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ELECTROPHILIC CATALYSIS IN SOLVOLYTIC REACTIONS

VII. SOLVENT EFFECT

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ABSTRACT

The rates of mercuric chloride catalyzed solvolysis of some alkyl chlorides in aqueous acetone and ethanol solvents have been compared. It is found that the increase in rate on changing from the acetone to the ethanol solvent is less in the catalyzed than in the normal reaction. On the basis that the electrophilic activity of the catalyst is less in aqueous ethanol than in aqueous acetone an explanation for the anomaly has been suggested. The effect, on the rates of solvolysis, of added chloride ions is in accord with the suggested explanation.

The rates of solvolysis of a number of alkyl chlorides, with and without mercuric chloride, in aqueous acetone and aqueous ethanol, together with the values of the heats and entropies of activation, are given in Tables I and II. The Hughes–Ingold theory requires that the rate of solvolysis of an alkyl chloride should increase on changing from aqueous acetone to aqueous ethanol (1). This can be put on a quantitative basis by using the Winstein equation $\log k/k_0 = m\mathrm{Y}$ (2). The data show that, while this is true of the normal solvolysis of all the alkyl chlorides, regarding the catalyzed reaction, *tert*-butyl and *tert*-amyl chloride behave abnormally, the rates in aqueous ethanol being lower. It can also be seen (Table I) that the ratio $k_{\text{ethanol}}/k_{\text{acetone}}$ for the normal solvolysis (k_{I}) is, in all cases, larger than the corresponding ratio for the catalyzed reaction (k_{II}). Since k_{I} varies over a wide range of values, to obtain a proper idea regarding the extent of abnormality in the rates of the catalyzed reaction of the different alkyl chlorides, a factor k_{III}, defined as $k_{\mathrm{II}}/k_{\mathrm{I}}$, has been calculated and included in the last column of Table I. It is evident that completely normal behavior will correspond to a value of 1 for k_{III}.

Since the k_{III} values of all alkyl chlorides are much less than 1, it was thought likely that the abnormal behavior might be due to a lower electrophilic activity of the catalyst in aqueous ethanol, particularly since Foote has shown that mercuric chloride does not form a complex with chloride ions in dry ethanol (3). This has been confirmed by solubility measurements which show that the $HgCl_2$:Cl^- (combined) ratios in 80% aqueous acetone and 80% aqueous ethanol at 31 °C are, respectively, 1:2.86 and 1:2.21, with a mercuric chloride concentration of 0.4 *M* (4). With a mercuric chloride concentration of 0.2 *M* the ratios have the values 1:4.38 and 1:3.0. It is clear that, since the number of chloride ions combining with a molecule of catalyst is less in aqueous ethanol, the electrophilic activity of the catalyst must be smaller in this solvent.* However, two points, namely the lower rates of catalyzed solvolysis in aqueous ethanol shown by *tert*-butyl and *tert*-amyl chloride and the wide variation in the k_{III} values, require explanation.

In Table II, a factor k_{IV} is introduced, which is the ratio of the rate, in aqueous acetone, due to the catalyst alone and the rate of the normal hydrolysis. If 1-chloropropylbenzene, 1-chloroisobutyl benzene, and (1-chloro-2,2-dimethylpropyl)benzene are excluded from consideration, it can be seen that the order of increasing k_{III} values parallels decreasing

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**This is an amplification of the argument in ref. 5. However, the effects, on the rate, due to a change in the electrophilic activity can be swamped by new kinetic factors introduced by the catalyst.*

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TABLE I

Kinetics of the solvolysis of alkyl chlorides (alkyl chloride = 0.1 *M*; $HgCl_2$ = 0.075 *M*;* *T* = 20 °C, in all except with *p*-$ClPhCH_2Cl$ where it is 68.2 °C)

RCl	10^7k_1 (normal)		10^6k_1 (catalyzed)		$k_{EtOH}/k_{acetone}$		$k_{III} = k_{II}/k_I$
	Acetone	EtOH	Acetone	EtOH	Normal (k_I)	Catalyzed (k_{II})	
(*i*) Solvent 80% v/v acetone/ethanol – water							
t-BuCl	10.4	50.9†	58.2	48.8	4.90	0.839	0.17
t-AmCl	14.7	91.6	105.	81.7	6.23	0.778	0.13
CHPhMeCl	4.03†	71.0§,‖	42.9‡	81.3	17.6	1.90	0.11
CHPhEtCl	0.935‡,‖	17.5§,‖	9.58‡,‖	23.0‖	18.7	2.41	0.13
CHPh-*i*-PrCl	0.238‡,‖	2.88§,‖	3.07‡,‖	6.73‖	12.1	2.19	0.18
CHPh-*t*-BuCl	0.0196‡,‖	0.0767§,‖	0.275‡,‖	0.606‖	3.90	2.20	0.56
CH(*p*-MePh)MeCl	178	3 400	3 545	5 237	19.1	1.48	0.077
$PhCH_2Cl$	0.0425‖	0.912‖	0.0240‖	0.212‖	21.46	8.83	0.41
p-$ClPhCH_2Cl$	7.83¶	98.30¶	5.12¶	42.20¶	12.56	8.24	0.65
t-BuCl	306	683	505	396	2.23	0.784	0.35

*For *p*-$ClPhCH_2Cl$, $HgCl_2$ = 0.3 *M*.
†Value calculated from ref. 14, 10^7k_1 = 48.7.
‡From ref. 9.
§Value calculated from ref. 27, 10^7k_1; CHPhMeCl = 71.00, CHPhEtCl = 18.10, CHPh-*i*-PrCl = 2.84, CHPh-*t*-BuCl = 0.076.
‖Calculated from higher temperatures.
¶From ref. 7, the temperature was wrongly given as 62.8 °C; it should be 68.2 °C.

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TABLE II

Kinetics of the solvolysis of alkyl chlorides

		Normal				Catalyzed			
		$\Delta H_{25^\circ}^\ddagger$ (kcal/mole)		$\Delta S_{25^\circ}^\ddagger$ (e.u.)		$\Delta H_{25^\circ}^\ddagger$ (kcal/mole)		$\Delta S_{25^\circ}^\ddagger$ (e.u.)	
RCl	$\frac{k_{\mathrm{cat}} - k_{\mathrm{normal}}}{k_{\mathrm{normal}}}(k_{\mathrm{IV}})^*$ (80% aq. acetone)	80% aq. acetone	80% aq. EtOH	80% aq. acetone	80% aq. EtOH	80% aq. acetone	80% aq. EtOH	80% aq. acetone	80% aq. EtOH
t-BuCl	57.97	22.0	22.3	−10.8	−6.6	17.9	19.8	−17.1	−11.8
t-AmCl	71.15	—	—	—	—	17.5	19.7	−16.9	−9.9
CHPhMeCl	102.7	21.1	19.8†	−15.5	−15.0	17.6	20.0	−18.5	−8.9
CHPhEtCl	101.5	22.6	20.1†	−13.6	−16.9	17.8	19.1	−20.7	−14.7
CHPh-*i*-PrCl	120.9	22.2	22.3†	−17.5	−12.1	17.9	17.9	−22.9	−21.3
CHPh-*t*-BuCl	148.6	24.9	24.8†	−14.1	− 9.8	19.0	19.6	−24.2	−20.4
CH(*p*-MePh)MeCl	198.2	—	—	—	—	—	—	—	—
$PhCH_2Cl$	4.65	21.4	20.9	−23.8	−23.9	17.5	19.7	−16.9	−9.9
p-$ClPhCH_2Cl$	1.40	—	—	—	—	—	—	—	—

*T = 20 °C in all except *p*-$ClPhCH_2Cl$ where it is 68.2 °C. The k_{IV} value for *p*-$ClPhCH_2Cl$ is not likely to be very different at 20 °C since for $PhCH_2Cl$, which shows similar behavior, the k_{IV} value at 82.3 °C is 2.9.

†Reference 27.

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k_{IV} values. This means that the abnormality in the rate of the catalyzed reaction in aqueous ethanol increases with the catalytic efficiency of the hydrolytic process. Provided the catalytic activity remains unchanged,* the sensitivity of the rate of solvolysis to the presence of the catalyst should be quantitatively similar in the two solvents. But any change in the catalytic activity will cause abnormal behavior, its extent varying with the alkyl chloride. Thus a substrate like 1-*p*-tolylethyl chloride, whose rate of hydrolysis is especially sensitive to the presence of the catalyst, will be most affected by such a change. On the other hand, the rates of hydrolysis of benzyl and *p*-chlorobenzyl chloride are little affected by the catalyst and so their rates of catalyzed solvolysis in aqueous ethanol will show the least abnormality, in agreement with observation. It may be noted that the two tertiary alkyl chlorides also fit into this pattern. The fact that the rates of their catalyzed solvolysis in aqueous ethanol is lower than the rate in aqueous acetone is accidental, caused by their abnormally low k_I values.†

The exceptional behavior shown by the other three alkyl chlorides has now to be explained. It has been argued that with the other alkyl chlorides, an inverse relationship exists between the extent of abnormal behavior (as shown by the k_{III} values) and the catalytic efficiency for the hydrolysis (as given by the k_{IV} values). These three alkyl chlorides, however, have k_{IV} values which are much larger than those expected on the basis of their k_{III} values. A possible explanation for this is as follows. The catalytic efficiency must increase with the ease with which the C—Cl bond can be heterolyzed (in other words, must increase with the inherent tendency of the substrate to adopt the S_N1 mechanism), and normally this will be the case. But if the catalyst is able to bring into play additional kinetic factors or to change the factors already present in the normal reaction significantly, the above rule may no longer hold. It has been argued on the basis of experimental evidence that the unduly high catalytic efficiency observed in the reactions of these three alkyl chlorides is due to the catalyst calling into play an additional inductomeric effect of substantial magnitude (9). The conclusion, therefore, is that the abnormally high k_{IV} values shown by these three alkyl chlorides are due to this special cause, which has no particular relevance to the argument presented here, so that its validity is not affected.

A closer inspection of the k_{III} values suggests that the explanation given above is not adequate, by itself, to account for the fact they are so much less than unity, even in favorable cases. Thus, according to the argument presented here, benzyl chloride and *p*-chlorobenzyl chloride should show the least abnormality. Yet the k_{III} values are only 0.42 and 0.65 respectively. In our studies of the kinetics of mercuric chloride catalyzed solvolysis of alkyl chlorides, we have found that the sensitivity of the rate to changes in the polarity of the medium is less in the presence of the catalyst than in its absence. Now, although the rates of solvolytic reactions of alkyl chlorides by both the S_N1 and S_N2 mechanisms are considerably accelerated by a change to a more polar solvent, the magnitude of the effect is greater for the S_N1 reaction (10). We believe that the inclusion of the catalyst molecule in the transition state will confer on it some of the properties of the transition state of an S_N2 reaction, in particular the relatively smaller response of the

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A referee has suggested consideration of the viewpoint that in a more ionizing solvent the effect of the catalyst may be expected to be less. We have not considered this possibility because the evidence available does not support it. Thus the value of the catalytic coefficient for the mercuric chloride catalyzed hydrolysis of benzyl chloride is almost constant over the solvent range 45–80% aqueous acetone (6), which involves a greater variation in the ionizing power than a change of solvent from 80% aqueous acetone to 80% aqueous ethanol. A similar situation obtains for the catalyzed solvolysis of p-chlorobenzyl chloride (7).

†*The low k_I values are presumably due to the fact that the tert-alkyl cations have relatively little stability (8).*

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rate of substitution to changes in the polarity of the environment, although we recognize that mercuric chloride is here the catalyst and not the substituting agent (11). This is in agreement with the views of Hammond *et al.* (12) that the transition state of the silver ion catalyzed hydrolysis of alkyl halides has a substantial S_N2 character. Other arguments in support of the above conclusion are as follows. (i) A convenient method of distinguishing solvolytic reactions occurring by the S_N1 and S_N2 mechanisms is by determining their *m* values by using the Winstein equation. The *m* values for the normal and catalyzed reactions of some of the alkyl chlorides are respectively (values taken from Fainberg and Winstein (13)): 1-phenethyl chloride, 1.056 (14), 0.40; *tert*-butyl chloride 1.00 (2), 0.50; *tert*-amyl chloride 1.10, 0.50; 1-chloropropyl benzene 0.62, 0.40; benzyl chloride 0.425 (15), 0.43; *p*-chlorobenzyl chloride 0.56, 0.44. Since a high *m* value signifies that the reaction belongs to the S_N1 category, the conclusion from the data is that the *m* values of the catalyzed reaction are more characteristic of S_N2 reactions. (ii) The magnitude of the ionic-strength effect is much less in the catalyzed than in the normal reaction; thus the ionic-strength effect in the hydrolysis of 1-phenethyl chloride is substantial (16), while it is barely detectable in the catalyzed reaction (17). (iii) The "medium effect" which is so characteristic of S_N1 solvolysis is much less marked in the catalyzed reaction; thus the rate of hydrolysis of *tert*-butyl chloride is rather sensitive to its concentration (18), while this is not the case with the catalyzed reaction (19).

With all alkyl chlorides except 1-chloroisobutyl benzene and (1-chloro-2,2-dimethylpropyl)benzene, the heats of activation for the catalyzed reaction in aqueous acetone are markedly lower than in aqueous ethanol, which contrasts with the normal reaction. It is suggested that this is due to the lower electrophilic activity in the ethanolic solvent. For the other two alkyl chlorides, the heats of activation in the two solvents are almost the same, suggesting that steric resistance to solvation is under observation (20). The trend in the entropy values is more difficult to explain. For the catalyzed reaction, the entropy values are more favorable in aqueous ethanol. This is possibly due to the orientational requirement in the transition state being more easily met in the ethanolic solvent consequent on the greater solvation of the catalyst. For 1-chloroisobutyl benzene and (1-chloro-2,2-dimethylpropyl)benzene, however, steric strain due to crowding in the transition state must be dominant, since the entropy values in the two solvents are relatively rather similar.

Addition of chloride ions reduces the rate of the catalyzed reaction because (i) by decreasing the catalyst concentration through formation of complexes like $HgCl_3^-$, $HgCl_4^=$ and (ii) by inducing a mass-law effect (17). An explanation for the latter observation has been given by Ingold (21) and Bunton (22). Of the alkyl chlorides studied (Table III), the mass-law effect is of importance only in the case of 1-phenethyl chloride (9, 17). So, with this exception, the reduction in rate due to added chloride ions must be due to the inactivation of the catalyst. It can be seen that the magnitude of reduction is approximately equal for the hydrolysis of all alkyl chlorides excepting 1-phenethyl chloride, in agreement with the above conclusion. But, the decrease in rate in aqueous ethanol is consistently smaller than in aqueous acetone. This again must be attributed to the greater solvation of the catalyst in this solvent. Further, while the rate decrease in the hydrolytic reaction appears to be little affected by changes in temperature (thus the rate reductions for five alkyl chlorides are about the same although the temperature varies by over 50 °C), this is not the case in aqueous ethanol where the decrease in rate appears to increase with temperature. It is suggested that this may be due to a negative temperature effect on the interaction between the mercuric chloride and the solvent. If this

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TABLE III

Effect of added sodium chloride on the rate of the catalyzed reaction ($HgCl_2$ = 0.075 M)

RCl	T (°C)	Solvent	10^6k_1		% reduction in rate	
			Cl = 0.05 M	Cl = 0.10 M	Cl = 0.05 M	Cl = 0.10 M
t-BuCl	20	60% acetone	346	235	31.5	53.5
t-BuCl	20	80% acetone	33.5	11.5	41.5	80.2
t-BuCl	20	60% EtOH	400	338	Nil	14.6
t-BuCl	20	80% EtOH	47.9	42.0	1.9	13.9
t-AmCl	20	60% acetone	508	334	30.5	54.3
t-AmCl	20	80% acetone	53.0	19.6	49.5	81.1
t-AmCl	20	60% EtOH	647	557	2.2	16.5
t-AmCl	20	80% EtOH	75.8	68.0	7.5	16.8
CHPhMeCl	20	80% acetone*	17.6	4.91	59.0	88.4
CHPhMeCl	20	80% EtOH	70.5	55.9	13.3	31.2
CHPhEtCl	45	80% acetone*	54.8	18.8	51.1	83.2
CHPhEtCl	45	80% EtOH	199	165	34.5	45.2
CHPh-*i*-PrCl	54.8	80% acetone*	40.2	14.3	51.2	82.6
CHPh-*i*-PrCl	54.8	80% EtOH	127	103	32.8	45.5
CHPh-*t*-BuCl	80	80% acetone*	35.5	14.6	49.7	79.3
CHPh-*t*-BuCl	80	80% EtOH	108	85.4	41.6	53.8

*Reference 9. Rate in the absence of chloride ions. CHPhEtCl: 80% acetone, 10^6k_1 = 112; 80% EtOH, 10^6k_1 = 304. CHPh-*i*-PrCl: 80% acetone, 10^6k_1 = 82.4; 80% EtOH, 10^6k_1 = 189; CHPh-*t*-BuCl: 80% acetone, 10^6k_1 = 70.5; 80% EtOH, 10^6k_1 = 185.

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is the case, the extent of complex formation between mercuric chloride and chloride ions (and hence the rate reduction) should increase with temperature.

EXPERIMENTAL

Materials

1-Phenethyl alcohol, 1-hydroxypropyl benzene, and 1-*p*-tolylethyl alcohol were prepared by the Meerwein-Pondorff reduction of the corresponding ketones. 1-Hydroxyisobutyl benzene and (1-hydroxy-2,2-dimethylpropyl)benzene were prepared by the Grignard reaction with magnesium isopropyl bromide and magnesium *tert*-butyl chloride, respectively. The alcohols were purified through their acid phthalates, prepared in the usual way (23). The alcohols were converted into the chlorides by reaction with thionyl chloride. *tert*-Butyl chloride (24) and *tert*-amyl chloride (25) were prepared by the usual methods.

The physical constants of the alkyl chlorides are given below.

Alkyl chlorides	Boiling point (°C)		n_D^{25}	
	Expt.	Lit.	Expt.	Lit.
CHPhMeCl	78–79/16 mm	81–82/17 mm (26)	1.5250	1.5250 (13)
CHPhEtCl	64/2 mm	61–62/0.5 mm (27)	1.5185	
CHPh-*i*-PrCl	65/1 mm	63–64/0.5 mm (27)	1.5150	
CHPh-*t*-BuCl	87–89/5 mm	89.5–90.5/6.7 mm (20)	1.5149	1.5142 (20)
t-BuCl	50–51/760 mm	50.8/760 mm (28)	1.3818	1.3819 (14)
t-AmCl	86–87/760 mm	86/760 mm (29)	1.4058	1.407 (18°)(29)
CH(*p*-MePh)MeCl	134/80 mm; 101/25 mm		1.5220	

A.R.(B.D.H.) mercuric chloride and sodium chloride were used. The latter was dried at 250 °C.

Acetone was purified and dried by the method of Conant and Kirner (30). Lime-dried ethanol was made absolute by refluxing with sodium and diethyl phthalate.

Kinetic Work

The term *x*% aqueous acetone or ethanol signifies solvent made up (at room temperature) with *x* volumes of dry acetone or ethanol and (100 − *x*) volumes of distilled water. A large stock of solvent was made up to facilitate comparative measurements.

A conventional thermostat (±0.03°) was used for rate measurements at higher temperatures while for work at below room temperature, a Gallenkamp low temperature thermostat fitted with a Jackson thermoregulator was used (±0.02°).

At the higher temperatures, the sealed-bulb technique was used. The appropriate quantity of alkyl chloride was taken in a 100 ml volumetric flask and accurately weighed quantities of mercuric chloride and (or) sodium chloride were transferred to the flask with the aid of the solvent. After dissolution, the solution was made up to the mark. Aliquots (5 ml) were pipetted into neutral glass ampoules (which conformed to the B.P. test for limits of alkalinity (31)), and the ampoules sealed. They were immersed in the thermostat and vigorously shaken for 2 min. Then one ampoule was taken out, immediately chilled to kill the reaction, washed, and broken, under 150 ml of cold, dry acetone/ethanol. The liberated acid was titrated against carbon dioxide free standard NaOH, lacmoid being used as the indicator. At suitable intervals, the other ampoules were removed and the acid estimated similarly. The "infinity" titer (mean of two concordant values) was taken after an interval equal to 8 half-lives. When mercuric chloride was present, a quantity of concentrated potassium iodide solution (neutralized to lacmoid) just sufficient to destroy the mercuric

TABLE IV

Illustrative kinetic run for the mercuric chloride catalyzed hydrolysis of *tert*-butyl chloride in 60% v/v acetone–water at 20.0 °C (initial concentration *t*-BuCl = 0.0980 *M*; $HgCl_2$ = 0.0750 *M*)

t (s)	NaOH titer (ml)*	10^4k_1	*t* (s)	NaOH titer (ml)*	10^4k_1
0	0.24	—	480	2.18	4.78
60	0.53	5.18	1 200	3.98	4.19
120	0.81	5.18	1 800	4.98	3.86
180	1.06	5.04	2 400	5.78	3.67
240	1.32	5.06	3 300	6.68	3.54
300	1.56	5.04	4 800	7.70	3.24
360	1.76	4.87	∞	9.70	—
420	1.96	4.78			

*Volume of 0.05050 *N* NaOH solution equivalent to 5.0 ml sample.

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chloride was added before titration. For work at low temperature, the pipetting was done directly from the volumetric flask which served as the reaction vessel.

The first-order rate coefficients were calculated from the formula $k = (1/t) \ln a/(a - x)$ and the values are expressed in reciprocal second. The values given are the mean from two experiments.

One point deserves mention. It was found for the catalyzed reaction (particularly in aqueous acetone) that the first-order rate coefficients were steady only over an initial limited portion of the reaction. This is illustrated in Table IV. The rate coefficients given are the mean of the values which show constancy derived from duplicate runs. The catalyzed hydrolysis of 1-*p*-tolylethyl chloride did not show even this initial constancy in the rate. To obtain the initial rate, therefore, log k was plotted against log $(a - x)$ a good straight line was obtained. The best straight line was obtained by the method of least squares. Duplicate runs gave good agreement.

REFERENCES

1. C. K. INGOLD. Structure and mechanism in organic chemistry. Cornell University Press, Ithaca. 1953. p. 345.
2. E. GRUNWALD and S. WINSTEIN. J. Am. Chem. Soc. **70**, 846 (1948).
3. H. W. FOOTE. Am. Chem. J. **42**, 620 (1905).
4. R. ANANTARAMAN and K. SARAMMA. Indian J. Chem. **2**, 335 (1964).
5. R. ANANTARAMAN and K. SARAMMA. Naturwissenschaften, **50**, 497 (1963).
6. S. KOSHY and R. ANANTARAMAN. J. Am. Chem. Soc. **82**, 1574 (1960).
7. R. ANANTARAMAN and K. SARAMMA. Z. Physik. Chem. Leipzig, **216**, 21 (1961).
8. C. G. SWAIN and B. R. MOSELY. J. Am. Chem. Soc. **77**, 3727 (1955). C. A. BUNTON and B. NAYAK. J. Chem. Soc. 1915 (1959).
9. R. ANANTARAMAN and K. SARAMMA. Tetrahedron. In press.
10. E. D. HUGHES and C. K. INGOLD. J. Chem. Soc. 252 (1935).
11. L. C. BATEMAN, K. A. COOPER, E. D. HUGHES, and C. K. INGOLD. J. Chem. Soc. 925 (1940).
12. G. S. HAMMOND, M. F. HAWTHORNE, J. H. WATERS, and B. M. GRAYBILL. J. Am. Chem. Soc. **82**, 704 (1960).
13. A. H. FAINBERG and S. WINSTEIN. J. Am. Chem. Soc. **78**, 2770 (1956).
14. A. H. FAINBERG and S. WINSTEIN. J. Am. Chem. Soc. **79**, 1597 (1957).
15. S. WINSTEIN, E. GRUNWALD, and H. W. JONES. J. Am. Chem. Soc. **73**, 2700 (1951).
16. E. D. HUGHES, C. K. INGOLD, and A. D. SCOTT. J. Chem. Soc. 1201 (1937).
17. R. ANANTARAMAN. Ph.D. Thesis, University of London. 1950.
18. E. D. HUGHES. J. Chem. Soc. 255 (1935).
19. P. J. CHAKKO. M.Sc. Thesis, Kerala University. 1961.
20. S. WINSTEIN and B. K. MORSE. J. Am. Chem. Soc. **74**, 1133 (1952).
21. C. K. INGOLD. Structure and mechanism in organic chemistry. Cornell University Press, Ithaca. 1953. p. 359.
22. C. A. BUNTON. Nucleophilic substitution at a saturated carbon atom. Elsevier. 1963. p. 154.
23. A. J. H. HOUSSA and J. KENYON. J. Chem. Soc. 2260 (1930).
24. A. I. VOGEL. A textbook of practical organic chemistry. Longmans, Green, London. 1959. p. 276.
25. E. D. HUGHES and B. J. MACNULTY. J. Chem. Soc. 1283 (1937).
26. A. M. WARD. J. Chem. Soc. 445 (1927).
27. G. BADDELEY, J. CHADWICK, and H. T. TAYLOR. J. Chem. Soc. 2405 (1954).
28. J. TIMMERMANS and Y. DELCOURT. J. Chem. Phys. **31**, 98 (1934).
29. C. D. HODGMAN (*Editor*). Handbook of chemistry and physics. Chemical Rubber Publishing Co., Ohio. 1944. p. 665.
30. J. B. CONANT and W. R. KIRNER. J. Am. Chem. Soc. **46**, 246 (1924).
31. British Pharmacopocia. 1953. p. 851.