PROGRESS REPORT

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BETWEEN THE

UNITED STATES ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION

AND

THE UNIVERSITY OF TENNESSEE

PERIOD

SEPTEMBER 15, 1974 TO SEPTEMBER 15, 1975

Title of Project

RESEARCH CONCERNING IONIC AND FREE RADICAL REACTIONS IN RADIATION CHEMISTRY

Principal Investigator

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MASTER

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A. Personnel

(1) Dr. T. Ffrancon Williams: Professor of Chemistry and Alumni Distinguished Service Professor.

(2) Dr. Koichi Nishikida: Postdoctoral Research Associate. After being associated with this research program since October 1, 1972, Dr. Nishikida left on July 31, 1975.

(3) Dr. Akinori Hasegawa: Postdoctoral Research Associate. Dr. Hasegawa joined the program on April 21, 1975. He is on a leave of absence from his position in the Department of Chemistry, Faculty of Science, at Hiroshima University, Japan.

(4) Mrs. Kathleen Webster: Research Assistant. Mrs. Webster is enrolled as a graduate student in the Institute of Radiation Biology at the University of Tennessee.

(5) Mr. Robert McNeil: Teaching Assistant. Mr. McNeil is a candidate for the Ph.D. degree in the Department of Chemistry.

(6) Mr. Reggie L. Hudson: Teaching Assistant. Mr. Hudson is a candidate for the Ph.D. degree in the Department of Chemistry. Mr. Hudson joined the group in the summer of 1975.

(7) Mr. James P. Watson: Undergraduate Research Participant. Mr. Watson carried out research in our group during the senior year (1974-75) of his B.S.-in-Chemistry degree program.

Employment. Dr. Williams devoted 1/4 of his time during the 1974-75 academic year to this research, this being a University contribution. He was also employed full time for three months in the summer of 1975. Dr. Nishikida and Dr. Hasegawa were employed full time during their specified employment periods. Mrs. Webster was employed from

November 1974 through March 1975. The other members of the group received no salary compensation under the contract.

B. Facilities and Equipment

During the past year we have added three major pieces of equipment to our ESR spectrometer/cryogenic systems, as follows:

(1) Signal Averaging System (Nicolet - 1074)

(2) Rapid Scan Unit (Varian V-4541)

(3) Helium Liquid Transfer System including cold end assembly and liquid helium container (Air Products and Chemicals LTD-3-110B1 and LT-3-110B1).

The other major facilities consisting of an ESR spectrometer system, a γ-radiation source, and cryogenic devices have been described in the last three Progress Reports (ORO-2968-78, -81, and -90).

C. Outline of Progress

Since last year's report (ORO-2968-81), a total of eight papers have been prepared of which six have been accepted for publication to date. Also, all previous reports issued under this Contract have been published with the exception of document ORO-2968-89 which is now in press (this paper was not submitted for publication until May 1975 because of the time needed to prepare a companion paper (ORO-2968-98)). The material appended to this report includes all these current documents together with reprints of papers previously included in preprint form.

The reports issued during the year provide an up-to-date account of the progress made under this Contract. Our accomplishments have included the ESR identification of several new radicals, including ClF_6, BrF_6, $Me_2Se{-}SeMe_2^{+}$, and F_3NO^{-}. Also, our description of the electronic structure of phosphoranyl radicals (J. Amer. Chem. Soc., 96, 5032 (1974)) has been corroborated by additional studies in this laboratory (ORO-2968-91) and by independent work carried out at the National Research Council of Canada by J. R. Morton and his collaborators. The titles and abstracts of our reports are listed, as follows:

CURRENT REPORTS

All reports issued under this Contract to date either have been published or are in press with the exception of ORO-2968-96 and ORO-2968-97.

I. [ORO-2968-91] LIGAND ELECTRONEGATIVITY EFFECT ON THE SPIN DISTRIBUTION IN PHOSPHORANYL RADICALS (Koichi Nishikida and Ffrancon Williams, J. Amer. Chem. Soc., 97, 0000 (1975)).

ABSTRACT: The trimethylphosphoranyl radical Me_3PH has been identified in γ-irradiated trimethyl phosphine at −196° by means of its esr spectrum consisting of an anisotropic ^{31}P doublet of isotropic ^{1}H doublets. Since this radical lacks electronegative groups which are thought to stabilize compounds and radicals of pentacoordinate phosphorus that assume trigonal bypyramidal geometry, the spin distribution is of particular interest. Comparison of the isotropic hyperfine splittings (A_{iso} (^{31}P) = 484 G; A_{iso} (^{1}H) = 182 G) with those obtained previously for alkoxyphosphoranyl radicals shows that the ^{31}P hfs decreases monotonically on progressive substitution of the two apical

alkoxy groups by alkyl or hydrogen ligands. In contrast, the large coupling to the hydrogen ligand in one apical position increases significantly when the other apical substituent is changed from an alkoxy to an alkyl group. These results indicate that the replacement of alkoxy groups by less electronegative ligands in the apical positions brings about a transfer of spin density from the orbitals of the central atom to the σ orbitals of the ligands leading to destabilization. This effect of electronegative substituents on the spin density distribution is in accord with the proposal that the half-occupied MO is largely localized along the axial three-center bond connecting the apical ligands and the central atom.

II. [ORO-2968-92] THE CHLORINE HEXAFLUORIDE RADICAL. PREPARATION, ELECTRON SPIN RESONANCE SPECTRUM, AND STRUCTURE (Koichi Nishikida, Ffrancon Williams, Gleb Mamantov, and Norman Smyrl, J. Amer. Chem. Soc., **97**, 3526 (1975)).

ABSTRACT: The previously unreported ClF_6 radical has been prepared by γ radiolysis of SF_6 containing 5 mole percent of ClF_5. Identification of the radical follows directly from its isotropic esr spectrum which consists of a 1:1:1:1 chlorine quartet of binomial fluorine septets. By including hyperfine interaction terms up to fourth order, the following esr parameters were obtained: a (^{35}Cl) = 771 G; a (^{37}Cl) = 642 G; a (^{19}F) = 89 G; and g = 2.015. The magnitude of the isotropic chlorine coupling is such that the unpaired electron must populate the chlorine 3s orbital for which a spin density of 0.46 is calculated. This finding

is consistent with the occupation of the totally symmetric a^*_{1g} orbital of ClF_6 in O_h geometry, a description which also accounts for the interaction with six equivalent fluorines. However, the possibility of large deformations from octahedral geometry similar to those observed for XeF_6 cannot be excluded and the large esr linewidths may be indicative of a fluctuating structure.

III. [ORO-2968-93] ESR SPECTRUM AND STRUCTURE OF BrF_6 (Koichi Nishikida, Ffrancon Williams, Gleb Mamantov, and Norman Smyrl, *J. Chem. Phys.*, 63, 1693 (1975)).

ABSTRACT: The BrF_6 radical was generated by a method analogous to that used in the preparation of ClF_6 (*J. Amer. Chem. Soc.*, 97, 3526 (1975)). A group of evenly-spaced lines detected between 6.5 and 7.5 kG were assigned to the superimposed $M_I = -3/2$ transitions of the ^{79}Br and ^{81}Br species, the substructure representing the additional coupling to several equivalent fluorines. The isotropic coupling constants were calculated from the Breit-Rabi equation, the average values being $a_{81} = 4494 \pm 2$ G, $a_{79} = 4163 \pm 2$ G, and $a_{19} = 89 \pm 1$ G. The ratio a_{81}/a_{79} is 1.079 in satisfactory agreement with $\mu_{81}/\mu_{79} = 1.078$, thereby confirming the analysis and the assignment of the spectrum to BrF_6. Employing the magnetic parameters calculated for the bromine 4s atomic orbital, these bromine coupling constants correspond to a 4s spin density of 0.54 on the central atom which compares closely with the value of 0.46 obtained for the chlorine 3s orbital in ClF_6. Thus the distribution of the unpaired electron between the ns orbital of the central atom and the fluorine ligands is very similar in the two radicals

and these results are consistent with the occupation of the totally symmetric a^*_{1g} orbital in O_h symmetry. However, these results do not exclude the possibility of large deformations about a mean of octahedral geometry, and the large ESR linewidths may be symptomatic of a fluctuating structure.

IV. [ORO-2968-94] THE ESR SPECTRUM AND STRUCTURE OF THE DIMER RADICAL CATION OF DIMETHYL SELENIDE ($Me_2Se\text{-}SeMe_2^+$) IN A γ-IRRADIATED SINGLE CRYSTAL (Koichi Nishikida and Ffrancon Williams, Chem. Phys. Letters, 34, 302 (1975))

ABSTRACT: The dimer radical cation of dimethyl selenide has been identified in a γ-irradiated single crystal of the parent compound, its main (^{even}Se) ESR spectrum showing hyperfine coupling to twelve equivalent hydrogens. Also, the relative intensity of the naturally abundant ^{77}Se satellite spectrum is in agreement with a hyperfine interaction involving two anisotropically equivalent selenium atoms. The principal values and direction cosines of the ^{77}Se hyperfine and g tensors have been determined and are shown to be satisfactorily interpreted in terms of a centrosymmetric structure, the unpaired electron occupying an antibonding (σ*) orbital built almost entirely from the p_σ orbitals of the two selenium atoms. Analysis of the g tensor components indicates that the CSeC planes are perpendicular to the direction of the Se-Se bond. It is also shown that the isotropic ^1H splitting and g factor obtained previously from solution ESR studies of the dimethyl sulphide dimer cation are consistent with the structure advanced for the selenium dimer. The results seem to rule out the possibility of any significant d orbital participation in the bonding.

V. [ORO-2968-95] MERCURY - 201 QUADRUPOLE INTERACTION IN THE ELECTRON SPIN RESONANCE OF THE CH_2HgCl RADICAL (Carolyn M. L. Kerr, Jorge A. Wargon, and Ffrancon Williams, *J. Chem. Soc., Faraday Trans. II*, in press).

ABSTRACT: The e.s.r. spectrum of the CH_2HgCl radical in γ-irradiated polycrystalline methyl mercuric chloride has been analyzed for quadrupole effects and a detailed interpretation yields the following set of parameters: $g_{\perp} = 1.990$; $^{1}A_{\perp}(2H) = 19.5$ G; $^{199}A_{\perp}(Hg) = -437$ G; $^{201}A_{\perp}(Hg) = +162$ G; e^2Qq_z (^{201}Hg) $= -900 \pm 50$ MHz. The value obtained for the ^{201}Hg nuclear quadrupole coupling constant is comparable to the results obtained in previous studies on mercuric chloride (from pure quadrupole resonance spectra of the solid) and methyl mercuric chloride (from microwave spectra of the gas).

VI. [ORO-2968-96] ELECTRON SPIN RESONANCE SPECTRA OF F_2NO AND F_3NO^-. A HYPERVALENT RADICAL FROM FIRST-ROW ELEMENTS (Koichi Nishikida and Ffrancon Williams, submitted for publication to *J. Amer. Chem. Soc.*).

ABSTRACT: The F_2NO and F_3NO^- radicals have been identified by means of their isotropic ESR spectra. Both radicals were generated by γ radiolysis of a solid solution of 5 mole % F_3NO in SF_6. The F_2NO spectrum shows a large ^{14}N hyperfine interaction ($a_N = 93.3$ G) and a fluorine coupling (a_F (2) $= 143.8$ G) indicative of a pyramidal radical analogous to the isoelectronic species, CF_3. The ESR parameters for F_3NO^- ($a_N = 147$ G, a_F (3) $= 195$ G, $g = 2.014$) are consistent with results obtained for radicals possessing thirty-three valence electrons derived from second-row elements. In particular, the large spin density (0.27) in the nitrogen 2s orbital is characteristic for this class of radicals and is predicted by INDO calculations based on either trigonal bipyramidal ($\underline{C}_s$) or $\underline{C}_{3v}$ geometry. The radiation chemistry and especially the large F_2NO/SF_5 signal intensity ratio are explained in terms of selective electron capture by F_3NO, the F_2NO and SF_5 radicals resulting from dissociation of the F_3NO^- and SF_6^- ions.

VII. [ORO-2968-97] DETECTION OF THIYL RADICALS BY SPIN TRAPPING IN THE RADIOLYSIS OF LIQUIDS (Jorge A. Wargon and Ffrancon Williams, submitted for publication to J. Chem. Soc., Chem. Comm.)

ABSTRACT: The e.s.r. spectra of thiyl nitroxides have been identified following the low-temperature radiolysis of alkanethiols containing t-BuNO as a radical trap. Thiyl radicals are also generated in the radiolysis of dimethyl sulphide and dimethyl disulphide.

VIII. [ORO-2968-98] ELECTRON SPIN RESONANCE STUDIES OF γ-IRRADIATED PHOSPHORUS COMPOUNDS CONTAINING PHOSPHORUS-CHLORINE BONDS (Carolyn M. L. Kerr, Kathleen Webster, and Ffrancon Williams, accepted for publication in J. Phys. Chem.)

ABSTRACT: Esr experiments similar to those described in the preceding paper [C. M. L. Kerr, K. Webster, and F. Williams, J. Phys. Chem., **79**, 0000] have been used to identify the radicals produced in a series of γ-irradiated phosphorus compounds containing phosphorus-chlorine bonds. The principal species formed from diethyl chlorophosphite are the

neutral radicals $\dot{P}(OEt)_2$ and $(EtO)_2\dot{P}Cl_2$ presumably by loss and addition of chlorine atoms, although there is evidence that the former species is produced at least in part by dissociative electron capture. On the other hand, the major radical derived from a series of chlorophosphate esters is invariably the chlorophosphoranyl radical anion formed by simple electron attachment to the parent molecule. In the dichlorophosphoranyl radicals, there is a large ^{35}Cl coupling from the two equivalent chlorines in the apical positions of a trigonal bipyramidal structure. Evidence for the anisotropy of this coupling suggests that a significant spin density resides in the $3p_\sigma$ orbitals of these chlorine ligands, in agreement with recent single crystal studies on $\dot{P}OCl_3^-$ [T. Gillbro and F. Williams, J. Amer. Chem. Soc., **96**, 5032 (1974)]. The much greater stability of radical anions derived from chlorophosphates relative to those from di- and tri-alkyl phosphate esters, which undergo efficient dissociation, is interpreted in terms of the effect of ligand electronegativity on the spin density distribution. This effect is consistent with recent MO descriptions which indicate that the half-occupied orbital in phosphoranyl radicals is largely localized along the axial three-center bond.

UPDATE OF PREVIOUS REPORTS

Three reports (86-88) issued as preprints in last year's Progress Report (ORO-2968-90) are now available as reprints. Also included in the present compilation is a preprint of document 89 which has been accepted for publication. All the other reports issued last year were furnished as reprints in ORO-2968-90.

IX. [ORO-2968-86] ELECTRON SPIN RESONANCE IDENTIFICATION OF THE DIMER RADICAL CATION $(MeO)_3P\text{-}P(OMe)_3^+$ IN γ-IRRADIATED TRIMETHYL PHOSPHITE FROM SECOND-ORDER HYPERFINE STRUCTURE (Tomas Gillbro, Carolyn M. L. Kerr, and Ffrancon Williams, *Mol. Phys.*, **28**, 1225 (1974)).

X. [ORO-2968-87] STRUCTURE AND REACTIVITY OF METHYL RADICAL - CYANIDE ION PAIRS IN CRYSTAL I AND CRYSTAL II OF ACETONITRILE (Estel Dean Sprague, Keiji Takeda, Jih Tzong Wang, and Ffrancon Williams, *Can. J. Chem.*, **52**, 2840 (1974)).

XI. [ORO-2968-88] METHYL RADICAL - METHANESULFENATE ANION PAIRS FORMED BY DISSOCIATIVE ELECTRON CAPTURE IN γ-IRRADIATED CRYSTALLINE DIMETHYL SULFOXIDE - d_6 AT 77K (Yoon Jin Chung, Koichi Nishikida, and Ffrancon Williams, *J. Phys. Chem.*, **78**, 1882 (1974)).

XII. [ORO-2968-89] ELECTRON SPIN RESONANCE STUDIES OF γ-IRRADIATED PHOSPHITE AND PHOSPHATE ESTERS: IDENTIFICATION OF PHOSPHINYL, PHOSPHONYL, PHOSPHORANYL, AND PHOSPHINE DIMER CATION RADICALS (Carolyn M. L. Kerr, Kathleen Webster, and Ffrancon Williams, accepted for publication in *J. Phys. Chem.*)

ABSTRACT: The powder esr spectra of several γ-irradiated phosphorus esters at 77 K have been analyzed into their distinguishable radical components, each spectrum being generally a composite of anisotropic features from a number of alkyl and phosphorus-centered radicals. Resolution of overlapping spectra has been achieved in some instances by radiation-chemical experiments designed to suppress or enhance

the products of electron capture relative to the radicals formed by other mechanisms. The identification of phosphorus-centered radicals is based on a number of criteria including the magnitude of the isotropic ^{31}P hfs which is highly characteristic for certain phosphoranyl radicals, the 3p/3s orbital ratio of phosphorus spin densities, and the results of chemical experiments. The radiation chemistry of dialkyl phosphites, $(RO)_2P(O)H$, is influenced by the ease with which the P-H bond in these compounds is broken, the principal radicals being the phosphonyl species $(RO)_2\dot{P}O$ and $RO\dot{P}(O)O^-$. Both of these species are thought to be the secondary products of hydrogen atom abstraction by the alkyl radical R• which is produced by dissociative electron capture. A similar primary step is shown to apply for the trialkyl phosphates, $(RO)_3PO$, but in this case only carbon-centered radicals are formed by secondary H-atom abstraction processes. Although the undissociated phosphoranyl radical anions are not detected in dialkyl phosphites, weak signals attributable to the corresponding anions are observed in trialkyl phosphates. Similarly, the phosphoranyl radical anion is tentatively identified in the spectrum of γ-irradiated dimethylacidpyrophosphate which also includes strong signals from methyl and phosphonyl radicals. The latter is thought to be formed by the loss of either the OH or the OMe group from the parent molecule rather than by scission of one of the P-O-P bridge bonds. Trialkyl phosphites, $(RO)_3P$, yield a large number of radicals including the phosphinyl species $(RO)_2\dot{P}$ by dissociative electron capture, the dimer radical cation $(RO)_3P-P(OR)_3^+$, and the phosphoranyl radicals $R\dot{P}(OR)_3$ and $\dot{P}(OR)_4$ by alkyl and alkoxy radical addition. The related tetraethylpyrophosphite yields $\dot{P}(OEt)_2$ and a dimer radical cation again characterized by two anisotropically equivalent phosphorus atoms indicative of P-P bond formation. However, the results for the pyrophosphite differ from those for the trialkyl phosphites in showing the absence of alkyl radicals or their phosphoranyl adducts and the formation of the phosphonyl species $(EtO)_2\dot{P}O$, the latter being produced presumably by cleavage of the P-O-P bridge. The esr parameters for each of the four main groups of phosphorus-centered radicals are summarized and the electronic structures of these radicals are discussed briefly. The novel dimer radical cations can be considered strictly analogous to the positive-hole V_K centers formed in irradiated alkali halides; the unpaired electron in the former occupies a σ^* orbital localized between the two strongly electronegative phosphorus atoms, the valence-shell configuration at phosphorus being close to tetrahedral.

CONFERENCE PRESENTATIONS

XIII. HYPERVALENT (EXCESS ELECTRON) RADICALS (Ffrancon Williams, Abstracts of the Edwin J. Hart Conference on Radiation Chemistry, Argonne National Laboratory, Argonne, Illinois, July 7-9, 1975).

ABSTRACT: Hypervalent (or electron-rich) radicals are odd-electron molecules possessing more electrons than can be accommodated by valence-bond structures based on the Lewis octet rule. In this contribution we shall discuss recent ESR studies in our laboratory on a wide variety of novel excess-electron species, including CH_3Br^-, $SO_2Cl_2^-$, $POCl_3^-$, ClF_6, BrF_6, $Me_2Se{-}SeMe_2^+$, and $(MeO)_3P{-}P(OMe)_3^+$. Each of these species has been generated by γ-irradiation of an appropriate solid matrix at low temperature.

The CH_3Br^- species** can be regarded as a methyl radical-bromide ion pair or as a molecule possessing a three-electron bond. ESR studies show that the spin density localized in the carbon 2p orbital is ∼0.9 and that the methyl configuration is planar, the remaining spin density being in the bromine 4p orbital. We shall review other examples of weakly interacting alkyl radical-anion pairs formed by dissociative electron capture in γ-irradiated crystalline solids.

Anisotropic ESR studies on the radical anions $SO_2Cl_2^-$ and $POCl_3^-$ have shown † that more than half the total spin density resides in the $3p_\sigma$ orbitals of the two equivalent chlorines which occupy the apical sites in a C_{2v}(C_s) trigonal bipyramidal structure. Taken together with the appreciable 3s spin density on the central atom, these results indicate that the unpaired electron occupies a linear three-center σ* orbital of a_1 (a') symmetry. This description is also consistent with the observation of a large isotropic coupling to hydrogen ligands in the apical sites of organophosphoranyl radicals. Detailed MO calculations support this three-center model for phosphoranyl and related radicals.

Recently, we succeeded †† in preparing the interesting radical ClF_6 which is isoelectronic with SF_6^-. The magnitude of the isotropic

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**E. D. Sprague and F. Williams, J. Chem. Phys. 54, 5425 (1971).
†T. Gillbro and F. Williams, J. Amer. Chem. Soc. 96, 5032 (1974).
††K. Nishikida et al., J. Amer. Chem. Soc., 97, 3526 (1975).

chlorine coupling is such that the unpaired electron must populate the chlorine 3s orbital for which a spin density of 0.46 is calculated. This finding is consistent with the occupation of the totally symmetric a^*_{1g} orbital of ClF_6 in O_h geometry, a description which also accounts for the interaction with six equivalent fluorines. However, the possibility of large deformations from octahedral geometry similar to those observed for XeF_6 cannot be excluded and the large ESR linewidths may be indicative of a fluctuating structure.

Finally, the dimer radical cations $(CH_3O)_3P{-}P(OCH_3)_3^+$ and $Cl_3PS{-}SPCl_3^+$ have been identified in γ-irradiated crystals of trimethyl phosphite[†] and thiophosphoryl chloride, respectively. These cations are directly comparable to the well-known positive-hole V_K center Cl_2^- formed in alkali chlorides, the unpaired electron occupying a σ* orbital localized between the two phosphorus (or sulfur) atoms. Presumably this antibonding orbital is low-lying because it is formed between two highly electronegative centers.

[†] T. Gillbro, C. M. L. Kerr, and F. Williams, Mol. Phys. 28, 1225 (1974).

Ligand Electronegativity Effect on the Spin Distribution in Phosphoranyl Radicals[1]

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Abstract: The trimethylphosphoranyl radical Me$_3$PH has been identified in γ-irradiated trimethyl phosphine at −196° by means of its esr spectrum consisting of an anisotropic ^{31}P doublet of isotropic ^{1}H doublets. Since this radical lacks electronegative groups which are thought to stabilize compounds and radicals of pentacoordinate phosphorus that assume trigonal bipyramidal geometry, the spin distribution is of particular interest. Comparison of the isotropic hyperfine splittings (A_{iso} (^{31}P) = 484 G; A_{iso} (^{1}H) = 182 G) with those obtained previously for alkoxyphosphoranyl radicals shows that the ^{31}P hfs decreases monotonically on progressive substitution of the two apical alkoxy groups by alkyl or hydrogen ligands. In contrast, the large coupling to the hydrogen ligand in one apical position increases significantly when the other apical substituent is changed from an alkoxy to an alkyl group. These results indicate that the replacement of alkoxy groups by less electronegative ligands in the apical positions brings about a transfer of spin density from the orbitals of the central atom to the σ orbitals of the ligands leading to destabilization. This effect of electronegative substituents on the spin density distribution is in accord with the proposal that the half-occupied MO is largely localized along the axial three-center bond connecting the apical ligands and the central atom.

A substantial body of esr data now exists for a wide variety of phosphoranyl radicals,[2] and this information has naturally stimulated interest in the structure of this important class of intermediates.[3,4] Although many esr studies have subscribed to the traditional view that the unpaired electron occupies essentially an equatorial sp^2 orbital of pentacoordinate (sp^3d hybridized) phosphorus in trigonal bipyramidal geometry, new light was shed on the electronic structure of these radicals by the recent finding[3] that large spin densities often reside in the σ orbitals of the axial ligands. While this latter result is difficult to reconcile with descriptions based on directed valence-bond theory, it becomes immediately understandable in terms of MO theory which assigns the unpaired electron in these radicals to an antibonding orbital of a_1 ($\underline{C}_{2v}$) or a' ($\underline{C}_s$) representation.[3] This orbital may be regarded as a three-center σ^* orbital derived from the axial ligand orbitals and the symmetry-allowed 3s and 3p orbitals of the phosphorus atom.

A corollary to this MO description is that the spin density distribution between the contributing group of ligand and central atom orbitals should be sensitive to the electronegativities of the ligands in the apical (axial) sites. In particular, the progressive replacement of two apicophilic electronegative groups by alkyl or hydrogen ligands should destabilize the radical,[3,5] the anticipated effect being to increase the spin populations on the apical ligands at the expense of the phosphorus atom.

Although the esr spectra of a number of organophosphoranyl radicals with only one electronegative ligand (alkoxy) have been documented,[6] as yet the only esr report describing a phosphoranyl radical without any electronegative ligands concerns the parent species PH_4.[7] However, the isotropic

^{31}P and ^{1}H splittings attributed to this radical appear to be quite anomalous and the identification has been seriously questioned.[8,9] In this paper we report the esr spectrum and spin density distribution for the trimethylphosphoranyl radical thereby completing the set of esr parameters for the series $R_nP(OR')_{4-n}$ (n = 0-4), where R is Me or H, and R' is Me, Et, or tert-Bu. Taken in conjunction with other work, our present results are shown to provide further evidence that the unpaired electron is largely localized along the axial three-center bond connecting the apical ligands and the central atom.

Experimental Section

Samples of trimethyl phosphine (Strem Chemicals Inc.) were prepared in Suprasil esr tubes by standard high-vacuum techniques. Attempts were made to obtain single crystals by a low-temperature technique[10] but our efforts in this direction were frustrated by the apparent occurrence of a phase transition in the solid below the melting point (-85°) and only partially oriented samples could be obtained for studies at -196°. However, even the small degree of preferential orientation induced by this method proved to be valuable in locating the characteristic features of the powder esr spectrum, as discussed below.

Irradiations were carried out at -196° in a cobalt-60 γ source and the samples were transferred promptly into a liquid nitrogen dewar which fitted into the cavity of a Varian (V-4502-15) X-band esr spectrometer. Spectra were recorded at sample temperatures above -196° by means of a variable-temperature accessory. Measurements of the magnetic field strength were made using a proton magnetic resonance probe (Walker/Magnemetrics Precision NMR Gaussmeter, Model G-502).

Results and Discussion

Figure 1 shows esr spectra of γ-irradiated trimethylphosphine at −196° recorded at two orientations. Apart from the radical of interest to us here, the spectrum consists of the intense doublet due to the hydrogen atom (a = 507 G) and the outermost pair of features which are thought to be the $(1, \pm 1)$ components of the dimer radical cation $\mathrm{Me_3P{-}PMe_3^+}$ analogous to the species produced in γ-irradiated trimethylphosphite.[11] The remaining features consisting of an anisotropic ^{31}P doublet of ^{1}H doublets are assigned to the $\mathrm{Me_3PH}$ radical, as indicated by the stick diagram. The integrity of this hyperfine structure was established by power saturation and annealing studies, as well as by the change of lineshape with orientation.

The sample used to obtain the spectra of Figure 1 was polycrystalline but apparently possessed some degree of preferential orientation. This was useful because the intensity of the parallel (outer) features could be enhanced for some directions,[12] as illustrated in the upper spectrum. As expected, the resolution is somewhat better at high field because the second-order downfields shifts are greater for the perpendicular than for the parallel features in the case of $|A_{\parallel}| > |A_{\perp}|$.[13] After second-order corrections had been applied,[13] the esr parameters were found to be $A_{\parallel}(^{31}\mathrm{P})$ = 537 G, $A_{\perp}(^{31}\mathrm{P})$ = 458 G; $A_{\parallel}(^{1}\mathrm{H})$ = 183 G, $A_{\perp}(^{1}\mathrm{H})$ = 181 G; and $g_{\parallel}$ = 2.0054, $g_{\perp}$ = 2.0026. The fairly small anisotropy associated with the smaller doublet splitting is fully consistent with the assignment to proton coupling.

The spin density distribution for the $\mathrm{Me_3PH}$ radical is shown in Figure 2. These values were derived in the usual way[3,11] from the isotropic and anisotropic components of the hyperfine couplings, viz., A_{iso} (^{31}P) = 484 G, $2B$ (^{31}P) = 2/3 ($A_{\parallel}$ (^{31}P) − $A_{\perp}$ (^{31}P)) = 53 G, and A_{iso} (^{1}H) = 182 G. The sum of the spin densities in the hydrogen 1s orbital and the phosphorus 3s and 3p orbitals is 0.75, so in the light of previous work[3] it is reasonable to assume that most of the remaining spin density resides in the σ orbital of the apical methyl group which contributes to the MO occupied by the unpaired electron. A direct measurement of the spin density in this methyl orbital would require a determination of the ^{13}C hfs tensor but this was not feasible in the present study.

It is instructive to compare (Table I) the isotropic hyperfine splittings for Me_3PH with those obtained previously for alkoxyphosphoranyl radicals. Evidently, the replacement of the apical alkoxy group in monoalkoxyphosphoranyl radicals by hydrogen or methyl results in a marked decrease of the ^{31}P hfs by _ca._ 140 G. This agrees with the previous trend along the series showing that the ^{31}P hfs increases monotonically according to the number of alkoxy groups in the organophosphoranyl radical. Also of interest is the significant increase in the hyperfine splitting of the apical hydrogen on substituting the alkoxy group in $Me_2PH(OR)$ by methyl. In fact, the proton coupling of 182 G for Me_3PH appears to be the largest value ever reported for radicals other than H-atom complexes and corresponds to a hydrogen 1s spin density of 0.36.

Therefore it appears that the destabilization incurred by the alkyl substitution of the alkoxy group in $Me_2PH(OR)$ is manifested directly by a transfer of spin density from the phosphorus 3s orbital to the σ orbitals of the apical ligands. This is consistent with the antibonding character of the half-occupied three-center orbital in these radicals,[3] and fully accords with our earlier expectations. Incidentally, these results must cast further doubt on the purported spectrum[7] of the PH_4 radical. Also, they reveal no indication of a marked change in the geometry of phosphoranyl radicals as the apical ligands become less electronegative.

In conclusion, it seems worthwhile to point out a simple implication of the three-center orbital description for the reactivity of phosphoranyl radicals.[14] It is natural to expect that as a greater spin density moves out from the phosphorus onto the apical ligands, so the lability of organophosphoranyl radicals to α-scission should be increased. Since monoalkoxytrialkylphosphoranyl radicals undergo α-scission quite readily with the loss of an alkyl radical,[6] this tendency should be even more pronounced for tetraalkylphosphoranyl radicals and might explain the difficulty of alkyl radical addition to trialkylphosphines[6] as compared to trialkylphosphites.[15]

References and Notes

(1) (a) This work was supported by the U.S. Atomic Energy Commission (Document No. ORO-2968-91); (b) the subject matter of this paper was originally submitted as a Communication (December 23, 1974).

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Table I. Isotropic Esr Parameters for Some Organophosphoranyl Radicals[a]

Radical	Number of Alkoxy Ligands	Temp. °C	$a(^{31}P)$ G	$a(^{1}H)$[b] G	*g*
Me_3PH[c]	0	-196	484	182	2.0035
$MePH_2(OR)$[d]	1	-85	631.5	139.6	
$Me_2PH(OR)$[d]	1	-65	631.4	142.9	
Me_3POR[d]	1	-81	618.7		
$MePH(OR)_2$[d]	2	-85	703.3		
$Me_2P(OR)_2$[d]	2	-65	713.7		
$MeP(OMe)_3$[e]	3	-70	783.1		2.003
$MeP(OEt)_3$[e]	3	-70	786.7		2.004
$EtOP(OMe)_3$[e]	4	-70	884.0		2.003
$P(OR)_4$[f]	4	-70	918		2.004

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[a] R = *tert*-Bu.

[b] Coupling to apical hydrogen ligand.

[c] This work; the isotropic parameters were deduced from the anisotropic couplings given in the text and the values showed no significant change between -196° and the temperature (-135°) at which the radicals disappeared on annealing.

[d] Reference 6.

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FIGURE CAPTIONS

Figure 1. First-derivative esr spectra of γ-irradiated trimethylphosphine at −196° recorded at two different orientations. The stick diagram refers to the parallel and perpendicular features of a ^{31}P doublet of ^{1}H doublets spectrum which is assigned to the Me_3PH adduct.

Figure 2. Molecular orbital occupied by the unpaired electron in the trimethylphosphoranyl radical. The values of the spin densities in the contributing atomic orbitals were calculated from the esr data.

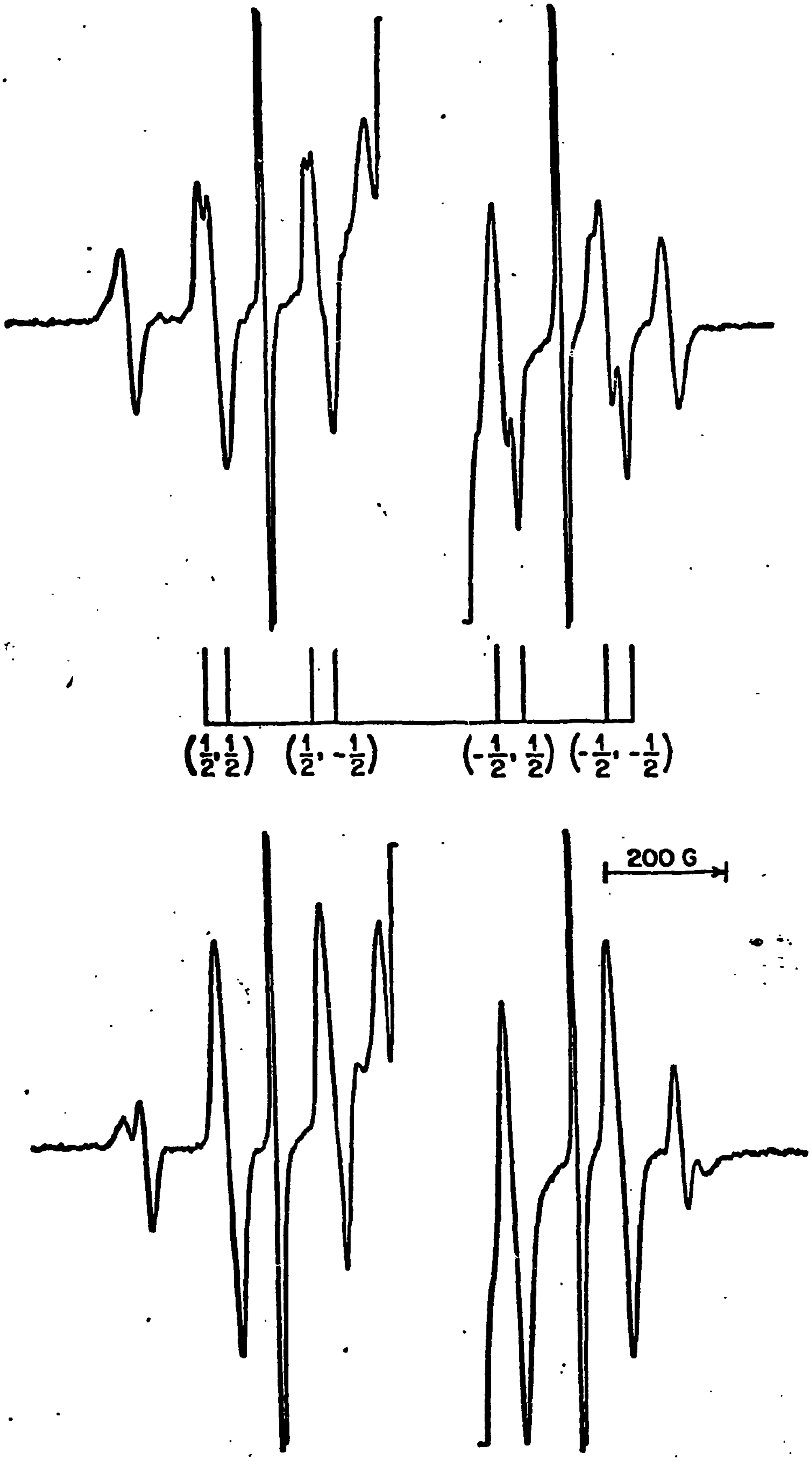

Figure 1. Nishikida and Williams

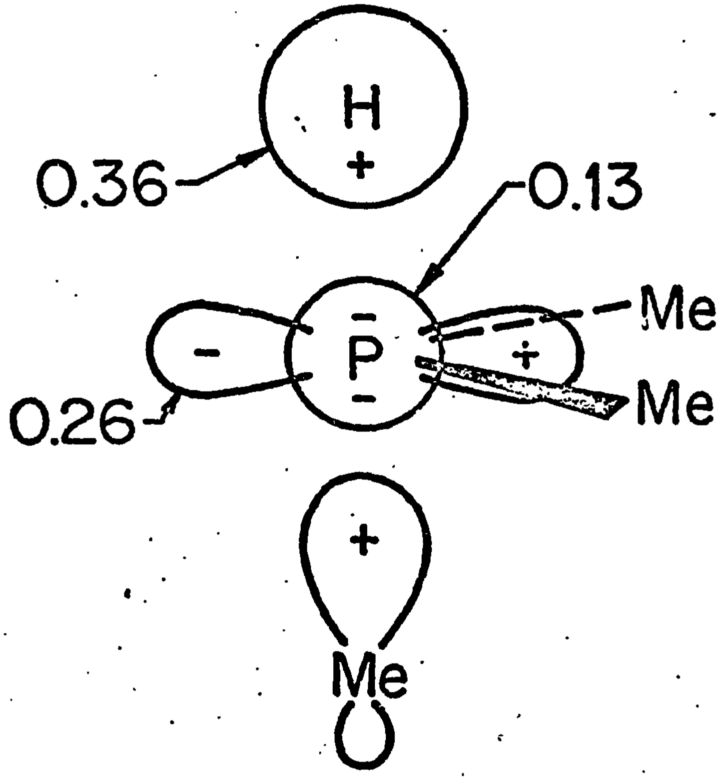

Figure 2. Nishikida and Williams

Mercury-201 Quadrupole Interaction in the Electron Spin Resonance of the CH_2HgCl Radical

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ABSTRACT

The e.s.r. spectrum of the CH_2HgCl radical in γ-irradiated polycrystalline methyl mercuric chloride has been analyzed for quadrupole effects and a detailed interpretation yields the following set of parameters: $g_\perp = 1.990$; ${}^{1}A_\perp(2H) = 19.5$ G; ${}^{199}A_\perp(Hg) = -437$ G; ${}^{201}A_\perp(Hg) = +162$ G; $e^2Qq_z\,({}^{201}Hg) = -900 \pm 50$ MHz. The value obtained for the ${}^{201}Hg$ nuclear quadrupole coupling constant is comparable to the results obtained in previous studies on mercuric chloride (from pure quadrupole resonance spectra of the solid) and methyl mercuric chloride. (from microwave spectra of the gas).

The e.s.r. spectrum of a mercury-containing radical normally consists of three sets of components resulting from the different isotopes of mercury, as exemplified in the present study of the CH_2HgCl radical in γ-irradiated methyl mercuric chloride. Thus in addition to the main spectrum corresponding to the even-numbered isotopes of zero spin, satellite spectra originate from the two magnetic isotopes ${}^{199}Hg$ ($I = 1/2$) and ${}^{201}Hg$ ($I = 3/2$) present in natural abundances of 17.0 and 13.2 percent, respectively. The ${}^{201}Hg$ spectrum of CH_2HgCl shows clear evidence for a quadrupole interaction so we have determined the ${}^{201}Hg$ nuclear quadrupole coupling constant by using the g and hyperfine parameters derived independently from the ${}^{even}Hg$ and ${}^{199}Hg$ spectra.

EXPERIMENTAL

Methyl mercuric chloride was used as received from Alfa Products (Ventron Corp.). Samples of the powdered solid were prepared in Suprasil tubes under vacuum and γ-irradiated at 77 K for doses of ca. 10 Mrad. The e.s.r. spectra were recorded as described previously[1] between 77 and 135 K, the resolution remaining largely unaltered in this temperature range. Magnetic field positions were determined from a calibration provided by the signals of the hydrogen-atom doublet ($a = 504$ G, $g = 2.0021$)[1,2] present in the spectra recorded below 120 K.

The e.s.r. parameters were evaluated by fitting the line positions calculated by matrix diagonalization to the experimental values. For the ^{201}Hg spectrum, quadrupole matrix elements were incorporated in the diagonalization program according to the spin Hamiltonian of Adrian _et al._[3]

Studies were also carried out on methyl mercuric bromide and methyl mercuric iodide but the e.s.r. spectra of the derived CH_2HgX radicals were poorly resolved and adequate only for identification purposes. Similar spectra for these two halides have been published recently by Fullam and Symons.[4] Evidently the replacement of chlorine by bromine or iodine increases the anisotropic halogen coupling so as to broaden the hyperfine components in the powder spectra of these radicals. Fullam and Symons[4] also reported the spectrum of the MeC(H)HgCl radical but the ^{201}Hg features were apparently too weak to be detected.

RESULTS AND DISCUSSION

The e.s.r. spectrum of γ-irradiated methyl mercuric chloride shown in fig. 1 is almost entirely attributable to the CH_2HgCl radical. The central spectrum consisting of a well-resolved triplet is assigned to the radical containing the even-numbered mercury isotopes (198, 200, 202, 204) with zero nuclear spin. This is flanked by a strong doublet of triplets from the ^{199}Hg isotope and a weaker quartet of triplets due to the ^{201}Hg radical. The triplet splitting ($\underline{A}(^1H)$ = 19.5 G[¶]) clearly arises from interaction with the methylene protons, and its magnitude is diagnostic of a carbon-centred radical. These assignments are indicated by the line positions marked below the spectrum. The relative intensities of the three component spectra were found to be approximately in the ratios calculated from the relative natural abundances of the mercury isotopes.

In addition to the hyperfine structure, the powder spectrum of fig. 1 is marked by two secondary characteristics. First, the lineshapes and intensity ratios of the individual ^{1}H triplets strongly suggest that the observed components are the perpendicular features of a spectrum possessing axially symmetric $\underline{g}$ and hyperfine tensors. Similar interpretations have previously been given for the powder spectra of several analogous substituted methyl radicals,[5-7] the reported values of $\underline{A}_{\perp}(^1H)$ ranging from 17.8 to 19.0 G being comparable to the 19.5 G coupling observed here. The cylindrical symmetry may be attributed to rotation of the CH_2 group[5] about the C-Hg-Cl($\underline{z}$) axis, assuming these atoms are collinear as in the neutral molecule.[8] Secondly, the spacing between the inner ($\underline{M}_{\underline{I}}$ = ± 1/2) components of the ^{201}Hg spectrum is markedly larger than the spacings between the inner and outer components. Symmetrical shifts of hyperfine components from the spectrum center are characteristic of quadrupole interactions, and a strong interaction is expected for CH_2HgCl as ^{201}Hg has a large nuclear quadrupole moment. Moreover, the axis

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[¶] G (gauss) = 10^{-4} T (tesla).

of the electric field gradient, which should be entirely due to the $6p_z$ electron in the linear *sp* bond-system of the mercury atom,[9] coincides with the z symmetry axis of the radical. The quadrupole coupling tensor should thus display the same cylindrical symmetry as the hyperfine interactions and the asymmetry parameter η was taken as zero in the ensuing calculations.

The analysis of powder e.s.r. spectra in this favorable case where the principal axes of the g, A, and e^2Qq tensors coincide has been discussed in detail by Adrian *et al.*[3] Although the perpendicular components are well defined in the present study and are interpreted below, there are no features which can be unambiguously assigned to the parallel spectrum. Two interpretatio are possible: either the mercury hyperfine coupling is essentially isotropic, the parallel features being masked throughout by the stronger perpendicular components, or it is appreciably anisotropic, the three weak lines indicated at extreme lowfield in fig. 1 being the outermost parallel features of the ^{199}Hg or (and) ^{201}Hg spectra. Considering the latter possibility, the apparent $A_{\|}(^{1}H)$ coupling of 27 G is close to that expected for a radical with a rotating CH_2 group,[10,11] but the mercury coupling implies a much larger anisotropy than previously observed for heavy-atom hyperfine splittings in radicals of this type.[6] In view of the scarcity of data on the anisotropic spectra of mercury-containing radicals,[12] it is not possible to say which is the more likely interpretation. Fortunately, it is still possible to obtain the value of the quadrupole coupling constant from the perpendicular spectrum by neglecting the mercury hyperfine anisotropy since the principal effect of the latter on the perpendicular spectrum is similar to that of changing $g_{\perp}$, namely, to shift the resonance positions without greatly altering the spacings between the mercury hyperfine components.

The following procedure was adopted in determining the e.s.r. parameters: $g_\perp$ and $^{199}A_\perp$ were obtained from the $^{\text{even}}$Hg and ^{199}Hg spectra and the value of $^{201}A_\perp$ calculated from the ratio of nuclear g factors, $^{201}g_N/^{199}g_N = 0.370$.[13] The derived parameters $g_\perp$ and $^{201}A_\perp$ were then employed together with varying values of e^2Qq_z to try to reproduce the experimental ^{201}Hg spectrum, the best fit being obtained (see below) for $|e^2Qq_z|$ in the region of 900 MHz. For such large values of the nuclear quadrupole coupling constant, it is no longer possible to describe spin states accurately in terms of the nuclear spin quantum number M_I as the quadrupole interaction causes substantial mixing of the M_I and $M_I \pm 2$ states unless the magnetic field is along the z principal axis. One result of this is that $\Delta M_I = \pm 2$ transitions become strongly allowed when the field is perpendicular to the symmetry axis and for $|e^2Qq_z| = 2|^{201}A_\perp|$ are as intense as those transitions formally described as $\Delta M_I = 0$. Furthermore, when this equality holds, two of the $\Delta M_I = \pm 2$ transitions coincide with the $\Delta M_I = 0$, $M_I = \pm 1/2$ transitions,[3] the remaining two lying close to the spectrum centre and therefore masked by the $^{\text{even}}$Hg spectrum. This situation is approximately realized for CH_2HgCl, as judged by the fact that a value of e^2Qq_z was found which both reproduces the experimental line positions and leads to the near superimposition of the $\Delta M_I = 0$ and $\Delta M_I = \pm 2$ lines as discussed above.

The results of the best-fit calculation are given in table 1. It was found that the calculated line positions were relatively insensitive to the choice of signs for the hyperfine and quadrupole coupling constants, the differences being much less than the estimated error of 5-10 G in locating the experimental line positions. Similarly, as already anticipated, the introduction of mercury hyperfine anisotropy into the calculations had only a minor effect on the results in comparison with the experimental uncertainty. On the other hand, the calculations were quite sensitive to the magnitude of the quadrupole coupling constant and values outside the range of 900 ± 50 MHz seem to be definitely excluded.

Although the signs of the hyperfine and quadrupole coupling parameters cannot be established from the results presented here, e^2Qq_z is taken to be negative since the quadrupole moment is positive[13] and the electric field gradient eq_z is negative as it is due to a single p_z electron.[9] The only published data with which to compare the value of e^2Qq_z obtained in this work is a nuclear quadrupole resonance study of mercuric chloride[14] which yielded an experimental value of 720 MHz. Allowing for the partially ionic character of the bonding in mercuric chloride, the latter value was used to predict a quadrupole coupling constant of -1000 MHz for a single p electron in the valence shell of mercury.[14] This is in good agreement with a tentative value of about 1100 MHz which has been estimated[15] from microwave studies on methyl mercuric chloride.[16] Thus the value of 900 MHz determined for CH_2HgCl in the present work can be considered reasonable in the light of these earlier results.

The mercury hyperfine coupling constants obtained here for CH_2HgCl are $^{199}A_\perp$ = 437 G and $^{201}A_\perp$ = 162 G, the former value being similar to the ^{199}Hg coupling of 439 G previously reported for CH_2HgBr.[4] There seems little reason to doubt that this mercury coupling arises mainly from spin polarization of the σ electrons in the C-Hg bond,[4] in which case the 6s spin density (calculated from $^{199}A_s$ = 12,000 G[12]) of 0.036 is negative. Accordingly, $^{199}A_\perp$ and $^{201}A_\perp$ have negative and positive signs, respectively, allowing for the signs of the magnetic moments. Assuming sp hybridization at mercury, the spin-polarization coefficient[5] becomes 0.072 which is considerably greater than the value of 0.022 reported for the CH_2PbMe_3 radical,[5] and even exceeds the coefficient of 0.043 for the unsubstituted methyl radical. Thus the degree of π-σ interaction appears to be unusually strong in the CH_2HgCl radical.

Finally, the value of $g_\perp$ (1.990) for the CH_2HgCl radical parallels the negative g-shifts from free-spin previously observed for the perpendicular spectra of the CH_2SnMe_3 and CH_2PbMe_3 radicals.[5] These latter results have been explained[5] in terms of a slight delocalization (1-2 percent) of the unpaired electron from the carbon 2p orbital into the vacant metal d(π) orbitals. A similar weak interaction is also plausible for the CH_2HgCl radical and might account for the low $g_\perp$ factor, although the contribution of the small spin density in the C-Hg σ orbital should also be considered in any detailed interpretation.

We thank Professor John Sheridan for his comments on the determination of the mercury-201 nuclear quadrupole coupling from microwave studies on methyl mercuric chloride. This work was supported by the U.S. Energy Research and Development Administration and this is Document No. ORO-2968-95.

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TABLE 1. - EXPERIMENTAL AND CALCULATED FIELD POSITIONS FOR PERPENDICULAR HYPERFINE COMPONENTS OF CH_2HgCl E.S.R. SPECTRA

Spectrum	Component[a]	Field Position/G	
		experimental	calculated[b]
^{even}Hg		3290	3288
^{199}Hg	$M_I = -1/2$	3050	3052
	$M_I = +1/2$	3489	3491
^{201}Hg	$M_I = +3/2$	2987	2980
	$M_I = +1/2$	3147	3135 (3141)[c]
	$M_I = -1/2$	3413	3415 (3421)[c]
	$M_I = -3/2$	3597	3583

[a] These are the central perpendicular components ($M_I(^1H) = 0$) of the ^1H triplets;

[b] calculated according to the microwave frequency $\nu = 9158$ MHz and the best-fit parameters $g_\perp = 1.990$, $A_\perp(^{199}Hg) = 437$ G, $A_\perp(^{201}Hg) = A_\parallel(^{201}Hg) = +162$ G, $e^2Qq_z = -900$ MHz; [c] $\Delta M_I = \pm 2$ transitions (see text).

CAPTION TO FIGURE

Figure 1. First-derivative e.s.r. spectrum of γ-irradiated polycrystalline methyl mercuric chloride recorded at 77 K after annealing to 133 K. The irradiation dose was 10 Mrad. The peak position of the central component in the main spectrum corresponds to a *g* factor of 1.990; the microwave frequency was 9158 MHz. The line positions of the perpendicular hyperfine components are marked below the spectrum; the assignment of the low-field lines indicated here as parallel features is discussed in the text.

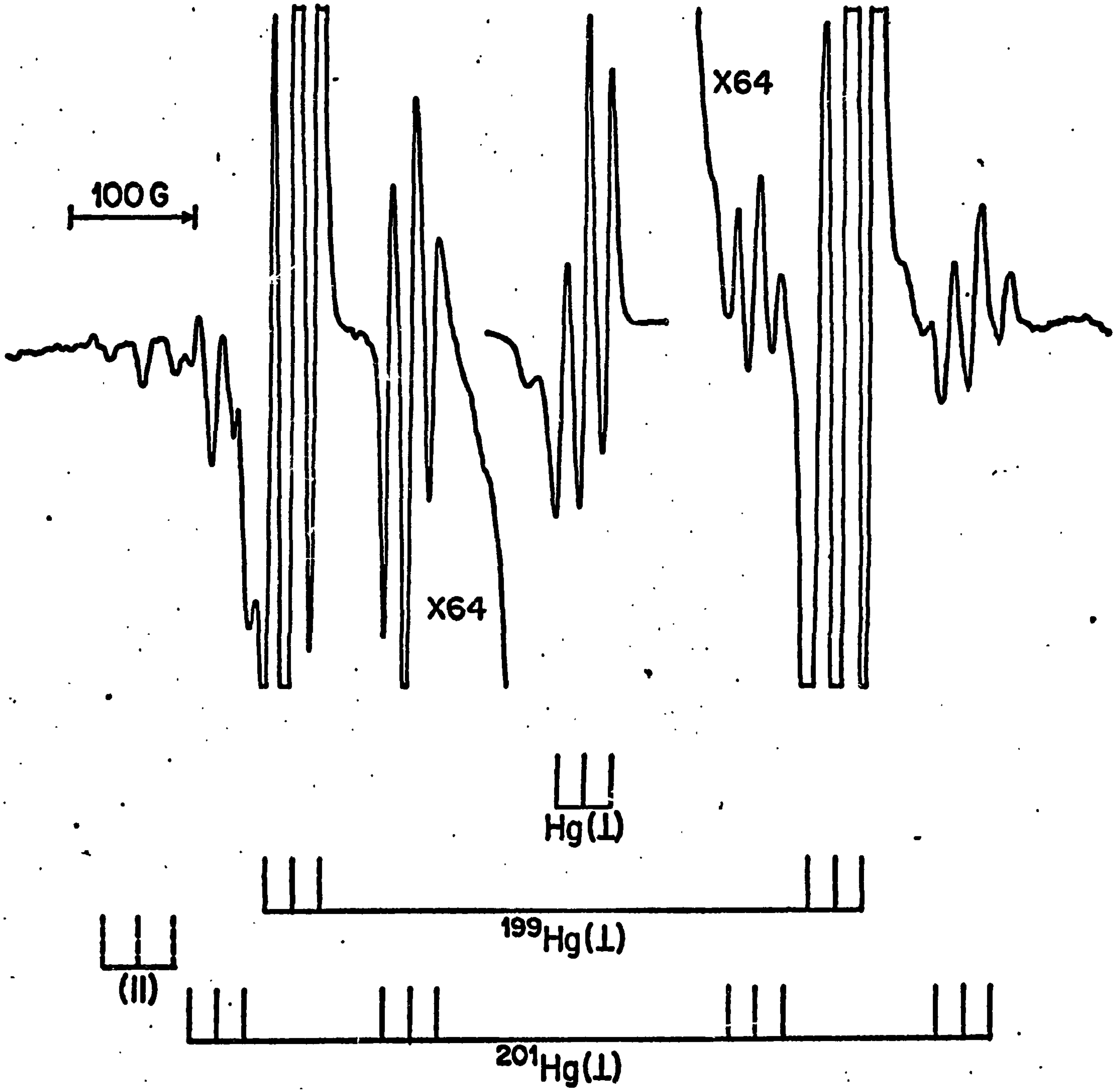

Figure 1. Kerr, Wargon, and Williams, "Mercury-201 Quadrupole Interaction......"

ELECTRON SPIN RESONANCE SPECTRA OF F_2NO AND F_3NO^-. A HYPERVALENT RADICAL FROM FIRST-ROW ELEMENTS

by

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ABSTRACT

The F_2NO and F_3NO^- radicals have been identified by means of their isotropic ESR spectra. Both radicals were generated by γ radiolysis of a solid solution of 5 mol % F_3NO in SF_6. The F_2NO spectrum shows a large ^{14}N hyperfine interaction ([illegible] = 93.3 G) and a fluorine coupling ($\underline{a}_F$ (2) = 143.8 G) indicative of a pyramidal radical analogous to the isoelectronic species, CF_3. The ESR parameters for F_3NO^- ($\underline{a}_N$ = 147 G, $\underline{a}_F$ (3) = 195 G, $\underline{g}$ = 2.014) are consistent with results obtained for radicals possessing thirty-three valence electrons derived from second-row elements. In particular, the large spin density (0.27) in the nitrogen 2s orbital is characteristic for this class of radicals and is predicted by INDO calculations based on either trigonal bipyramidal ($\underline{C}_s$) or $\underline{C}_{3v}$ geometry. The radiation chemistry and especially the large F_2NO/SF_5 signal intensity ratio are explained in terms of selective electron capture by F_3NO, the F_2NO and SF_5 radicals resulting from dissociation of the F_3NO^- and SF_6^- ions.

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Electron Spin Resonance Spectra of F_2NO and F_3NO^-.
A Hypervalent Radical from First-Row Elements[1]

Sir:

We wish to report the identification of the difluoronitroxide radical, F_2NO, and of the trifluoramine oxide radical anion, F_3NO^-, by ESR spectroscopy. The latter species is of particular interest because it represents the first example of a radical possessing thirty-three valence electrons derived solely from first-row elements, although the related phosphoranyl radicals PF_4[2] and Cl_3PO^-[3] are well established.

Recent work[4-7] has exploited the usefulness of the SF_6 matrix for isotropic ESR studies of trapped inorganic radicals, a technique first employed by Fessenden and Schuler.[2] In the present study, solid solutions containing 1 - 10 mol % trifluoramine oxide[8] in SF_6 were γ irradiated at -196° and the ESR spectra recorded at -170°. Optimum signal intensities for the F_2NO and F_3NO^- radicals relative to those of the SF_5 radical[2,9] were obtained from a 5 mol % solution irradiated for 0.3 Mrad.

The ESR spectrum shown in Figure 1 is dominated by a pattern consisting of a 1:2:1 triplet of 1:1:1 triplets with the central lines of the 1:2:1 triplets resolved into their two second-order components of equal intensity. This hyperfine structure is attributable to the interaction of the unpaired electron with two equivalent ^{19}F ($\underline{I} = 1/2$) nuclei and one ^{14}N ($\underline{I} = 1$) nucleus, the corrected ESR parameters being $\underline{a}_F$ (2) = 143.8 G, $\underline{a}_N$ = 93.3 G, and $\underline{g}$ = 2.0058 ± 0.0002.[10] Assignment of this spectrum to the F_2NO radical is based on the similarity of the ^{19}F coupling to the corresponding value of 142.4 G for the isoelectronic CF_3 radical in a xenon matrix,[11] and on the large ^{14}N coupling which is diagnostic of a pyramidal nitrogen-centered radical analogous to CF_3.[11] Moreover, the g factor is typical of those obtained for nitroxide radicals.[12] Finally, confirmation of the F_2NO identification was obtained through the detection of an identical ESR spectrum from a γ-irradiated solution of FNO in SF_6,[13] fluorine atom addition to the solute being expected on the basis of previous results.[2,4,6,7]

In addition to the lines from SF_5 and F_2NO, a family of weaker spectral components can be seen in Figure 1 under conditions of high gain. Starting from the wings, the well-resolved outer lines are easily grouped into two sets of 1:1:1 triplets whose individual spacings are in accord with the second-order shifts attributable to a ^{14}N interaction. Although some inner components of the spectrum are overlapped by the strong lines from the spectra of H, SF_5, and F_2NO, sufficient structural detail is present to analyse the pattern into a 1:3:3:1 quartet of ^{14}N triplets, each of the central lines from the quartets being resolved into two 1:2 second-order components, as shown in the stick diagram. The quartet hyperfine structure is interpreted in terms of coupling to three equivalent fluorines and the corrected ESR parameters are a_F (3) = 195 G, a_N = 147 G, and g = 2.014.

The identification of this second radical as F_3NO^- is strongly supported by the large value of a_N which corresponds to an unprecedented spin-density of 0.27 in the nitrogen 2s orbital. This is quite comparable to the spin densities in the central atom 3s orbitals of phosphoranyl and related radicals possessing fluorine ligands.[3,14] However, the equivalence of the three fluorines in F_3NO^- cannot be explained in terms of a trigonal bipyramidal (C_s) structure characteristic of phosphoranyl radicals unless there is rapid exchange of the fluorine ligands between the axial and equatorial sites of a fluxional radical. On the other hand, if F_3NO^- retains the $\underline{C}_{3v}$ symmetry of the parent molecule, the fluorines are always isotropically equivalent since the unpaired electron occupies an a_1 orbital composed largely from the antibonding combination of the nitrogen 2s and fluorine $2p_\sigma$ orbitals. INDO calculations for each of these geometries predict nitrogen 2s spin densities of 0.20 ($\underline{C}_s$) and 0.30 ($\underline{C}_{3v}$) which are reasonably close to the experimental value and they are also able to reproduce the approximate magnitude of the fluorine splitting. In contrast, the calculations for the radical cation F_3NO^+ with the expected $\underline{C}_{3v}$ symmetry indicate that most of the spin density now resides in an oxygen 2p orbital perpendicular to the $\underline{C}_{3v}$ axis, and the symmetry of the half-occupied MO excludes the direct participation of the nitrogen 2s orbital. Considering other possible species, the isotropic parameters reported recently for NF_3^+ [15] are quite different from those obtained here for F_3NO^-.

In conclusion, we note that the radiation chemistry of this system is consistent with F_2NO and F_3NO^- formation by electron capture reactions. ESR studies with a wide variety of solutes in SF_6 show that the SF_5 radical is generally the most abundant radical produced by radiolysis and its formation is thought to proceed by dissociative electron capture,[9,16] the undissociated species SF_6^- being produced in much smaller yield.[2,5,9] The present results are remarkable in terms of the large F_2NO/SF_5 intensity ratio indicating therefore that F_3NO competes very favorably with SF_6 for electron capture, although SF_6 is itself known to be an extremely efficient electron scavenger.[16] The high F_2NO/F_3NO^- ratio is explained if the dissociative path is favored, as seems to be the case for SF_6.

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pattern becomes typical of a highly anisotropic powder spectrum from a stationary radical. These results suggest that intramolecular motion, probably inversion coupled with rotation, is responsible for the nearly isotropic appearance of the F_2NO spectrum in a randomly oriented sample at -196°. An inversion barrier of only 0.064 kcal mol^{-1} has been calculated theoretically for the H_2NO radical (Y. Ellinger, R. Subra, A. Rassat, J. Douady, and G. Berthier, *J. Am. Chem. Soc.*, **97**, 476 (1975)).

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(13) An unidentified spectrum derived from an irradiated solution of NO in SF_6 was previously analyzed[2] as a ^{19}F doublet (a'_F = 187 G) of ^{19}F triplets (a_F (2) = 143 G). The spectrum of F_2NO would fit this description exactly if the central components of the ^{14}N triplets were masked by the usually more intense lines of SF_5 (see Figure 1) thereby converting the ^{14}N triplet interaction to an apparent doublet ($2a_N = a'_F$). Accordingly, a previous tentative assignment[9] to $ONSF_4$ can probably be discounted.

(14) F_3NO^- and the valence-isoelectronic species F_3SO (J. R. Morton and K. F. Preston, *J. Chem. Phys.*, **58**, 2657 (1973) and Ref. (2)) possess the same spin density in the central-atom *ns* orbital and the sums of the fluorine couplings are 585 G (F_3NO^-) and 555 G (F_3SO).

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CAPTION TO FIGURE

Figure 1. Second-derivative ESR spectra of a γ-irradiated solid solution of 5 mol % F_3NO in SF_6. The sample was irradiated at -196° and the spectra recorded at -170° immediately after irradiation. The lower spectrum was recorded at high gain to reveal the hyperfine components of the F_3NO^- radical anion which are much weaker than those of the SF_5 and F_2NO radicals shown in the upper spectrum.

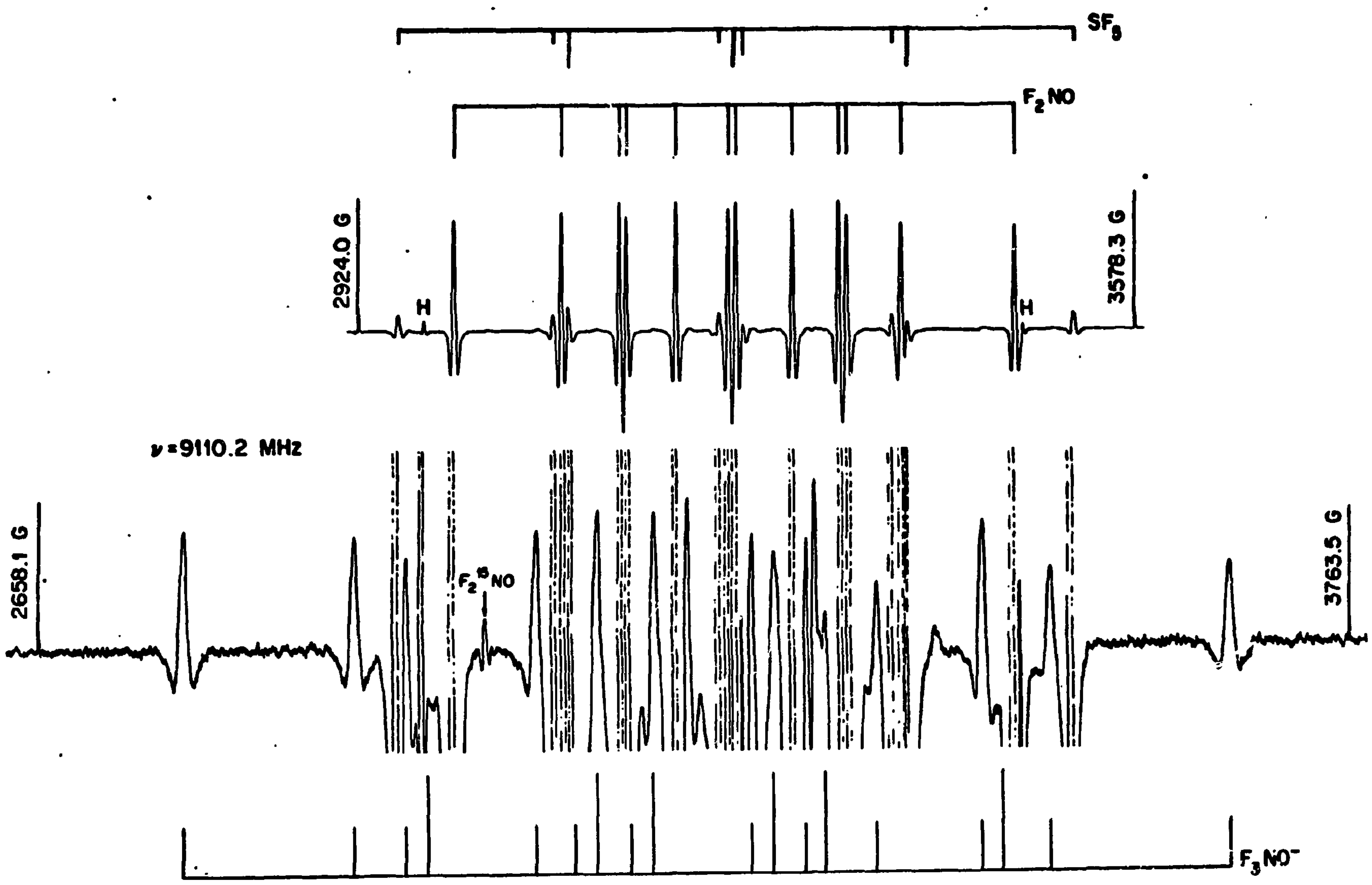

FIGURE 1. Nishikida and Williams

Detection of Thiyl Radicals by Spin Trapping in the Radiolysis of Liquids

By Jorge A. Wargon and Ffrancon Williams*

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Summary The e.s.r. spectra of thiyl nitroxides have been identified following the low-temperature radiolysis of alkanethiols containing *t*-BuNO as a radical trap. Thiyl radicals are also generated in the radiolysis of dimethyl sulphide and dimethyl disulphide.

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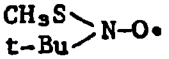
Although thiyl (RS•) radicals are thought to be important intermediates in mechanisms of radioprotection involving thiol compounds,[1] their unequivocal e.s.r. detection in radiolysis does not appear to have been achieved for two reasons. First, direct e.s.r. detection in the liquid state is considered highly improbable on account of the π - orbital degeneracy of these radicals,[2] and secondly, it was pointed out recently[3] that many of the solid-state e.s.r. spectra previously attributed to RS• radicals can be more reasonably assigned on the basis of their $\underset{\sim}{g}$ tensors to adduct radicals of the type $RS \overset{\bullet}{-} SR_2$. However, these limitations can be circumvented by the spin-trapping technique,[4] and here we report convincing e.s.r. evidence for the intermediacy of thiyl radicals in the liquid-phase radiolysis of compounds containing thiol, sulphide, and disulphide groups.

As in the previous study of methanol,[5] 2-methyl-2-nitrosopropane (t-BuNO) was used as the diamagnetic scavenger to produce long-lived nitroxide radicals at low temperatures. Solutions ($\sim 10^{-1}$ M) prepared by high-vacuum techniques were kept at room temperature before irradiation to allow for dissociation of the inactive t-BuNO dimer, the γ irradiations and subsequent e.s.r. observations being carried out in the range between -50° and -110° depending on the thermal stability of the derived nitroxides. N.m.r. studies[6] have shown that when t-BuNO solutions are cooled below room temperature, the monomer-dimer equilibrium is not rapidly attained and a high monomer concentration persists for much longer than the typical irradiation time (ca. 10 min) in these experiments.

The e.s.r. spectrum obtained after γ radiolysis of a methanethiol solution at -110° (see Figure) is dominated by a ^{14}N triplet of well-resolved 1:3:3:1 quartets indicating clearly that the trapped radical possesses three equivalent hydrogens. Assignment of this pattern to the methane-thiyl t-butyl nitroxide  $\begin{smallmatrix}CH_3S\\ \underline{t}\text{-}Bu\end{smallmatrix}\!>\!N\text{-}O\cdot$ is supported by the similarity of the e.s.r. parameters (a_N = 18.9 G, g = 2.0064) to those of the simple triplet spectrum generated by the u.v. photolysis of butane-1-thiol solutions and ascribed to the butane-1-thiyl t-butyl nitroxide (a_N = 18.5 G, g = 2.0071). The observation of the ^1H coupling for the methane-thiyl spin adduct, a_H (3) = 1.2 G, provides conclusive evidence for the identification. This coupling is comparable to the corresponding value of 1.4 G for the methoxyl radical adduct,[5] although the ^{14}N couplings and g factors for these S- and O- nitroxides differ appreciably, as expected.

In the radiolysis of several other alkanethiols at -110°, the corresponding thiyl nitroxide was produced almost exclusively in every case. However, irradiation at -70° gave additional weaker signals from mercaptoalkyl nitroxides suggesting the onset of secondary radical reactions at the higher temperature. The radiolysis of dimethyl sulphide and of dimethyl disulphide solutions resulted similarly in the trapping of methanethiyl radicals but in these systems there was also a signal of comparable intensity from the spin adduct of the methyl radical. The e.s.r. parameters for the thiyl nitroxides are summarized in the Table.

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(Received, August 1975; Com.)

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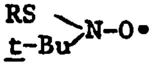
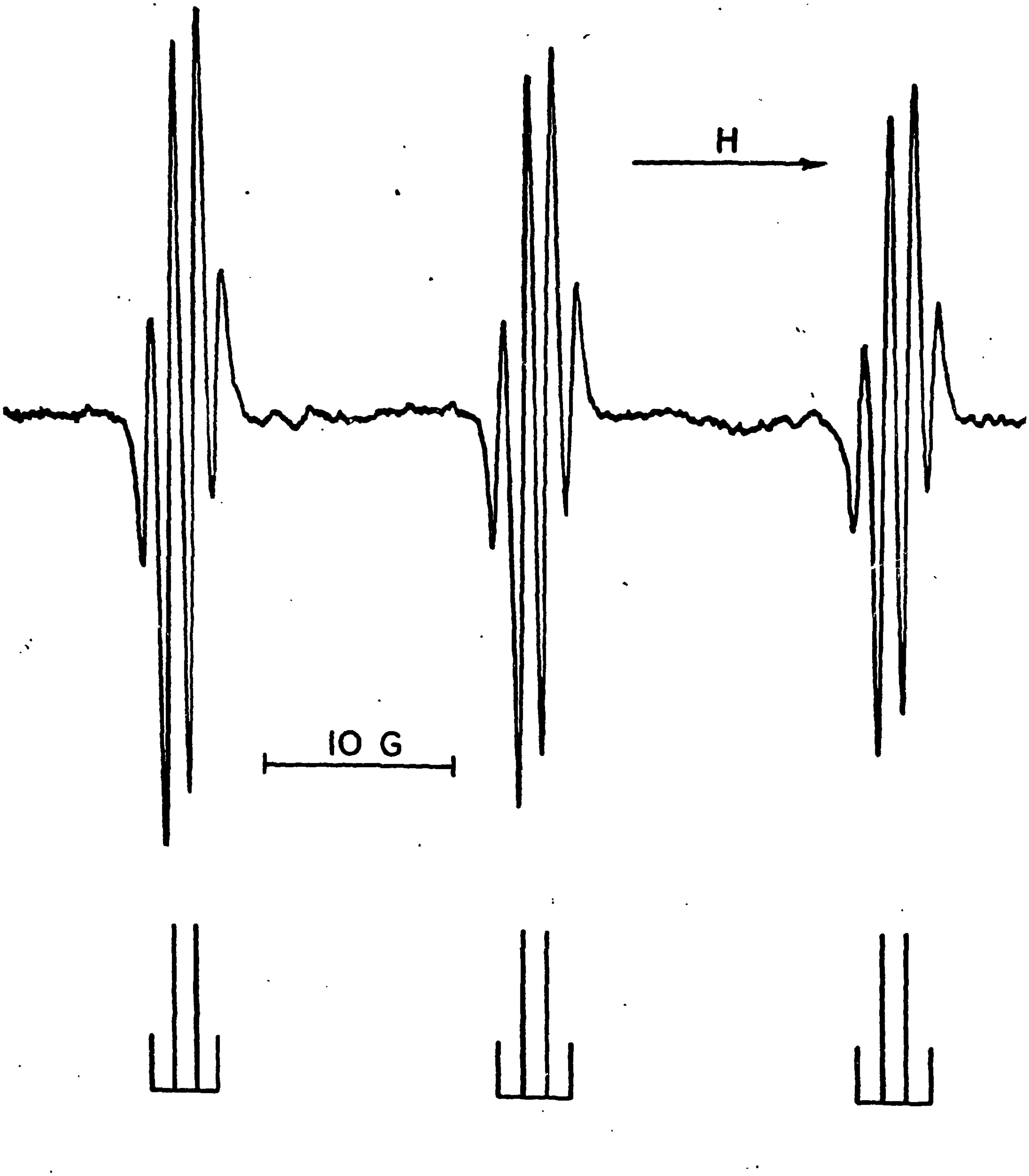
TABLE. Isotropic e.s.r. parameters for thiyl nitroxides 
$(RS)(t\text{-}Bu)N\text{-}O^{\bullet}$
generated by the radiolysis of the corresponding thiols (RSH) in the presence of *t*-BuNO.

Trapped Radical	Temp./°C	Hyperfine couplings/G		*g*
RS•		a_N	a_N (3)	
MeS•	-103	18.9	1.2	2.0064
EtS•	-92	17.4		2.0063
n-PrS•	-85	17.8		2.0063
i-PrS•	-97	16.7		2.0062
n-BuS•	-73	17.8		2.0063

FIGURE CAPTION

First-derivative e.s.r. spectrum of a γ-irradiated solution of methanethiol containing 0.05 M t-BuNO. The sample was irradiated for a dose of 0.07 Mrad at -110° and the spectrum recorded at -90°.



Wargon and Williams "Detection of Thiyl Radicals....."

Electron Spin Resonance Studies of γ-Irradiated Phosphite and Phosphate Esters: Identification of Phosphinyl, Phosphonyl, Phosphoranyl, and Phosphine Dimer Cation Radicals[1]

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ABSTRACT

The powder esr spectra of several γ-irradiated phosphorus esters at 77 K have been analyzed into their distinguishable radical components, each spectrum being generally a composite of anisotropic features from a number of alkyl and phosphorus-centered radicals. Resolution of overlapping spectra has been achieved in some instances by radiation-chemical experiments designed to suppress or enhance the products of electron capture relative to the radicals formed by other mechanisms. The identification of phosphorus-centered radicals is based on a number of criteria including the magnitude of the isotropic ^{31}P hfs which is highly characteristic for certain phosphoranyl radicals, the 3p/3s orbital ratio of phosphorus spin densities, and the results of chemical experiments. The radiation chemistry of dialkyl phosphites, $(RO)_2P(O)H$, is influenced by the ease with which the P-H bond in these compounds is broken, the principal radicals being the phosphonyl species $(RO)_2\dot{P}O$ and $RO\dot{P}(O)O^-$. Both of these species are thought to be the secondary products of hydrogen atom abstraction by the alkyl radical R• which is produced by dissociative electron capture. A similar primary step is shown to apply for the trialkyl phosphates, $(RO)_3PO$, but in this case only carbon-centered radicals are formed by secondary H-atom abstraction processes. Although the undissociated phosphoranyl radical anions are not detected in dialkyl phosphites, weak signals attributable to the corresponding anions are observed in trialkyl phosphates. Similarly, the phosphoranyl radical anion is tentatively identified in the spectrum of γ-irradiated dimethylacidpyrophosphate which also includes strong signals from methyl and phosphonyl radicals. The latter is thought to be formed by the loss of either the OH or the OMe group from the parent molecule rather than by scission of one of the P-O-P bridge bonds. Trialkyl phosphites,

$(RO)_3P$, yield a large number of radicals including the phosphinyl species $(RO)_2\dot{P}$ by dissociative electron capture, the dimer radical cation $(RO)_3P\text{-}P(OR)_3^{+}$, and the phosphoranyl radicals $R\dot{P}(OR)_3$ and $\dot{P}(OR)_4$ by alkyl and alkoxy radical addition. The related tetraethylpyrophosphite yields $\dot{P}(OEt)_2$ and a dimer radical cation again characterized by two anisotropically equivalent phosphorus atoms indicative of P-P bond formation. However, the results for the pyrophosphite differ from those for the trialkyl phosphites in showing the absence of alkyl radicals or their phosphoranyl adducts and the formation of the phosphonyl species $(EtO)_2\dot{P}O$, the latter being produced presumably by cleavage of the P-O-P bridge. The esr parameters for each of the four main groups of phosphorus-centered radicals are summarized and the electronic structures of these radicals are discussed briefly. The novel dimer radical cations can be considered strictly analogous to the positive-hole V_K centers formed in irradiated alkali halides; the unpaired electron in the former occupies a σ^* orbital localized between the two strongly electronegative phosphorus atoms, the valence-shell configuration at phosphorus being close to tetrahedral.

Introduction

The radiolysis of phosphate esters is relevant to radiobiology and to the use of these compounds as solvents in extraction processes for the separation of nuclear fuels from highly radioactive fission products. Despite these areas of interest, relatively little is known about the detailed radiation chemistry of simple organophosphorus compounds. A key practical finding[3] is that the radiolysis of liquid trialkyl phosphates in bulk or in aprotic solutions results in the formation of acidic esters which have deleterious effects on the efficiency of these solvents in extraction processes. If a similar non-aqueous reaction (i.e. a pseudo-hydrolysis) were to occur under radiobiological conditions resulting in the rupture of the phosphodiester linkage in the polynucleotide chain, such a direct mechanism of radiation damage would be of considerable significance. With this background of interest, we have turned to esr studies to obtain information about the possible intermediates which participate in the radiation chemistry of some simple organophosphorus compounds.

Esr studies on γ-irradiated single crystals[4-6] have provided definitive identification of and accurate parameters for a few phosphorus-centered radicals. These include the well-known species $\dot{P}O_3^{2-}$ [4] and $H\dot{P}O_2^{-}$ [5] in ionic crystals and the radicals $(C_6H_5)_2\dot{P}O$ [6a] and $C_6H_5\dot{P}(O)OH$[6b] from diphenyl phosphine oxide and phenylphosphinic acid, respectively. In each case the radical is formed as a result of the net loss of a hydrogen atom bonded to phosphorus from the parent anion or molecule. In addition, there have been numerous studies of γ-irradiated inorganic phosphate glasses,[7] but these have provided few unambiguous results as the only spectral features capable of yielding structural information are the anisotropic ^{31}P doublet features which in general are rather poorly resolved. The same limitations apply to previous studies of γ-irradiated organophosphorus compounds[8] in the glassy or polycrystalline state with the additional complication that several paramagnetic species are usually formed. However, the formidable problem of radical identification in these systems has been eased considerably by two recent developments. First, unambiguous esr spectra have become available for a variety of organic phosphonyl ($R_2\dot{P}O$) and phosphoranyl ($R_4\dot{P}$) radicals in solution[9-12] thereby providing accurate isotropic ^{31}P hfs constants which are frequently diagnostic of radical structure. Second, a simple general technique has been described[13] which in favorable cases allows the chemical resolution of a complex esr spectrum from a γ-irradiated solid into its individual radical components. This is done by carrying out radiation-chemical experiments to eliminate or enhance the paramagnetic species formed by the specific process of electron attachment.

In this and the following contribution, we report the results of a fairly detailed study of radiation damage to organophosphorus derivatives. In addition to identifying most of the radical products, we have established some mechanisms of formation through the use of competitive scavenging experiments. An attempt has also been made to relate the nature of the intermediates formed in the γ-irradiated solid at low temperature to the results of product analyses in the liquid-phase radiolysis of trialkyl phosphites and trialkyl phosphates.

Experimental Section

Materials and Sample Preparation. Dimethyl phosphite, diethyl phosphite, trimethyl phosphite, triethyl phosphite, trimethyl phosphate, triethyl phosphate, dimethyl methyl phosphonate, tetraethylpyrophosphite, and dimethylacidpyrophosphate were all obtained from the Aldrich Chemical Company and generally used as received. Samples of dimethyl phosphite and trimethyl phosphite purified by fractional distillation using a Nester-Faust spinning-band column gave esr results which were identical with those obtained from the corresponding untreated compounds. Methyl bromide was obtained in a lecture bottle from the Matheson Company and ethyl bromide (A.C.S. certified grade) was supplied by the Fisher Scientific Company; both of these materials were used as received. 2-Methyltetrahydrofuran (MTHF) was obtained from Eastman Organic Chemicals Company. It was washed with 1 N sodium hydroxide solution and then with water, after which it was dried with calcium sulfate. The compound was then distilled at atmospheric pressure using a Nester-Faust spinning-band column and the middle fraction retained at 87°C.

All the materials used were degassed by several freeze-pump-thaw cycles. With the exception of the high-boiling pyrophosphite and pyrophosphate compounds, the esters were dried and distilled on the vacuum line before sample preparation in 4 mm i.d. Suprasil tubes. Solutions of methyl or ethyl bromide (5-10 mol%) in the esters, and of the esters (ca. 10 mol%) in MTHF, were prepared with ca. 10% accuracy as previously indicated.[14] All samples were shock-cooled in liquid nitrogen and formed clear glasses. As esr tubes containing trimethyl phosphate, triethyl phosphate, and dimethyl methyl phosphonate frequently cracked on cooling, only limited studies on these compounds were carried out by this preparative technique and an alternative method was used in which glass beads were prepared by dropping degassed ester or solution into liquid nitrogen.

γ-Irradiations. Samples were irradiated at 77K in an AECL Gammacell-200 cobalt-60 source at a nominal dose rate of 0.45 Mrad hr^{-1}. Total doses of 0.1-0.3 Mrads were used for scavenging experiments involving observation of alkyl radicals whereas doses of 2-5 Mrads were required for observation of the broad spectra of phosphorus-centered radicals. In cases where it was desirable to compare the signal intensities from samples of a compound with and without an electron scavenger, these samples were always irradiated together to the same total dose.

Esr Measurements. At 77K these were made with the sample tubes contained in a liquid nitrogen dewar which extended into the sensitive region of the Varian V-4502 spectrometer cavity. For measurements at higher temperatures, the Varian V-4557 variable-temperature accessory was used with the appropriate controller. Experimental field positions for the esr transitions were determined by reference to the spectrum of the hydrogen atom present as an internal standard and to the spectrum of an aqueous solution of Mn^{2+} using a V-4532 dual-sample cavity. The g and hfs parameters were calculated from the experimental data by means of matrix diagonalization calculations on an ICL 1907 computer. This method gives more accurate results than the use of the Breit-Rabi formula which is only strictly applicable to calculations on isotropic spectra.[15,16] In particular it was found that for axially symmetric g and hfs tensors, the results obtained by the matrix diagonalization method differ appreciably from those obtained by the Breit-Rabi method in the values for

$g_{\|}$ and $g_{\perp}$. Essentially the Breit-Rabi correction overcompensates for the downfield second-order shifts in the positions of the parallel components, and conversely for the perpendicular components, resulting in corrected values of $g_{\|}$ and $g_{\perp}$ which are therefore too small and too large, respectively. As an illustration of this difference, $g_{\|}$ and $g_{\perp}$ for the radical $Me\dot{P}(OMe)_3$ in γ-irradiated trimethyl phosphite ($A_{\|}$ = 884 G, $A_{\perp}$ = 724 G) were calculated by the matrix diagonalization method to be 2.0021 and 2.0016, respectively, whereas the corresponding values obtained by a Breit-Rabi procedure are 1.9989 and 2.0041. As expected, the differences between the hfs parameters calculated by the two procedures are less pronounced, these being less than 1 G in the above example and therefore insignificant in comparison with the accuracy of the experimental data derived from powder spectra.

Results

Dimethyl and Diethyl Phosphite. We have reported briefly on the esr identification of phosphorus-centered radicals in these γ-irradiated compounds at 77K.[13] In the present paper we wish to deal more fully with the radiation-chemical significance of the work. As shown in Figure 1, the esr spectrum (A) of γ-irradiated diethyl phosphite $(EtO)_2P(O)H$ consists of overlapping anisotropic features positioned outside the hydrogen-atom doublet and a central spectrum which includes well-resolved lines from the ethyl radical for which the isotropic ^1H coupling of 27 G to the methyl hydrogens is diagnostic.[17] Since the outer features must originate from phosphorus-centered radicals, it is evident that the radiation chemistry of these compounds involves a variety of bond-breaking processes.

The resolution of the anisotropic outer features was accomplished by additional experiments involving glassy solutions of methyl bromide in the diethyl ester, and of the ester in 2-methyltetrahydrofuran (MTHF). These studies exploit the well-known properties of alkyl bromides as excellent electron scavengers[18] and of MTHF as a suitable matrix for the stabilization of anionic species by electron attachment.[14] Thus, it was anticipated that esr signals from the products of electron capture by the ester would be suppressed in the presence of methyl bromide but should appear clearly in the MTHF glass. As will now be described, the results are in keeping with these expectations.

In the spectrum B of Figure 1, careful inspection of the central spectrum reveals that the hfs of the 1:3:3:1 quartet with narrow lines is now 23 G and not 27 G as in spectrum A. Clearly, the methyl radical has been produced in the sample doped with methyl bromide, largely to the exclusion of the ethyl radical formed in the pure ester. In addition, the outer spectrum of the doped sample consists of only one ^{31}P doublet with lineshapes characteristic of axially symmetric hfs and g tensors. The complementary experiment in the MTHF glass shows (spectrum C) that a different ^{31}P doublet is produced as a result of electron capture, and comparison of all three spectra reveals that both of these ^{31}P doublets are superimposed on each other in the spectrum of the pure ester. Thus it is clear that the radical products from the radiolysis of the pure ester include the ethyl radical and a phosphorus-centered radical, both originating from electron capture, as well as another phosphorus-centered radical formed in comparable amount by some other process.

The esr parameters of the two phosphorus-centered radicals are listed in Table I. The radical having the larger anisotropic ^{31}P splittings is readily identified as the diethoxyphosphonyl radical $(EtO)_2\dot{P}O$ since the derived value of the isotropic hfs is in good agreement with that obtained for this radical in the liquid state.[9] For the other radical produced by electron capture, the $3\underline{p}/3\underline{s}$ ratio of orbital spin densities again is approximately 3, indicating that this radical is also a phosphonyl radical in which the phosphorus atom is tetravalent. The most reasonable assignment is to the species $EtO\dot{P}(O)O^-$ which can be regarded as a derivative of PO_3^{2-}. The isotropic ^{31}P coupling of 557 G lies below the range (597-697 G) found for this radical in salts of diethyl phosphoric acid.[19a] However, as observed for PO_3^{2-},[19b] the 3s spin density on phosphorus is markedly dependent on the nature of the associated cation,[19a] so the lower value obtained for $EtO\dot{P}(O)O^-$ in γ-irradiated organic glasses is probably attributable to the separation of the anion from its nearest cation by several solvent molecules.

Returning to the central portion of spectrum A in Figure 1, the spectrum of the ethyl radical is overlapped to some extent by broad lines which probably arise from the alkyl radical produced by the loss of a hydrogen atom from the CH_2 carbon of the ethyl group. While this radical may have been produced in part by secondary processes of hydrogen atom abstraction, the possibility of its direct formation in primary radiation-chemical processes cannot be excluded.

The results for dimethyl phosphite are entirely analogous to those obtained for diethyl phosphite, the esr spectra showing the formation of the corresponding phosphorus-centered radicals with almost identical esr parameters (Table I). Therefore, the size of the alkyl group appears to be of secondary importance in affecting the radiation chemistry of these compounds, and the fundamental processes are not confined to the alkyl groups alone.

Trimethyl and Triethyl Phosphite. Irradiation of trimethyl phosphite at 77K yields the complex esr spectrum A shown in Figure 2. The central spectrum is composed mainly of an anisotropic triplet ($\underline{A} \approx 20$ G) with a sharp center line and broad outer components. This pattern is typical of powder spectra for $\cdot CH_2X$ species,[17,20] and can be assigned to the $\cdot CH_2OP(OMe)_2$ radical. Although not evident in spectrum A, a very weak signal from the methyl radical quartet was detected when the spectrum was recorded immediately after irradiation.

The intense central triplet is flanked in spectrum A of Figure 2 by doublet features within the hydrogen-atom lines. The high-field component of this doublet has the form of a parallel feature but the shape of the low-field line appears to be distorted by the superposition of another resonance. This interpretation is verified by examining spectrum B of the sample doped with methyl bromide. In this case, the doublet signal as evidenced by the high-field feature is extremely weak in comparison with the low-field resonance whose assignment will be discussed subsequently. Confirmation of the doublet parallel features is provided by spectrum C of the MTHF glass where there is no distortion of the low-field line indicating the complete absence of the interfering resonance. Although the perpendicular features corresponding to this ^{31}P doublet ($\underline{A}_{||} = 269$ G) cannot be observed in these spectra, an analogous doublet having an almost identifical hfs for the parallel features ($\underline{A}_{||}$ = 280 G) is found to be associated with a very narrow hfs for the perpendicular features in the spectrum of γ-irradiated tetraethylpyrophosphite (see below). Thus, it seems likely that the perpendicular features are obscured in the present case by the other more intense resonances which are present near $\underline{g}$ = 2 in all three samples. The esr parameters of the inner doublet are also very similar to those (Table II) of the $\dot{P}(OEt)_2$ radical generated unambiguously from $ClP(OEt)_2$ by electron capture so these features are assigned to the dimethoxyphosphinyl radical $\dot{P}(OMe)_2$. The evidence showing that this radical is not produced in the sample doped with methyl bromide whereas it is formed in the MTHF glassy solution strongly suggests that $\dot{P}(OMe)_2$ is the product of a dissociative electron attachment reaction.

The region between the hydrogen-atom doublet and the broad outer features in spectrum $\underset{\sim}{A}$ of Figure 2 contains contributing signals from at least three phosphorus-centered radicals. The most prominent signal, which is the only one observed in this region in spectrum $\underset{\sim}{B}$ of the methyl bromide - doped sample, is assigned to the radical $Me\dot{P}(OMe)_3$ formed by the addition of the methyl radical to the parent ester. The esr parameters for this phosphoranyl radical are given in Table III, the derived isotropic ^{31}P hfs agreeing fairly well with the value reported for this radical in solution.[12] Analysis of the anisotropic signals positioned outside the hydrogen-atom lines in spectrum $\underset{\sim}{C}$ of the MTHF sample suggests that these other resonances consist of two anisotropic ^{31}P doublets with the approximate hfs parameters $\underline{A}_{||}$ = 730 G, $\underline{A}_{\perp}$ = 550 G and $\underline{A}_{||}$ = 830 G, $\underline{A}_{\perp}$ = 675 G. It is uncertain whether the weak lines in the corresponding portion of spectrum $\underset{\sim}{A}$ also belong to these doublets. In any event, the identities of the radicals responsible for these doublet spectra are not known.

Turning now to the broad outermost features in spectra A and B of Figure 2, these are assigned to the (1,+1) and (1,-1) components of a ^{31}P dimer spectrum. If this radical possesses two anisotropically equivalent phosphorus atoms, the complete spectrum should consist of two additional components in the central region resulting from the large second-order splitting of the $M_I = 0$ degenerate transition.[21] Although the (0,0) component is masked by the intense signal of the central triplet from the $\cdot CH_2OP(OMe)_2$ radical, the (1,0) component of the dimer spectrum is observed about 120-140 G downfield of the free-spin region and was previously described as the resonance superimposed on the low-field parallel feature of $\dot{P}(OMe)_2$ in spectrum A. Fortunately, this (1,0) component is completely exposed in spectrum B, the asymmetry of the line being attributable to the overlapping of the parallel and perpendicular features. Relative to the outer features, this line is much narrower leading to a marked enhancement of the signal height. All four components of this ^{31}P dimer spectrum have been observed in the single crystal spectra of γ-irradiated trimethyl phosphite[21] so this eliminates a possible alternative assignment of the downfield resonance to a singlet spectrum with a g factor of ca. 2.10. The dimer cation assignment is also supported by chemical evidence, the intensity of the spectrum being undiminished by predoping the glassy sample with electron scavengers. Consistent with this finding, the radical does not appear in the spectrum of the dilute MTHF glass. The esr parameters for this dimer cation $(MeO)_3P\text{-}P(OMe)_3^{+\bullet}$ and similar species are listed in Table IV.

On warming the γ-irradiated trimethyl phosphite sample above 100K, a slow decay of all the radicals was accompanied by the simultaneous growth of a spectrum assigned to the phosphoranyl radical $\dot{P}(OMe)_4$. This radical also decayed out above 110K. Its identification is based upon the good agreement between the derived isotropic values of the esr parameters (Table III) and the results obtained for tetra-alkoxyphosphoranyl radicals in solution.[10-12]

Additional electron scavenging experiments were carried out using solutions of ethyl bromide in trimethyl phosphite. A strong signal from the ethyl radical was detected after irradiation but it was not at all clear if the weak signal of the methyl radical ordinarily present in the spectrum of the γ-irradiated undoped ester had been suppressed in this case. Thus, it is difficult to say whether or not the methyl radicals are produced by electron capture in the irradiation of the bulk ester. Irrespective of the primary mechanism of methyl radical formation, the strength of the $Me\dot{P}(OMe)_3$ signal in the bulk material and its enhancement in samples containing methyl bromide combine to indicate that methyl radicals are formed in good yield by irradiation of the pure ester but that they add rapidly to the phosphite in the glassy state. In contrast to these results for glasses, irradiation studies on single crystals of trimethyl phosphite[21] provide evidence for a photobleachable intermediate which is thought to be the radical anion. These findings call attention to an important effect of phase on the stability of the trimethyl phosphite radical anion in solids.

Triethyl phosphite gave results almost parallel to the trimethyl compound on γ irradiation. The esr spectrum of the bulk material showed signals in the center from $\dot{C}_2H_4OP(OEt)_3$ and the ethyl radical (weak), strong lines due to $\dot{P}(OEt)_2$ and $(EtO)_3P\text{-}P(OEt)_3^{+\bullet}$, and features from several radicals in the intermediate region just outside the hydrogen atom doublet. Inclusion of methyl bromide resulted in the production of methyl radicals, although again it could not be determined whether the signal of the ethyl radical was affected; additional changes induced by the presence of an electron scavenger were a decrease in the yield of $\dot{P}(OEt)_2$ and the removal of all radicals except $R\dot{P}(OEt)_3$ in the intermediate region. It is likely that the spectrum assigned to $R\dot{P}(OEt)_3$ contains contributions from R = Me and Et since the esr parameters would be very similar.[10-12] Warming the bulk sample produced the same spectral changes over the same temperature range as for the trimethyl ester, although the amount of $\dot{P}(OEt)_4$ formed was less than that of $\dot{P}(OMe)_4$ in the methyl ester.

In comparison with the dialkyl phosphites, the trialkyl esters appear to be somewhat less efficient electron scavengers. Thus the MTHF solutions of trialkyl esters examined immediately after irradiation showed a faint blue color associated with solvent-trapped electrons whereas this was not observed in the MTHF solutions of dialkyl esters. Also the complementary behavior of samples containing alkyl bromide and MTHF solutions which so strongly characterized the results for the dialkyl phosphites is less pronounced in the case of the trialkyl phosphites. Of course, the greater variety of phosphorus-centered radicals produced in the latter compounds is attributable partly to the fact that compounds of trivalent phosphorus are excellent radical scavengers resulting in the formation of phosphoranyl radicals. Also contributing to the abundance of phosphorus-centered radicals in phosphites is the preferential formation of dimer cations in competition with other reactions of positive ions, such as proton transfer, which lead to carbon-centered radicals.

Tetraethylpyrophosphite. This compound $(EtO)_2POP(OEt)_2$ contains two trivalent phosphorus atoms and, not unexpectedly, its radiation chemistry bears a marked resemblance to that of triethyl phosphite, although the esr results for tetraethylpyrophosphite are apparently simpler. This can be seen from spectrum $\underset{\sim}{A}$ of the irradiated bulk material in Figure 3 which is analyzed in terms of three phosphorus-centered radicals as indicated by the stick diagrams. In addition, there is a weak underlying spectrum in the center thought to be mainly due to carbon-centered radicals produced by the net loss of a hydrogen atom. Ethyl radicals are not observed in this system.

The inner of the two ^{31}P doublets is clearly attributable to a phosphinyl radical on the basis of the ^{31}P hfs parameters. Two structures are possible, i.e. $\dot{P}(OEt)_2$ and $(EtO)_2PO\dot{P}OEt$. Although the electron scavenging studies do not discriminate between these possibilities, it is evident from the reduced intensity of the inner doublet in spectrum $\underset{\sim}{B}$ of the sample containing methyl bromide that the phosphinyl radical is formed predominantly via electron capture. The esr parameters listed in Table II are close to those of $\dot{P}(OEt)_2$ formed in γ-irradiated chlorodiethyl phosphite[22] and this assignment is further supported by the good agreement between the isotropic ^{31}P hfs and the value observed in solution studies of $\dot{P}(OEt)_2$.[23] Moreover, there is no suggestion of a secondary ^{31}P doublet splitting in the spectrum as might have been expected for the alternative species $(EtO)_2PO\dot{P}OEt$ by analogy to carbon-centered radicals possessing phosphorus atoms in a β position (see below). Thus it seems likely that $\dot{P}(OEt)_2$ is the phosphinyl radical produced from tetraethylpyrophosphite.

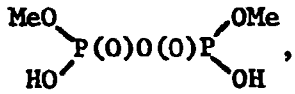
The doublet spectrum with the larger principal values of the ^{31}P hfs tensor can be definitely assigned to the diethoxyphosphonyl radical

$(EtO)_2\dot{P}O$ on the basis of the similarity of the esr parameters (Table I) to those of the same radical observed in γ-irradiated diethyl phosphite (see above) and in the liquid phase.[9] It might be noted that the formation of this radical is accompanied by a change from trivalent phosphorus in the neutral molecule to tetravalent phosphorus in the radical. Thus the unpaired electron is largely localized on phosphorus rather than on oxygen even though bond scission occurs in the β position relative to this phosphorus atom.

By analogy with the results for the trialkyl phosphites, the outermost features in spectrum A (Figure 3) belonging to the third phosphorus-centered radical are assigned to a dimer cation possessing two strongly coupled and anisotropically equivalent ^{31}P atoms by virtue of a three-electron (σ^*) P - P bond. As before, the spectrum should consist of four anisotropic components but only the (1,+1) and (1,-1) lines are visible in spectrum A. In spectrum B, however, the (1,0) component is partly resolved as a result of a reduction in the intensity of the overlapping doublet spectrum assigned to $\dot{P}(OEt)_2$. The (0,0) component should be located in the region near g = 2 but it is hidden by the considerably more intense signals from other radicals.

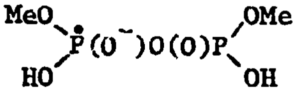
Inclusion of methyl bromide, as stated previously, has the effect of reducing the intensity of the phosphinyl radical spectrum whereas that of the phosphonyl radical and dimer cation spectra are hardly affected. The signal from methyl radicals, which is extremely weak in spectrum B, decayed rapidly on standing at 77K after γ irradiation and there are strong indications that two secondary radicals are formed. Superimposed on the perpendicular features of the $\dot{P}(OEt)_2$ radical in the central region of spectrum B is a quintet spectrum with an approximately binomial intensity distribution. This can be assigned to the $CH_3\dot{C}HOP(OEt)OP(OEt)_2$ radical produced as a result of hydrogen atom abstraction from the ester by methyl radicals. In addition, there are anisotropic features absent in spectrum A which partly overlap the doublet spectrum of the phosphonyl radical outside the lines of atomic hydrogen. These extra features are most reasonably assigned to the methyl radical adduct of tetraethylpyrophosphite. However, the anisotropic esr parameters given in Table III are intermediate between those of the tri- and tetra-alkoxyphosphoranyl radicals derived from trialkyl phosphites so the identification is provisional.

It is noteworthy that spectrum A of the undoped ester contains no contribution from the spectra of ethyl radicals or their adducts. This suggests that alkyl radicals are not produced from pyrophosphite esters in marked contrast with the results of radiation damage to the trialkyl phosphites. It appears, therefore, that the P-O-P linkage in the pyrophosphite plays a significant role in the radiation chemistry of this compound and this conclusion is further borne out by the formation of the phosphonyl radical in this system.

<u>Dimethylacidpyrophosphate</u>. In this molecule,  $^{MeO}_{HO}{>}P(O)O(O)P{<}^{OMe}_{OH}$, the P-O-P linkage occurs between tetravalent phosphorus atoms. This structural feature is also present in the biologically important compounds adenosine-di-phosphate and adenosine-tri-phosphate and often is referred to as the energy-rich bond in the phosphorylation cycle. Since previous studies of radiation damage to monophosphate esters[3,17,24,25] have shown the importance of de-esterification and the formation of carbon-centered radicals, it is of interest to see if such results are modified by the introduction of the pyrophosphate group.

The esr spectrum of the γ-irradiated bulk material at 77K is shown in the upper part of Figure 4. The central portion consists of overlapping signals from the methyl radical and the $\cdot CH_2OP\lessgtr$ radical formed by removal of a hydrogen atom from the methyl group of the parent molecule. Outside the hydrogen-atom doublet, the broad overlapping lines can be decomposed into the parallel and perpendicular features of two ^{31}P doublets, as indicated by the stick diagram. This analysis is helped by examination of the simpler spectrum $\underset{\sim}{B}$ recorded after warming the sample to 153K, the signals from the methyl radical quartet and the outer ^{31}P doublet having disappeared during the annealing process.

From the accurate ^{31}P hfs parameters of the inner doublet, as measured from spectrum $\underset{\sim}{B}$ and listed in Table I, the 3p/3s orbital hybridization ratio for the unpaired electron in this radical is found to be close to 3 suggesting an assignment to a phosphonyl radical. Conceivably, three species of this type could be formed by scission of one of the P-OR bonds (R = H, Me, MeOP(O)OH) in the parent molecule. The species containing one phosphorus atom, $MeO\dot{P}(O)OH$, is the protonated form of the radical $MeO\dot{P}(O)O^-$ believed to be formed in γ-irradiated dimethyl phosphite so it might be expected that the difference between the isotropic ^{31}P hfs of these two species would be comparable to the range of 80-110 G found for other phosphonyl radicals which exist as acid-base pairs ($\dot{P}O_3H^-$ and $\dot{P}O_3{}^{2-}$, $C_6H_5\dot{P}O_2H$ and $C_6H_5\dot{P}O_2{}^-$).[4-6] Although $\underset{\sim}{A}_{iso}$ for the species in question (756 G) exceeds that for $MeO\dot{P}(O)O^-$ (556 G), this being the order expected for this correlation, the difference is much larger than in the other known cases. Therefore the assignment must be left open to include the possibility that the phosphonyl radical is one of the forms containing two phosphorus atoms produced by loss of OH or OMe from the parent molecule.

The outer ^{31}P doublet in spectrum A of Figure 4 is most reasonably assigned to a phosphoranyl radical from both the magnitude of $\underline{A}_{iso}$ and the 3p/3s spin density ratio of ca. 2 derived from the experimental hfs parameters in Table I. The most likely candidate is the radical anion  $(MeO)(HO)\dot{P}(O^-)O(O)P(OMe)(OH)$ formed by electron capture but this proposal is tentative since no studies were made of the effect of electron scavengers on the phosphorus-centered radicals.

As reported earlier,[17] the methyl radicals are definitely formed in this system by a mechanism of dissociative electron capture paralleling the results obtained for the trialkyl phosphate. This conclusion was established by the use of ethyl bromide as a competitive electron scavenger. Outside the methyl radical quartet and the spectrum of the $\cdot CH_2OP\lessgtr$ radical which is discussed below, the center portion of the spectrum A in Figure 4 is flanked by weak doublet features separated by about 140 G. These are assigned to the formyl radical, $H\dot{C}O$. A weak signal from this radical was also noted in the spectrum of γ-irradiated trimethyl phosphate.[24]

The pattern in the central region of spectrum B in Figure 4 is solely attributable to the $\cdot CH_2OP\lessgtr$ radical. The most interesting feature of this spectrum is that the narrow $\underline{M}_I = 0$ component of the anisotropic triplet resulting from interaction with two equivalent α hydrogens in clearly split into a sharp doublet by the phosphorus. Careful examination of the broader low-field feature indicates a similar secondary splitting. This ^{31}P hfs of about 8G is evidently isotropic, as judged by the excellent resolution of the split central component, and is quite comparable to the average value of 10.4 G obtained for the analogous $\cdot CH_2OP(O)(OMe)_2$ radical in aqueous solution,[26] and to the $\underline{A}(^{31}P)$ of 7 G found for $CH_3\dot{C}HOPO_3Et^-$ in γ-irradiated silver diethyl phosphate at 250°K.[27] In contrast, a ^{31}P hfs of only 4 G was reported for the $\cdot CH_2OP(O)(OMe)_2$ radical in γ-irradiated trimethyl phosphate at 120K.[24] Despite the poorer resolution in the solid state, the difference has been ascribed[24] to a temperature-dependent conformational effect. However, a comparison of the spectra obtained for the bulkier radical in the present system at 77 and 153K (Figure 4) provides little indication that the ^{31}P hfs is strongly dependent on temperature in this range.

Trialkyl Phosphates. Independent esr studies by two groups of workers[17,25] have shown that the radiation-induced production of alkyl radicals in solid trialkyl phosphates is strongly affected by the incorporation of strong electron scavengers such as organic halides and nitrous oxide. Thus a mechanism of alkyl radical formation by dissociative electron capture is established for these compounds. Less attention has been devoted to the spectra of phosphorus-centered radicals in these γ-irradiated esters because the signals are comparatively weak making it difficult to resolve the individual spectra of the radical components. However, we have confirmed the presence of a ^{31}P doublet with the approximate parameters reported earlier ($\underline{A}_{\parallel}$ = 969 G, $\underline{A}_{\perp}$ = 814 G)[8] in the spectrum of γ-irradiated trimethyl phosphate subjected to large doses (>10 Mrad). This doublet was attributed[8] to the oxygen-centered radical $(RO)_2P(O)\dot{O}$ but the ^{31}P hfs parameters are clearly inconsistent with such an assignment, the values being quite similar to those of tetraalkoxyphosphoranyl radicals (Table III). Therefore, the radical structure is likely to be $\dot{P}(OMe)_4$ or $\dot{P}(O^-)(OMe)_3$, the latter species originating from electron capture. A recent report[28] suggests that overlapping ^{31}P doublets corresponding to both $\dot{P}(O^-)(OMe)_3$

and $\dot{P}(O)(OMe)_2$ are present in this system. However, the outer doublet attributed to the phosphoranyl radical appears to predominate, especially at lower doses.[8]

Dimethyl methyl phosphonate. As in the case of trimethyl phosphate, the esr spectrum of γ-irradiated dimethyl methyl phosphonate showed a strong signal from methyl radicals produced mainly by dissociative electron capture.[17] Although this suggests a similar reaction involving the ester groups, the possibility that some methyl radicals originate from a rupture of the $Me-P(O)(OMe)_2$ bond cannot be overlooked. Unfortunately, no detailed study was made of the phosphorus-centered radicals produced in the phosphonate and the radiation chemistry of compounds containing phosphorus-carbon bonds requires a separate investigation.

Electronic Structure of Phosphorus-Centered Radicals

The phosphorus radicals reported here have been classified together with previously known analogous species into four categories consisting of the novel phosphine dimer radical cations[21,31] and the well-established triad of phosphinyl, phosphonyl, and phosphoranyl radicals. The esr data for these groups of radicals are summarized in Tables I - IV. In a few instances these compilations also include measurements carried out on the same radical under different preparative conditions from those employed here. Bearing in mind that the outer features of the dimer radical cation spectra are separated by twice the ^{31}P hfc, examination of the esr parameters reveals that spectral differentiation is readily achieved between these four radical categories, except possibly between phosphonyl and phosphoranyl radicals. Even in this case, however, the p/s ratios of orbital spin densities on phosphorus differ significantly and there is no appreciable overlap between the ^{31}P doublet hfs parameters for the dialkoxyphosphonyl and the tri- (or tetra-) alkoxyphosphoranyl radicals considered here. Thus, radical identification on the basis of the esr parameters can be considered to be fairly reliable in these systems, especially when the assignments are supported by the results of chemical experiments as mentioned earlier.

Phosphinyl Radicals. This class is represented in this work (Table II) by the $\dot{P}(OMe)_2$ and $\dot{P}(OEt)_2$ radicals. The powder spectrum of $\dot{P}(OEt)_2$ in tetraethylpyrophosphite shows that the parallel and perpendicular components are widely separated and this evidence of a large ^{31}P hfs anisotropy for these radicals has been directly and quantitatively confirmed by recent studies on the $\dot{P}(OMe)_2$ species in a γ-irradiated single crystal of trimethyl phosphite,[33] the radical being produced in this case by photobleaching the precursor species thought to be the trimethyl phosphite radical anion. In considering the signs of the ^{31}P hfs tensor components, a negative rather than positive sign is preferred for $\underline{A}_{\perp}$ since this choice leads to $\underline{A}_{iso}$ in much better agreement with the result from solution studies.[23]

From these results it can be calculated (Table II) that the large ^{31}P hfs anisotropy of $\dot{P}(OEt)_2$ corresponds to a spin density of 0.95 in a phosphorus 3p orbital. Even allowing for some uncertainty in this value because of differences in the atomic parameter $2\underline{B}_0$ for phosphorus,[29] it is clear that the $\dot{P}(OR)_2$ species are π radicals with the unpaired electron largely concentrated on the phosphorus atom. The spin densities in the phosphorus 3s and 3p orbitals of $\dot{P}(OEt)_2$ are quite similar to those obtained for $\dot{P}F_2$[29] and $\dot{P}Cl_2$,[34,35] such results conforming to the Walsh MO description[36] of BAB radicals with 19 valence electrons. According to a simpler model which considers the phosphorus lone pair as a third ligand, four of the five valence electrons of phosphorus can be assigned to three sp^2 hybridized orbitals such that the O-P-O bond angle is not 180°, the additional unpaired electron occupying essentia the p orbital perpendicular to the molecular plane. In the MO description,[36] this π orbital is antibonding with respect to the corresponding ligand p orbitals and most of the spin density is localized on the central atom for the radicals of interest here. A similar structure was recently shown to apply for the 19-valence electron BAC radicals exemplified by $O\dot{Se}Cl$, $O\dot{S}Cl$ and $O\dot{S}Br$,[37] a change in the electronegativity of the outer atoms having only a relatively minor effect on the spin density distribution.

Phosphonyl Radicals. This work has furnished anisotropic esr parameters for the species $(RO)_2\dot{P}O$ and $RO\dot{P}(O)O^-$ derived from dialkyl phosphites (Table I). In each case the 3p/3s ratio of orbital spin densities is remarkably close to 3, thereby confirming the expected sp^3 tetrahedral configuration at the phosphorus atom for these radicals. The parameters are also very similar to those obtained for the prototype species $\dot{P}O_3^{2-}$ which has been studied exhaustively.[4,19,38] There appears to be a smaller total spin density on phosphorus in the free anionic species $RO\dot{P}(O)O^-$ as compared to the neutral radical $(RO)_2\dot{P}O$, and this can be interpreted in terms of an increase in the oxygen electronegativity on replacement of $-O^-$ by $-OR$. Since the unpaired electron occupies an antibonding MO distributed between phosphorus and oxygen atomic orbitals,[38] a greater effective electronegativity for oxygen should force more spin density on phosphorus, as observed. Unfortunately, the same trend of decreasing spin density on phosphorus with increasing negative charge is not clearly apparent from data on $EtO\dot{P}O_2^-$ and the th member of this series, $\dot{P}O_3^{2-}$,[19a] although it should be pointed out that this comparison is suspect since $\dot{P}O_3^{2-}$ and $EtO\dot{P}O_2^-$ were not observed in identical crystalline hosts.

As mentioned earlier, the 3*p*/3*s* ratio of spin densities on phosphorus remains essentially constant for the radicals $\dot{P}O_3^{2-}$, $RO\dot{P}(O)O^-$, and $(RO)_2\dot{P}O$. This is in contrast to the results obtained for the analogous series $\dot{P}O_3^{2-}$, $Ph\dot{P}O_2^-$, and $Ph_2\dot{P}O$ where the ratio increases markedly from 3 to 5.5,[6] the radical changing from a pyramidal to a more planar geometry with increasing substitution of oxyl (O^-) by the more electropositive phenyl groups. Since the spin density on phosphorus remains constant along the series, there is no spin delocalization into the phenyl groups and the tendency toward planarity may be attributed to the decrease in ligand electronegativity[39] as well as to the steric effects of the bulky phenyl groups.[6] Evidently the difference between the electronegativities of O^- and OR is too small to have any measurable effect on the geometry of the alkoxyphosphonyl radicals.

Phosphoranyl Radicals. The electronic structure of phosphoranyl radicals had recently been discussed in terms of a trigonal bipyramidal geometry with particular reference to the relatively large spin densities (*ca.* 0.3) which reside in the σ orbitals of the apical ligands when one or both of these sites are occupied by hydrogen or chlorine.[40] The present results summarized in Table III refer mainly to organophosphoranyl radicals with two apical alkoxyl groups for which it is not possible to obtain the ligand spin densities without the use of ^{17}O labeled compounds.[38] However, the anisotropic ^{31}P splittings have been analyzed in the usual way to give 3*s* and 3*p* spin densities on phosphorus and the most interesting result is the change in this spin distribution in going from $\dot{P}(OR)_4$ to $R\dot{P}(OR)_3$. Previous studies of isotropic spectra[10-12] have clearly established that ρ_{3s} decreases when an alkoxyl is replaced by an alkyl group, and this is confirmed by the present data which in addition show that this is accompanied by a corresponding increase in ρ_{3p}, the ρ_{3p}/ρ_{3s} ratio increasing from 1.9 for $\dot{\mathrm{P}}(\mathrm{OMe})_4$ to 2.4 for $\mathrm{Me}\dot{\mathrm{P}}(\mathrm{OMe})_3$.

The total spin density on phosphorus for these tri- and tetra-alkoxyphosphoranyl radicals is *ca.* 0.7 leaving a deficit of only 0.3, presumably shared between the apical ligand orbitals.[40] However, considering the various uncertainties in the determination of the phosphorus *p*-orbital contribution from a powder spectrum, the results should not be regarded as inconsistent with individual spin densities of *ca.* 0.25 in the apical positions. What does seem to be clear from this and previous work[40] is that a greater spin density resides in the phosphorus 3*p* orbital when organic ligands replace the more electronegative halogen atoms in the apical sites, and that this increase occurs partly at the expense of the spin density in the phosphorus 3*s* orbital.

Phosphine Dimer Radical Cations. For these novel centrosymmetric species,[21,31] almost the entire spin density is located on the two anisotropically equivalent phosphorus atoms, the ρ_{3p}/ρ_{3s} ratio being close to 2 in each case. Although these radicals have unit positive charge, their structure is best considered in terms of the electron-excess center which would be formed by electron addition to the hypothetical dipositive cation $\mathrm{YX_2\overset{+}{P}-\overset{+}{P}X_2Y}$ in which both of the positively charged and therefore highly electronegative phosphorus atoms are tetravalent with a closed-shell structure. Thus, the phosphine dimer radical cations are directly comparable to $\mathrm{Cl_2^-}$, the excess electron occupying a σ^* orbital between the two phosphorus atoms. Presumably this orbital is low-lying because it is formed between two highly electronegative centers.

Assuming to a first approximation that the extent of $\underline{s}$ admixture is the same for the σ and σ^* orbitals of the three-electron P-P bond in the dimer radical cation, the approximately $\underline{sp}^2$ hybridization for the orbital occupied by the unpaired electron suggests that the geometry about the $\underline{C}_3$ axis is more pyramidal than in the ideal tetrahedral $\underline{sp}^3$ structure. This is in marked contrast to the esr results[41] for the monomer radical cations PH_3^+ and PEt_3^+ where the phosphorus $3\underline{p}/3\underline{s}$ spin density ratios are 6.5 and 9.3, respectively, indicating that these monomer cations are considerably less pyramidal at phosphorus than their parent closed-shell molecules. A similar conclusion has been reached from studies of photoelectron spectroscopy.[42] Therefore it appears that the approximately tetrahedral configuration of the neutral $\ddot{P}X_3$ molecule is retained to a much greater degree in forming the dimer than the monomer radical cation.

Mechanisms of Radiation-Induced Reactions

A number of reviews have appeared in recent years on the radiation-induced reactions of phosphorus compounds.[43] In general, the emphasis has been largely confined to the study of gross chemical changes. Although some inferences have been made in regard to the reaction mechanisms, relatively little prior work has been concerned with the direct identification of intermediates. In this section we summarize the pattern of radical formation for each class of compounds, distinguishing where possible between primary and secondary elementary processes. The likely role of organophosphorus radicals in subsequent reactions leading to stable radiolysis products is also briefly discussed. For convenience, compounds of tricoordinate phosphorus are considered first.

Trialkyl Phosphites. In a γ-irradiated single crystal of trimethyl phosphite, the radical products consist uniquely of the dimer radical cation and a photobleachable species thought to be the monomer radical anion.[21]

$$P(OR)_3 \rightsquigarrow P(OR)_3^{+} + e^{-} \qquad (1)$$

$$P(OR)_3^{+} + P(OR)_3 \longrightarrow (RO)_3P\text{-}P(OR)_3^{+} \qquad (2)$$

$$P(OR)_3 + e^{-} \longrightarrow P(OR)_3^{-} \qquad (3)$$

This simple result is modified considerably when the compound is irradiated in the glassy state. In addition to the dimer radical cation, the major species identified in the glass include $\dot{P}(OR)_2$ and $R\dot{P}(OR)_3$ as well as the carbon-centered radical R'• formed by loss of a hydrogen atom from the parent compound. Although the radiation-chemical experiments clearly establish that $\dot{P}(OR)_2$ is formed by a dissociative electron attachment reaction, viz.,

$$P(OR)_3 + e^{-} \longrightarrow [P(OR)_3^{-}] \longrightarrow \dot{P}(OR)_2 + RO^{-} \qquad (4)$$

the other two neutral species must originate largely, if not entirely, from the secondary reactions of an alkyl radical as represented in (5) and (6).

$$R\bullet + P(OR)_3 \longrightarrow R\dot{P}(OR)_3 \qquad (5)$$

$$R\bullet + P(OR)_3 \longrightarrow RH + R'\bullet \qquad (6)$$

In fact, only a weak signal was observed for the alkyl radical R• itself, strongly suggesting that reactions (5) and (6) proceed rapidly in the glass at 77K. As a result of this complication, it proved impossible to establish whether or not the radical R• is formed by the dissociative electron-capture process (7). However, the complete absence of the dialkoxyphosphonyl radical

$$P(OR)_3 + e^- \rightarrow (RO)_2PO^- + R\cdot \qquad (7)$$

$(RO)_2\dot{P}O$ in this system appears to rule out the formation of alkyl radicals by homolytic scission of the carbon-oxygen bond in the parent compound.

The formation of the tetraalkoxyphosphoranyl radical $\dot{P}(OR)_4$ on annealing the glass is directly attributable to the addition of an alkoxy radical to trialkyl phosphite. Unfortunately, alkoxy radicals cannot be detected by esr in either the liquid or solid state unless the orbital angular momentum arising from the π-orbital degeneracy is quenched.[44] Even in the solid state where quenching is more likely to occur, an authentic spectrum for $RO\cdot$ radicals does not appear to have been reported.[45] In the absence of any positive identification, it is not clear whether an alkoxy radical is produced during irradiation and reacts only on annealing the matrix. Such behavior would be in marked contrast to the apparently high reactivity of alkyl radicals in bulk trialkyl phosphites at 77K. Moreover, it is known that the $\dot{P}(OMe)_4$ species is formed at 77K in a γ-irradiated solution of trimethyl phosphite in methanol,[31] the methoxy radical probably originating in this case from a primary ion-molecule reaction in the methanol.[46] Therefore it is conceivable that the formation of an alkoxy radical in bulk trialkyl phosphites occurs by secondary processes during annealing. Two possible examples of such processes are illustrated in reactions (8) and (9); the former is an electron

$$(RO)_3P\text{-}P(OR)_3^{+\cdot} + RO^- \rightarrow 2\ P(OR)_3 + RO\cdot \qquad (8)$$

$$R\dot{P}(OR)_3 \rightarrow RP(OR)_2 + RO\cdot \qquad (9)$$

transfer reaction resulting in charge neutralization and the latter involves the fragmentation of α-scission of the previously-identified phosphoranyl radical.

The radiolysis of trialkyl phosphites in the liquid phase leads to the formation of the corresponding trialkyl phosphates $(RO)_3PO$ and phosphonates $(RO)_2P(O)R$.[47] These products are easily accounted for in terms of the well-known reactions (10) and (11) involving the β-scission of the phosphoranyl radicals $\dot{P}(OR)_4$ and $R\dot{P}(OR)_3$.[10-12,48] Since the published

$$(RO)_3\dot{P}OR \longrightarrow (RO)_3PO + R\bullet \tag{10}$$

$$(RO)_2\dot{P}(OR)R \longrightarrow (RO)_2\dot{P}(O)R + R\bullet \tag{11}$$

_G_-values are close to 10,[47] a short chain reaction appears to be involved in each case. It should be noted, however, that the chain formation of trialkyl phosphate requires that the alkyl radical ejected in (10) be replaced by an alkoxy radical to yield $\dot{P}(OR)_4$ on subsequent addition to the trialkyl phosphite. Such a transformation would be represented by a combination of reactions (5) and (9).

It is less easy to rationalize the formation of dialkyl phosphites $(RO)_2P(O)H$ which have also been reported as one of the major radiolysis products of trialkyl phosphites.[47] Neither the dialkoxyphosphonyl radical $(RO)_2\dot{P}O$ nor phosphoranyl radicals with hydrogen ligands were detected in the present work although these species represent the most likely intermediates in any radical mechanism of dialkyl phosphite formation.

Tetraethylpyrophosphite. As expected, some of the radicals produced from $(EtO)_2POP(OEt)_2$ are similar or identical to those formed in triethyl phosphite. Both compounds yield dimer radical cations and $\dot{P}(OEt)_2$, these radicals being the products of positive ion and electron capture reactions, respectively. On the other hand, the absence in tetraethylpyrophosphite of ethyl radicals or of the phosphoranyl radical produced by ethyl radical addition is a major point of difference. Also, the diethoxyphosphonyl radical, $(EtO)_2\dot{P}O$, is formed only in the pyrophosphite.

The absence of ethyl radical formation suggests that electron capture by the pyrophosphite occurs by (12) to the exclusion of (13). This would also

$$(EtO)_2POP(OEt)_2 + e^- \longrightarrow (EtO)_2PO^- + \dot{P}(OEt)_2 \qquad (12)$$

$$(EtO)_2POP(OEt)_2 + e^- \longrightarrow (EtO)_2POP(O^-)(OEt) + Et\bullet \qquad (13)$$

explain why the yield of $\dot{P}(OEt)_2$ relative to the dimer radical cation is higher in tetraethylpyrophosphite than in triethyl phosphite, assuming that reaction (7) competes with (4) in the latter case. Thus it appears that the $>$P–O–P$<$ bridge bonds are dissociated preferentially following electron capture, although it must be emphasized that this conclusion depends crucially on our assignment of the phosphinyl radical spectrum to $\dot{P}(OEt)_2$ rather than to $EtO\dot{P}OP(OEt)_2$.

The phosphonyl radical $(EtO)_2\dot{P}O$ does not appear to be a product of ionic reactions. Since there is no evidence to suggest that it is formed in secondary radical reactions, a homolytic primary process may be involved. Irrespective of the mechanism, the fact that this radical is formed in the pyrophosphite but not in trialkyl phosphites indicates again that the $>$P–O–P$<$ structure is vulnerable to some form of radiation damage. A study of the stable radiolysis products would be of interest in this connection but we are not aware of any work along these lines.

Dialkyl Phosphites. These compounds of tetracoordinate phosphorus are characterized by weak P-H bonds such that hydrogen atom transfer reactions are common. One illustration relevant to our study is provided by the radical chain mechanism of phosphonate formation through the addition of olefins to dialkyl phosphites,[43b,48,49] reactions (14) and (15) constituting the essential propagation steps. In (15) the $(RO)_2\dot{P}O$ radical is

$$(RO)_2\dot{P}O + RCH{=}CH_2 \longrightarrow (RO)_2P(O)CH_2\dot{C}HR \tag{14}$$

$$(RO)_2P(O)CH_2\dot{C}HR + (RO)_2P(O)H \longrightarrow (RO)_2P(O)CH_2CH_2R + (RO)_2\dot{P}O \tag{15}$$

produced as a result of hydrogen atom abstraction by an alkyl radical and we shall now invoke similar reactions to explain some of our results.

Electron capture by a dialkyl phosphite can be considered to give initially the phosphoranyl radical anion $(RO)_2\dot{P}(O^-)H$ but since this intermediate was not detected under our conditions, it is assumed to dissociate spontaneously by β-scission to give the observed alkyl radical as represented in (16). The other observed radical product of dissociative electron capture

$$(RO)_2P(O)H + e^- \longrightarrow [(RO)_2\dot{P}(O^-)H] \longrightarrow RO(O)P(O^-)H + R\bullet \tag{16}$$

is considered to be the phosphonyl radical $RO\dot{P}(O)O^-$ and it is suggested that this species is formed by a subsequent hydrogen atom transfer between the products of (16), this reaction (17) occurring geminately. This simple scheme

$$RO(O)P(O^-)H + R\bullet \longrightarrow RO\dot{P}(O)O^- + RH \tag{17}$$

explains why the two radicals are always associated with an electron capture mechanism, even in the MTHF matrix. Moreover, it accounts for the absence of this phosphonyl radical when alkyl radicals are produced independently by the different electron capture process in glassy solutions of alkyl halides (Figure 1).

There is indirect evidence that the neutral dialkoxyphosphonyl radical $(RO)_2PO$ is formed by hydrogen atom abstraction from the parent molecule, as in reaction (18). Thus we find that the integrated signal intensity from

$$R\bullet \; + \; (RO)_2P(O)H \longrightarrow (RO)_2\dot{P}O \; + \; RH \qquad (18)$$

$(RO)_2\dot{P}O$ greatly exceeds that of the alkyl radical, even in the alkyl bromide solutions where a high yield of alkyl radicals would be expected in the absence of secondary reactions. All the results are explicable if most of the alkyl radicals produced initially in the dialkyl phosphites are converted by reactions (17) and (18) into the two phosphonyl radicals. Although it is concluded that secondary reactions such as (18) are mainly responsible for $(RO)_2\dot{P}O$ formation, a contribution from positive-ion processes, such as proton transfer from the parent ion, cannot be ruled out.

In a recent note,[50] Symons has reported the hfs parameters for a species derived from dimethyl phosphite and thought to be either of two phosphoranyl radicals, $(MeO)_2\dot{P}(O^-)H$ or $(MeO)_2\dot{P}(OH)H$. However, no details were given of the γ-irradiation conditions and his results may refer to methanol solutions of dimethyl phosphite which might well give the hydrogen-atom adduct. In any event we were unable to detect the species with the parameters reported by Symons[50] and, as already mentioned, our results are consistent with the dissociation of the dialkyl phosphite radical anion in aprotic solvents.

Trialkyl Phosphates. The esr results for trialkyl phosphates are unusually simple in that the main primary species which has been identified is the alkyl radical produced by dissociative electron capture. Only a weak signal was detected for the phosphoranyl radical thought to be either $\dot{P}(OR)_4$ or, more probably, the radical anion $(RO)_3\dot{P}O^-$. These results can be interpreted to mean that the radical anion is formed initially but that it has a high probability of undergoing fragmentation by β-scission with the ejection of an alkyl radical, as in reaction (19). The subsequent reactions of these alkyl

$$(RO)_3PO + e^- \longrightarrow (RO)_3\dot{P}O^- \longrightarrow (RO)_2P(O)O^- + R\cdot \qquad (19)$$

radicals appear to involve hydrogen atom abstraction from the neutral ester.[17]

The demonstration of reaction (19) affords an attractive mechanism to account for dialkyl phosphoric acid as a major radiolysis product of trialkyl phosphates.[3] However, the simultaneous formation of the monoalkyl phosphoric acid in about one-tenth the yield of the dialkyl phosphoric acid is not so readily explained by this mechanism unless the acid products are considerably more efficient than the neutral ester in capturing electrons. If this were the case, one would expect the yield of monoalkyl phosphoric acid to increase with irradiation dose but the available data[3,43] do not clearly reveal an effect of this sort.

A positive-ion mechanism was suggested earlier on the basis of mass-spectrometric data to explain the formation of alkyl phosphoric acids in the radiolysis of trialkyl phosphates.[3c] The essential feature of this mechanism is the decomposition of the closed-shell species $(RO)_3P^+OH$ by a series of dealkylation reactions to give protonated phosphoric acids of the general formula $(RO)_{\underline{n}}P^+(OH)_{4-\underline{n}}$ with $\underline{n} \leq 3$. The original precursor of these species is the parent radical cation $(RO)_3\overset{+}{\dot{P}}O\cdot$ which should have a powder esr spectrum similar to that of the isoelectronic species $\dot{P}O_4^{2-}$.[51] However, the radical cation was not detected in the present work and this could be due to the formation of $(RO)_3P^+OH$ by hydrogen atom abstraction from a neutral molecule. The frequent failure to detect radical cations in organic systems is undoubtedly due to the prevalence of such transfer reactions.

Dimethylacidpyrophosphate. The results are similar to those obtained for trimethyl phosphate insofar as the observation of the methyl radical, the $\dot{C}H_2OP\lessdot$ species, and a low yield of the $H\dot{C}O$ radical is concerned. However, only the pyrophosphate gives strong signals for phosphorus-centered radicals, two such species being produced. The radical having the larger ^{31}P couplings has been tentatively identified as the phosphoranyl radical anion. If this assignment is correct, the electron capture mechanism is analogous to (19) for trialkyl phosphates, the only difference being that the pyrophosphate radical anion is apparently more stable to β-scission at 77 K.

The most notable difference between the findings for the trialkyl phosphates and dimethylacidpyrophosphate is the formation of a phosphonyl radical in the latter compound. Although the assignment is not entirely unambiguous, the esr parameters tend to favor the radical produced by loss of OH or OMe from the parent molecule. In this connection it is interesting to note that the phosphonyl radical $EtO\dot{P}(O)O^-$ has been reported as a radiolysis product from certain salts of diethyl phosphoric acid,[19a,52] indicating that an alkoxyl group is lost more readily when the parent phosphate also possesses an OH group in either of its acidic or basic forms. Finally, while these esr results do appear to suggest that P-O-P bonds are less susceptible to radiation damage in the pyrophosphate than in the pyrophosphite, more evidence is clearly needed on this question before it can be answered definitively.

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(15) The calculation of esr parameters from spectra with large anisotropic hfs constants has been discussed by several authors. Solutions of the Hamiltonian which are pertinent to the present studies are given by B. Bleaney, *Phil. Mag.*, **42**, 441 (1951).

(16) To second order,[15] the downfield shifts of the esr transitions for a nucleus with $I = 1/2$ and an axially symmetric hfs tensor are given by $A_{\perp}^{2}/4H$ and $(A_{\parallel}^{2} + A_{\perp}^{2})/8H$ for the parallel and perpendicular components, respectively. More exact expressions can be readily derived from the basic results given by Horsfield *et al.*[4] Employing an obvious notation and assuming that $g_{\parallel}\beta_0$ and $g_{\perp}\beta_0$ each greatly exceed $g_N\beta_N$, the corrected positions of the low-field and high-field parallel transitions are given by the expressions,

$$H_0 - \frac{A_{\parallel}}{2} = \frac{H_1}{2} + \frac{H_1}{2}\left(1 + \frac{A_{\perp}^{2}\,g_{\perp}^{2}}{H_1^{2}\,g_{\parallel}^{2}}\right)^{1/2}, \text{ and}$$

$$H_0 + \frac{A_{\parallel}}{2} = \frac{H_2}{2} + \frac{H_2}{2}\left(1 + \frac{A_{\perp}^{2}\,g_{\perp}^{2}}{H_2^{2}\,g_{\parallel}^{2}}\right)^{1/2}$$

Similarly, we obtain for the corresponding perpendicular transitions,

$$H_0 - \frac{A_{\perp}}{2} = \frac{H_1}{2}\left\{1 + \left(\frac{A_{\parallel}g_{\parallel} - A_{\perp}g_{\perp}}{2H_1g_{\perp}}\right)^{2}\right\}^{1/2} + \frac{H_1}{2}\left\{1 + \left(\frac{A_{\parallel}g_{\parallel} + A_{\perp}g_{\perp}}{2H_1g_{\perp}}\right)^{2}\right\}^{1/2}, \text{ and}$$

$$H_0 + \frac{A_{\perp}}{2} = \frac{H_2}{2}\left\{1 + \left(\frac{A_{\parallel}g_{\parallel} - A_{\perp}g_{\perp}}{2H_2g_{\perp}}\right)^{2}\right\}^{1/2} + \frac{H_2}{2}\left\{1 + \left(\frac{A_{\parallel}g_{\parallel} + A_{\perp}g_{\perp}}{2H_2g_{\perp}}\right)^{2}\right\}^{1/2}$$

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TABLE I: Esr Parameters[a] of Phosphonyl Radicals

System	Radical	^{31}P hyperfine splittings $A_{\|\|}$	$A_{\perp}$	A_{iso}	$g_{\|\|}$	$g_{\perp}$	g_{iso}	ρ_{3s}[b]	ρ_{3p}[b]	ρ_{3p}/ρ_{3s}	Reference
$(MeO)_2P(O)H$	$(MeO)_2\dot{P}O$	795	630	685	1.999	2.001	2.001	0.188	0.534	2.84	This work
$(MeO)_2P(O)H$/MeBr	$(MeO)_2\dot{P}O$	794	627	683	2.001	2.002	2.002	0.188	0.539	2.87	This work
$(MeO)_2P(O)H$	$(MeO)_2\dot{P}O$	803	632	689	2.023	2.027	2.026				8[c]
uv/$(MeO)_2P(O)H$/ t-BuOO-t-Bu	$(MeO)_2\dot{P}O$			700			2.004				9
$(EtO)_2P(O)H$	$(EtO)_2\dot{P}O$	784	614	671	2.001	2.000	2.001	0.184	0.549	2.98	This work
$(EtO)_2P(O)H$	$(EtO)_2\dot{P}O$	784	615	671	2.023	2.027	2.026				8[c]
uv/$(EtO)_2P(O)H$/ t-BuOO-t-Bu	$(EtO)_2\dot{P}O$			687			2.005				9
$(EtO)_2POP(OEt)_2$	$(EtO)_2\dot{P}O$	777	611	667	2.002	2.002	2.002	0.183	0.534	2.92	This work
$(MeO)_2P(O)H$/MTHF	$MeO\dot{P}(O)O^-$	649	510	556	1.999	2.002	2.001	0.153	0.452	2.95	This work
$(EtO)_2P(O)H$/MTHF	$EtO\dot{P}(O)O^-$	651	510	557	2.002	2.001	2.001	0.153	0.452	2.95	This work
$(Na^+)_2HPO_3^{2-}\cdot 5H_2O$	$\dot{P}O_3^{2-}$	702.5	540.5	594.5	1.9994	2.001	2.000	0.163	0.524	3.22	4[d]
(MeO)(HO)P(O)O (O)P(OH)(OMe)	(RO)$\dot{P}$(O)O[e] (O)P(OH)(OMe)	868	685	746	2.002	1.999	2.000	0.205	0.592	2.89	This work[e]

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[a] ^{31}P hyperfine splittings in gauss; A and g values obtained in this work have been corrected for second-order effects using a matrix diagonalization method; the estimated experimental errors are ±5 G and ±0.002.

[b] Spin densities in 3s and 3p orbitals of phosphorus calculated using A_0 = 3640G and $2B_0$ = 206 G, respectively, and taking the signs of the ^{31}P hfs tensor components as positive.

[c] The magnitudes of the g factors suggest that the parameters are uncorrected for second-order effects.

[d] Hyperfine splittings converted from values in MHz given in Ref. 4.

[e] These are the parameters obtained from spectrum B of Figure 4; the radical identification (R = H or Me) is tentative (see text).

TABLE II: Esr Parameters[a] of Phosphinyl Radicals

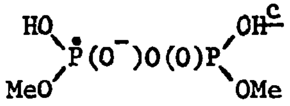
System	Radical	^{31}P hyperfine splittings $A_{\parallel}$	$A_{\perp}$	A_{iso}	$g_{\parallel}$	$g_{\perp}$	g_{iso}	ρ_{3s}[b]	ρ_{3p}[b]	ρ_{3p}/ρ_{3s}	Reference
$(\mathrm{MeO})_3\mathrm{P/MTHF}$	$\dot{\mathrm{P}}(\mathrm{OMe})_2$	269			2.002						This work
$(\mathrm{EtO})_3\mathrm{P/MTHF}$	$\dot{\mathrm{P}}(\mathrm{OEt})_2$	269			2.002						This work
$(\mathrm{EtO})_2\mathrm{PCl/MTHF}$	$\dot{\mathrm{P}}(\mathrm{OEt})_2$	277			2.002						22
$(\mathrm{EtO})_2\mathrm{PCl}$	$\dot{\mathrm{P}}(\mathrm{OEt})_2$	278	-15[c]	83	2.001	2.002	2.002	0.023	0.948	41.5	22
$(\mathrm{EtO})_2\mathrm{POP(OEt)}_2$	$\dot{\mathrm{P}}(\mathrm{OEt})_2$	280	-12[c]	85	2.002	2.002	2.002	0.023	0.945	40.5	This work
uv/$(\mathrm{EtO})_2\mathrm{PP(OEt)}_2$/ *t*-BuOO-*t*-Bu	$\dot{\mathrm{P}}(\mathrm{OEt})_2$			78.5			2.002				23
$\mathrm{PF_3/Xe}$	$\dot{\mathrm{P}}\mathrm{F}_2$	308.1	-27.2	84.6	2.0027	2.0016	2.0020	0.023	1.085	46.8	29
$\mathrm{PF_3/C_2F_6}$	$\dot{\mathrm{P}}\mathrm{F}_2$			81.3			1.9994				30
uv/$\mathrm{PF_2Cl}$	$\dot{\mathrm{P}}\mathrm{F}_2$			82.0			1.9997				30

[a] ^{31}P hyperfine splittings in gauss and *g* factors obtained in this work have been corrected in cases when the parallel and perpendicular components were both observed; the corrections were made according to the simple second-order equations given in footnote 16. The estimated experimental errors in the hfs and g factors are ± 5 G and ± 0.002.

[b] Spin densities in 3*s* and 3*p* orbitals of phosphorus calculated using A_0 = 3640 G and $2B_0$ = 206 G, respectively.

[c] Negative sign is assumed for $A_{\perp}$ since this leads to a value of A_{iso} in better agreement with that obtained directly from the spectrum of the radical in solution (Ref. 23).

TABLE III: Esr Parameters[a] of Phosphoranyl Radicals

System	Radical	^{31}P hyperfine splittings									Reference
		$A_{\parallel}$	$A_{\perp}$	A_{iso}	$g_{\parallel}$	$g_{\perp}$	g_{iso}	ρ_{3s}[b]	ρ_{3p}[b]	ρ_{3p}/ρ_{3s}	
$(MeO)_3P$	$Me\dot{P}(OMe)_3$	879	719	773	2.002	2.000	2.001	0.212	0.515	2.43	This work
$(MeO)_3P/MeBr$	$Me\dot{P}(OMe)_3$	884	724	778	2.002	2.001	2.001	0.214	0.515	2.41	This work
uv/$(MeO)_3P$/ MeN=NMe/c-C_6H_{12}	$Me\dot{P}(OMe)_3$			783.1			2.003				12
$(EtO)_3P$	$Et\dot{P}(OEt)_3$	876	721	773	2.001	1.999	2.000	0.212	0.500	2.36	This work
$(EtO)_3P/MeBr$	$Et\dot{P}(OEt)_3$	886	728	781	2.000	1.999	1.999	0.215	0.510	2.37	This work
$(EtO)_2POP(OEt)_2/MeBr$	$Me(EtO)_2\dot{P}OP(OEt)_2$[c]	937	764	822	1.998	2.001	2.000	0.226	0.558	2.47	This work
$(MeO)_3P$	$\dot{P}(OMe)_4$	967	825	873	2.001	2.000	2.000	0.240	0.456	1.90	This work
$(MeO)_3P/MeOH$	$\dot{P}(OMe)_4$	990	840	890				0.245	0.485	1.98	31
$(MeO)_3PO$	$\dot{P}(O^-)(OMe)_3$	969	814	866	2.035	2.040	2.038				8[d] [e]
$(MeO)_3PO$	$\dot{P}(O^-)(OMe)_3$	970	805	860				0.236	0.534	2.26	28
$(EtO)_3P$	$\dot{P}(OEt)_4$	963	817	866	2.003	2.002	2.002	0.238	0.471	1.98	This work
uv/$(EtO)_3P$/EtOOEt/ c-C_6H_{12}	$\dot{P}(OEt)_4$			884.5			2.003				12
$(EtO)_3PO$	$\dot{P}(O^-)(OEt)_3$	975	825	875	2.035	2.040	2.038				8[d] [e]
Dimethylacid-pyrophosphate	 $(HO)(MeO)\dot{P}(O^-)O(O)P(OH)(OMe)$[c]	1252	1063	1126	2.002	2.000	2.001	0.309	0.612	1.98	This work
Phenacite $(Be^{2+})_2SiO_4^{4-}/PO_4^{3-}$	$\dot{P}O_4^{4-}$	1242	1113	1156				0.318	0.418	1.31	32

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[a] ^{31}P hyperfine splittings in gauss; A and g values reported in this work have been corrected for second-order effects using a matrix diagonalization method; the estimated experimental errors are ±5 G and ±0.002.

[b] Spin densities in 3s and 3p orbitals of phosphorus calculated using A_0 = 3640 G and $2B_0$ = 206 G, respectively, and taking the signs of the ^{31}P hfs tensor components as positive.

[c] Radical assignment is tentative (see text).

[d] The magnitudes of the g factors suggest that the parameters are uncorrected for second-order effects,

[e] Radical assignment differs from that $((RO)_2P(O)\dot{O})$ given in Ref. 8.

TABLE IV: Esr Parameters[a] of Phosphine Dimer Radical Cations

	Radical Cation	^{31}P hyperfine splittings									
System	$YX_2P{-}PX_2Y^{+\bullet}$	$A_{\parallel}$	$A_{\perp}$	A_{iso}	$g_{\parallel}$	$g_{\perp}$	g_{iso}	ρ_{3s}[b]	ρ_{3p}[b]	ρ_{3p}/ρ_{3s}	Reference
$(MeO)_3P$	X = Y = OMe	727	619	655	1.998	2.000	2.000	0.180	0.350	1.94	This work
$(MeO)_3P/MeBr$	X = Y = OMe	731	622	658	1.999	2.001	2.000	0.181	0.354	1.96	This work
$(MeO)_3P/MeOH$	X = Y = OMe	720	615	650				0.179	0.340	1.90	31
$(EtO)_3P$	X = Y = OEt	726	618	654	2.000	2.000	2.000	0.180	0.350	1.94	This work
$(EtO)_3P/MeBr$	X = Y = OEt	721	615	650	1.997	1.999	1.998	0.179	0.345	1.93	This work
$(EtO)_2POP(OEt)_2$	X = OEt Y = $OP(OEt)_2$	742	631	668	2.005	2.000	2.002	0.184	0.359	1.95	This work
$(EtO)_2POP(OEt)_2/MeBr$	X = OEt Y = $OP(OEt)_2$	737	633	667	1.999	1.998	1.998	0.183	0.340	1.86	This work

[a] ^{31}P hyperfine splittings in gauss; A and g values reported in this work have been corrected for second-order effects using a matrix diagonalization method; the estimated experimental errors are ±5 G and ±0.002.

[b] Spin densities in 3s and 3p orbitals of phosphorus calculated using A_0 = 3640 G and $2B_0$ = 206 G, respectively, and taking the signs of the ^{31}P hfs tensor components as positive.

FIGURE CAPTIONS

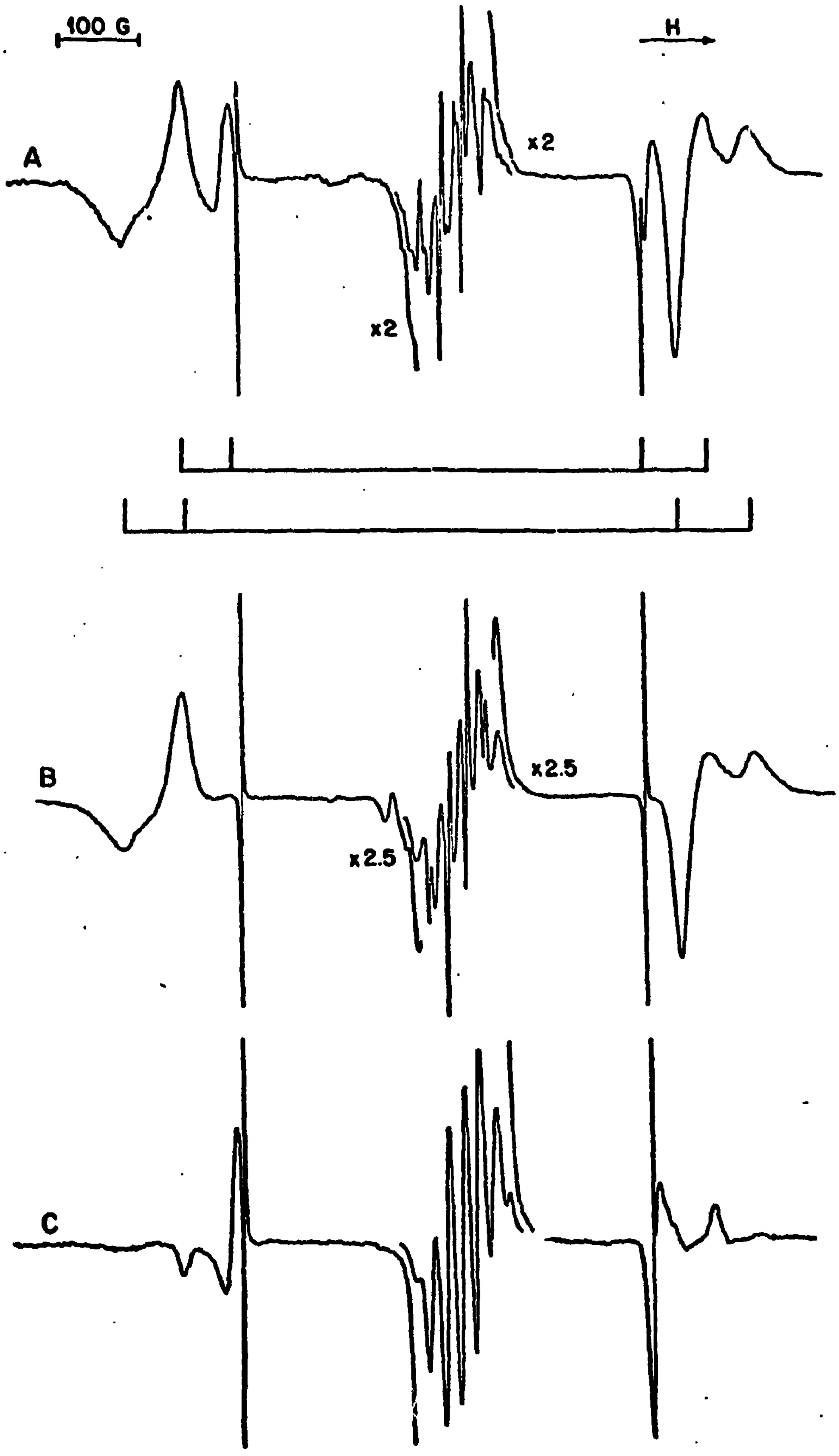
Figure 1. Esr spectra of γ-irradiated diethyl phosphite glasses at 77 K: A, diethyl phosphite; B, diethyl phosphite doped with 8 mol % methyl bromide; C, 10 mol % solution of diethyl phosphite in MTHF. The stick diagrams under spectrum A indicate the parallel and perpendicular doublet features of $EtO\dot{P}(O)O^-$ and $(EtO)_2\dot{P}O$. The signal in the central portion of spectrum C (attenuation factor of 10) is due to solvent radicals. The hydrogen-atom doublet is present in these and most of the spectra shown in the following figures.

Figure 2. Esr spectra of γ-irradiated trimethyl phosphite glasses at 77 K: A, trimethyl phosphite; B, trimethyl phosphite doped with 6 mol % methyl bromide; C, 10 mol % solution of trimethyl phosphite in MTHF. The stick diagrams under spectrum B refer to the anisotropic features from the doublet and second-order triplet spectra of $Me\dot{P}(OMe)_3$ and $(MeO)_3P\text{-}P(OMe)_3{}^+$, respectively.

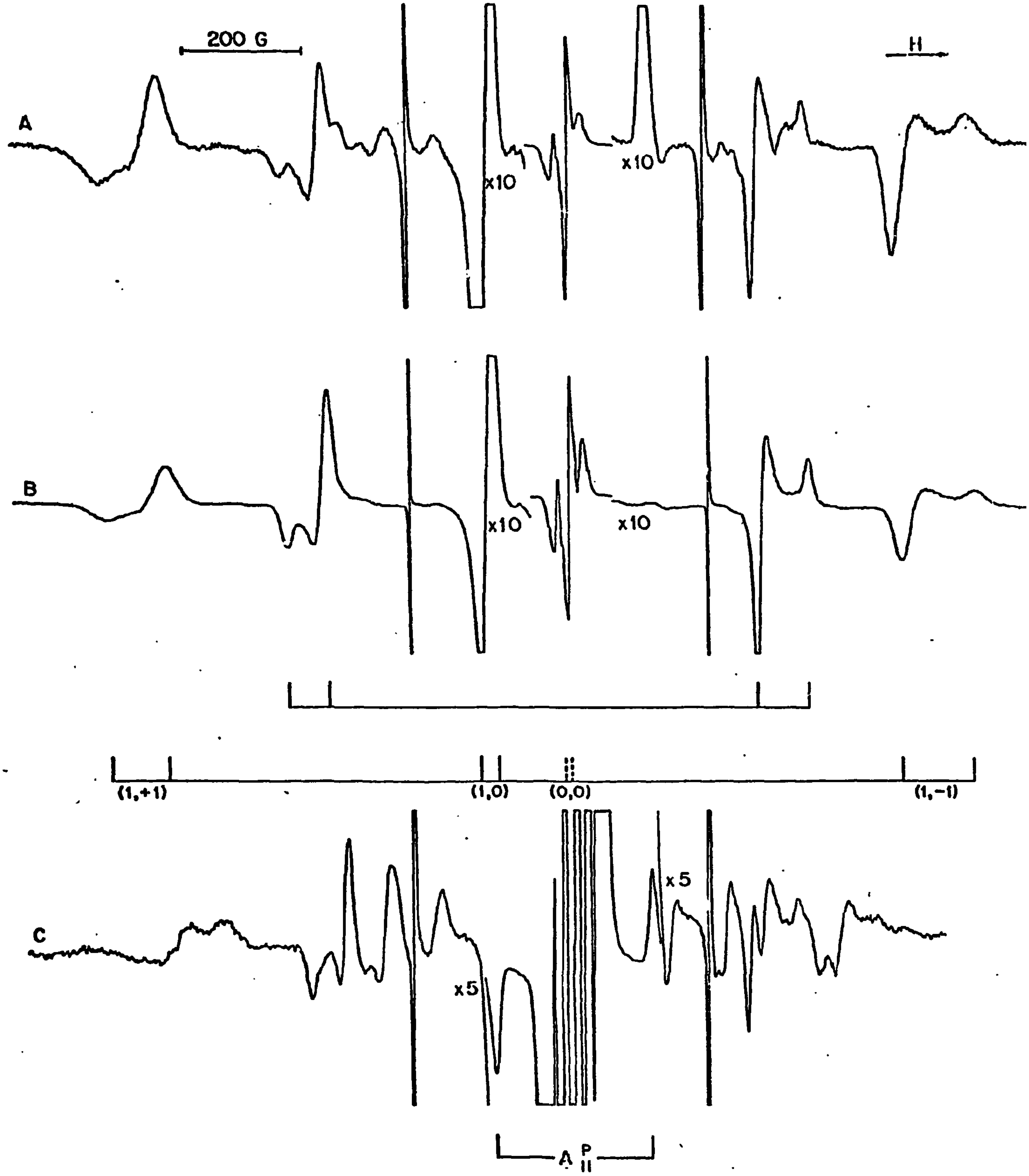
Figure 3. Esr spectra of γ-irradiated tetraethylpyrophosphite samples at 77 K: A, tetraethylpyrophosphite; B, tetraethylpyrophosphite doped with 8 mol % methyl bromide. The stick diagrams under spectrum A refer to the anisotropic features of $\dot{P}(OEt)_2$ (inner doublet), $(EtO)_2\dot{P}O$ (outer doublet), and $[(EtO)_2POP(OEt)_2]_2{}^+$ (second-order triplet).

Figure 4. Esr spectra of γ-irradiated dimethylacidpyrophosphate: A, at 77 K; B, recorded at 153 K after warming sample from 77 K. The stick diagrams under spectrum A refer to the anisotropic features of the phosphoranyl and phosphonyl

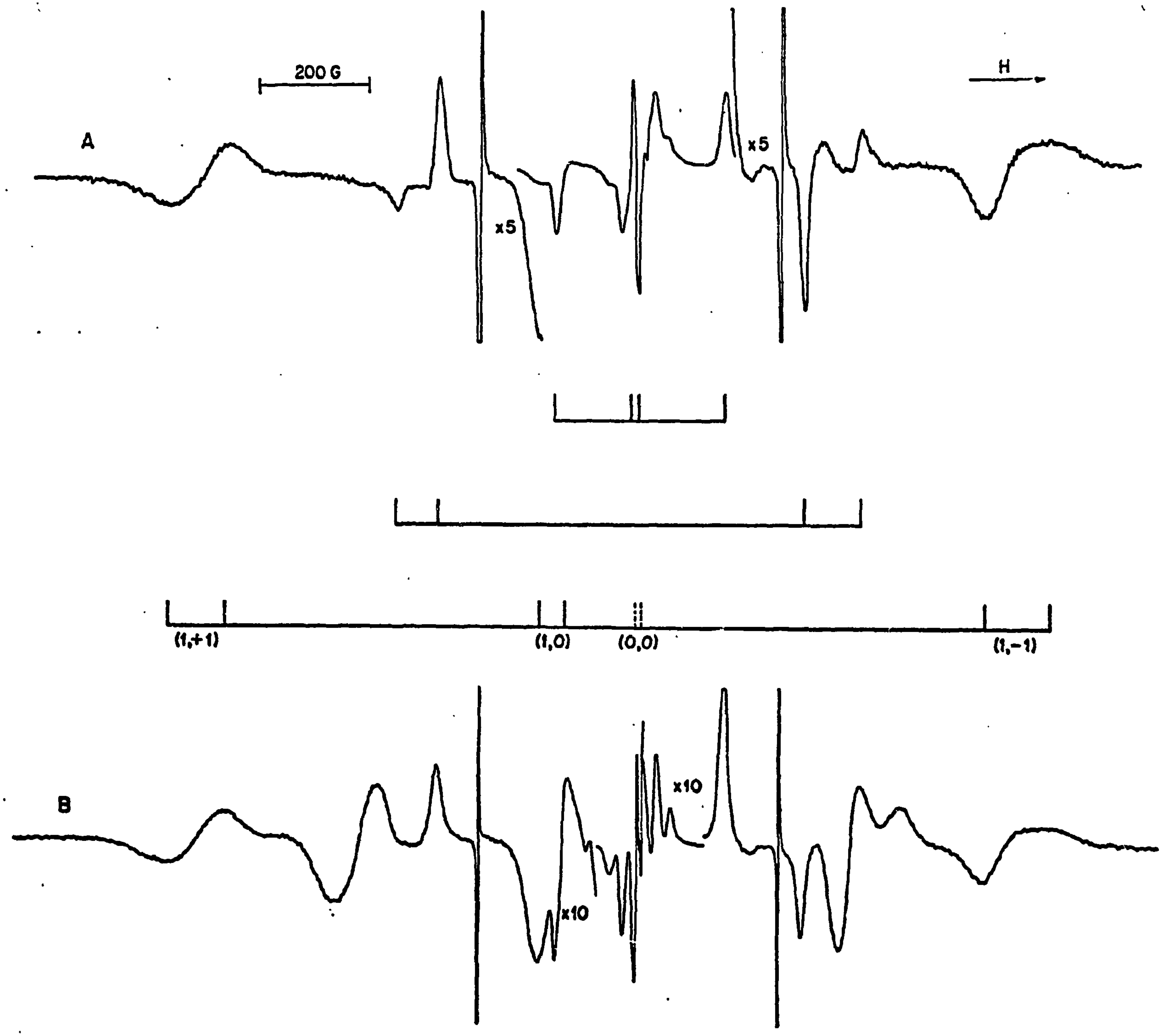
radicals discussed in the text; the narrowly separated lines drawn under the central portion of spectrum B refer to the ^{31}P splitting for the central component of the $\cdot\mathrm{CH_2OP}<$ radical derived from dimethylacidpyrophosphate.



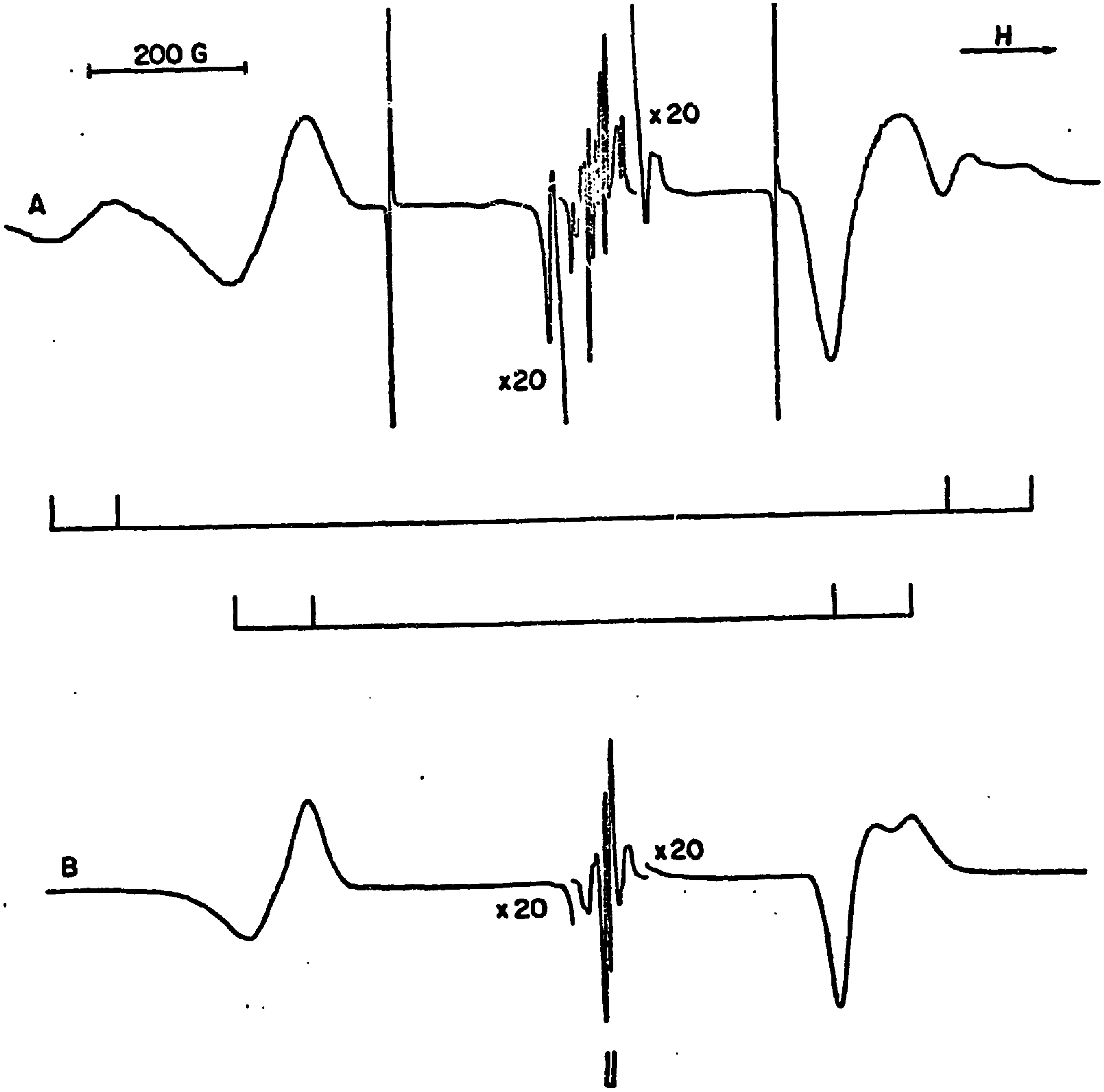
Kerr et al., "ESR Studies of γ-Irradiated Phosphite and Phosphate Esters:..."
Figure 1.



err et al., "ESR Studies of γ-Irradiated Phosphite and Phosphate Esters:..." Figure 2



Kerr et al., "ESR Studies of γ-Irradiated Phosphite and Phosphate Esters:..." Figure 3



Kerr et al.. "ESR Studies of γ-Irradiated Phosphite and Phosphate Esters:..." Figure 4

Electron Spin Resonance Studies of γ-Irradiated Phosphorus Compounds Containing Phosphorus-Chlorine Bonds[1]

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ABSTRACT

Esr experiments similar to those described in the preceding paper [C. M. L. Kerr, K. Webster, and F. Williams, J. Phys. Chem., 00, 0000] have been used to identify the radicals produced in a series of γ-irradiated phosphorus compounds containing phosphorus-chlorine bonds. The principal species formed from diethyl chlorophosphite are the neutral radicals $\dot{P}(OEt)_2$ and $(EtO)_2\dot{P}Cl_2$ presumably by loss and addition of chlorine atoms, although there is evidence that the former species is produced at least in part by dissociative electron capture. On the other hand, the major radical derived from a series of chlorophosphate esters is invariably the chlorophosphoranyl radical anion formed by simple electron attachment to the parent molecule. In the dichlorophosphoranyl radicals, there is a large ^{35}Cl coupling from the two equivalent chlorines in the apical positions of a trigonal bipyramidal structure. Evidence for the anisotropy of this coupling suggests that a significant spin density resides in the $3p_\sigma$ orbitals of these chlorine ligands, in agreement with recent single crystal studies on $\dot{P}OCl_3^-$ [T. Gillbro and F. Williams, J. Amer. Chem. Soc., 96, 5032 (1974)]. The much greater stability of radical anions derived from chlorophosphates relative to those from di- and tri-alkyl phosphate esters, which undergo efficient dissociation, is interpreted in terms of the effect of ligand electronegativity on the spin density distribution. This effect is consistent with recent MO descriptions which indicate that the half-occupied orbital in phosphoranyl radicals is largely localized along the axial three-center bond.

Introduction

Recent esr studies[3,4] have shown that the radicals formed by γ irradiation of compounds containing phosphorus-chlorine bonds can include both neutral and ionic species. The two major radicals identified in γ-irradiated phosphorus trichloride at 77K are $\dot{P}Cl_2$ and $\dot{P}Cl_4$,[3,4] the results being very similar to those obtained by uv photolysis[5] in which case the reactions probably involve the homolytic scission and addition of chlorine atoms. However, the role of ionic processes in the radiation chemistry of phosphorus chlorides is also indicated by the identification of the radical anion $\dot{P}OCl_3^-$ in γ-irradiated phosphorus oxychloride at 77K.[3,4,6]

In the preceding paper[7] we have summarized the results of esr studies on γ-irradiated organophosphorus esters. The present contribution describes similar investigations on γ-irradiated phosphorus chlorides, including organophosphorus derivatives containing both P-OR and P-Cl bonds. One of the main conclusions to emerge from this work is that radical anions of phosphate esters are stabilized by the presence of P-Cl bonds, a finding which contrasts with the well-known propensity of compounds containing C-Cl bonds to undergo dissociative electron capture. Although this difference might seem surprising at first sight, it is entirely consistent with a theoretical analysis of the factors governing the stability of phosphoranyl radicals.[6,8]

Experimental Section

Materials. Phosphorus oxychloride (Matheson, Coleman, and Bell), phosphorus trichloride (Alfa Inorganics), and methyl bromide (Matheson Co.) were used as received. The organophosphorus chlorides were obtained from Aldrich Chemical Co., and consisted of diethyl chlorophosphite, diethyl chlorophosphate, ethyl dichlorophosphate and phenylphosphonic dichloride. The diethyl chlorophosphite was purified by distilling it twice on the vacuum line, the middle fraction (*ca.* 20%) being retained both times. This purified sample gave a considerably simpler esr spectrum on γ irradiation than the starting material. Methyltetrahydrofuran (MTHF) was supplied by Eastman Organic Chemicals Co. and purified as before.[7]

Sample Preparation, γ-Irradiation, and Esr Measurements. These techniques were similar to those described in the previous paper.[7] All the samples used in the present work were shock-cooled in liquid nitrogen and formed clear glasses with the exception of bulk phosphorus trichloride and phosphorus oxychloride which were polycrystalline.

Results

Phosphorus Trichloride. The esr spectrum of γ-irradiated PCl_3 is shown in Figure 1 (A). Its appearance is very similar to the spectrum reported for the photolyzed material,[5] showing characteristic features which can be likewise assigned to the $\dot{P}Cl_2$ and $\dot{P}Cl_4$ radicals. Only the perpendicular features ($A_\perp(^{31}P)$ *ca.*20G) of the $\dot{P}Cl_2$ spectrum are observable in the present case but this is not surprising since the parallel features reported earlier[5] are much weaker and broadened by chlorine hyperfine coupling. The esr parameters of $\dot{P}Cl_2$ and related radicals are listed in Table I.

The $\dot{P}Cl_4$ spectrum lies outside the sharp isotropic doublet of the hydrogen atom, and consists of an incompletely resolved ^{31}P doublet of chlorine septets. It was originally suggested[5] that this hyperfine structure should be associated with the perpendicular features but more recent single crystal studies[6] of the analogous species $\dot{P}OCl_3^-$ would seem to indicate that these are probably the parallel components for which direction the chlorine hfs assumes its maximum value. In any event, the hyperfine structure of the $\dot{P}Cl_4$ spectrum is clearly indicative of strong interaction with one phosphorus and only two equivalent chlorine nuclei, the weak coupling from the other two chlorines (ca. 7.5 G)^5 being unresolved in the present case. The ^{31}P and ^{35}Cl hfs parameters for $\dot{P}Cl_4$ are given in Table II and these are comparable to the corresponding values for $\dot{P}OCl_3^-$ and the other isostructural species.

Diethyl Chlorophosphite. The lower esr spectrum (B) in Figure 1 was obtained from γ-irradiated diethyl chlorophosphite at 77K. As for phosphorus trichloride, there are features present both inside and outside the hydrogen-atom doublet which can be assigned to two phosphorus-centered radicals. The inside features have the typical appearance of an axially symmetric doublet spectrum with a large hyperfine anisotropy, and the parallel and perpendicular components are indicated by the stick diagram. The spectrum parameters given in Table I are comparable to those recorded for other phosphinyl radicals such as $\dot{P}(OEt)_2$ in γ-irradiated tetraethylpyrophosphite^7 and $\dot{P}Cl_2$ in a uv-photolyzed 1:10 PF_3/PCl_3 mixture,^{5} so the radical is clearly of this general type. A closer examination of the esr parameters further suggests that the spectrum can be probably assigned to $\dot{P}(OEt)_2$ rather than the alternative species $Cl\dot{P}OEt$ which also could be formed directly from the parent compound. Firstly, in contrast to the results for $\dot{P}Cl_2$ where $A_{\parallel}(^{35}Cl) = 15$ G,^{5} the parallel components show no substructure and a linewidth which is inconsistent with an unresolved coupling of more than 10 G to a single chlorine nucleus. Second, the parameters $A_{\perp}(^{31}P)$ and $g_{\perp}$ are nearly identical to those obtained for $\dot{P}(OEt)_2$ whereas it might be expected that the values for $Cl\dot{P}OEt$ would be intermediate between the perpendicular parameters for $\dot{P}(OEt)_2$ and $\dot{P}Cl_2$ which differ significantly (Table I). Although these arguments are not compelling, they definitely favor the $\dot{\mathrm{P}}(\mathrm{OEt})_2$ assignment. However, if for some reason the ^{31}P hfs and g parameters of $\dot{\mathrm{P}}(\mathrm{OEt})_2$ and $\mathrm{Cl\dot{P}OEt}$ were to be very similar, then obviously the results would be consistent with the formation of either or both of these radicals.

The outer features of the spectrum of γ-irradiated diethyl chlorophosphite (Figure 1B) strongly resemble those of $\dot{\mathrm{P}}\mathrm{Cl}_4$ except for the somewhat poorer resolution and the presence of a broad signal which overlaps the outermost lines, especially at high field. The latter is presumed to be formed from an impurity since its intensity was reduced after purification of the diethyl chlorophosphite. Despite this extraneous signal, the spectrum can be analyzed as for $\dot{\mathrm{P}}\mathrm{Cl}_4$ in terms of a ^{31}P doublet of chlorine septets, as shown by the stick diagram. This similarity suggests that the spectrum can be assigned to $\mathrm{Cl_2\dot{P}(OEt)_2}$. The ^{31}P hfs for this radical is somewhat lower than that for $\dot{\mathrm{P}}\mathrm{Cl}_4$ while the hfs from the two equivalent chlorines is very close to that found for $\dot{\mathrm{P}}\mathrm{Cl}_4$ and $\dot{\mathrm{P}}\mathrm{OCl}_3^-$ (Table II). Again it is likely that these hfs parameters obtained from the polycrystalline spectrum refer to the parallel components.[6]

Additional esr experiments were carried out with glassy solutions containing methyl bromide but the presence of the alkyl halide had only a minor effect on the results. That is, the signal intensities from the two phosphorus-centered radicals were only slightly diminished whereas the spectrum of methyl radicals was extremely weak indicating that selective electron capture by the methyl bromide is inefficient in this system. Consistent with this conclusion is the finding that diethyl chlorophosphite is a good electron scavenger as judged by the fact that glassy MTHF solutions of this solute turned yellow instead of blue on γ irradiation, the latter color being characteristic of the solvent-trapped electron in MTHF.[9] Additional evidence for electron capture by diethyl chlorophosphite comes from the esr spectrum of the γ-irradiated MTHF solution showing, apart from the strong central lines of the MTHF radical, parallel features of a ^{31}P doublet spectrum whose parameters ($\underline{A}_{\parallel} = 277$ G, $\underline{g}_{\parallel} = 2.0019$) agree closely with those obtained for the $\dot{\mathrm{P}}(\mathrm{OEt})_2$ radical ($\underline{A}_{\parallel} = 269$ G, $\underline{g}_{\parallel} = 2.0015$) in a γ-irradiated solution of triethyl phosphite in MTHF.[7] As discussed earlier, it is not certain that the esr spectra of $\dot{\mathrm{P}}(\mathrm{OEt})_2$ and $\mathrm{Cl}\dot{\mathrm{P}}\mathrm{OEt}$ can be differentiated so we must leave open the additional possibility that the latter radical is formed. In any event, we can conclude that one or both of these phosphinyl radicals are formed by dissociative electron capture.

Phosphorus Oxychloride. Polycrystalline[3,4] and single-crystal[6] esr studies have been reported previously, the most thoroughly identified species being the radical anion $\dot{\mathrm{P}}\mathrm{OCl}_3^-$.

Additional work is described here on solutions of phosphorus oxychloride in MTHF. On γ irradiation at 77K, the glass became yellow indicating efficient electron capture, and a typical powder esr spectrum is reproduced in Figure 2 (A). This spectrum consists of a strong central seven-line signal due to solvent radicals and, outside the hydrogen-atom lines, a ^{31}P doublet of chlorine septets attributable to $\dot{\mathrm{P}}\mathrm{OCl}_3^-$. The $\dot{\mathrm{P}}\mathrm{OCl}_3^-$ spectrum is poorly resolved on the low-field side but the high-field features exhibit the same characteristic shape already described for $\dot{\mathrm{P}}\mathrm{Cl}_4$ and $\mathrm{Cl}_2\dot{\mathrm{P}}(\mathrm{OEt})_2$ and the seven parallel components are clearly visible. The large chlorine hfs of *ca*. 65 G is, within experimental error, the same as that obtained from the polycrystalline spectrum and corresponds closely to the maximum (parallel) splitting recorded for the single-crystal spectrum.[6] However, the spectrum in the MTHF glass shows no substructure due to the weaker interaction of the third chlorine and the ^{31}P splitting of ca. 1280 G is significantly less than the value of ca. 1370 G derived from the polycrystalline spectrum. Both of these differences are probably attributable to the much poorer resolution in the glassy state rather than to any perturbation of the $\overset{\bullet}{P}OCl_3^-$ structure by the changed environment. Moreover, it should be emphasized that because of the additional coupling to the chlorines, the anisotropy of the ^{31}P splitting is lost in these powder spectra and consequently the measured splitting represents some intermediate value which is not necessarily the isotropic splitting.

Ethyl Dichlorophosphate. After γ irradiation of the bulk material in the glassy state at 77K, its esr spectrum consisted of a weak signal from ethyl radicals superimposed on a broad singlet of unknown origin. In addition, the features in the wings were analyzed into a doublet of septets and ascribed to the radical anion $Cl_2\overset{\bullet}{P}(O)OEt^-$ ($A(^{31}P) = 1084$ G; $A(^{35}Cl) = 64$ G). Incorporation of methyl bromide decreased the intensity of the radical anion spectrum to about 2/3 of the value in the undoped sample and yielded a central spectrum consisting of a superimposition of signals from methyl and ethyl radicals. The methyl radicals decayed selectively leaving behind an ethyl radical signal of approximately the same intensity as in the undoped sample, indicating that the formation of ethyl radicals is largely unaffected by the presence of methyl bromide.

A γ-irradiated glassy solution of ethyl dichlorophosphate in MTHF yielded the spectrum shown in Figure 2 (B). This is analogous to the corresponding spectrum from phosphorus oxychloride and, apart from the hydrogen-atom doublet and central lines of the solvent radicals, it consists exclusively of features attributable to the $Cl_2\overset{\bullet}{P}(O)OEt^-$ radical anion. It is noteworthy that although the low-field group clearly shows the chlorine septet structure, the lines are broad and there appears to be only one set of features. In contrast, the high-field group shows additional structure although it is insufficient for a complete analysis of the anisotropy. This difference in appearance between the high-field and low-field groups is explained by the fact that the second-order downfield shifts are greater for the perpendicular than for the parallel features, assuming $|\underline{A}_{||}(^{31}P)| > |A_{\perp}(^{31}P)|$.[7] Finally, a fairly accurate value for the parallel ^{35}Cl hfs was obtained from the high-field structure where the outer components corresponding to the $^{35}Cl^{37}Cl$ combinations are partially resolved. The esr parameters obtained for the ethyl dichlorophosphate radical anion in the different systems are listed in Table II. All the samples became yellow on γ irradiation and the color is probably associated with the radical anion.

<u>Phenylphosphonic dichloride</u>. On γ irradiation in the glassy state at 77K, this compound yielded an esr spectrum consisting of outer features and a complex poorly-resolved signal in the center which was not analyzed. The structure of the outer features indicated septet patterns, the spectrum being similar to that observed for ethyl dichlorophosphate but with a smaller ^{31}P doublet splitting such that the innermost high-field component overlapped the hydrogen high-field line. By analogy, this spectrum is assigned to the radical anion $Cl_2\dot{P}(O)C_6H_5^-$ formed by electron capture. Similarly, the results obtained for the methyl bromide and MTHF solutions parallel those of ethyl dichlorophosphate. Thus, only a small (<u>ca.</u> 20%) decrease in the intensity of the radical anion signal resulted from the inclusion of methyl bromide in the bulk material and a similar but better resolved spectrum was obtained for the MTHF glass (Figure 2C).

The esr parameters derived from this latter spectrum are given in Table II.

In addition to the spectral features of the radical anion and the MTHF radical, the spectrum of Figure 2C includes a pair of weak lines lying just inside the hydrogen-atom doublet. These lines probably constitute the perpendicular features of a ^{31}P doublet in which case the magnitude of the coupling (<500 G) is suggestive of the phosphonyl radical $Ph\dot{P}(O)Cl$ produced by dissociative electron capture, the smaller ^{31}P hfs relative to other phosphonyl radicals[7,9] of the type $(RO)_2\dot{P}O$ being attributable to delocalization of the unpaired electron into the phenyl group. However, without the observation of clearly recognizable parallel features, this assignment must be tentative.

Diethyl Chlorophosphate. The esr spectra obtained from this compound under a variety of irradiation conditions are shown in Figure 3. After γ irradiation of the neat compound, spectrum A clearly shows the presence of the ethyl radical with the characteristic quartet splitting of 27 G from the isotropic methyl protons. In addition, the features outside the hydrogen doublet can be assigned to three different phosphorus-centered radicals. The outermost lines belong to the $Cl_2\dot{P}(O)OEt^-$ radical anion presumably formed from ethyl dichlorophosphate present as an impurity. Although some of the features are obscured by overlap in the 77K spectrum, the identification was established by annealing the sample to 133K at which point the spectra from the other two radicals had disappeared and the spectrum corresponded to that of the $Cl_2\dot{P}(O)OEt^-$ species observed in the ethyl dichlorophosphate systems.

The sharp features lying immediately outside the hydrogen-atom doublet in spectra A and B of Figure 3 are almost certainly the perpendicular components of $(EtO)_2\dot{P}O$ since the experimental splitting of 615 G corresponds closely to the value obtained for this radical in γ-irradiated glasses of diethyl phosphite and tetraethylpyrophosphite.[7] A relatively weak signal from these features is also present in the spectrum of the MTHF glass (C). The spectrum of the third phosphorus-centered radical is strongly overlapped in spectra A and B of the bulk material but is clearly observed in the MTHF glass (C). As shown in the stick diagram, a spectral analysis based on axially symmetric hyperfine tensors for one phosphorus and one chlorine is seen to fit the experimental spectrum reasonably well, though no more than three of the expected four lines from the chlorine substructure are resolved for any component. The esr parameters are listed in Table II and the hyperfine pattern is assigned to the $(EtO)_2\overset{\bullet}{P}(O)Cl^-$ radical anion formed by electron capture. This identification rests not only on the radiation chemical evidence of formation in the MTHF glass but also on the general similarity of the derived isotropic parameters ($\underline{A}_{iso}(^{31}P)$ = 918 G; $\underline{A}_{iso}(^{35}Cl)$ = 35 G) to those obtained from solution studies of analogous chlorophosphoranyl radicals[10] such as $(EtO)_2\overset{\bullet}{P}(O\text{-}\underline{t}\text{-}Bu)Cl$ for which $\underline{A}_{iso}(^{31}P)$ = 1037 G and $\underline{A}_{iso}(^{35}Cl)$ = 47.2 G. While closer agreement between the esr parameters for these two radicals, differing as they do by only one ligand group, might have been expected, it must be realized that the analysis of the complex anisotropic spectrum in terms of axial symmetry may be oversimplified and consequently the derived isotropic parameters can only be regarded as rough estimates in this instance.

Comparison of the spectra A and B in Figure 3 indicates that the signal intensity of the radical anion spectrum is slightly reduced relative to the intensity of the $(EtO)_2\overset{\bullet}{P}O$ spectrum in the sample containing methyl bromide. Also the 23 G quartet splitting in the center of spectrum B is diagnostic of the methyl radical, presumably formed through dissociative electron capture by the alkyl halide. These results point to competitive electron scavenging, the bulk diethyl chlorophosphate competing effectively with 10 mole% methyl bromide.

Electronic Structure of Phosphorus-Centered Radicals

<u>Phosphinyl Radicals</u>. The present study provides an additional set of parameters for the phosphinyl radical thought to be $\dot{\mathrm{P}}(\mathrm{OEt})_2$. These results together with corresponding data for $\dot{\mathrm{P}}\mathrm{Cl}_2$[5,11] and $\dot{\mathrm{P}}(\mathrm{C_6H_5})_2$[12] are presented in Table I. As indicated in the previous paper,[7] the ^{31}P couplings are only slightly affected by the nature of the ligands so that there is little evidence for any substantial delocalization of the unpaired electron from the phosphorus 3p orbital into the ligand p or π orbitals which are perpendicular to the plane of the radical. This conclusion is also in keeping with the very similar parameters reported recently for $\dot{\mathrm{P}}(\mathrm{SR})_2$ radicals.[13]

<u>Chlorophosphoranyl Radicals</u>. The structure of the $\dot{\mathrm{P}}\mathrm{OCl}_3^-$ radical anion has been discussed in detail elsewhere,[6] and the main conclusions concerning the nature of the half-occupied MO were shown to be relevant to a wide variety of phosphoranyl radicals.[6,8] An important feature of the $\dot{\mathrm{P}}\mathrm{OCl}_3^-$ radical structure is the relatively large spin density which resides in each of the $3p_\sigma$ orbitals of the axial chlorines. This was revealed only through a study of the ^{35}Cl anisotropy in a single crystal[6] because, in general, the anisotropic parameters cannot be extracted from the powder spectra of chlorophosphoranyl radicals. For this reason, considerable caution must be exercised in the interpretation of the parameters listed in Table II. Nevertheless, using the relation between the powder and single crystal spectra of $\dot{\mathrm{P}}\mathrm{OCl}_3^-$ as a guide,[3,6]

it may be inferred that the observed ^{35}Cl coupling of ca. 60 G for the radicals possessing two axial chlorine ligands is close to the maximum (parallel) value. This proposal is supported by the fact that the isotropic ^{35}Cl couplings for analogous radicals measured in solution[10] are significantly less than 60 G. Thus the observed ^{35}Cl couplings appear to provide a qualitative indication of appreciable anisotropy similar to that documented for $\dot{\mathrm{P}}\mathrm{OCl}_3^{-}$,[6] suggesting again that appreciable spin populations reside in the $3p_\sigma$ orbitals of the axial chlorine ligands. This generalization is reinforced by the results for the diethyl chlorophosphate radical anion showing clear evidence of anisotropic coupling to the single chlorine ligand (Table II).

Turning to the ^{31}P couplings, the values for the chlorophosphoranyl radical anions and the neutral species in Table II decrease monotonically as the number of chlorine ligands in the radical is reduced by replacement with alkoxyl groups. A similar trend is established by the isotropic data on a similar series of neutral chlorophosphoranyl radicals,[10] and the results are readily interpreted in terms of the effect of ligand electronegativity on the spin distribution. These results, as well as previous data on organophosphoranyl radicals,[14] show that the progressive introduction of less electronegative groups brings about a decrease in the 3s spin density on phosphorus, the effect being attributed to the antibonding character of the half-occupied MO in these radicals.[6,15]

It was recently suggested[8] that a decrease in ligand electronegativity might also bring about the destabilization of a phosphoranyl radical through a possible increase in the spin populations on the apical ligands at the expense of the phosphorus atom.[8] When applied to the present case, this argument suggests that relative to the effect of the alkoxy groups in the phosphate ester radical anions, the more electronegative chlorine ligands should stabilize the chlorophosphate radical anions. This proposal seems to be in accord with the chemical results showing that electron capture by chlorophosphate esters is non-dissociative whereas the corresponding process is known to be largely dissociative for trialkyl and dialkyl phosphates.[7,16]

Mechanisms of Radiation-Induced Reactions

Phosphorus Trichloride and Diethyl Chlorophosphite. These tricoordinate compounds can be discussed together because in each case the results are very similar, the two main radicals being formed by net processes of chlorine atom removal and addition. Since the same radical products are also produced by uv photolysis in the case of PCl_3,[5] it is tempting to suggest that the homolytic reactions exemplified by (1) and (2) are also involved in the radiolysis.[3]

$$(EtO)_2PCl \rightarrow (EtO)_2P\bullet + Cl\bullet \qquad (1)$$

$$Cl\bullet + (EtO)_2PCl \rightarrow (EtO)_2\overset{\bullet}{P}Cl_2 \qquad (2)$$

Indeed, except for the possibility of chlorine atom transfer from an ionic intermediate, it is difficult to visualize alternative paths leading to the formation of the neutral chlorophosphoranyl radical, the addition reaction (2) representing a very facile general reaction in the free radical chemistry of tricoordinate phosphorus compounds[10,14] which is entirely analogous to the process of alkyl radical addition in the radiolysis of trialkyl phosphites.[7] Regarding the formation of the phosphinyl radical, a mechanism of dissociative electron capture (3) is also implicated by the identification of the $\overset{\bullet}{P}(OEt)_2$ radical in a γ-irradiated $(EtO)_2PCl$/MTHF glass. This reaction is formally

$$(EtO)_2PCl + e^- \rightarrow \bullet P(OEt)_2 + Cl^- \qquad (3)$$

similar to the process of dissociative electron capture in trialkyl phosphites.[7,9]

Chlorophosphate Esters. The present work furnishes unambiguous chemical evidence for radical anion formation in this class of compounds since the characteristic esr spectrum of the derived chlorophosphoranyl radical was obtained by the γ irradiation of each compound in an MTHF glass, this method of generation being diagnostic of electron capture.[9,17] The radical anion was also identified by its esr spectrum in the neat material after γ irradiation so electron attachment to the parent molecule (4) is clearly an important general process for

$$EtOP(O)Cl_2 + e^- \rightarrow EtO\overset{\bullet}{P}(O)Cl_2^- \qquad (4)$$

these compounds. Esr evidence for radical anion formation from phenylphosphonic dichloride and phenyl phosphonothionic dichloride [$PhP(S)Cl_2$] has been also reported by Mishra and Symons,[18] and the same authors have claimed that a similar reaction occurs when the cyclic trimer of phosphonitrilic chloride is γ irradiated at 77°K.[19] Therefore there is overwhelming evidence for a process of type (4) in these chlorinated compounds of tetracoordinate phosphorus.

As already mentioned in the previous section on the structure of these radical anions, the contrasting results for chlorophosphate and alkyl phosphate esters[7] can be attributed to the much greater stability of the chlorophosphate radical anions to dissociation. Thus, while dissociative electron capture to form the alkyl radical predominates in the trialkyl phosphates,[7,16] we find that this reaction becomes progressively less important along the series $(EtO)_3PO$, $(EtO)_2P(O)Cl$, $EtOP(O)Cl_2$. It is also significant that the chlorine-containing esters appear to be more efficient electron scavengers than the trialkyl esters. This was revealed by comparative experiments on the neat materials showing a lower efficiency of electron scavenging by methyl bromide in the chloroesters. Also, the solute concentration required to prevent the formation of the characteristic blue color from the solvent-trapped electron in a γ-irradiated MTHF glass was invariably smaller for the chloresters than for the trialkyl esters.

An alternative mode of dissociation (5) involving the ejection of

$$(EtO)_2\dot{P}(O)Cl^- \rightarrow (EtO)_2\dot{P}O + Cl^- \qquad (5)$$

a chloride ion from the diethyl chlorophosphate radical anion does not seem to be responsible for the appreciable yield of the phosphonyl radical produced in the neat material. This conclusion is based on the much lower yield of the phosphonyl radical relative to that of the chlorophosphoranyl radical anion in the MTHF glass (Figure 3). This finding would be consistent however with a mechanism involving the homolytic cleavage of the phosphorus-chlorine bond in the radiolysis of the bulk compound.

The main conclusion to be drawn from these studies is that a large variety of competing ionic reactions can take place in the radiolysis of phosphorus compounds. Perhaps the most striking result is the sensitivity of certain reactions to substitutional factors, as exemplified by the dissociation behavior of phosphoranyl radical anions.

References and Notes

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TABLE I: *Esr Parameters*[a] *of Phosphinyl Radicals*

System	Radical	^{31}P hyperfine splittings (G)								$\rho_{3p}/$	Reference
		$A_{\parallel}$	$A_{\perp}$	A_{iso}	$g_{\parallel}$	$g_{\perp}$	g_{iso}	ρ_{3s}	ρ_{3p}	ρ_{3s}	
$(\mathrm{EtO})_2\mathrm{PCl}$	$\dot{\mathrm{P}}(\mathrm{OEt})_2$	278 (±5)	-15[b] (±5)	83 (±5)	2.001	2.002	2.002	0.0228	0.948	41.5	This work[c]
$(\mathrm{EtO})_2\mathrm{POP}(\mathrm{OEt})_2$	$\dot{\mathrm{P}}(\mathrm{OEt})_2$	280 (±5)	-12 (±5)	85 (±5)	2.002	2.002	2.002	0.0234	0.945	40.7	7
uv/10% PF_3 in PCl_3	$\dot{\mathrm{P}}\mathrm{Cl}_2$	269	-28	71	2.001	2.021	2.014	0.0195	0.961	49.3	5
Δ/PCl_3	$\dot{\mathrm{P}}\mathrm{Cl}_2$	293	-30.5	77.3	2.002	2.001 1.996	2.000	0.0212	1.047	49.4	11
$(\mathrm{C}_6\mathrm{H}_5)_3\mathrm{PO}$	$\dot{\mathrm{P}}(\mathrm{C}_6\mathrm{H}_5)_2$	269.7	∿0	89.8	2.0021	2.0094 2.0039	2.0051	0.0247	0.873	35.3	12

[a] The parameters for $\dot{\mathrm{P}}(\mathrm{OEt})_2$ were corrected according to the second-order equations given in footnote 16 of Ref. 7.

[b] Negative signs are assumed for $A_{\perp}$ (see Ref. 7).

[c] Spin densities in 3s and 3p orbitals of phosphorus calculated using A_0 = 3640 G and $2B_0$ = 206 G, respectively.

TABLE II: *Esr Parameters*[a] *of Chlorophosphoranyl Radicals*

System	Radical	Axial Chlorine ligands	Hyperfine Couplings (G) $\underline{A}(^{31}P)$	$\underline{A}(^{35}Cl)$	$\underline{g}$	Reference
PCl_3	$\dot{P}Cl_4$	2	1217	60	2.013	This work
$P(O)Cl_3$/MTHF	$\dot{P}(O)Cl_3^-$	2	1284	65	2.014	This work
$(EtO)_2PCl$	$(EtO)_2\dot{P}Cl_2$	2	1109	66	2.010	This work
uv/$EtOPCl_2$/$\underline{t}$-BuOO-$\underline{t}$-Bu/C_3H_8	$EtO\dot{P}(O\text{-}\underline{t}\text{-}Bu)Cl_2$	2	1145[b]	34.1[b]	2.011[b]	10
$EtOP(O)Cl_2$	$EtO\dot{P}(O)Cl_2^-$	2	1084	64	2.006	This work
$EtOP(O)Cl_2$/MTHF	$EtO\dot{P}(O)Cl_2^-$	2	1078	63	2.008	This work
$PhP(O)Cl_2$/MTHF	$Ph\dot{P}(O)Cl_2$	2	938	56	2.007	This work
$(EtO)_2P(O)Cl$/MTHF	$(EtO)_2\dot{P}(O)Cl^-$	1	1081($\parallel$)	49($\parallel$)	1.985($\parallel$)	This work
			837($\perp$)	28($\perp$)	2.001($\perp$)	
uv/$(EtO)_2PCl$/$\underline{t}$-BuOO-$\underline{t}$-Bu/$\underline{c}$-C_5H_{10}	$(EtO)_2\dot{P}(O\text{-}\underline{t}\text{-}Bu)Cl$	1	1037[b]	47.2[b]	2.009[b]	10

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[a] ^{31}P couplings and $\underline{g}$ factors obtained in this work have been corrected using the Breit-Rabi formula. Unless otherwise indicated, the anisotropy of the parameters was not observed. The ^{35}Cl couplings are thought to represent the parallel components (see text). The estimated errors in the hfs and g parameters are ± 5G and ± 0.002.

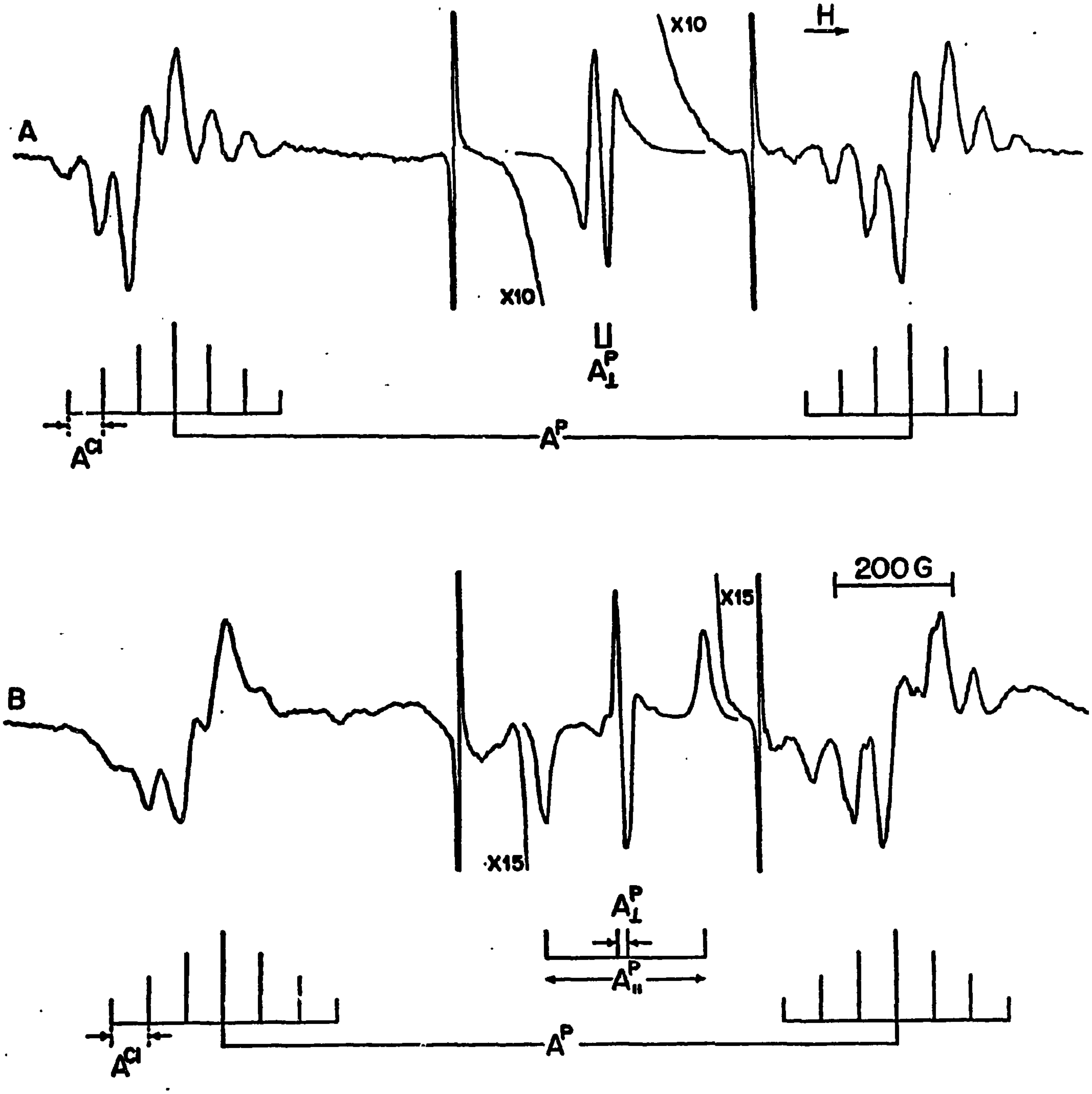
[b] Isotropic values obtained from solution esr spectra.

CAPTIONS TO FIGURES

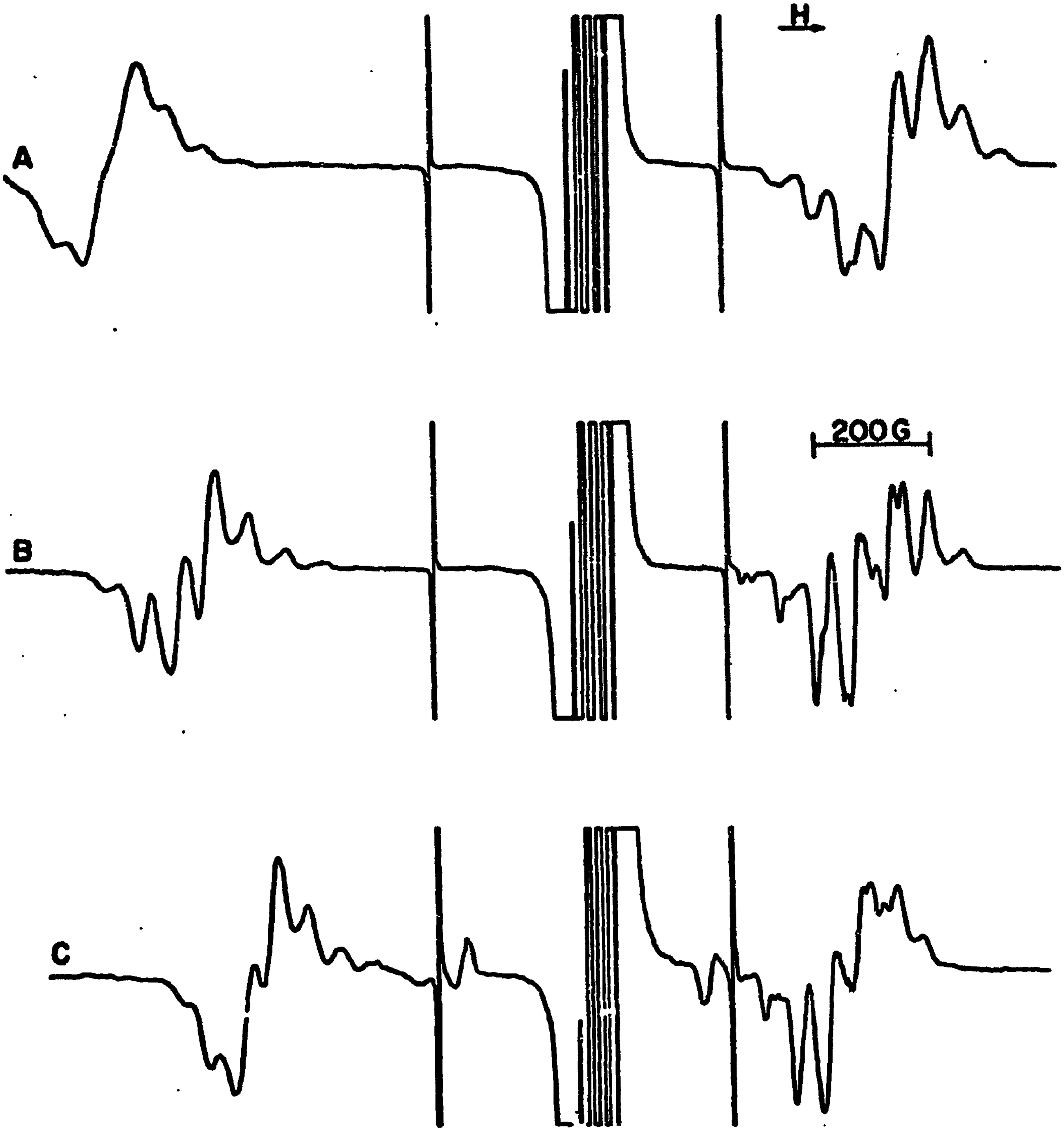
FIGURE 1. (A) First-derivative esr spectrum of γ-irradiated polycrystalline phosphorus trichloride at 77°K, showing the perpendicular features of the PCl_2 radical in the center and the doublet of septets assigned to the PCl_4 radical in the outer regions. (B) First-derivative esr spectrum of a γ-irradiated diethyl chlorophosphite glass at 77°K showing spectra assigned to the $P(OEt)_2$ radical (anisotropic ^{31}P doublet inside hydrogen-atom lines) and the $(EtO)_2PCl_2$ radical (^{31}P doublet of ^{35}Cl septets). The irradiation dose was ca. 3 Mrad in each case.

FIGURE 2. Esr spectra of γ-irradiated glassy solutions of three chlorine-containing phosphorus compounds in MTHF. The solution concentrations were ∿10 mole% and the irradiation doses 2-5 Mrad. Irradiations and esr measurements were carried out at 77°K. The first-derivative spectra shown are of solutions containing (A), phosphorus oxychloride; (B), ethyl dichlorophosphate; (C) phenylphosphonic dichloride.

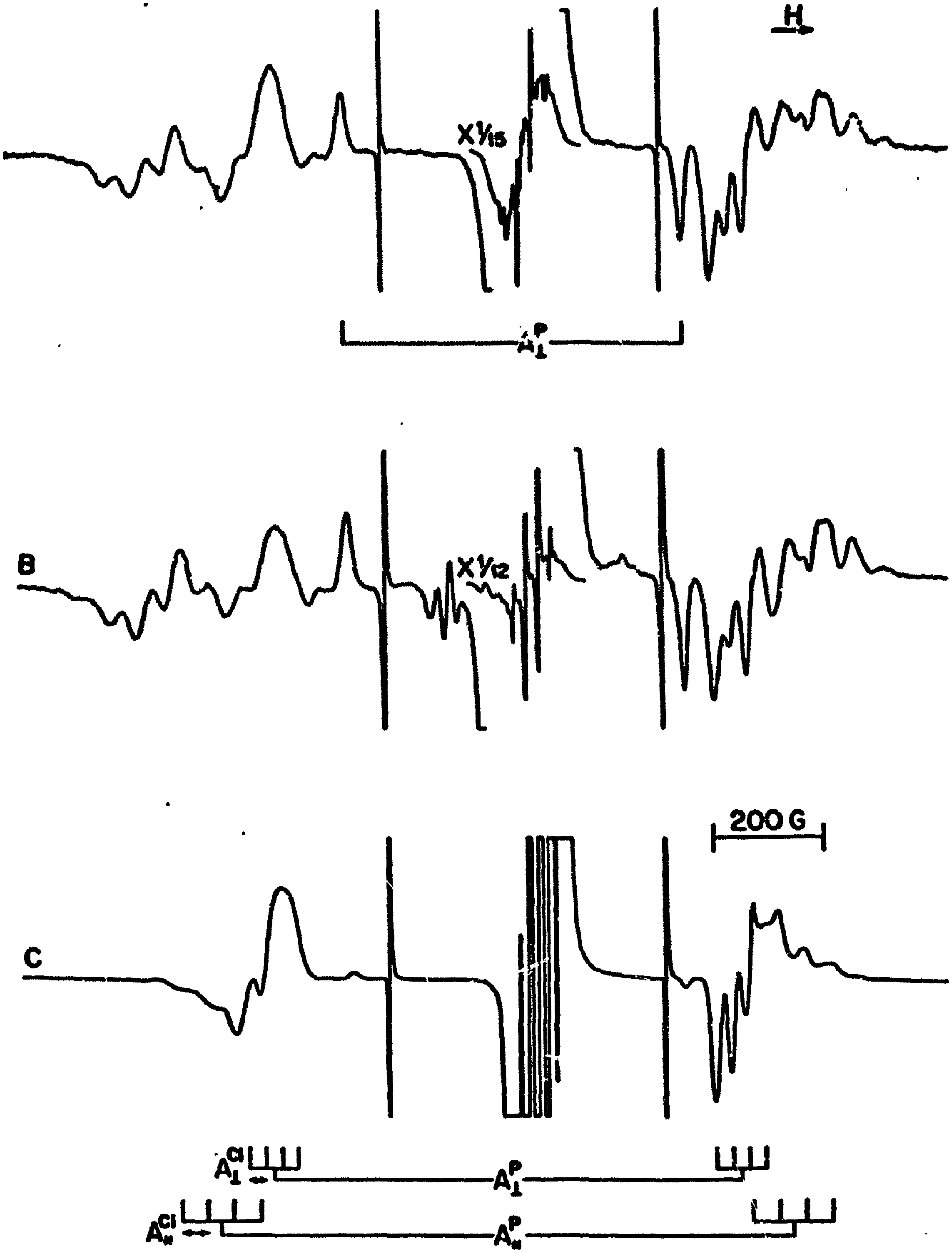
FIGURE 3. First-derivative esr spectra of γ-irradiated diethyl chlorophosphate samples at 77°K: (A) bulk diethyl chlorophosphate (dose, 2 Mrad); (B) diethyl chlorophosphate containing ∿10 mole% methyl bromide (dose, 2 Mrad); (C) 10 mole% diethyl chlorophosphate in MTHF (dose, 3 Mrad).



Kerr *et al.*, "ESR Studies of γ-Irradiated Compounds Containing Phosphorus-Chlorine Bonds." Figure 1



Kerr et al., "ESR Studies of γ-Irradiated Compounds Containing Phosphorus-Chlorine Bonds." Figure 2



Kerr *et al.*, "ESR Studies of γ-Irradiated Compounds Containing Phosphorus-Chlori Bonds." Figure 3