Br^{80} organic yield after 3 hr. irradiation should be indistinguishable from that for the (n, γ) process, in accord with previous observations.[12]

Expected Effects of γ-Dose in Other Systems.—In systems where radiolysis does not produce a substance which can react with the radioactive inorganic compounds produced by the (n, γ) process no increase in organic yield would be expected as a result of increased γ-dosage. The (n, γ) reaction on organic chlorides seems to produce 10% of the radiochlorine as Cl_2 and 70% as HCl.[13] The latter reacts very slowly with olefins, hence the radiolytic production of olefins might increase the usual organic yield of 20% to a maximum of 30%. Organic iodides liberate free iodine when exposed to high γ-dosage. This would serve to reduce organic yields of the (n, γ) reaction because of the scavenger effect.[2] It is to be expected that some compounds, including some bromides other than n-C_3H_7Br may show higher sensitivity of their organic yields to γ irradiation than does the latter.

Acknowledgment.—This work was supported in part by the Atomic Energy Commission and in part by the University Research Committee with funds supplied by the Wisconsin Alumni Research Foundation.

MADISON, WISCONSIN

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[13] J. C. W. Chien and J. E. Willard, THIS JOURNAL, **75**, 6160 (1953).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MICHIGAN]

The Exchange of Isotopic Chlorine between HCl and the Series CH_3Cl, CH_2FCl, CHF_2Cl and CF_3Cl[1,2]

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CH_3Cl exchanges chlorine with HCl in the gas state in Pyrex vessels at a rate $R = 1.4 \times 10^9 e^{-43,600/RT}$ [CH_3Cl] moles liter^{-1} sec.$^{-1}$ at a surface–volume ratio of 7.4 cm.$^{-1}$. For the exchange between CH_2FCl and HCl the rate is $R = 1.4 \times 10^9 e^{-47,100/RT}$ [CH_2FCl] moles liter^{-1} sec.$^{-1}$ at surface/volume = 7.4 cm.$^{-1}$. These two reaction rates are directly proportional to the surface–volume ratio and depend strongly on the condition of the surface. CHF_2Cl exchanges chlorine with HCl at a rate $R = 9 \times 10^4 e^{-30,200/RT}$ [CHF_2Cl]$^{1/2}$[HCl]$^{1/2}$ moles liter^{-1} sec.$^{-1}$ in a reaction which is independent of the surface area or condition. The CF_3Cl–HCl exchange rate is much slower.

The progressive substitution of fluorine atoms in an organic molecule has been shown to effect a marked change in the structural parameters of that molecule.[3,4] There is also a good deal of qualitative information regarding the effect of such substitution on chemical activity, but little quantitative work of this nature is available. It was decided, therefore, to make a comprehensive study of a chemical reaction involving a series of compounds containing progressively larger numbers of fluorine atoms. It was hoped that the rates and mechanisms of such a reaction might enable the effect of the fluorines on the reactivity of the molecules to be understood.

An isotopic exchange reaction seemed to offer many advantages since the products would not be chemically different from the reactants and interpretation of the results might be simpler. The reaction chosen was the exchange of chlorine between HCl and the individual members of the series CH_3Cl, CH_2FCl, CHF_2Cl and CF_3Cl in the gas phase.

While this work was in progress, Peri and Daniels[5] reported the results of an investigation of the exchange of radioactive bromine between C_2H_5Br and Br_2, HBr and DBr. They observed the same rate law as is reported here for chlorine exchange in the CH_3Cl–HCl and CH_2FCl–HCl systems.

Experimental Procedures

Materials.—All of the organic chlorides were dried by passing them several times through a tube filled with P_2O_5, non-condensable impurities were removed by repeatedly freezing *in vacuo*, and the compounds were then fractionally distilled. Absence of foreign lines in the mass spectra of the purified materials was used as the criterion of purity.

The HCl used was generated by dropping C.p. hydrochloric acid solution into C.p. sulfuric acid. After concentration of the heavier isotope by thermal diffusion, the gas was passed through P_2O_5, repeatedly frozen *in vacuo*, and fractionally distilled.

Isotopic Separation.—A thermal diffusion column was constructed to separate the chlorine isotopes. This has been described in detail elsewhere.[1] The HCl used in this work varied from 40.9 to 68.2% Cl^{37}, compared with the normal concentration of 24.6% Cl^{37}.

Isotopic Analysis.—Isotopic analyses were performed on a model 21-201 Consolidated-Nier mass spectrometer. Chlorine isotopic ratios could be determined directly in the organic chlorides without separating them from their mixtures with HCl. The Cl^{37}/Cl^{35} ratio was read from the peaks corresponding to the undissociated molecules in the cases of CH_3Cl and CH_2FCl. For CHF_2Cl and CF_3Cl it was more practical to use the CHFCl and CF_2Cl peaks, respectively.

The chlorine isotopic ratio could not be read directly in the HCl molecule because of an intense memory effect for this compound that was observed in the mass spectrometer. When successive samples with different Cl^{37}/Cl^{35} ratios were analyzed, the ratio obtained for the second sample would initially be close to that of the first sample, drifting slowly over a period of many hours toward the correct value for the new sample. HCl was apparently absorbed on the walls of the instrument in such a way that it could not be pumped off in any reasonable time, but could be rapidly displaced by or undergo chlorine exchange with additional HCl in the gas phase. An effort to analyze the HCl after

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(1) Abstracted from the dissertation of J. E. B. submitted in partial fulfillment of the requirements for the Ph.D. degree in Chemistry, Summer, 1952. More complete details of this investigation may be obtained from the dissertation filed in the library of the University of Michigan.

(2) Presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society, Los Angeles, California, March 15–19, 1953.

(3) L. O. Brockway, *J. Phys. Chem.*, **41**, 185 (1937).

(4) L. O. Brockway and C. G. Thornton, paper presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society, Los Angeles, California, March 15–19, 1953.

(5) J. B. Peri and F. Daniels, THIS JOURNAL, **72**, 424 (1950).

conversion to *t*-butyl chloride by reaction with *t*-butyl alcohol was only partially successful since this compound also exhibited a mass spectrometer memory effect, although not nearly as strong as with HCl.

After the study of the exchange reaction between CH_3Cl and HCl had progressed a little way, it was found that under the proper conditions the wall-catalyzed exchange came to equilibrium quickly and reproducibly in packed tubes. This provided the basis for a satisfactory method for determining the chlorine isotopic ratio in HCl. The sample of HCl was allowed to come to isotopic exchange equilibrium with an equal volume of CH_3Cl containing the normal chlorine isotope ratio by heating for 1 hour at 400° in a packed tube. The isotopic ratio was then measured in the CH_3Cl and that originally present in the HCl was calculated, assuming an equilibrium constant of unity for the exchange reaction. This assumption is certainly nearly correct, but it could not be checked because no independent method for determining the chlorine isotopic ratio in HCl was devised.

The Exchange Reactions.—Most of the data were gathered from individual runs in sealed reaction tubes made from 8 mm. Pyrex glass tubing, carefully selected to have an internal diameter of 6.0 ± 0.1 mm. In some of the experiments, especially with CH_3Cl and CH_2FCl, the surface of the reaction tubes was conditioned by a preliminary heating to 450–500° while the tubes were being evacuated. The tubes were then filled to the desired pressure with the prepared gas mixture and sealed off. The gas mixture left in the vacuum manifold was returned to the storage bulb, and samples taken for mass spectroscopic analysis showed that no measurable contamination or exchange occurred during handling in the vacuum manifold.

The filled reaction tubes, which had a volume of 3.1 cc. and an interior surface of 23 sq. cm., were sealed to a length of 1 mm. glass rod which served as a handle. Trial runs showed that no isotopic exchange was caused by the glassblowing operations. The filled tubes were next heated for various lengths of time in an electrically heated tube furnace. Temperatures were measured by means of iron–constantan or chromel–alumel thermocouples which were calibrated at 419.5° by determining the melting point of a specimen of zinc furnished by the National Bureau of Standards. The temperature of the furnace was constant within ±0.25° throughout the region where the samples were placed. After the reaction tubes had been heated for the desired length of time, they were removed from the furnace, cooled and sealed with Apiezon wax into a breakoff device on a vacuum line. Here the reaction tube was broken and the contents transferred to a sample tube for isotopic analysis in the mass spectrometer.

The CH_3Cl–HCl and CH_2FCl–HCl Exchange Reactions

Somewhat similar results were obtained with the first two members of the series studied. The first exchange experiments performed showed that the rate of chlorine exchange with these compounds was strongly dependent on the nature of the glass surface. Different sample tubes drawn from the same section of glass tubing gave greatly different rates. It was found, however, that fairly reproducible results could be obtained if the reaction tubes were conditioned by being pre-heated at 450–500° for 4 hr. on the vacuum line before being filled. If this treatment was omitted the exchange reaction would always go very much faster. Very commonly the reaction would reach equilibrium in unbaked tubes under conditions of time and temperature which would produce only 10% exchange in baked tubes.

Even with the preliminary baking, consistent results were not invariably obtained. About one sample in four would still show much greater exchange than others run at the same time with the same treatment. Longer baking of the reaction tubes produced no additional improvement in the reproducibility and a higher temperature could not be used without danger of collapsing the evacuated Pyrex vessels. These abnormal results were easily recognized since the deviation, if present at all, was of considerable magnitude and was always in the direction of more rapid reaction. A typical set of values for the rate constant obtained from baked tubes is: $k' = 1.7, 1.7, 2.2, 2.3, 2.4, 2.6, 2.9, 13.1, 304$ and ∞. While the first seven of these values have a mean deviation of ±0.3 from their average of 2.2, the deviations from the mean of the last three are 8.9, 302 and ∞, all in the direction of more rapid reaction. Consequently it is assumed that the variations among the first seven are essentially random, while the last three are the result of failure to bring the glass surface into the same condition as prevailed for the rest. Such abnormally large values were discarded. The smallest difference between the values used and one discarded appeared in the series shown in Table II for both gases at 125 mm. pressure and 420°. The reported $k_{1,0}$ values, 1.8, 2.3, 2.5 and 2.9, give an average of 2.4 ± 0.3, while the values 6.5 and ∞ were discarded.

It is customary to treat the kinetics of isotopic exchange reactions in terms of the apparent rate constant, k', which is always first order regardless of the true order of the reaction.[6] This constant is evaluated from the equation $k' = -(1/t)\ln(1-\alpha)$, where α is the fraction of complete exchange which has occurred at time t. For a reactant, x, representing a single isotopic species, $\alpha = ([x]_t - [x]_0)/([x]_\infty - [x]_0)$. The true order of the exchange reaction can be determined by varying the initial concentrations of the reacting materials. If the true rate, R, is $R = k[a]^m[b]^n$ for the reacting materials a and b, then $k = k'[a]^{1-m}[b]^{1-n}/([a] + [b])$, where [a] is the total concentration of all isotopic species of the compound a, and [b] is similarly defined.

A series of runs was made to determine the validity of the first order apparent rate law as applied to this reaction. Tubes of the standard type described above were heated at 450–500° for four hours on the vacuum line and then filled with a mixture of equal parts of CH_3Cl and HCl (enriched in Cl^{37}) to a total pressure of 250 mm. at room temperature. The tubes were heated at 405° for various times with the results shown in Table I. The indicated uncertainties represent the average deviation of the individual results from their mean. It can be seen that the first-order apparent rate law is valid over the range tested.

Table I

Test of Constancy of First-order Apparent Rate Constant

405°, pressure CH_3Cl = pressure HCl = 125 mm.

Time, hr.	No. of runs	α, fraction exchanged	k', (sec.$^{-1}$ × 10^6)
2	4	0.15 ± 0.01	2.3 ± 0.2
4	7	.28 ± .04	2.3 ± .4
8	7	.46 ± .04	2.1 ± .2

Next the initial concentrations of CH_3Cl and HCl or of CH_2FCl and HCl were varied so that the true order of the exchange reaction could be determined.

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(6) H. A. C. McKay, *Nature*, **142**, 997 (1938).

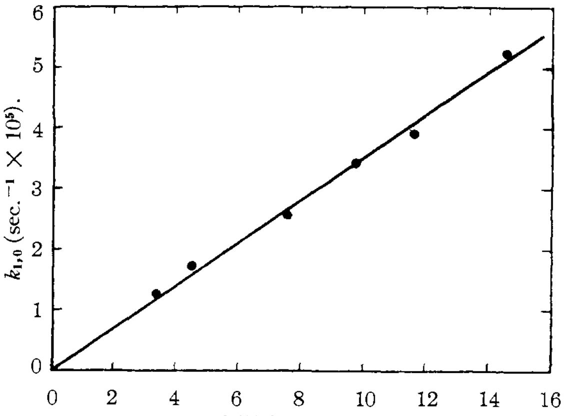

Fig. 1.—Effect of surface–volume ratio on the rate constant for chlorine exchange between CH_3Cl and HCl.

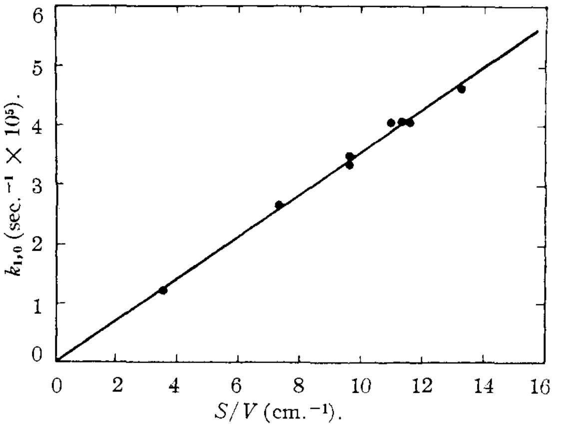

Fig. 2.—Effect of surface–volume ratio on the rate constant for chlorine exchange between CH_2FCl and HCl.

The results obtained are shown in Tables II and III. In both cases the data are consistent with a rate law that is first order with respect to the organic chloride concentration and independent of the concentration of HCl. The corresponding rate constants, $k_{1,0}$ are given in Tables II and III.

TABLE II

EFFECT OF INITIAL PRESSURE ON CH_3Cl-HCl EXCHANGE RATE

Temp., °C.	Time, (hr.)	CH_3Cl pressure (mm.)	HCl pressure (mm.)	No. of runs	α fraction exchanged	$k_{1,0}$ (sec.$^{-1}$ × 10^5)
375	6	125	62.5	2	0.14 ± 0.005	0.22 ± 0.005
	6	125	125	4	.09 ± .01	.22 ± .02
					Av.	.22 ± 0.01
405	4	62.5	62.5	4	.29 ± .04	1.2 ± 0.2
	[a]	125	125	18	[a]	1.1 ± .15
	4	250	250	4	.27 ± .04	1.0 ± .15
					Av.	1.1 ± 0.15
420	2	62.5	125	2	.23 ± 0.01	2.4 ± 0.1
	2	83	166	2	.25 ± .03	2.7 ± .3
	2	125	62.5	3	.40 ± .02	2.3 ± .2
	4	125	125	4	.49 ± .05	2.4 ± .3
	2	250	125	3	.40 ± .02	2.3 ± .2
					Av.	2.4 ± 0.2

[a] Average of determinations listed in Table I.

TABLE III

EFFECT OF INITIAL PRESSURE OF CH_2FCl-HCl EXCHANGE RATE

480°, 2 hr.

CH_2FCl pressure (mm.)	HCl pressure (mm.)	No. of runs	α fraction exchanged	$k_{1,0}$ sec.$^{-1}$ × 10^5
25	125	3	0.20 ± 0.02	2.6 ± 0.3
125	25	3	.67 ± .03	2.6 ± .2
125	125	3	.20 ± .01	2.5 ± .03
125	625	2	.22 ± .005	2.8 ± .05
625	125	2	.66 ± .005	2.5 ± .05
			Av.	2.6 ± 0.2

A series of experiments was now performed to determine whether the surface area of the reaction tubes as well as the condition of that surface affected the reaction rate. The strong catalytic action of the untreated glass surface considerably limited the range of surface–volume ratios which could be studied since reaction vessels packed with glass wool or small glass tubing always gave abnormally high results, even though the outer tube was given a preliminary baking. This occurred even when the tubes used for packing were drawn down from the same piece used for the outer tube and all edges were carefully fire-polished. In all successful experiments the surface–volume ratio was varied by changing the shape of the reaction tubes. The results obtained are shown in Figs. 1 and 2, where the rate constants are plotted against the surface–volume ratios. It can be seen that the rate of the reaction is directly proportional to the surface–volume ratio for both CH_3Cl and CH_2FCl.

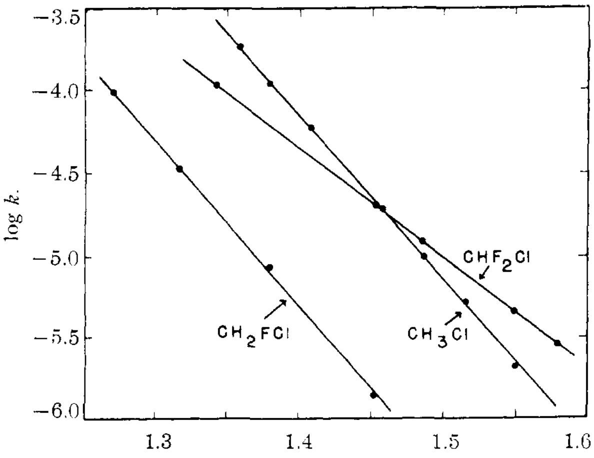

Fig. 3.—Effect of temperature on the rate constant for chlorine exchange in the systems CH_3Cl-HCl, CH_2FCl-HCl and CHF_2Cl-HCl.

The rate constants were next evaluated at a number of different temperatures so that the energies of activation could be calculated. The results obtained are given in Tables IV and V. All of the experiments except those previously reported were with 125 mm. pressure of the organic chloride and 125 mm. pressure of HCl. The results are shown graphically in Fig. 3, where the logarithm of the rate constant is plotted against the reciprocal of the absolute temperature. From the slope of this line the activation energy for the exchange reaction between CH_3Cl and HCl at a surface–volume ratio of 7.4 cm.$^{-1}$ is calculated to be 43.6 kcal./mole and $k_{1,0} = 1.4 \times 10^9 e^{-43,600/RT}$ sec.$^{-1}$. For the CH_2FCl–HCl exchange the activation energy at the same surface–volume ratio is 47.1 kcal./mole and $k_{1,0} = 1.4 \times 10^9 e^{-47,100/RT}$ sec.$^{-1}$.

TABLE IV

EFFECT OF TEMPERATURE ON CH_3Cl–HCl EXCHANGE RATE

Temp., °C.	Time (hr.)	No. of runs	α fraction exchanged	$k_{1,0}$ (sec.$^{-1}$ × 10^5)
375	6	6	[a]	0.22 ± 0.01
390	4	2	0.13 ± 0.00	.48 ± .00
405	[a]	26	[a]	1.1 ± .15
420	[a]	14	[a]	2.4 ± .2
435	2	3	0.47 ± 0.02	4.4 ± .2
450	1.5	6	.58 ± .09	8.2 ± 2.1
465	1.5	2	.83 ± .005	16.7 ± .3

[a] Listed in Table II.

TABLE V

EFFECT OF TEMPERATURE ON CH_2FCl–HCl EXCHANGE RATE

Temp., °C.	Time (hr.)	No. of runs	α fraction exchanged	$k_{1,0}$ (sec.$^{-1}$ × 10^5)
420	8	2	0.08 ± 0.005	0.155 ± 0.010
450	1.5	2	.08 ± .005	.82 ± .05
480	2	13	[a]	2.6 ± .2
510	1.5	4	.61 ± .05	8.9 ± 1.3

[a] Listed in Table III.

An examination of the mass spectra of the reaction mixtures after they had been heated discloses no significant changes in the peaks other than those resulting from the chlorine exchange reaction. If, however, the reaction mixture had been heated in an unbaked or packed tube, or had undergone abnormal wall catalysis for any other reason, certain new peaks became evident. In the case of CH_3Cl, small peaks corresponding to the various isotopic combinations of CH_2Cl_2 appeared. With CH_2FCl, fairly strong peaks corresponding to CH_2Cl_2 and to CH_2F_2 were found. In spite of the formation of these new substances the chlorine isotopic ratio in the parent molecules would always be that predicted for isotopic equilibrium without decomposition, so that the exchange reaction must have proceeded to completion before appreciable decomposition occurred.

The CHF_2Cl–HCl and CF_3Cl–HCl Exchange Reactions

Strikingly different results were obtained for the last two members of the series. With CHF_2Cl no catalysis by the glass walls of the reaction vessels was noted. The same results were obtained whether or not the reaction tubes were previously baked in the manner described above. The results were uniformly concordant without any of the abnormally high values obtained with CH_3Cl and CH_2FCl. Even the presence of glass wool or glass tubing as packing in the reaction vessels did not cause acceleration of the rate. Table VI summarizes some experiments testing the effect of surface–volume ratio on the rate constant. For the first five entries, the tube shape was altered; for the last three, packing was used.

TABLE VI

EFFECT OF SURFACE–VOLUME RATIO ON CHF_2Cl–HCl EXCHANGE RATE

420°, 2 hr., pressure CHF_2Cl = pressure HCl = 125 mm.

Surface area (cm.^{2})	Vol. (cm.^{3})	S/V (cm.$^{-1}$)	α fraction exchanged	$k_{1/2,1/2}$ (sec.$^{-1}$ × 10^5)
23	5.8	4.0	0.30	2.5
23	3.1	7.4	.30[a]	2.5[a]
15	1.4	10	.33	2.8
20	1.6	13	.28	2.3
19	1.4	13	.31	2.6
39	2.5	16	.41	3.6
2,600	3.0	870	.20	1.6
28,000	15.0	1800	.25	2.0

[a] Average of 4 determinations listed in Table VII.

The true order for the CHF_2Cl–HCl exchange was determined as before by varying the initial concentrations of the reactants. The results are shown in Table VII. It was found that a constant value for the rate constant could not be obtained using the rate law that was fitted by the data for CH_3Cl and CH_2FCl, but that the results obtained indicated the rate of exchange was proportional to the concentration of CHF_2Cl to the one-half power and to the concentration of HCl to the one-half power. The values obtained for the corresponding rate constant, $k_{1/2,1/2}$, are given in Table VII.

TABLE VII

EFFECT OF INITIAL PRESSURE ON CHF_2Cl–HCl EXCHANGE RATE

420°, 2 hr.

CHF_2Cl pressure (mm.)	HCl pressure (mm.)	No. of runs	α fraction exchanged	$k_{1/2,1/2}$ (sec.$^{-1}$ × 10^5)
25	125	4	0.36 ± 0.01	2.3 ± 0.1
125	25	3	.40 ± .02	2.7 ± .1
125	125	4	.30 ± .02	2.5 ± .2
125	250	4	.34 ± .002	2.7 ± .03
125	625	4	.36 ± .01	2.4 ± .05
625	125	4	.39 ± .01	2.6 ± .05
			Av.	2.5 ± .15

In order to calculate the activation energy, the rate constant was determined at a series of temperatures with the results shown in Table VIII. All of the experiments were performed with 125 mm. pressure of CHF_2Cl and 125 mm. of HCl except those at 420° which were previously listed in Table VII. These values are graphed in Fig. 3 along with those for the earlier members of the series. From this curve the energy of activation for the CHF_2Cl–HCl exchange reaction was calculated to be 30.2 kcal./mole, and $k_{1/2,1/2} = 9 \times 10^4 e^{-30,200/RT}$ sec.$^{-1}$.

TABLE VIII

EFFECT OF TEMPERATURE ON CFH_2Cl–HCl EXCHANGE RATE

Temp., °C.	Time (hr.)	No. of runs	α fraction exchanged	$k_{1/2,1/2}$ (sec.$^{-1}$ × 10^5)
360	8	5	0.15 ± 0.002	0.28 ± 0.004
375	8	7	.26 ± .01	0.53 ± .03
405	4	8	.34 ± .03	1.47 ± .15
420	2	23	[a]	2.5 ± .15
465	1.5	4	.61 ± .03	8.7 ± .7

[a] Listed in Table VII.

An examination of the mass spectrum of the products of the CHF_2Cl–HCl exchange reaction showed the formation of very small amounts of CHF_3 and possibly traces of CF_4. If the reaction mixture was heated for a long period of time—approximately 50 half-lives—the presence of CF_2Cl_2 could also be detected. This latter compound might also have been present after shorter heating time, but identification of small traces of it was hampered by the interference of the unresolved doubly ionized mercury band. When the reaction mixture was heated to 510° for 4 hr., very extensive decomposition occurred, forming a complex mixture of products. This behavior contrasts sharply with that of CH_2FCl–HCl mixtures, which gave no appreciable decomposition at this temperature.

The exchange reaction between CF_3Cl and HCl has not been thoroughly investigated. No exchange could be detected after 2 hr. heating at 405° either in empty tubes or in tubes packed with glass wool up to a surface–volume ratio of 1800 cm.$^{-1}$. This means that at 405° the apparent rate constant, k', must be less than 0.02×10^{-5} sec.$^{-1}$. The apparent rate constant for the CHF_2Cl–HCl exchange at this temperature was 2.9×10^{-5} sec.$^{-1}$. Three runs at $510 \pm 5°$ for 125 hr. gave an apparent rate constant, k', of $0.066 \pm 0.011 \times 10^{-5}$ sec.$^{-1}$. By extrapolation of the curve in Fig. 3, the apparent rate constant for CHF_2Cl at 510° can be calculated to be 30×10^{-5} sec.$^{-1}$.

Attempts to speed up the CF_3Cl–HCl exchange by raising the temperature failed because of very severe decomposition which occurred at these higher temperatures. A tube filled with CF_3Cl–HCl mixture and heated for 2 hr. at 600° (at which temperature the Pyrex tube sagged and threatened to collapse) showed that a high fraction of the organic compound had been converted to CO_2, presumably by reaction with the glass wall. A tube similarly treated but initially packed with glass wool showed no gaseous product except CO_2.

Discussion of Results

Because of the striking differences observed in the kinetic behavior of the exchange reactions of the first two members of the series studied as compared with CHF_2Cl, it appears that an entirely different mechanism must prevail for the latter compound. Possible mechanisms for the CH_3Cl–HCl and CH_2FCl–HCl exchanges have been discussed in detail by one of us.[1] The wall-dependent step may be either the dissociation of the organic chloride, which must be only weakly adsorbed on the surface, or the reaction of the organic chloride with adsorbed HCl, which must be so strongly adsorbed that the fraction of the surface covered is independent of the HCl pressure in the gas phase. The data do not permit a positive choice between these alternatives, but some arguments can be adduced that favor the organic chloride dissociation. In this case the dissociation at the wall would be the rate-determining step, followed by a rapid exchange between atomic chlorine and HCl. This is the mechanism favored by Peri and Daniels[5] for bromine exchange between HBr and C_2H_5Br. Further work to clarify this mechanism is contemplated.

The CHF_2Cl–HCl exchange most likely involves a chain mechanism, but none has been worked out in detail which can explain the observed dependence of the rate on the concentrations. Since the rate is independent of the surface–volume ratio, the reaction must either be completely homogeneous or consist of a chain which both starts and ends at the wall.

Since the order and homogeneity of the exchange of CF_3Cl with HCl were not thoroughly studied, no conjectures can be made concerning the mechanism of this reaction.

It has long been thought that the introduction of fluorine atoms into organic halides on the halogen-bonded carbon atom tends to make the halogen less reactive. This concept is based mostly on qualitative observations regarding ease of hydrolysis and further fluorination.[7] The present study shows, however, that this generalization at least does not apply to all reactions of such a halogen. In this connection the work of Reed and Rabinovitch[8] on the carbon–chlorine bond strength[9] in the series CH_3Cl, CH_2FCl, CHF_2Cl and CF_3Cl is significant. By experiments on the sodium diffusion flames of these compounds, they have found that in CH_3Cl the carbon–chlorine bond has a strength of 80.7 kcal. and that the bond is a few kcal. stronger than this in CH_2FCl and CHF_2Cl, but a few kcal. weaker in CF_3Cl.

One of the most interesting observations to be made from the present study is the sharp change in mechanism that occurs in the middle of a series of such similar-appearing reactions as chlorine exchange between HCl and CH_3Cl, CH_2FCl, CHF_2Cl and CF_3Cl. A simple comparison of the relative rates of these reactions without a thorough study of the kinetic details could lead to some very wrong conclusions.

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ANN ARBOR, MICHIGAN

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[7] A. L. Henne and T. Midgley, Jr., THIS JOURNAL, **58**, 882 (1936).

[8] J. F. Reed and B. S. Rabinovitch, paper presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society, Los Angeles, California, March 15–19, 1953.

[9] Defined as the energy required to separate the molecule into an organic radical and chlorine atom, all substances being in the gas state.