ELECTRON SPIN RESONANCE STUDIES OF RADIATION EFFECTS

Progress Report

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ABSTRACT

The effects of γ radiation and X-rays on organic and inorganic solids have been studied by electron spin resonance (ESR) spectroscopy. Paramagnetic species produced by radiation damage and identified by their ESR spectra include organic and inorganic free radicals, transition metal ions and V centers. Information concerning the stabilities of these species in the solid state, and their reactions and conformational changes with temperature, has been obtained.

The structures and conformational changes of alicyclic radicals trapped in an adamantane matrix have been studied and the effects of substituents on the barriers to ring inversion in some five- and six-membered rings have been evaluated. The possible use of hexamethylenetetramine instead of adamantane as a solid-state matrix for the ESR investigation of free radicals has been studied. The geometric and electronic structures of bromo- and iodo-radicals have been established and the nuclear hyperfine interactions characteristic of these species determined. An experimental and theoretical investigation of tunneling motions in the methyl radical has been completed.

ESR studies of radiation damage in transition metal cyanides and fluorides have been made. New complexes of iron, nickel and cobalt have been obtained in which the metals have unusual valence states; hyperfine interactions with metal and ligand have been used to establish the structures of these species. While irradiated oxyfluoride complexes appear to preferentially gain or lose an electron on irradiation, it has been shown that most fluoro complexes give rise to the V center F_2^- as one of the radiation products. Improvements have been made in the computer programs used for

theoretical calculation of trial ESR spectra and for quantum chemical calculations of radical geometries and electron distributions.

SUMMARY OF PROGRESS

Summaries of investigations carried out during 1976 are presented here. Complete reports on some of the topics are available and are listed in the Bibliography of Reprints and Preprints at the end of this report.

A. RADIATION DAMAGE IN ORGANIC SOLIDS

1. ESR Study of γ -Irradiated Bromo- and Iodo-Acids and Amides

Although the structures of fluorine and chlorine substituted radicals are generally well established there is a continuing major controversy concerning the simple aliphatic bromo- and iodo-radicals and there is no general agreement as to whether the observed halogen hyperfine structure in the ESR spectra arises from α - or β -halogen substitution. In an effort to decide this question in the case of the bromo radical obtained by γ -irradiation of deuterated bromomalonamide, we are attempting to obtain the complete bromine and hydrogen hyperfine splitting tensors for the radical. The magnitudes and directions of the tensor components should establish whether the radical is $\cdot\text{CHBrCONH}_2$ or a species such as $\text{CH}_2\text{Br}\dot{\text{C}}\text{ONH}_2$ or $\dot{\text{C}}\text{H}_2\text{-CBr(O)NH}_2$. A complete set of ESR spectra of γ -irradiated $\text{CHBr}(\text{CONH}_2)_2$ have been obtained about three crystallographic axes. Analysis of many of the spectra has been possible using the computer program MAGNSPEC to compute theoretical spectra for various choices of ESR parameters. However, problems arising because of the large bromine quadrupole interaction have made analysis of some spectra difficult and we have not yet completed the data necessary for obtaining the desired hyperfine tensors.

Since the single crystal ESR spectra show hyperfine splitting by one hydrogen in both the radical obtained by γ -irradiation of bromomalonamide and iodoacetamide, we believe that these radicals must be $\cdot\text{CH}_2\text{CONH}_2$ and $\cdot\text{CHICONH}_2$ rather than $\text{CH}_2\text{Br}\dot{\text{C}}\text{ONH}_2$ and $\text{CH}_2\text{I}\dot{\text{C}}\text{ONH}_2$ as suggested by M.C.R. Symons.

2. Bromine-substituted Radicals in Liquid and Solid Phases

In an attempt to obtain simple α - or β -bromo radicals in an adamantane matrix, solid solutions of several bromine compounds in adamantane have been γ -irradiated. The ESR spectra obtained from cyclopentyl bromide show only the cyclopentyl radical. Similar results with a number of other bromine-substituted aliphatic compounds have been obtained suggesting that the bromo radicals first formed are short-lived and decay rapidly with loss of the bromine to leave a hydrocarbon radical.

3. ESR Studies of γ -Irradiated Chlorofluorocarbons

A study has been made of the radical obtained on γ -irradiation of an adamantane solid solution of 1,2-dichloro tetrafluorocyclobutene. The ESR spectra are consistent with a radical having two equivalent chlorine atoms and three or four different fluorines. A nonplanar radical cation appears to be the most likely product but further work with related compounds will be needed to establish the structure with certainty.

The ESR spectra of γ -irradiated bis-dichlorofluoroacetone in adamantane have also been analyzed. The radical produced is $\dot{\text{C}}\text{FCICOC}\text{Cl}_2\text{F}$ and the chlorine and fluorine hyperfine splitting constants have been measured. Chlorofluorocarbons appear to give rather stable radicals on γ -irradiation.

4. ESR Studies of Ring Inversion in Cyclic Radicals

An extensive investigation of cyclic radicals in the adamantane matrix has been made. The radicals are generally stable over a wide temperature range so that the temperature dependence of the ESR spectra can be determined and the presence or absence of ring inversion noted. The materials studied may be divided into several classes:

(a) For precursors giving rise to cyclic radicals whose ESR spectra show no temperature dependence, no information concerning interconversion among conformational isomers can be obtained from these spectra. These include cyclopentanone, where the radical appears to be rapidly interconverting even at -140°C , and cyclopentyl chloride, where the radical is obtained and is apparently planar.

(b) Precursors giving rise to radicals with temperature dependent ESR spectra. Here there is a possibility of determining the barriers to interconversion between different ring conformations. These include cyclohexane, cyclopentane, 1,4-dioxane, tetrahydropyran, cyclopentylamine, cyclopentyl chloride and cyclopentane carboxylic acid.

Detailed studies of the radical from cyclohexane and the radical from cyclopentanecarboxylic acid have been carried out. The line shapes at different temperatures were fit by a computer program to values of the rate of inversion and the barrier hindering inversion obtained in each case from an Arrhenius plot of the inversion rate versus reciprocal temperature. The barriers are 4.9 kcal/mole for cyclopentylcarboxyl radical. A more detailed discussion is given in the enclosed preprint C00-1385-70.

5. Tunneling Rotations in Simple Radicals

The methyl radical in sodium acetate trihydrate single crystals gives a simple ESR spectrum above 40°K consisting of four lines of relative intensity 1:3:3:1. Below about 20°K a spectrum of eight lines of equal intensity is obtained. We have observed the spectra in the range 4°K to 40°K and have developed a theory to describe the orientation dependence of the low temperature spectra. At 4.2°K the radical is tunneling at a rate about 6×10^4 MHz.

Details of these experiments and calculations are given in the enclosed reprint, J. Chem. Phys. 65, 580 (1976), of document C00-1385-67.

Evidence of tunneling for the trifluoromethyl radical in γ -irradiated trifluoroacetamide single crystals has been sought but not observed. We now believe that tunneling motion may be unimportant in this radical at low temperatures.

6. Hexamethylenetetramine as a Matrix for ESR Studies

Adamantane is an excellent matrix for study of a variety of free radicals but many polar precursors are not soluble in it. We have attempted to prepare solid solutions of a number of these materials in hexamethylenetetramine (HMTA) in the hope that it would prove to be suitable for some of them. n-Butylamine, 2-methylpentene, isopropylamine, n-propylamine and isobutylamine were tried; HMTA was dissolved in the amine, filtered; and pressed into pellets in a pellet press. These were γ -irradiated for several hours at 77°K. In most cases usable ESR spectra were not obtained. Isopropylamine gave isotropic ESR spectra of $(\text{CH}_2)_2\dot{\text{C}}\text{NH}_2$ but they were not as good as in adamantane. In most other cases the radicals were either unstable in HMTA (even at 77°K) or the precursors did not dissolve sufficiently to give

adequate radical concentrations on irradiation. In most cases only the spectra of the matrix itself were observed. It therefore appears that HMMA will find only limited use as a matrix for radical studies. It is not a plastic solid and this may help account for our results. Future work will concentrate on true plastic solids, such as camphor, as possible matrices.

B. RADIATION DAMAGE IN INORGANIC COMPOUNDS

1. V-Centers in γ -Irradiated Fluorometallates

Single crystals of Cs_2ZrF_6 were γ -irradiated at 77°K. Two V centers of the type F_2^- , in somewhat different environments, are identified in the ESR spectra. A preliminary X-ray investigation in this laboratory indicates that the crystals are rhombohedral with space group $\text{P}\bar{3}\text{m1}$. ESR spectra have been taken for rotations with the magnetic field in the ac and ab planes. However, the complete tensors for both V-centers have not yet been obtained because of the complexity of some of the spectra.

γ -Irradiated single crystals of K_2NbF_7 and of K_2TaF_7 also show the presence of V centers (F_2^- radicals). In both cases other species which show metal hyperfine structure are also present and complete analysis of the ESR spectra is not at present possible. It does appear that F_2^- is relatively stable and is very often one of the paramagnetic products of irradiation of the fluoro complexes of the metals.

2. ESR Study of Irradiated Cyanide Complexes

Efforts this year have concentrated on studies of γ -irradiated alkali halides doped with transition metal cyanides. The spectra can often be interpreted, as a result of the high symmetry, and the hyperfine interactions with both metal and ligand nuclei obtained.

Crystals of KBr doped with $K_4Fe(CN)_6$ were irradiated at 77°K. The ESR spectra at -140°C show the presence of the Fe(I) species $[Fe(CN)_6]^{5-}$. A set of spectra taken for rotation about the cubic axis have given the g tensor. When the crystals are heated to 200°C and examined again at -140°C the spectrum of $[Fe(CN)_5Br]^{5-}$ is seen. The bromine hyperfine splittings ($a_{Br}^{||} \approx 32.5$ G, $a_{Br}^{\perp} \approx 20$ G) have been determined from a set of spectra taken on rotation about a cubic axis. The large bromine hyperfine interaction indicates that the Fe-Br bond is partially covalent.

Crystals of CsCl doped with $K_2Ni(CN)_4$ and γ -irradiated at room temperature show the presence of both Ni(I) and Ni(III) species. The spectra are rather complex and further work, including Q-band measurements, will be required to obtain the g tensors. Crystals of NaCl doped with $K_2Pt(CN)_4$ and γ -irradiated show the presence of a Pt(I) or Pt(III) species and the platinum hyperfine splitting has been measured. Construction of the g and A(Pt) tensors is in progress.

3. ESR Studies of Paramagnetic Fluoroxo Complexes of Transition Ions

The ESR spectra of the d^1 complex CrO_3F^- in γ -irradiated single crystals of $KCrO_3F$ have been studied. The matrix crystals, $KCrO_3F$, are tetragonal with the Scheelite structure. The ESR spectra are consistent with the hypothesis that the CrO_3F^- species have the fluorines randomly distributed among the four tetrahedral positions. As a result, the ESR spectra are rather complex and have not yet been analyzed completely.

4. ESR Studies of Oxygen-17 Enriched Complexes

The complex ion $[Mo(V)OF_5]^{2-}$ enriched in oxygen-17 has been prepared in a frozen aqueous HF matrix. The ESR spectra show satellite lines from hyperfine interaction with oxygen-17 ($A_{||}^{(17O)} = 20$ G). It has not

been possible to obtain the complete oxygen hyperfine tensor from the powder spectra because the fluorine hyperfine lines from the parallel and perpendicular orientations overlap and interfere. Single crystal data will probably be necessary to complete the analysis.

C. STUDIES OF SHORT-LIVED RADICALS

Several years ago a Micro-Now Model 509 ESR spectrometer with 2 MHz modulation was purchased and a student of Prof. Enke's has been interfacing this to a PDP-8 computer so that short-lived radicals produced by a Xenon flashlamp could be studied. No other commercial instrument for this purpose is available and the Micro-Now instrument has required extensive redesign and rebuilding. The instrument is now capable of observing radicals with half-lives of 100 microseconds or longer but is not yet in routine use so no results were obtained from it in 1976 with bromo radicals.

D. THEORETICAL INVESTIGATIONS

1. Quantum Chemical Studies of Free Radicals

An extensive study of the equilibrium geometry of hydroxy-benzyl radical, $C_6H_5\dot{C}H(OH)$ has been completed using our INDO-level program. It has been shown that the planar arrangement is most stable and any rotation of the α -hydrogen or hydroxyl out of the plane of the ring is energetically less stable. Also, the hydroxyl hydrogen is cis to the benzene ring in the most stable configuration.

The program GAUSSIAN 70 was modified to run on our CDC-6500 computer and the program POLYATOM, which is capable of making calculations on radicals with second-row elements (Si, P, S, Cl), also became available; these will be used in future work instead of the INDO program.

2. Spin Hamiltonian parameters from ESR Spectra

A revised version of the computer program MAGNSPEC has now been prepared and is operating on the CDC-6500 computer. This will calculate positions and intensities of ESR spectral lines for sets of spin Hamiltonian parameters including quadrupolar interactions. It has been used to calculate single-crystal spectra for the $\cdot\text{CHBrCONH}_2$ and $\cdot\text{CHICONH}_2$ radicals, where the bromine and iodine quadrupole interactions are large.

Principal Investigator's Time Contribution

5/1/76 - 6/15/76 40% of full time
 6/15/76 - 8/31/76 100% of full time, 10 weeks, Summer
 9/1/76 - 12/31/76 40% of full time
 1/1/77 - 4/30/77 40% of full time will be contributed

Bibliography of Reprints and Preprints for 1976

Reprints

- COO-1385-58 The Kinetics of Some Gas Phase Reactions of Chlorine-Monofluoride and Chlorine Trifluoride, J. Inorg. Nucl. Chem., Supplement 149-153 (1976).
 COO-1385-67 Tunneling Rotation of the Methyl Radical in Solids, J. Y. Lee and M. T. Rogers, J. Chem. Phys. 65, 580-81 (1976).

Preprints

- COO-1385-70 Conformational Studies of Some Cyclic Radicals in Adamantane, M. T. Rogers, and Choo Song, to be submitted for publication.
 COO-1385-71 Electron Spin Resonance Studies of Radiation Effects, M. T. Rogers, 1975 Annual Progress Report, Contract EY-76-S-02-1385 001.

*Reprints +
Preprints
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