509. *The Kinetics of the Hydrolysis of Some Tertiary Aliphatic Halides.*

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Velocity constants and (usually) Arrhenius constants have been measured for the unimolecular hydrolysis, in aqueous alcohol, of three series of tertiary aliphatic chlorides and iodides, namely,

I CMe_3X, CMe_2EtX, $CMeEt_2X$, CEt_3X;
II CMe_2RX, where R = Me, Et, Pr^n, Bu^n, or *n*-amyl;
III CMe_2RX, where R = Me, Et, Pr^i, or Bu^t.

Replacement of methyl by ethyl always increases reactivity, but other substitutions have more complex results. The structural influence is discussed (*a*) in terms of a competition between electron release and steric effects and (*b*) in terms of the view that the electron-release effect is itself composite.

Chlorides have lower Arrhenius non-exponential factors than have iodides, and appear to demand a greater contribution from solvation energy (achieved by more precise orientation of solvent molecules).

The influence of alkyl groups on rates and equilibria is perplexing, because some of the phenomena stand in sharp contrast with others, and quite diverse effects have been postulated to explain experimental results. It was thought that a study of the influence of structure on the rate of hydrolysis of tertiary aliphatic halides might contribute to the clarification of the problem.

Ingold, Hughes, and others have made extensive studies of the hydrolysis of *tert.*-butyl and *tert.*-amyl halides (*J.*, 1935, 255; 1937, 1183, 1187, 1280, 1283; 1938, 881. Summaries in *Trans. Faraday Soc.*, 1938, **34**, 185; 1941, **37**, 603; *J.*, 1946, 968). The hydrolysis of these compounds in aqueous solvents does not require the presence of hydroxyl ions, being kinetically of order zero with respect to them, and of first order with respect to the halide. The kinetics suggest a rate-determining ionisation :

$$R_1R_2R_3CX + \text{solvent} = \underset{\text{solvated}}{R_1R_2R_3C^+} + \underset{\text{solvated}}{X^-}$$

The carbonium ion is supposed to react rapidly with any nucleophilic reagent present :

$$R_1R_2R_3C^+ + \genfrac{}{}{0pt}{}{H_2O}{EtOH} = \text{Tertiary alcohol, ether, or olefin} + \underset{\text{solvated}}{H^+}$$

(The part played by the solvent molecules in the first stage is a matter open to question but need not be considered here.)

The mechanism applies to tertiary halides and to the first-order hydrolysis of secondary halides, and has been confirmed by numerous observations on solvent and structural effects, stereochemistry, analysis of reaction products, and isotope exchange.

The present work consists of a survey of the reactivities of a considerable number of higher tertiary chlorides and iodides of varied structure. The compounds not available commercially were prepared from the alcohols which in turn were made by Grignard reactions.

The hydrolysis in aqueous alcoholic solution was followed by conductometric determination of the hydrogen halide formed.

EXPERIMENTAL.

Materials.—The solvent used throughout was a mixture of ethyl alcohol (76% by weight) and water and was thus approximately of the same composition as the " 80% alcohol " (by volume) used in the work of Hughes and Ingold. It was made up from specially dried and fractionated alcohol. One single batch was used for the entire investigation.

The method employed for following the reaction did not require a given halide to be absolutely pure provided that no other tertiary halide was present, and, since many of these compounds are difficult to separate completely from the alcohols, we preferred, rather than to devote considerable time to the fractionation of elaborately dried products, to use the specimens as prepared by direct treatment of the corresponding alcohol with the hydrogen halide. It was then shown that possible solvent effects of impurities would not affect the conclusions. The identity of the compounds is quite certain from the mode of preparation, and, as will appear, the velocity constants of all the halides form a coherent system. The preparations are exceedingly unlikely to yield any tertiary halides but those expected, and compounds other than tertiary have rates of hydrolysis quite negligible in comparison.

tert.-Butyl iodide and chloride, and *tert.*-amyl chloride : commercial specimens were available of purity over 90%, which was sufficient for the purpose.

tert.-Amyl iodide : a commercial specimen was fractionated as carefully as possible but the final specimen contained only 65% of the tertiary compound. The remainder, which may have been *neo*pentyl iodide, was hydrolysed so slowly that it had no influence on the measurements with the *tert.*-amyl iodide itself.

Higher tertiary alcohols and halides : the alcohols were prepared by one or other of the following Grignard reactions :

$$\begin{array}{llll}(a) & R{\cdot}CO_2Et + 2EtMgBr & \longrightarrow & REt_2C{\cdot}O{\cdot}MgBr + MgBr{\cdot}OEt \\ & REt_2C{\cdot}O{\cdot}MgBr + H_2O & \longrightarrow & REt_2C{\cdot}OH + MgBr{\cdot}OH \\ (b) & Me_2CO + RMgBr & \longrightarrow & RMe_2C{\cdot}O{\cdot}MgBr \\ & RMe_2C{\cdot}O{\cdot}MgBr + H_2O & \longrightarrow & RMe_2C{\cdot}OH + MgBr{\cdot}OH\end{array}$$

The tertiary alcohols were distilled, the middle fractions being collected and converted into halides by saturation with the gaseous hydrogen halide. After removal of excess of the hydrogen halide and of any iodine and water, the tertiary halides were generally used for the kinetic studies without further attempts to separate them from unchanged alcohols. The specimens usually contained from 50 to 80% of tertiary halide. In two cases (dimethyl-*n*-butyl- and dimethyl*iso*propyl-carbinyl iodides) the crude halide was distilled under reduced pressure so as to raise the purity to about 80%.

Hydrolysis Measurements.—All the tertiary halides were assumed to hydrolyse by the above-mentioned mechanism, and the reaction was assumed to be irreversible under the conditions of the experiment, as shown by Hughes for *tert.*-butyl and *tert.*-amyl halides in " 80% alcohol." On this basis conductometric measurement of the rate of formation of hydrogen halide indicates the course of the simple unitary ionisation process.

In dilute solution the hydrogen halides are completely ionised and their ions are effectively the only conducting species present. The conductivity was assumed to be proportional to the concentration of the hydrogen halide and to indicate at any instant the amount of hydrolysis that had occurred. In the concentration range employed the equivalent conductivities were thus regarded as constant, an assumption justified by the results. Good first-order curves were obtained, and the constants for *tert.*-butyl and *tert.*-amyl halides were in essential agreement with those of Hughes for a solvent of nearly the same composition. Variations in equivalent conductivities would be revealed by deviations from first-order law. The conductometric method was applicable to reactions with times of half change from 40 seconds to many hours, and its ease and speed allowed numerous readings to be taken in a given experiment. In all but the slowest reactions the hydrolysis could be followed nearly to the end, and often a direct reading of the end-point was possible. The concentration range was below M/20. This was necessary to ensure the validity of the assumption of constant mobilities, and also to diminish solvent effects, which appear when large amounts of halide are added to the solvent (Hughes, *J.*, 1935, 255).

The conductivities were measured on a direct-reading oscillator bridge (Cambridge Instrument Co.). The same tube constituted reaction vessel and conductivity cell. It had platinum-black electrodes which did not need to be re-platinised during the course of the work. Since the bridge readings could be used directly in the calculation of velocity constants, the first-order constant being independent of concentration units, the cell constant had not to be determined. Electrically controlled oil-, water- or glycerol-thermostats were used (with cooling coils when necessary), adjustable to 0·05° and checked against standard thermometers.

General Experimental Procedure.—About 40 ml. of aqueous alcohol were placed in a closed tube in the thermostat, alongside a second tube containing 0·2—0·3 ml. of tertiary halide (or a corresponding amount of solid halide, finely ground) and a third tube containing the electrode unit with leads connected to the bridge. When the tubes had reached a steady temperature the halide was rapidly poured into the solvent which was vigorously stirred while a stop watch was started. The electrode unit was then inserted into the reaction tube, and the change of conductivity with time was measured. According to the speed of the reaction one of two methods of taking the readings was employed. If the rate was low, the bridge could be balanced and read in the normal way; if high, the bridge was set ahead of the balance point and, when extinction of sound in the earphones occurred, the stop-watch reading was taken. Observations were made for as long as required by the method to be used for evaluating the results (see below).

Evaluation of Velocity Constants and Arrhenius Constants.—With some of the halides the end-point could be measured directly or obtained by a short extrapolation, and one of the usual methods was used for evaluating velocity constants. When, however, the reaction was too slow to be followed conveniently over more than about 75% of its course, the velocity constants were computed by a special method. This applied mainly to the chlorides. Even though some of them admitted direct observation of the end-point, experiments with chlorides did not give good results when the usual method was used. During the last 10% of the reaction there was a deviation from the first order and the observed end-point appeared too high as judged from the earlier part of the curve. The cause of the effect is not known but it may have been due to some electrode phenomenon. Accordingly all the velocity constants for chlorides were computed by a method which did not involve more than about 80% of the reaction or require a knowledge of the end-point.

When the end-point could be observed directly, the graph of conductivity against time was plotted and a new zero selected to eliminate errors due to uncertainty about the initial time. Conductivity was then taken as proportional to amount of reaction, and final conductivity to initial concentration of halide. A graph of percentage reaction against time was then plotted from the new origin and values of k were calculated from the readings for 0 and 50%, 10 and 60%, and so on up to 40 and 90%, whereby equal weight was given to all parts of the curve. The method is illustrated in Table I for the hydrolysis of dimethyl-*n*-propylcarbinyl iodide at 25·0°. Even with the faster reactions the average error of the five values of the constant usually did not exceed 2% and generally was about 1%. Moreover, the constants seldom showed any systematic trend. The absolute error of the mean value was probably between 1 and 2%. Three separate determinations for *tert.*-butyl iodide at 35·0° gave for k the values 3·10, 3·11, and 3·15 × 10^{-3} sec.$^{-1}$.

With iodides whose reactions went to completion too slowly for convenience the end-point was obtained by extrapolation. The method was to estimate approximately the time of half change from the reaction curve up to about 97% and then to calculate an increment to apply to the last reading taken. The method is illustrated in Table II for the hydrolysis of methyldiethylcarbinyl iodide at 5·0°.

When the end-point was unknown, as with all the chlorides and with dimethyl-*tert.*-butylcarbinyl iodide at 5·0°, the following method was used. If in the formula $k = \frac{2{\cdot}303}{t_2 - t_1} \log \frac{a - x_1}{a - x_2}$ the values of x_1 and x_2 are taken so that $t_2 - t_1$ is constant, $(a - x_1)/(a - x_2)$ is also constant $= c$. Therefore, $x_1 = cx_2 + a(1 - c)$. From the linear plot of x_1 against x_2 c can be found and, from it and the value of $t_2 - t_1$, k can be calculated. The method gave good results with $t_2 - t_1$ approximately equal to $t_{1/2}$. The reproducibility of the results is illustrated in Table III.

A more detailed example is shown in Table IV.

The constants of the Arrhenius equation were calculated in the usual way from graphs of log k against $1/T$. The activation energies so obtained are probably correct to within about 300 cals./mole. Values of velocity constants are given in Tables V and VI, and of Arrhenius constants in Table VII.

Effect of Impurities.—Hughes found the velocity of hydrolysis of certain tertiary halides to be rather sensitive to changes in the composition of the solvent, which alter the non-exponential factor of the Arrhenius equation (*J.*, 1935, 255). The *tert.*-amyl iodide used in the present work may have contained some *neo*pentyl iodide, but the two substances are so similar that the impurity should cause no appreciable solvent effect. The most important impurity was in general the corresponding alcohol. If this exerted any serious solvent effect the velocity constants should change systematically as reaction proceeds:

no such effect has been found. Experiments made with *tert.*-butyl iodide showed that much larger amounts of ether than could possibly have been left from the Grignard preparation exerted no detectable solvent effect (compare Tables VI and V).

TABLE I.

*Hydrolysis of dimethyl-*n*-propylcarbinyl iodide at* 25·0°.

Directly measured end-point, 0·00688; new origin at t = 120 secs.; new end-point 0·00688 − 0·00136 = 0·00552.

Time (sec.).	Conductivity (mhos).	Time from new zero.	% change from new zero.
54	0·0007		
72	0·0009		
102	0·0012		
134	0·0015	14	2·5
166	0·0018	46	8·0
201	0·0021	81	13·4
226	0·0023	106	17·0
252	0·0025	132	20·7
18 other readings			
1800	0·00656	1680	94·1
2100	0·00670	1980	96·6

x_2. %	x_1. %	t_2.	t_1.	$k = \frac{2{\cdot}303}{t_2 - t_1}\log_{10}\frac{a - x_1}{a - x_2}$ (sec.$^{-1}$).
50	0	399	0	$1{\cdot}735 \times 10^{-3}$
60	10	525	58	1·735
70	20	690	125	1·740
80	30	925	204	1·735
90	40	1323	295	1·740

Mean value of $k = 1{\cdot}735 \times 10^{-3}$ sec.$^{-1}$ at 25·0°.

TABLE II.

Hydrolysis of methyldiethylcarbinyl iodide at 5·0°.

Last reading taken, 0·00310 at 230 mins. Approx. time of half change, 43 mins. (= $t_{1/2}$). 230 = $5{\cdot}35t_{1/2}$ approx. Therefore change at 230 mins. = 97·4%. Thus end-point is at 0·00310 × 100/97·4 = 0·00318. New origin at t = 10 mins. New end-point = 0·002705.

Range, %	0—50	10—60	20—70	30—80	40—90
10^2k (min.$^{-1}$)	1·522	1·522	1·530	1·526	1·533

Mean value of $k = 1{\cdot}527 \times 10^{-2}$ min.$^{-1}$ = $2{\cdot}55 \times 10^{-4}$ sec.$^{-1}$.

TABLE III.

Reproducibility of results; k *in sec.*$^{-1}$.

	I.	II.	
CMe_3Cl, 35°	4·02	4·12	$\times 10^{-5}$
CMe_3Cl, 70°	1·55	1·525	$\times 10^{-3}$
CMe_2EtCl, 45°	1·98	1·945	$\times 10^{-4}$
CMe_2Bu^nCl, 35°	5·42	5·45	$\times 10^{-5}$

TABLE IV.

*Hydrolysis of dimethyl-*n*-propylcarbinyl chloride at* 35·0°.

$t_2 - t_1$ = 200 mins.

Time (mins.)	10	20	30	40	. . . 25 other . . .	405	421
Cond. (mhos) × 10^6	343	591	810	1015	. . . readings . . .	4980	5060

t_1.	t_2.	10^6x_1.	10^6x_2.	t_1.	t_2.	10^6x_1.	10^6x_2.
20	220	591	3570	120	320	2370	4445
40	240	1010	3760	140	340	2650	4580
60	260	1395	3945	160	360	2910	4710
80	280	1745	4120	180	380	3145	4830
100	300	2065	4280				

c = 1·99, whence $k = 5{\cdot}74 \times 10^{-5}$ sec.$^{-1}$ at 35·0°.

TABLE V.

Velocity constants.

Compound.	Temp.	10^5k (sec.$^{-1}$).	Compound.	Temp.	10^5k (sec.$^{-1}$).
$\mathrm{CMe_3I}$	15	25·5	n-$\mathrm{C_5H_{11}{\cdot}CMe_2I}$	15	42·0
	25	92·6		25	143
	35	310		35	474
	45	980		45	1440
$\mathrm{CMe_2EtI}$	15	52·3	$\mathrm{CMe_3Cl}$	35	4·07
	25	188·5		45	12·5
	35	575		60	59·3
	45	1670		70	153·8
$\mathrm{CMeEt_2I}$	5	25·5	$\mathrm{CMe_2EtCl}$	35	6·55
	15	95·1		45	19·62
	25	324		60	89·75
	35	975		70	224·8
$\mathrm{CMe_2Pr^nI}$	15	50·0	$\mathrm{CMeEt_2Cl}$	25	2·95
	25	173·5		35	9·06
	35	550		45	28·1
	45	1625		60	129·5
$\mathrm{CMe_2Pr^iI}$	15	41·5	$\mathrm{CEt_3Cl}$	25	3·27
	25	149·5		35	10·6
	35	504		45	31·3
	45	1395		60	141·5
$\mathrm{CEt_3I}$	5	42·2	$\mathrm{CMe_2Pr^nCl}$	35	5·72
	15	152			
	25	453	$\mathrm{CMe_2Pr^iCl}$	35	3·49
	35	1360			
			$\mathrm{CMe_2Bu^nCl}$	35	5·43
$\mathrm{CMe_2Bu^nI}$	15	45·4			
	25	165	$\mathrm{CMe_2Bu^tCl}$	35	4·52
	35	543			
	45	1595	n-$\mathrm{C_5H_{11}{\cdot}CMe_2Cl}$	35	4·94
$\mathrm{CMe_2Bu^tI}$	5	19·0			
	15	71·6			
	25	263			
	35	821			

TABLE VI.

Solvent effect (at 35°) of impurities.

Impurity.	Vol. (in 40 ml.) of impurity.	Vol. of $\mathrm{CMe_3I}$.	10^5k.
Diethyl ether	0·1 ml.	0·2 ml.	310, 312
Light petroleum	0·2 ml.	0·1 ml.	294, 295

TABLE VII.

Constants of Arrhenius equation, $k = Ae^{-E/RT}$.

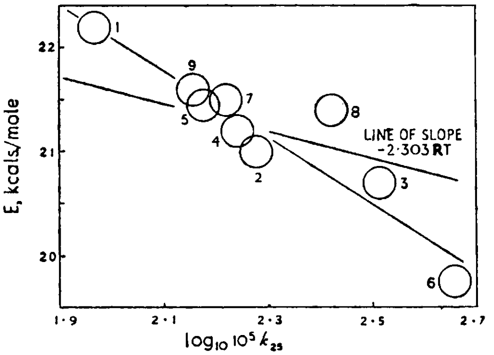
Compound.	E, cals./mole.	$A \times 10^{-10}$	Compound.	E, cals./mole.	$A \times 10^{-10}$.
$\mathrm{CMe_3I}$	22,200	1740	$\mathrm{CMe_2Bu^tI}$	21,400	1260
$\mathrm{CMe_2EtI}$	21,000	480	n-$\mathrm{C_5H_{11}{\cdot}CMe_2I}$	21,600	1050
$\mathrm{CMeEt_2I}$	20,700	470	$\mathrm{CMe_3Cl}$	21,700	10·5
$\mathrm{CMe_2Pr^nI}$	21,200	603	$\mathrm{CMe_2EtCl}$	21,200	6·9
$\mathrm{CMe_2Pr^iI}$	21,450	710	$\mathrm{CMeEt_2Cl}$	21,500	16·9
$\mathrm{CEt_3I}$	19,750	145	$\mathrm{CEt_3Cl}$	21,250	12·9
$\mathrm{CMe_2Bu^nI}$	21,500	960			

In order to find an extreme upper limit to any effect of other impurities *tert.*-butyl iodide containing about 70% of light petroleum was tested and found to give a velocity constant at 35·0° only about 5% lower than the normal. No more unfavourable impurity than this completely non-polar substance could possibly have been present in anything like this amount, so that this experiment provides a severe test. Even if all the impurity in each halide were assumed to be of the nature of light petroleum and due allowance made for the solvent effect, the conclusions to be drawn in the Discussion would not be changed.

Comparison with the Results of Hughes for tert.-*Butyl and* tert.-*Amyl Halides.*—The solvent used in this work is slightly different from that used by Hughes, so that only approximate agreement can be expected. For *tert.*-butyl iodide Hughes (*J.*, 1937, 1183) found $k = 9{\cdot}13 \times 10^{-4}$ sec.$^{-1}$ at 25·15° compared with the present value of $9{\cdot}26 \times 10^{-4}$ at 25·0°. When allowance is made for the slight difference of temperature, the latter result is about 6% higher. Hughes found $E = 22{,}400$ between 0° and 25°; we find 22,200 between 15° and 45°. With *tert.*-amyl iodide Hughes (*J.*, 1937, 1283) obtained $k = 1{\cdot}74 \times 10^{-3}$ sec.$^{-1}$ at 25·2°, whereas we find $1{\cdot}885 \times 10^{-3}$ at 25·0°. Corrected for temperature difference, the latter result is about 12% higher. In view of the sensitiveness of the reactions to solvent influences the agreements are satisfactory. For *tert.*-butyl chloride Hughes (*J.*, 1935, 255) gives $k = 3{\cdot}25 \times 10^{-5}$ at 35° and $10{\cdot}4 \times 10^{-5}$ sec.$^{-1}$ at 45°. The present values are $4{\cdot}07 \times 10^{-5}$ and $12{\cdot}5 \times 10^{-5}$, respectively, that is about 20% higher. Between 8° and 45° Hughes found 23,060 for the activation energy, whereas between 35° and 70° we find 21,700. For *tert.*-amyl chloride Hughes (*J.*, 1937, 1283) found $k = 2{\cdot}85 \times 10^{-4}$ sec.$^{-1}$ at 50°, compared with the present value (interpolated) of $3{\cdot}16 \times 10^{-4}$ which is about 10% higher. From Hughes's values of k at 25·2° and 50°, the activation energy is 22,700 compared with our value of 21,200.

FIG. 1.

E *against log* k *for tertiary iodides.*



1, CMe_3I. 2, CMe_2EtI. 3, $CMeEt_2I$. 4, CMe_2Pr^nI. 5, CMe_2Pr^iI. 6, CEt_3I. 7, CMe_2Bu^nI. 8, CMe_2Bu^tI. 9, $n\text{-}C_5H_{11}{\cdot}CMe_2I$.

On the whole, therefore, the results for the chlorides agree less closely than those for the iodides with those obtained by Hughes. This probably is due to the more important part which the solvent appears to play in the hydrolysis of the chlorides. The difference in activation energy may depend to some extent upon a variation of E with temperature for *tert.*-butyl and *tert.*-amyl chlorides, both the present series of measurements having covered a higher temperature range than that used by Hughes. A change of E with T in this sense is not unreasonable in itself. Everett and Wynne-Jones (*Trans. Faraday Soc.*, 1939, **35**, 1380) have shown that in the dissociation of organic acids there is a difference in the specific heats of the undissociated acid and the ions which causes a marked variation in ΔH with T. C_p for undissociated acid and solvent is greater than for the solvated ions where solvent molecules are oriented with loss of various degrees of freedom. The orientation of solvent molecules in the transition state for the halide ionisation should produce a diminution of specific heat and consequent variation of E with T according to the equation $dE/dT = C_p(\text{transition state}) - C_p(\text{initial state})$ which will predict a negative value. Such an effect should be more important for the chlorides, where solvation seems to play a greater part than with the iodides (see later).

DISCUSSION.

Relation between E *and log* k *for the Tertiary Iodides.*—In Fig. 1 are plotted values of E and of $\log_{10} 10^5 k_{25}$ for these compounds. In general, increased reactivity is associated with a diminution in activation energy, although the position of dimethyl-*tert.*-butylcarbinyl iodide is anomalous in this respect. If the non-exponential factor, A, were constant throughout, the points would lie around a line of slope $-2{\cdot}303\boldsymbol{R}T$, whereas actually a trend of greater slope is indicated. A varies so as to compensate partly the changes in E. Such compensation effects are not at all uncommon (references : Hinshelwood, " Kinetics of Chemical Change," Oxford, 1940, p. 257).

Differences between Iodides and Chlorides.—In general the tertiary iodides are about 100 times as reactive as the corresponding chlorides, the difference residing mainly in *A*. The obvious interpretation of the lower values for the chlorides is that these require a more highly ordered and so less probable arrangement of the solvent molecules in the transition state. In this sense solvation might be said to play a more important part in the ionisation of the chlorides than in that of the iodides.

FIG. 2.

Effect of structure on reactivity for tertiary chlorides.

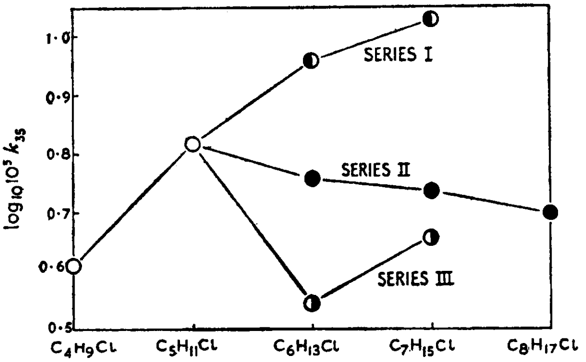
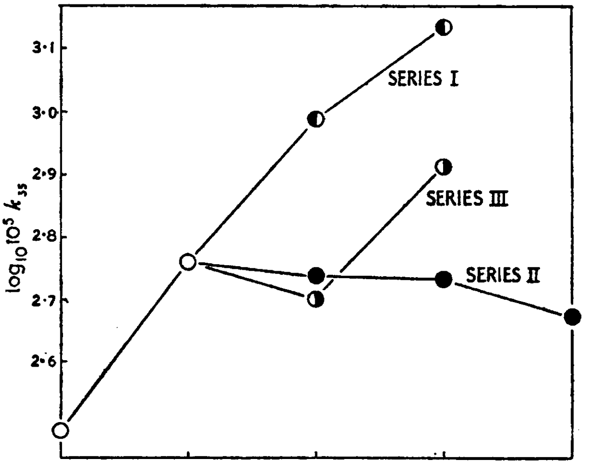


FIG. 3.

Effect of structure on reactivity for tertiary iodides.



There is independent evidence that this is so from the values of *E* themselves. For the chlorides they are little different from those of the iodides. The activation energies for the formation of unsolvated ions would be considerably greater for the chlorides and, since they are not so for the reactions in solution, it seems that the chlorides make the greater use of solvation energy. For this purpose more exact orientation is demanded, with the result that, although the values of *E* are not very different from those of the iodides, the non-exponential factor is adversely affected.

Variation of Reactivity with Structure.—$\text{Log}_{10}k_{35}$ will be taken as a measure of the reactivity. The halides are conveniently classified into three series :

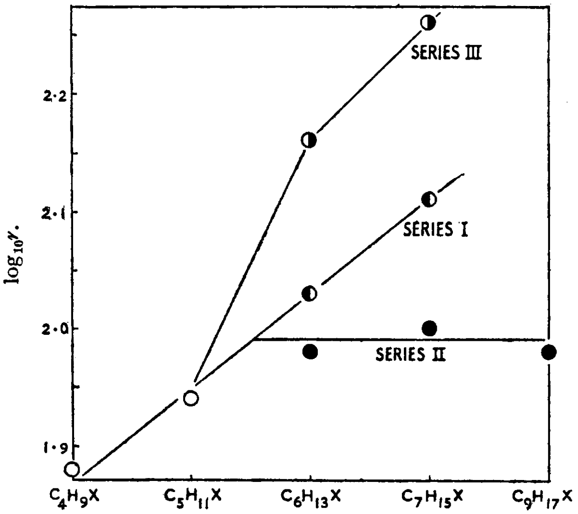
I. CMe_3X, CMe_2EtX, $CMeEt_2X$, and CEt_3X.
II. CMe_2RX, where R = Me, Et, Pr^n, Bu^n, or *n*-amyl.
III. CMe_2RX, where R = Me, Et, Pr^i, or Bu^t.

The variations in these series for chlorides and iodides respectively are shown in Figs. 2 and 3, and a comparison of chlorides and iodides is shown in Fig. 4. The essential results are as follows. In series I a continuous increase occurs through the series. This increase is not linear, but is subject to a saturation effect which is more marked with the chlorides than with the iodides. The logarithm of the velocity ratio (r) increases linearly. For the iodides, E changes progressively in the direction corresponding to the change in reactivity. The values for the chlorides cover a smaller range and show anomalies probably attributable to experimental error, and possibly also to dependence of E on T.

In series II a maximum reactivity occurs with R = Et, the longer-chain compounds becoming progressively less reactive. With both chlorides and iodides a slight arrest in the fall occurs at R = Bu^n. The velocity ratio increases to a limit in the higher members. E for the iodides varies in the direction required by the reactivity changes, although the variation is scarcely significant in the latter part of the series.

FIG. 4.

Comparison of corresponding tertiary chlorides and iodides.



$$r = \frac{k_{35}\text{ (iodide)}}{k_{35}\text{ (chloride)}}$$

In series III, both with iodides and with chlorides, a fall in reactivity occurs when R is changed from Et to Pr^i, and an increase when the latter is replaced by Bu^t. With the chlorides the Pr^i compound is actually less reactive than the Me compound, and the Bu^t than the Et compound. The velocity ratio increases through the series, the step from R = Et to R = Pr^i being the most marked. The increased reactivity of the iodide with R = Bu^t relative to the Pr^i compound seems to be due to an increased non-exponential factor rather than to a decreased E. The significance of this is hard to assess. M. G. Evans and Polanyi (*Trans. Faraday Soc.*, 1936, **32**, 1333) have indeed argued that trends in E at the ordinary temperature may be misleading and may not reflect directly trends in E at the absolute zero, which are the ultimate true measure of reactivity. They consider that, in general, values of log k at a fixed temperature are more significant. If this is so in the present example, the anomalous activation energy may have no special importance and may be disregarded. It must, however, be noted.

Theories of the Influence of Structure upon Reactivity of Tertiary Halides.—The most important effect of alkyl groups depends on their release of electrons, for which the following order of efficacy is often assumed :

$$\text{Me} < \text{Et} \begin{array}{l} < \text{Pr}^n < \text{Bu}^n < n\text{-amyl} \\ < \text{Pr}^i < \text{Bu}^t \end{array}$$

The number of reactions which are explicable in a straight-forward manner on this basis is, however, small (for an example, see Kharasch and Flenner, *J. Amer. Chem. Soc.*, 1932, **54**, 674) and special hypotheses are often introduced. In certain examples, indeed, electronic effects have been supposed not to be the chief factors at work (A. G. Evans, " The Reactions of Organic Halides in Solution," Manchester, 1946, p. 28).

In the hydrolysis of the tertiary halides, electronic effects should be of primary importance, ionisation being favoured by the more electron-releasing alkyl groups which should facilitate the removal of the halogen ion and stabilise the carbonium ion by dispersing the positive charge. The variation of reactivity in the three series is obviously not directly explicable on the basis of the above order which would require a continuous increase through series II and III. If the order in question is to be accepted, an additional factor must be introduced.

There are two main possibilities : (*a*) the normal electronic is in competition with a steric effect, and (*b*) the electronic effect is itself complex and does not in fact increase uniformly with increasing chain length or with the branching of the alkyl group.

The possibility (*a*) will be considered first. In series I the replacement of methyl by ethyl invariably increases reactivity, and the only reasonable explanation of this is that ethyl has a greater electron release than has methyl. Whatever the precise mechanism of the electronic effect may be, it will certainly involve various dipoles, and the saturation effect can be explained by mutual induction effects, each dipole reducing to some extent the influence of the others. This saturation effect is more marked in the chlorides than in the iodides, the ratio r rising through the series. The electronic effects should be similar in both but, since an increase in the size of the alkyl groups probably screens the nascent ions from the solvent and reduces the part played by solvation, a new effect will operate. Everett and Wynne-Jones (*loc. cit.*) have brought forward evidence that the larger alkyl groups in the fatty acids screen the ions from the solvent, and A. G. Evans (*op. cit.*, p. 13) has calculated heats of solvation for the ions Me^+, Et^+, Pr^{i+}, Bu^{t+} which are in accordance with this view. Diminution in solvation energy, leading to reduced reactivity, will be a more serious matter for the chlorides where, by the argument advanced above, solvation plays a more important part.

The combination of the electron-release effect and a steric effect, each increasing with chain length, could be responsible for the maximum in reactivity at $R = Et$ in series II. The ratio r, however, rises to a limit with the higher members of the series, a fact which might mean either that the assumed steric effect is unimportant in the iodides and reaches a limit with the chlorides, or else that the steric effect comes, for the higher compounds, to operate equally on the chlorides and the iodides. The first interpretation is inconsistent with the explanation of the reactivity maximum. The second would mean that with increasing distance from the central carbon atom the solvation shell became more and more nearly of the same pattern in both chlorides and iodides.

In series III both a maximum at $R = Et$ and a minimum at $R = Pr^i$ occur, and the usual order postulated for electron release certainly will not account for this. Anomalies are not unusual but generally consist in a complete reversal of the expected order or in the occurrence of either a maximum or a minimum. It is, however, interesting to note that a similar anomaly occurs in the strengths of the branched-chain fatty acids.

The combination of the steric effect with the electron-release effect provides a possible explanation. The rise in r as R changes from Et to Pr^i indicates a marked increase in the steric effect which may outweight the greater electron release of the *iso*propyl group. A further increase, though less pronounced, occurs in the steric effect when R becomes Bu^t, and this may be insufficient to counteract the electron release of the new methyl, so that on balance there is an increase in reactivity.

This brings us to the interesting possibility (*b*), namely that the reactivity maximum in series II and III, and the minimum in series III, may really correspond to a maximum and a minimum in the electron release itself (though steric effects must of course be retained to explain differences in behaviour between iodides and chlorides).

Although the electron release is commonly assumed to increase with chain length, a different assumption has occasionally been made. Certain gas-phase reactions of the paraffins have been interpreted in the light of the idea that there is a specific electron-releasing influence of the methyl group but that this is damped rather than enhanced by intervening methylene groups (Hinshelwood, *J.*, 1948, 531). Such an idea has some theoretical support (Coulson, *Quart. Reviews*, 1947, **1**, 172; also, private communications). The symmetry properties of the orbitals of the methyl group favour delocalisation of the C–H bonds and transmission of negative charge to the fourth bond. The electron-releasing effect is probably a manifestation of this and might be transmitted along a chain to some extent, but, in general, methylene groups would damp the influence. As far as this goes, electron release should diminish with increasing chain length and, as stated, certain reactions of the paraffins can be explained on this basis. Reactions in solution, however, usually require for their explanation that the methylene groups should make some positive contribution of their own to the total electron release, and this, in principle, they may do in virtue of the C–H dipoles they contain.

It may be expedient to assume two effects. On the one hand, there is the special effect of methyl groups which has been ascribed above to their symmetry and assumed to be damped by methylene groups intervening between them and the centre of reaction. On the other hand, methylene groups may be assumed to make a contribution of their own, which will gradually increase to a limiting value as their number increases.

Suppose that there is one methyl group with n methylene groups intervening. The damped influence of the methyl will be of the general form Be^{-bn}, where B and b could be more or less constant. The total influence of the methylenes could be roughly expressed in the form Cn^x where x is a power, not necessarily constant, but certainly less than unity. The total effect is expressed by $Be^{-bn} + Cn^x$. Such an expression could have a maximum at different values of n according to the constants. In the gaseous oxidation reactions of the paraffins the maximum could occur with $n = 0$, in the tertiary halide hydrolysis at $n = 1$ and so on. Quite complicated variations could occur, such as may possibly be responsible for the complex dependence of the strengths of the fatty acids on structure. The contribution of the methylene groups may well depend on whether stabilisation of a free radical or of an ion is required. It might be suggested that special polarisability effects are called into play in reactions involving the heteropolar formation or breaking of bonds (there is, however, no clear theoretical justification for this).

With regard to the effect of branched-chain structures the contribution of the CH group must be assumed to be almost negligible, and the additional methyl group in *iso*propyl supposed unable to compensate the loss of the methylene group. Hence the fall in reactivity. In *tert.*-butyl, however, the second and third methyl groups together, possibly because they form with the first a highly symmetrical system, more than make up for the loss of the methylene group (though with the chlorides the result is somewhat obscured by the steric effect).

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