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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 radical products were deduced from the ESR parameters.

The objectives of this project for 1974 were met. Several investigations were completed, seven scientific articles published, four accepted for publication and two produced in preprint form. ESR studies of radiation damage in organic acids and amides resulted in the first complete single-crystal ESR studies of alpha-bromine- and iodine-substituted radicals. The first well-characterized β -bromo radical was obtained by irradiation of isobutyl bromide in an adamantane matrix. Radiation damage in ammonium salts of the fluoroacetic acids and in mandelic acid was studied by ESR. Hole centers in several irradiated fluorometallates were investigated. General methods for obtaining g and hyperfine tensors from g -value differences and general methods for determining axial g 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 as well as a new method of obtaining nuclear quadrupole coupling constants in liquids from NMR and Raman data.

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More detailed description of investigations completed during 1974 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 are to be continued.

A. RADIATION DAMAGE IN ORGANIC AND INORGANIC COMPOUNDS

A major goal of this project has been the study of radiation damage in carboxylic acids and their salts, and in amides. Radicals produced by γ -irradiation, X-irradiation or electron irradiation tend to be rather stable in the host crystals, especially at 77°K. Detailed single-crystal ESR investigations, which permit characterization of the radicals and description of their electronic and geometric structures, have been emphasized. Where the structure of the host crystal is not known, we have begun to determine these structures in order to relate the orientation of the radical to that of the undamaged molecule. Since the structures of these crystals involve extensive hydrogen-bonding networks, they are also of considerable intrinsic interest. The effects of substituents on the stability, geometry and electronic distribution in radicals of the type $\cdot\text{CHXY}$ ($\text{X} = \text{Cl}, \text{Br}, \text{F}, \text{I}, \text{phenyl}$; $\text{Y} = \text{CONH}_2, \text{COO}^-, \text{OH}$) have been investigated recently.

I. Radicals in γ -Irradiated Bromomalonamide

Until recently very few ESR spectra of radicals showing bromine hyperfine interactions had been reported despite the considerable body of results for analogous fluorine and chlorine-containing radicals. Of the few reports in the literature, none permitted unequivocal characterization of

the radical. We have now obtained excellent ESR spectra of a radical in γ -irradiated bromomalonamide and have characterized it as $\cdot\text{CDBrCOO}^-$. There is extensive electron delocalization into the bromine p_π orbitals and the radical is probably non-planar. An article describing this work has appeared in J. Chem. Phys. 61, 4814 (1974). The deuterated species was used to eliminate proton hyperfine interactions and simplify the spectra.

II. Crystal Structure of Bromomalonamide

In order to determine whether the radical in γ -irradiated bromomalonamide is an electron adduct or hole species based on the undamaged molecule $\text{CDBr}(\text{CONH}_2)_2^+$ or $^-$, or a derivative of trivalent carbon, the crystal structure of the amide was determined. The C-Br direction in the radical and in the undamaged molecule proved to be quite different suggesting that the radical is formed by breaking a bond to give $\cdot\text{CHBrCONH}_2$. The three-dimensional hydrogen-bonding network in $\text{CHBr}(\text{CONH}_2)_2$ is interesting and the thermal motions are unusual. These results are outlined in a recent paper, J. Chem. Phys. 61, 4808 (1974), which was placed by the journal alongside the ESR article mentioned above.

III. The Radical $\cdot\text{CHICONH}_2$ in γ -Irradiated $\text{CH}_2\text{ICONH}_2$

No well-characterized ESR spectra of an iodine-containing radical have been available. We were able to carry out a complete single-crystal study of the radical $\cdot\text{CHICONH}_2$ in γ -irradiated iodoacetamide. Extensive delocalization of the odd electron into the iodine $5p_\pi$ orbitals is found and suggests that the radical is non-planar, although further work is underway to settle this point. This work is described in Journal of Magnetic Resonance, 14, 279 (1974).

IV. Crystal Structure of Ammonium Difluoroacetate

Study of the radicals $\cdot\text{CF}_2\text{H}$, $\cdot\text{CFHCOO}^-$ and $\cdot\text{CF}_2\text{COO}^-$ in γ -irradiated single crystals of $\text{CF}_2\text{HCOONH}_4$ was reported last year in AEC Document COO-1385-56. These studies have been continued and the crystal structure of $\text{CF}_2\text{HCOONH}_4$ has now been completed. The orientation of the radicals with respect to the undamaged molecules provides some clues as to the mechanism of formation of the radicals and will be discussed in an article which is being prepared.

V. Radicals in γ -Irradiated Mandelic Acid

The study of radicals in γ -irradiated mandelic acid has been continued. Further INDO calculations on the geometry of the hydroxybenzyl radical $\text{C}_6\text{H}_5\dot{\text{C}}\text{HOH}$ have been carried out and these confirm that the lowest ground state energy is for a planar radical. An ESR spectrum tentatively attributed to a cyclohexadienyl radical we now believe is that of a radical pair and further work is planned to establish the exact nature of this species.

VI. Radicals in γ -Irradiated Alkyl Halides

Radicals showing hyperfine interaction with a beta halogen have not been much studied and the only well-known examples are those with beta fluorine substituents. They are of considerable interest since the hyperfine splittings depend on the dihedral angle between the odd electron orbital on the alpha carbon and the $\text{C}_\beta\text{-Halogen}$ bond direction; the ESR data thus give the conformation of the radical rather precisely. We have now been able to prepare the first well-characterized β -bromo radical, $\text{CH}_2\text{Br}-\dot{\text{C}}(\text{CH}_3)_2$, by γ -irradiation of isobutyl bromide in adamantane. The isotropic ESR spectrum shows a small bromine hyperfine interaction indicating that the bromine is in the nodal plane of the odd electron orbital.

We have also been able to make $\dot{\text{C}}\text{H}_2\text{Cl}-\text{C}(\text{CH}_3)_2$ and here the β -chlorine hyperfine interaction is large and shows that chlorine is eclipsed with the odd electron orbital. These results are presented in a Communication, J. Amer. Chem. Soc., 96, 7130 (1974). The reasons for the difference between the bromo- and chloro-radical are not known.

VII. ESR Study of γ -Irradiated Chloromalonamide

No radical in which the only hyperfine interaction is with a single chlorine has been studied in detail by single-crystal ESR. We devoted considerable effort attempting to analyze the spectra of the radical $\cdot\text{CCl}(\text{CONH}_2)_2$ in γ -irradiated malonamide using the complete Hamiltonian and the MAGNSPEC computer program to simulate spectra. Despite the apparent simplicity of the system we were never successful. An x-ray investigation of the crystal structure (in collaboration with Dr. B. L. Barnett) now reveals that the crystal shows disorder with chlorines in two sets of positions with relative intensities about 60:40. This means that the ESR spectra are superpositions or averages and so would be very difficult to unravel. Further work on the ESR problem has been abandoned but we may publish our partial crystal structure as a note.

VIII. V Centers in γ -Irradiated K_2TaF_7 and Refinement of Crystal Structure

A number of fluoride complexes lead to the production of V centers, F_2^- , rather than to oxidation or reduction of the central metal atom. This is true for both K_2NbF_7 and K_2TaF_7 . In order to relate the orientation of the V centers to the crystal structure, the structure of K_2TaF_7 , which had been reported in 1941, was subjected to refinement using modern techniques.

The resulting structure is interesting because it reveals a number of details of coordination about tantalum and will be submitted for publication by itself (AEC Document COO-1385-63). The ESR results will be written up as a separate article.

IX. Paramagnetic Species from γ -Irradiated $[\text{Co}(\text{CN})_6]^{3-}$

There have been several studies of γ -irradiated cobalticyanides and it has been shown that $\text{K}_3\text{Co}(\text{CN})_6$ itself, or $[\text{Co}(\text{CN})_6]^{3-}$ doped into an alkali halide lattice, yield both $\text{Co}(\text{CN})_5^{3-}$ and $\text{Co}(\text{CN})_6^{4-}$ ions by addition of an electron and possibly loss of a cyanide ion. The ESR results of Danon et al. (1967) suggested to them that two of the cyanide ligands of the latter product had turned around so that the structure of $\text{Co}(\text{CN})_6^{4-}$ in the irradiated crystal should actually be written as the diisocyanide $[\text{Co}(\text{CN})_4(\text{NC})_2]^{4-}$ with the nitrogens of the axial ligands bonded to cobalt. We have now shown that this explanation is probably wrong and that all six cyanide carbons are bonded to cobalt but the two axial cyanides are bent from linear. The carbon-13 hyperfine interactions which we observed in irradiated, ^{13}C -enriched material support the latter hypothesis. This work is in press in J. Magnetic Resonance, AEC Document No. COO-1385-62.

X. An ESR Study of Hole Species in γ -Irradiated $\text{K}_2\text{NbOF}_5 \cdot \text{H}_2\text{O}$

A variety of products is often obtained by γ -irradiation of fluoro complexes. In the case of $\text{K}_2\text{NbOF}_5 \cdot \text{H}_2\text{O}$, V centers of the type F_2^- were not observed but rather the electron adduct $[\text{NbOF}_5]^{3-}$ plus the ESR lines of two additional species. We have identified the latter as the hole species NbOF_4 and $[\text{NbOF}_5]^-$. It is interesting that both electron and hole species

are formed on irradiation of this compound and that both contain niobium. The ESR evidence has been presented in an article submitted to J. Magnetic Resonance (AEC Document COO-1385-64).

B. GENERAL METHODS FOR ANALYSIS OF ESR SPECTRA OF CRYSTALS

Although procedures for determining symmetric, second rank tensors (such as g or hyperfine tensors) from experimental data obtained by rotating a crystal about three orthogonal axes had been published as early as 1958, no general treatment, considering all possible types of axis sets, had been carried out. Also, the additional information obtainable from the usual inherent overdetermination of the tensor elements has usually not been utilized. We have now completed an exhaustive theoretical analysis of the problem in its most general aspects and the results are available in three articles. In the initial publication last year (J. Magn. Resonance, 9, 92(1973)) a generalization of methods for determining g tensors was presented. This year our contribution to the subject has been completed with the publication of two additional articles.

A series of computer programs has been written to accompany each article and copies are being distributed free to interested persons. These make it possible for anyone to use these powerful methods without themselves having to go through the details of the complex algebra.

The objective of this work was to investigate all the possible experimental situations and provide the theory (plus a computer program) for obtaining the g tensor in each case plus the additional information from the overdetermination of tensor elements. We show that it is often more practical to use rotations about non-orthogonal axes. The methods apply to hyperfine or to zero-field splitting tensors as well as to g tensors.

I. Determination of g Tensors from g-Value Differences

When only limited data are available, the difference Δg between the maximum and minimum g values in each of three orthogonal planes of rotation may be used to give the g tensor. A method for improving the precision of g-tensor parameters obtained from such limited data is treated in J. Magn. Resonance, 13, 53 (1974).

II. Methods for Determining Axial g Tensors

Less information is required when the g tensor is axial and general methods for determining such axial tensors are developed in the final article of this series which is in press in Journal of Magnetic Resonance (to appear in Vol. 17, 1975). AEC Document No. COO-1385-59.

C. NUCLEAR QUADRUPOLE RESONANCE SPECTROSCOPY

No new experimental research was carried on in this area in 1974 but two extensive older studies were completed and published. The objective of our work in NQR spectroscopy was to obtain information concerning structure and bonding in solids, particularly compounds of the heavier elements which are difficult to study by other methods.

The temperature dependence of nuclear quadrupole coupling constants in crystals was related by Bayer to vibrational frequencies characteristic of the solid and succeeding modifications of the Bayer theory have improved it. We made an extensive test of current theories utilizing data on perhenates and periodates. Our work was characterized by three unusual features:

- (1) The quadrupolar nuclei are at the centers of near tetrahedra of oxygen atoms,
- (2) All the salts studied had the same crystal structure (scheelite),

and (3) Raman-infrared data gave all the vibrational frequencies, including low-frequency lattice vibrations, so that the theories could be applied with no adjustable parameters.

I. Temperature Dependence of NQR Spectra of Perrhenates and Periodates

In this work we combined experimental pure quadrupole spectroscopic measurements of nuclear quadrupole coupling constants of $^{185,187}\text{Re}$ in MReO_4 solids ($\text{M} = \text{K}, \text{Na}, \text{Ag}$), and ^{127}I in NaIO_4 , with Raman-infrared data for the vibrational frequencies of the crystals. The observed frequencies were used with a modified Bayer-Brown theory to calculate the temperature dependence for each crystal. These curves were then compared with the experimental ones. The differences obtained indicate that even in these series, all with the same crystal structure, the change in field gradient with expansion of the lattice must be appreciable, and must depend on cation, since that is the most important term omitted in our theoretical calculations.

This work was presented at the First International Symposium on Nuclear Quadrupole Resonance (London, Sept. 28-29, 1972), and has now appeared as article No. 22 in the proceedings of that conference, "Advances in Nuclear Quadrupole Resonance", Vol. I, J. A. S. Smith, editor, Heydon, London, 1974.

II. Anomalous Temperature Dependence of NQR Frequency in NH_4ReO_4

In the previous study, it was noted that ammonium perrhenate did not conform to Bayer theory, even qualitatively, in that its NQR frequency increased with increasing temperature. A study of both the NQR frequency and the Raman-infrared frequencies as functions of temperature have shown that the temperature dependence of the reorientation of the ammonium ion is probably the cause of the anomalous NQR results. A short article (J. Magn. Resonance, 15, 584 (1974)) describing this work has now appeared.

III. NQR Coupling Constants in Liquids

A new method for estimating nuclear quadrupole coupling constants in liquids is suggested. At present there is no direct experimental method for liquids but we have employed an indirect method based on experimental measurements of nuclear quadrupole relaxation from NMR studies of liquids. Utilizing the rotational correlation time obtained from parallel Raman lineshape measurements, one may obtain an estimate of e^2qQ for the quadrupolar nucleus.

An article describing application of the proposed method to deuterium in deuteriochloroform and deuterobromoform is in press. (J. Chem. Phys. 63, 0000 (1975), preprint enclosed), AEC Document No. COO-1385-61.

D. Kinetics of Gas Phase Reactions of Some Interhalogen Compounds

In order to give proper credit for AEC support, a publication based on a previous AEC contract is included here. This is the thesis of James P. Phelps, which is to be published as an article in the H. Hyman memorial issue of Journal of Inorganic and Nuclear Chemistry in 1975 (preprint enclosed). This work which was done in the period 1953-56 has been available only as an AEC publication but will now be available in the regular literature. AEC Document No. COO-1385-58.

Partially Completed Projects

Several projects were worked on during 1974 but not completed. To avoid repetition, the current status of many of these will be discussed only in the next section, "Proposed Technical Program for 1975-76" since they would be continued if this contract is renewed.

Principal Investigator's Time Contribution

5/1/74-6/19/74	30% of full time
6/20/74-8/31/74	60% of full time, 10 weeks, Summer
9/1/74-12/31/74	30% of full time
1/1/75-4/30/75	40% of full time will be contributed.

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- COO-1385-63 Refinement of the Structure of Potassium Heptafluorotantalate, L. V. Giurgiu, B. L. Barnett and M. T. Rogers, to be submitted for publication.
- COO-1385-64 An ESR Study of Hole Species in γ -Irradiated $\text{K}_2\text{NbOF}_5 \cdot \text{H}_2\text{O}$, J. R. Shock and M. T. Rogers, submitted to Journal of Magnetic Resonance.
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