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MASTER

A RADICALS IN IRRADIATED CRYSTALS STUDIED BY ESR SPECTROSCOPY

1. Trifluoromethyl and other Radicals in Irradiated Single Crystals of Trifluoroacetamide

The ESR spectra of $\cdot CF_3$ in CF_3CONH_2 have been analyzed and the radical has been shown to be non-planar.

This article has now been published (J. Chem. Phys., **46**, 3193 (1967)) as Document No. COO-1385-17.

2. ESR Study of CF_2COO^- Radicals in Irradiated Single Crystals of Sodium Chlorodifluoroacetate.

In a preprint of an article submitted last year (COO-1385-18) it was shown that single crystals of $CClF_2COONa \cdot 2H_2O$ irradiated and observed at 77°K contain several inequivalent $\cdot CF_2COO^-$ radicals. The original X-band ESR investigation has now been extended by a Q-band study of these radicals. Comparison of the spectra at 10 Gcs and at 35 Gcs has shown some errors in the original interpretation of the spectra.A revised manuscript is in preparation.

3. Some Effects of Crystal Structure on Production of Radicals in Irradiated Crystals.

The nature of radicals stable in irradiated acetate salts at 77°K has been shown to depend to some extent on the crystal structure. In metal acetates with several molecules of water of crystallization the methyl radical predominates. As the number of molecules of water of crystallization is reduced other radicals, particularly CH_2COO^-, become of comparable stability and predominate in anhydrous acetates. The more open structure of the hydrogen-bonded hydrates appears to favor the loss of CO_2 and production of methyl radicals. Some other effects of crystal structure on radical stability are also reviewed.

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This work is accepted for presentation at the International Conference on Radiation Chemistry to be held at Argonne National Laboratory, August 1968. It will be printed in the Proceedings of the Conference and a preprint is enclosed (Document No. COO-1385-22).

4. Electron Spin Resonance Studies of Radicals in Irradiated Crystals.

The electronic structures of the radicals produced in some irradiated aliphatic acids and amides have been deduced from the ^{1}H, ^{19}F and ^{13}C hyperfine splitting tensors of magnetic nuclei in the radicals. An interpretation of the isotropic and dipole-dipole hyperfine components for the radicals $\cdot CH_3$, $\cdot CF_3$, $\cdot CF_2CONH_2$, $\cdot CF_2COO^-$ and $\cdot OOCF_2COO^-$ was presented in a plenary lecture at the International Conference on Spectroscopy, Bombay, India, January, 1967. This review of some recent work on the present project has now been published in the Proceedings of the Conference. A reprint is enclosed as Document COO-1385-20.

5. Trichloromethyl Radical in Irradiated Trichloroacetamide

Single crystals of monoclinic trichloroacetamide irradiated and observed at 77°K show very complex ESR spectra. However, when the magnetic field lies in the ab plane at 30° to the a-axis the spectrum can be interpreted as the superposition of three sets of ten equally spaced lines, the relative intensities within each set being 1:3:6:10:12:12:10:6:3:1 as expected for $\cdot CCl_3$. Equivalent lines of the three sets have relative intensities in agreement with the calculated natural abundance ratios for the radicals $\cdot C^{35}Cl_3$, $\cdot C^{35}Cl_2\,{}^{37}Cl$ and $\cdot C\,{}^{35}Cl\,{}^{37}Cl_2$ i.e., 27:27:9. The fourth set of unit intensity due to $\cdot C\,{}^{37}Cl_3$ is too weak to be observable. In this selected orientation some ^{13}C satellite lines may be seen, and the values of the ^{35}Cl and ^{13}C hyperfine splitting tensors appear to be near the maximum principal values so some conclusions concerning the electronic structure of the radical can be made.

A note will be submitted shortly as Document COO-1385-23 but copies are not yet available.

6. Conversion of $\cdot CH_3$ to $\cdot CH_2COO^-$ in Irradiated Sodium Acetate Crystals

At 77°K $\cdot CH_3$ is the principal radical observed in irradiated $CH_3COONa \cdot 3H_2O$ but on warming these ESR lines disappear and are completely replaced at 180°K by the lines due to $\cdot CH_2COO^-$. Measurements of the intensities of the $\cdot CH_3$ lines, and of the increase in the $\cdot CH_2COO^-$ lines after conversion, were made at 77°K in a single crystal mounted with $H||a$. The intensities of the two sets are equal within the experimental errors involved (some care was taken to reduce the rather large errors inherent in experiments of this type) so the number of $\cdot CH_3$ radicals disappearing is about equal to the number of $\cdot CH_2COO^-$ radicals appearing. This would suggest that conversion occurs by abstraction of a hydrogen of an acetate ion by methyl:

$$\cdot CH_3 + CH_3COO^- \rightarrow CH_4 + \cdot CH_2COO^-$$

The information is of interest since little is known concerning the mechanisms of the reactions of radicals in crystals. A note is in preparation.

7. Irradiated Polycrystalline Fluorocarbon Derivatives

In the course of a search for new fluorocarbon radicals both barium dichlorofluoroacetate $Ba(CFCl_2COO)_2$ and ammonium difluoroacetate $CF_2HCOONH_4$ were irradiated. The ESR spectra are rather complex and indicate that the expected radicals $\cdot CCl_2F$ and $\cdot CHF_2$ are not obtained even at 77°K. An attempt is now being made to prepare single crystals of these materials.

The following pure liquids have been irradiated at 77°K and the ESR spectra observed at the same temperature: CF_3CH_2OH, $CF_3CF_2CF_2CH_2OH$, 2-fluoropyridine, $CH_3OOC\text{-}CCl_2F$. In all cases good spectra showing nuclear hyperfine splittings are obtained. The following compounds gave a single broad line or no signal: octafluoronaphthalene, trifluoroacetanilide, $CH_3CHOH\ C_6F_5$, ϕ_3SiF, ϕ_4Ge, ϕ_3Bi.

Further work to identify the radicals in each case is in progress.

8. Radicals in Irradiated Amides

In earlier work from this laboratory [COO-1385-9] ESR spectra of polycrystalline amides were reported. In order to identify the radicals with more certainty, to study their structures, and perhaps their motions and reactions, we have prepared single crystals of acetamide, isobutyramide and trimethylacetamide. These have now been irradiated and ESR spectra observed at 77°K and at room temperature as a function of orientation.

The room temperature radicals from isobutyramide and trimethylacetamide appear to be $(CH_3)_2\ \overset{\circ}{C}CONH_2$ and $(CH_3)_3C\cdot$ as was found for the powders. The ESR spectra are nearly isotropic even in single crystals so the radicals must undergo considerable motion. The proton hyperfine splittings $A_H \simeq 25$ Gauss are those expected for freely rotating β-methyl protons in aliphatic radicals.

At 77°K the ESR spectra are quite different with fourteen or more lines for isobutyramide and considerable anisotropy. Either new radicals have been formed or the freezing out of motions has made protons non-equivalent at 77° that were equivalent at 300°K. The proton hyperfine splitting tensors are being determined from analysis of the spectra and work is underway to identify the radicals with the aid of isotopic substitution.

9. Radicals Trapped in Irradiated Clathrates

Single crystals of ϕ_3CH and ϕ_3SiH were prepared from C_2H_5OH and irradiated at 77°K. The ESR spectra were not of the expected $\phi_3C\cdot$ and $\phi_3Si\cdot$radicals but rather of a radical derived from C_2H_5OH (probably $CH_3\overset{\circ}{C}HOH$). The solvent has been incorporated into the crystals and, on irradiation, it is the ethanol which suffers radiation damage. Crystals of ϕ_3CH from dimethylsulfoxide show, on irradiation, an ESR spectrum characteristic of radicals from $(CH_3)_2SO$ rather than from ϕ_3CH.

Although the crystal structures of the solvated crystals are not known it seems likely that the solvent molecules are trapped in holes in the hydrocarbon lattice much as in clathrates. The method is being explored as a possible means to stabilize radicals difficult to study otherwise.

10. Radicals in Fluoroacetamide Irradiated at 77°K

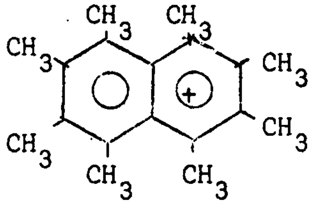
It was shown several years ago [Cook, Rowlands and Whiffen, 1963] that fluoroacetamide gives the radical $\cdot CHFCONH_2$ on irradiation at room temperature. We have studied the products of irradiation at 77°K with the hope of trapping $\cdot CH_2F$ radical. However, the most abundant radical is $\cdot CH_2CONH_2$ under these conditions. It was further found that weak lines due to radical pairs $\cdot CH_2CONH_2 \ldots \cdot CHFCONH_2$ were present, the second part of the pair having come from abstraction of a proton from a neutral molecule by $F\cdot$.

Before our work could be completed an article appeared [Iwasaki and Toriyama, 1967] reporting essentially the same findings. We have accordingly stopped work on this project and started studies of ammonium fluoroacetate with our original objective still in mind.

B. Stable Radicals in Solution Studied by ESR Spectroscopy

1. Octamethylnaphthalene Cation

A new synthesis of completely methylated naphthalene [Oku, Kakihana and Hart, 1967] has made this material available and Prof Hart kindly supplied us with a sample along with some partly methylated naphthalenes. When dissolved in 98% H_2SO_4 these yield paramagnetic solutions which show excellent ESR spectra. These cation radicals are of considerable interest structurally since it is known that there are important steric interactions between the methyl groups. We have, therefore, measured the proton hyperfine splittings for both types of methyl groups on the radical (I); the values are A_1 = 6.30 G and A_2 = 1.91 G.



The higher value is close to that found for hexamethylbenzene cation [Carter and Vincour, 1967] and the lower value is similar to A_{CH_3} = 1.62 found for 2,3,6,7-tetramethylnaphthalene negative ion [Howarth and Fraenkel, 1966]. We have not found rearrangement products comparable to the hexamethylbenzyl radical formed from hexamethylbenzene [Singer and Lewis, 1965].

This work is being prepared for publication and some molecular orbital calculations of spin densities will be added.

2. Hexamethylnaphthalene cations

1,2,3,4,6,7-hexamethylnaphthalene and 1,2,3,4,6,8-hexamethylnaphthalene also give radical cations in H_2SO_4 but the radicals are rather unstable and ESR spectra must be taken immediately after preparation. The spectra are more complex and we are analyzing them by comparing observed with computer simulated spectra.

The cations from these compounds undergo rearrangements, possibly with methyl group migrations, and the ESR spectra change with time. An effort is being made to identify some of the intermediate stages in the decomposition of the original radical.

C. Nuclear Magnetic Resonance and NQR Spectroscopy

1. Computer Analysis of NMR Spectra

An article entitled "The Evaluation of Matrix Elements of the High-Resolution NMR Spin-Coupling Hamiltonian using a Digital Computer" has now appeared and is COO-1385-11.

Y. K. Pan and M. T. Rogers, Journal of Computational Physics, 2, 27-31 (1967).

2. Chlorine Quadrupole Resonance Study of Some Molecular Adducts of Phosphorus Oxychloride

The chlorine quadrupole resonance frequencies of Lewis acid-base adducts have been used to derive the order of Lewis acid strength for the series $SbCl_5$, $FeCl_3$, $SnCl_4$ and $TiCl_4$.

This article, COO-1385-19 is in press in Journal of Physical Chemistry.

3. Rhenium Pure Quadrupole Resonance Spectrum of Potassium Perrhenate

The nature of chemical bonds in the heavier metals can be investigated from the pure nuclear quadrupole resonance spectra. In the case of rhenium such a resonance has been reported up to now only for one compound, dirhenium decacarbonyl [Segel and Barnes, 1957]. We have recently been able to detect both the ^{185}Re and ^{187}Re resonances in $KReO_4$. This result is rather unexpected since most tetroxide species are tetrahedral. However, the crystal structure suggests that ReO_4^- is a distorted octahedron in $KReO_4$ [Morrow, 1960]. The contributions to the field gradient tensor at the Re nucleus from the chemical bonds and from the electric charges of the species in the tetragonal lattice have been separately evaluated and the results shown to be consistent with a tetragonal bisphenoidal structure for the ion in $KReO_4$. The Re-O bonds have considerable covalent character. The asymmetry parameter is zero within the errors of observation or calculation.

An article describing these results has been submitted to Journal of Chemical Physics and a preprint is enclosed, COO-1385-24.

4. NQR Study of Charge Transfer Complexes

Bromine pure NQR resonances have been observed in the molecular charge transfer complex 2-bromopyridine$\cdot Br_2$. Comparison of these with the resonance frequencies for pure 2-bromopyridine and pure Br_2 reveals important changes in the ^{79}Br frequencies on complex formation. One bromine of Br_2 [γ= 382.4 MHz] has dropped to 165.6 MHz and the other risen to 301.5. Formation of an N-Br bond of the type $C_5H_4BrN....Br-Br$ would account for these changes. The bromine frequency of the ring substituent rose from 265.21 to 267.16 MHz and would result from charge moving toward Br_2 in the complex making the C-Br bond to the ring less ionic.

This work is being prepared for publication.

5. Point-charge Calculations of Electric Field Gradients in Crystals

Since the chemist is interested in the use of pure quadrupole spectroscopic data for the study of chemical bonding it is important to be able to estimate and correct for the electric field gradient tensor arising solely from the electric charges distributed through the lattice. A computer program based on that of DeWette and Schacher (1965) has been developed here with the kind assistance of Dr. Schacher. This has already been applied to calculations of field gradients in molecular adducts [COO-1385-19] and in $KReO_4$ [COO-1385-24].

We have now made calculations on a series of metal halides of known crystal structure in which two or more chemically equivalent halogens have crystallographically nonequivalent positions. The results permit us to estimate the importance of the Sternheimer antishielding factor and are in agreement with recent ideas that for crystals where partly covalent bonding occurs the Sternheimer factor has much smaller values than are appropriate for the true ionic crystals.

This work is complete and will be submitted for publication shortly.

Bibliography of Preprints and Reprints 1967-68

Reprints

COO-1385-10 Keto-Enol Tautomerism Studied by Nuclear Magnetic Resonance Spectroscopy. III. Studies of Proton Chemical Shifts and Equilibrium Constants at Different Temperatures, J. L. Burdett and M. T. Rogers, J. Phys. Chem. 70, 939 (1966) and J. Phys. Chem. 71, 4587 (1967). Through an oversight AEC support was not properly acknowledged in the original and the correction is made in the second reference.

COO-1385-11 The Evaluation of Matrix Elements of the High-Resolution NMR Spin-Coupling Hamiltonian Using a Digital Computer, Y. K. Pan and Max T. Rogers, J. Computational Physics, 2, 27-31 (1967).

COO-1385-17 Trifluoromethyl and Other Radicals in Irradiated Single Crystals of Trifluoroacetamide, Max T. Rogers and L. D. Kispert, J. Chem. Phys. 46, 3193-3199 (1967).

COO-1385-20 Electron Spin Resonance Studies of Radicals in Irradiated Crystals, Max T. Rogers and L. D. Kispert, Proceedings of the International Conference on Spectroscopy, Bhabba Atomic Research Center, Bombay, India, Vol. II, 1967,pp.376-382.Copies were mailed March 21,1967 along with form AEC-427 to AEC-Chicago.A duplicate set is enclosed now with information concerning the publisher and a title page from the two-volume proceedings.

Preprints

COO-1385-22 Some Effects of Crystal Structure on the Production of Radicals in Irradiated Crystals, Max T. Rogers and L. D. Kispert, to be presented at the International Conference on Radiation Chemistry, Argonne National Laboratory, August, 1968, and to be published in the Proceedings of the Conference (ACS Advances in Chemistry Series).

COO-1385-23 Trichloromethyl Radical in Irradiated Trichloroacetamide, Max T. Rogers and L. D. Kispert, to be submitted to Journal of Physical Chemistry. Preprints will not be mailed with the report but will be sent in two to three weeks.

COO-1385-24 Rhenium Pure Quadrupole Resonance Spectrum of Potassium Perrhenate, Max T. Rogers and K. V. S. Rama Rao, submitted to Journal of Chemical Physics.