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ELECTRON SPIN RESONANCE STUDIES OF RADIATION EFFECTS

Annual Progress Report

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ABSTRACT

This project is primarily devoted to a study of the effects of high-energy radiation, particularly γ -rays, on nonmetallic solids. Electron spin resonance spectroscopy (ESR) has been used to identify paramagnetic species produced, study their molecular and electronic structures, and follow their reactions and decay. Fundamental processes in the radiation chemistry of solid organic and inorganic compounds were studied by ESR. The effects of radiation depend strongly on the chemical constitution of the solid and a wide variety of materials have been examined to identify the more stable paramagnetic products and search for general principles governing radiation damage. Structure and bonding in radicals were deduced from the ESR parameters.

The objectives of this project for 1973 were met to an unusual degree with several investigations completed, six scientific articles published, five accepted for publication and two advanced to preprint stage. ESR studies of radiation damage in organic acids and amides resulted in the first complete ESR studies of bromine- and iodine-substituted radicals and a partial study of trichloromethyl. The effects of changing the central atom in $\cdot\text{MXYZ}$ radicals, and of replacing F with CF_3 groups in $\cdot\text{CF}_3$, were explored. Radiation damage in ammonium salts of the fluoroacetic acids and in mandelic acid was studied by ESR. Hole centers in irradiated hexafluorometallates and in hydrazinium dihalides were discovered. General methods for obtaining g and hyperfine tensors were developed to provide improved techniques for analyzing ESR data. Finally, a number of older studies of nuclear quadrupole resonance in perhenates and periodates were published.

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More detailed description of investigations completed during 1973 are given below and summarize the contents of the "Reprints and Preprints" listed at the end of this section. Partly completed investigations are discussed later under "Proposed Technical Program" in case they would be continued.

A. Radiation Damage in Organic and Inorganic Compounds

I. V Centers and H Atoms in Irradiated Hydrazinium Dihalides

Hydrazine (N_2H_4) forms a series of dihalides ($N_2H_4F_2$, $N_2H_4Cl_2$, $N_2H_4Br_2$) which have ionic crystal structures related to fluorite with the $N_2H_6^{++}$ cation replacing the alkaline earth cation. We found that γ -irradiation of the chloride and bromide produces the V centers Cl_2^- and Br_2^- , respectively, and these species have ESR rather similar to the same species trapped in cubic alkali halide lattices. However, the g and hyperfine tensors for Cl_2^- and Br_2^- are not axial in the hydrazinium salts. The fluoride is of particular interest since F_2^- is not detected but, apparently, an electron adduct of $N_2H_6^{++}$. We have analyzed the ESR spectra and believe that they arise from the species $N_2H_6^+$ (or $N_2H_6^{3+}$). A preliminary report of this work appeared in 1973 in the Proceedings of the XVII Colloque Ampere and the problem is being investigated further. It now appears that V centers are quite commonly the only stable paramagnetic species observed when inorganic and organic halides are irradiated at 77°K.

A rather different hole species, F_3^{2-} , is observed when $KAsF_6$ is γ -irradiated but no arsenic-containing radical is produced. Although F_3^{2-} had been observed in γ -irradiated LiF it is rather surprising that it would be the preferred product when a complex ion, AsF_6^- , is γ -damaged.

This radical is found from the ESR parameters to be bent with $\angle F-F-F=150^\circ$. INDO calculations show that it is a σ -type radical with the odd electron density concentrated in the orbitals in the plane of the radical. A complete description has been published in J. Chem. Phys. 58, 3082 (1973).

II. γ -Irradiated Molecular Solids - Some Substituted Amides

Amides form rather open structures with three-dimensional hydrogen-bonded frameworks. On irradiation rather large radicals are produced and become trapped in the crystal so that they are fairly stable. This provides a good way to study by ESR radicals of the type $\cdot CHXCONH_2$ ($X=F, Cl, Br, I$). We have, as yet, been unable to obtain any other trivalent carbon species with α -bromine or iodine substituents stable enough to permit a complete analysis of the ESR spectra.

ESR data for $\cdot CHFCONH_2$ and $\cdot CHClCONH_2$ have been available in the literature for several years and the analogous radicals $\cdot CHBrCONH_2$ and $\cdot CHICONH_2$ were of particular interest since they would allow us to compare bonding and structure as a function of halogen substituent in a series. We have now been able to prepare these by the processes:

and analysis of the ESR spectra has been completed.

It appears that unpaired spin density is extensively transferred to the ρ_π orbitals of the halogen atoms with a maximum at bromine. The spin densities in the $4\rho_\pi$ and $5\rho_\pi$ orbitals of bromine and iodine are 0.28 and 0.21, respectively, whereas in $\cdot CHFCONH_2$ and $\cdot CHClCONH_2$ $\rho_{2\rho_\pi}(F)=0.12$ and $\rho_{3\rho_\pi}(Cl)=0.15$. The overlap integrals $S(2\rho_\pi, n\rho_\pi)$ between the carbon and halogen π orbitals appear to go in the same order so the direct transfer through overlap would account for the large spin densities in the ρ_π halogen

orbitals. The radicals are known from observed ^{13}C hyperfine interactions to be planar for $\text{X} = \text{F}, \text{Cl}$ but the geometry is as yet unknown for $\text{X} = \text{Br}, \text{I}$.

A complete description of this work is contained in two articles which have been submitted for publication (J. Chem. Phys., 1974, and J. Magn. Resonance, 1974). These are the first complete ESR studies of carbon-centered radicals with α -bromine and α -iodine substituents so much work remains to be done in the area.

The crystal structure of bromomalonamide was carried out to supplement the ESR work. The results were important since they showed that the C-Br bond direction in the radical was 70° away from that of an undamaged molecule and the radical could not be simply an electron adduct of $\text{CHBr}(\text{CONH}_2)_2$. The structure is of interest since the three-dimensional hydrogen bonded framework is different from that in other diamides in that the molecules have a mirror plane. This work is being reported in an article in J. Chem. Phys. (1974).

III. Irradiated Ammonium Fluoroacetates

Carboxylic acids and their salts usually produce trivalent carbon species on irradiation by breakage of a C-H or C-C bond. We therefore attempted to obtain the radicals $\cdot\text{CHF}_2$ and $\cdot\text{CH}_2\text{F}$ for ESR single-crystal study by irradiating $\text{CHF}_2\text{COONH}_4$ and $\text{CH}_2\text{FCOONH}_4$. Actually, the former yielded both the species $\cdot\text{CHF}_2$ and $\cdot\text{CHFCOO}^-$ and the spectra as yet have not been resolved well enough to analyze. $\text{CH}_2\text{FCOONH}_4$, on the other hand, gave no $\cdot\text{CH}_2\text{F}$ but only $\cdot\text{CHFCOO}^-$ at room temperature. The g and $A(\text{F})$ tensors for this radical were obtained and their temperature dependence down to 137°K studied. The radicals move somewhat on warming and begin to undergo torsional vibrations of rather large amplitude.

A study of the radicals $\cdot\text{CF}_3$ and $\cdot\text{CF}_2\text{COO}^-$ in $\text{CF}_3\text{COONH}_4$ was made to complete our investigation of irradiated fluoroacetates. This work is described in a preprint enclosed.

IV. Radicals in Irradiated Group IVA Halides

(a) The radicals $\cdot\text{CF}_n(\text{CF}_3)_{3-n}$ ($n=0-2$) were produced by UV photolysis of the perfluoriodides in the presence of di-tertiary-butylperoxide (DTBP). The reactions appear to be

and the radicals are stable enough in solution in the DTBP to be studied by ESR. The radicals $\cdot\text{CF}_2\text{CF}_3$, $\cdot\text{CF}(\text{CF}_3)_2$ and $\cdot\text{C}(\text{CF}_3)_3$ were prepared in this way and the isotropic fluorine hyperfine interactions measured. The results show that the radicals become more nonplanar with more fluorine substituents on the trivalent carbon. As CF_3 groups replace fluorine the radicals become more nearly planar since CF_3 is less electronegative than fluorine. Where $\cdot\text{CF}_3$ is nearly tetrahedral we estimate that $\cdot\text{C}(\text{CF}_3)_3$ is bent only about 5° from the plane. An article describing this work has appeared (J. Amer. Chem. Soc. 95, 1512 (1973).)

(b) Silicon-, Germanium-, and Tin-centered Radicals

It is interesting to compare the ESR parameters of series of radicals of the type $\cdot\text{MXYZ}$, where $\text{M} = \text{C}, \text{Si}, \text{Ge}, \text{Sn}$ and to observe the effect of the central atom on radical geometry. We have prepared a number of these radicals by γ -irradiation of organometallic halides and methyls in

an adamantane matrix. The radicals are trapped in the matrix but are free to rotate and give isotropic ESR spectra. Thus, $\text{Ge}(\text{CH}_3)_4$ and $\text{Sn}(\text{CH}_3)_4$ give $\cdot\text{Ge}(\text{CH}_3)_3$ and $\cdot\text{Sn}(\text{CH}_3)_3$ on irradiation, while $(\text{CH}_3)_3\text{SnCl}$, $(\text{CH}_3)_2\text{SnCl}_2$, CH_3SnCl_3 or (SnCl_4) give $\cdot\text{Sn}(\text{CH}_3)_2\text{Cl}$, $\cdot\text{Sn}(\text{CH}_3)\text{Cl}_2$, and $\cdot\text{SnCl}_3$, respectively. The chlorine, germanium and (where possible) the tin hyperfine splittings were observed; these show that the radicals are all quite nonplanar with $\cdot\text{M}(\text{CH}_3)_3$ bent about 13° - 14° out of the plane for $\text{M} = \text{Si}, \text{Ge}, \text{Sn}$ (but only 5° for t-butyl). Similarly, the carbon radical in the series $\cdot\text{MCl}_3$ is least bent ($\cdot\text{CCl}_3$ about 8°) while the rest appear to be nearly tetrahedral ($\cdot\text{SiCl}_3$, $\cdot\text{GeCl}_3$, $\cdot\text{SnCl}_3$, $\cdot\text{SnCl}_2(\text{CH}_3)$, $\cdot\text{SnCl}(\text{CH}_3)_2$).

This work has appeared in J. Amer. Chem. Soc. 95, 2459 (1973).

B. Determination of g Tensors

The usual method of analyzing ESR spectra to obtain g tensors utilizes three sets of spectra taken by rotating the crystal about three axes and obtaining spectra with the magnetic field 5 - 10° apart in each plane. Often these spectra cannot all be analyzed because lines overlap or several radicals are present. A method has been developed for obtaining g tensors from limited data using only the difference between the maximum and minimum g value, Δg , in each of three orthogonal planes. A convenient computer program was written and a description of the technique given (J. Magn. Resonance, 13, 000 (1974)).

C. Nuclear Quadrupole Resonance Spectroscopy

No new work in this field was done in 1973 but some older work was prepared for publication.

The objective of our work in NQR spectroscopy is to study chemical bonding and structure in a variety of solids where other methods (IR, Raman, NMR) are of limited use. In particular, we have studied compounds of the heavier elements, such as rhenium, bromine and iodine. The rhenium and iodine resonances in ReO_4^- and IO_4^- salts are particularly sensitive probes of solid-state properties since these ions in solution are presumably tetrahedral and the field gradient at the central atom would be zero.

I. NQR Spectra of Perrhenates and Periodates.

The ^{185}Re and ^{187}Re NQR resonances in several perrhenates MReO_4 ($\text{M}=\text{K}, \text{Ag}, \text{NH}_4, \text{Na}$) were observed. The finite electric field gradient q at the rhenium nucleus could come from distortion of the ion (q_p) in the solid, or from the charge distribution (q_e) in the tetragonal crystal. We have estimated the latter by a point-charge calculation in those cases where the crystal structures are known. By also estimating the covalent contribution q_p we have obtained approximate values of the Sternheimer coefficient γ_∞ in these compounds by use of the equation:

$$q_{\text{obs}} = q_p + q_e [1 - \gamma_\infty]$$

The value $\gamma_\infty \sim -16$ was obtained for KReO_4 and appears reasonable.

The periodates similarly show a ^{127}I resonance which arises in part from distortion of IO_4^- from tetrahedral in the crystal and, in part, from the lattice charges. Again, the experimental field gradient tensor is consistent with a Sternheimer coefficient of about -20.

This work has appeared in J. Chem. Phys. 58, 3233 (1973).

II. Temperature Dependence of NQR Spectra of Perrhenates and Periodates

The temperature dependence of NQR spectra is usually attributed to vibrations and accounted for by a modification of the Bayer theory. We have measured the $^{185,187}\text{Re}$ and ^{127}I resonances in a series of perrhenates and periodates and have also made detailed analyses of the Raman spectra of the crystals. The experimental NQR curves were compared with those calculated with Bayer-Brown theory using the Raman data. The differences are believed to result from neglect of the effect of volume on the field gradient tensor. Since we had quite complete data on the lattice frequencies, we were able to provide a stringent test of the theory. This work is published in the Proceedings of the International Symposium on NQR (1974).

The case of NH_4ReO_4 is particularly interesting since the temperature coefficient of the rhenium NQR frequency is positive over the range 245°K-387°K. We studied this anomalous coefficient in detail and conclude that it is associated with the temperature dependence of the reorientation of the ammonium ion. A preprint of this work is enclosed and it will be submitted to J. Magn. Resonance.

Partially Completed Projects

Several projects were worked on during 1973 but not completed. To avoid repetition the current status of these will be discussed only in the next section, "Proposed Technical Program for 1974-75" since they would be continued if this contract is renewed.

Principal Investigator's Time Contribution

5/1/73-6/19/73	30% of full time
6/20/73-8/31/73	60% of full time, 10 weeks, Summer
9/1/73-12/31/73	30% of full time
1/1/74-4/30/74	30% of full time will be contributed.

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