316. *The Influence of the Reaction Medium on the Relative Apparent Electron-donating Effects of Different Alkyl Groups.*

By E. SPINNER.

This study of the rates of ionisation of the halides $R\cdot CMe_2Cl$ ($R = Me, Et, Pr^i, Bu^t$) in five widely differing solvents was undertaken to elucidate further the nature of the Baker–Nathan effect which is variously attributed to hyperconjugation and to steric resistance to bond contraction. The former theory is shown to demand that the effect, being of a polar nature, be most pronounced in the best cation-solvating solvents, while the latter theory demands the reverse. Actually, the relative rates of ionisation vary greatly from solvent to solvent, and the data, though somewhat irregular, are much more readily reconciled with the latter view.

ALKYL groups may stabilise electron-deficient molecules by two different mechanisms; one type of stabilisation, increasing from Me to Bu^t, is due to the inductive effect of alkyl groups; the other type, increasing in the order $H < Bu^t < Pr^i < Et < Me$ and known as the Baker–Nathan effect, is the subject of controversy. Baker and Nathan[1] ascribed it to a mesomeric or electromeric electron release by alkyl groups (hyperconjugation) which is possible if at least one hydrogen atom is linked to a carbon atom attached to an unsaturated centre and which increases in importance with the number of hydrogen atoms so linked; structures like $H^{+}CH_2{:}CH\cdot\overset{-}{C}H_2$ in the case of propene are considered to contribute.

Burawoy and Spinner,[2] on the other hand, have criticised the theory of hyperconjugation and ascribed the Baker–Nathan effect to steric resistance to bond contraction. When an atom acquires a (partial) positive charge its bond radius contracts and the linkages attached to it become stronger with a consequent stabilisation of the molecule.[3] Such stabilisations will be referred to as contraction stabilisations. The contraction stabilisation incurred when the atom to which an alkyl group is attached acquires a (partial) positive charge decreases with the size of the group, *i.e.*, in the order $Me > Et > Pr^i > Bu^t$ ($\gg$ H*), owing to intramolecular steric repulsions.

One important difference between these two theories lies in the fact that hyperconjugation effects, like all mesomeric and electromeric effects, are true polar effects, *i.e.*, stabilisation is due to the transfer of electronic charge from the alkyl group to the electron-deficient centre. The contraction effect, on the other hand, is not a polar effect, contraction stabilisation being due essentially to increased orbital overlap giving rise to stronger σ-bonds. (This effect must not be confused with the bond shortening due to increased double-bond character which is demanded by the theory of hyperconjugation and inseparable from the electron-donating effect.) The total stabilisation of an electron-deficient entity by an alkyl group, due to the *sum* of the inductive + hyperconjugation *or* contraction effects, which will be called the apparent electron-donating effect of the alkyl group, is influenced by the reaction medium. It will be shown by a complete analysis of the energetics of a typical heterolytic reaction, *viz.*, the dissociation $R\cdot CMe_2Cl \longrightarrow R\cdot\overset{+}{C}Me_2 + \overset{-}{Cl}$ (studied in the present work), that the two theories lead to opposite predictions concerning the relative prominence of the Baker–Nathan effect in different media.

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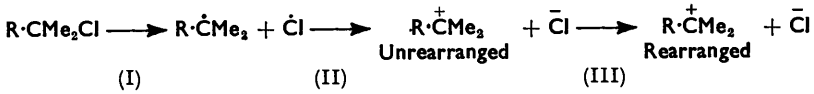
* The contraction of the C–H bond would be resisted by very formidable *internuclear* repulsions.

[1] Baker and Nathan, *J.*, 1935, 1844.

[2] Burawoy and Spinner, *J.*, 1954, 3752.

[3] Burawoy, "Contribution à l'Étude de la Structure Moléculaire," Desoer, Liège, 1948, p. 73; *Trans. Faraday Soc.*, 1944, **40**, 537; *Chem. and Ind.*, 1944, **63**, 434.

For energetic purposes the reaction may be considered to proceed by the following stages :



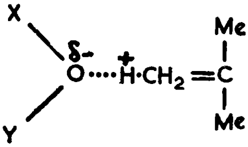
$$R{\cdot}CMe_2Cl \xrightarrow{(I)} R{\cdot}\dot{C}Me_2 + \dot{C}l \xrightarrow{(II)} \underset{\text{Unrearranged}}{R{\cdot}\overset{+}{C}Me_2} + \overset{-}{Cl} \xrightarrow{(III)} \underset{\text{Rearranged}}{R{\cdot}\overset{+}{C}Me_2} + \overset{-}{Cl}$$

[The relative positions of the atoms in $R{\cdot}CMe_2$ are considered to remain unchanged during stages (I) and (II).]

The (electronic) potential energy difference between the initial and the transition state consists of : (1) the energy of heterolytic fission of the C–Cl bond; (2) the ionisation potential of $R{\cdot}\dot{C}Me_2$ and the electron affinity of Cl, the latter being independent of R ; (3) the energy of rearrangement of the ion $R{\cdot}\overset{+}{C}Me_2$; (4) the difference between the energies of solvation of $R{\cdot}CMe_2Cl$ on the one hand and of $R{\cdot}\overset{+}{C}Me_2$ and $\overset{-}{Cl}$ on the other; (5) the difference in intramolecular van der Waals–London cohesion energy * between $R{\cdot}CMe_2Cl$ and $R{\cdot}\overset{+}{C}Me_2 + \overset{-}{Cl}$.

Factor (1) is almost independent of the polar effect of R but is affected by its size; if R is bulky, dissociation relieves intramolecular steric strain.[5] The ionisation potential of $R{\cdot}CMe_2$ (2) is determined by the polar effects of R, *i.e.*, by its ability to transfer electronic charge to C^+. Such a transfer will be strongly facilitated by the vicinity near R of the negative pole(s) of polar (or polarised) molecules. Factor (3) is composed of the relief in intramolecular steric strain obtained when the ion becomes planar [5] and the contraction stabilisations in the ion; both will be almost unaffected by the nature of the solvent.

The energy of solvation of $R{\cdot}\overset{+}{C}Me_2$ (4) is determined to some extent, but by no means wholly, by the ease with which the negative poles of the solvent molecules can approach C^+; this will be reduced if R is bulky,[6,5] the reduction being greatest in the solvents which solvate the cation most effectively. However, the transition state obtained in ionisation reactions consists of a pair of *partially* solvated ions; [7] the access of solvent molecules to C^+ is restricted in any case; the attractions between solvent and R itself (which is accessible) cannot be ignored. The intramolecular van der Waals–London attractive forces (5) stabilise the undissociated halide, stabilisation increasing with the number of atoms in R. However, these forces (which will be discussed fully in another publication) tend to be relatively less important in saturated systems; they will only be affected slightly by the solvent.



(IV)

Assistance of hyperconjugation by a solvent molecule, which increases with the electron availability on O, *illustrated for the* $[Me_3C]^+$ *ion.*

In most heterolytic reactions stabilisations due to polar effects (polar stabilisations) are decisive and factor (2) overshadows all others. Hyperconjugation transfers electronic charge more effectively than does the inductive effect and is the potentially stronger polar effect; Shiner [8] has already pointed out that it should be favoured by solvents which are good acceptors in hydrogen-bond formation (see IV). Kloosterziel and Backer [9] found that the (negative) Hammett's σ-value for the Me group is highest in the most polar solvent, but this can be due to enhancement of either the inductive or the hyperconjugation effect.

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* This type of molecular energy was first considered by Eyring.[4]

[4] Eyring, *J. Amer. Chem. Soc.*, 1932, **54**, 3191.

[5] Brown and Fletcher, *ibid.*, 1949, **71**, 1845; Brown and Stern, *ibid.*, 1950, **72**, 5068.

[6] Shorter and Hinshelwood, *J.*, 1949, 2412.

[7] Cf., *e.g.*, Ingold, " Structure and Mechanism in Organic Chemistry," Bell, London, 1953, p. 312.

[8] Shiner, *J. Amer. Chem. Soc.*, 1953, **75**, 2925; 1954, **76**, 1603.

[9] Kloosterziel and Backer, *ibid.*, 1952, **74**, 5806.

(The reaction studied, *viz.*, the addition of a proton to *p*-toluidine, is closely comparable to the ionisation of an alkyl halide. It is noteworthy that the σ-value of Me is highest in the most polar medium, although the better solvation of the N^+ atom could conceivably reduce the electron demand on the Me group.)

Since the Baker–Nathan effect is not observed in electronic absorption spectra, Burawoy and Spinner[10] conclude that it is not a polar effect, but related to factor (3). Energies of electronic excitation are composed of factors of the type of (2), (4), and (5), but not (1) or (3), and in some of the systems studied the polar stabilisation of the excited state by alkyl groups is very great. Sweeney and Schubert,[11] on the basis of the same evidence, also concluded that the Baker–Nathan effect cannot be a polar effect; confining their attention to cations (in general), they ascribe it to steric inhibition of solvation of the ion, *i.e.*, they regard it as related to factor (4) (this view has been criticised by Burawoy and Spinner[10]). To summarise, if the Baker–Nathan effect is a polar effect, *i.e.*, is due to hyperconjugation, *or* if it is due to steric inhibition of solvation, it should be most pronounced in solvents which solvate cations most effectively; if it is due to neither of these causes, these will be just the solvents in which the inductive effect is most prominent.

Little previous work on the variation with solvent of the apparent electron-donating effects of alkyl groups has been carried out. Hughes, Ingold, and Taher[12] found the Baker–Nathan effect in the solvolysis rates of the *p*-alkyldiphenylmethyl chlorides to be more prominent in 80% aqueous acetone than in pure ethanol. Berliner, Beckett, Blomers, and Newman[13] observed a pure Baker–Nathan order in the rates of alkaline hydrolysis of the ethyl *p*-alkylbenzoates in 85% aqueous ethanol, but a pure inductive order for the same reaction when carried out in 56% aqueous acetone (in which solvent the σ-value for Me itself is higher). The significance of these data (collected in Table 1) was difficult to assess. Ethanol and 80% aqueous acetone are solvents of similar ionising power; 56% aqueous acetone is a more highly polar medium than 85% aqueous ethanol.

TABLE 1. *Velocity constants in different solvents.*

Reaction		Medium	H	Me	Et	Pr^i	Bu^t
p-$C_6H_4R{\cdot}CHPhCl$ = *p*-$C_6H_4R{\cdot}CHPh^+ + Cl^-$	(*a*)	80% $COMe_2$	7·28	156	126	101	79·6
		EtOH	5·30	124	120	106	98·7
p-$C_6H_4R{\cdot}CO_2Et + OH^-$ = *p*-$C_6H_4R{\cdot}CO_2^- + EtOH$	(*b*)	56% $COMe_2$	2·89	1·18	1·06	0·964	0·908
		85% EtOH	0·614	0·273	0·293	0·314	0·342

(*a*) Values of 10^5k_1 (sec.$^{-1}$) at 25°. (*b*) Values of 10^3k_2 (l. mole^{-1} sec.$^{-1}$) at 25°.

In the present work the rates of ionisation of the series of halides $R{\cdot}CMe_2Cl$ (R = Me, Et, Pr^i, Bu^t) were studied in a number of solvents varying widely in polar properties. The results are collected in Table 2. Such halides undergo solvolysis by a unimolecular mechanism (ionisation) even in solvents of low polarity.[14] *iso*Propyl chloride (R = H) was not studied because the mechanism of solvolysis is uncertain in many solvents. The complete series of halides has been examined in 80% aqueous ethanol by Shorter and Hinshelwood[6] and by Brown *et al.*[5] Their results are included in Table 2.

The solvolyses in 70% aqueous methanol, 90% aqueous propan-1-ol, and 90% aqueous acetone are free from kinetic complications. In the case of the hydrolyses in 94% formic acid, which contained 1% of water, a slight excess of calcium formate over alkyl halide, and 5% of acetone (the presence of which is essential to ensure speedy dissolution of the higher halides at the commencement of reaction), the first-order velocity coefficients decrease as the reaction proceeds, presumably owing to reversibility of heterolysis (see Table 5); the values of the " constants " given in Table 2, being average values, are of little absolute significance, but they represent the relative reactivitites of the halides quite accurately. Measurement of the rate of hydrogen chloride generation in absolute propanol is complicated by the fact that there is appreciable reaction between hydrogen chloride and solvent at 35°; the allowance made for this is rather approximate. The accuracy

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[10] Burawoy and Spinner, *J.*, 1955, 2085.
[11] Sweeney and Schubert, *J. Amer. Chem. Soc.*, 1954, **76**, 4625.
[12] Hughes, Ingold, and Taher, *J.*, 1940, 949.
[13] Berliner, Beckett, Blommers, and Newman, *J. Amer. Chem. Soc.*, 1952, **74**, 4940.
[14] Hughes, *J.*, 1935, 255; Cooper and Hughes, *J.*, 1937, 1183.

TABLE 2. *Velocity constants for the reaction* $R{\cdot}CMe_2Cl \longrightarrow R{\cdot}CMe_2^+ + Cl^-$ *in different solvents.*[a]

Solvent	Temp.	R =	Me	Et	Pr^i	Bu^t
94% $H{\cdot}CO_2H$	15°	k_1 (1)	1·08	1·98	1·44	2·52
		(2)	1·02	1·74	1·32	2·40
		mean	1·05	1·86	1·38	2·46
		$k_{rel.}$	1·0	1·8	1·3	2·3
70% MeOH	35	k_1 (1)	0·830	1·65	1·13	1·88
		(2)	0·852	1·62	1·12	1·82
		mean	0·841	1·64	1·12	1·85
		$k_{rel.}$	1·00	1·95	1·33	2·20
80% EtOH	25 [b]	10^2k_1	3·3	5·5	2·9	4·0
		$k_{rel.}$	1·00	1·66	0·88	1·21
	35 [c]	10^2k_1	4·07	6·55	3·49	4·52
		$k_{rel.}$	1·00	1·61	0·86	1·11
90% Pr^nOH	35	10^2k_1 (1)	1·84	2·90	1·51	1·92
		(2)	1·87	2·91	1·54	1·92
		mean	1·86	2·91	1·53	1·92
		$k_{rel.}$	1·00	1·56	0·82	1·03
90% $COMe_2$	35	10^3k_1 (1)	1·43	2·20	1·46	2·76
		(2)	1·46	2·21	1·47	2·79
		mean	1·45	2·21	1·47	2·78
		$k_{rel.}$	1·00	1·52	1·01	1·92
100% Pr^nOH	35	10^3k_1 (1)	0·78	1·40	0·91	1·31
		(2)	0·82	1·45	0·92	1·33
		mean	0·80	1·43	0·92	1·32
		$k_{rel.}$	1·00	1·8	1·15	1·65

(*a*) For composition of solvents see Experimental section.
(*b*) Brown and Fletcher; Brown and Stern.[5]
(*c*) Shorter and Hinshelwood.[6]

of the absolute velocity constants obtained in this solvent is uncertain, but the relative rates are fairly accurate.

The order in which the various alkyl groups facilitate the ionisation of $R{\cdot}CMe_2Cl$ varies considerably from solvent to solvent; in formic acid and 70% aqueous methanol the inductive effect is preponderant, while in 90% aqueous propanol the inductive and the Baker–Nathan effect are about equally strong. There is, however, not complete regularity as between solvents; the ion-solvating powers decrease from 70% aqueous methanol to 80% aqueous ethanol to 90% aqueous propanol to 100% propanol, but these solvents do not form a continuous sequence. In Table 3 the solvents are listed in the order in which they enhance the activating effects of the various alkyl groups relative to methyl, and it is seen that for all groups the order is 70% MeOH $\gg$ 94% $H{\cdot}CO_2H$ > 80% EtOH > 90% PrOH; these solvents may be regarded as "normal." The positions of 90% aqueous acetone and propanol in the lists are, however, not fixed, and these two solvents, especially the latter, must be regarded as anomalous.

In Table 3 the solvents are also compared as regards their effects on absolute rates of ionisation, *i.e.*, their ionising power, and as regards the electrical conductivities which hydrogen chloride exhibits in them. All the lists are headed by the most polar solvents, but there is no strict parallelism between any of the properties listed.

The ionising power of a solvent depends on its ability to solvate both anion and cation (and solvation of the small anion is likely to be more important). The dimensions of the transition state, especially the C–Hal distance, will also be determined by the ionising power of the solvent, and since this factor could conceivably be of some importance there might be a parallelism between the solvent effects on absolute ionisation rates and the enhancement by the solvent of the activating effect of alkyl groups. Actually, there is no close parallelism, and this factor seems to be overshadowed (at least in the case of the "normal" solvents). As shown above, the apparent electron-donating effect of alkyl groups should depend on the ability of the solvent to solvate the cation. The electrical conductivities of the hydrogen chloride solutions depend on the basicities and ionising powers of the media, and on the mobility of the ions (*i.e.*, the weight and size of the solvent molecules); basicity and cation-solvating power are closely related properties depending on the electron availability at the negative pole of the molecule.

90% Aqueous acetone, which might be expected to be similar to 90% aqueous propanol, is more "polar" than expected as regards both its conducting power and its ability to enhance the apparent electron-donating effect of alkyl groups (especially of Bu^t). This is undoubtedly due to the structure of the acetone molecule: the negative end of the dipole, the oxygen atom, is readily accessible, while the positive end, the carbonyl-carbon atom, is inaccessible. As a result, acetone molecules should solvate anions very poorly but cations very effectively; the cation-solvating power of acetone will be further enhanced by the high polarisibility of the carbonyl group in the direction towards the oxygen atom. In view of Burawoy's arguments[3] against the concept of the delocalisation of electrons, the author regards this polarisibility as wholly inductomeric in nature, but according to conventional views the carbonyl group can also be regarded as possessing a high electromeric polarisibility towards oxygen.

TABLE 3. *Relative reactivities and absolute ionisation rates of* $\mathrm{R{\cdot}CMe_2Cl}$, *and the electrical conductivity of* HCl *solutions: order of solvents.*

Et/Me Rate ratio	70% MeOH	>	Pr^{n}OH	>	$\mathrm{H{\cdot}CO_2H}$	>	80% EtOH	>	90% Pr^{n}OH	>	90% $\mathrm{COMe_2}$
	1·95		1·8		1·8		1·61		1·56		1·52
Pr^i/Me Rate ratio	70% MeOH	>	$\mathrm{H{\cdot}CO_2H}$	>	Pr^{n}OH	>	90% $\mathrm{COMe_2}$	>	80% EtOH	>	90% Pr^{n}OH
	1·33		1·3		1·15		1·01		0·86		0·82
Bu^t/Me Rate ratio	70% MeOH	≈	$\mathrm{H{\cdot}CO_2H}$	>	90% $\mathrm{COMe_2}$	>	Pr^{n}OH	>	80% EtOH	>	90% Pr^{n}OH
	2·20		2·3		1·92		1·65		1·11		1·03
Absolute k_1 at 35° (a)	$\mathrm{H{\cdot}CO_2H}$	>	70% MeOH	>	80% EtOH	>	90% Pr^{n}OH	>	90% $\mathrm{COMe_2}$	>	Pr^{n}OH
	~20 (b)		1		5×10^{-2}		2×10^{-2}		2×10^{-3}		10^{-3}
$10^4 \times$ Spec. cond. of N/200-HCl in solvent at 35°	70% MeOH	>	$\mathrm{H{\cdot}CO_2H}$ (c)	≈	80% EtOH	>	90% $\mathrm{COMe_2}$	>	90% Pr^{n}OH	>	Pr^{n}OH
	7·2		4·2		4·1		3·1		1·9		1·3

The rate ratios in the solvent 94% $\mathrm{H{\cdot}CO_2H}$ given here were determined at 15°; they must be lowered slightly to be comparable with the other rate ratios, determined at 35°.

(*a*) Approx. average for all chlorides. (*b*) Estimated.

(*c*) Estimated; the conductivity of N/200-HCl in pure $\mathrm{H{\cdot}CO_2H}$ at 25° is 0·00035,[15] that of 80% EtOH at 25° is 0·00034.

Propan-1-ol, the least polar of the solvents examined, has the lowest ionising and conducting powers, but it does not occupy an extreme position as regards its ability to enhance the apparent electron-donating effects of alkyl groups. For some reason the higher alkyl halides ionise more readily in this solvent than might be expected. In water-free solvents of very low polarity the solvation of the cation is probably due largely to van der Waals–London as well as electrostatic attractive forces. In addition, the nature of the transition state is likely to be somewhat different in these solvents.

As regards the "normal" solvents, the position is clear. The order in which these solvents favour the inductive effect at the expense of the Baker–Nathan effect is 70% MeOH ≈ 94% $\mathrm{H{\cdot}CO_2H}$ > 80% EtOH > 90% Pr^{n}OH; *i.e.*, the inductive order becomes more prominent as the cation-solvating power of the solvent increases. This supports the idea that the Baker–Nathan effect is neither a polar effect, *i.e.*, not due to hyperconjugation, nor the consequence of steric inhibition of cation solvation (which is completely over-shadowed by other effects; the greater the intramolecular transfer of electronic charge to the C^+ atom, the less will be the importance of solvation of that atom). The results are in agreement with the view that the Baker–Nathan effect is due to steric resistance to bond contraction, and that the only *true* polar effects exerted by alkyl groups are of the inductive and inductomeric type.

EXPERIMENTAL

Materials.—Liquid alkyl halides were purified by alternate fractional distillation and fractional freezing; *tert.*-butyl chloride had b. p. 49·5°/736 mm., m. p. −23°; 1 : 1-dimethylpropyl chloride had b. p. 85°/750 mm., m. p. −73°; 1 : 1 : 2-trimethylpropyl chloride had b. p.

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[15] Schlesinger and Martin, *J. Amer. Chem. Soc.*, 1914, **36**, 1589.

110°/770 mm., m. p. −11°. 1 : 1 : 2 : 2-Tetramethylpropyl chloride[16] was purified by recrystallisation from absolute methanol and sublimation *in vacuo* to give transparent plates of m. p. 129° (in a sealed capillary tube).

Solvents.—70% Aqueous methanol : 600 ml. of water made up to 2 l. (at room temp., *ca* 17·5°) with pure lime-dried methanol. 90% Aqueous propan-1-ol and 90% aqueous acetone : 200 ml. of water made up to 2 l. (at room temperature) with pure lime-dried propanol and pure Anhydrone-dried acetone, respectively. 100% Propanol was lime-dried. 94% Formic acid : see below.

Rate Determinations in Solvents Other than 94% Formic Acid.—Normally, 0·7—0·9 g. of alkyl halide at 35° was dissolved in 100 ml. of solvent at 35°. In the case of 1 : 1 : 2 : 2-tetramethylpropyl chloride in 70% aqueous methanol, direct dissolution being too slow, the halide was dissolved quickly in 36·6 ml. of pure methanol and a mixture of 15 ml. of water and 50 ml. of aqueous methanol at 35° was added rapidly and with stirring, giving a final solvent composition identical with that of 70% aqueous methanol. In all other instances the same sample of solvent was used for all halides.

The rate of hydrogen chloride generation was followed conductometrically; the cell was fitted with platinised-platinum electrodes and a mechanical stirrer, and the cell constant was checked before and after each determination. Charts showing conductivity against hydrogen chloride concentration were prepared for each solvent used. The conductivities of hydrogen chloride solutions in absolute propanol decrease with time, quite rapidly at first, more slowly later (after some water has been formed); the conductivities used in the chart were those obtained after time intervals comparable with those encountered in rate determinations.

The reactions in 70% aqueous methanol were followed to completion, equilibrium corresponding to about 99% of solvolysis. In the other solvents reactions were pursued up to 10—15% of solvolysis; the velocity coefficients calculated are those for first-order irreversible reactions. In all cases total halide contents (ionised + labile organic) were estimated by titration of samples of the reaction mixture by Volhard's method. Data for one typical solvolysis in each solvent are shown in Table 4. The reaction between hydrogen chloride and absolute propanol is responsible for the observed gradual decrease in the velocity coefficient in this solvent.

TABLE 4. *Solvolyses at 35°.**

CMe_2Pr^iCl in 70% aq. MeOH : a = 69·8			CMe_2EtCl in 90% aq. $COMe_2$: a = 70·9			CMe_2Bu^tCl in 90% aq. Pr^nOH : a = 67·5			CMe_3Cl in Pr^nOH : a = 54·3		
t (min.)	x	10^2k	t (hr.)	x	10^3k	t (hr.)	x	10^2k	t (hr.)	x	10^4k
5	6·1	1·83	2	0·31	2·19	0·5	0·63	1·88	16	0·7	8·1
10	11·9	1·87	4	0·63	2·23	1·0	1·28	1·91	20	0·85	7·9
15	17·1	1·87	6	0·94	2·22	1·5	1·90	1·92	24	1·02	8·0
20	21·75	1·87	8	1·24	2·19	2·0	2·55	1·93	40	1·68	7·8
25	26·0	1·86	10	1·53	2·19	2·5	3·17	1·93	44	1·82	7·7
30	29·7	1·85	25	3·77	2·18	3·0	3·76	1·91	48	2·0	7·8
35	33·5	1·87	27·5	4·14	2·19	3·5	4·36	1·91	64	2·63	7·8
40	36·75	1·87	30	4·52	2·20	4·0	4·96	1·91	68	2·77	7·7
45	39·75	1·87	32	4·80	2·19	4·5	5·57	1·91	72	2·93	7·7
50	42·5	1·88	47·5	7·13	2·23	5·0	6·16	1·91	88	3·50	7·6
55	44·9	1·87	50	7·48	2·23	5·5	6·76	1·91		Mean	7·8
60	47·2	1·88	52·5	7·82	2·23	6·0	7·37	1·93			
70	51·1	1·88	55	8·17	2·22	6·5	7·98	1·94			
80	54·3	1·88		Mean	2·21	7·0	8·53	1·93			
90	57·0	1·89				7·5	9·07	1·93			
100	59·2	1·90				8·0	9·65	1·93			
110	60·9	1·90					Mean	1·92			
120	62·4	1·91									
∞	69·2	—									
	Mean	1·88									

* a and x denote the initial concentration of alkyl halide and the concentration of hydrogen chloride after time t (in ml. of N/10), respectively.

Rate Determinations in 94% Formic Acid.—These were carried out by a modification of the method of Bateman and Hughes.[17] A solution of calcium formate (0·32 g.) and water (0·5 ml.)

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[16] Calingaert, Soroos, Hnidza, and Shapiro, *ibid.*, 1944, **66**, 1389.

[17] Bateman and Hughes, *J.*, 1937, 1187; 1940, 935.

TABLE 5. *Hydrolysis of* CMe_2RCl *in* 94% *formic acid, in the presence of excess of calcium formate, at* 15°.*

t (min.)		5	10	15	20	25	30	40	50	60	∞ †
Me	x	3·77	6·1	8·4	9·25	—	12·05	14·0	—	18·0	32·3
$a = 33·3$	10^2k	2·4	2·0	1·9	1·6	—	1·5	1·4	—	1·3	1·8 ‡
Me	x	3·15	5·22	6·8	8·1	—	10·75	13·1	—	17·0	29·3
$a = 30·2$	10^2k	2·2	1·9	1·7	1·6	—	1·5	1·4	—	1·4	1·7 ‡
Et	x	8·15	10·85	13·55	16·0	17·75	19·7	24·8	—	—	32·5
$a = 36·5$	10^2k	5·0	3·5	3·2	2·9	2·8	2·7	3·0	—	—	3·3 ‡
Et	x	5·7	9·0	12·15	14·7	17·7	18·95	23·1	—	—	32·7
$a = 35·0$	10^2k	3·6	3·0	2·8	2·7	2·9	2·6	2·8	—	—	2·9 ‡
Pr^i	x	4·8	7·6	—	13·05	—	17·0	20·05	23·0	25·4	33·2
$a = 36·6$	10^2k	2·8	2·4	—	2·2	—	2·1	2·0	2·0	2·1	2·2 ‡
Pr^i	x	5·7	8·6	—	12·9	—	17·0	20·05	22·8	24·9	33·05
$a = 36·35$	10^2k	3·4	2·7	—	2·2	—	2·1	2·1	2·0	2·0	2·4 ‡
Bu^t	x	7·35	10·95	14·2	16·8	18·85	20·65	23·3	—	—	29·25
$a = 31·25$	10^2k	5·5	4·4	4·3	4·2	3·7	3·8	3·7	—	—	4·2 ‡
Bu^t	x	—	10·9	13·85	16·55	18·65	20·2	24·0	—	—	28·3
$a = 30·7$	10^2k	—	4·4	4·0	4·0	3·9	3·7	4·2	—	—	4·0 ‡

* a and x are the initial concentration of alkyl halide and the concentration of chloride ion after time t respectively. † 20—30 Hr. ‡ Average value of 10^2k.

in formic acid (m. p. 8·3°) (total volume 50 ml.) at 15° was added to a solution of alkyl halide (0·35—0·5 g.) in acetone (2·5 ml.) rapidly and with vigorous shaking; 5-ml. samples were pipetted into tubes which after specified periods were immersed in solid carbon dioxide; carbon tetrachloride (15 ml.) was added, the mixture was extracted with water (2 × 15 ml.), and the chloride was titrated (Volhard's method). The total halide content (ionised + labile organic) was estimated similarly, 5-ml. portions of formic acid solution being added directly to excess of silver nitrate solution (containing some ethanol).

The velocity coefficients are those for a first-order reaction opposed by one of the second order. (The occurrence of the reverse reaction between *tert.*-butyl alcohol and calcium chloride was observed in this medium.) The coefficients decrease as the reaction proceeds; for *tert.*-butyl chloride the *initial* coefficient agrees closely with the value obtained by Bateman and Hughes[17] for hydrolysis in slightly aqueous formic acid containing no calcium formate ($2·3 \times 10^{-2}$ min.$^{-1}$). Complete results appear in Table 5.

FACULTY OF TECHNOLOGY, UNIVERSITY OF MANCHESTER. [*Received, July* 19*th*, 1955.]