(n,γ)I^{128} reaction in gaseous ethyl iodide at low pressure are positively charged as a result of internal conversion of some of the capture γ-rays. Similar evidence has been reported for a positive charge on Br^{80},[23b] Br^{82},[23b] Au^{107},[23c] and In^{116},[23c] follow-radiative neutron capture.

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MADISON 6, WISCONSIN

[CONTRIBUTION FROM THE BEACON LABORATORIES OF THE TEXAS COMPANY]

Isotopic Exchange Rates as Criteria of Surface Heterogeneity[1]

BY R. P. EISCHENS

RECEIVED MAY 9, 1952

The exchange between gaseous CO and CO chemisorbed on iron has been studied. The most weakly bonded CO exchanges the fastest. The exchange data show that the iron is heterogeneous. Kinetic treatment of the data indicates that the heterogeneity is due to differences between a relatively few homogeneous portions rather than to a spectrum of chemisorption bond strengths. In some cases it is not possible to distinguish between the two types of heterogeneity.

Introduction

The question of the degree of heterogeneity of catalyst surfaces has long been of interest to those concerned with fundamental catalyst studies. Despite the considerable attention this problem has received, there remains a wide divergence of opinion concerning this basic surface property. This disagreement stems from the fact that the adsorption of gases, the primary tool of surface chemistry, is inherently unsuited to resolve the question.

When attempts are made to study surface heterogeneity by means of rates of adsorption, heats of adsorption or related methods, the results are such that it is practically impossible to differentiate between heterogeneity as a true surface property and an apparent heterogeneity introduced by variation in the amount of gas on the surface.

The study of the exchange between adsorbed and non-adsorbed gas is not subject to the uncertainties caused by variation in the amount of gas on the surface. During the exchange the adsorbed molecule is displaced by another from the gaseous phase and the amount of gas on the surface remains constant.

When reduced iron is exposed to carbon monoxide at low temperature the gas is rapidly adsorbed.[2] That part of the adsorbed carbon monoxide which is not easily removed by pumping is designated as chemisorbed. Although the chemisorbed carbon monoxide is not easily removed by pumping, it does exchange with carbon monoxide from the gaseous phase. This exchange was first observed over synthetic ammonia catalysts.[3]

The work to be described in this paper is concerned with the study of the exchange between chemisorbed and gaseous carbon monoxide over unpromoted iron. The exchange was followed by introducing radioactive carbon monoxide as the chemisorbed phase and measuring the rate of its appearance in the gaseous phase.

Experimental

Apparatus—A functional sketch of the chemisorption–exchange apparatus is shown in Fig. 1.

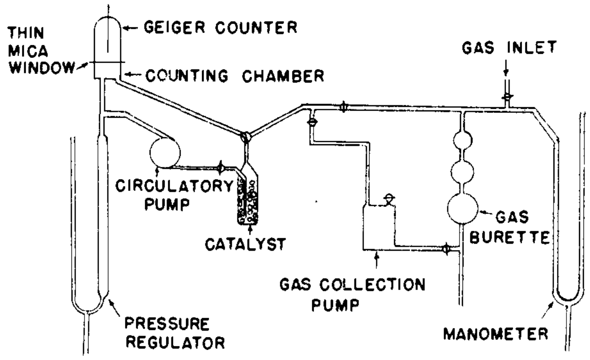

Fig. 1.—Functional sketch of chemisorption-exchange apparatus.

The Geiger counter was assembled from a commercial kit.[4] The counter was modified for gas counting by replacing the sealing ring with a brass chamber.[5] A non-recording Tracerlab Autoscaler was used.

A combination mercury diffusion-Sprengel pump was used to collect the gas pumped off at low pressure.[6] The circulating pump is of the magnetically activated plunger type. It operates at 500 cc./min. The volume of the gaseous phase was approximately 200 cc. The circulating pump was found to be essential to ensure uniformity of the isotopic composition of the gaseous phase. Uniformity of the gaseous phase could be attained in about one minute with the pump whereas it required several hours without it.

The pressure regulator is operated by changing the level of the contained mercury. It is used to adjust the initial pressure to the predetermined level and to compensate for small changes of pressure during the exchange run.

The inlet tube of the catalyst chamber extends to the bottom. The lower part is packed with glass beads so the entering gas can attain temperature equilibrium before reaching the catalyst. Both inlet and outlet of the catalyst chamber are protected from mercury vapor by gold leaf traps.

Materials.—The iron samples were prepared from the oxide by hydrogen reduction. The oxide was prepared by heating the hydroxides obtained by precipitation from a nitrate solution with ammonium hydroxide.[7] The chemicals

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(1) Parts of this paper were presented at the 1951 Gordon Research Conference on Catalysis and the Symposium on Colloid Chemistry of Catalysts at the 1951 A.C.S. Meeting in New York.

(2) S. Brunauer and P. H. Emmett, THIS JOURNAL, **62**, 1732 (1940).

(3) J. T. Kummer and P. H. Emmett, *ibid.*, **73**, 2886 (1951).

(4) Mark 7, Model 1, Radiation Counter Laboratories, Inc., Chicago, Illinois.

(5) J. T. Kummer, *Nucleonics*, **3**, 27 (1948).

(6) I. E. Puddington, *Ind. Eng. Chem.*, *Anal. Ed.*, **16**, 592 (1944).

(7) The oxide was prepared by Mr. L. W. Cook of this Laboratory.

used were of C.P. grade. Spectrographic analysis of the iron showed trace quantities of Cu and Si. The over-all purity of the iron was 99.9%. The iron was used in the form of $^1/_4$" pellets.

The hydrogen used in the reduction was ordinary tank hydrogen purified by passing over copper at 400° and through two liquid nitrogen traps packed with glass wool. The reductions were carried out at 300° for a period of four days at a space velocity of 1000 v./v./hr. After reduction the samples were pumped for 24 hours at a pressure of 1×10^{-5} mm. at 300°.

Despite attempts to prepare the samples in a reproducible manner, there were variations in the specific surface areas as determined by the B.E.T. nitrogen method. The areas ranged from 2–6 m.^{2}/g.

The ratio of the volume of carbon monoxide chemisorbed at −78° to the amount of nitrogen in the B.E.T. monolayer was usually about 1.1. When the iron sample was to be used in an exchange run the area determination was not made until after the run so as to prevent contamination of the surface by nitrogen.

The radioactive carbon monoxide, which is a mixture of $\mathrm{C^{14}O}$ and CO, is designated as $\mathrm{C^*O}$. The $\mathrm{C^*O}$ was prepared by reducing $\mathrm{C^*O_2}$ obtained by addition of perchloric acid to $\mathrm{BaC^*O_3}$.[8] The $\mathrm{C^*O_2}$ was reduced over zinc at 400°.[9] The $\mathrm{C^*O}$ prepared in this manner is almost 99% pure. The principal impurities are hydrogen, 1% and methane, 0.2%.

Self absorption corrections were made with the aid of experimentally determined curves showing the activity of the $\mathrm{C^*O}$ as a function of pressure.

The normal carbon monoxide was prepared free of all impurities except water vapor by addition of phosphoric acid to formic acid. The purity was checked by mass spectrometer analysis. The water was removed in a liquid oxygen trap prior to use in the exchange experiments.

Procedure.—All of the exchange runs to be reported here were conducted at −78° and at pressures a few cm. less than one atmosphere.

A quantity of $\mathrm{C^*O}$ in excess of the amount required to form a monolayer was admitted to the reduced iron at −78°. The $\mathrm{C^*O}$ was allowed to stand over the iron for about 20 hours at pressures near one-half atmosphere. The non-adsorbed gas was pumped off with a manual Toepler pump until the pressure appeared to be zero on an ordinary mercury manometer. This pressure will be referred to as 0.1 mm. The difference between the amount of $\mathrm{C^*O}$ added and that pumped off is taken as the amount chemisorbed.

In some cases carbonyl formation can cause serious difficulties. A description of these effects is not within the scope of this paper since it was not a serious obstacle in the runs to be described.

After the non-adsorbed $\mathrm{C^*O}$ had been pumped off, normal carbon monoxide was measured in. It was separated from the catalyst until the two stopcocks on the catalyst chamber were opened to start the experiment. The exchange was followed by measurement of the $\mathrm{C^*O}$ content of the gaseous phase. The first reliable data were not obtained until about a minute after the exchange had started. The counting level changed from 1 to about 100 times background during the course of the run. The background was 1–2 counts per second (c./sec.). All data were corrected for this background level.

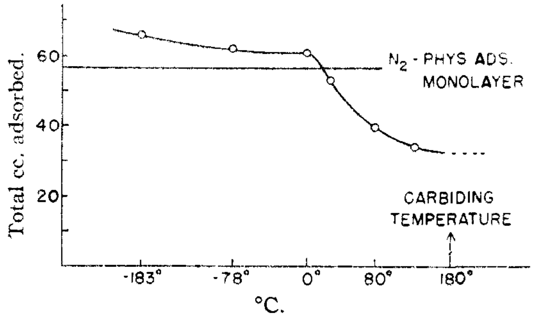

Fig. 2.—The effect of temperature on the chemisorption of CO at 0.1 mm. on a 48.9-g. sample of reduced iron.

The data for Fig. 2 were obtained in the following manner. Carbon monoxide was introduced to the reduced iron at −183° and allowed to stand for one hour at a pressure of 35 cm. The excess carbon monoxide was pumped off until the pressure fell to 0.1 mm. The difference between the amount added and that pumped off was considered to be chemisorbed. The other data points were obtained by raising the temperature, waiting for one hour and again pumping down to a pressure of 0.1 mm. No carbon monoxide was added after the first batch at −183°.

The data in Fig. 3 were obtained by pumping off the chemisorbed gas and measuring the amount of $\mathrm{C^*O}$ in each batch collected. The three batches were collected at −78, −33 and 0° with pumping periods of 72, 24 and 16 hours, respectively. The gas collection pump operated at a pressure of 1×10^{-4} mm. After the period of pumping at 0°, hydrogen was introduced and the remaining $\mathrm{C^*O}$ reduced from the surface. The total C* recovered by exchange, pumping and reduction was 95% of that initially chemisorbed.

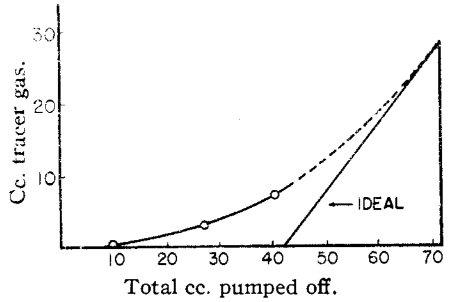

Fig. 3.—The amount of $\mathrm{C^*O}$ pumped off as a function of the total carbon monoxide removed. At the start of the pumping the iron had adsorbed 72 cc. of carbon monoxide, 29 cc. of which was $\mathrm{C^*O}$. The $\mathrm{C^*O}$ was on the sites where exchange was slowest. The three data points represent gas pumped off at −78, −33 and 0°.

Results and Discussion

Chemisorption.—A preliminary chemisorption study was carried out to determine the experimental conditions which would be suitable for an exchange run. The results of this study also illustrate the meaning of the term "chemisorption" as used in this paper.

In Fig. 2 the total volume (cc. S.T.P.) of carbon monoxide chemisorbed on a 48.9-g. sample of reduced iron is given as a function of temperature.

The straight horizontal line at 56 cc. represents the nitrogen in the B.E.T. monolayer at −196°.

The horizontal part of the carbon monoxide curve between −183 and 0° is thought to represent a monolayer of carbon monoxide on iron. The slightly higher value at −183° is probably due to the inclusion of some physically adsorbed gas as chemisorbed. The second horizontal portion which appears to be starting at the higher temperatures is probably due to the incidence of carbide formation.

The chemisorption results indicated that −78° would be a convenient temperature at which to conduct the first chemisorption–exchange runs, since it is about in the middle of the temperature range in which the iron is covered with a monolayer of CO.

General Characteristics of the Exchange Data.—On the basis of a considerable number of exchange experiments it has been learned that the data from a typical run at −78° have the following general characteristics. There is an initial rapid exchange which is so fast that $^1/_5$ to $^1/_3$ of the total amount of

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[8] The $\mathrm{BaC^*O_3}$ was obtained from the A.E.C.

[9] R. B. Bernstein and T. I. Taylor, *Science*, **106**, 498 (1948).

chemisorbed carbon monoxide has exchanged in the minute required to obtain the first radioactivity measurement. The rapid exchange is followed by a period of several hours during which the exchange proceeds at a conveniently measurable rate. Another $^1/_5$ to $^1/_3$ of the chemisorbed gas is involved in this measurable exchange. Finally there is a period in which the exchange is very slow. The exchange rate for the slow portion is so small that in some cases the exchange appears to stop and an apparent equilibrium is reached at a counting level below that calculated for complete mixing This slow exchange portion is also found with the synthetic ammonia catalysts.[3]

At room temperature all of the chemisorbed carbon monoxide exchanges rapidly and the theoretical equilibrium value is reached in a few minutes. The theoretical equilibrium value is calculated from the relative amounts of the chemisorbed and gaseous phases and the initial activity of the C*O.

Rate of Exchange and Chemisorption Bond Strength.—The term "heterogeneous" as applied to catalyst surfaces generally means that the component parts of the surface differ in the tenacity with which they bond adsorbed gases. For this reason an attempt was made to determine whether the variation in exchange rate reflects differences in the strengths of the chemisorption bonds.

This was done by replacing part of the chemisorbed C*O with CO and then pumping to determine whether C*O or CO could be more easily pumped off. The replacement was carried out by a series of five consecutive exchange reactions. In this series of consecutive exchanges, the gaseous phase was replaced with CO after the apparent equilibrium was reached. The sample of reduced iron had initially chemisorbed 72 cc. of C*O. In the five separate exchange runs which comprised the consecutive series the volumes of C*O displaced from the surface were 23.9, 14.0, 4.0, 0.7 and 0.9 cc. The remaining 28.5 cc. of C*O was concentrated on the parts of the surface where the exchange was slow.

Figure 3 shows the amount of C*O pumped off as a function of the total gas removed. If there were no relationship between the rate of exchange and bond strength, the gas pumped off would be a random mixture of CO and C*O, and the data would fall in a straight line from the lower left to the upper right. However, Fig. 3 shows that the gas pumped off is poorer in C*O than would be expected from random mixing. From this it is concluded that the variation in exchange rate on different parts of the surface does reflect a difference in the chemisorption bond strength and the chemisorbed carbon monoxide which is the most easily removed by pumping is that which exchanges at the fastest rate.

Although there is a definite relationship between bond strength and rate of exchange, there is a variation from the "ideal" line. This line illustrates the result which would be expected if there were a clear demarcation in the strengths of the chemisorption bonds and all of the sites of weaker bonding were covered with CO. If this were true, no C*O would be removed in the first 43.5 cc. pumped off. The deviation from the "ideal" may indicate that there is only a partial correlation between bond strength and rate of exchange. However, the deviation may also be caused by surface migration resulting from the higher temperatures used in pumping off the chemisorbed gas.

Kinetic Treatment of Exchange Data.—As previously discussed the data indicate that the surface may be divided into portions in which the exchange rates are fast, medium and slow. The exchange method as used here is not sensitive enough to detect differences within the fast and slow portions. However, the medium rate portion goes at a conveniently measurable rate and is amenable to kinetic treatment.

The kinetics of an isotopic exchange may be expressed by the equation[10a,b]

$$-\ln(1 - X/X_\infty) = R't(a + b)/ab$$

When this equation is applied to the chemisorption-exchange, X is the amount of C*O in the gaseous phase at time t, X_∞ is the amount at infinite time, b and a are constants which represent the volumes of gas in the chemisorbed and gaseous phases, respectively, and R' is the rate of exchange. If R' is a constant a plot of $-\ln(1 - X/X_\infty)$ *vs.* t will give a straight line of slope $R'(a + b)/ab$. The units of R' obtained from the slope are expressed as cc./min. In this case where the exchange may be assumed to be a direct function of the amount of gas on the portion it is possible to express the rate, R, for each portion in terms of (cc./min.)/cc. by dividing R' by the number of cc. of gas adsorbed on the portion. All of the rates will be given in the latter units.

This equation was derived for a single phase system in which there was only one R'. Application of the equation to two phase systems imposes certain limitations. A discussion of the factors involved in such application has been presented by Norris.[11] If diffusion effects are not involved the equation may be used for two-phase systems.

If there is more than one rate of exchange, it is necessary that the differences in rates must be large enough so that each may be considered separately. This means that for the medium exchange rates, an experimentally determined X_∞ must be used instead of the theoretical X_∞ which is calculated from the ratio of the two phases. The initial rapid exchange does not interfere with the use of this equation because the gas which is chemisorbed in the portion where exchange is rapid may be considered to be part of the gaseous phase, since it is in isotopic equilibrium with that phase. Thus the exchange in the rapid portion effects only the values of the constants a and b.

Carbon monoxide which is physically adsorbed during the exchange run is considered to be in isotopic equilibrium with the gaseous phase.

The McKay equation has been used by Winter[12] in a study of the exchange between gaseous oxygen and metallic oxides.

Figure 4 shows an exchange run plotted as $-\ln(1 - X/X_\infty)$ *vs.* t. The X_∞ used is the experi-

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[10] (a) H. A. C. McKay, *Nature*, **142**, 997 (1948); (b) R. B. Duffield and M. Calvin, THIS JOURNAL, **68**, 557 (1946).

[11] T. H. Norris, *J. Phys. Colloid Chemistry*, **54**, 777 (1950).

[12] E. R. S. Winter, *J. Chem. Soc.*, 1170 (1950).

mental value of 158 c./sec. (the theoretical X_∞ for complete mixing is 304 c./sec.). Figure 4 includes the fast and medium exchange rates for this run. The ordinate for this plot is shown on the right. The corresponding values of X/X_∞ are shown on the left. An X/X_∞ value of 1 would indicate that the medium rate exchange had reached equilibrium.

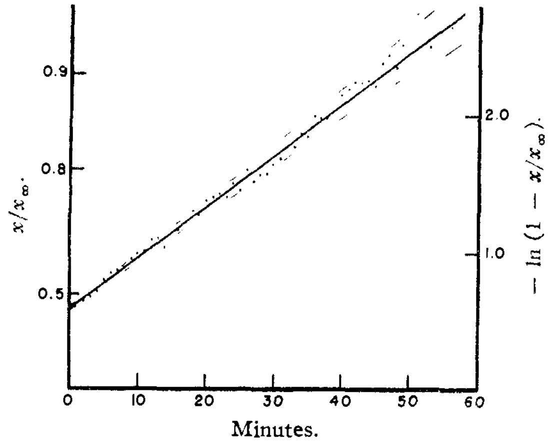

Fig. 4.—Exchange between gaseous and chemisorbed carbon monoxide. Plot of $\ln(1 - x/x_\infty)$ *vs.* time. In this run the final exchange rate was so slow that it could be considered to be zero and the experimental equilibrium value was used for the x_∞. There was 72 cc. in the chemisorbed phase and 145 cc. in the gaseous phase.

The dashes on each side of the straight line represent the spread expected from the statistical nature of the counting. This spread, which is $\pm\sqrt{n}/n$, where n is the number of counts, amounts to $\pm 1.6\%$ for the points shown. The error caused by the statistical randomness becomes large as $X/X_\infty \rightarrow 1$.

The results indicate that the conveniently measurable portion of the exchange proceeds with a single R of 3.5×10^{-2}.

The above treatment is a special case which is simple because the slow exchange rate may be taken as zero. When the slow rate cannot be taken as zero, the kinetic treatment can still be simple if either of the two phases is large compared to the other. Then the exchange may be expressed as a sum of exponentials and treated like a radioactive decay.[13]

This method is illustrated in Fig. 5. A plot of $1 - X/X_\infty$ *vs.* t on semi-log paper gives a curve concave upward which ends in a straight line. This straight line represents the slowest exchange rate. The terminal straight line is extrapolated to $t = 0$ and the extrapolated line subtracted from the original curve. The residual curve also terminates in a straight line. This line represents the next slowest rate. In theory this process could be repeated many times but in practice it is difficult to resolve more than three rates. The rates and extents of the portions are obtained from the straight lines by use of the equation

$$1 - X/X_\infty = \sum_{i=1}^{i=n} a_i e^{-R_i t}$$

where the intercept a_i is the ratio of the extent of the portion to the total surface, and the slope of the line gives the rate of exchange, R_i, for the ith portions.

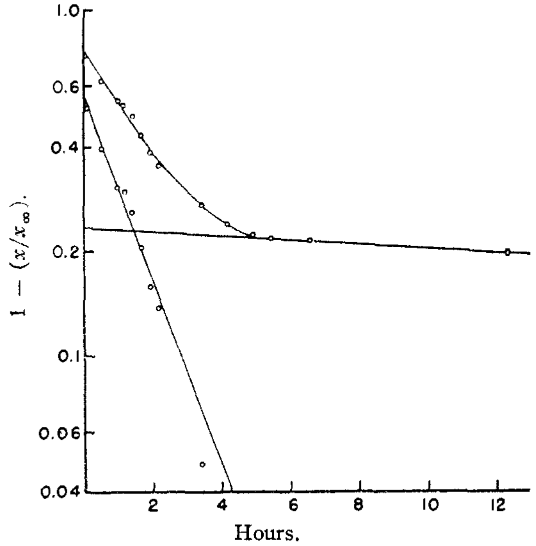

Fig. 5.—Plot of $\ln(1 - x/x_\infty)$ *vs.* time for the exchange between gaseous and chemisorbed carbon monoxide on iron at −78° in presence of mercury vapor. There was 56 cc. in the chemisorbed phase and 195 cc. in the gaseous phase. The data are treated as those from a radioactive decay.

The exact values for the rates and size of portions are only approximately correct for these exchange runs where the gaseous phase is about five times as large as the chemisorbed phase. In this case the error in the rates and portion sizes caused by treating the exchange data as a radioactive decay is less than 10%.[14] The approximation does not involve the interpretation with regard to the number of rates needed to describe the results. A rigorous mathematical treatment of simultaneous exchange reactions has been published.[15]

There is a gap in the data for Fig. 5 between the sixth and twentieth hours. The point at 12 hours represents an interpolation from the points at 20 hours and beyond. This is done so the time scale may be spread out.

The expected standard deviation for the counting data is $\pm 1.6\%$. Figure 5 shows that the exchange data may be expressed by three rates. The first involves 22% of the chemisorbed gas and is immeasurably fast. The second rate which involves 55% of the chemisorbed gas is 1.0×10^{-2}. The remaining 23% of the chemisorbed gas exchanges at a rate of 2.3×10^{-4} or slower.

The experimental conditions for the runs illustrated in Figs. 4 and 5 differ in that the mercury vapor traps were removed and mercury was deliberately added to the catalyst chamber prior to the latter run. Other work has indicated that the differences in the two runs are not necessarily due to the presence of mercury.

More than twenty exchange runs have been conducted. In all of these runs the exchange data in-

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(13) Friedlander and Kennedy, "Introduction to Radiochemistry," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 288.

(14) Private communication, J. J. Mitchell, this Laboratory.

(15) C. W. S. Sheppard and A. S. Householder, *J. App. Phys.*, **22**, 510 (1951).

dicate an over-all heterogeneity. In some cases it is not possible to determine whether the data should be interpreted on the basis of a few rates or a spectrum of rates. This difficulty arises from the fact that it is sometimes possible to describe curves, such as those obtained in these runs, by a sum of a few exponentials even though a large number of rates are involved.

The conclusion that only a few rates are involved is based on the fact that there are examples where the medium rate is much faster than the slow rate. When $R_2 \gg R_3$ (the initial fast rate for which there are no data being R_1) curves are obtained which may be plotted to appear as a series of relatively straight portions with most of the curvature concentrated in sharp knees.[16] Although there may be differences within the R_2 portion these differences are small compared to the differences between the portions.

The data in Figs. 4 and 5 indicate that the surface of the catalyst may be described on the basis of a relatively few portions which differ from each other but are homogeneous within themselves. The term homogeneous should be interpreted to include the possibility of exchange occurring only at a few sites with rapid surface migration within each portion.

The cause of the over-all heterogeneity has not been determined. There is a temptation to identify each of the homogeneous portions as exposed crystal faces. However, difficulties inherent in powder samples such as adsorbed gases, traces of oxide and concentration of impurities on the surface make it impossible to come to a definite conclusion. Neither an increase in the severity of the reduction conditions nor the deliberate addition of oxygen has a marked effect on the general characteristics of the exchange.

Isotopic Effect.—The study of the chemisorption-exchange is simplified if there is no appreciable difference in the chemical properties of C^*O and CO. In order to determine whether the isotopic factor was appreciable, radioactive measurements were made on the excess C^*O over the catalyst during the chemisorption period. If either the $C^{14}O$ or CO were preferentially adsorbed from the C^*O, the calibration activity of the C^*O would change.

No differences greater than the limit of experimental accuracy of 1% could be detected after 20 hours contact with the iron. These results indicate that the isotopic factor can be neglected in the chemisorption-exchange experiments.

Acknowledgment.—The author is grateful to Supervisor L. C. Roess and the members of the Physical Research Department for their interest and suggestions and to A. K. Blom and E. J. Bane for their help with the experimental work.

BEACON, N. Y.

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[16] R. P. Eischens, *J. Chem. Phys.*, **19**, 377 (1951).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

The Fast Electron and X-Ray Decomposition of the Alkyl Halides[1,2]

BY ROBERT H. SCHULER[3] AND WILLIAM H. HAMILL

RECEIVED MAY 5, 1952

The liquid phase decomposition of a number of alkyl halides upon exposure to fast electrons and energetic X-radiation has been investigated in the region of 0.5 to 2.0 million volts. Alkyl iodides decompose in high yield to free iodine and exhibit considerable radiation-induced exchange with radioiodine present in the system during irradiation. Decomposition of the alkyl bromides yields mainly hydrogen bromide and small amounts of free bromine and is in general complicated by secondary effects. These reactions are sensitive to small amounts of additives present in the reaction. Processes which are peculiar to the radiation chemistry of the system are illustrated, particularly in the decomposition of methyl iodide.

There are evident similarities between radiation chemistry and photochemistry but there is little information permitting direct comparison of the relative effects of both types of irradiation for the same system.[4] The alkyl halides have been chosen for the present survey because of the possibility of conveniently and arbitrarily restricting observations to the displaced halogens[5] and because of the information available from photochemical studies of the alkyl halides, in particular a parallel investigation of the alkyl iodides.[6] Prior to initiation of this work there was little information available on the radiation chemistry of the alkyl halides[7a]; more recently observations on the radiation decomposition of the alkyl iodides have been reported by Williams[5] and others.[7b]

Experimental

The source of radiation used in these investigations was an electrostatic accelerator (Van de Graaff Generator) operated by the Department of Physics of the University of Notre Dame. This instrument supplies a high energy monochromatic beam of electrons in the 1–2 Mev. region. The energy of the beam, previously calibrated by the Physics group, is known to better than 1%. The current in the elec-

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[1] Presented at the 115th Meeting of the American Chemical Society in San Francisco, March, 1949. From the doctoral dissertation of Robert M. Schuler, University of Notre Dame, 1949.

[2] This work was supported in part under contract N6 ori 165, T.O. II with the Office of Naval Research.

[3] Peter C. Reilly Fellow.

[4] A very recent example of such a comparative study is provided by the work of R. R. Hentz and M. Burton, THIS JOURNAL, **73**, 532 (1951).

[5] This limitation is particularly well justified for the iodides because it can be expected that interaction with ionizing radiations will be largely confined to iodine, due to its large atomic number. Energy absorption therefore becomes rather specific in effect, for the C–I bond, as in the photochemical case. Confirmation of this view is supplied by the work of L. H. Gevantman and R. R. Williams, Jr., *J. Phys. Chem.*, **56**, 569 (1952).

[6] W. H. Hamill and R. H. Schuler, THIS JOURNAL, **73**, 3466 (1951).

[7] (a) A. Kailan, *Monatsh.*, **38**, 537 (1918); P. Gunther, *Z. angew. Chem.*, **41**, 1357 (1928); (b) P. Sue and E. Saeland, *Bull. soc. chim. France*, 437 (1949); M. Lefort, P. Bonet-Maury and M. Frilley, *Compt. rend.*, **226**, 1904 (1948).