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ELECTRON SPIN RESONANCE STUDIES OF RADIATION EFFECTS

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TECHNICAL REPORT

Jan. 1, 1969 - Dec. 31, 1969

A. RADICALS IN IRRADIATED CRYSTALS STUDIED BY ESR SPECTROSCOPY

1. ESR Study of γ -Irradiated Acetamidine Hydrochloride

Radiation damage in amides has been extensively studied so it was felt that a study of the paramagnetic species in γ -irradiated acetamidine $\text{CH}_3-\text{C}(\text{NH}_2)=\text{NH}$ would be of considerable interest. Single crystals of acetamidine hydrochloride $[\text{CH}_3-\text{C}(\text{NH}_2)=\text{NH}_2]^+ \text{Cl}^-$ were prepared and the unit cell and space group determined by X-ray analysis. ESR spectra of crystals irradiated at 77°K showed *only* the V center, Cl_2^- . As the temperature was allowed to rise from 77°K to 125°K the V center lines disappeared and were replaced by a set of lines attributed to the new radical $[\cdot\text{CH}_2-\text{C}(\text{NH}_2)=\text{NH}_2]^+$. Two amino protons and the two α protons of the methylene group show hyperfine interaction with the odd electron and these tensors were measured and have been discussed.

A preprint describing this work is enclosed as AEC Document No. COO-1385-31.

2. V Centers in Irradiated Hydrazine Salts

V centers such as Cl_2^- are well known from ESR studies of irradiated alkali halides. However, they have only recently been reported in two irradiated organic chloride salts, hydroxylamine hydrochloride (Ueda, 1964) and glycine hydrochloride (Box *et.al.*, 1969). We have now observed additional examples of the stability of these species. Cl_2^- has been identified in γ -irradiated acetamidine hydrochloride at 77°K (above). Also, we find

the radical Cl_2^- in irradiated hydrazinium dichloride at 77°K. (A second radical predominates at -80°C but has not been identified). In hydrazinium dibromide we find the species Br_2^- at 77°K; on warming this is converted to a new radical, possibly a peroxide. These V centers, which show axial symmetry in the alkali halides, become less symmetric in the cases we have studied, indicating that weak interactions with molecules of the lattice occur. However, the isotropic chlorine and bromine hyperfine splittings do not change much with matrix.

A preprint, AEC Document No. COO-1385-32, describing this work is enclosed.

3. Radicals in Irradiated Trimethylacetamide

It had been shown many years ago [Rogers, et.al., 1965] from powder ESR spectra that trimethylacetamide γ -irradiated at room temperature gave the t-butyl radical and the hyperfine splitting tensor for this radical has been reported [Hamrick et.al., 1968]. We have now found that γ -irradiation at 77°K, followed by observation of the ESR spectrum without warm-up, leads to the lines of a new radical $\cdot\text{CH}_2-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{CONH}_2$. The hyperfine splitting tensor for the two equivalent α protons has been determined from single crystal ESR studies and the reaction of these radicals to give t-butyl radical has been studied as a function of temperature. The unit cell and space group for the crystal were determined from x-ray measurements. It has also been possible to estimate the ^{13}C hyperfine splitting in the $(\text{CH}_3)_3^{13}\text{CCONH}_2$ radical; from this we conclude that the radical is slightly nonplanar.

4. Radicals in γ -Irradiated sec-Butyramide

The radical $(\text{CH}_3)_2\dot{\text{C}}\text{H}$ has been reported in γ -irradiated single crystals of $(\text{CH}_3)_2\text{CHCONH}_2$ at room temperature from ESR studies [Hamrick et.al., 1968] and they also report the unit cell and space group for the crystal. We have found a new radical in single crystals of this amide irradiated at 77°K. The ESR spectrum indicates that this is the radical $\cdot\text{CH}_2-\overset{\text{CH}_3}{\underset{|}{\text{CH}}}-\text{CONH}_2$ and the hyperfine splitting tensor for the β proton, and for the two equivalent α protons, have been determined. This radical converts on warming to the room temperature radical and the interconversion has been followed.

5. Radicals in Irradiated Hydrazinium Difluoride

Hydrazinium difluoride does not give a V-center on irradiation at 77°K, unlike the dichloride and dibromide; instead the ESR spectrum of the hydrogen atom is seen along with a very complex group of lines which probably arises from the radical $[\text{N}_2\text{H}_6]^+$. In addition the lines of a radical pair, possibly formed from N_2H_6^+ and a hydrogen atom, are seen. Work on this interesting group of paramagnetic species is continuing.

6. Halogen-Substituted Radicals

A number of compounds have been irradiated to try to obtain chlorine or bromine substituted radicals since no example of this class has been completely worked out. Dichloromalonamide appears to give the $\dot{\text{C}}\text{ONH}_2$ radical while monobromomalonamide gives either $\text{CONH}_2-\dot{\text{C}}\text{Br}-\text{CONH}_2$ or $\text{CONH}_2\dot{\text{C}}\text{Br}_2$ (or both). Also, irradiation of CBr_4 gives a radical believed to be $\cdot\text{CBr}_3$ and cyanogen bromide gives $(\text{CNBr})^\cdot$. Work on these bromine-containing radicals is being continued.

7. Fluorocarbon Radicals

In an effort to prepare the $\cdot\text{CF}_2\text{H}$ and $\cdot\text{CFH}_2$ radicals for ESR study we have irradiated the ammonium salts of monofluoroacetic acid and difluoroacetic acid. We do not obtain the simple radicals desired, even at 77°K, but instead the $\cdot\text{CF}_2\text{COO}^-$ and $\cdot\text{CFHCOO}^-$ radicals by loss of a hydrogen atom. The hyperfine splitting tensors for each of these radicals is being evaluated and rather complete studies of these radicals, already known in other matrices, will be carried out.

8. Radicals in Irradiated Inorganic Compounds

Irradiated polycrystalline arsenic trifluoride and arsenic trichloride have been examined by ESR. The paramagnetic species produced are the negative molecule-ions formed by adding an electron to the molecule. Considerable information about the structures of these new species should be obtainable from the spectra.

Single crystals of KIO_4 and NaIO_4 give a paramagnetic species, probably IO_4^- , which shows a rather small iodine hyperfine interaction. Further work on periodates and perrhenates appears worthwhile.

9. Radiation Damage Studies in Various Solids

A number of materials have been irradiated by γ -rays or high-energy electrons, usually at 77°K, and the ESR spectra examined, but at present results are incomplete. These include KHF_2 (gives a strong impurity spectrum), tetrazole (powder spectra only) and pentachlorophenol.

B. Nuclear Quadrupole Resonance Spectroscopy

1. NQR Spectra of Nitrogen Compounds

A spectrometer operating over the range 2.5 - 15 MHz has been completed and has been used to detect the ^{14}N pure quadrupole resonance in methylurea. A study of the resonance frequency as a function of temperature is also being made. Other substituted ureas and some related nitrogen compounds are being examined for new ^{14}N resonances.

2. NQR Spectra of Inorganic Chlorine Compounds

The chlorine pure quadrupole resonance in $\text{BiCl}_3 \cdot \text{H}_2\text{O}$ has been observed and studies on other halides of the heavy metals are underway. A number of air or water sensitive heavy metal halides are being studied, carrying out all preparations and transfers in a dry-box. Previous failures to detect resonances may have been a result of impurities and a reexamination of these using more careful handling techniques seems worthwhile.

3. Electric Field Gradient Tensors from X-ray Data

The calculation of the electric field gradient tensor at a given nucleus in a solid may be carried out several ways. For largely ionic substances the gradient is computed from the magnitudes and locations of the electric charges but the value so obtained must be multiplied by the Sternheimer polarization factor to obtain the true field gradient at the nucleus and the calculation of this factor presents difficulties. For crystals in which the bonding is partly covalent one must also calculate the gradient from the bonding electrons, particularly those occupying p orbitals, and again such calculations are difficult.

We are now computing the value of the electric field gradient tensor at a given nucleus from the experimental electron density map obtained from an x-ray diffraction study. This involves dividing the unit cell into (say) $30 \times 30 \times 30$ elements and assigning each an electronic charge from the Fourier map. A computer program then adds these contributions for a large number of unit cells and gives the resultant tensor. Preliminary results for iodine monochloride are promising although various problems remain to be solved in carrying out the calculations.

4. Temperature Dependence of NQR Spectra of MO_4^{n-} Ions

The dependence on temperature of the ^{127}I resonance in various periodates such as NH_4IO_4 , NaIO_4 and KIO_4 is being studied along with that of the ^{185}Re resonance in NH_4ReO_4 , KReO_4 , etc. The ^{185}Re frequency decreases with temperature in the usual manner in KReO_4 whereas it increases with increase in temperature in NH_4ReO_4 . The anomalous temperature dependence in NH_4ReO_4 could result from a number of causes and further efforts are being made to find the origin of the effect.

Bibliography of Preprints and Reprints 1969-70

Reprints

- COO-1385-25 An ESR Study of the Radical Cations from Octamethylnaphthalene and Two Hexamethylnaphthalenes, K. D. J. Root and M. T. Rogers, Journal of Magnetic Resonance, 1, 568-574 (1969).

Preprints

- COO-1385-28 Nuclear Quadrupole Zeeman Studies of p-Bromobenzenesulfonyl Chloride and p-Bromoaniline Hydrochloride, K. V. S. Rama Rao and M. T. Rogers, to be submitted to Journal of Chemical Physics.
- COO-1385-29 Electron Spin Resonance Spectra of Inorganic Radicals and Radical Ions, K. D. J. Root and M. T. Rogers, Chap. X in "Spectroscopy in Inorganic Chemistry", Vol. II, Edited by C. N. R. Rao and J. R. Ferraro, Academic Press, New York, 1970.
- COO-1385-31 Radicals in Irradiated Acetamidine Hydrochloride, J. C. Watson and M. T. Rogers, to be submitted to Journal of Chemical Physics.
- COO-1385-32 V Centers and U Centers Irradiated Hydrazinium Salts, J. C. Watson and M. T. Rogers, to be submitted to Journal of Chemical Physics.