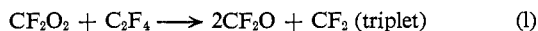
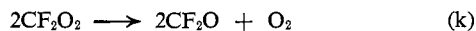
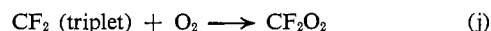
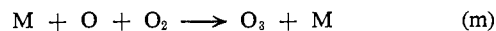


Figure 5. Log-log plot of $\Phi(\text{cyclo-C}_3\text{F}_6)/[\Phi_0(\text{cyclo-C}_3\text{F}_6) - \Phi(\text{cyclo-C}_3\text{F}_6)]$ vs. $(\text{C}_2\text{F}_4)/(\text{O}_2)$ with 500 mm. of N_2O present.

mechanism is



If the intermediate $\text{C}_2\text{F}_4\text{O}$ is present, then it too could be scavenged by O_2 and produced by CF_2O_2 attack on C_2F_4 . The ozone-producing reaction has been in-



vestigated by many workers.²³⁻²⁸ The results have been critically analyzed by Leighton²⁹ and by Kaufman.¹⁰ The generally accepted rate constant is about $10^8 \text{ l.}^2/\text{mole}^2 \text{ sec.}$ Under our conditions, this reaction would be considerably less important than (f), but could play some role at high $(\text{O}_2):(\text{C}_2\text{F}_4)$ ratios.

As the $\text{O}_2:\text{C}_2\text{F}_4$ ratio is enhanced, the cyclo- C_3F_6 diminishes. This can be explained by a competition between the O_2 and C_2F_4 for triplet CF_2



In the presence of excess N_2O , the competition leads to the approximate result

$$\frac{\Phi(\text{cyclo-C}_3\text{F}_6)}{\Phi_0(\text{cyclo-C}_3\text{F}_6) - \Phi(\text{cyclo-C}_3\text{F}_6)} \approx \frac{k_n (\text{C}_2\text{F}_4)}{k_j (\text{O}_2)} \quad (4)$$

where $\Phi_0(\text{cyclo-C}_3\text{F}_6)$ is the quantum yield of cyclo- C_3F_6 in the absence of O_2 . Figure 5 shows a log-log graph of the left-hand side of eq. 4 vs. $(\text{C}_2\text{F}_4)/(\text{O}_2)$. The best straight line of slope unity is plotted. The intercept yields a value of 0.40 for k_n/k_j .

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Electron Paramagnetic Resonance Studies of Irradiated γ -Silica in Static Systems and under Dynamic Flow Conditions

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Contribution from the Frick Chemical Laboratory, Princeton University, Princeton, New Jersey. Received December 16, 1964

An electron spin resonance study has been carried out on the interaction of irradiated silica with oxygen, nitric oxide, and a number of gases. The appearance of a doublet characterized the adsorption of the oxygen and nitric oxide, and this was shown to be due to the relaxation of spins on the surface of the irradiated silica. A flow system was developed to study by pulse techniques the interaction of gases with the solid.

Introduction

Electron spin resonance has been used to study the effect of high energy radiations on surfaces¹⁻⁶ and also the effect of adsorbed gases in static systems.⁷

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The present investigation is a study of the effects of oxygen and nitric oxide and a number of other gases on the electron spin resonance signal of irradiated silica in static systems and under dynamic flow conditions. The latter type of investigation permits the observation of transients that occur when a pulse of a gas passes over a surface.

Experimental

Materials. Silica gel was prepared by hydrolysis of ethyl orthosilicate and was evacuated at 600° and 10^{-5} mm. for 12 hr. The ethyl orthosilicate (Fisher Laboratory chemical) was distilled before the hy-

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drolisis. The sample tubes were made out of G.E. Special Purity quartz (5-mm. o.d., 4-mm. i.d. tubing) which had a quartz-Pyrex graded seal for attachment to a conventional vacuum manifold. The samples were sealed under high vacuum conditions so as to have a tube with two pointed ends. They were irradiated with a γ -source from spent fuel elements. The dose was about 10^7 r., and the irradiations were carried out at about 50° . Before the e.s.r. measurements were performed, the powdered samples, about 0.2 g. in weight and 3 cm. in length, were kept in one end of the tube while the other end was heated with a flame to eliminate the e.s.r. signal found in the irradiated quartz tubes. The powder was then transferred to the annealed part of the tube, and the e.s.r. spectrum was measured.

Helium (General Dynamics Grade A) was dried by passing over silica gel.

Oxygen (General Dynamics Industrial Grade) was purified in the same way. All other gases were obtained from Matheson Co.

Apparatus. A Varian spectrometer (Model V4500) operating at 9.5 kMc./sec. and at TE₁₀₂ mode was employed. The magnetic field was modulated at 100 kc./sec. and was controlled by a Field-Dial regulator V-FR-2200. This enabled us to keep the magnetic field at a predetermined value for periods of time and to observe variation in signal intensity at this particular magnetic field setting.

A Wilkins A-90-0 aerograph gas chromatograph was used with a thermal conductivity detector.

A microsyringe was used to inject the various gases and liquids through a rubber septum situated just above the sample tube. Glass 2-mm. capillary tubing was used to connect various parts of the apparatus. The gas chromatograph had a soap bubble flowmeter on the exit side.

Procedure. The e.s.r. measurements of samples in evacuated sealed tubes were carried out in the conventional way. For the flow experiments the samples were introduced into the helium flow line with a polyethylene tube connection, and the end closer to the source of helium was broken through the polyethylene under a pressure of helium. Then, with a pressure of helium in the sample, slightly above atmosphere, the other end was broken off and attached with polyethylene tubing to the flow system. The carrier gas flow rate was varied from 5 to 60 cc./min. The gas flowed through one thermoconductivity cell of the gas chromatograph, over the silica gel sample in the cavity, and then back through the other thermoconductivity compartment. E.s.r. measurements could be made varying the composition of the flowing gas by scanning at various rates and through various ranges of the magnetic field by means of the Field-Dial unit. Another procedure was to set the Field-Dial unit at an appropriate value of the magnetic field and then inject various amounts of gases, recording simultaneously the variation both in e.s.r. signal intensity and in the readings of the gas chromatograph.

Results

(1) *E.s.r. Measurements on γ -Irradiated Silica Gel under Vacuum.* The complex e.s.r. spectrum obtained varies with experimental conditions of measurements,

namely, modulation amplitude, frequency, and power. The effect of modulation amplitude is shown in Figure 1. The total width of the spectrum is 4 gauss, and the peak to peak separations are between 0.5 and 1 gauss. In all cases, the modulation amplitude was kept less than the peak to peak separation. As the modulation amplitude is increased from 15 mgauss, the first part of the spectrum to the left of the dotted line in Figure 1 increases as expected whereas the second part to the right of the dotted line, particularly the last peak on the high-field side, progressively decreases. At about an amplitude of modulation of 150 mgauss this peak appears on the other side of the zero line and increases with intensity on further increase of the modulation amplitude. With a low amplitude of modulation, though the conditions are favorable to obtain a derivative of the absorption mode for the first part of the signal, this is not the case for the second part which is apparently out of phase with the first part. This is because of the difference in the spin-lattice relaxation times of the two parts of the spectrum.

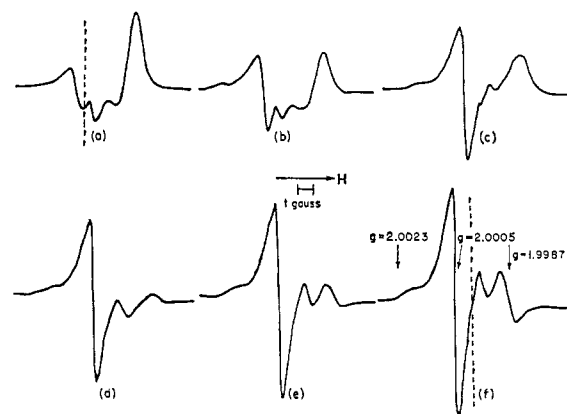


Figure 1. Effect of modulation amplitude on e.s.r. signal of silica gel under vacuum. Power 7 mw., scanning rate 2.5 gauss/min., modulation frequency 100 kc./sec., modulation amplitude in mgauss: (a) 15, (b) 60, (c) 120, (d) 150, (e) 192, (f) 240.

This unusual behavior of phase reversal has been previously reported for F centers in irradiated LiF but with a change in frequency of the modulating field.^{8,9} The change takes place owing to the change in the rapid passage conditions of resonance.

Instead of changing the amplitude of modulation to bring about the phase reversal, the same effect was obtained by admission of oxygen and nitric oxide (NO). In no case did an out-of-phase component appear in the presence of these paramagnetic gases.

Since the above-mentioned authors found a phase reversal with a change in frequency of modulation, the effect of frequency was studied. At 400-c.p.s. modulation frequency and an amplitude of 220 mgauss, the signal obtained shows the same shape as far as the first part of the spectrum is concerned, but in the region of the second part the results were indeterminate because of poor signal to noise ratio.

The phase reversal of a resonance signal as mentioned earlier is due to the change in the resonance passage

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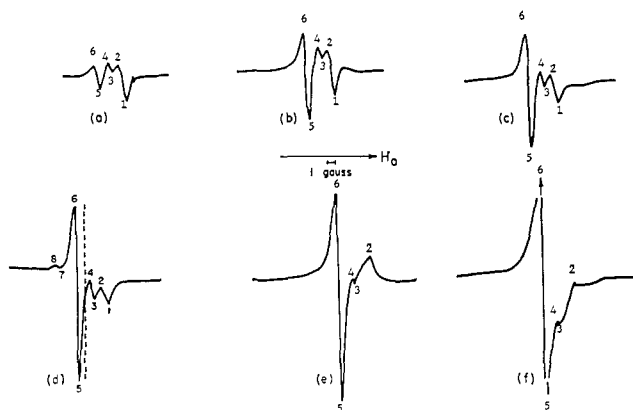


Figure 2. Saturation behavior of e.s.r. signal of sample under vacuum. Modulation frequency 100 kc./sec., modulation amplitude 600 mgauss, scanning 2.5 gauss/min. Power in mw.: (a) 2.2, (b) 3.5, (c) 4.4, (d) 7.0, (e) 22, (f) 165.

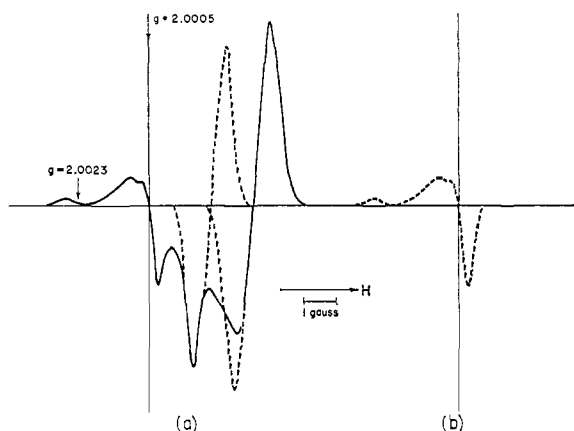


Figure 3. Peak analysis of e.s.r. signal of sample in helium. Modulation frequency 100 kc./sec., amplitude 15 mgauss, power 7 mw., scanning 2.5 gauss/min.; (a) solid line is original signal; dotted lines indicate two resolved peaks; (b) residual signal after subtracting the two resolved peaks.

conditions given by the relation

$$\gamma_e H_1 > \frac{\omega_m H_m}{H_1} \gg \frac{1}{T_1}$$

for rapid passage where γ_e is the magnetogyric ratio of the electron, H_1 is the half-amplitude of the microwave resonance field, ω_m and H_m are the frequency and the amplitude of the modulating field, and finally T_1 is the spin-lattice relaxation time of the electron.

The phase reversal was observed at a modulation amplitude of 150 mgauss, a frequency of 100 kc./sec., and H_1 equal to about 100 gauss. This gives an approximate value of 10^{-5} sec. for T_1 .

(2) *Saturation Behavior of the Spectra.* E.s.r. signals for the γ -irradiated silica gel under vacuum at various power levels are shown in Figure 2 for a modulation amplitude of 600 mgauss.

On comparison of Figures 2d and e, one can notice that the last peak between points 1 and 2 which was an in-phase signal until a power level of 7 mw. was reached on further increase of power to 22 mw. has changed phase. This is to be expected on the relation given above since the increase of H_1 in the denominator has the same effect as the decrease in either modulation

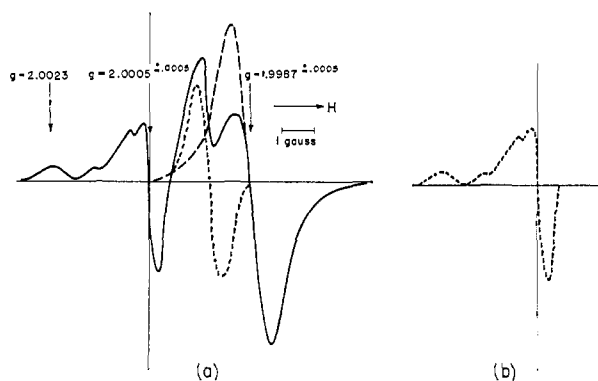


Figure 4. Peak analysis of e.s.r. signal of sample in oxygen. Modulation frequency 100 kc./sec., amplitude 60 mgauss, scanning 2.5 gauss/min., power 7.0 mw.; (a) solid line is original signal, dotted lines indicate the two resolved peaks; (b) residual signal after subtracting the two resolved peaks.

amplitude or frequency. Therefore, during the progressive saturation method, the increase in power level changes the passage conditions.

From the saturation experiments carried out on the peaks between the points 1 and 2, and 5 and 6, the following results were obtained for a sample under vacuum and also in oxygen. The peak between 5 and 6 progressively increases in amplitude with H_1 , showing no saturation even at the maximum power available. This may be due to the inhomogeneous character of line broadening which, of course, could not be ascertained for lack of sufficiently high power. The peak between 1 and 2 for a sample under vacuum saturates at relatively low power level; however, it could not be completely suppressed, which again is an indication of the inhomogeneous character of the line. The remaining intensity of the peak is apparently due to the unresolved hyperfine structure. In oxygen, the peak between 1 and 2 shows no saturation whatsoever, thereby indicating that the relaxation time is considerably shortened.

(3) *Resolution of E.s.r. Spectra.* The resolution of the spectrum obtained with a low amplitude of modulation (15 mgauss) for a sample in helium is shown in Figure 3a. The solid line represents the original signal; the dotted lines indicate two resolved peaks. These two peaks, though in phase with each other, are out of phase with the residual signal (Figure 3b) obtained by subtracting the two resolved peaks from the original signal. The very appearance of the signal without any resolution indicates this out-of-phase component.

A similar resolution was performed on a signal obtained for a sample in the presence of oxygen (Figure 4a). This again gives two well-resolved peaks at the same location as those obtained in helium. These two peaks are in phase with each other and also in phase with the residual signal (Figure 4b) obtained by subtracting the two resolved peaks from the original spectrum.

Although the two resolved peaks for a sample in helium and for a sample in oxygen occur at the same location (Figures 3a and 4a, dotted lines), they are exactly 180° out of phase with respect to each other.

An alternative way to analyze the spectrum obtained for samples in O_2 or NO consists of subtracting the corresponding spectra in helium from the respective

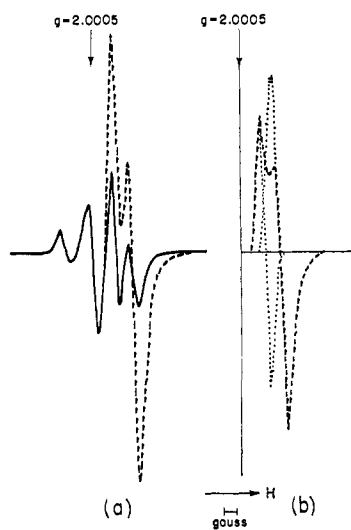


Figure 5. Peak analysis of e.s.r. signal of sample in oxygen (1 atm.). Modulation frequency 100 kc./sec., amplitude 600 mgauss, scanning 3.5 gauss/min.; (a) solid line, sample in vacuum; dashed line, sample in 1 atm. of O_2 ; (b) dashed line, residual signal obtained after subtracting the signal under vacuum from that in O_2 ; dotted lines represent resolution of residual signal into two peaks.

spectra obtained in O_2 or NO. The residual in each case will be due to the effect of O_2 or NO on the signal. Figure 5 represents such an analysis for oxygen and Figure 6 for nitric oxide (NO). In both cases the residual signal consists of two peaks with a slight overlap which can be resolved into separate peaks (Figures 5b and 6b, dotted lines).

A similar analysis performed on signals of deuterated silica gel in oxygen results in a residual signal which again shows the characteristic feature as those with nondeuterated silica gel in O_2 . In the spectrum of the deuterated silica gel in helium, the intensity of the second part of the spectrum relative to the first part is small, unlike that observed in a nondeuterated sample. On the other hand, many more satellites appear on either side of the main peak. The intensities of the satellites are of the same order of magnitude as the second part of the spectrum.

(4) *E.s.r. Measurement under Pulse Conditions.* In order to study the effect of oxygen on the e.s.r. signal in the flow system, small amounts of O_2 were introduced by means of a gastight microsyringe through the rubber septum. The magnetic field was kept constant during each experiment at selected values of magnetic field corresponding to different peak maxima. If the peak is affected by oxygen, a deviation from the otherwise constant e.s.r. recording is observed. A typical series of such e.s.r. recordings obtained with various amounts of oxygen injected is shown in Figure 7. Also the simultaneously recorded changes of the heat conductivity device of the gas chromatograph are given. The recordings show that the effect of oxygen on the e.s.r. signal is reversible. Both e.s.r. and heat conductivity recordings show a tailing-off effect which is, however, more pronounced with the gas chromatograph signals.

In this way different peaks as numbered in Figure 2d have been tested for oxygen sensitivity. It was found that the intensities relative to the original peak changed in the following way: while peak 1 increases in the

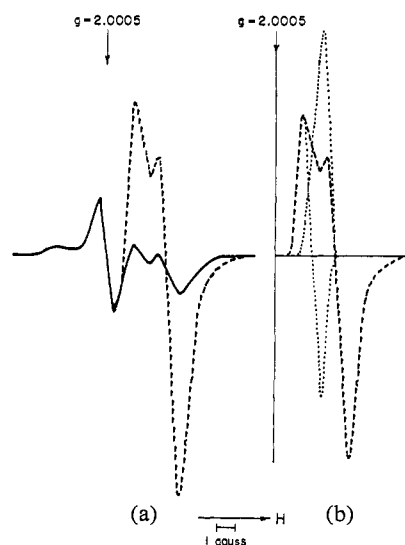


Figure 6. Peak analysis of e.s.r. signal obtained in NO (1 atm.). Modulation frequency 100 kc./sec., amplitude 600 mgauss, scanning 2.5 gauss/min. (a) solid line, sample under vacuum; dashed line, sample in NO (1 atm.); (b) dashed line, residual signal obtained after subtracting the signal under vacuum from that in NO; dotted lines represent resolution of residual signal into two peaks.

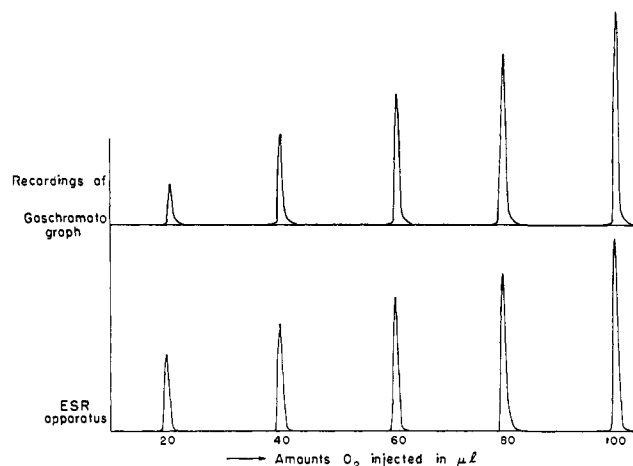


Figure 7. E.s.r. and gas chromatograph recordings obtained on injection of O_2 into a helium flow containing γ -irradiated silica gel. Magnetic field kept constant at maximum of peak 1. The amount of O_2 in milliliters is indicated on the recordings. Helium flow rate 18 ml./min., modulation frequency 100 kc./sec., amplitude 600 mgauss, power 7 mw.

direction of the peak, peaks 2-5 change in the opposite direction. No effect on peaks 6-8 could be detected.

Using various amounts of injected O_2 , it is possible to determine an isotherm of the oxygen effect. As the amount increases, the amplitude changes increase, apparently approaching limiting values. The effect is shown for different peaks being most pronounced for peak 1.

As the flow rate decreases, the area of the e.s.r. peak increases following an inverse relationship within the accuracy of measurement. This can be due either to the shorter residence times in which the O_2 is interacting with the surface defects or to a smaller number of such defects which are affected. Considering the peaks recorded by the gas chromatograph, it is found that the area of the peak changes with flow rate, being largest

at the lowest flow rate. Apparently, this is due to the passage of the carrier gas through the sample bed consisting of porous particles. Before any conclusions can be drawn from these preliminary experiments, the effect of flow rate on the gas chromatographic recordings should be tested without a sample in the flow system.

In a number of experiments the effect of gases other than oxygen were studied in the flow system. It was found that NO and, to a lesser extent, CO have the same effect as oxygen. In each case the magnetic field was set at the maximum of peak 1 (see Figure 2d for peak numbering) and 100 ml. of the gas was injected. A comparison of the peaks shows that the effect of O₂ and NO is practically the same, whereas CO has only an effect of about 15% of the former gases. With NO it was also found that the various peaks are affected in the same way as by oxygen. The isotherm of the NO effect was carried out with a sample in helium stream using a low modulation of 15 mgauss which produced an out-of-phase peak in the original sample. Therefore, no quantitative results were obtained for the dependence of the NO effect on the amount of gas injected. The effect of CO has been verified with several different samples and also in a static experiment by Dr. Nozaki.

No effect on the oxygen-sensitive peak could be detected with the following substances: H₂, C₂H₄, N₂, N₂O, CO₂, SO₂, H₂S, NH₃, BF₃, and Cl₂, as well as with H₂O and H₂O₂.

Discussion

The asymmetric e.s.r. signal that was observed for γ -irradiated silica gel at room temperature under vacuum and in helium flow was resolved into two parts—one which was only slightly affected by O₂ and NO and another that was markedly changed by the interaction of these gases with the surface of the solid.

The asymmetric signal on γ -irradiation of silica gel and its enhancement by oxygen was observed in this laboratory by Dr. Fumio Nozaki, and the findings were presented at the Third International Congress of Catalysis, Amsterdam, 1964.

It was also found that small amounts of alumina change this signal to one characterized by six lines due to the aluminum hyperfine structure, indicating that the aluminum defects had a greater affinity for the electrons than the defects in the silica. The e.s.r. signal of γ -irradiated silica gel was also observed by Kohn¹⁰ and by Kazansky, Parisky, and Voevodsky.¹¹ The latter authors found that admission of oxygen does not affect the strong signal which was observed and therefore assigned to volume defects which are assumed to be due to capture of electrons by oxygen lattice vacancies. The changes of other parts of the signal were not further studied.

In order to resolve further the e.s.r. spectrum, the signals in helium flow were subtracted from those in O₂ and NO. The residual signals obtained in this way have the same shape consisting of two superimposed peaks. A similar residual peak was obtained by subtracting the signal of a deuterated silica in helium from the corresponding signal in oxygen. This is strong

evidence for the conclusion that the signal is not due to electron transfer from the solid to the adsorbed gas since one would expect different hyperfine structure for a negatively charged oxygen or nitric oxide ion. Furthermore, an electron transfer to any species associated with H can be excluded since the residual signal obtained after the peak analysis shows a similar doublet.

For a further interpretation of the oxygen effect it is important to note that the enhanced peaks due to O₂ and NO simply overlap with those already present in the original spectrum of the γ -irradiated silica either under vacuum or in helium (Figures 3–6). The shape of the signals, as well as the *g*-values, is the same, and only the intensities are different.

A possible explanation of the observed doublet follows. Since the amount of Si²⁹ is only 4% and no triplet with deuterated silica gel was observed, the doublet cannot be due to the interaction of the trapped electron either with the nuclear spin ($I = 1/2$) of Si²⁹ or with the proton. A similar doublet was also formed with ZnO¹² supporting the view that it could not be due to Si²⁹. A center created by the capture of an electron by an oxygen lattice vacancy from a neighboring oxygen atom results in a hole on the atom which can form an electron-hole pair. Alternatively, the electron captured from elsewhere can form an electron-electron pair with an unpaired electron in the neighboring oxygen atom. This may account for the observed doublet. Owing to low concentration of surface defects, consisting of trapped electrons, the spin-spin interaction of these pairs is not averaged out into a single broad line but results in a well-resolved doublet (Figure 3). Because of this low concentration of centers the observed spin-lattice relaxation time is relatively long.

Paramagnetic gases like O₂ and NO when admitted on collision with the surface cause a large perturbing field. The spin-lattice relaxation time of the centers is shortened, thus enhancing the doublet signal. This doublet is an inhomogeneously broadened resonance signal due to the varying local environment surrounding the individual centers.

The strong line ($g = 2.0005$) which changes only slightly with admission of O₂ and NO could be due to one or both of the following types of defects. There may be clusters of defects on the surface. In such a cluster the local field produced is large so as to cause a broadening of the line and also a shift in the *g*-value. However, this is not the case with this line, but an exchange interaction among the trapped surface electrons within this cluster can account for the observed narrow line, the *g*-value close to that for free electrons, the short spin-lattice relaxation time as indicated by the nonsaturation character of the line (Figure 2), and also for the absence of hyperfine structure (doublet) due to the pair formation. Since exchange interactions generally furnish a strong relaxation mechanism, admission of O₂ or NO practically has no effect on the relaxation. Consequently, only a slight effect of the above-mentioned gases on these peaks has been observed.

In such exchange narrowed lines, one would expect a change in line shape as saturation sets in. In our experiment this behavior could not be observed since it was not possible even at the maximum available

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(12) R. J. Kokes, *ibid.*, in press.

micropower level to reach the point of saturation. In exchange narrowed lines, one does not have the usual effect of saturation broadening but rather a narrowing of the central part of the line.

Alternatively the strong line can be due to the defects in the bulk of the silica gel as has also been suggested by Kazansky, *et al.*,² who interpret the defects as trapped electrons in oxygen vacancies. If the defects are far below the surface, admission of O₂ and NO could not relax these centers by dipolar interaction. Since the dipolar interaction varies inversely as the cube of the distance between defect and paramagnetic molecule, only small effects, if any, can be expected.

The results obtained in the present study indicate that the effect of O₂ and NO is due to magnetic dipolar

interaction of the paramagnetic molecules and the trapped electrons on the surface. The molecules can either be physically adsorbed or just be present in the vicinity of the surface defect without being adsorbed. By change in temperature of the system it is possible to differentiate between the two possibilities.

The present observation indicates the care that must be taken in obtaining meaningful e.s.r. measurement of surface defects and their interaction with gaseous molecules.

Acknowledgment. We wish to acknowledge the support given to this investigation by the U. S. Atomic Energy Commission and the technical help of George Kemmerer and Don Isgan. We wish to thank Mr. Richard F. Bailey of the RCA group of the Industrial Reactor Laboratories for the irradiations of the silica.

Heat Capacity of Activation in Hydrolytic Displacement from a Tertiary Carbon¹

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Contribution from the Division of Pure Chemistry, National Research Council, Ottawa, Canada. Received June 24, 1964

Values of the heat capacity of activation (ΔC_p^) for the hydrolysis of 2-chloro-2-methylbutane, 2-chloro-2-methylpropyl methyl ether, and *t*-butyldimethylsulfonium ion were determined for hydrolysis in water. These values were shown to support a working hypothesis based on the recognition that part of the energy requirement in the activation process is the work required to break down the initial state solvation shell. Differences in ΔC_p^* values can be understood in terms of modification of the initial state solvation shell through the presence of a lyophilic group or of a charge, and by modification of the degree of solvent disorganization in the transition state through a change of mechanism.*

The experimental fact that ionogenic reactions such as the hydrolysis of alkyl halides in water³ or the ionization of weak acids⁴ are characterized by large negative heat capacity changes has long been recognized.^{5,6} It is accepted that these large negative temperature coefficients reflect mainly the summation of heat capacity changes associated with the reorganization of a number of adjacent water molecules as a consequence of developing electrostatic interaction. Since interaction between the neutral solute and the water molecules in the solvent sheath is small compared to ion-

water interaction, the simplest explanation would seem to be that the water is frozen down about the formed (or forming) ions, reference being made to the well-known heat capacity change of -9 cal./mole deg. for the freezing of water to ice. This argument is undoubtedly an oversimplification in the case of weak acid ionization⁶ and as normally applied^{5,7,8} is probably incorrect for the activation process accompanying solvolysis.⁹

Glew and Moelwyn-Hughes¹⁰ were among the first to recognize that the hydrogen-bonded solvation shell about alkyl halides in aqueous solutions is an important factor in hydrolysis.^{11,12} While subsequent research does not appear to support their detailed mechanism, all pertinent work has tended to reinforce the basic idea that for ionogenic reactions in water the free energy change (ΔF_s^*) associated with the breakdown of the solvent shell about neutral solutes is a significant factor in the activation process, particularly with respect to the associated ΔC_p^* values. The kinetic solvent isotope effect (k_{D_2O}/k_{H_2O})¹³ and the phenomena associated with the curious term "hydrophobic bond"¹⁴ are further examples in which the importance of this solvent shell is made evident.

(1) Issued as N. R. C. No. 8461.

(2) National Research Council of Canada Postdoctorate Fellow, 1959-1961.

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