Ring-opening Reactions of Cyclic Ethers. IX.[1] Molecular Weight Distribution of Adducts in the Acid-catalyzed Reactions of Epichlorohydrin with Alcohols

Shizen Sekiguchi,* Yasushi Hasegawa, Kenji Nakamura, Kohji Matsui,
and Kensuke Nagahama
Department of Synthetic Chemistry, Gunma University, Tenjincho, Kiryu, Gunma 376

(Received November 21, 1975)

It was found that the molecular weights of adducts in the acid-catalyzed reactions of epichlorohydrin with alcohols obey the Weibull-Nycander distribution but not the Flory distribution. The distribution constants ($C=k_i/k_0$) were found to be smaller than 1, indicating that the reaction rate of the initial stage (k_0), *i.e.*, the reaction of epichlorohydrin with a starting alcohol, is greater than the rates of the later stages (k_i), *i.e.*, the reactions of epichlorohydrin with its adducts. The results indicate that the reaction proceeds *via* an "borderline" A-2 mechanism.

Nonionic surface active agents, prepared from the successive addition reaction of alkylene oxides to aliphatic carboxylic acids, aliphatic amines, and esters of polyhydric alcohols, have recently attracted much attention. They are used as commercial surfactants to a greater extent than anionic ones.

Several papers have appeared dealing with basic studies on the preparation of surfactants. The molecular weight distribution (MWD) of the adducts in the sodium hydroxide-catalyzed addition reaction of ethylene oxide (EO) or propylene oxide to lower alcohols was determined by Shigematsu *et al.*,[2,3] who indicated that it obeys the Weibull-Nycander distribution.[4] Shoda *et al.*[5] studied the MWD of the products in the sodium hydroxide-catalyzed addition reaction of EO to the reduced alcohol of coconut oil and showed that it obeys the Flory distribution,[6] that is, the Poisson one. Nagase and Sakaguchi[7] indicated that the MWD of the adducts in the sodium-catalyzed addition reaction of EO to dodecyl alcohol obeys the Weibully-Nycander distribution better than the Flory one. Karabinos and Quinn[8] studied the potassium hydroxide-catalyzed reactions of EO with lauryl alcohol and showed that the MWDs of the adducts deviate from the Flory distribution. Tischbirek[9] discussed the effects of reaction temperature, pressure of reaction systems, concentration of EO, rate of stirring, and kinds of alcohols and catalysts on the MWD of the adducts in the acid- or base-catalyzed reactions of EO with alcohols (C_2, C_6, and C_{12} alcohols). Thus few papers have appeared on the MWD of adducts in the acid-catalyzed reactions of epoxides with alcohols.

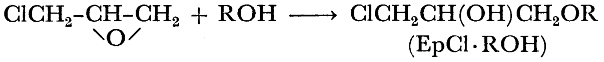
On the other hand, the mechanism of the acid-catalyzed ring-opening reactions of epoxides has been discussed by many workers.[10—13] Briggs *et al.*[14] discussed the mechanism of the acid-catalyzed alcoholysis of epoxides in detail, criticizing our previous work.[11]

In order to confirm the mechanism of the acid-catalyzed alcoholysis of epichlorohydrin (EpCl), we have determined the distribution constant (C), which is the ratio of the rate constant of the later stages (k_1, k_2, ...) to that of the initial stage (k_0), and which distribution the MWD in these reactions would obey.

Experimental

Materials. Methyl, propyl, butyl, *s*-butyl, and isobutyl alcohols were purified by the usual method. Boron trifluoride etherate ($BF_3 \cdot Et_2O$) and EpCl were repeatedly distilled through a rectifying column (Kyowa VI-DL Concentric Tube Fractionater, theoretical plate number 80); $BF_3 \cdot Et_2O$ bp 125 °C; EpCl 114—115 °C, d_4^{20} 1.1682, n_D^{20} 1.4326.

Synthes is of 1 : 1 (EpCl·ROH) and 2 : 1 (3EpCl·ROH) Adducts. Epichlorohydrin reacts with an alcohol in the presence of an acid to give the following adducts.[11,15,16]



$$\underset{\diagdown O \diagup}{ClCH_2\text{-}CH\text{-}CH_2} + ROH \longrightarrow \underset{(EpCl \cdot ROH)}{ClCH_2CH(OH)CH_2OR} \qquad (1)$$

Table 1. Syntheses of 1 : 1 and 2 : 1 adducts

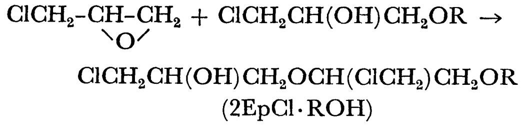
Run	Adduct	ROH[a)] g(mol)	EpCl g(mol)	Catalyst g(mol)	React temp (°C)	React time (h)	Bp (°C/mmHg)	Yield[b)] (%)
1	EpCl·n-C_4H_9OH	1280(17.3)	200 (2.16)	8 (0.078)[c)]	117—121	12	72.6—74.6/2	60
2	EpCl·i-C_4H_9OH	1280(17.3)	200 (2.16)	8 (0.078)[c)]	108—112	17.5	74.0—76.0/4	72
3	EpCl·s-C_4H_9OH	1280(17.3)	200 (2.16)	8 (0.078)[c)]	99—103	26	86—88/8	80
4	2EpCl·n-C_4H_9OH	298(1.78)	20.8(0.224)	1.18(8.37×10^{-3})[d)]	110—130	31	140—144/1	34
5	2EpCl·i-C_4H_9OH	238(1.42)	16.3(0.176)	1.13(7.99×10^{-3})[d)]	110—130	30	145—150/4	52
6	2EpCl·s-C_4H_9OH	284(1.70)	19.8(0.211)	1.16(8.17×10^{-3})[d)]	110—130	34	168—170/12	29
7	EpCl·CH_3OH	480(15.0)	140 (1.5)	2.8 (2.7×10^{-2})[c)]	67—68	12	93.2—93.5/ 48—50	83.3
8	EpCl·n-C_3H_7OH	520(8.65)	100 (1.08)	1.6 (1.5×10^{-2})[c)]	96—98	10	73—75/8	56.3

a) Alcohols used are *n*-, *i*-, and *s*-C_4H_9OH, CH_3OH, and *n*-C_3H_7OH in the case of Runs 1—3, 7 and 8, respectively; EpCl·ROH(1 : 1 adduct) in the case of Runs 4—6. b) Based on initial EpCl. c) 95% H_2SO_4 used as a catalyst. d) $BF_3 \cdot Et_2O$ used as a catalyst.

Table 2. Refractive indices and elemental analyses of adducts

Run	Adduct	Ref. index[a)] (n_D^t)	Elemental anal. (%)			
			Calcd		Found	
			C	H	C	H
1	EpCl·n-C_4H_9OH	1.4437(23.8) [1.4441(23.5)][11a]	50.45	9.07	50.31	9.22
2	EpCl·i-C_4H_9OH	1.4399(23.8)	50.45	9.07	50.37	9.06
3	EpCl·s-C_4H_9OH	1.4420(23.2) [1.4425(23.8)][11a]	50.45	9.07	50.30	9.09
4	2EpCl·n-C_4H_9OH	1.4652(25.0)	46.33	7.77	46.50	7.71
5	2EpCl·i-C_4H_9OH	1.4597(26.5)	46.33	7.77	46.31	7.74
6	2EpCl·s-C_4H_9OH	1.4593(25.4)	46.33	7.77	46.48	7.67
7	EpCl·CH_3OH	1.4488(15.4) [1.4488(15.4)][11a]	38.57	7.28	38.58	7.42
8	EpCl·n-C_3H_7OH	1.4443(15.4) [1.4447(19.5)][11a]	47.22	8.58	47.08	8.39

a) Figures in parentheses indicate the temperature of measurement.



$$ClCH_2\text{-}\underset{\diagdown O \diagup}{CH\text{-}CH_2} + ClCH_2CH(OH)CH_2OR \rightarrow ClCH_2CH(OH)CH_2OCH(ClCH_2)CH_2OR \quad (2EpCl\cdot ROH) \tag{2}$$

Higher adducts are formed, depending on the reaction conditions, especially on the molar ratio of EpCl to alcohol. These adducts were synthesized for the preparation of calibration curves in vapor phase chromatography (VPC).

In the case of EpCl·CH_3OH, a typical procedure is described below. One hundred and forty grams (1.5 mol) of EpCl was added dropwise at room temperature to a stirred solution of 480 g (15 mol) of methyl alcohol and 2.8 g (2.7×10^{-2} mol) of H_2SO_4. EpCl had to be carefully added to prevent bumping. After addition of EpCl the mixture was further refluxed for 12 h. After the mixture had been neutralized with a concentrated sodium hydroxide solution, and dried over anhydrous sodium sulfate, methyl alcohol was distilled off and the residue was distilled under reduced pressure.

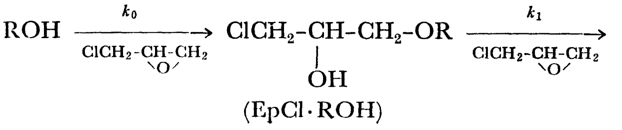
The reaction conditions, boiling points and yields for the preparation of the adducts are shown in Table 1, and the physical properties and results of elemental analyses in Table 2.

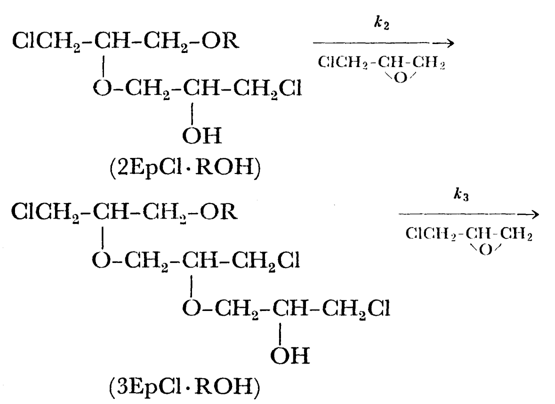
Determination of Unreacted Alcohols and Epichlorohydrin, and Adducts. The amount of the unreacted EpCl and Alcohols, and adducts were determined by VPC on a column packed with 10% polydiethylene glycol succinate (2 m) on Diasolid M at 100 °C for unreacted EpCl and alcohols (toluene used as an internal standard), 190 °C for 1 : 1 adducts and 200 °C for 2 : 1 adducts (in these cases, nitrobenzene used as an internal standard). Helium was used as a carrier gas.

Theoretical

Theories on molecular weight distribution have been worked out by several workers, the Flory[17] and Weibull-Nycander distributions[18] being often used. Molecular weight distribution can be calculated if certain assumptions are made on the relative reactivities of a starting alcohol and its adducts.

The reaction path of addition is expressed as follows:





$$ROH \xrightarrow[ClCH_2\text{-}CH\text{-}CH_2 \,(\diagdown O \diagup)]{k_0} \underset{(EpCl\cdot ROH)}{ClCH_2\text{-}\underset{OH}{CH}\text{-}CH_2\text{-}OR} \xrightarrow[ClCH_2\text{-}CH\text{-}CH_2 \,(\diagdown O \diagup)]{k_1} \underset{(2EpCl\cdot ROH)}{ClCH_2\text{-}\underset{O\text{-}CH_2\text{-}\underset{OH}{CH}\text{-}CH_2Cl}{CH}\text{-}CH_2\text{-}OR} \xrightarrow[ClCH_2\text{-}CH\text{-}CH_2 \,(\diagdown O \diagup)]{k_2} \underset{(3EpCl\cdot ROH)}{ClCH_2\text{-}\underset{O\text{-}CH_2\text{-}\underset{O\text{-}CH_2\text{-}\underset{OH}{CH}\text{-}CH_2Cl}{CH}\text{-}CH_2Cl}{CH}\text{-}CH_2\text{-}OR} \xrightarrow[ClCH_2\text{-}CH\text{-}CH_2 \,(\diagdown O \diagup)]{k_3} \tag{3}$$

Flory distribution (or Poisson distribution)

If $k_0=k_1=k_2=\cdots=k_n=\cdots$ in Eq. 2, we obtain

$$\frac{n_i}{n_{00}} = e^{-v}\cdot\frac{v^i}{i!} \tag{4}$$

Weibull-Nycander distribution

If $k_0=k_1=k_2=\cdots=k_n=\cdots$in Eq. 1 we have

$$v = C\cdot\ln\frac{n_{00}}{n_0} - (C-1)\left(1-\frac{n_0}{n_{00}}\right) \tag{5}$$

and

$$\frac{n_i}{n_{00}} = \frac{C^{i-1}}{(C-1)^i}\left\{\frac{n_0}{n_{00}}-\left(\frac{n_0}{n_{00}}\right)^C\sum_{j=0}^{i-1}\frac{1}{j!}\left[(C-1)\ln\frac{n_{00}}{n_0}\right]^j\right\} \tag{6}$$

n_{00}; mole of a starting alcohol
n_i; mole of i-th mer (iEpCl·ROH)
v; average mole of added EpCl per one mole of the starting alcohol
C; distribution constant (k_i/k_0)

Thus we can calculate the v-value if the amount of unreacted EpCl is determined. Once the v-value is determined, the expected amounts of i-th mers formed in the Flory distribution can be calculated by means of Eq. 4. Furthermore, if the amount of unreacted alcohol is also determined, a C-value can be calculated by means of Eq. 5. Using the C-value and Eq. 6, one can estimated the expected amounts of i-th mers in the Weibull-Nycander distribution.

Table 3. Determination of adducts[a)]

Run	Alcohol	Catalyst[b)] (mol%)		React. temp (°C)	v	Observed values n_0/n_{00}	n_1/n_{00}	n_2/n_{00}	C
9	n-C_4H_9OH	$BF_3 \cdot Et_2O$	0.108	50	0.996	0.154	0.761	0.103	0.14
10		$BF_3 \cdot Et_2O$	0.109	70	1.000	0.160	0.743	0.101	0.16
11		$BF_3 \cdot Et_2O$	0.054	70	0.917	0.200	0.754	0.079	0.14
12		$SnCl_4$	0.109	70	1.000	0.112	0.845	0.031	0.08
13		$ZnCl_2$	1.99	70	0.845	0.239	0.779	0.025	0.12
14		H_2SO_4	2.00	70	0.184	0.814	0.180	trace	0.10
15	i-C_4H_9OH	$BF_3 \cdot Et_2O$	0.108	50	0.994	0.150	0.716	0.113	0.13
16		$BF_3 \cdot Et_2O$	0.106	70	1.000	0.155	0.699	0.117	0.15
17		$SnCl_4$	0.109	70	1.000	0.129	0.733	0.097	0.10
18	s-C_4H_9OH	$BF_3 \cdot Et_2O$	0.109	50	1.000	0.157	0.701	0.124	0.15
19		$BF_3 \cdot Et_2O$	0.109	70	1.000	0.169	0.650	0.127	0.17
20		$SnCl_4$	0.109	70	1.000	0.129	0.733	0.097	0.10
21		$ZnCl_2$	2.00	70	0.902	0.167	0.712	0.067	0.07
22	CH_3OH	$BF_3 \cdot Et_2O$	0.063	55	0.980	0.158	0.725	0.108	0.13
23	n-C_3H_7OH	$BF_3 \cdot Et_2O$	0.035	70	0.882	0.235	0.678	0.108	0.17

a) Thirty grams (0.324 mol) of EpCl was used. The molar ratio of each alcohol to EpCl is one. b) Based on the amount of EpCl.

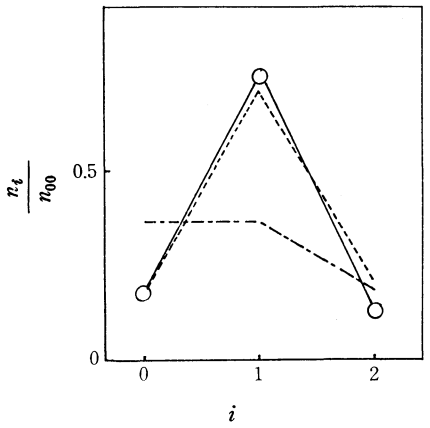


Fig. 1. The relationship between n_i/n_{00} and i.
——: observed, ——: Flory distribution, ----: Weibull-Nycander distribution.

Results and Discussion

The results of determination of the adducts are given in Table 3. Through all runs, the recovery of initial EpCl summing up unreacted and transformed EpCl ranged from 95 to 100%, and, moreover, most of it was found to be transformed EpCl. Thus it seems that a very small amount of initial EpCl changed into unidentified products.[19)]

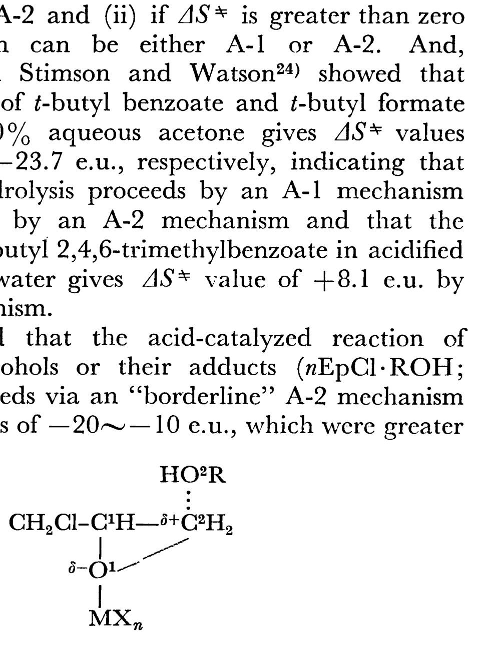
The results indicate that the distribution constant was smaller than 1, the 1 : 1 adduct being produced to a greater extent than the 2 : 1 one in every case. The observed values (n_i/n_{00}) in the case of Run 9 are compared with those calculated on the basis of the Flory and Weibully-Nycander distributions by use of C (0.14) (Fig. 1). The MWD in Run 9 clearly obeys the Weibully-Nycander one. Similar results were also obtained in the other runs.

The mechanism of acid-catalyzed ring-opening reactions of epoxides have been discussed by several workers. Long *et al.*[10)] concludedthat the acid-catalyzed hydrolysis of epoxides proceeds *via* a "borderline" A-1 mechanism,[10,20)] *viz.*, the carbonium ion formed through the co-ordination of an acid (catalyst) to the oxygen atom of epoxides reacts with nucleophiles.

On the other hand, Koskikallio and Whalley[12)] and leNoble and Duffy[13)] found that the volume of activation ($\Delta V^{\neq}$) is negative in the acid-catalyzed hydrolyses of epoxides and they concluded that the hydrolysis proceeds *via* an A-2 mechanism. Briggs *et al.*[14)] reported that the acid-catalyzed alcoholysis of styrene oxide proceeds *via* a "borderline" A-2 mechanism.

Entropy of activation as a criterion for reaction mechanism is discussed by many workers.[21)] Whalley[22)] deduced that (i) if $\Delta S^{\neq}$ is less than zero the reaction was probably A-2 and (ii) if $\Delta S^{\neq}$ is greater than zero the mechanism can be either A-1 or A-2. And, Stimson[23)] and Stimson and Watson[24)] showed that the hydrolysis of t-butyl benzoate and t-butyl formate in acidified 60% aqueous acetone gives $\Delta S^{\neq}$ values of +9.5 and −23.7 e.u., respectively, indicating that the former hydrolysis proceeds by an A-1 mechanism and the latter by an A-2 mechanism and that the hydrolysis of t-butyl 2,4,6-trimethylbenzoate in acidified 90% ethanol–water gives $\Delta S^{\neq}$ value of +8.1 e.u. by an A-1 mechanism.

We reported that the acid-catalyzed reaction of EpCl with alcohols or their adducts (nEpCl·ROH; n=1,2,3) proceeds via an "borderline" A-2 mechanism with $\Delta S^{\neq}$ values of $-20\sim-10$ e.u., which were greater to some extent than those of usual A-2 mechanism and proposed the following transition state.[11)] The distribution constants of *ca.* 0.10 correspond to this



$$\begin{array}{c} \phantom{CH_2Cl\text{-}C^1H—\delta+}HO^2R \\ CH_2Cl\text{-}C^1H—{}^{\delta+}C^2H_2 \\ {}^{\delta-}O^1 \\ MX_n \end{array}$$

proposition, since if this transition state is assumed, the reaction rate of the first stage will be greater than those of the later ones owing to the steric crowding of the bulkier adducts (RO^2H) at C^2 atom. If the carbonium ion such as $ClCH_2(O\overset{-}{M}X_n)\overset{+}{C}H_2$ were formed, the 1 : 1 adducts should be produced less than as shown in Fig. 1 and the MWD should obey the Flory distribution since this situation indicates that $k_0=k_1=\cdots$.

Although Briggs *et al.* stated that the choice of EpCl is not appropriate for the elucidation of the mechanism or ring-opening reaction of epoxides, we found that the determination of MWD of adducts in the acid-catalyzed reaction of EpCl with alcohols is very useful. It is concluded that in the presence of acidic catalysts EpCl reacts with alcohols *via* an "borderline" A-2 mechanism.

References

1) Part VIII; S. Sekiguchi, K. Matsui, and Y. Yasuraoka, *Bull. Chem. Soc. Jpn.*, **43**, 2523 (1970).

2) H. Shigematsu, Y. Miura, and Y. Ishii, *Kogyo Kagaku Zasshi*, **65**, 64 (1962).

3) H. Shigematsu, Y. Nishikawa, and Y. Ishii, *Kogyo Kagaku Zasshi*, **65**, 111 (1962).

4) B. Weibull and B. Nycander, *Acta Chem. Scand.*, **8**, 847 (1954).

5) Y. Shoda, T. Yamamoto, and T. Shimojima, *Yukagaku Kyokai Shi*, **7**, 8 (1958).

6) P. Flory, *J. Am. Chem. Soc.*, **62**, 1561 (1949).

7) K. Nagase and K. Sakaguchi, *Kogyo Kagaku Zasshi*, **63**, 588 (1960).

8) J. V. Karabinos and E. J. Quinn, *J. Am. Oil Chemists Soc.*, **33**, 223 (1956).

9) G. Tischbirek, *Vortraege Originalfass. Intern. Kongr. Grenzflaechenaktive Stoffe*, 3, Cologne, **1**, 126 (1960).

10) (a) F. A. Long and J. G. Pritchard, *J. Am. Chem. Soc.*, **78**, 2663 (1956); (b) J. G. Pritchard and F. A. Long, *ibid.*, **78**, 2667 (1956); (c) J. G. Pritchard and F. A. Long, *ibid.*, **78**, 6008 (1956); F. A. Long, J. G. Pritchard, and F. E. Stafford, *ibid.*, **79**, 2362 (1957); (d) L. L. Ingraham and S. Winstein, *ibid.*, **74**, 1160 (1952).

11) (a) S. Sekiguchi, I. Takase, and K. Matsui, *Kogyo Kagaku Zasshi*, **66**, 1827 (1963); *ibid.*, **68**, 286, 945, 2414 (1965); (b) S. Sekiguchi, S. Ishii, and K. Matsui, *ibid.*, **68**, 286 (1965); (c) S. Sekiguchi and S. Ishii, *ibid.*, **70**, 47 (1967).

12) J. Koskikallio and E. Whalley, *Trans. Faraday Soc.*, **55**, 815 (1959).

13) W. J. leNoble and M. Duffy, *J. Phys. Chem.*, **68**, 614 (1964).

14) (a) J. Briggs, N. B. Chapman, A. F. Finch, and V. Wray, *J. Chem. Soc., B*, **1971**, 55; (b) J. Briggs, N. B. Chapman. and V. Wray, *ibid.*, **1971**, 63, 66, 71.

15) F. G. Ponomarev, *Zhur. Obshchei. Khim.*, **22**, 128, 9291 (1952); *Chem. Abstr.*, **46**, 11105 (1952); *ibid.*, **47**, 3794 (1953).

16) (a) J. Novák, *J. Chromatogr.*, **31**, 137 (1967); (b) J. Novák and J. Reznicek, *ibid.*, **43**, 437 (1969).

17) P. Flory, *J. Am. Chem. Soc.*, **62**, 1561 (1940).

18) B. Weibull and B. Nycander, *Acta Chem. Scand.*, **8**, 847 (1954).

19) Unidentified products may be considered to involve higher adducts or isomeric adducts such as [$ClCH_2CH(OR)$-CH_2OH) and its higher ones. However, as their amounts were very small, they were neglected.

20) R. E. Parker and N. S. Isaacs, *Chem. Rev.*, **59**, 768 (1959).

21) (a) M. L. Bender, "Technique of Organic Chemistry," Vol. VIII, Part II, ed. by S. L. Friess, E. S. Lewis, and A. Weissberger, Interscience, New York, N. Y. (1963), p. 1427; (b) R. W. Taft, Jr., *J. Am. Chem. Soc.*, **74**, 5374 (1952); (c) R. W. Taft, Jr., E. L. Purlee, P. Riesz, and G. A. DeFrazio, *ibid.*, **77**, 1584 (1955); (d) G. Kohnstam, *Adv. Phys. Org. Chem.*, **5**, 121 (1967); (e) E. H. Cordes, *Prog. Phys. Org. Chem.*, **4**, 1 (1967).

22) E. Whalley, *Trans. Faraday Soc.*, **55**, 798 (1959).

23) V. R. Stimson, *J. Chem. Soc.*, **1955**, 4020.

24) V. R. Stimson and E. J. Watson, *J. Chem. Soc.*, **1954**, 2848.