

[CONTRIBUTION FROM THE RICHARD BENBRIDGE WETHERILL LABORATORY OF CHEMISTRY, PURDUE UNIVERSITY]

The Heterogeneous Exchange Reaction between Hydrogen Chloride and Chlorine on Glass and Fluorocarbon^{1a,b}

BY J. R. WALTON² AND W. H. JOHNSTON

RECEIVED AUGUST 23, 1956

The heterogeneous exchange reaction between hydrogen chloride and chlorine was studied on Pyrex and Vycor glasses and on fluorocarbon using chlorine-36. Evidence was obtained that this reaction proceeds through catalysis by adsorbed water which was removed both by evacuations at elevated temperatures and by treatment with diborane at room temperature. By varying the amount of adsorbed water, half-times of exchange were obtained from one minute to six days. The rate law of the reaction producing exchange was determined on Vycor and found to be consistent with equilibria adsorptions and a rate-controlling surface reaction. The rate in moles liter⁻¹ sec.⁻¹ was $5.0 \times 10^{-6}(\text{HCl})^{0.37}(\text{Cl}_2)^{0.37}$ for concentrations in moles liter⁻¹.

Introduction

In 1951 Johnston and Libby reported a rapid heterogeneous exchange reaction between hydrogen chloride and chlorine in the gaseous state.³ The present paper describes further experiments on several glasses and fluorocarbon and reports the discovery that adsorbed water is responsible for the catalytic activity of these surfaces. Originally, the adsorbed water was removed by evacuation at elevated temperatures. In order to avoid possible structural changes accompanying these evacuations, additional experiments were done in which the water was removed by chemical treatment with diborane at room temperature. A rate law is reported and related to a proposed mechanism for exchange. No evidence was found for an homogeneous dark reaction.

Experimental

The radioactive chlorine-36 was obtained from the Isotopes Division, Oak Ridge National Laboratory, U.S.A.E.C. as high specific activity dilute hydrochloric acid. A small amount of this solution was mixed with excess concentrated ammonium hydroxide and evacuated to dryness in a glass bulb. Following extensive evacuation, a large excess of anhydrous hydrogen chloride was added to the vessel. The radioactive ammonium chloride was sublimed carefully to the upper half of the bulb. By this procedure the chlorine-36 was efficiently introduced into the anhydrous hydrogen chloride.

The procedure for measuring exchange was essentially the same as that described previously.³ In each experiment the gases were mixed in the dark and separated by passage through two traps in series under vacuum. The first trap for chlorine was maintained at -125 to -130° by an ethanol bath; the trap for hydrogen chloride was immersed in liquid nitrogen. In each experiment the initial and final specific activities were determined by measuring the activities in an annular Geiger counter as a function of pressure. The over-all recoveries of pressure and activity were determined in each experiment and found to be 90 to 100%.

Preparation of Surfaces.—In the thermal preparation of the Pyrex surface, a 500-ml. virgin Pyrex flask was successively evacuated by heating for two days at 150 – 170° and by a series of heatings for $1/2$ -hour each at 250 – 400° with a glass-working torch. Each evacuation was at a pressure of less than 10^{-3} mm. The Vycor surface was a 800-ml. Kjeldahl flask which was initially cleaned with chromic acid cleaning solution and carefully steamed. It was successively evacuated at less than 10^{-3} mm. by a series of heatings for $1/2$ hour each at 250 – 400° and by heating under vacuum at 700° for one week.

The fluorocarbon surface was a mixture of saturated long-

chain fluorocarbons, du Pont perfluorolube oil FCX-335. The reaction vessel was a 500-cc. Pyrex flask which was coated with the fluorocarbon by melting it at 60 – 90° . This vessel was evacuated at less than 10^{-3} mm. for one week at room temperature.

In several experiments adsorbed water was added to the Pyrex and fluorocarbon surfaces by introducing 2 mm. of water vapor and evacuating at 10^{-3} mm. for 3 hours.

In an effort to chemically remove adsorbed water, a 270-cc. Pyrex flask was given a series of pre-treatments with diborane at room temperature. The diborane was prepared by the reaction between boron trifluoride etherate and lithium aluminum hydride and purified by distillation.⁴

Results and Discussion

Catalysis by Adsorbed Water.—The half-times for isotopic exchange between hydrogen chloride and chlorine on fluorocarbon, Pyrex and Vycor following various thermal pre-treatments under vacuum are shown in Table I. It is interesting to note the wide range of speeds of this heterogeneous reaction; the half-time of exchange ranged from a few minutes to almost a week.

TABLE I
HETEROGENEOUS EXCHANGE BETWEEN HYDROGEN CHLORIDE AND CHLORINE ON FLUOROCARBON, PYREX AND VYCOR AT 20°

Surface	Treatment ^a	Half-time ^b
Fluorocarbon	1. 25° for 1 week	38.0
	2. 25° for 10 min.	39.0
	3. Plus 2 mm. of H ₂ O	0.8
	4. 25° for 3 hours ^c	16.0
Pyrex	1. 170 – 200° for 2 days	1.2
	2. 250 – 400° for $1/2$ hr.	3.3
	3. 250 – 400° for $1/2$ hr.	5.6
	4. 250 – 400° for $1/2$ hr.	7.3
	5. Plus add. H ₂ O ^d	0.2
Vycor	1. 250 – 400° for $1/2$ hr.	1.5
	2. 250 – 400° for $1/2$ hr.	3.7
	3. 250 – 400° for $1/2$ hr.	5.1
	4. No additional treat.	5.1
	5. 700° for 1 week	134.0
	6. No additional treat.	134.0

^a Sequence of evacuations (at 10^{-3} mm.) or additions. ^b Isotopic exchange half-time in hours. ^c Adsorbed water remaining from run 3. ^d Added as in run 4-fluorocarbon.

With each successive evacuation at an elevated temperature, the rate of exchange was slower. This observation suggested an adsorbed catalyst which was progressively removed by the evacuations. Prior to runs fluorocarbon-4 and Pyrex-5

(1) (a) This work was supported in part by the A.E.C. under Contract At(11-1)-166 with Purdue University; (b) parts of this paper were presented at the XIIth International Congress of Pure and Applied Chemistry on September 10, 1951, in New York.

(2) A. E. C. Research Assistant.

(3) W. H. Johnston and W. F. Libby, *THIS JOURNAL*, **73**, 854 (1951).

(4) A. E. Finholt, A. C. Bond, Jr., and H. I. Schlesinger, *ibid.*, **69**, 1199 (1947).

water was adsorbed on the reaction surfaces. As shown in Table I, the rate of exchange was greatly increased on both surfaces. During run fluorocarbon-3 a small amount of water was present in the gas mixture. In this case the reaction rate was 48 times faster than runs 1 and 2.

The inference that adsorbed water is the catalyst on these surfaces raises the question of possible surface structural changes at the elevated temperatures of evacuation. Therefore, an attempt was made to remove adsorbed water by chemical treatment at room temperature. The chemical reaction was that between diborane and water to form hydrogen and boric oxide. A Pyrex flask was chosen as the reaction vessel since boric oxide is a normal constituent of this glass.

The removal of adsorbed water was accomplished in a series of successive contacts for 10–12 hours with initially 3 mm. B₂H₆ and evacuations for 1–2 days at 10⁻³ mm. at room temperature. Prior to the first contact with B₂H₆ the average half-time of exchange was 1.1 min. following room temperature evacuation at less than 10⁻⁴ mm. for three weeks. After the first contact with B₂H₆ the half-times of four successive runs were 37, 40, 39 and 37 min. After a second contact the half-time was 67 min. and after a third contact with B₂H₆ two successive half-times were 231 and 215 min.

Although the evidence of the thermal evacuations, the additions of H₂O, and the treatments with B₂H₆ is qualitative, the conclusion is clear that the exchange reaction between HCl and Cl₂ on Pyrex, Vycor and fluorocarbon is catalyzed by adsorbed water.

Rate Law and Mechanism.—A number of authors have discussed the relationship between the observed rate of isotopic exchange and the kinetics of the reaction producing exchange.⁵ In the absence of an isotope effect and in the case of a reaction which is not complex, the equation relating these rates may be expressed in the logarithmic form

$$\log [t(\text{HCl} + 2\text{Cl}_2)] = (1 - m)\log x + C \quad (1)$$

where t is the half-time of exchange, (HCl) and (Cl₂) are the concentrations of reactants, C is a constant, x is the concentration of either reactant with the other one held constant, and m is the order of reaction of the varying species.

Table II shows the effect of varying the concentrations of chlorine and hydrogen chloride by a factor of four in the Vycor vessel which was evacuated at 700° (see Table I). These experiments were done at 35.0° because of the experimental difficulties due to the slowness of the reaction on this surface.

(5) (a) H. A. C. McKay, *Nature*, **142**, 997 (1948); (b) R. B. Duffield and M. Calvin, *THIS JOURNAL*, **68**, 557 (1946); (c) T. H. Norris, *J. Phys. Colloid Chem.*, **54**, 777 (1950); (d) G. M. Harris, *Trans. Faraday Soc.*, **47**, 716 (1951).

TABLE II
CONCENTRATION STUDIES ON VYCOR^a

HCl ^b	Cl ₂	Half-time, hr.	$t(\text{HCl} + 2\text{Cl}_2)$ ^c
0.62	0.49	109	174
.62	0.99	106	276
.61	1.93	91	407
.62	1.95	93	418
.31	0.98	85	193
.62	.99	106	275
1.22	.97	144	455
0.31	.48	99	126

^a Evacuated at 10⁻³ mm. for 1 week at 700°; runs were made at 35.0°. ^b All concentrations in millimoles liter⁻¹. ^c See eq. 1; units of hr. millimoles liter⁻¹.

If the data of the last column of Table II are graphically inserted in eq. 1 as a function of the appropriate varying concentration, it is found that this equation is obeyed for m values of 0.37 for both Cl₂ and HCl. This corresponds to an actual rate of exchange of $k(\text{HCl})^{0.37}(\text{Cl}_2)^{0.37}$ over the region studied. Using this relationship the last line of Table II fits both the functions for varying Cl₂ and varying HCl.

Using these coefficients the specific rate constant of isotopic exchange, k , may be found by expressing eq. 1 in the form

$$\log k = 0.63 \log (\text{HCl}) + 0.63 \log (\text{Cl}_2) - \log [t(\text{HCl} + 2\text{Cl}_2)] + \log 0.693 \quad (2)$$

If the data of Table II are inserted in eq. 2, the average specific rate constant is 0.00180 ± 0.00011 in millimoles^{0.26} liters^{-0.26} hours⁻¹, where the variation is the experimental standard deviation. The rate of exchange in moles liter⁻¹ sec.⁻¹ is $5.0 \times 10^{-6} (\text{HCl})^{0.37}(\text{Cl}_2)^{0.37}$ for concentrations in the corresponding units.

This expression for the rate of exchange of hydrogen chloride and chlorine on Vycor may be explained as equilibrium adsorptions and a second order surface reaction. The adsorption isotherms approximate the Freundlich type with exponents of 0.37 for both gases over the range studied. These exponents are reasonable at room temperature.⁶

The role of the adsorbed water probably involves hydrogen bonding of the hydrogen chloride and chlorine on the surface and may participate in the formation of the activated complex. In view of the well-known affinity of glass surfaces for water, the severity of the treatments to remove water and the wide range of the rates of exchange are not surprising. The latter suggests an interesting test for adsorbed water on glass.

LAFAYETTE, INDIANA

(6) J. W. McBain, "The Sorption of Gases and Vapors by Solids," Routledge and Sons, Ltd., London, 1932, p. 5.