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FINAL SCIENTIFIC REPORT

SPECTROSCOPIC STUDIES OF CHEMICAL REACTIONS IN THE SOLID STATE

submitted by

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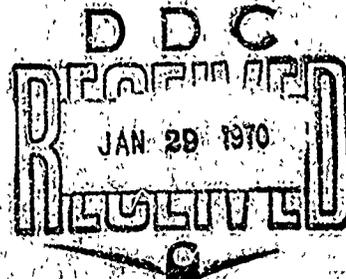
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ABSTRACT

>Solid state chemical reactions of simple organic and inorganic ions have been studied in pressed alkali halide disks of infrared spectroscopy. These reactions were induced thermally or by irradiation with gamma rays, and then they were followed spectroscopically. In thermal decomposition reactions involving weight changes, the kinetic results obtained with these disks by infrared spectroscopy agreed with those from thermal gravimetric analysis. In gamma irradiation studies, ion free radicals were trapped readily in these disks even at room temperature, and the decay of these radicals was followed by infrared spectroscopy or by electron paramagnetic resonance spectroscopy. The concentrations of the free radicals were sufficient to determine some chemical and physical properties of these ion free radicals. The pressed disks were also found to be suitable as matrices for the study of environmental effects on the internal and external motions of the impurity ions.

INTRODUCTION

This investigation concerns the uses of the well known pressed alkali halide disks of infrared spectroscopy in quantitative kinetic studies of solid state chemical reactions, in matrix isolation studies of unstable molecules including free radicals, and in spectroscopic studies of solvent-solute interactions in the solid state.

Exploratory work with these pressed disks was initiated with a National Science Foundation grant (G-17346, June 1961 to August 1964), and subsequent studies were carried out with support from the Directorate of Chemical Sciences, AFOSR, and from the Bureau of Radiological Health, PHS. The former support (Grant AFOSR-907-65, 67) extended over the period from June 1965 to December 1969 and covered the chemical kinetics aspects of our research objectives. The PHS Grant RH-433 (March 1966 to August 1970) dealt with the radiation damage studies with the pressed disks.

Research progress made during the period from June 1965 to December 1969 is described in this report.

THERMAL DECOMPOSITION STUDIES

Solutes for pressed disks in kinetic studies were selected on the basis: that they can be used as test cases for comparison of the experimental results with those from the traditional experimental techniques of thermal gravimetric analysis (TGA) and

differential thermal analysis (DTA); that they can be possible sources of ion free radicals whose subsequent identifications can lead to a better understanding of the reaction mechanisms; that their chemistries are related; and that they are of biological interest. Ions chosen for our studies were the formate, the oxalate, the acetate, and the bicarbonate.

The results from the thermal decomposition studies of the formate and oxalate ions have been published (Publications No. 2, 3, and 4). In these publications and in Publication No. 5, comparison of the TGA/DTA techniques with our infrared spectroscopic method was made. Generally, the infrared technique was superior to the TGA/DTA methods, and furthermore, these disks themselves were found to be excellent samples for the TGA runs. The alkali halide pressed disks provided better isothermal conditions in strongly exothermic or endothermic reactions and minimized complications arising from surface reactions in the decompositions of pure solids. Also, the disks allowed TGA runs on compounds whose melting points were below the decomposition temperature.

Sodium acetate dissolved readily in a KI matrix, and on heating such a disk the solute decomposed smoothly by a first order rate law. The major ionic product was the formate, but it also decomposed eventually. During the initial stages of the reaction, the rate constant from the formate growth was the same experimentally as that from the acetate decay. In the temperature

range of 480 to 574°C, the Arrhenius parameters from these rate constants were $\log A = 8.80 \pm 0.04$ (sec^{-1}) and $E = 46.65 \pm 0.15$ kcal/mol.

Considerable decomposition of the acetate occurred during the dissolution of the solute in a KBr matrix, while in a KCl matrix practically all of the solute decomposed before a solution could be made. The major reaction product in both matrices was the carbonate ion. Some formate was always present in the KBr matrix, but none was observed in the KCl matrix. In the temperature range of 399 to 640°C, the Arrhenius activation energy for the decay of the acetate ion in a KBr matrix was 22.61 ± 0.47 kcal/mol but the frequency factor was only $\log A = 2.78 \pm 0.13$ (sec^{-1}).

There appears to be no doubt that the carbon dioxide anion free radical (Publication No. 1) is involved in the production of the formate from the acetate ion. Evidences for this view are as follows. When the acetate- d_3 was decomposed in a KBr matrix, both formate-h and formate-d were observed. From the decomposition of $^{13}\text{CH}_3\text{CO}_2^-$, only traces of formate- ^{13}C and no bicarbonate- ^{13}C were observed, while both C-13 isotopic formate and bicarbonate were formed from the decomposition of $\text{CH}_3^{13}\text{CO}_2^-$. Also, gamma irradiation of the acetate ion in a KBr matrix gave an EPR signal of the CO_2^- radical, and dissolution of one such disk in water generated methane and ethane. Results from these isotopic studies and those from the thermal decompositions are being prepared for publication (Publication No. 10).

During the thermal decomposition of the formate, oxalate, and acetate ions, we invariably observed traces of the bicarbonate ion. This bicarbonate, however, was the monomeric ion, and its infrared spectrum was quite different from that of the ordinary potassium bicarbonate which consists of bicarbonate dimers (Publication No. 5). Although the decomposition of pure potassium bicarbonate gave only the expected products carbonate, carbon dioxide and water, the same decomposition in a KBr matrix produced some monomeric bicarbonate ions. At a low concentration of about 0.05 mg of potassium bicarbonate in a gram of KBr matrix, the decomposition at about 300°C gave essentially only the monomer. However, as the solute concentration was increased, more and more carbonate was formed. The carbonate yield was about 75% when the initial solute concentration was 0.6 mg/g.

Further heating of the bicarbonate monomer at about 500°C gave an unexpected product, the formate ion. The rate of appearance of the formate was the same experimentally as the rate of decay of the bicarbonate, and both were first order in the bicarbonate. Although more kinetic runs need to be made, the reaction activation energy appears to be about 32 kcal/mol. Also, if a one-to-one reactant/product is assumed, then the strongest infrared band of the bicarbonate monomer at 1697 cm^{-1} has a molar extinction coefficient of 2.99×10^3 liter/mol-cm for the KBr matrix. The most intense infrared band of the formate ion at 1633 cm^{-1} has, in comparison, an extinction coefficient of 1.81×10^3 liter/mol-cm.

Since the final decomposition products of the perchlorate ion are the chloride ion and the oxygen gas, this ion appears to be a convenient reagent to study the oxidation reactions of various solutes in pressed KCl disks. Unfortunately, the kinetics of the thermal decomposition of the perchlorate ion is not understood even today, so this reaction was studied by our pressed disk method.

Appreciable concentrations of the perchlorate ion can be forced to dissolve into the KCl matrix by heating. The infrared spectrum of such a disk displayed the expected infrared fundamental bands of a tetrahedral solute ion. The most intense band (molar extinction coefficient of 9.55×10^3 liter/mol-cm) was at 1133 cm^{-1} , and it showed a resolved satellite band at 1119 cm^{-1} due to the Cl-37 isotope in natural abundance. The remaining infrared fundamental was a weak band at 640 cm^{-1} , and this band, with an extinction coefficient of 0.90×10^3 liter/mol-cm showed no Cl-37 component.

When a KCl disk containing the perchlorate ion was heated above about 450°C , the perchlorate decomposed smoothly and the chlorate ion (1015 cm^{-1} , extinction coefficient of 3.24×10^3 liter/mol-cm; Cl-37 band at 1005 cm^{-1}) appeared as a reaction intermediate. The maximum concentration of the chlorate observed during the reaction was greater the higher the initial concentration of the perchlorate and the higher the reaction temperature. Also, the higher the concentration of the chlorate, the slower was

the rate of decay of the perchlorate. As long as the concentration of the chlorate was low (optical density less than 0.1), the decay of the perchlorate was second order in the reactant over 80-85% of the reaction. The Arrhenius parameters for the temperature range of 447 to 534°C were $\log A = 12.90 \pm 0.13$ (liter/mol-sec) and $E = 44.31 \pm 0.43$ kcal/mol. During the initial stages of these reactions, one mole of perchlorate produced one mole of chlorate. When the chlorate concentration was high, the reaction order was less than 2 and often closer to one. Also, when the initial perchlorate concentration was high and complete dissolution of the solute could not be assured spectroscopically, the perchlorate decay in such a disk followed a first order rate law. However, these runs also showed relatively high concentrations of the chlorate intermediate. Experimental results from these studies are being summarized for Publication No. 11. To complete this research, however, it may be necessary to investigate the decomposition of the chlorate ion and also study the kinetics in KBr and KI matrices. In the latter matrix, the oxidation of the iodide ion occurs.

The simplest hydride of nitrogen whose decomposition can be studied by the infrared pressed disk method is the hydrazinium ion, $N_2H_5^+$. Since the kinetics of this ion may be related to the radiation chemistry of hydrazine and since this ion may serve as a model of the amino group in a more complex amino acid, we have initiated the study of the pyrolysis reaction of the hydrazinium

ion in a KBr matrix. Although the infrared spectrum of this ion has not yet been assigned, it showed that the ion exists in two forms, A and B, in the KBr matrix. When the concentration of the solute was low or when the disk was prepared by the freeze-dry method, the solute ion was in form B. Form A, on the other hand, was produced when the concentration of the solute was higher (greater than about 1.0 mg of N_2H_5Br per gram of KBr) or when form B in a KBr disk was heated below about 150°C. However, form B was not converted into A when the heating was done at above about 250°. In fact, at these higher temperatures A changed to B, while they decomposed. Both A and B produced the ammonium ion as the ionic reaction product, and these decomposition reactions were first order in the reactant. The Arrhenius parameters were $\log A = 4.82 \pm 0.12$ (sec^{-1}) and $E = 16.96 \pm 0.29$ kcal/mol for species A in the temperature range of 157 to 211°C, and $\log A = 6.30 \pm 0.11$ (sec^{-1}) and $E = 21.28 \pm 0.24$ kcal/mol for species B in the temperature range of 168 to 236°C. Stoichiometry indicated that one mole of A produced 0.5 mole of ammonium ion while one mole of the product was obtained from one mole of B. Attempts were made to study the deuterium isotope effect, but $N_2D_5^+$ exchanged rapidly with traces of H_2O present in the disk.

The isomerization of the maleate ion to the fumarate was also studied by the disk method. This is a reaction which cannot be studied by TGA and which is of particular interest because it involves an internal rotation about a double bond. In addition, the

fumarate ion can be used as a relatively stable model compound of a carbon-carbon double bonded system in the solid state. Publications No. 5 and 7 describe the results from this study.

Finally, Publication No. 6 summarizes our spectroscopic study of the tetramer of phosphonitrilic chloride. This study and an earlier one on the trimer of this compound were made in order to obtain basic infrared data which were to be used in a subsequent kinetic study of these compounds. We expect that both the polymerization and halogen exchange reactions of these phosphonitrilic halides can be investigated by the infrared pressed disk method.

MATRIX ISOLATION OF ION FREE RADICALS

Publication No. 1 reported our matrix isolation study of the carbon dioxide anion free radical. In this study we had assumed that the intensity of the 1665 cm^{-1} infrared band of CO_2^- in KBr was the same as the intensity of the 1633 cm^{-1} band of the HCO_2^- ion. We have since been able to obtain a better estimate of the radical's infrared band intensity by making absolute concentration determinations from EPR scans of our disks. The molar extinction coefficient of the 1665 cm^{-1} band of the radical in a KBr matrix at room temperature is 8.66×10^3 liter/mol-cm, which may be compared to 1.81×10^3 liter/mol-cm for the formate band. Since the specified concentration error in the EPR standards was about 25%, our infrared extinction coefficient of

the radical may have a comparable error. The new extinction coefficient of the radical is 4.8 times greater than that assumed in Publication No. 1.

The principal mode of decay of the radical observed earlier was its reaction with traces of water present in the alkali halide pressed disk to give bicarbonate and formate as reaction products. Subsequently, we have been able to study this decay under anhydrous condition by using the radicals themselves as scavengers of water. A pressed disk was irradiated with gamma rays and then heated, and this process was repeated four to six times. After such a treatment the radical decayed by a bimolecular process, and good second order kinetic plots over two to three half-life were obtained from both the EPR and the infrared methods. In the KCl matrix, where we made a reasonable assumption that the infrared band of the radical has the same intensity as in the KBr matrix, the Arrhenius parameters were $\log A = 9.37 \pm 0.10$ (liter/mol-sec) and $E = 18.93 \pm 0.20$ kcal/mol for the temperature range of 140 to 215°C. The corresponding parameters in a KBr matrix were $\log A = 6.59 \pm 0.08$ and $E = 11.89 \pm 0.15$ for the temperature range of 97 to 200°C. The decay of the radical in the KBr matrix was faster by a factor varying from about four to about ten than the rate in the KCl matrix. The decay in the KI matrix was apparently even faster since it was not possible to trap at room temperature sufficient concentrations of the radical to study its decay by the infrared method. The decay products were diamagnetic, and the carbonate ion was observed to be the principal ionic product

in all matrices. Experimental determinations of the stoichiometry of the ionic species indicated that the other unobserved carbon product was the CO gas. These were just the products observed from the decomposition of the oxalate ion (Publications No. 3 and 4). Although there were considerable uncertainties due to overlapping of the infrared bands, traces of oxalate also seemed to be present after the decay of the radical in the KCl matrix.

The carbonate anion free radical, CO_3^- , was produced by gamma irradiation of monomeric bicarbonate in a pressed disk. At room temperature, the maximum concentration of this radical we were able to trap was less than the CO_2^- case by a factor of about ten. Typical concentrations of the radical in 0.5 g disks were $2-5 \times 10^{-8}$ mole. Since we expected the infrared spectrum of this radical to be essentially the same as that of the carbonate ion, whose strongest infrared band near 1400 cm^{-1} is not only very broad but has an extinction coefficient of only 0.511×10^3 liter/mol-cm in the KBr matrix, it was not profitable to attempt a kinetic study of this radical by the infrared method. Thus, all kinetic studies were made by EPR spectroscopy.

Unlike the CO_2^- radical, the carbonate anion free radical did not react with water. It decayed only by a bimolecular process giving diamagnetic products. From three kinetic runs made at 72, 96 and 118°C in a KCl matrix, the Arrhenius parameters were $\log A = 10.3 \pm 0.4$ (liter/mol-sec) and $E = 14.8 \pm 0.8$ kcal/mol. These parameters in a KBr matrix from four runs were $\log A = 9.6 \pm 0.5$ and $E = 11.9 \pm 0.8$ for the temperature range of 23 to 70°C . The

decay rate in the KI matrix was the same experimentally as in KBr.

When the initial concentration of the radical was high, the decay products in KCl and KBr matrices displayed the same blue color and showed the same weak band at 703 millimicron. However, heating of the disk at 150°C for 15 min destroyed the color and the band. Since the temperature dependence of the color and the absorption band did not agree with the behavior of F-centers created by radiation damage of the matrix, the decay product or products must give rise to the observed band and color. A known oxide of carbon which is consistent with our observations is the peroxydicarbonate ion, $C_2O_6^{2-}$. This peroxy ion is known to decompose thermally into carbon dioxide and the peroxide ion and to hydrolyze in acid to give carbon dioxide and hydrogen peroxide. Not only did our disks give positive tests for peroxide, but in two samples which were hydrolyzed the colorimetric titration with iodide gave the same concentration of the peroxide as was expected from the initial known concentration of the free radical. We propose, therefore, that the bimolecular decay of the CO_3^- radical produces the diamagnetic $C_2O_6^{2-}$ as the initial product, and that this peroxy compound is either trapped in the matrix at lower temperature or is decomposed further into carbon dioxide and peroxide ion at higher temperatures.

The EPR spectrum of the CO_2^- radical trapped in a KCl matrix showed a single symmetric line at $g = 2.0005$ and with a line-width of 14 gauss (Publication No. 1). Neither the line-width nor the

g-value showed any observable temperature dependence from room temperature to near liquid nitrogen temperature. The spectrum of the CO_3^- radical, on the other hand, had a sharp symmetric line at $g = 2.0113$ and with a line-width of only 3.7 gauss at room temperature. However, as the temperature of the disk was reduced below about -150°C , the line broadened and its g-value changed. At -184°C , the line-width was 5.2 gauss and $g = 2.0130$. Not only were these changes reversible, but the temperature dependence of the line-width followed an Arrhenius type equation with an activation energy of $1,024 \pm 60$ cal/mol. At our lowest attainable temperature of -196°C , the line finally split into three components with g-values of 2.0057, 2.0088, and 2.0162. No such splitting was observed with the KBr and KI matrices, and the activation energies in these matrices were also lower, being 527 ± 47 and 108 ± 12 cal/mol, respectively. What these observations suggest is that the CO_3^- radicals trapped in these pressed disks are rotating freely at room temperature. Moreover, as the temperature is decreased, the rotation becomes hindered, and in KCl matrix the rotation ceases at the lowest temperature. These experimental results together with those from kinetic studies of CO_2^- and CO_3^- are being summarized into Publication No. 9.

ENVIRONMENTAL EFFECT STUDIES

The vibrational analysis of the infrared spectrum of the cyanate ion in potassium halide matrices has been discussed in detail in Publication No. 8. This publication constituted the first part of a three part study. In Part II, we plan to report the experimental data on the sodium and rubidium halide matrices while in Part III we hope to present some interpretation of the combined experimental results from the three series of alkali metal halide matrices. More limited studies have also been made on the nitrate ion (Publication No. 12), and interesting conclusions from both sets of studies are summarized below.

As we had hoped, the infrared spectroscopic data from our pressed disks were identical to those obtained by other investigators who used doped single crystals of the same matrices. Our experimental technique allowed saving of considerable amount of experimental time in sample preparation, and in addition, permitted studies of simple organic or inorganic ions whose decomposition temperatures are far below the melting points of the common matrix salts. An example of the latter study was our work on the formate ion (Publication No. 2) which most certainly will decompose completely if one tried to dissolve it in molten potassium bromide. The pressed disk technique allowed us to prepare potassium halide matrices doped with the formate ion and to examine interesting changes in the infrared spectrum of the solute ion. One additional advantage of the pressed disk is that they are insensitive to sudden changes in temperature. These disks can be

cooled rapidly to liquid nitrogen temperature or heated to high temperatures rapidly. On the other hand, single crystals of most alkali halides are notoriously sensitive to thermal shock.

When the experimental frequencies from the cyanate ion (total of 86, 92, and 73 isotopic infrared bands were recorded with KCl, KBr, and KI matrices, respectively) were fitted to a vibrational energy expression which included terms quadratic in the quantum numbers, it was found that only the harmonic energy terms changed significantly from one matrix to another. The anharmonicity constants, on the other hand, were essentially the same experimentally in all three potassium halide matrices. Similar results were obtained from the nitrate ion, although in this case there were insufficient number of infrared bands to determine the complete set of vibrational parameters. Thus, even though the absolute values of the potential constants of the impurity ion may differ significantly depending on whether the observed or the harmonic frequencies are used in the calculation, we can expect that the changes in these potential constants from one matrix to another is reasonably independent on which kind of frequencies were used. This conclusion is encouraging since generally it is not possible to determine the anharmonicity constants of a molecule.

The infrared fundamental bands of the cyanate and nitrate ions exhibited Lorentz band shapes. At 320°K the most intense cyanate band at 2181.8 cm^{-1} in the KCl matrix had a band width

of 1.4 cm^{-1} and a molar extinction coefficient of 7.0×10^3 liter/mol-cm. In KBr and KI matrices the band widths were slightly larger and the extinction coefficients somewhat smaller. The strongest band of the nitrate ion in a KCl matrix had a frequency of 1395.0 cm^{-1} and a band width of 3.6 cm^{-1} at 300°K . Its molar extinction coefficient was 4.4×10^3 liter/mol-cm. The widths of these intense bands of the cyanate and nitrate, as well as the widths of other fundamental bands of these ions, showed an Arrhenius type temperature dependence. The activation energies of the strongest bands were 2.1 and 1.6 kcal/mole, respectively, for the cyanate and the nitrate ion.

In addition to absorption bands arising from the internal vibrational modes of the impurity ion, there were also satellite bands which appeared in combination with the intense internal mode bands. One set of sharp satellite bands was due to the coupling between two impurity ions. The intensities of these bands were proportional not to the first power of the concentration but to the square of the concentration of the impurity ion. Both the nitrate and the cyanate displayed such bands. Another set of satellites arose from the coupling of the external mode, either translational or rotational, of the impurity ion with the internal mode of the same impurity. These bands, which again were observed for both cyanate and nitrate, have been interpreted by earlier investigators as super-optical and gap modes arising from the presence of the impurity in the host crystal lattice. There were

also unresolved broad absorptions near the intense internal mode bands, and these were presumably due to combination of the host lattice modes with the internal mode of the impurity. Much information concerning the nature of the ionic crystal with an impurity can be obtained by the pressed disk technique, and the ease with which these experiments can be carried out should allow considerable progress in this field.

PUBLICATIONS

1. "Infrared Spectrum of Carbon Dioxide Anion Radical," K. O. Hartman and I. C. Hisatsune, *J. Chem. Phys.*, 44, 1913 (1966).
2. "The Kinetics of Formate Ion Pyrolysis in Alkali Halide Matrices," K. O. Hartman and I. C. Hisatsune, *J. Phys. Chem.*, 70, 1281 (1966).
3. "The Kinetics of Oxalate Ion Pyrolysis in a Potassium Bromide Matrix," K. O. Hartman and I. C. Hisatsune, *J. Phys. Chem.*, 71, 392 (1967).
4. "The Kinetics of Calcium Oxalate Pyrolysis," F. E. Freeberg, K. O. Hartman, I. C. Hisatsune, and J. M. Schempf, *J. Phys. Chem.*, 71, 397 (1967).
5. "Chemical Reactions in Ionic Matrices," I. C. Hisatsune, *Nippon Kagaku Zasshi*, 89, 1143 (1968).
6. "The Assignment of the $(\text{PNCl}_2)_4$ Vibrational Spectrum," I. C. Hisatsune, *Spectrochim. Acta*, 25 A, 301 (1969).
7. "Thermal Isomerization of the Maleate Ion in Potassium Halide Matrices," I. C. Hisatsune, R. Passerini, R. Pichai, and V. Schettino, *J. Phys. Chem.*, 73, 3690 (1969).
8. "Infrared Spectrum of Matrix Isolated Cyanate Ion. I. Vibrational Analysis, Band Widths, and Absolute Intensities in Potassium Halides," V. Schettino and I. C. Hisatsune, *J. Chem. Phys.*, in press.
9. "The Decay Kinetics of Carbon Dioxide and Carbonate Anion Free Radicals," I. C. Hisatsune, E. C. Beahm, and T. Adl, in preparation.
10. "Thermal Decomposition of the Acetate Ion in Potassium Halide Matrices," I. C. Hisatsune and E. C. Beahm, in preparation.
11. "Thermal Decomposition of the Perchlorate Ion in a Potassium Chloride Matrix," I. C. Hisatsune and D. G. Linnehan, in preparation.
12. "Infrared Spectrum of Matrix Isolated Nitrate Ion", M. Tsuboi and I. C. Hisatsune, in preparation.

PERSONNEL

Individuals who assisted in this research project, the durations of their participations, and their research subjects are summarized below. Also during the project period, the principal investigator was away from the university twice. He served as a Visiting Professor at the Molecular Spectroscopy Laboratory of the University of Florence, Italy, from June to December 1966 and again as a Visiting Professor at the Department of Chemistry of the University of Tokyo, Japan, from March to September 1968.

Senior Research Personnel:

1. M. C. Dodge (Ph. D., Univ. of Calif., Berkeley, 1968): March to September 1969; thermal decomposition of the hydrazinium ion.
2. R. Pichai (Ph. D., Annamalai Univ., India, 1967): August 1967 to August 1968; thermal isomerization of the maleate ion.
3. V. Schettino (Ph. D., Univ. of Florence, Italy, 1965): July 1967 to June 1968; vibrational analysis of the matrix isolated cyanate ion and thermal isomerization of the maleate ion.
4. M. Tsuboi (D. Sc., Univ. of Tokyo, Japan, 1953): July and August 1969; vibrational analysis of the matrix isolated nitrate ion.

Junior Research Personnel and Degrees Earned from this University:

1. T. Adl (M.S., March 1969): March 1966 to March 1969; matrix isolation and decay kinetics of the carbonate anion free radical and thermal decomposition of the bicarbonate ion (exploratory).
2. E. C. Beahm: March 1967 to October 1969; thermal decomposition of the acetate ion and the decay kinetics of the carbon dioxide anion free radical.
3. M. L. Franklin (M.S., September 1966): June 1965 to September 1966; radiation damage of nitrate and nitrite ions (exploratory).
4. K. O. Hartman (Ph.D. September 1965): June 1965 to September 1965; thermal decomposition of formate and oxalate ions and matrix isolation of the carbon dioxide anion free radical.
5. R. J. Kempf (Ph.D., September 1967): June to September 1967; radiation damage of acetate ion and ESR study of the carbonate anion free radical (exploratory).
6. D. G. Linnehan (M.S., December 1969): April 1966 to December 1969; thermal decomposition of the perchlorate ion.
7. G. E. McGraw (Ph.D., December 1965): June to December 1965; matrix isolation of some carbonium ions (exploratory).
8. J. J. Stacy (B.S., June 1966): June 1965 to June 1966; thermal decomposition of perchlorate and chlorate ions (exploratory).