dictions are indeed verified by the data. Relative rates are C_2H_5I:*n*-C_3H_7I:*sec*-C_4H_9I:*i*-C_3H_7I::1:5:21:22.

Reaction 8 as written is similar to the bimolecular elimination reaction (E_2) known to occur in solution. As an ionic process it occurs as a concerted single step reaction.[19] With secondary butyl iodide one would predict *trans*-butene-2 to be formed from an E_2 reaction. In the present work *trans*-butene-2 constituted at least 85% of the butene formed from secondary butyl iodide. Probably reaction 8 also occurs as a concerted single step reaction.

The mechanism proposed to explain the present data is based mainly on (1), (2), (7) and (8). Reaction 3 and possibly reaction 4 may occur to some extent on the walls. Reaction 9 may occur if hydrogen iodide is allowed to accumulate. Evidence in favor of (1), (2), (7) and (8) being the important steps is very strong but not in all cases absolutely conclusive.

ROCHESTER, NEW YORK

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[19] E. D. Hughes and C. K. Ingold, *Trans. Faraday Soc.*, **37**, 657 (1941).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NEW MEXICO]

The Kinetics of the Exchange of Chlorine between Hydrogen Chloride and Acetyl Chloride in the Vapor Phase[1]

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A measurable exchange has been observed between hydrogen chloride and acetyl chloride in the vapor phase. The exchange reaction was investigated over a temperature range from 0 to 29.6°; the concentration of acetyl chloride ranged from 0.0026 to 0.0106 *M* and of hydrogen chloride from 0.0031 to 0.0080 *M*. Over the range of conditions studied the rate of exchange can be represented by $R = 0.17e^{-1550/RT}$ (HCl) (CH_3COCl) where the units of *R* are liter × $mole^{-1}$ × $sec.^{-1}$. A more complicated rate expression cannot be excluded but is not called for by the data.

Introduction

This paper is concerned with the kinetics of the exchange of chlorine atoms between hydrogen chloride and acetyl chloride in the vapor phase. The reaction was found to be first order with respect to each reactant and homogeneous.

Experimental

Radioactivity.—The 3.08×10^5-year chlorine-36, which was used as tracer in all experiments, was obtained from Oak Ridge in the form of a dilute solution of hydrochloric acid (5.5 ml. of 0.37 *M* hydrochloric acid contained 20 μc. of chlorine-36).

Chemicals.—Merck reagent grade acetyl chloride was further purified according to the method of Fieser.[2] All other chemicals were of analytical grade and were used without further purification. Standard active solutions of potassium chloride were prepared by inoculating weighed amounts of potassium chloride with the active hydrochloric acid solution and diluting to volume.

Procedure.—Reaction mixtures of hydrogen chloride and acetyl chloride were prepared employing ordinary vacuum-line techniques. Purified acetyl chloride was fractionally distilled under vacuum and allowed to vaporize at a pressure determined by an appropriate constant-temperature bath; the vapor was frozen in a trap prior to the introduction of hydrogen chloride.

Radioactive hydrogen chloride, generated by adding sulfuric acid to dry, radioactive potassium chloride, was passed over phosphorus pentoxide before being admitted to the reaction vessels and subsequently frozen in the trap with the acetyl chloride. The frozen mixture was allowed to vaporize and diffuse into the reaction vessels over a period of 30 minutes, at room temperature, in the presence of red light. The reaction vessels which were inverted U-tubes were isolated from each other with stopcocks and sealed off from the vacuum line after freezing the reactants with liquid nitrogen. Only about 30 seconds were required to freeze the contents of eight tubes. The sealed tubes were immersed in a constant-temperature water-bath and allowed to come to thermal equilibrium over a period of 30 minutes. Zero time was reckoned from the time the first sample was taken from the bath. In most instances the reaction was allowed to proceed to within 65–84% of completion.

The concentrations of the reactants in each experiment were determined by dissolving the contents of each of two reaction vessels of known volume in water and analyzing the resulting solution for total hydrogen ion and chloride ion.

Separation Procedure.—Acetyl chloride was condensed in one arm of the U-tube with a Dry Ice-acetone bath; the hydrogen chloride was frozen in the other arm with a liquid nitrogen bath. The arm containing the acetyl chloride was then cracked and immersed immediately in water. The purity of the separated acetyl chloride proved to be greater than 99%; the separated hydrogen chloride fraction was contaminated with acetyl chloride. The fraction exchange in each instance was calculated from the activity in the separated acetyl chloride. For most of the runs the half-time for exchange was determined on the basis of five samples.

Measurement of Radioactivity.—The chlorine-36 activity was detected according to the procedure of Kahn, Freedman, Feltham and Lark[3] which is based on the precipitation of mercurous chloride. The samples were placed directly below the 4.8-mg./cm.^{2} dural window of a methane-flow proportional counter operated at atmospheric pressure and 4,200 volts. A model PA-1 pulse amplifier fed into a model SC-2 scaler supplied by the Los Alamos Scientific Laboratory.

Results and Discussion

The reaction studied is

$$CH_3COCl(g) + HCl^*(g) = CH_3COCl^*(g) + HCl(g)$$

where the asterisks indicate radioactive atoms. The constant rate of exchange *R* of chlorine atoms between acetyl chloride and hydrogen chloride in any one experiment was evaluated with the aid of the logarithmic form of the isotopic exponential ex-

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[1] This communication is based on work done under the auspices of the Los Alamos Scientific Laboratory and the Atomic Energy Commission and submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the University of New Mexico, June, 1957, by Warren J. Neill.

[2] L. F. Fieser, "Experiments in Organic Chemistry," 2nd Ed., D. C. Heath and Co., New York, N. Y., 1941, p. 380.

[3] M. Kahn, A. J. Freedman, R. D. Feltham and N. L. Lark, *Nucleonics*, **13**, 58 (1955).

change law.[4] The pertinent data and experimental results are summarized in Table I.

TABLE I

RESULTS OF EXCHANGE EXPERIMENTS

Temp., °C.	(HCl), M	(CH_3COCl), M	$t_{1/2}$, sec.	k, l. mole^{-1} sec.$^{-1}$
29.6	0.0080	0.0037	4860	0.0122
29.6	.0048	.0106	3300	.0137
29.6	.0041	.0093	4080	.0127
29.6	.0042	.0049	6120	.0125
29.6	.0039	.0050	5880	.0133
13.8	.0056	.0043	6360	.0110
13.8	.0043	.0050	7200	.0103
13.8	.0032	.0038	9000	.0110
0	.0033	.0054	8040	.0098
0	.0042	.0029	9900	.0098
0	.0051	.0054	7080	.0093
0	.0031	.0026	12060	.0100
0	.0038	.0055	8100	.0092

Dependence on Acetyl Chloride and Hydrogen Chloride.—The dependence of *R*, the rate of exchange, on the concentration of acetyl chloride and hydrogen chloride was found to be

$$R = k(CH_3COCl)(HCl)$$

where *k* is the specific rate constant.

Effect of Light on the Rate of Exchange.—The results of an experiment carried out at 29.6° in room light (daylight + fluorescent lighting) indicated that light has no effect on the rate of the exchange reaction. Nevertheless, all reactions were carried out in the presence of red light.

Effect of Glass Surface on the Rate of Exchange.—No variation in the rate of exchange was observed at 0° when the surface was increased approximately ten-fold using Pyrex glass wool.

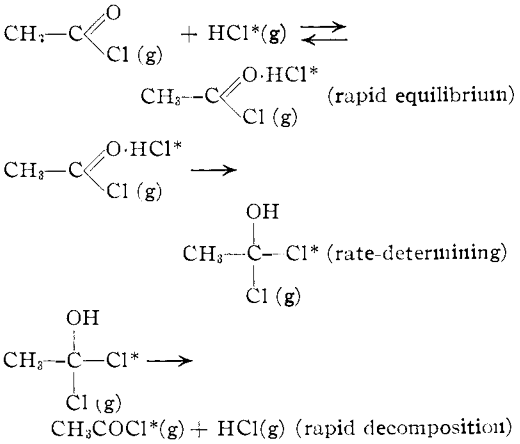
Activation Energy.—The slope of the linear semi-logarithmic plot of the average values for the specific reaction rate *k* against the reciprocal of the absolute temperature was evaluated by the method of least squares. The values of $\ln \bar{k}$ were weighted according to the procedure of Worthing and Geffner.[5] The experimental activation energy and its probable error as calculated from the slope is 1550 ± 110 cal.

The Rate Law.—The exchange reaction was found to be first order with respect to each reactant and homogeneous over the temperature range 0 to 29.6°. The concentration of the acetyl chloride varied from 0.0026 to 0.0106 *M* while the concentration of the hydrogen chloride varied from 0.0031 to 0.0080 *M*. Over the range of conditions studied the rate law for the exchange reaction is

$$R = 0.17e^{-1550/RT}(HCl)(CH_3COCl)$$

where *R* is expressed in liter mole^{-1} sec.$^{-1}$. A more complicated rate expression cannot be excluded but is not called for by the data.

The Mechanism.—A mechanism which is consistent with the observed rate law is represented by equations 1, 2 and 3.



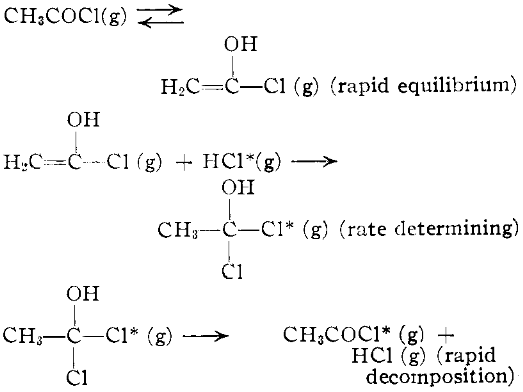
$$CH_3-C(=O)Cl(g) + HCl^*(g) \rightleftarrows CH_3-C(O\cdot HCl^*)Cl(g) \quad \text{(rapid equilibrium)} \quad (1)$$

$$CH_3-C(O\cdot HCl^*)Cl(g) \longrightarrow CH_3-C(OH)(Cl^*)Cl(g) \quad \text{(rate-determining)} \quad (2)$$

$$CH_3-C(OH)(Cl^*)Cl(g) \longrightarrow CH_3COCl^*(g) + HCl(g) \quad \text{(rapid decomposition)} \quad (3)$$

where reaction 1 represents hydrogen bond formation.

Another possible mechanism, which is similar to that proposed by Hertel, Becker and Clever,[6] for the chlorination of acetyl chloride in the liquid phase, is shown below.



$$CH_3COCl(g) \rightleftarrows H_2C=C(OH)-Cl(g) \quad \text{(rapid equilibrium)} \quad (4)$$

$$H_2C=C(OH)-Cl(g) + HCl^*(g) \longrightarrow CH_3-C(OH)(Cl^*)Cl(g) \quad \text{(rate determining)} \quad (5)$$

$$CH_3-C(OH)(Cl^*)Cl(g) \longrightarrow CH_3COCl^*(g) + HCl(g) \quad \text{(rapid decomposition)} \quad (6)$$

where equation 4 represents enolization of acetyl chloride in the vapor phase. However, this mechanism is not plausible because the energy of activation for the rate-determining step, based on the assumptions discussed below, turns out to be negative.

Conant and Carlson[7] have estimated the free energy of enolization in the vapor phase for a compound of the type $R_2CHCOOC_2H_5$ to be between 14 and 16 kcal. and for compounds of the type $R_2CHCOCH_3$ to be between 10 and 12 kcal. Considering the effect of resonance on the inhibition of enolization of such compounds,[8] one estimates a free energy of enolization for acetyl chloride in the vapor phase to be 14 kcal. Because the entropy change accompanying an isomeric change is generally small,[7] the heat of enolization for acetyl chloride should be approximately 14 kcal. The difference between the observed energy of activation, 1.55 kcal., and 14 kcal., which should approximate the energy of activation for the rate-determining step (equation 5), is −12.5 kcal.

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[4] G. Friedlander and J. W. Kennedy, "Nuclear and Radiochemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, p. 315.

[5] A. G. Worthing and J. Geffner, "Treatment of Experimental Data," John Wiley and Sons, Inc., New York, N. Y., 1950, pp. 243, 247–249.

[6] E. Hertel, G. Becker and A. Clever, *Z. physik. Chem.*, **B27**, 303 (1934).

[7] J. B. Conant and G. H. Carlson, THIS JOURNAL, **54**, 4048 (1932).

[8] A. E. Remick, "Electronic Interpretations of Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 59.