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Observations of the Thermal Behavior of Radicals in Gamma-Irradiated Ice*

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Ice was subjected to γ radiation at 77°K and the EPR spectra of the radicals produced were examined as a function of temperature. The spectrum consisted essentially of a doublet centered at $g=2.008\pm0.002$ and split by 40 gauss; the corresponding spectrum of irradiated D_2O consisted of a triplet with approximately 6 gauss between adjacent lines. The doublet decayed rapidly above 100°K leaving a residual broad line which was thermally stable until approximately 145°K. The main spectrum has been attributed to the OH radical and the residual line assigned to the HO_2 radical. The decay process of the OH radicals was shown to follow the rate law $d(\text{OH})/dt=-k(\text{OH})^{\frac{3}{2}}$ where $k=8.5\times10^{12}\exp-6000/RT$ (liter/mole)$^{\frac{1}{2}}$ sec^{-1}. The magnitude of the rate constant was shown to be a function of the total irradiation damage experienced by the ice sample.

Stabilization of OH radicals at 77°K was studied as a function of total irradiation dosage; saturation is reached at an OH concentration of $1.8\times10^{-3}M$ or 0.003 mole %. The EPR spectrum of a frozen aqueous NO solution was also observed; it consisted of a broad line centered at approximately $g=2.08$.

I. INTRODUCTION

In the last few years a great amount of effort has been expended in research on the stabilization of free radicals at low temperatures. However, little is known of the mechanism of the stabilization processes or of the forces which the radicals experience in the trapping matrix. It was thought at this laboratory that an important contribution to the understanding of the nature of the stabilizing forces might be obtained from isothermal kinetic studies on the stabilization and recombination of radicals trapped at low temperatures. Also, these experiments could shed light upon the nature and energetics of the diffusion process.

The kinetics was studied by following the growth and decay of the EPR spectrum of radicals produced by the γ irradiation of ice at 77°K. The use of EPR techniques was considered the most desirable method with which to obtain accurate data since the radicals can be observed continuously and the method of detection perturbs the observed systems only to a negligible extent. Also, observations of the line shape and width as a function of concentration and temperature yield information on the magnitude and nature of the matrix perturbations.

Irradiated ice was chosen as the first system to study because of the considerable amount of work done on the radiation chemistry of water at room temperature. It was hoped that the behavior of the radicals formed at low temperatures might be correlated with postulated mechanisms at room temperature. There is some controversy in the literature over the shape and interpretation of the spectrum of irradiated ice[1,2]; it was hoped that this study would help settle this question.

II. EXPERIMENTAL

Sample Preparation

Samples of distilled water weighing 0.4–0.6 g were degassed under high vacuum, frozen in cylindrical Pyrex molds, and transferred from the molds to the precooled microwave cavity with only slight melting on the surface. The samples were irradiated in the cavity at 77°K by means of an 800-curie cobalt-60 source at a dose rate of approximately 1.0×10^5 rep/hr. Most of the data were obtained from samples irradiated to a total dosage of approximately 1.6×10^6 rep (about 0.9×10^{20} ev/g).

Paramagnetic Resonance Equipment

Spectra were obtained with a Varian Associates V-4500 EPR Spectrometer equipped with a 12-in. magnet system and low temperature accessories. The output from the crystal detector is an ac signal (400 cps) which, after ac amplification, is passed through a phase detector to a graphic recorder; the recorder presentation is approximately the derivative of the resonance line. Most of the quantitative work was done at power levels which were shown by experiment to be low enough to avoid power saturation effects on the OH spectrum. The microwave frequency was near 9.4 kMc and was measured with a calibrated tunable cavity. The magnetic field was calibrated with respect to the six absorption lines of Mn^{++} in zinc-blende[3] and the resonance line of solid DPPH.[4]

Concentration Determinations

The concentrations of OH were estimated by a comparison between the values of (height×width^2) for the absorption derivative curves for OH and for a known

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* This research is being supported by a contract with the Air Force Office of Scientific Research.

[1] M. S. Matheson and B. Smaller, J. Chem. Phys. **23**, 521 (1955).

[2] R. Livingston, H. Zeldes, and E. H. Taylor, Discussions Faraday Soc. **19**, 166 (1955).

[3] J. S. Van Wieringen, Discussions Faraday Soc. **19**, 118 (1955).

[4] A. N. Holden, W. A. Yager, and F. R. Merritt, J. Chem. Phys. **19**, 1319 (1951).

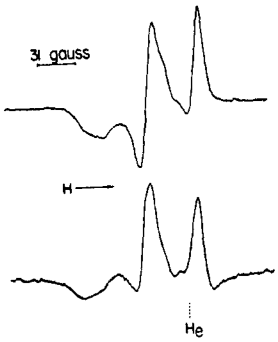

FIG. 1. Paramagnetic resonance spectrum of γ-irradiated H_2O at 77°K. The upper and lower spectra are the absorption and dispersion signals, respectively. In this and the following figures H_e represents the free electron resonance as given by the equation $h\nu=g_e\mu_0 H_e$ where $g_e=2.0023$.

quantity of Wurster's blue perchlorate (WBP) dispersed in an ice sample of identical size and geometry at 77°K. The product of the height of an absorption derivative curve and the square of the width at maximum height is directly proportional to the area under the absorption curve, and the proportionality constant is a function of line shape only. Inspection of the shapes of the dispersion derivative curves for OH and WBP showed that the OH curve was very nearly Gaussian while the WBP line was very nearly Lorentzian. It can be shown that for two absorption derivative lines of identical area, one Lorentzian (L) and the other Gaussian (G), that $(hw^2)_G/(hw^2)_L=3.49$. Using this correction factor, and allowing for both lines of the OH doublet, a comparison of (hw^2) for the two systems yielded a value of 8×10^{-4} moles/liter for the OH concentration after 16.5 hr of irradiation (1.6×10^6 rep). The absolute values of the concentrations are estimated to be good to within a factor of two.

They are in excellent agreement with values which we obtained in calorimetric studies of irradiated ice (to be published), based on the assumption that OH recombination ($\Delta H\cong-26$ kcal/mole OH) was[5] responsible for an exotherm observed on warming irradiated ice to 100°K.

Temperature Control

The EPR cavity was mounted in a double Dewar system designed for liquid helium. For temperatures above 77°K, the inner Dewar and its vacuum jacket were filled with nitrogen gas and the outer Dewar with liquid nitrogen. Warming of the cavity was accomplished by blowing a stream of dried nitrogen at room temperature into the volume surrounding the cavity but not impinging directly on the cavity. A calibrated copper-constantan thermocouple was in intimate contact with the lower part of the sample cavity and was insulated from the immediate surroundings by $\frac{1}{4}$-in. styrofoam. The thermocouple output was recorded continuously by a recording potentiometer. The potentiometer was fitted with electrical contacts which, though an electronic relay, caused a solenoid valve to open and close, controlling the warm nitrogen flow around the cavity. This control system was sensitive to about ±0.05°K (1μv) and maintained the sample temperature continuously to within ±0.2°K maximum variation at temperatures from 85° to 150°K. In one experiment, a second thermocouple was frozen directly into a sample inside the cavity; the temperature of the inner thermocouple was within 0.5°K of that of the outer control thermocouple.

Rate Measurements

After irradiation of a sample the concentration of stabilized OH was determined at 77°K for use as an initial value in the kinetic calculations. The sample was then warmed rapidly (about 10°/min) to the reaction temperature, and rate measurements were begun within about three minutes, the time required to retune the apparatus at the higher temperature. A reference portion of the absorption derivative spectrum was scanned repeatedly at 30–60 second intervals during decay at constant temperature. Occasional scans of the entire spectrum showed that no noticeable changes in line shape occurred before about 90% decomposition, after which perturbations from the overlapping spectra of other trace radicals became appreciable. Within the region of constant line width, relative OH concentrations were taken to be proportional to the height of the low-field component of the doublet.

III. RESULTS AND DISCUSSION

Description of the Observed Spectra in Irradiated Ice

A. H_2O

The EPR spectrum of degassed ice irradiated and observed at 77°K consists essentially of a partially resolved doublet and a broad hump at the low field end of the spectrum (Fig. 1). The doublet has a hyperfine splitting constant of 110±5Mc/sec and a g value of 2.008 ± 0.002. The members of the doublet have a line width at half height of approximately 17 gauss. The line widths of the doublet components do not vary measurably with changes in the concentration of radicals present, which indicates that the line width is due to spin-matrix interactions rather than electronic spin-spin interactions. The doublet begins to disappear slowly at 90°K, and at 110°K the spectrum decays very rapidly. The broad side band has essentially the same temperature dependence as the doublet.

After the spectrum described above has disappeared, a weak, broad, unresolved line remains (Fig. 2) until the temperature reaches about 145°K, at which point the line begins to lose intensity measurably with time.

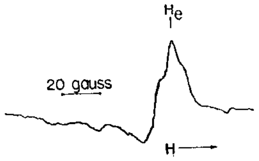

FIG. 2. Absorption spectrum of γ-irradiated H_2O at 77°K after annealing at 110°K.

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[5] P. A. Giguère, J. Chem. Phys. **30**, 322 (L) (1959).

This line has a width of approximately 20 gauss. The height of the line relative to one of the peaks of the doublet depends upon the total irradiation dosage; the larger the dosage the greater the relative height. After a dosage of 0.9×10^{20} ev/g the relative height was ~4%, while after 2.7×10^{20} ev/g the relative height was ~8%.

B. D_2O

The EPR spectrum of a D_2O sample irradiated and observed at 77°K consists of a poorly resolved triplet and a broad band on the low field side of the spectrum (Fig. 3). The triplet has approximately the same g value as the doublet observed in the H_2O system and has a hyperfine splitting constant of 17 Mc/sec. The ratio of the observed splittings of the doublet and triplet is in excellent agreement, within experimental error, with the reported[6] free atom ratio of $H/D=6.5$.

The line widths of the triplet components are about 5 gauss. The ratio of the line widths in the spectra of irradiated H_2O and D_2O is in good agreement with the ratio of the magnetic moments of the proton and deuteron. This good agreement, together with the observations that the line width did not appreciably change with spin concentration or with temperature from 77° to 107°K, indicates that the main cause of line width is the magnetic interactions of the free electron and the nuclei of the matrix.

The field position of the broad band on the low field side of the spectrum is essentially the same as that of the broad band in the irradiated H_2O spectrum.

Interpretation and Assignment of Spectra

The transformation of the observed doublet in the spectrum of irradiated H_2O into a triplet in the spectrum of irradiated D_2O strongly indicates that the responsible paramagnetic species contains only one interacting hydrogen atom. The radicals containing one hydrogen atom that are most likely to be formed during the irradiation process are H, OH, and HO_2.

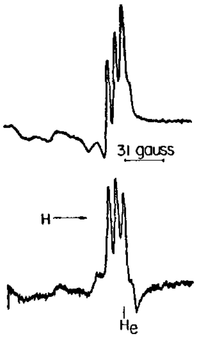

FIG. 3. Paramagnetic resonance spectrum of γ-irradiated D_2O at 77°K. The upper and lower spectra are the absorption and dispersion signals, respectively.

Matheson and Smaller,[1] using a 350 Mc/sec quarter-wave coaxial line oscillator detector, observed a doublet at $g=2.0$ in the spectrum of γ-irradiated ice which they attribute to strongly perturbed H atoms; this doublet is probably the same as the one reported here.[7] However, recently the spectra of ice, irradiated at 4°K with high voltage electrons and with γ rays, were observed at the Varian Associates Laboratory[8] and at this laboratory, respectively. The 4°K spectrum contains the doublet described above (split by 40 gauss) superimposed on a broad background; it also contains a doublet centered about $g=2.0$ and split by approximately 500 gauss. It seems very probable that the latter doublet, which has a hyperfine splitting constant very close to that of a free H atom, is due to trapped H atoms. Also, H atoms have been trapped in a variety of other matrices, at this laboratory and elsewhere, including acidified ice,[2,9] wet glass surfaces,[2] solid hydrogen,[8,10] and sodium *meta*-silicate. The EPR spectra of all these systems contained a doublet which was split within 20 Mc of the free hydrogen atom value. The maximum temperature at which the hydrogen atoms were stable in the various matrices varied from 40° to above 100°K; microwave power saturation studies indicated that the relaxation times for the trapped hydrogen atoms also varied appreciably. In view of the constancy of the splittings found for H atoms perturbed by their environment to considerably different extents, it seems very unlikely that the 40-gauss doublet is due to trapped hydrogen atoms.

Several other investigators have reported spectra similar to the residual broad line left after the disappearance of the doublet[10,11]; they have, on various reasonable arguments, tentatively attributed this line to the HO_2 radical. The line shape is similar to that found for the corresponding salt NaO_2.[12] Examination of the EPR spectrum of a 0.01 M aqueous H_2O_2 solution irradiated at 77°K in our laboratory showed that the height of the broad line relative to that of the doublet was considerably greater (~30%) than in plain H_2O (~4%). Experiments performed here on frozen aqueous solutions have shown that considerable energy is released upon irradiation and that chemical reactions readily take place during irradiation even at 77°K.[13]

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[6] J. E. Nafe and E. B. Nelson, Phys. Rev. **73**, 718 (1948).

[7] However, Matheson and Smaller report a splitting constant of 85.5 Mc/sec while the value reported here is 110±10 Mc/sec. The difference in the two values is larger than experimental error; the reason for the difference is not immediately obvious.

[8] L. H. Piette, R. C. Rempel, H. E. Weaver, and J. M. Flournoy, J. Chem. Phys. **30**, 1623 (1959).

[9] R. Livingston, H. Zeldes, and E. H. Taylor, Phys. Rev. **94**, 725 (1954).

[10] C. K. Jen, S. N. Foner, E. L. Cochran, and V. A. Bowers, Phys. Rev. **112**, 1169 (1958).

[11] R. Livingston, J. Ghormley, and H. Zeldes, J. Chem. Phys. **24**, 483 (L) (1956).

[12] J. E. Bennett, D. J. E. Ingram, M. C. R. Symonds, P. George, and J. S. Griffith, Phil. Mag. **46**, 443 (1956).

[13] Two degassed aqueous solutions, one 0.01 M in acrylamide and the other 0.01 M in $FeSO_4$, were irradiated at 77°K. Examination of their EPR spectra showed a marked decrease in the intensity of the observed doublet, as well as modifications in the shape of the spectra, compared to the spectrum observed from irradiated pure ice.

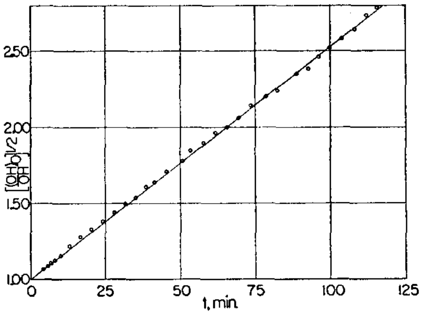

FIG. 4. Disappearance of OH radicals in ice at 100°K; OH_0= initial OH concentration.

Also, Foner and Hudson[14] have shown that the reaction $H_2O_2+OH \rightarrow H_2O+HO_2$ occurs readily in the gas phase. Thus it seems quite probable that the broad line is due to HO_2 and that the reaction stated above does take place during irradiation of the H_2O_2 solution. On this basis the doublet spectrum in irradiated ice and the triplet spectrum in irradiated D_2O can be readily attributed to the OH and OD radicals, respectively.

An important objection which might be raised to the above identification is that the ground electronic state of the OH radical in the gas phase is $^2\Pi$. Molecules in the $^2\Pi_{1/2}$ state should be essentially nonparamagnetic and those in the $^2\Pi_{3/2}$ state should have a g value appreciably different from $g=2.0$. However, an OH radical trapped in an H_2O lattice will experience quite intense crystalline fields. It would not be improbable for the crystalline field interactions to uncouple the spin and orbital angular momenta, yielding a spectrum centered about $g=2.0$ due to the residual Kramers' doublet. We have, in fact, observed a spectrum centered about $g=2.0$ for a frozen aqueous solution of NO ($^2\Pi$ electronic state) which tends to confirm that quenching of the orbital momentum can take place in an ice matrix. (The NO observations are discussed below.) For the remainder of the paper the identification of the doublet as the OH radical will be considered correct.

Kinetics

The rate law $d(OH)/dt=-k'(OH)^{3/2}$ was found to describe accurately the decrease of OH concentration with time in ice at temperatures from 92–107°K. The validity of the $\frac{3}{2}$ order law was confirmed in separate experiments in which the initial concentrations differed by a factor of 5.5. Figure 4 gives a plot of $(OH_0/OH)^{1/2}$ vs time obtained in one of the runs at 100°K.

The magnitude of the rate constant k' was found to depend upon the history of the sample. In order to assure a constant sample weight and geometry in the microwave cavity, some samples were used for several kinetic runs by warming the cavity (without melting the sample) to destroy the residual radicals, and then reirradiating at 77°K. It was found that the magnitude of the rate constant was a function of the cumulative dosage even at the same initial OH concentrations; an increase in cumulative dosage by a factor of more than 20, from 0.9×10^{20} to 20×10^{20} ev/g, resulted in an increase in the observed rate constant by a factor of 3.5. Corrections were therefore necessary in comparisons between rate constants for new and reirradiated samples. The uncertainty in the activation energy due to the incorporation of these corrections is only about 0.3 kcal/mole.

The uncorrected molar reaction rate constants (k') are tabulated in Table I, along with the constants (k) which are corrected for cumulative irradiation effects. The uncertainty in the 77°K rate constant is due to the possibility that the very slow decrease in spectral intensity (*ca.* 2%/day) may have been due in part to drift in the sensitivity of the EPR spectrometer. The uncertainty in the rate constants due to graphing errors is estimated at ±10%. An Arrhenius plot, illustrating the temperature dependence of the rate constant k, is given in Fig. 5. The corrected rate constant can be expressed by the following Arrhenius expression

$$k=8.5\times10^{12}\exp-6000/RT\ (\text{liters/mole})^{1/2}\ \text{sec}^{-1}$$

over the entire temperature range studied, representing a maximum change in rate constant of a factor of 10^4. The uncertainty in the activation energy is estimated to be less than ±0.5 kcal.

Experiments involving OD in D_2O indicate that the activation energy for the deuterated system is, within experimental error, the same as that for OH in H_2O.

The most likely uncharged products formed during the irradiation of ice at 77°K are OH, HO_2, H_2O_2, and H_2; there may also be very small amounts of H atoms present ($<10^{12}$ spins/cc). An attempt to derive a $\frac{3}{2}$ order rate law for the disappearance of OH in terms of various reaction mechanisms using the above species was unsuccessful. One problem is that there is considerable doubt about the identities of the primary products from the OH decay. The concentration of H_2O_2 after melting the samples was found, using approximate colorimetric methods, to be considerably less than that predicted on the basis of the reaction $2OH \rightarrow H_2O_2$

TABLE I. Molar rate constants.

k', (liter/mole)$^{1/2}$ sec^{-1}	k,[a] (liter/mole)$^{1/2}$ sec^{-1}	T, °K	Total dosage,[b] ev/g$\times10^{-20}$
5×10^{-4}	2×10^{-4}	77	8.5
0.12	0.085	92.0	4.2
0.12	0.12	94.8	0.9
0.79	0.79	100.1	0.9
1.06	0.79	100.1	3.5
3.33	2.72	103.9	2.6
6.32	5.67	106.7	1.7

[a] These constants are corrected for cumulative irradiation damage; all values are normalized to a total dosage of 0.9×10^{20} ev/g.

[b] This quantity is the total irradiation dosage received by the sample.

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[14] S. N. Foner and R. L. Hudson, J. Chem. Phys. **23**, 1364 (L) (1955).

alone. Ghormley and Stewart,[15] using more exact analytical methods, after melting the irradiated samples determined the concentration of H_2O_2 produced with irradiation dose rates of 3.0×10^{18} ev/g hr and 4.2×10^{19} ev/g hr (5.3×10^{18} ev/g hr was the dose rate in the experiments described in this paper). Their results indicated H_2O_2 concentrations which were a factor of 4 to 5 smaller than those predicted on the basis of the stabilized OH concentrations determined by the present authors for the same dosage. The yields of hydrogen and oxygen were found in our experiments to be somewhat smaller than the yields of stabilized hydroxyl radicals; however, the experimental conditions were such that the differences are not too significant. The significant fact is that the above products are not present in large excess of the stabilized OH radicals (see next section). The problem is further complicated by the fact that the analysis of products is made after melting the sample; thus effects due to reactions occurring during the melting process must also be considered.

An important and complicating feature of the system under consideration is that the reaction is taking place at low temperatures between species embedded in a solid matrix. The problem of encounter rates is much more difficult in the solid phase than in the liquid or gaseous phases. In the solid state there is no translational motion in the ordinary sense and mass transfer is accomplished by a limited degree of diffusion which probably depends upon complex mechanisms. Also, in a polycrystalline sample there is a considerable amount of internal surface area, as well as a large number of grain boundaries, which would be important in the diffusion process. The fractional order of the observed rate law could be due to the mechanism of mass transfer.[16] The observed increase in the rate constant with increased irradiation damage certainly suggests that the diffusional process is very important. An activation energy of 6 kcal/mole is consistent with the idea that the rate-controlling step is the diffusional process since hydroxyl radicals are probably involved in the elaborate hydrogen bond network in ice. The energy of a normal hydrogen bond in ice is approximately 5 kcal/mole.[17]

A kinetic run at 100°K was made on a sample of ice which was prepared from 0.01 *M* aqueous H_2O_2 and was irradiated to produce an OH concentration of 4×10^{-4} *M*. The peroxide concentration in this experiment was nearly two orders of magnitude greater than the amount normally found after irradiation of pure ice, but the rate of disappearance of OH was only about twice the normal rate, initially, and approached the normal rate as the reaction proceeded. The relatively slight effect of the peroxide on the rate indicates that H_2O_2 is not a principal reactant in the rate determining step. However, the kinetics were somewhat perturbed, in that the peroxide run followed closely a second order rate law in OH, instead of the normal $\frac{3}{2}$ order law, during the two half-lives for which data were obtained. The effects of the peroxide are not well understood, but may be due to perturbation of the crystal lattice of the ice matrix which might affect the diffusion mechanism of OH.

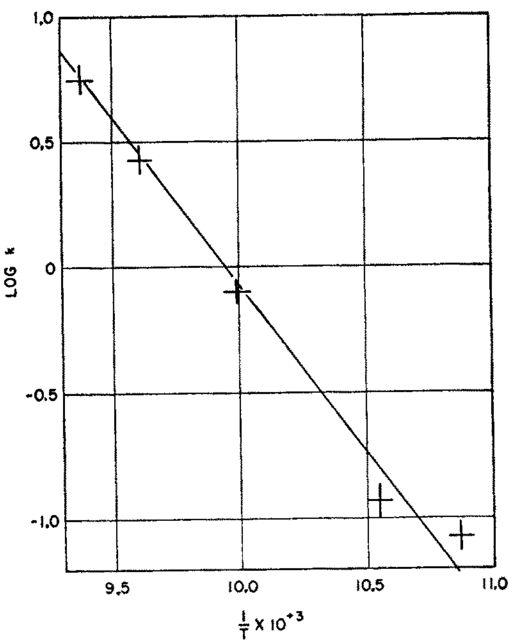

FIG. 5. Temperature dependence of rate of disappearance of OH in irradiated ice.

Production of Stabilized Radicals

Stabilization of OH radicals at 77°K was studied as a function of total irradiation dosage. The irradiation was stopped at intervals and the EPR spectrum examined. The effect of stopping the irradiation at intervals was shown in separate experiments to be negligible. Since the line width did not change with concentration the peak height was taken to be proportional to concentration, and the absolute concentration was determined at only one point. The concentration of stabilized OH radicals is shown as a function of cumulative dosage in Fig. 6. "Saturation" is reached at an OH concentration of $1.8\times10^{-3}M$ or 0.003 mole %.

An attempt to fit the experimental curve to a rate law of the form $d(\mathrm{OH})/dt=a-k(\mathrm{OH})^n$, where a and n are empirical constants, showed that the best fit is obtained when $n=\frac{1}{4}$. The rate of stabilization was not sensitive

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[15] J. A. Ghormley and A. C. Stewart, J. Am. Chem. Soc. **78**, 2934 (1956).

[16] *Note added in illustration*: In the case of certain catalyzed, heterogeneous, diffusion-controlled, bimolecular reactions the apparent concentration dependence is $\frac{3}{2}$ order [P. H. Emmett, *Catalysis* (Reinhold Publishing Corporation, New York, 1955), Vol. II, p. 131]. It is not suggested that exactly the same conditions exist in the case under discussion; rather, the example is given only to illustrate the effect that the physical mass transfer process can have on the apparent concentration dependence of a chemical reaction.

[17] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1948), p. 301.

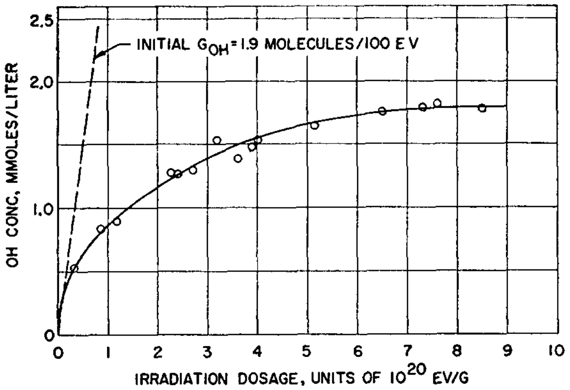

FIG. 6. Stabilization of OH radicals in γ-irradiated ice at 77°K as a function of cumulative dosage. A constant dose rate of 5.3×10^{18} ev/g hr was used.

to the past irradiation damage to the sample as was the case of the decay process. The latter observation, together with the fact that the concentration dependence is not $\frac{3}{2}$ order, indicates that the mechanism of destruction of radicals is completely different during irradiation from the mechanism during the decay process. Work is in progress on the effect of different irradiation levels and sample geometry; any further speculation on the mechanism of stabilization and the theoretical significance of the empirical rate law will be deferred until this work is completed.

An interesting feature of the stabilization curve is that the initial slope corresponds to an irradiation yield $G_{OH}=1.9$ radicals/100 ev; the corresponding value[18] for pure H_2O at 300°K is $G_{OH}=2.05$. This close agreement (even taking into account the uncertainty of the concentration determination) suggests that the mechanism of radical formation by ionizing radiation is essentially the same at 300° and 77°K. In water at 300°K molecular hydrogen and hydrogen peroxide are thought to form in regions of dense energy release, i.e., at the ends of the tracks of slow secondary electrons. The radicals H and OH diffuse out of the tracks from regions of less dense energy release; the radiation yield measures the number of radicals which do not recombine immediately.[19] Stabilization of essentially the same number of OH radicals at 77°K as survive to diffuse out of the "spurs" at room temperature illustrates the effectiveness of the ice matrix as a radical trap at low concentrations.

The initial slope of the OH stabilization curve (Fig. 6) represents a minimum value for the rate of formation OH (and H) during irradiation; it is of interest to consider the destruction reactions which are responsible for the decrease in yield of stable OH with prolonged irradiation. Toward this end, the final yields of the molecular products H_2 and H_2O_2 were determined, after melting, for a sample which had been irradiated to saturation with respect to OH ($1.8\times10^{-3}M$ after a dosage of 2×10^{21} ev/g). Extrapolation of the initial slope of Fig. 6 to this dosage indicated that at least 6×10^{-2} moles/liter of H and OH should have been formed during the irradiation. However, on the basis of the observed EPR spectra, 97% of the OH and 100% of the H had disappeared, presumably through the reactions:

$$2OH\rightarrow H_2O_2 \tag{1}$$

$$H+OH\rightarrow H_2O \tag{2}$$

$$2H\rightarrow H_2. \tag{3}$$

Analysis of the sample after melting showed that the final H_2O_2 and H_2 concentrations were both somewhat less than 10^{-3} M, i.e., of the order of 1% of the values which would have been expected if reactions (1) and (3) were predominant during irradiation. Thus, the destruction of OH apparently occurs principally through recombination with H. This conclusion is a reasonable one in view of the wide difference in stability between H and OH. The absence of stable H at 77°K indicates that H is more mobile than OH, the latter probably being strongly hydrogen-bonded in the ice matrix. Therefore reaction (1) is quite unfavorable with respect to (2) and (3). The relative importance of (2) and (3) depends on the concentration ratio (OH)/(H), which rapidly becomes quite large as OH accumulates, causing (2) to predominate after a short time. In evaluating these conclusions, it must be remembered that the product analysis was made after the sample melted. The desirability of product analysis at low temperatures is obvious; low temperature infrared techniques would be useful in this regard.

NO in Ice

It was thought that since NO has a similar ground electronic state to OH in the gas phase, the electron paramagnetic resonance spectrum of NO in a crystal matrix would be of great interest. Jen *et al.*[10] failed to observe a spectrum for NO either in an argon matrix at 4°K or in a CO_2 matrix at 77°K. The absence of a spectrum was attributed to crystal anisotropy coupled with the $^2\Pi$ state of NO. However, since the H_2O matrix would provide stronger electric fields than argon or CO_2 it seemed desirable to attempt to observe NO in an ice matrix.

FIG. 7. Absorption spectrum of an aqueous NO solution at 77°K.

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[18] C. J. Hochanadel and S. C. Lind, Ann. Rev. Phys. Chem. 7, 83 (1956).

[19] J. L. Magee, J. Am. Chem. Soc. 73, 3270 (1951).

Gaseous NO (fractionally distilled to remove most of the NO_2) was dissolved in previously degassed H_2O at room temperature. The resulting solution was quickly frozen under a partial pressure of NO of about 60 cm Hg, and the EPR spectrum was taken at 77°K (no irradiation). The observed spectrum is shown in Fig. 7.

The presence of a broad spectrum at $g=2.08\pm0.02$ indicates that the orbital angular momentum is largely uncoupled from the spin momentum since molecules in the ${}^2\Pi_{\frac{1}{2}}$ state would be nonparamagnetic and those in the ${}^2\Pi_{\frac{3}{2}}$ state would have a g value near $\frac{4}{5}$. However, the broad unresolved physiognomy of the spectrum and the deviation of g from 2.002 suggests that the quenching of the angular momentum is not complete. The fact that the line was not appreciably power saturated at the highest klystron power output available to us, more than 230 mw, confirms that the relaxation time is quite short, as would be expected for such a system. The line shape remained approximately constant from 77° to 180°K; it could not be ascertained accurately, because of tuning problems, whether or not the line was appreciably broadened at the higher temperatures.

The observation that the angular momentum of NO is only partly quenched in ice ($g=2.08$) while the angular momentum of OH is rather completely quenched ($g=2.008$) is at first somewhat surprising, since the two radicals are quite similar electronically in the gas phase. However, it must be remembered that the radicals are imbedded in an ice matrix and that the OH radical would be much more intimately involved in the hydrogen-bonded network than would NO. In fact, the structural description of the OH radical in ice is probably incomplete without inclusion of the hydrogen-bonding interactions between the hydroxyl oxygen atom and the H atoms belonging to the neighboring water molecules. The line width in the case of the OH radical was shown above to be largely determined by the magnetic perturbation produced by the magnetic moments of the matrix nuclei. Also, the magnitude of the line width did not appreciably change over the temperature range studied. The last observation strongly indicates that the OH radical is held tightly in the hydrogen bonded cage, since any appreciable motion of the radical would result in line narrowing as the temperature increased. If the line broadening is due primarily to spin-spin dipolar interactions between the free electron and two equivalent hydrogen-bonded hydrogen nuclei, then a line width of 17 gauss corresponds to an average distance of 1.1 A between the free electron and either of the interacting nuclei. This distance is noticeably shorter than Pauling's value of 1.7 A for the O···H separation in ice.[17] The hydrogen atom which is directly bonded to the oxygen atom on which the free electron is localized contributes a larger dipolar splitting, which together with the isotropic hyperfine splitting accounts for the observed splitting of 40 gauss.

FIG. 8. An unidentified spectrum observed in several samples of γ-irradiated H_2O and D_2O.

A detailed calculation of the line shape expected for such a model as described above is underway.

Unidentified Triplet Spectrum

A triplet spectrum, which does not decay appreciably below about 200°K, was observed in several H_2O samples which had been irradiated at 77°K (Fig. 8). The same spectrum was observed in some of the D_2O samples. The splitting between adjacent lines is 20 gauss in both the H_2O and D_2O samples; therefore, the responsible paramagnetic species does not contain an interacting hydrogen atom. The spectrum is centered at $g=2.002\pm0.001$. The component lines have line widths of approximately 3 gauss in both the H_2O and D_2O matrices; thus, the magnetic nuclei of the lattice are not interacting appreciably with the unpaired electron. Another interesting feature of the triplet spectrum is that the relative intensities of the lines change with temperature. At 77°K the relative intensities are 1:1.7:1.2, going from high to low field; as the temperature increases the relative intensities approach 1:2:1. Also, the absolute height of the lines increases with temperature while the line width does not decrease noticeably.

The conditions under which the triplet is formed upon irradiation are not well understood. In the degassed samples the triplet seldom occurred on short irradiations; when it did appear its intensity relative to the main spectrum (described above) was weak. Upon long irradiations the triplet increased in intensity. It was thought that the triplet might be due to residual gas left after imperfect degassing, although this seemed doubtful, or to O_2 formed during the irradiation process. However, H_2O samples which were frozen while saturated with air produced little or no triplet upon irradiation at 77°K. On the other hand, samples saturated with O_2, N_2, or Ar all produced a large amount of triplet after irradiation; in fact, with the O_2 saturated sample the normal spectrum was almost completely absent. This last series of experiments indicates that the species responsible for the triplet may be due to reactions involving the radicals responsible for the normal spectrum, i.e., OH radicals. The disappearance of the triplet upon warming above 200°K is an irreversible process since the spectrum fails to reappear on cooling again to 77°K. This confirms the fact that the spectrum is due to an unstable species formed during the irradiation.

IV. CONCLUSION

The growing importance of free radical research and low temperature reactions lends interest to the results described in this paper. The techniques described here can be used for investigating diffusion-controlled processes in a variety of systems. Correlation of line widths and thermal stability should give important information on the relaxation processes and on the binding forces present in the solid state. Further work is in progress at this laboratory along these lines.

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Rate Constants at Low Concentrations. V. Mechanism of Reaction of Ozone with Photolyzing Nitrogen Dioxide in Presence of Excess Oxygen*

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Trace concentrations of ozone and nitrogen dioxide in pure, dry air at atmospheric pressure were exposed to a known intensity of 3660 A radiation in a stirred flow reactor at 300°K. An increase of steady-state concentrations of ozone and nitrogen dioxide above their dark values was observed and measured. A value of $k_7K_{eq}=0.44$ sec^{-1} ($NO_3+NO\rightarrow 2NO_2$, k_7, $NO_2+NO_3\rightleftharpoons N_2O_5$, K_{eq}) was obtained from the data using a postulated mechanism. The good agreement between this value and the values of 1.0 sec^{-1} obtained by I. C. Hisatsune, B. Ogg, and R. A. Crawford [J. Am. Chem. Soc. **79**, 4648 (1957)] supports the validity of the proposed mechanism.

THE authors have reported the results of an investigation of the reaction of ozone with nitrogen dioxide[1] in which the following method was used. The reactants and pure, dry air were passed into a stirred flow reactor at measured flow rates. The steady-state effluent concentrations were measured both with the reactor dark and with irradiation. Checks were made on the equality of the influent and effluent concentrations of each of the reactants in the absence of the other.

Data obtained in those experiments with no irradiation allowed a calculation of the rate constant for reaction (4) in the following, previously reported.[1] However, the data obtained with these mixtures irradiated with a known light intensity at 3660 A have not been previously reported because the fate of atomic oxygen produced by photolysis of nitrogen dioxide was not sufficiently understood. Now that the reactions of atomic oxygen have been better established[2-4] we can propose a reaction mechanism and interpret the data with greater confidence.

The experimental results are shown in Table I. It is apparent that both reactants were consumed in the dark reaction, and this result can be accounted for by reactions previously discussed.[1] When the mixture was irradiated following attainment of dark steady state, both of the effluent reactant concentrations increased to irradiated steady-state values (see columns 3, 4, 6, and 7, Table I). Ozone effluent concentrations were higher than influent concentrations in two instances, whereas nitrogen dioxide did not attain its influent concentration. These small differences between influent and effluent dioxide concentrations can be used to estimate some of the reaction constants in the mechanism proposed below.

According to published rate constants,[2,4] atomic oxygen is important only in its reaction with molecular oxygen to form ozone when such a large excess of oxygen is present. The mechanism shown in Table II is proposed.

The steady-state stirred reactor equations were used to obtain a relationship between the reaction constants and the data. The residence time in the reactor was so long that the rate of removal by reactor flow of the species O, NO, and NO_3 was insignificant in comparison with their rate of reaction. By use of this assumption and after considerable algebraic manipulation, the expression

$$\frac{k_7k_6}{k_5}\left[\frac{Q/V}{k_6}+1\right]=\frac{\{2k_4(O_3)_{si}(NO_2)_{si}-[Q/V][(NO_2)_0-(NO_2)_{si}]\}\{k_3(O_3)_{si}(NO_2)_{si}\}}{\{KI\phi(NO_2)_{si}+[Q/V][(O_3)_0-(O_3)_{si}]-k_4(O_3)_{si}(NO_2)_{si}\}\{(NO_2)_0-(NO_2)_{si}\}}$$

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[1] H. W. Ford, G. J. Doyle, and N. Endow, J. Chem. Phys. **26**, 1336 (1957).

[2] S. W. Benson and A. E. Axworthy, Jr., J. Chem. Phys. **26**, 1718 (1957).

[3] H. W. Ford and N. Endow, J. Chem. Phys. **27**, 1156 (1957).

[4] H. W. Ford and N. Endow, J. Chem. Phys. **27**, 1277 (1957).