69. *The Kinetics of Halogen Substitution. Part V. Halogen Addition. Part XIV. Catalysis by Electrolytes in Acetic Acid Solution.*

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Measurements have been made of the catalysis of bromination by various electrolytes, such as $HClO_4$, $LiClO_4$, LiCl, LiBr, H_2SO_4, NaOAc, in acetic acid solution, of (*a*) *m*-xylene and *β*-bromostyrene; (*b*) allyl bromide and 3 : 4- and 2 : 6-dichlorostyrene; (*c*) ethyl acrylate, maleic acid, and sodium ethylenesulphonate. Three types of catalysis are differentiated: (*a*) for normal electrophilic substitution or addition, the effectiveness being $HClO_4 > H_2SO_4$ and $LiClO_4 >$ LiCl; the catalysis is in the order of the conductivities, and has the nature of a salt (activity) effect; (*b*) for electrophilic addition when a $+T$, $-I$ group is joined to an ethylene carbon atom; LiCl $> LiClO_4$ and LiCl > LiBr; (*c*) when nucleophilic reactivity is possible by the action of a $-T$, $-I$ group; LiCl $> LiClO_4$ and LiBr > LiCl.

Catalysis of chlorine substitution and addition is slight. Iodine addition shows a relatively low catalysis by $LiClO_4$ and $HClO_4$, but a large catalysis by LiCl and LiBr.

It has been shown that perchloric acid may catalyse considerably halogen addition in acetic acid solution to unsaturated aldehydes (*J.*, 1945, 888), and likewise lithium chloride accelerates bromine addition to such compounds as allyl chloride and vinyl bromide (*J.*, 1945, 131; 1947, 630). Perchloric acid and lithium chloride may also act as catalysts, although less efficiently, in halogenation reactions which have the normal electrophilic character, *e.g.*, in the bromination of mesitylene, or in bromine addition to such ethylene derivatives as β-bromostyrene. As acetic acid is a solvent of low dielectric power, and since the ionisation of a halogen atom would appear to be a rate-determining process, it was suggested in our earlier communications that such catalysis might be of the nature of a salt effect, for according to Kolthoff and Willman (*J. Amer. Chem. Soc.*, 1934, **56**, 1007) perchloric acid and lithium chloride are electrolytes in acetic acid solution. Perchloric acid is a strong electrolyte compared, for example, with nitric acid, as its equivalent conductivity is 400 times greater than that of nitric acid at the same molar concentration, but on the other hand it is a weak electrolyte in the sense that in 0·01M-solution it is dissociated to the extent of less than 1%. That is equally true of lithium chloride, which has similarly a small degree of dissociation, and obeys the Ostwald dilution law over the concentration range examined by Kolthoff and Willman. In spite of the relatively small dissociation of lithium chloride, it appears to have an activity effect in the isomerism of α-phenylallyl acetate in acetic acid solution (for reference and discussion, see Catchpole and Hughes, *J.*, 1948, 3), whilst for lithium and potassium acetate the effect is considerably smaller. These results are consistent with the values for the molecular conductivities (quoted after Table I, p. 295), and correspondingly it will be shown that the catalytic efficiencies of lithium chloride and sodium acetate in the reactions now studied have a similar order.

Certain typical reactions have been examined in greater detail than previously, and the conductivities of perchloric acid and lithium chloride measured over a higher concentration range than that studied by Kolthoff and Willman. The results reveal that these solutions show minima in the molecular conductivities (at M/64 for perchloric acid, and M/32 for lithium chloride), indicating the formation of triple ions. In Fig. 1 are shown the results obtained for the bromination of *m*-xylene with different amounts of added perchloric acid.

In Fig. 2 are the results for the lithium chloride-catalysed addition of bromine to β-bromostyrene; included also in the diagram are the measurements at double the lower concentration, giving an order, $n = 3·0$, for the uncatalysed reaction, and a corrected order, $n = 2·3$, for the catalysed reaction. Inset are plotted (circles) the ratios of velocities of catalysed (corrected by subtraction of uncatalysed rate) and uncatalysed reactions against the concentrations of the electrolytes, whilst the broken curves show the specific conductivities of the solutions over this concentration range (the arrow indicates minimum molecular conductivity). With different amounts of catalyst for the same reaction, the catalytic activity is approximately proportional to the conductivity of the solutions. The deviation from linearity is in the reverse sense to that required if the electrolyte showed simple dissociation; but an exact proportionality between catalytic activity and conductivity is not necessarily to be expected, as the effects caused by single and triple ions may be somewhat different. Similar results were obtained for certain other reactions, chlorination of *m*-xylene ($HClO_4$), bromination of *m*-xylene (LiCl), and bromine addition to bromostyrene ($HClO_4$).

Table I summarises the relative efficiency of different catalysts in such reactions, as ratio of rates of corrected catalysed to uncatalysed reactions, the halogen being at M/80- and the catalyst at M/20-concentration.

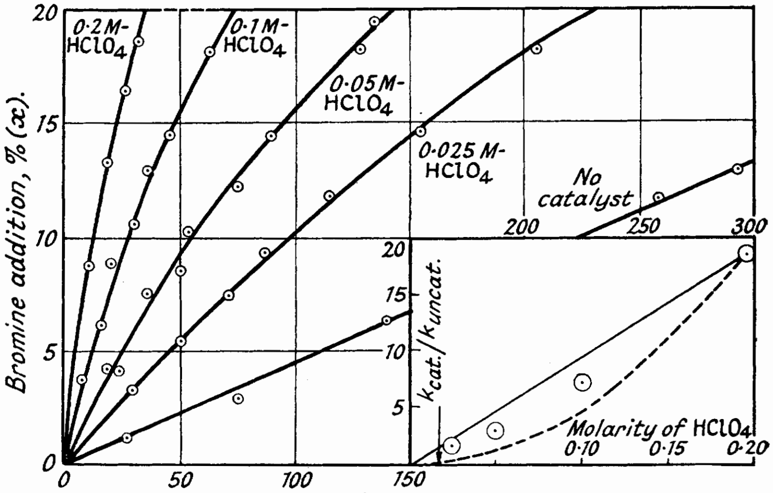
TABLE I.

	m-Xylene and chlorine.	*m*-Xylene and bromine.	Bromostyrene and bromine.	Undecenoic acid and iodine.
$HClO_4$	0·9	3·1	1·3	1·4
$LiClO_4$	—	—	1·3	1·5
LiCl	0·25	1·0	0·5	7·4
H_2SO_4	—	0·3	0·2	0·3
NaOAc	—	0·2	0·1	—

The molecular conductivities of the electrolytes, M/20, in acetic acid at 25° are as follows :

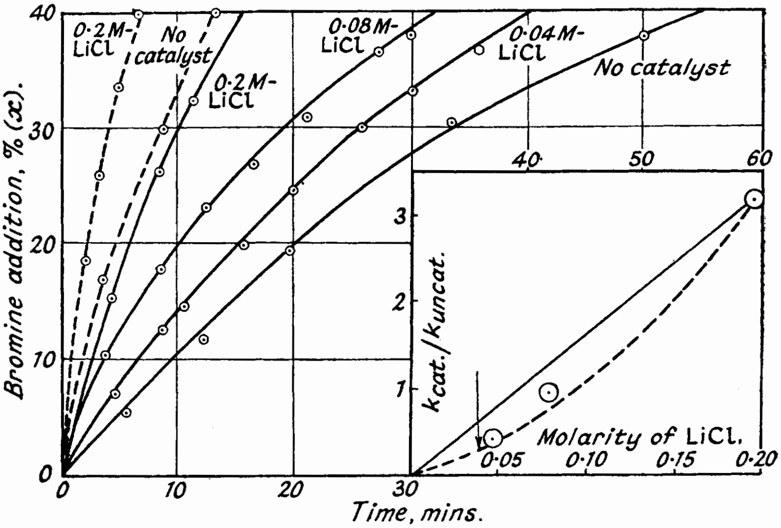
$HClO_4$.	$LiClO_4$.	LiCl.	NaOAc.	H_2SO_4.
1·50	0·81	0·23	0·18	0·09

FIG. 1.



m-*Xylene*, M/8 ; *bromine*, M/80, *with* $HClO_4$.

FIG. 2.



β-Bromostyrene–bromine : — M/10, M/80 ; - - - M/5, M/40 *with* LiCl.

It is apparent that there is a general relationship between the molecular conductivity and the catalytic activity, more especially when pairs of related electrolytes, *e.g.*, $LiClO_4$ and LiCl,

$HClO_4$ and H_2SO_4, are considered. The parallelism between the two types of reaction, the catalytic efficiency for bromine substitution being approximately double that for bromine addition, indicates that a similar mechanism is in operation, and this is regarded as a salt (activity) effect. In the presence of such a catalyst as lithium chloride, however, it has been found (with stilbene, M/80 + Br_2, M/80 + LiCl, M/4) that the reaction product contains not only the dibromo-, but also a large amount of the chlorobromo-compound, with some bromoacetate also. It is therefore evident that the chloride ion is effective in completing the second stage of the reaction, and if the catalysis is an activity effect, this second stage does not appear to be rate-determining. When the chloride ion does appear to take part in a rate-determining step (compounds in Table II), then the catalytic activities of lithium perchlorate and chloride become reversed, *i.e.*, are no longer in the order of their conductivities. The activity effect would seem, in both substitution and addition, to involve the stretching of the Br–Br link in the intermediate, with the resultant anionisation of one of the bromine atoms. But in substitution the process also includes the stretching of the C–H link with proton formation, and this difference may be the reason for the superior catalytic activity of electrolytes in the substitution reaction.

The weak catalysis by sodium acetate, possibly related to the fact that this compound is a base in acetic acid solution, is especially to be noted with regard to the substitution reaction. Since sodium acetate is a proton-acceptor, such small catalysis suggests that the removal of a proton is not a rate-determining step. Such a result should be contrasted with the conclusion reached by Bennett *et al.* (*J.*, 1947, 474) for nitration in sulphuric acid solution. In nitration the electrophilic reagent is the NO_2^+ ion, whereas in halogenation the attack is by a neutral molecule, the reaction being one of mutual interchange in which the proton removal is part of the actual process (cf. Hinshelwood, Presidential Address, *J.*, 1947, 694).

TABLE II.

	3 : 4-Dichloro-styrene.	2 : 6-Dichloro-styrene.	Allyl bromide.
$HClO_4$	—	1·3	1·3
$LiClO_4$	—	1·3	1·3
LiCl	1·7	2·0	4·0
LiBr *	0·9	1·5	2·8

* These values are not corrected for the small (unknown) uncatalysed rate.

On comparing different halogens, it is seen that the relative catalysis is less for chlorine than for bromine, and this may be related to the superior ionising power of the chlorine. But the comparison is complicated by the fact that there is a change in the reaction order, chlorine addition being of the second and bromine addition of the third order. Actually the difference in effect would be still greater if the second-order reactions of each halogen could be compared. Both bromine and iodine addition are of third order under the experimental conditions, and it is found that lithium perchlorate, for instance, has the same catalytic effect in each reaction; there is, however, an abnormally large catalysis of iodine addition by lithium chloride. One possibility is that the chloride ion takes part in the second stage of the iodine addition by a rate-determining step, being differentiated from the perchlorate ion in its effect owing to its power of forming a covalent link with carbon. If this is so, lithium bromide, which is more ionised than the chloride, should be superior as a catalyst. Actually, it shows considerable catalytic activity (ratio, 6·9, in comparison with LiCl, 7·4) but $LiBrI_2$ formation would tend to reduce this value, and such an effect would be greater than with lithium chloride. On the other hand, there is the possibility with lithium chloride of iodine chloride formation (as in the reaction between mercuric chloride and iodine in this solvent), and this may cause in part the catalysis by lithium chloride, for even if the amount of iodine chloride formed might be very small, it has a high reactivity (10^5 greater than that of iodine).

Whereas, in what may be termed the normal electrophilic addition of bromine, the electrolytes lithium perchlorate and perchloric acid are superior as catalysts to lithium chloride, for certain compounds the reverse effect is observed; examples of this are shown in Table II, where the catalytic activities have the same significance as for Table I, being for Br_2, M/80, and catalyst, M/20.

The compounds in Table II are of the type, $CHR'{:}CH_2$, where R′ is a group of opposing electronic requirement. This is shown for instance by bromomethyl, which is chiefly *o,p*-directing, with a small *m*-directing power. In the 3 : 4-dichlorophenyl group, the introduction of the two chlorine atoms reduces the rate of bromine addition by a factor of 200, so that here also the tautomeric effect which favours the addition is offset by an inductive effect. The 2 : 6-dichlorophenyl group is similar, although with this compound there is the possibility of steric hindrance also (the rate of 2 : 6-dichlorostyrene being less than that of styrene by a factor of 10^4). Vinyl bromide would also be included in this class, and special mechanisms involving an initial attack by chloride ions were proposed to explain the abnormally high catalysis by lithium chloride of bromine addition to the allyl halides and vinyl bromide (*loc. cit.*). An alternative mechanism, however, is also possible, namely, an initial electrophilic attack by halogen, followed by a rate-determining stage in which the addition of the chloride ion to the intermediate, $\overset{+}{C}HR'-CH_2-\overset{-}{Br}-Br$, is aided by the withdrawal of electrons by the group R′. Whereas the catalysis with lithium chloride becomes greater for this type of compound, the efficiency of perchloric acid and lithium perchlorate does not increase. Such a specific effect for the chloride ion is attributed to the fact that it can form a covalent link with the carbon atom to which it becomes attached, whereas this is not possible for the perchlorate ion. Equally the bromide ion can form a covalent link, and lithium bromide should be expected to be more efficient than the chloride (molecular conductivities, LiCl, 0·23; LiBr, 0·45) but its effect is offset by the removal of bromine as $LiBr_3$. It is to be noted that the lithium bromide catalysis increases in the same order as for lithium chloride (Table II).

Another class of compound is characterised by showing a considerable catalysis of bromine addition by lithium chloride, and a still larger catalysis by the bromide, whilst the effect with the perchlorate remains relatively small. The catalytic ratios for certain of these compounds (bromine at M/80 and 4 mols. of catalyst, except for maleic acid, where these amounts are doubled) are shown in Table III; with the first two compounds, sodium acetate is present to prevent acid catalysis.

We have shown, in previous communications, that the addition of bromine to acrylic and maleic acids in acetic acid solution is greatly catalysed by hydrogen bromide, and we have produced evidence, mainly from the effect of constitution of the olefin on the rate of reaction, that such additions proceed by a nucleophilic mechanism. We have further shown that hydrogen chloride is also a catalyst for bromine addition to related compounds, *e.g.*, the 1 : 2-unsaturated aldehydes, and although considerably less effective than hydrogen bromide, it is more efficient than would be expected from a comparison with certain other acids, which are more ionised in the solvent, acetic acid. The evidence indicated that the reagents in these reactions were HBr_3 and $HClBr_2$, and similarly for ethyl acrylate and maleic acid (Table III) it is concluded that the catalysis is due to $LiBr_3$ and $LiClBr_2$, or more particularly to Br_3^- and $ClBr_2^-$ ions, as lithium bromide and lithium chloride themselves are appreciably dissociated in acetic acid solution. There is also evidence, of a constitutional nature, that these reactions are nucleophilic in character : thus the rate of bromine addition to maleic acid in the presence of lithium chloride is 8 times faster than to citraconic acid, whereas in aqueous acetic acid, *i.e.*, under electrophilic conditions, this order is reversed (*J.*, 1945, 129). With regard to the actual formulation of such nucleophilic reactions, it is not yet established whether the organic compound reacts according to a resonance structure (I), or whether solvent molecules are required to establish, by a hydrogen bond, the positive charge on the β-carbon atom (II).

TABLE III.

	$CH_2{:}CH{\cdot}CO_2Et$.	$CH(CO_2H){:}CH{\cdot}CO_2H$.	$CH_2{:}CH{\cdot}SO_3Na$.
$LiClO_4$	0·8	0·2	0·7
LiCl	10	6	6·7
LiBr	33	30	—

$$\overset{\oplus}{C}H_2{-}CH{=}C(OEt){-}\overset{\ominus}{O}$$

(I.)

$$\overset{\oplus}{C}H_2{-}CH{=}C(OEt){-}\overset{\frac{1}{2}\ominus}{O}\ldots H\ldots\overset{\frac{1}{2}\ominus}{O}Ac$$

(II.)

The corresponding catalytic ratios of lithium chloride for chlorine addition have also been measured, *viz.*, ethyl acrylate (~0·1), maleic acid (0·35). The catalysis tends to be small, as for chlorine substitution (Table I). The larger effect for maleic acid is attributed to the influence of the electron-attracting carboxyl group on the β-carbon atom in aiding the second stage of the electrophilic substitution (as for compounds in Table II).

Sodium ethylenesulphonate (Table III) similarly shows a large lithium chloride catalysis, even although the uncatalysed (electrophilic) rate is relatively high owing to the ionisation of the compound. Ethylenesulphonic acid itself, whilst not showing acid catalysis of bromine addition with perchloric acid, gives a large catalysis with hydrogen bromide. Compounds with the SO_2R group, therefore, appear also capable of nucleophilic reactivity, and the initial attack in the catalysis of sodium ethylenesulphonate could therefore be expressed by $\mathrm{Cl\overset{-}{B}r_2\overset{\curvearrowright}{\ }\overset{+}{C}H_2{-}CH{=}\overset{-}{S}O_2{\cdot}ONa}$.

The results obtained in the present investigation for the catalysis of bromine addition by electrolytes in acetic acid solution reveal that unsaturated compounds are divisible into three classes, which may be specified, with reference to the nomenclature proposed by Ingold (cf. Ingold and Ingold, *J.*, 1931, 2354), as follows :

Class I. Compounds of the types $\mathrm{CHR{:}CH_2}$ and $\mathrm{CHR\overset{\curvearrowright}{:}CHX}$ (the arrows indicating the point of electrophilic attack), where R is a group (+*I* or +*T*), and X a halogen atom or group such as chloromethyl (−*I*), or a group such as phenyl which in this position may exert a relatively weak tautomeric effect (−*T*). Actually, compounds, $\mathrm{CHR{:}CH_2}$, where R is phenyl or an alkyl, are too reactive for convenient measurement, but allyl esters, $\mathrm{CH(CH_2{\cdot}O{\cdot}COR)\overset{\curvearrowright}{:}CH_2}$, approximate to this type. The relative catalysis is $LiClO_4 > LiCl$, being in the order of their molecular conductivities, and is apparently chiefly a salt (activity) effect; further $LiCl > LiBr$.

Class II. Compounds of the type $\mathrm{CHR'\overset{\curvearrowright}{:}CH_2}$, where R′ is a group of opposing electronic requirements, such as bromomethyl (+*T*, −*I*). The relative efficiency is $LiCl > LiClO_4$, as the chloride ion becomes involved in a rate-determining step of the reaction; here also $LiCl > LiBr$.

Class III. Compounds of the type $\mathrm{CH_2\overset{\curvearrowright}{:}CHX}$, where X is a group like carboxyl (−*T*, −*I*). The catalysed reactions now proceed by a nucleophilic mechanism, and the active reagent in catalysis by lithium chloride is the $ClBr_2^-$ ion. The effect here may be considerable, whereas the lithium perchlorate catalysis remains small, as for Classes I and II. The relative efficiency is $LiCl > LiClO_4$, and $LiBr > LiCl$. This class would also include compounds of the type $\mathrm{CHX{:}CHX}$ (*e.g.*, maleic acid), as well as compounds, $\mathrm{CHR{:}CHX}$ (when X is a strong −*T* group). The compound $\mathrm{CHPh{:}CH{\cdot}NO_2}$ was selected as a representative example; considerable lithium chloride catalysis was established (in presence of sodium acetate), but the exact catalytic ratio could not be determined as the uncatalysed reaction appeared to be accompanied by polymerisation.

EXPERIMENTAL.

The technique and materials were as previously described. In addition there were used ethyl acrylate, b. p. 95·5—96·5°/725 mm., and 2 : 6- and 3 : 4-dichlorostyrene. For the last two substances we are indebted to the kindness of Dr. C. S. Marvel, University of Illinois; the compounds were distilled under reduced pressure before measurement, and showed the theoretical bromine absorption. The solutions of catalysts were prepared as previously described. In addition, standard lithium perchlorate was prepared by mixing equal volumes of equimolecular lithium chloride and perchloric acid solutions; hydrogen chloride was freely evolved and dry nitrogen was bubbled through the solution until it gave a negative test for chloride. Catalytic ratios for sodium ethylenesulphonate are quoted in Table III, and more detailed results for the rates, etc., of this compound will be given in a later communication. Herewith details of a typical experiment.

M/10-*β-Bromostyrene* + M/80-*bromine* + M/25-LiCl *in acetic acid at* 24°. Reaction mixture 10 ml.; 1 ml. titrated with N/80-$Na_2S_2O_3$.

Time, mins.	0	4	10·5	20	30	44	60
Titre	1·97	1·83	1·64	1·43	1·27	1·10	0·96

From curve : $x = 20, t = 14{\cdot}3$. Second expt. : $x = 20, t = 14{\cdot}3$.

There follows a summary of further results quoted as times (t), in mins., for % halogen absorption, for dark reactions in acetic acid at 24°. *m*-Xylene, M/80, + Cl_2, M/80, $x = 20$, $t = 1{\cdot}80$; +LiCl, M/10, $t = 1{\cdot}20$; +$HClO_4$, M/20, $t = 0{\cdot}94$. *m*-Xylene, M/8, +Br_2, M/80, $x = 10$, $t = 225$; +LiCl, M/20, $t = 110$; +$HClO_4$, M/20, $t = 54$; +NaOAc, M/10, $t = 160$. (In the sodium acetate catalysis, interference from liberated hydrogen bromide is negligible, as from $x = 0$ to $x = 10$, [NaOAc]/[HBr] = 160, and from experiments with added hydrogen bromide the effect of an equal amount of this is very small.) *β*-Bromostyrene, M/8, + Br_2, M/80, $x = 20$, $t = 17$; +$HClO_4$, M/20, $t = 7{\cdot}5$; +H_2SO_4, M/10, $t = 11{\cdot}2$. *β*-Bromostyrene, M/10, +Br_2, M/80, $x = 20$, $t = 20{\cdot}5$; +LiCl, M/20, $t = 13{\cdot}5$; +$LiClO_4$, M/20, $t = 9{\cdot}5$; +$HClO_4$, M/20, $t = 9{\cdot}5$. Undecenoic acid, 0·47M, +I_2, 0·0125M, $x = 10$, $t = 6{\cdot}5$; +$HClO_4$, M/10, $t = 1{\cdot}7$; +LiCl, M/40, $t = 2{\cdot}0$; +H_2SO_4, M/10, $t = 4{\cdot}0$. Undecenoic acid, 0·23M, +I_2, 0·0125M, $x = 10$, $t = 11{\cdot}5$; +LiCl, M/20, $t = 1{\cdot}4$; +$LiClO_4$, M/20, $t = 4{\cdot}6$; +$HClO_4$, M/20, $t = 5{\cdot}2$. 2 : 6-Dichlorostyrene, M/80, +Br_2, M/80, $x = 10$, $t = 11{\cdot}5$; +LiCl, M/20, $t = 3{\cdot}7$; +LiBr, M/20, $t = 6{\cdot}5$; $LiClO_4$, M/20, $t = 4{\cdot}9$; +$HClO_4$, M/20, $t = 4{\cdot}9$. 3 : 4-Dichlorostyrene, M/80, +Br_2, M/80, $x = 50$, $t = 1{\cdot}95$; +LiCl, M/10, $t = 0{\cdot}45$, +LiBr, M/10, $t = 2{\cdot}15$. Allyl bromide, M/80, +Br_2, M/80, $x = 20$, $t = 19{\cdot}0$; +LiCl, M/20, $t = 3{\cdot}9$; +LiBr, M/20, $t = 6{\cdot}8$; +$LiClO_4$, M/20, $t = 8{\cdot}5$; +$HClO_4$, M/20, $t = 8{\cdot}5$. Ethyl acrylate, M/5, +Cl_2, M/80, +NaOAc, M/80, $x = 20$, $t = 42$; +LiCl, M/5, $t = 30$. Ethyl acrylate, M/80, +Br_2, M/80, $x = 20$, $t = 5160$; +$LiClO_4$, M/20, $t = 2760$; +LiCl, M/20, $t = 480$; +LiBr, M/20, $t = 150$. Maleic acid, M/5, +Cl_2, M/80, +NaOAc, M/80, $x = 5$, $t = 2400$; +LiCl, M/5,

$t = 1{,}000$. Maleic acid, M/10, $+Br_2$, M/40, +NaOAc, M/40, $x = 20$, $t = 3{,}000$; $+NaClO_4$, M/10, $t = 2{,}500$; +LiCl, M/10, $t = 430$; +LiBr, M/10, $t = 100$.

The ratios quoted in the tables are for the corrected catalysed rates to the uncatalysed rates, calculated for the most part at $x = 10$ or 20% halogen absorption; the ratios diverge slightly from these results as x increases. The catalytic ratios quoted in previous communications are given the same significance by the subtraction of unity.

The conductivities of perchloric acid and lithium chloride, represented in Figs. 1 and 2, are from measurements by Mr. W. S. Metcalf, of Victoria University College, and a further account will be given in a separate communication. We express our thanks to him, and to Dr. P. B. D. de la Mare, University College, London, for helpful discussion at various stages of the present investigation.

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