777. *The Common-ion Effect in the Unimolecular Solvolysis of t-Butyl Chloride.*

By C. A. Bunton and B. Nayak.

The solvolysis of t-butyl chloride in aqueous methanol is accompanied by exchange of chloride between it and radioactive chloride ion. This exchange is apparently not an S_N2 reaction between chloride ion and alkyl chloride, but is caused by capture of some of the carbonium ions by chloride ions instead of by water. This intervention by chloride ions is compared with that by azide ions.

The classical work on the solvolysis of t-butyl chloride provided one of the earliest examples of an S_N1 reaction.[1] The carbonium ion so formed would be expected to be short-lived, and the hydrolysis of optically active 3-chloro-3,7-dimethyloctane (which is structurally similar to t-butyl chloride) gives an alcohol of inverted configuration, with *ca.* 80% loss of optical activity.[2] Thus the carbonium ion is captured by water molecules before it attains its most stable, planar configuration. Somewhat similarly the product of methanolysis of the hydrogen phthalate of 3,5-dimethylhexan-3-ol has an inverted configuration, with appreciable racemisation.[3]

It has been suggested that the solvolysis of t-butyl chloride in aqueous ethanol should be taken as an example of a limiting S_N1 reaction, and its rate has been taken as a standard in setting up a scale of ionising power for a variety of solvents.[4] The relations between solvent composition and both products and reaction rates have been studied in great detail.[5]

Alkyl halides, *e.g.*, diphenylmethyl chloride, which give comparatively stable carbonium ions, show a characteristic kinetic retardation of solvolysis by the common (chloride) ion, because the carbonium ion (R^+) may react either with this, to regenerate the alkyl halide, or with the solvent:[6]

$$\mathrm{R{-}Cl} \underset{+\mathrm{Cl}^-}{\overset{-\mathrm{Cl}^-}{\rightleftharpoons}} \mathrm{R}^+ \xrightarrow{\mathrm{H_2O}} \mathrm{R{\cdot}OH} + \mathrm{H}^+$$

This retardation has not been observed in hydrolyses of t-alkyl halides. This may be simply because the retarding effect of the common ion was obscured by the acceleration due to increase in the ionic strength. There was an indication, from a decrease of the rate constant in the latter part of the reaction of t-butyl chloride, that such an effect was only just outside the limits of detection, and there was strong evidence of an effect of azide upon the carbonium ion.[1b] It was, however, possible that there was some real mechanistic difference between the solvolyses of t-alkyl halides and of, *e.g.*, diarylmethyl halides. Our work was designed to avoid this difficulty by using an isotopic tracer to prove incorporation of chloride ions into the unhydrolysed t-butyl chloride and to show that this was not a bimolecular reaction between chloride ions and t-butyl chloride itself.

t-Butyl chloride was allowed to hydrolyse in alkaline aqueous methanol containing $\mathrm{Na^{36}Cl}$ in several-fold excess over the alkyl halide. After a time sufficient for partial reaction, the t-butyl chloride, with other volatile substances, was pumped off, and its

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[1] (*a*) Hughes, *J.*, 1935, 255; (*b*) Bateman, Hughes, and Ingold, *J.*, 1940, 960; Bateman, Church, Hughes, Ingold, and Taher, *J.*, 1940, 979.

[2] Hughes, Ingold, Martin, and Meigh, *Nature*, 1950, **166**, 679.

[3] Doering and Zeiss, *J. Amer. Chem. Soc.*, 1953, **75**, 4733.

[4] Grunwald and Winstein, *ibid.*, 1948, **70**, 846.

[5] (*a*) Olson and Halford, *ibid.*, 1937, **59**, 2644; Speith, Ruelesamen, and Olson, *ibid.*, 1954, **76**, 6253; Speith and Olson, *ibid.*, 1955, **77**, 1412; (*b*) Bateman, Hughes, and Ingold, *J.*, 1940, 881.

[6] Ingold, "Structure and Mechanism in Organic Chemistry," Bell, London, 1953, p. 360.

specific activity determined. All the exchange experiments were made with alkali in excess over t-butyl chloride to eliminate chloride exchange *via*:

$$\mathrm{Me_3C{\cdot}OH + HCl \rightleftharpoons Me_3CCl + H_2O}$$
$$\mathrm{Me_2C{:}CH_2 + HCl \rightleftharpoons Me_3Cl}$$

(cf. exchange between t-butyl chloride and hydrogen chloride in formic acid[7]). Control experiments were done to ensure that (*a*) no chloride ion came over as a spray in the distillate, and (*b*) a representative sample of t-butyl chloride was pumped over (see p. 3857).

Results of these exchange experiments are given in Table 1; the ratio $k_E/(k_E + k_C)$ gives the proportion of carbonium ions which are captured by chloride ions and regenerate t-butyl chloride. The rates of solvolysis are given in Table 2. The amount of olefin elimination was measured (see p. 3857); it is similar to that found in other solvents. The kinetic form also is similar to that found for other solvents, and added salts increase the rate. Lyate ions (OH^- and OMe^-) have little effect (see ref. 8).

TABLE 1. *Isotopic exchange between chloride ions and t-butyl chloride.* 35·0°. $[Bu^tCl] \approx 0{\cdot}085$M. Methanol–water 80 : 20 (v/v).

[NaCl] (M)	[NaN$_3$] (M)	Exchange (%) †	$\frac{k_E}{k_E + k_C}$
0·30	—	6·0 (5·9) at 50% reaction	0·09
,,	—	10·9 (11·0) at 75% reaction	0·07
Methanol-water 75 : 25 (v/v)			
0·50	—	7·1 (6·9) at 50% reaction ‡	0·1
,,	—	14·4 (13·4) at 75% reaction	0·1
0·25	0·25	4·4 at 53% reaction	0·06
,,	,,	8·5 at 75% reaction	0·06
,, *	0·75	3·1 (2·6) at 50% reaction	0·04
,, *	,,	6·4 at 75% reaction	0·04

* LiCl. † The figures in parentheses are for redistilled samples.
‡ With reagent concentration as used here, n-butyl chloride gave <0·1% exchange in 65 min.

TABLE 2. *First-order rate constants of solvolysis in aqueous methanol.* $[Bu^tCl] \sim 0{\cdot}085$M. Methanol–water 80 : 20 (v/v).

Reagent	—	NaCl		NaOH
[Reagent] (M)	—	0·25	0·50	0·118
10^5k_1 (sec.$^{-1}$) 25·0°	2·12	2·48	2·64	2·19
10^5k_1 (sec.$^{-1}$) 35·0°	7·45	8·55	9·35	7·78

Methanol-water 75 : 25 (v/v)

Reagent		NaCl		NaOH	NaOH	NaCl
[Reagent] (M)	—	0·25	0·50	0·112	0·097	0·50
10^5k_1 (sec.$^{-1}$) 25·0°	4·25	4·68	5·06	4·30	—	
10^5k_1 (sec.$^{-1}$) 35·0°	14·7	16·6	17·9	14·7	17·7	
Reagent	NaN$_3$	NaOH	NaN$_3$	LiOH	LiCl	NaN$_3$
[Reagent] (M)	0·50	0·095	0·50	0·112	0·25	0·75
10^5k_1 (sec.$^{-}$) 25·0°	—	—		—		
10^5k_1 (sec.$^{-}$) 35·0°	22·4	22·5		23·7		

It could reasonably be suggested that this exchange is a bimolecular reaction between t-butyl chloride and chloride ions, but this is most unlikely, because n-butyl chloride does not exchange its chlorine under conditions in which t-butyl chloride does, and a primary is much more reactive than a tertiary alkyl halide by the S_N2 mechanism. Also the bimolecular exchange between halide ions and a tertiary alkyl halide in acetone is very slow, and from this, and the known effect of solvent changes upon the rates of S_N2 reactions,

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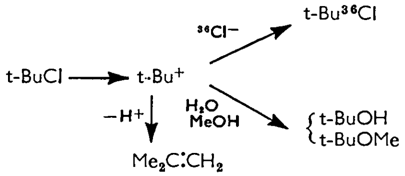
[7] Koskoski, Thomas, and Fowler, *J. Amer. Chem. Soc.*, 1941, **63**, 2451.
[8] Benfey, Hughes, and Ingold, *J.*, 1952, 2494.

we can be reasonably certain that there is no such bimolecular exchange in the conditions of our experiments.[9] Thus the mechanism of exchange must be:



In this representation it is not suggested that the t-butyl carbonium ion has attained its most stable, planar, configuration before its capture, because the solvolysis product of a structurally similar optically active compound is not racemic.[2] This can be considered as a " shielding " by the departing ion.[10] It could also be explained in terms of Winstein's ion-pair hypothesis,[11] although the present evidence for such intermediates comes from reactions carried out in solvents of low dielectric constant.

The exchange experiments show that with [chloride ion] = 0·5M about 10% of the carbonium ions (or ion pairs) return to t-butyl chloride, and, with the results of the stereochemical experiments, they show that these ions are not captured immediately by the adjacent water molecules, but exist for a time sufficient for approach of the common (chloride) ion. The experiments are therefore very similar in scope to those on the oxygen exchange and racemisation of secondary alcohols in acid.[12]

With t-butyl chloride the extent of common-ion intervention is small, relative to that for diarylmethyl halides, but it is generally found that the most reactive species will discriminate least towards reagents. Thus the reactive t-butyl carbonium ion will be captured preferentially by the most abundant reagent, *i.e.*, the solvent molecules.

These interventions by chloride, in the hydrolysis of t-butyl chloride, are similar to those of azide ions, and it is possible to carry out a competition experiment between azide and chloride ions. Addition of azide ions decreases the extent of chloride exchange. The effect is small (Table 1), and large concentrations of azide were used; this is because with t-butyl chloride the extent of anion intervention is itself small. From these experiments we calculate the extent of carbonium ion capture by chloride and azide ions. In methanol–water (75 : 25 v/v), 0·5M-chloride ions capture *ca.* 10% of the carbonium ions, whereas the same concentration of azide ion captures *ca.* 13% (Tables 1 and 3). The extent of intervention by azide ions is similar to that observed for other solvolyses of t-butyl halides.[1b]

TABLE 3. *Intervention by azide ion.*

Solvent: Methanol–water 75 : 25 (v/v). 35·0° [t-BuCl] ≈ 0·085M.

[NaOH] (M)	—	—	0·10	0·10	0·113 *
[LiCl] (M)	—	—	—	—	0·25
[NaN$_3$] (M)	0·50	1·00	0·50	1·00	0·75
Yield of Bu^{t}N$_3$ (mole %)	13·4	22·6	11·8	19·7	17·0

* LiOH.

EXPERIMENTAL

Materials.—t-Butyl chloride (B.D.H.) was distilled, and a sample with b. p. 51° collected. Methanol was dried by distillation over magnesium. Sodium and lithium chlorides were oven-dried at 250°. Sodium [^{36}Cl]chloride was prepared by neutralisation of H^{36}Cl with sodium hydroxide. Sodium chloride solution was then added to give radioactive sodium chloride of the required activity; this was purified by recrystallisation from water and oven-dried at

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[9] de la Mare, Fowden, Hughes, Ingold, and Mackie, *J.*, 1955, 3200.

[10] Hughes, Ingold, and Masterman, *J.*, 1937, 1196.

[11] Fainberg and Winstein, *J. Amer. Chem. Soc.*, 1956, **78**, 2763, and accompanying papers.

[12] Bunton, Konasiewicz, and Llewellyn, *J.*, 1955, 604; Bunton and Llewellyn, *J.*, 1957, 3402; Bunton, Llewellyn, and Wilson, *J.*, 1958, 4747; Grunwald, Heller, and Klein, *J.*, 1957, 2604.

250°. Lithium [^{36}Cl]chloride was prepared by neutralisation of H^{36}Cl with lithium hydroxide in aqueous methanol.

Kinetics.—The reaction was followed by titration of the acid produced. Aliquot parts (5 c.c.) were titrated in acetone with lacmoid as indicator. For runs in which azide ion was present phenolphthalein was used as indicator and 95% ethanol as titration solvent.

Integrated first-order rate constants k_1, were calculated from the equation: $k_1 = (2{\cdot}3/t) \log a/(a - x)$, where a is the concentration of t-butyl chloride initially, $a - x$ that at time t,

TABLE 4.

Solvent: methanol–water (80 : 20 v/v); 25°. [Bu^{t}Cl] initially ~0·088M; $(a - x)$ expressed in c.c. of 0·054N-NaOH per 5 c.c. portion. The time zero is arbitrary.

Time (min.)	0	30	60	90	120	180	240
Titre (c.c.)	0·22	0·52	0·85	1·07	1·35	1·92	2·35
10^5k_1 (sec.$^{-1}$)	—	2·08	2·23	2·04	2·08	2·16	2·10
Time (min.)	300	360	420	480	541	575	∞
Titre (c.c.)	2·85	3·25	3·62	3·98	4·27	4·40	8·36
10^5k_1 (sec.$^{-1}$)	2·16	2·15	2·10	2·10	2·12	2·08	—

Mean $10^5k_1 = 2{\cdot}12 \pm 0{\cdot}05$ (sec.$^{-1}$).

and t is in seconds. From the results of runs at 25·0° and 35·0° we can calculate approximate values of the Arrhenius parameters: in methanol–water (80 : 20 v/v), $E = 23$ kcal. mole^{-1}; $A = 10^{12}$ sec.$^{-1}$; in methanol–water (75 : 25 v/v), $E = 23$ kcal. mole^{-1}; $A = 2 \times 10^{12}$ sec.$^{-1}$. These values are similar to those found for solvolyses of t-butyl chloride in other solvents. Details of a typical run are in Table 4.

Estimation of Olefin.—Aliquot portions of t-butyl chloride in alkaline aqueous methanol were sealed in tubes. After a convenient time, two tubes were removed. In one, the extent of reaction was determined by acid–base titration; the other was broken under acidic methanol at 0°, an excess of standard bromine in methanol added, the flask swirled, potassium iodide added and the iodine titrated with thiosulphate. Control tests were made on samples taken at the beginning of reaction.

[Bu^{t}Cl] = 0·085M; [NaOH] = 0·10—0·13M. Methanol–water (80 : 20 (v/v).

	25·0°	35·0°
Elimination/Total reaction (moles %)	13·7; 13·1 *	15·3

* Methanol–water 75 : 25 (v/v).

The percentage of olefin elimination is similar to those found for other *E*1 eliminations from t-butyl compounds.[13]

Azide Intervention.—The extent of this was determined at complete reaction, by estimation of acid. The change of azide-ion concentration during reaction was small.

Isotopic Exchange.—A solution of Na^{36}Cl (or Li^{36}Cl) was prepared in aqueous methanol, and the specific activity of a portion determined by using a halogen-quenched liquid counter tube and an Ekco scaler. To the rest, t-butyl chloride was added (at thermostat temperature). After *ca.* one half-life, half the solution was removed and cooled to 0°, and part evaporated under the vacuum of a rotary oil pump. Dry air was passed in to prevent bumping, and the distillate passed through a ½ l. round-bottomed flask. The distillate was trapped in two traps, in series, cooled to −80°. The contents of the traps were treated with sodium hydroxide to hydrolyse the t-butyl chloride. The amount of chloride was determined by potentiometric titration with N/100-silver nitrate. The specific activity was then determined. This procedure was repeated with the residue of the reaction solution after *ca.* 2 half-lives.

It was necessary to make various tests on this method of separation. All experiments were made with alkali in excess over the t-butyl chloride, therefore there was no risk of hydrogen chloride distilling over. (*a*) A portion of the distillate was redistilled under reduced pressure; the specific activity of this redistilled portion was very close (within experimental error) to that of the original distillate. (*b*) Control experiments on the distillation were made (i) with unlabelled t-butyl chloride and sodium chloride and (ii) with radioactive sodium chloride and t-butyl alcohol. The distillates had no perceptible radioactivity.

[13] Ref. 6, p. 442.

TABLE 5.

[Bu^{t}Cl] = 0·085M; [NaOH] = 0·115M; [NaCl] = 0·50M; (A) Solution of Na^{36}Cl used. (B) Distillate pumped off after 50% reaction. (C) Solution (B) after redistillation. (D) Distillate pumped off after 75% reaction. (E) Solution (D) after redistillation.

[NaCl] (mM)	Background			Solution			Specific activity counts (min.$^{-1}$ mmole^{-1} l.)
	Time	Counts	Counts/min.	Time	Counts	Counts/min.	
(A) 4·9	15	165	11	25	25,323	1013	207
	20	220		50	50,640		
(B) 2·87	12	141	11·7	15	711	47·6	12·2
	24	283		28	1335		
				30	1432		
(C) 1·73	7	84	12	18	605	32·7	12·0
	12	145		40	1309		
				42	1360		
(D) 2·18	16	191	11·9	28	1864	66·8	25·2
	20	230		30	2014		
	22	270					
(E) 0·878	30	345	11·9	31	1019	32·4	23·4
	45	554		15	470		

(The differences between counts are within the coincidence error.)

The relative values of the first-order constants for exchange, k_E, and chemical reaction, k_C, were calculated from the equation

$$k_E/k_C = \log\{100/(100 - \%\ \text{exchange})\}/\log\{a/(a - x)\}$$

The change in chloride-ion concentration during the run was ignored; this causes little error for samples taken at 1 half-life. Table 5 contains details of an exchange experiment in methanol–water 75 : 25 (v/v) at 35·0°.

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WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES,
UNIVERSITY COLLEGE, GOWER ST., LONDON, W.C.1.

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