tained by Stein and Vogel[2] from measurements of the refractive indices (Na D line) and densities of the liquids.

No single value of the atomic refraction of fluorine will, when combined with the standard refractions of other atoms, produce good agreement with the observed molar refractions of all fluorine-containing compounds. It is usually possible to select a satisfactory value of this quantity suitable for use in any given series of compounds, but in the case of the halogen fluorides the refractions of the other halogen atoms in their higher valence states are also unknown. If we use the value 1.35 cc./mole for the atomic refraction of fluorine and make no correction for change of valence state then the calculated molar refractions of the halogen fluorides are as shown in Table I. The fair agreement with experiment is probably fortuitous since the refraction of the central atom should decrease with the increase in oxidation number. It is possible that an increasing use of d-orbitals in π-bond formation in the tri- and pentafluorides produces a compensating increase in polarizability.

A value of 1.10 cc./mole for the atomic refraction of fluorine when combined with standard refractions of other atoms[7] leads to the calculated values of the molar refractions of the fluorocarbon derivatives shown in Table I. Since an atom refraction of fluorine of about 0.8 cc./mole is found for the monofluorides there is an increase in polarizability of fluorine in the polyfluorides; this may be associated with the increase in double-bond character of the carbon–fluorine bonds in the polyfluorides.[8]

Acknowledgments.—This work was supported by the Atomic Energy Commission through Contract AT-(11-1)-151. We are indebted to Dr. W. H. Pearlson and the Minnesota Mining and Mfg. Co. for the gift of purified samples of fluorocarbon derivatives.

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[7] A. I. Vogel, *J. Chem. Soc.*, 1833 (1948). Although our values are for $\lambda = 5461$ they have been compared with literature values for $\lambda = 5893$ with no correction for dispersion since the latter would be less than our experimental error.

[8] See, for example, L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940.

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The Oxygen-induced Hydrogen–Deuterium Exchange[1,2]

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Received March 7, 1955

Oxygen in concentrations as low as two parts per 1000 in a hydrogen–deuterium mixture increases the rate of exchange over that of oxygen-free mixtures by a factor of 100 or more. This induced exchange results from a chain mechanism in which initiation occurs at the wall and termination in the gas phase. It is postulated that, in the presence of oxygen, OH radicals are produced at the wall, leading to a higher steady-state H-atom concentration in the gas phase than for an oxygen-free system. The terminating step is $H + O_2 + M \rightarrow HO_2 + M$ and not the atom recombination reaction operative in the uninduced exchange.

Introduction

Farkas and Farkas[4] studied the hydrogen–deuterium exchange in fused silica vessels in the temperature region 575 to 750°. They showed that the exchange is predominantly homogeneous and proceeds *via* the atomic processes

$$H + D_2 \rightleftarrows HD + D$$

and

$$D + H_2 \rightleftarrows HD + H$$

Initiation and termination of these reaction chains were shown to occur *via* the continuously maintained equilibria

$$H_2 \rightleftarrows 2H;\ D_2 \rightleftarrows 2D;\ \text{and } HD \rightleftarrows H + D$$

Van Meersche[5] also studied this reaction and extended the lower portion of the temperature range to 450°. His results are in complete agreement with an Arrhenius extrapolation of the Farkas and Farkas data.

Mund, *et al.*,[6–8] investigated the α-particle-initiated hydrogen–deuterium exchange in the temperature range 12 to 60°. Even at these temperatures reaction proceeds by an atomic chain sequence. It was shown that chain termination by the processes

$$H + O_2 \longrightarrow HO_2 \text{ and } D + O_2 \longrightarrow DO_2$$

becomes important in the presence of small amounts of oxygen and the exchange is inhibited. The HO_2 and DO_2 may undergo further reactions but do not regenerate the chain carriers H and D.

We find that traces of oxygen accelerate the rate of the hydrogen–deuterium exchange in fused silica vessels in the neighborhood of 500°. As little as 2 or 3 parts per 1000 of oxygen in a hydrogen–deuterium mixture increase the initial rate of HD formation by a factor of 100 or more, depending on the pretreatment of the vessel walls. The experimental results can be explained on the basis of a chain mechanism with wall initiation and gas-phase termination.

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[1] This research was supported in part by Headquarters, Air Research and Development Command Office of Scientific Research, under Order No. CS-670-54-9, through Project SQUID.

[2] Presented at 127th meeting of the American Chemical Society, Division of Physical and Inorganic Chemistry, March 29 to April 7, 1955, in Cincinnati, Ohio.

[3] (a) Olin Mathieson Chemical Corp., New Haven, Conn. (b) General Electric Co., Cincinnati, Ohio.

[4] (a) A. Farkas and L. Farkas, *Nature*, **132**, 894 (1933); (b) *Proc. Roy. Soc.* (*London*), **A152**, 124 (1935).

[5] M. Van Meersche, *Bull. soc. chim. Belg.*, **60**, 99 (1951).

[6] W. Mund, L. Kaertkemeyer, M. Vanpee and A. Van Tiggelen, *ibid.*, **49**, 187 (1940).

[7] W. Mund, Th. De Menten De Horne and M. Van Meersche, *ibid.*, **56**, 386 (1947).

[8] W. Mund and M. Van Meersche, *ibid.*, **57**, 88 (1948).

Experimental

A 5-cm. diameter fused silica bulb, immersed in a manually controlled, electrically heated furnace, communicated with a high-vacuum manifold, a quartz spiral manometer, and a mixing vessel containing the hydrogen–deuterium mixture. Provision was made for analyzing the reaction mixture with a mass spectrometer[9] both before and after reaction. Oxygen-free hydrogen and deuterium were prepared by diffusion through palladium. Mixtures containing 2 to 3 parts per 1000 of oxygen were made from hydrogen and deuterium taken directly from commercial cylinders after passage through a liquid nitrogen trap.

The effect of surface on the reaction rate was determined from a series of experiments involving the following pretreatments of the reaction vessel (I) cleaned with nitric acid, washed with distilled water and evacuated to 10^{-6} mm. at 547°; (II) evacuated at 800°, for three hours and cooled to 547°; (III) evacuated at 800°, cooled to 25°, and exposed to the atmosphere for 16 hours; (IV) evacuated at 800°, cooled to 25°, and exposed to dry air for 16 hours; and (V) evacuated at 800°, cooled to 25°, and exposed to water vapor (P = 25 mm.) for 16 hours.

Results

The extent of the reaction was characterized by values of the ratio $(HD)_t/(HD)_\infty$, where $(HD)_t$ is the measured concentration of HD at time t and $(HD)_\infty$ is the calculated equilibrium concentration of HD for the reaction mixture.

Effect of Oxygen. (a) **Surface Active.**—Experiments 1 and 2 of Table I illustrate the effect of oxygen on the exchange in the fused silica vessel. The presence of 2 to 3 parts per 1000 of oxygen in the H_2–D_2 mixture resulted in almost 100 times more exchange than was observed[4b,5] in the uninduced reaction under the same conditions of pressure, temperature and time. Reduction of the oxygen concentration to less than the limit of detectability of the mass spectrometer lowered the amount of exchange to approximately nine times the uninduced value.

(b) **Surface Inactive.**—4 and 5, Table I, demonstrate that the Farkas and Farkas values could be reproduced in the absence of oxygen if the vessel wall was previously outgassed at 800°.

Effect of Surface.—Table II shows the effect of vessel pretreatment. Pretreatments II and IV resulted in less activity than III and V.

An eightfold increase in the surface-to-volume ratio resulted in an increase in the amount of HD formed from 26 to 95% of the equilibrium value in the time indicated. (Compare 1 and 5 of Table II.)

TABLE I

EFFECT OF OXYGEN ON THE HYDROGEN–DEUTERIUM EXCHANGE

$$T = 537 \pm 1°;\ \frac{(H_2)_0}{(D_2)_0} = 1$$

	Vessel pretreatment	Total pressure, mm.	Time, sec.	$(O_2)_0$, parts/1000	$\frac{(HD)_t}{(HD)_\infty}$	$\frac{(HD)_t}{(HD)_\infty}$[a] uninduced—no oxygen present
1	I	62.5	720	3	0.96	0.01
2	I	62.5	720	0[b]	.09	.01
3	IV	62.5	720	3	.34	.01
4	II	62.5	2160	0[b]	.06	.03
5	II	45.4	57600	0[b]	.34	.48

[a] From the data of references 4 and 5. [b] Oxygen was not detected by the mass spectrometer. The limit of detectability was estimated to be 1 part in 10,000.

TABLE II

EFFECT OF VESSEL PRETREATMENT, SURFACE TO VOLUME RATIO AND ADDED DILUENT

$T = 537 \pm 1°$; $(H_2O)_0/(D_2)_0 = 1$; $(O_2)_0$ = 2–3 parts/1000; t = 720 sec.

	Vessel pretreatment	S/V, cm.$^{-1}$	Total pressure, mm.	$\frac{(HD)_t}{(HD)_\infty}$
1	II	1.2	47.7	0.26
2	IV	1.2	62.5	.34
3	III	1.2	62.5	.96
4	V	1.2	55.5	.94
5	II	10.0	51.0	.95
6	V	1.2	62.5	.94

Discussion

The direct dependence of the rate of the oxygen-induced hydrogen–deuterium exchange on the surface-to-volume ratio of the reaction vessel clearly excludes a bimolecular gas phase reaction, and chain reactions with chain initiation and termination in the gas phase, chain initiation and termination at the wall, or chain initiation in the gas phase with termination at the wall. There are two processes, a hydrogen–deuterium exchange on the surface, and chain initiation at the wall with chain termination in the gas phase, that lead to the surface-to-volume ratio dependence indicated in Table II.

A surface exchange as the mechanism for the oxygen-induced hydrogen–deuterium exchange reaction is highly improbable in view of the following consideration. Water adsorbed on the surface increases the rate of oxygen free hydrogen–deuterium exchange somewhat, possibly by a surface exchange. However, oxygen has a very pronounced effect on the rate whether water is adsorbed on the surface or not (1 and 3, Table I). Since the adsorption of oxygen on silica is negligible under the conditions prevailing in the induced exchange experiments, oxygen at 0.2 mm. and 537°, a wall initiated chain reaction rather than a surface exchange must be the mechanism for the oxygen-induced hydrogen–deuterium exchange. A reasonable initiation step, and one that leads to a higher atom concentration than would arise from merely thermal dissociation of hydrogen, is that suggested for the slow rate region of the hydrogen-oxygen reaction,[10] namely

$$H_2 + O_2 \xrightarrow{\text{wall}} 2OH$$

The OH radicals produce H atoms in the gas phase by $H_2 + OH \rightarrow H_2O + H$.

The chain-terminating step could be (1) the atom recombination in the gas phase (recombination on the walls is ruled out by the surface-to-volume dependence of the rate), or (2) $H + O_2 + M \rightarrow HO_2 + M$ in which the HO_2 diffuses to the wall and is destroyed. It will be shown that the second alternative is correct. The reaction mechanism can be written as

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(9) Consolidated Model 21-610.

(10) G. von Elbe and B. Lewis, THIS JOURNAL, **59**, 656 (1937).

$$\begin{aligned} H_2 + O_2 &\xrightarrow{K_1 \text{ wall}} 2OH \\ OH + H_2 &\xrightarrow{k_2} H_2O + H \\ H + H_2 &\xrightarrow{k_3} H + H_2 \\ H + O_2 + M &\xrightarrow{k_4} HO_2 + M \end{aligned}$$

All permutations of the hydrogen isotope species are admissable in the scheme. Because zero-point energy differences result in different rates of reaction for different isotopes, the changing concentration of hydrogen species during the exchange reaction is accompanied by small changes in the concentration of the chain carriers. However, to a very good approximation

$$\frac{d(H)}{dt} = \frac{d(D)}{dt} = \frac{d(OH)}{dt} = \frac{d(OD)}{dt} = 0$$

In the kinetic treatment the specific reaction rate constants for similar isotopic reactions will be assumed equal. The exchange reaction involves long chains and hence the initiating and terminating steps affect the kinetics only in establishing a stationary atom concentration.[11]

$$\frac{d(HD)}{dt} = k_3\left[(H)(D_2) + (D)(H_2) - \frac{(H)(HD)}{2} - \frac{(D)(HD)}{2}\right]$$

If A and B are the initial concentrations of H_2 and D_2, then

$$(H) = \frac{A}{A+B}[(H) + (D)] \text{ and}$$

$$(D) = \frac{B}{A+B}[(H) + (D)]$$

$$\frac{d(HD)}{dt} = k_3[(H) + (D)]\left\{\frac{2AB}{A+B} - HD\right\}$$

The rate is thus proportional to the total atom concentration. Since initiation and termination rates are equal, steady-state conditions prevailing

$$\overline{[(H) + (D)]} = \frac{I}{k_4(O_2)(M)}$$

where I is the rate of initiation per unit volume, M is a third body (H_2, D_2, HD, O_2, or H_2O, for example), and $\overline{[(H) + (D)]}$ is the average chain carrier concentration in the vessel. $\overline{[(H) + (D)]}$ may be substituted for $[(H) + (D)]$. It is easy to show that $\overline{[(H) + (D)]}$ and $[(H) + (D)]$ differ only slightly under the experimental conditions employed. In a spherical vessel, the steady state requires that

$$\frac{D}{r}\frac{\partial^2(Cr)}{\partial r^2} - \beta C = \frac{\partial C}{\partial t} = 0 \qquad (1)$$

where $C = [(H) + (D)]$, $\beta = k_4(M)(O_2)$, the diffusion coefficient D is independent of concentration, and r is the distance from the center of the vessel. The boundary conditions are (1) C is finite at the origin, and (2) $I = \int_0^R 4\pi r^2 \beta C \, dr$, where R is the vessel radius. This gives

$$C = \frac{I}{4\pi} \frac{(\sinh \sqrt{\beta/D}\, r)/r}{R\sqrt{D\beta} \cosh \sqrt{\frac{\beta}{D}}\, R - D \sinh \sqrt{\frac{\beta}{D}}\, R}$$

In a 2.5 cm. radius vessel with $(O_2) = 4.0 \times 10^{-9}$ moles/cc. and $(M) = 1.2 \times 10^{-6}$ moles/cc., $C_{r=R}/C_{r=0} = 1.06$. Substitution of $\overline{[(H) + (D)]}$ for $[(H) + (D)]$ is justified therefore, and

$$\begin{aligned}(HD) &= \frac{2AB}{A+B}\left(1 - e^{-\frac{k_3 I t}{k_4(O_2)(M)}}\right) \\ &= (HD)_\infty (1 - e^{-kt}) \qquad (2)\end{aligned}$$

k is established by an experimental value of HD at time t. Initial rate is given by $(d(HD)/dt)_{t=0} = k(HD)_\infty$. The atom concentration in the presence of oxygen can be calculated by

$$[(H) + (D)]_{\text{induced}} = \frac{\left(\frac{d\,(HD)}{dt}\right)_{t=0\,(\text{induced})}}{\left(\frac{d\,(HD)}{dt}\right)_{t=0\,(\text{uninduced})}} [(H) + (D)]_{\text{uninduced}} \qquad (3)$$

$[(H) + (D)]_{\text{uninduced}}$ can be calculated from thermodynamic data. This gives, for 1, Table I, $[(H) + (D)] = 7.13 \times 10^{-16}$ moles/cc., without particularizing the terminating reaction. The ratio of rates of the two postulated terminating steps, $H + O_2 + M \xrightarrow{k_4} HO_2 + M$ and $H + H + M \xrightarrow{k_4'} H_2 + M$, is in these experiments $k_4(O_2)/k'[(H) + (D)] = 7500$ since k_4' has the well established value of 10^{16} cc.^{2}/mole^2 sec. and $k_4 = 1.34 \times 10^{13}$ cc.^{2}/mole^2 sec.[12] The atom recombination is negligible, therefore, compared to the atom–molecule reaction.

An independent check of the value for the reaction rate constant k_4 can be obtained from the data of Mund and Van Meersche.[8] These experiments were done on the α-particle-initiated hydrogen–deuterium exchange in the presence of 1 part per 1000 of oxygen. For their system

$$k_4 = \frac{I}{[(H) + (D)]\,(O_2)(M)}$$

with

$$I = 6.15 \times 10^{-13} \text{ mole/cc. sec.}$$
$$(M) = 3.72 \times 10^{-5} \text{ mole/cc.}$$
$$(O_2) = 2.3 \times 10^{-8} \text{ mole/cc.}$$

and

$$[(H) + (D)] = 2.16 \times 10^{-14} \text{ mole/cc.}^{13}$$
$$k_4 = 3.4 \times 10^{13} \text{ cc.}^2/\text{mole}^2 \text{ sec. at } 12°$$

This agrees remarkably well with Lewis and von Elbe's value of $k_4 = 0.6 \times 10^{13}$ cc.^{2}/mole^2 sec., and the previous conclusion that $H + O_2 + M \xrightarrow{k_4} HO_2 + M$ terminates the chain in the oxygen-induced exchange is further strengthened.

PITTSBURGH, PA.

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[11] A lower bound for the chain length is $[d(HD)/dt]_0/I$. From 1, Table I, I is calculated as 4.7×10^{-17} moles/cc. sec. and $[d(HD)/dt]_0 = 2.7 \times 10^{-9}$ moles/cc. sec. giving a chain length of at least 6×10^7.

[12] B. Lewis and G. von Elbe, "Combustion, Flames and Explosions of Gases," Academic Press, Inc., New York, N. Y., 1951, p. 59.

[13] This was calculated, as previously, from the relationship (3). $(d(HD)/dt)_{t=0\,(\text{uninduced})}$ was calculated from the data of Farkas and Farkas, and Van Meersche extrapolated to 12°. $[(H) + (D)]_{\text{uninduced}}$ was calculated from thermodynamic data at 12°.