from the lesser tendency of the latter to form a covalent bond with the metal, which is to say, it is less distorted by the presence of the metal. These observations refer to the potential of zero charge, which shows that even an uncharged surface exerts an "electrostatic" influence on a polarizable anion. The electrostatic influence arises from the attraction between the electrons in the iodide ion and the mercury ions in the surface. The electrons associated with the latter are able to move away sufficiently to make the net result a decrease in free energy, whereupon the process continues until the change of free energy resulting from additional motion of the center of charge of the anion becomes zero.

In the discussion of chemical binding it is usually convenient to distinguish between electrostatic and covalent forces, even while recognizing that the latter are in the last analysis electrostatic. As the preceding discussion indicates, however, this distinction breaks down rather badly and may have to be abandoned altogether in order to get a valid picture of the factors influencing the behavior of the electrical double layer.

There is a further equation relating to the inner region of the double layer which has not been used in this work. It is

$$\psi^{02} = -4\pi q(\beta + \gamma)/DD_0 \qquad (18)$$

which is the ordinary equation for a two-plate condenser applied to the inner region under conditions of constant n^i. From equation 4 we have

$$(\partial\psi^v/\partial n^i)_q = -4\pi\gamma/DD_0 = -\lambda \qquad (19)$$

where λ is not necessarily to be regarded as independent of q. From equations 18 and 19 it follows that

$$\lambda q/\psi^{02} = \gamma/(\beta + \gamma) \qquad (20)$$

Values of $\gamma/(\beta + \gamma)$ computed in this manner are shown in Fig. 9. The disagreement with the values computed through equations 12 and 13 is marked. What this means is that D in equation 4 is not identical with D in equation 18. This possibility was considered in ref. 2 where a prime was put on the D of what is here called equation 18. The ratio of $\gamma/(\beta + \gamma)$ found in the two ways equals the ratio of the two kinds of D.

Conclusion

The method of calculation adopted in this work makes great demands upon the precision of the experimental data. An alternative and possibly less demanding method of calculation would be to assume the linearity of the curves in Fig. 6 and to calculate from these the differential capacity. By comparison with the observed values of the latter, one could in principle select the best values of the parameters controlling the curves shown in Fig. 6. This procedure is mathematically possible but would represent a very formidable task even by modern methods of computation. Another disadvantage of this procedure is that one would be obliged to make certain auxiliary assumptions which ought to be tested further by the direct method of computation used here.

The computations employed in this work are based upon a combination of thermodynamics and Gouy–Chapman theory, as modified by Stern and as further modified by the author with respect to the nature of the inner region of the double layer. These latter modification, at least, are by no means universally accepted, and it may be that later work will indicate a need for their revision. The most that can be said is that the present picture of the electrical double layer serves as a convenient frame of reference which fits the facts well enough to serve as a basis for detailed calculations.

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Reactions of the High Voltage Discharge Products of Water Vapor

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The recombination of the high voltage discharge products of water vapor has been investigated on the surface of silica gel. The recombination reaction was accompanied by a temperature increase and a green luminescence on the surface on the gel. The principal products of the reaction were H_2 and O_2. Both the H atom and OH radical were removed as a result of the surface reaction but the silica gel surface did not catalyze the recombination of H atoms. It was concluded that the surface reaction is: $S + OH = S\text{-}OH$, $S\text{-}OH + H = S\text{-}O + H_2$, $2S\text{-}O = 2S + O_2$ where S is the surface. A study of the intensity of the luminescence on the surface of the gel as a function of time and the temperature to which the gel was preheated showed that the activity of the gel was initially high and then decreased to an equilibrium value after 30 minutes. The water content of the gel controlled its activity in these recombination reactions. The addition of sodium ions to the gel resulted in a change in the color of the luminescence from green to yellow indicating that the luminescence is a result of an excitation of the surface caused by the exothermic reactions occurring thereon. The reactions of the water vapor discharge products in a liquid air trap were also studied. H_2O_2, H_2O, H_2 and O_2 were formed and the molar ratios of product to water vapor admitted to the system were 26.8, 38.0, 35.2 and 4.2%, respectively. On the basis of two simple assumptions, it was possible to show that the reactions in the trap leading to O_2 are $H + OH = H_2 + O$, $2O = O_2$; and to account approximately for the observed product distribution.

Introduction

The recombination of the high voltage discharge products of water vapor on solid surfaces such as KCl, K_2CO_3, Al_2O_3 and KOH has been studied by several authors.[1-4] Taylor and Lavin[1] observed a

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(1) H. S. Taylor and G. I. Lavin, This Journal, **52**, 1910 (1930).

(2) A. A. Frost and O. Oldenburg, *J. Chem. Phys.*, **4**, 642 (1936).

(3) W. V. Smith, *ibid.*, **11**, 110 (1943).

(4) D. R. Warren, *Trans. Faraday Soc.*, **53**, 206 (1957).

green or green-blue luminescence on the surface of these solids when they were exposed to the water vapor discharge. Badin[5] noted a blue-green luminescence on KCl during the reaction of H atoms and O_2 molecules. The present authors have observed a similar phenomenon on the surface of silica gel. This investigation was initiated to study the intensity of the luminescence on the surface of silica gel when exposed to the water vapor discharge as a function of time and the temperature to which the gel was preheated. The effect of a silica gel surface on the distribution of products in the liquid air trap located directly below the discharge was also studied in an attempt to elucidate the mechanism of the reaction occurring on the surface.

Several runs were made without a reactive surface in the system in order to study the reactions of H atoms and OH radicals in the liquid air trap.

Experimental

Materials.—Three different batches of silica gel were used. Batch no. 1 was a commercially available gel (Davison Chemical Co.) which had been purified by extensive treatment with 10% HCl. Batch no. 2 was given to the authors by Dr. George Zimmerman of Bryn Mawr College who had purified the gel by repeated treatment with concentrated HCl and HNO_3 over a period of several months. Batch no. 3 was also a commercially available gel which had been purified by extensive treatment with HCl. The hydrogen was manufactured by Pascal Oxygen Co. (99.5% pure).

Apparatus and Procedure.—The apparatus used was similar to that described by Jones and Winkler.[6] The water flow was determined by observation of the water level in a precision bore capillary. The pressure of the water vapor on the inlet side of the discharge tube was determined by means of a McLeod gauge which was maintained at about 60°. The water vapor flow was controlled by means of a needle valve and a capillary constriction. The discharge tube was the "U" type 104 cm. long, constructed of 25 mm. o.d. Pyrex tubing and water jacketed. The electrodes were isolated from the body of the discharge tube by means of two connecting tubes to prevent metal particles sputtered from the surface of the electrodes from falling into the body of the tube. Similarly, the metal leads were protected by 4 mm. o.d. tubing. The transformer used was a Thordarson No. T-21 P79 which had a maximum output of 7500 volts at 800 milliamps. The current used was 200 or 250 milliamps. The current was controlled by means of a 10,000 ohm resistor in series with the tube.

One of two reaction chambers was attached to the discharge tube at the bend of the "U" by means of a ground glass joint. Apiezon wax was used on the joint. The reaction chamber was connected to a removable trap, and a high capacity Welch Duo-Seal pump was used to evacuate the system.

Reaction chamber no. 1 was a straight glass tube, 20 mm. o.d. and 30 cm. long. The substance under investigation was coated on the inside of the tube by first carefully cleaning the tube with hot cleaning solution; then adding a water slurry of the material to the tube and rotating it in a stream of air until a uniform dry coating formed on the inside; finally baking the coating on the glass by heating it to 250 to 300° for 12 to 15 hours.

Reaction chamber no 2 (Fig. 1) was used to study the intensity of the luminescence on the surface of silica gel by means of a photomultiplier tube. The silica gel was coated on the face of a tapered cylindrical quartz platform (1 cm. in diameter, 3 cm. high) by the method described above; however, the drying temperature varied. The weight of the silica gel sample was about 30 mg. The platform fitted over the end of a ground glass plug and was held in place by means of a Teflon ring. The face of the platform was located about two cm. from the gas stream. The photomultiplier tube (RCA 931-A) was located directly opposite the face of the platform. The response of the photomultiplier passed through a cathode follower and was recorded on a Leeds and Northrup Speedomax. The reaction chamber was made light tight by wrapping it in black tape. Light leaks were found to constitute a small constant fraction of the total intensity.

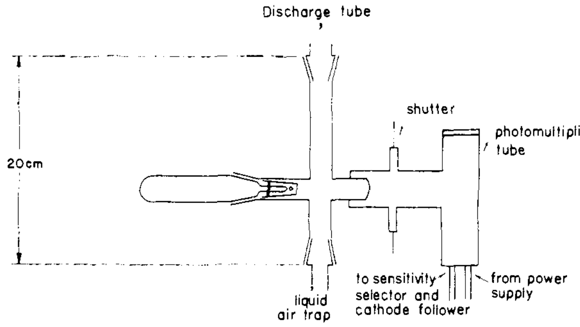

Fig. 1.

At the end of a run the trap was removed and weighed. Hydrogen peroxide was determined by titration with standard permanganate and water determined by difference. Non-condensable products were presumed to be H_2 and O_2 and the amounts were calculated from a material balance. All of the runs were of one hour duration except for eight of the blanks (runs 8 to 20, Table I) which were one-half hour long. The relative yields were independent of the duration. The frozen products near the top of the trap generally showed a yellow-brown tint, which also has been noted by Giguere.[7]

Atomic hydrogen was produced by passing tank hydrogen saturated with water vapor at 30° through the discharge tube. The presence of atomic hydrogen in the reaction chamber was verified by reduction of MoO_3 which was coated on the face of the quartz platform and placed in the apparatus as shown in Fig. 1.

Results

Reaction on the Surface of Silica Gel.—A sample of silica gel from batch no. 1 was coated on the inside of reaction chamber #1 and inserted between the discharge tube and the trap. The effect on product distribution is shown in Table I, runs 1 and 2. Without the silica gel coating, the yields were as shown in runs 3 and 4. These results show that the principal products of the surface reaction were H_2 and O_2. The absence of H_2O_2 in the trap indicates that all of the OH radicals were removed by the surface reaction. The top of the silica gel-coated tube became very warm, but the temperature decreased rapidly along the tube to room temperature at a distance of 4 cm. A green luminescence was visible at the top of the tube and similarly decreased along the tube.

In another experiment, it was found that the gases entering the trap after passing through the silica gel-coated tube did not reduce a tungstic acid coating on the walls of the trap. Without the silica gel on the tube, reduction of tungstic acid to the blue lower oxides was almost immediate. We conclude that H atoms as well as OH radicals are removed by the reaction on the silica gel surface.

It was also shown that the silica gel surface does not catalyze the recombination of H atoms alone. In these experiments, the silica gel surface was alternately exposed to the water vapor discharge and the hydrogen discharge. Silica gel was coated on the face of a quartz platform and inserted in the apparatus as shown in Fig. 1. When exposed to the water vapor discharge, a temperature rise and the green luminescence were observed. However,

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(5) E. J. Badin, This Journal, **70**, 3651 (1948).

(6) R. A. Jones and C. A. Winkler, *Can. J. Chem.*, **29**, 1010 (1951).

(7) P. A. Giguere and E. A. Secco, *J. phys. radium*, **15**, 508 (1954).

TABLE I

EFFECT OF VARIABLES ON YIELD

Run no.	Catalyst	Preheat temp., °C.	Flow, mmoles H_2O per hr.	Pressure, mm.	Current, mamp.	Moles of product per mole of water input × 100			
						H_2O_2	H_2O	H_2	O_2
1[a]	SiO_2 gel	250–300	19.00	0.3	200	0	12.3	87.7	43.9
2[a]	SiO_2 gel	250–300	19.64	.3	200	0	13.9	86.1	43.0
3[a]	None		22.00	.1	200	25.6	40.2	34.2	4.3
4[a]	None		15.96	.1	200	25.3	41.2	33.5	4.1
5[b]	SiO_2 gel	110	18.30	.1	250	25.4	40.2	34.7	4.8
6[b]	SiO_2 gel	300	18.54	.1	250	25.6	39.5	34.8	4.6
7[b]	SiO_2 gel	525	18.64	.1	250	25.5	39.8	34.7	4.6
8–13[b]	None		[c]	.1	200	26.6[i]	37.5[i]	35.9[i]	4.6[i]
14–20[b]	None		[d]	.1	250	27.0[i]	38.4[i]	34.6[i]	3.8[i]
8–20	None		...	.1	..	26.8 ± 0.3[i]	38.0 ± 0.6[i]	35.2[i]	4.2[i]
21[b,h]	None		19.30	.3	200	0.0	35.7	64.2	32.1
22[b,h]	None		19.16	.3	200	0.0	36.7	63.3	31.6
G[e]	None		560	.1	[g]	25.0	41.1	33.9	4.5
J & W[f]	None		15.27	.1	200	24.5	38.6	36.9	6.2

[a] Reaction chamber no. 1. [b] Reaction chamber no. 2. [c] Varied from 20.75 to 22.02. [d] Varied from 18.10 to 28.24. [e] Calculated from the data of Giguere.[8] [f] Calculated from the data of Jones and Winkler.[6] [g] Electrodeless discharge. [h] Trap cooled in Dry Ice instead of liquid air. [i] Mean values; ranges are the most probable error of the mean, 95% confidence limits.

when exposed to hydrogen discharge, no temperature rise or luminescence was observed.

The Luminescence of the Silica Gel Surface.—Shown in Fig. 2 are the results of the study of the intensity of the luminescence as a function of the time and temperature to which the gel was preheated (batch no. 1). The same sample of gel was preheated to three different temperatures, 110, 325 and 525°. As the temperature of preheating was increased, the initial intensity of the surface luminescence increased and in all three cases decreased with time, reaching the same constant value after about 1/2 hour. Since the intensity is dependent on the amount of energy transferred to the surface, we conclude that the intensity of the luminescence is proportional to the activity of the gel in catalyzing these recombination reactions. This agrees with Badin's[5] observation in the case of KCl that the luminescence is most intense when the activity of the surface is greatest. The most plausible explanation of these observations is that the activity of the gel is increased by dehydration at higher temperatures (an effect observed by Badin[5] in the case of KCl) and that some water is readsorbed on the surface as the recombination reactions proceed. The weight of the silica gel sample was determined before and after each run and was found to remain essentially constant (±0.3%). The presence of the silica gel surface in the system reduced the hydrogen peroxide yield by 1 to 1.5% (Table I, runs 5, 6 and 7 compared to runs 8 to 20).

Samples of silica gel from batches 2 and 3 exhibited the same green luminescence when exposed to the products of the water vapor discharge. The intensity of the luminescence was least in the case of the extensively purified batch (batch no. 2), which suggests that the luminescence may arise from the presence of impurities in the gel.

In the initial stages of the studies of the intensity of the luminescence, the platforms used were made of Pyrex glass. The face of the platform was coated with silica gel (batch no. 1) and dried at 110°. It was observed that if the sample of the gel and platform were heated to this temperature for a fairly long period of time (about three days), the color of the luminescence on the surface upon exposure to the discharge products of water vapor was a bright yellow rather than the green usually observed. However, after exposure to the discharge products for three minutes, the yellow luminescence had diminished considerably and the usual green luminescence appeared. Apparently sodium ions from the glass migrated to the surface of the gel and the energy liberated by the exothermic reactions occurring on the surface was sufficient to excite them. The energy liberated at the surface is probably large enough to drive sodium ions off the surface of the gel causing the yellow luminescence to diminish with time. In a later experiment the silica gel was purposely contaminated with a sodium salt by treating the gel with a dilute solution of NaI. Upon exposure to the discharge products of water vapor, the surface exhibited a brilliant yellow luminescence which did not diminish significantly with time.

From these experiments it is concluded that the luminescent phenomenon observed on the surface of silica gel is the result of an excitation of the surface caused by the exothermic reactions occurring thereon.

The green luminescence also was observed by means of a small hand spectroscope. The spectrum in the visible region appeared to be continuous with a broad green band. The luminescence observed on the surface of silica gel contaminated with sodium ions also showed a continuous spectrum in the visible region with a broad yellow band.

Reactions in the Liquid Air Trap.—With the reaction chamber no. 2 inserted between the discharge tube and the trap a number of blank runs were made, *i.e.*, runs in which a reactive surface was not present in the system. Some 13 such runs were made over a period of five months. The results are shown in Table I, runs 8 to 20, along with the data of Jones and Winkler[6] and Giguere.[5] These three independent results are strikingly

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(8) P. Giguere, E. A. Secco and R. S. Eaton, *Disc. Faraday Soc.*, **14**, 104 (1953).

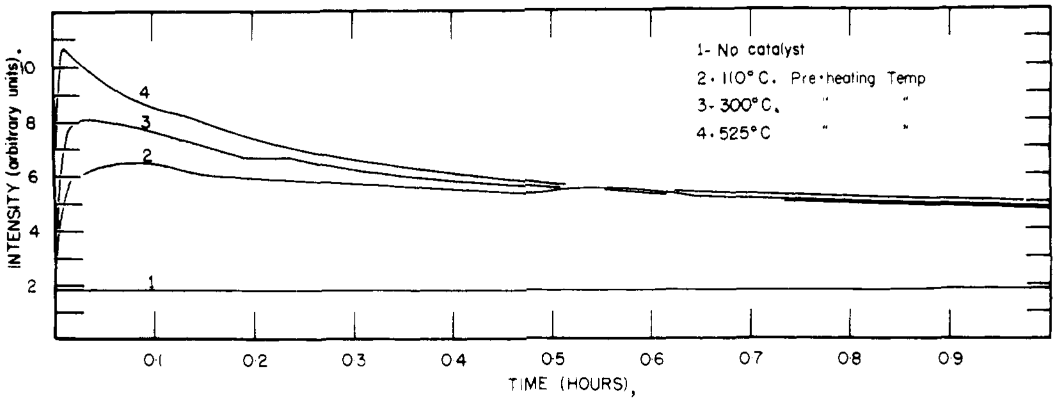

Fig. 2.—Variation of the intensity of luminescence with time and preheating temperature.

similar when one considers that they are derived from apparatus which are different in design. Giguere used an electrodeless discharge, the flow of water vapor through the system being the largest yet reported. Jones and Winkler inserted their liquid air trap directly below the discharge tube while the present authors placed the trap about 22 cm. from the discharge. The pressure in all three cases was about the same, *i.e.*, 0.1 to 0.2 mm. Giguere claimed complete dissociation of the water vapor while Jones and Winkler claimed about 75% dissociation. The present authors applied Giguere's criterion for complete dissociation to the present apparatus. It was found that between currents of 200 and 250 milliamp., the pressure on the exit side of the liquid air trap remained essentially constant and therefore had reached its maximum value, indicating complete dissociation. Jones and Winkler suggest that the amount of water frozen out at Dry Ice temperature is the amount which passes through the discharge undissociated, since no hydrogen peroxide is formed in the trap at this temperature. The present authors made two consecutive blank runs using a Dry Ice trap. These results are shown in Table I (runs 21 and 22). From these results, the degree of dissociation of the water vapor in this investigation was only about 64% according to the criterion of Jones and Winkler. So that, although the results of all three authors are very similar, there is considerable disagreement as to the extent of dissociation of the water.

The present authors are inclined to place more confidence in Giguere's criterion than in that of Jones and Winkler, since it seems reasonable that an increase in current through the tube should increase the number of water molecules dissociated and therefore increase the pressure of non-condensable gases. Furthermore, analysis of the data from the two series of runs, 8–13 and 14–20, at 200 and 250 milliamp., respectively, shows that there is no statistically significant difference between them, although at liquid air temperatures the yield of products, particularly H_2O_2, should vary with the current through the tube if the degree of dissociation of water vapor were less than 100%. We note also that in the studies of the reactions on the surface of silica gel using reaction chamber no. 1 (runs 1 and 2), the yield of water was only about 13%. If the dissociation of water into H and OH were only 64%, the water yield would never fall below 36% under any circumstances. Sanders, *et al.*,[9] have suggested that a species other than H and OH is present in the water vapor discharge. However, this new species has not been identified.

Discussion

The Reactions of H Atoms and OH Radicals in the Liquid Air Trap.—The results of the blank runs, 8–20, can be used as a basis for the interpretation of the phenomena occurring in the liquid air trap. We can account qualitatively for the three of the four products of these reactions by the following simple recombination reactions occurring on the walls of the trap.

$$H + H = H_2 \quad \Delta H = -103.2 \text{ kcal./mole}^{10} \quad (1)$$

$$OH + OH = H_2O_2 \quad \Delta H = -\ 53.6 \text{ kcal./mole}^{11} \quad (2)$$

$$H + OH = H_2O \quad \Delta H = -119.9 \text{ kcal./mole}^{12} \quad (3)$$

The reaction leading to the formation of O_2 is not as straightforward, however. Jones and Winkler[6] have shown that most of the O_2 is evolved from the trap when the temperature is increased above $-120°$. They considered this temperature to be the decomposition temperature of the "abnormal" form of H_2O_2 postulated by Gieb and Harteck.[13] However, the existence of such a form is open to doubt.[14] Giguere[3] has suggested that the reaction leading to the formation of O_2 is

$$OH + OH = H_2 + O_2 \quad \Delta H = -18 \text{ kcal.} \quad (4)$$

However, according to the semi-empirical relationships developed by Hirschfelder[15] this reaction has a high activation energy (about 55 kcal.). Jones and Winkler[6] found 0.4% ozone in the gases evolved from the trap and we have detected ozone qualitatively by odor, suggesting that the reaction forms O atoms originally. The only other reaction which could form O from OH radicals is

$$H + OH = H_2 + O \quad \Delta H = -2.2 \text{ kcal.} \quad (5)$$

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[9] T. M. Sanders, G. C. Dousmanis, A. L. Schawlow and C. H. Townes, *J. Chem. Phys.*, **22**, 245 (1954).

[10] A. G. Gaydon, "Dissociation Energies," Dover Publications, New York, N. Y., 1950, p. 209.

[11] J. Weiss, "Advances in Catalysis," Academic Press, New York, N. Y., 1952, p. 361.

[12] I. M. Klotz, "Thermodynamics," Prentice-Hall, New York, N. Y., 1950, p. 52.

[13] K. H. Geib and P. Harteck, *Ber.*, **65**, 1551 (1932).

[14] C. W. Bawn and M. A. Hogg, *Disc. Faraday Soc.*, **14**, 141 (1953).

[15] J. O. Hirschfelder, *J. Chem. Phys.*, **9**, 645 (1941).

Reaction 5 has a much lower activation energy than (4) according to Hirschfelder[15] (about 5.5 kcal.). Oxygen molecules formed from the union of two O atoms could then be occluded in the frozen products or form a loose adduct with H_2O_2 or H_2O as Ruhrwein and Edwards have suggested.[16]

There is another argument which we believe will not only show that (5) is reaction leading to the formation of O_2 but also will enable us to calculate the yields of products. This argument is based on the simple assumption that the principal process governing the distribution of products is the random recombination of the H atoms and OH radicals. Such an argument predicts that the yields should be 25% H_2O_2, 50% H_2O, 25% H_2 and 0% O_2, if the water vapor is completely dissociated. We note that the calculated H_2O_2 yield is close to that observed (Table I, runs 8–20), so that no other reaction involving two OH radicals can occur to any significant extent. On the other hand, the water yield is 12% lower than that predicted, which suggests that reaction 5 has occurred.

Assuming that the process leading to the formation of O_2 is (5), then an examination of the data of runs 8–20 will show that a reasonably constant fraction of the OH radicals combining with H atoms follows this path (0.17 in this investigation, 0.18 according to Giguere,[8] and 0.24 according to Jones and Winkler[6]). We may account for this observation as follows.

The combination of H atoms and OH radicals proceeds along one of two paths, (3) or (5). We assume that the relative probabilities of these reactions are determined by the relative probabilities of the colliding H atom striking the oxygen atom (3) or the hydrogen atom (5) of the hydroxyl radical. Therefore, the probability, P_A, of forming H_2O is approximately proportional to the collision area of the oxygen atom in the OH radical and a hydrogen atom, which in turn is proportional to the square of the collision diameter for this pair. So that

$$P_A = k(R_H + r_0)^2 \qquad (6)$$

where

R_H = Bohr radius of the H atom

r_0 = covalent radius of the oxygen atom in the OH radical

Similarly

$$P_B + k(R_H + r_H)^2 \qquad (7)$$

where P_B is the probability of (5) and r_H is the covalent radius of the H atom in the OH radical. The covalent radii of the hydrogen atom and the oxygen atom are 0.31 and 0.66 Å., respectively[17]; while the Bohr radius of the hydrogen atom is 0.53 Å., so that

$$X = \frac{P_A}{P_A + P_B} = 0.67 \qquad (8)$$

We now proceed to calculate the distribution of products on the assumptions outlined above, *i.e.*, (a) the H atom and OH radicals combine in a perfectly random manner in the trap, (b) the reaction leading to the formation of oxygen in the trap is (5), and (c) there are two possible reactions of H atoms and OH radicals, (3) and (5), and their relative probabilities are given by (6) and (7). We have shown that every mole of water admitted to the system is completely dissociated. *i.e.*

$$H_2O(1\text{ mole}) = H(1\text{ mole}) + OH(1\text{ mole}) \qquad (9)$$

On the basis of our first assumption, we get

$$OH(0.5\text{ mole}) = H_2O_2(0.25\text{ mole}) \qquad (10)$$

$$H(0.5\text{ mole}) = H_2(0.25\text{ mole}) \qquad (11)$$

the remaining H and OH radicals react by either of two paths.

$$OH(0.5\,X\text{ mole}) + H(0.5\,X\text{ mole}) = H_2O(0.5\,X\text{ mole}) \qquad (12)$$

$$OH(0.5(1 - X)\text{ mole}) + H(0.5(1 - X)\text{ mole}) = H_2(0.5(1 - X)\text{ mole}) + O_2(0.25(1 - X)\text{ mole}) \qquad (13)$$

where X is given by (8). The total products can now be obtained by summing equations 9 to 13, *i.e.*

$$H_2O(1\text{ mole}) = H_2O_2(0.25\text{ mole}) + H_2(0.25 + 0.5(1 - X)\text{ mole}) + H_2O(0.5X\text{ mole}) + O_2(0.25(1 - X)\text{ mole}) \qquad (14)$$

Using (14) the yields of products should be: H_2O_2, 25.0%; H_2O, 33.3%; H_2, 41.7%; O_2, 8.3%.

We note that (14) predicts a larger fraction of OH radicals reacting to form $H_2 + O_2$ than is actually observed. However, in this highly simplified calculation we have assumed that all configurations of the activated complex are equally probable, but as a matter of fact the most likely configuration is that which minimizes the potential energy, *i.e.*, a linear configuration with the H atom preferentially approaching the oxygen atom in the hydroxyl radical. This is particularly true for reactions involving "s" electrons.[15] The effect of this preference would be to reduce the fraction of OH radicals reacting through (5).

The Reaction of H and OH on the Surface of Silica Gel.—The experimental facts regarding this reaction may be summarized as follows: (1) the H atom and the OH radical are both removed; (2) the principal products of the reaction are H_2 and O_2; (3) the silica gel surface does not catalyze the recombination of H atoms; (4) the green luminescence observed on the surface is the result of an excitation of the surface caused by exothermic reactions occurring thereon; (5) studies of the intensity of the luminescence as a function of time and the temperature to which the gel was preheated indicate that the water content of the gel controls its activity.

Laidler[18] and Schuler and Laidler[19] have shown that the most probable mechanism of the recombination of free radicals on surfaces is a reaction between an adsorbed species and a gas phase species. Therefore, the failure of the silica gel surface to catalyze the recombination of H atoms indicates either that the surface cannot adsorb H atoms or that they are adsorbed in a way that makes reaction with gas phase H atoms impossible. In either case, it appears that in catalyzing the recombination of the discharge products of water vapor, the silica gel surface first adsorbs the OH radical. The adsorbed hydroxyl radical then reacts with some species from

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(16) R. Ruhrwein and J. W. Edwards, Free Radical Symposium, National Bureau of Standards, Washington, D. C., Sept. 1957.

(17) L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1948, pp. 164, 168.

(18) K. J. Laidler, *J. Chem. Phys.*, **53**, 712 (1949).

19) K. A. Schuler and K. J. Laidler, *ibid.*, **17**, 1212 (1949).

the gas phase to form the observed products. Of the two possible reactions, *i.e.*, a reaction with a gas phase OH radical or H atom to form $H_2 + O_2$, the reaction with the H atom should again have the lower activation energy.

We suggest, therefore, that the mechanism of this surface reaction is

$$S + OH = S\text{-}OH \quad (15)$$

$$S\text{-}OH + H = S\text{-}O + H_2 \quad (16)$$

$$S\text{-}O + S\text{-}O = 2S + O_2 \quad (17)$$

where S is the surface. The OH radical is probably bound to the surface through the oxygen atom. This orientation would greatly increase the probability of forming $H_2 + O_2$ upon reaction of an H atom from the gas phase, as is experimentally observed.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF MANCHESTER]

Radical and Molecular Yields in the γ-Irradiation of Liquid Methanol

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Fe(III) salts and benzoquinone are reduced during the γ-irradiation of methanol and the extent of reduction is a measure of G(radicals). These solutes also decrease $G(H_2)$, $G(CH_4)$ and G(glycol) while at the same time increasing $G(CH_2O)$. The observations are accounted for by the oxidants reacting with the radicals H, CH_2OH and CH_3 and the results are analyzed to give $G(H)$, $G_m(H_2)$, $G(CH_2OH)$, $G(CH_3)$, $G_m(CH_2O)$, G_m(glycol) and $G_m(CH_4)$. Appreciable differences in $G(H)$ and $G(CH_3)$ are observed between pure methanol and methanol which is 0.1 N in sulfuric acid.

Values of the total radical yields have been obtained for various organic solvents subjected to ionizing radiation by using scavengers such as iodine[1] and diphenylpicryl hydrazyl,[2] and also from measurements of the initiation rates of polymerization.[3] So far the separation of these total yields into the yields of individual radicals has not been made as it has for water. The present work is an application to methanol of the use of ferric salts and quinones as radical scavengers.[4-6] These have been fruitful in aqueous systems where the radicals reduce the scavengers and, in suitable conditions, the extent of this reduction is a measure of $G_w(H) + G_w(HO)$. More detailed analyses of the product yields in various conditions also enables the individual radical and molecular yields to be obtained.

We found in preliminary experiments that Fe(III) and quinones are also reduced during the irradiation of their solutions in organic liquids. Methanol was chosen for a detailed study because the work of McDonell and Newton[7] and McDonell and Gordon[8] has shown that the irradiation products are ethylene glycol, formaldehyde, hydrogen, methane and carbon monoxide, all of which can be determined at low conversions.

Experimental

Materials.—Methanol of analytical reagent grade was dried by refluxing with magnesium methoxide. Traces of formaldehyde were removed by refluxing with dinitrophenylhydrazine. Benzoquinone was purified by low temperature sublimation *in vacuo*. Ferric chloride hydrate (described as $FeCl_3 \cdot 6H_2O$) was analytical reagent grade and was used without further purification.

Analyses.—Gases were collected and measured as described previously[5] and analyzed mass spectroscopically. The formaldehyde in the irradiated methanol (10^{-4} to 10^{-3} M) was determined with chromotropic acid[9] and glycol by treating with periodic acid.[10]

We found it possible to extend the latter method to concentrations of the order 10^{-4} M. With a 50% excess of periodic acid the time for complete reaction was about 12 hours when the analysis mixture contained about 20% methanol + 80% water. More than 20% methanol slowed the reaction considerably and also gave rise to a reduction of periodic acid over and above that due to glycol. Hence to determine the smaller amounts of glycol, the original methanol solution was concentrated by distillation *in vacuo* and then diluted with water.

Fe(III), because of its absorption in the ultraviolet, interferes with this method of analysis and was removed before the addition of periodate by running the solution (diluted to 20% methanol) through an ion-exchange resin (Amberlite I.R. 120) in the sodium form. Tests showed that the eluent gave some reaction with periodic acid even in the absence of glycol, due presumably to traces of material from the resin. This was corrected for by running blanks through the same resin but the procedure introduced an error of about ±0.05 into the glycol yields. Since in the presence of Fe(III) these are only of the order of 0.2 the possible error in the yields in these conditions is considerable. Benzoquinone interferes with both glycol and formaldehyde analyses and we have been unable to overcome this difficulty. Hence in benzoquinone + methanol mixtures we can only report the gas yields.

With these exceptions tests with known solutions containing all the materials present in the irradiated solutions established the reliability of the analytical methods for glycol and formaldehyde.

When the extent of reduction of Fe(III) or quinone was small, the Fe(II) and hydroquinone produced were determined by their reduction of ferriin as described previously.[5,6] When the change was appreciable, as at the lower Fe(III) and quinone concentrations, it was measured by the decrease in absorption of Fe(III) at 249 mμ and of benzoquinone at 246 mμ. We have been unable to obtain hydroquinone

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[1] F. N. Weber, P. F. Forsyth and R. H. Schuler, *Radiation Research*, **3**, 68 (1955).

[2] A. Prevost-Bernas, A. Chapiro, C. Cousin, Y. Landler and M. Magat, *Disc. Faraday Soc.*, **12**, 98 (1952).

[3] W. H. Seitzer and A. V. Tobolsky, THIS JOURNAL, **77**, 2687 (1955).

[4] E. J. Hart, *ibid.*, **77**, 5786 (1955).

[5] J. H. Baxendale and D. Smithies, *Z. physik. Chem.*, **7**, 242 (1956).

[6] J. H. Baxendale and G. Hughes, *ibid.*, **14**, 324 (1958).

[7] W. R. McDonell and A. S. Newton, THIS JOURNAL, **76**, 4651 (1954).

[8] W. R. McDonell and S. Gordon, *J. Chem. Phys.*, **23**, 208 (1955).

[9] C. E. Bricker and H. R. Johnson, *Ind. Eng. Chem.* (*Anal. Ed.*), **17**, 400 (1945).

[10] G. O. Aspinall and R. J. Ferrier, *Chem. Ind.*, 1216 (1957).