401. *Electrophilic Catalysis in Nucleophilic Substitution and Elimination. Part II.* Kinetics and Mechanisms of Reaction of t-Butyl Chloride with Pyridine, Tribenzylamine, Radio-chloride Ions and Hydrogen Radio-chloride in Nitromethane.*

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Measurements are reported on the kinetics of elimination from and radio-chloride exchange in t-butyl chloride in nitromethane. The elimination of hydrogen chloride in the presence of pyridine, tribenzylamine, or low concentrations of tetraethylammonium chloride has the characteristics of a unimolecular process. At higher chloride concentrations a small incursion of a second-order component of elimination is also observed. The dilution of tracer during the reaction with saline radio-chloride is almost entirely due to the elimination so there is little or no substitution by chloride ions.

The isotope exchange with hydrogen radio-chloride is stoicheiometrically a substitution in which the rate rises linearly with the acid concentration. The second-order component is about 10 times faster than the corresponding component of elimination produced by chloride ions. The rate-determining step in the second-order component of exchange with hydrogen radio-chloride is taken to be the electrophilically assisted ionisation of t-butyl chloride by molecular hydrogen chloride to give the t-butyl cation and the hydrogen dichloride anion. This conclusion is supported by the observation that chloride ions reduce this rate by combining with the electrophilic catalyst. It is also shown that the stoicheiometric composition of the transition state accords with the principle of microscopic reversibility.

Molecular hydrogen chloride is a recognised electrophilic catalyst for such ionic processes as the rearrangement of camphene hydrochloride to isobornyl chloride in nitrobenzene,[1] the racemisation and the radio-halogen exchange of 1-phenylethyl chloride in nitromethane,[2] and the methanolysis, and benzyl-alcoholysis of triphenylmethyl chloride in benzene.[3a,b] For a detailed understanding of this type of catalysis the kinetics of the isotopic halogen exchange between t-butyl chloride and hydrogen radio-chloride have been investigated in nitromethane. This proved advantageous in that it provided an independent check of some of the mechanistic conclusions deduced from the kinetics of

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* Part I, *J.*, 1959, 1179.

[1] Bartlett and Pöckel, *J. Amer. Chem. Soc.*, 1938, **60**, 1585.

[2] Pocker, " Kinetics and Mechanisms of Exchange and Racemization in Aralphyl Halides," paper presented at the Informal Faraday Society Meeting on Isotope Exchange Reactions held in Leeds, September 25—26th, 1958, abstracts in: *Trans. Faraday Soc.*, 1959, **55**, 1266.

[3] (*a*) Hughes, Ingold, Mok, and Pocker, *J.*, 1957, 1238. (*b*) Hughes, Ingold, Patai, and Pocker, *ibid.*, p. 1255.

addition of hydrogen chloride to isobutene.[4] For completeness the present paper includes also a parallel study of the reaction of t-butyl chloride in the absence of electrophilic catalysis.

(1) *Elimination of Hydrogen Chloride from t-Butyl Chloride.*—This reaction can only be observed in the absence of free hydrogen chloride. It was investigated by measuring the development of acidity in the presence of pyridine, tribenzylamine, or tetraethylammonium chloride. The rate coefficient of acid production is practically identical with the corresponding values for production of chloride and of olefin (Table 1). At low concentrations of tetraethylammonium chloride, the rate of elimination is practically identical with that in the presence of pyridine or tribenzylamine. When the amount of saline chloride is increased the first-order rate coefficient of the elimination of t-butyl chloride rises, indicating the incursion of a small component of elimination which is of first order in saline chloride. Apart from the latter variation, our conclusion is that the elimination becomes observable only in the presence of amine or of saline chloride, but its rate is approximately independent of their concentrations. These conclusions can only be reconciled on the assumption that the elimination is unimolecular and depends for its rate on that of the ionisation of t-butyl chloride, and that pyridine and tetraethylammonium chloride act by retarding the retrograde addition to the olefin, the former by combining with the acid to give amine hydrochloride, and the latter by complex-formation with hydrogen chloride to give hydrogen dichloride ions.[4] The slow increase in the rate of elimination with increasing concentration of tetraethylammonium chloride is not entirely an ionic-strength effect since the corresponding perchlorate has a smaller effect on this rate. It cannot be due to an increase of suppression of the back addition of hydrogen chloride to olefin because an upper limit to such a possible effect is set by removing the acid completely, *i.e.*, by addition of pyridine. If one neglects steric considerations, it is also difficult to visualise its being caused by a minor bimolecular component of elimination since the more basic pyridine does not show such an effect. One is therefore led to the conclusions that the slow increase in elimination rate is due in part to a general salt effect and in part to a more specific interaction between chloride ions and t-butyl chloride ion-pairs.

TABLE 1. *Initial first-order rate coefficients* (k_1 *in sec.*$^{-1}$) *of acid production* (d[H$^+$]/d*t*) *from t-butyl chloride in the presence of pyridine, tribenzylamine, or tetraethylammonium chloride in nitromethane at* 75°.

[Bu^{t}Cl] ...	0·021	0·042	0·084	0·168	0·21	0·21	0·21	0·21	0·21	0·21
[C_5H_5N] ...	0·022	0·022	0·022	0·022	0·011	0·022	0·033	0·033	0·033	0·066
10^6k_1	2·42	2·49	2·46	2·38	2·56	2·40	2·42	2·36 *	2·48 †	2·50

At 25°: [Bu^{t}Cl] = 0·1032; [C_5H_5N] = 0·1185; 10^9k_1 = 7·5 sec.$^{-1}$.

[Bu^{t}Cl]	0·21	0·21	0·21	0·21
[(Ph·CH$_2$)$_3$N]	0·0050	0·010	0·020	0·040
10^6k_1	2·40	2·48	2·36	2·42

[Bu^{t}Cl] ...	0·02075	0·1037	0·2075	0·2075	0·2075	0·2075	0·2075	0·2075	0·2075	0·224
10^4[NEt$_4$Cl]	47·5	47·5	47·5	47·5	47·5	95	190	488	1075	1075
10^6k_1	2·56	2·54	2·50	2·46 *	2·55 †	2·76	3·14	4·0	5·85	5·80

[Bu^{t}Cl] ...	0·224	0·224	0·224	0·224	0·224
10^4[NEt$_4$Cl]	192	192	192	1040	100
[NEt$_4$ClO$_4$]	—	0·0425	0·0850	—	0·090
10^6k_1	3·1	3·5	4·0	5·9	3·7

[Bu^{t}Cl] = 0·224; [(n-Bu)$_4$NCl] = 0·050; 10^6k_1 = 4·2 sec.$^{-1}$.
[Bu^{t}Cl] = 0·224; [(n-Bu)$_4$NCl] = 0·1075; 10^6k_1 = 5·86 sec.$^{-1}$.

At 25°: [Bu^{t}Cl] = 0·1032; [NEt$_4$Cl] = 0·058; 10^9k_1 = 8 sec.$^{-1}$.

* From d[olefin]/d*t*. † From d[Cl$^-$]/d*t*.

(2) *Reaction between Radio-chloride Ions and t-Butyl Chloride.*—This reaction was studied

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[4] Pocker, *J.*, 1960, 1292.

by observing the dilution of tracer accompanying the reaction between ordinary chlorine of t-butyl chloride and chloride ions made radioactive with chlorine-36 and supplied in the form of tetraethylammonium chloride. The concurrent elimination produces hydrogen chloride, which instantaneously exchanges its chlorine with that of the saline chloride so that dilution of tracer is not in itself an indication that chlorine is being exchanged with t-butyl chloride. Indeed, the rates of tracer dilution are about the same as the rates of production of hydrogen chloride. The results are given in Table 2*a*. From these it can be deduced that there is little or no concurrent substitution by chloride ions. This conclusion was further confirmed by showing that, as long as there is free Cl^- left, tracer is not being introduced into t-butyl chloride. It is of interest that in the reaction of t-butyl bromide with tetraethylammonium chloride in nitromethane the elimination process also contains both a zeroth and a first-order component in chloride ions,[5] with little or no substitution accompanying it (Table 2*b*).

TABLE 2*a*. *Initial first-order rate coefficients* (k_1* *in* sec.$^{-1}$) *of tracer dilution in the reaction of t-butyl chloride with tetraethylammonium radio-chloride in nitromethane at* 75·0°.

Bu^{t}Cl	0·224	0·224	0·224	0·224	0·224
$NEt_4{}^{36}Cl$	0·0194	0·0244	0·0488	0·1075	0·1375
10^6k_1 *	3·0	3·2	4·0	5·6	6·6

TABLE 2*b*. *Initial first-order rate coefficients* (k_1 *in* sec.$^{-1}$) *of production of bromide ions, of hydrogen ions, and of olefin from t-butyl bromide in nitromethane at* 25·0° *as a function of the concentration of added tetraethylammonium chloride.*

Bu^{t}Br	NEt_4Cl	Method	10^5k_1	Bu^{t}Br	NEt_4Cl	Method	10^5k_1
0·02	0·01	+d[H$^+$]/d*t*	0·45	0·02	0·12	d[H$^+$]/d*t*	1·24
0·02	0·01	+d[Br$^-$]/d*t*	0·44	0·02	0·12	d[Br$^-$]/d*t*	1·2
0·02	0·01	+d[olefin]/d*t*	0·42	0·02	0·12	d[olefin]/d*t*	1·16
0·02	0·01	−d[Cl$^-$]/d*t*	~0	0·02	0·12	−d[Cl$^-$]/d*t*	~0

(3) *Isotopic Chlorine Exchange between t-Butyl Chloride and Hydrogen Radio-chloride.*—This reaction was studied over a range of reagent concentrations in nitromethane, the basic measurement being that of isotopic exchange between ordinary chlorine of t-butyl chloride and chlorine made radioactive with chlorine-36 supplied in the form of hydrogen chloride. The stoicheiometric reaction is one of substitution since d[olefin]/d*t* = 0. It is slow at 25·0° but proceeds at convenient speed at 75·0°. The results are given in Table 3. With acidities below 0·10M-hydrogen chloride, the first-order rate coefficients increase linearly with the concentration of hydrogen chloride. This rise is well represented by the equation 10^6k_1 (sec.$^{-1}$) $= 2{\cdot}4 + 340$[HCl]. The component of exchange which is of first order in alkyl halide and of zeroth order in hydrogen chloride, $10^6k_1 = 2{\cdot}4$ sec.$^{-1}$, has practically the same value as that for elimination (sections 1 and 2). This indicates that whatever the stoicheiometry of these reactions, substitution or elimination, the rates are controlled by a common process which is identified as the slow ionisation of the alkyl halide.

The component of exchange which is of first order in alkyl halide and of first order in hydrogen chloride might be mechanistically interpreted in three possible ways. One possibility is that an S_N2 substitution is taking place. If this were true the order in which the substituting agents should stand would be the order of nucleophilic power, $Cl^- > HCl_2{}^- > HCl$. But the reaction with chloride ions, supplied as tetraethylammonium radio-chloride, leads to elimination with little or no substitution. Another possibility would be that of *E*2 elimination which is irreversible when chloride ions are present but is strongly reversed when free hydrogen chloride is present. But if this were true the order of such eliminating agents should be the order of their basicity, $Cl^- > HCl_2{}^- > HCl$.

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[5] de la Mare, Hughes, Ingold, and Pocker, *J.*, 1954, 2930.

Actually, the second-order component of chlorine exchange with hydrogen radio-chloride is *ca.* 10 times faster than that for elimination, as observed in the presence of chloride ions. The third interpretation is therefore the correct one: the hydrogen chloride molecule is intervening in the rate-controlling step of the second-order process by virtue of its capacity to form a hydrogen bond with the chlorine of the t-butyl chloride and thus assists electron transfer and bond heterolysis.

Since hydrogen chloride is assumed to act as an electrophilic catalyst then added saline chloride should not accelerate the radio-chlorine exchange between hydrogen chloride and t-butyl chloride, but should suppress it by combining with the catalyst.[4] The results are given in Table 3*b*, where the exchange rates are evaluated as of first order in alkyl halide. At constant concentration of hydrogen chloride, these decrease with increasing amounts of added tetraethylammonium chloride. This reduction is ascribed to the removal of free hydrogen chloride by the reaction: $Cl^- + HCl \rightleftharpoons HCl_2^-$, so that the concentration of free acid $[HCl]_f$ is smaller than that of the stoicheiometric acid $[HCl]_s$. Consequently we write $[HCl]_f = [HCl]_s - [HCl_2^-]$. If in the region where the concentration of stoicheiometric acid is higher than that of added saline chloride, we assume that $[HCl_2^-] \simeq [NEt_4Cl]_0$ then $[HCl]_f \simeq [HCl]_s - [NEt_4Cl]_0$. The ratio $(10^5k_1 - 0{\cdot}24)/([HCl]_s - [NEt_4Cl]_0)$ is roughly constant in the region $[NEt_4Cl]_0/[HCl]_s < 3/4$ and is about equal to the second-order component in the absence of tetraethylammonium chloride.

In the region $[HCl]_s > [NEt_4Cl]_0$ the situation is similar to that in the absence of saline chloride inasmuch as the stoicheiometric reaction is one of substitution and little or no elimination can be detected, *i.e.* $d[H^+]/dt \sim 0$. Under these conditions isobutene adds hydrogen chloride rapidly and almost completely and, because of the direction of the thermodynamic control, we obtain overall exchange rather than elimination. When $[NEt_4Cl]_0 \sim [HCl]_s$ the stoicheiometric reaction is still essentially one of substitution, but concurrent elimination occurs, as measured by the development of acidity. Initially, acid is formed at nearly the rate of dilution of tracer but the amount of acid ultimately developed is only *ca.* 10% of the amount of $NEt_4HCl_2^-$ present. Thus at 75·0° the first-order rate coefficient of radio-chlorine exchange between 0·2M-t-butyl chloride and 0·02M-$NEt_4HCl_2^-$ is $10^6k_1 = 3{\cdot}18$ sec.$^{-1}$, while the rate coefficient of acid development during the first 30 minutes is $10^6k_1 = 3{\cdot}2$ sec.$^{-1}$, but within 2 hours the latter rate falls to zero. It should also be noted that at 75·0° the initial rate of elimination of hydrogen chloride from t-butyl chloride at low concentrations of tetraethylammonium chloride is about the same as that with $NEt_4HCl_2^-$.

TABLE 3*a*. *First-order rate coefficients (k_1 in sec.$^{-1}$) of chlorine exchange between hydrogen radio-chloride and t-butyl chloride in nitromethane at* 75·0°.

$[Bu^tCl]$	0·204	0·204	0·204	0·204	0·204	0·204	0·204	0·204	0·0204	0·0204	0·0204
$[H^{36}Cl]$	0·005	0·010	0·020	0·029	0·040	0·050	0·0584	0·074	0·08	0·12	0·14
10^6k_1	4·1	5·7	9·4	12·6	16·0	18·9	23·1	27·0	29·8	39	45
$(10^5k_1 - 0{\cdot}24)/[HCl]$	34	33	35	35	34	33	35·5	33·2	34·2	32	30·4
$[Bu^tCl]$	0·051	0·102	0·204	0·408							
$[H^{36}Cl]$	0·04	0·04	0·04	0·04							
10^6k_1	15·8	15·5	16·0	16·4							

At 25·0°; $[Bu^tCl] = 0{\cdot}204$M; $[H^{36}Cl] = 0{\cdot}0163$M; $10^8k_1 = 6{\cdot}3$ sec.$^{-1}$.

TABLE 3*b*. *Effect of added tetraethylammonium chloride on the rate of chlorine exchange between hydrogen radio-chloride and t-butyl chloride in nitromethane at* 75·0°.

$[Bu^tCl]$	0·233	0·233	0·233	0·233	0·233	0·233	0·233
$[H^{36}Cl]$	0·080	0·080	0·080	0·080	0·080	0·080	0·080
$[NEt_4Cl]$	—	0·020	0·025	0·040	0·060	0·080	0·090
10^6k_1	29·8	22·2	19	15·4	9·6	4·0	3·9
$(10^5k_1 - 0{\cdot}24)/([HCl] - [NEt_4Cl])$	34·2	33	30·2	32·5	36	—	—

Discussion.—We had for kinetic reasons to describe the reaction between t-butyl cation and hydrogen dichloride anion as being slower than the proton loss.[4] For independent kinetic reasons presented above we have to describe the rate-determining step in the second-order component of chlorine exchange between t-butyl chloride and hydrogen radio-chloride as an electrophilically assisted ionisation of the former by the latter to produce a t-butyl cation and a hydrogen dichloride anion. Because of the direction of the thermodynamic control we obtain overall exchange rather than overall elimination. Actually these conclusions are correlated by theory, and the rate-determining step of either process (addition or exchange) could be deduced from the other by the principle of microscopic reversibility. The transition state when approached from either direction has the same stoicheiometric composition:

$$(CH_3)_2C{=}CH_2,2HCl \equiv (CH_3)_3C^+HCl_2^- \equiv (CH_3)_3CCl,HCl$$

These considerations are independent of whether we describe the intermediate as a kinetically free t-butyl cation (scheme *a*) or as a t-butyl hydrogen dichloride ion-pair (scheme *b*). Indeed both descriptions are consistent with the observation that the rate of deuterium exchange is *ca.* 9 times faster than that of the radio-chlorine exchange.[6] This observation only means that the t-butyl cation (either as the kinetically free entity or paired with a hydrogen dichloride anion) has in the presence of free hydrogen chloride a sufficiently long existence to enable it to exchange by elimination and back addition all nine of its hydrogen atoms before it reacts with one of the chlorines of the dichloride anion. In scheme (*a*) we have for kinetic reasons to picture the elimination of the proton either as a unimolecular proton loss or as one directly assisted by a solvent molecule but not as a proton extraction by hydrogen dichloride ion. No such kinetic restriction exists for the ion-pair picture except that the hydrogen dichloride anion cannot be external and must be part of the ion-pair.

Scheme (*a*)

$$Bu^tCl + HCl \xrightleftharpoons[2]{} (Bu^t)^+ + HCl_2^-$$

$$(Bu^t)^+ \xrightleftharpoons[4]{3} (CH_3)_2C{=}CH_2 + H^+$$

$$H^+ + HCl_2^- \xrightleftharpoons[6]{5} 2HCl$$

Rates: $5 > 6 > 4 > 3 > 2 > 1$

Scheme (*b*)

$$Bu^tCl + HCl \xrightleftharpoons[2]{1} (Bu^t)^+HCl_2^- \xrightleftharpoons[4]{3} (CH_3)_2C{=}CH_2 + 2HCl$$

Molecular hydrogen chloride induces ionisation of alkyl and aralkyl chlorides in solvents where the hydrogen dichloride ion is a relatively stable entity, *e.g.*, nitromethane,[2] nitrobenzene,[1] and benzene.[3] These organic chlorides are, however, subject to little or no catalysis by this mechanism in solvents where the hydrogen dichloride ion is unstable irrespective of whether the dissociation of the acid to a proton and a chloride anion is large, as in water, methanol, or ethanol, or whether it is small and the bulk of the acid is largely undissociated as in acetic acid. In the latter type of solvent, however, alkyl chlorides are subject to catalysis by acids stronger than hydrogen chloride, *e.g.* perchloric acid. In n-heptane the radioactive exchange between t-butyl chloride and hydrogen chloride is of first order in alkyl halide and roughly of second order in hydrogen chloride; [6] an observation which could in fact be predicted from the third-order dependence on acid in the addition of hydrogen chloride to isobutene in n-heptane,[7] by the principle of microscopic reversibility. These observations indicate that in n-heptane and possibly in other weakly solvating media, the hydrogen dichloride ion can undergo further hydrogen

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[6] Pocker, unpublished observations.

[7] Mayo and Katz, *J. Amer. Chem. Soc.*, 1947, **69**, 1339.

bonding with another hydrogen chloride molecule so that the composition of the transition state for both exchange and addition becomes more complex and may be represented by:

$$(CH_3)_3CCl,2HCl \equiv (CH_3)_3C^+Cl^-(HCl)_2 \equiv (CH_3)_3C^+H_2Cl_3^- \equiv (CH_3)_2C{=}CH_2,3HCl$$

At the high temperatures employed in the gas-phase eliminations of alkyl halides the conjugate acid of HCl_2^-, *i.e.* $(HCl)_2$, is unstable; this explains why the unimolecular gas-phase elimination of t-butyl chloride is not catalysed by the hydrogen chloride produced in the elimination process.[8,9] This observation could also be predicted by the principle of microscopic reversibility since the gas-phase addition of hydrogen chloride to isobutene is a bimolecular homogeneous reaction of first-order in each reactant.[10] Water molecules are stable to quite high temperatures, which explains why the gas-phase elimination of t-butyl alcohol is catalysed by hydrogen chloride.[11]

EXPERIMENTAL

Materials.—The methods of preparation and purification of the materials used have been previously described,[4,12] except for t-butyl chloride and hydrogen radio-chloride. t-Butyl chloride was dried (phosphoric oxide) and fractionated; it had b. p. 50·9°.

Hydrogen radio-chloride. A solution of this material in nitromethane was prepared by adding concentrated sulphuric acid to 2N-[^{36}Cl]hydrochloric acid supplied by the Radiochemical Centre, Amersham. The gas was dried by concentrated sulphuric acid and dissolved in nitromethane. The system was then flushed with small amounts of ordinary hydrogen chloride. The resulting solution was sealed in dry ampoules which were kept at −80° to suppress the decomposition of the nitromethane by hydrogen chloride.

Kinetic Measurements.—For measuring the dilution of radioactive tracer in the reaction between t-butyl chloride and tetraethylammonium radio-chloride the bulbs were cooled and broken in dry ether (100 ml.) to precipitate the saline material ($NEt_4Cl + NEt_4HCl_2$). The coagulated precipitate was filtered off (a No. 4 porosity sintered-glass filter being used), washed with dry ether, and dissolved by drawing three portions of distilled water (5 ml. each) through the filter. The aqueous solution was counted in a Geiger–Müller liquid-sample tube of about 12 ml. capacity, an Ekco Type 529 scaler being used. After the counting, portions (5 ml.) were titrated potentiometrically against standard silver nitrate to obtain specific activity.

For measuring the radioactive exchange between hydrogen radio-chloride and t-butyl chloride, bulbs were broken in cold ether containing triethylamine. The saline precipitate (NEt_3HCl) was filtered off, washed with ether, and dissolved in distilled water. The aqueous solution was analysed as described above. If a and b respectively are the concentrations of t-butyl chloride and hydrogen chloride and if c and $c - x$ are respectively the specific activities of the hydrogen chloride in the initial solution (counted as NEt_3HCl) and of a solution of acid recovered from a reaction stopped after time t, then the first-order rate coefficient k_2 was obtained by plotting $\log\{1 - (a + b)x/ac\}$ against t and multiplying the slope of the line by $-2{\cdot}303b/(a + b)$.

For measuring the radioactive exchange between hydrogen radio-chloride and t-butyl chloride in the presence of added tetraethylammonium chloride, bulbs were broken in cold ether containing triethylamine. The precipitate ($NEt_4Cl + NEt_3HCl$) was treated as above. The first-order rate coefficients k_1 were obtained by plotting $\log\{1 - (a + b + [NEt_4Cl])x/aC\}$ against t and multiplying the slope of the lines by $-2{\cdot}303b/(a + b)$.

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[8] Breasly, Kistiakowsky, and Stauffer, *J. Amer. Chem. Soc.*, 1936, **58**, 143.

[9] Barton and Onyon, *Trans. Faraday Soc.*, 1949, **45**, 725.

[10] Kistiakowsky and Stauffer, *J. Amer. Chem. Soc.*, 1937, **59**, 165.

[11] Maccoll and Stimson, *Proc. Chem. Soc.*, 1958, 80.

[12] Pocker, *J.*, (*a*) 1958, 240; (*b*) 1959, 1179; (*c*) 1959, 2319; (*d*) 1959, 3939, 3944.