

# Microwave Absorption and Molecular Structure in Liquids. LXXIII. A Dielectric Study of Solute-Solvent Interactions<sup>1</sup>

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**Abstract:** Measurements of dielectric constant and loss at 0.2, 1.2, 3.2, 10.0, and 25.0 cm have been made for seven chloroethanes in dilute cyclohexane, benzene, *p*-xylene, mesitylene, and *p*-dioxane solutions at 20–55°. The data have been used to calculate mean relaxation times and apparent dipole moments. For each ethane the mean relaxation time increases with increased solvent basicity, and an approximately linear relationship exists between the solute relaxation time and the ionization potential for the hydrocarbon solvents. In general, this behavior is interpreted in terms of weak solute-solvent interaction, probably C-H hydrogen bonding, hindering the rotation of the chloroethanes. The relative interactions for the solutes in each of the solvents capable of acting as proton acceptors are obtained by reference to their relaxation times in cyclohexane and may be expressed in terms of the increased free energies of activation for molecular rotation amounting to 150–850 cal/mol. In certain cases interaction is also evidenced by the solvent dependency of the apparent dipole moments.

Extensive work has been carried out on the subject of C-H groups as proton donors in hydrogen bonding.<sup>3</sup> The potential of dielectric relaxation measurements as a method of studying weak molecular interactions has been illustrated for chloroform<sup>4</sup> and for some haloethanes,<sup>5,6</sup> whose relaxation times are appreciably longer in aromatic solvents than in cyclohexane or hexane, with which there is no specific interaction.<sup>7</sup> So far the work has been limited to several haloethanes in cyclohexane and *p*-xylene solutions at 25°<sup>6</sup> and to 1,2-dichloroethane in cyclohexane, hexane, carbon tetrachloride, benzene, and *p*-xylene at 20°.<sup>5</sup> Infrared spectroscopy, the most characteristic method for the detection of hydrogen bonding, is relatively insensitive to C-H-B hydrogen bonding, where B is a  $\pi$ -base proton acceptor. Thus, an extensive study of the dielectric behavior of the chloroethanes at low concentration to minimize solute-solute interactions, in non-polar solvents capable of acting as proton acceptors (benzene, *p*-xylene, mesitylene, and *p*-dioxane) and an inert reference solvent (cyclohexane), was proposed. An additional object of this work was to investigate the effect of solvent upon the apparent dipole moment, which, in the case of 1,2-dichloroethane, is rather large.<sup>5</sup>

## Experimental Section

**Materials.** The chloroethanes were all dried over calcium chloride prior to fractional distillation. Pentachloroethane and 1,1,2,2-tetrachloroethane were distilled under reduced pressure, and the small center fractions collected for use were stored in dark bottles over calcium chloride. Cyclohexane, benzene, *p*-xylene, and mesitylene were dried over and distilled from sodium. *p*-Dioxane was twice refluxed for 10 hr over sodium and then distilled from sodium.

**Methods of Measurement.** Dielectric constants and losses were measured at 0.20, 1.2, 3.2, 10.0, and 25.0 cm by methods which

have been described previously.<sup>8-12</sup> The static dielectric constants were measured at 575 m with a heterodyne beat apparatus.

The dielectric constants and losses for the solutions were corrected for the solvent absorptions which have been discussed elsewhere.<sup>13,14</sup>

## Results

The measured values of the dielectric constants  $\epsilon'$  and losses  $\epsilon''$ , which were considered too numerous for publication,<sup>15</sup> were fed into an IBM 7094 computer programmed to solve the Cole-Cole equations<sup>16</sup> for the most probable relaxation time  $\tau_0$ , distribution parameter  $\alpha$ , and optical or infinite-frequency dielectric constant  $\epsilon_\infty$ .

Dipole moments were obtained from the Debye equation (eq 1) for dilute solutions in which  $\epsilon_1$  is the static

$$\mu = 0.01281 [3T(\epsilon_0 - \epsilon_\infty)M_2/(\epsilon_1 + 2)^2w_2d_1]^{1/2} \quad (1)$$

dielectric constant of the solvent,  $d_1$  is its density,  $w_2$  is the weight fraction of the solute, and  $M_2$  is its molecular weight.

The free energy of activation difference ( $\Delta\Delta G_0^\ddagger$ ) for molecular reorientation in two solvents may be calculated using<sup>5</sup> eq 2, in which  $\tau_{0B}$  and  $\tau_{0cyc}$  are the most probable

$$\tau_{0B}/\tau_{0cyc} = \exp(\Delta\Delta G_0^\ddagger/RT) \quad (2)$$

relaxation times in the solvents capable of acting as proton acceptors (benzene, *p*-xylene, mesitylene, and *p*-dioxane) and in cyclohexane, respectively.

Table I lists the most probable relaxation times (in picoseconds), distribution parameters, and dipole moments for the chloroethanes at mole fraction  $f_2$  and temperature  $t$  in the different solvents. The calculated  $\Delta\Delta G_0^\ddagger$  values are given in Table II.

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(15) Tables of  $\epsilon'$  and  $\epsilon''$  values will be made available on request.

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(1) This research was supported by the Office of Naval Research and the U. S. Army Research Office (Durham).

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**Table I.** Most Probable Relaxation Times ( $\tau_0$ ), Distribution Parameters ( $\alpha$ ), and Dipole Moments ( $\mu$ ) for Chloroethanes at Mole Fraction ( $f_2$ ) and Temperature ( $t$ ) in Various Solvents

Solvent	$f_2$	$t, ^\circ\text{C}$	$\tau_0$ (psec)	$\alpha$	$\mu, \text{D.}$
1,1-Dichloroethane					
Cyclohexane	0.0254	25	2.7	0.02	1.95
Benzene	0.0251	25	4.2	0.00	1.88
<i>p</i> -Xylene	0.0265	25	4.5	0.02	1.89
Mesitylene	0.0292	25	4.7	0.07	1.91
<i>p</i> -Dioxane	0.0228	25	5.8	0.02	1.98
1,2-Dichloroethane					
Cyclohexane	0.0463	20	2.1	0.10	1.46
	0.0423	55	1.6	0.06	1.44
Benzene	0.0389	20	3.5	0.13	1.83
	0.0389	50	2.9	0.03	1.76
<i>p</i> -Xylene	0.0560	20	4.8	0.05	1.58
	0.0560	25	4.5	0.07	1.58
	0.0560	55	3.3	0.09	1.58
Mesitylene	0.0643	20	5.8	0.08	1.49
	0.0643	25	5.3	0.08	1.51
	0.0643	55	4.0	0.09	1.51
<i>p</i> -Dioxane	0.0334	20	6.9	0.08	1.82
	0.0232	25	5.9	0.07	1.88
1,1,1-Trichloroethane					
Cyclohexane	0.0294	25	2.9	0.02	1.84
	0.0294	55	2.1	0.06	1.87
Benzene	0.0275	25	3.7	0.03	1.82
	0.0275	55	2.8	0.03	1.82
<i>p</i> -Xylene	0.0417	25	4.0	0.07	1.76
	0.0417	55	2.7	0.06	1.85
Mesitylene	0.0495	25	4.8	0.07	1.77
	0.0495	55	3.2	0.08	1.81
<i>p</i> -Dioxane	0.0291	25	5.8	0.06	1.87
1,1,2-Trichloroethane					
Cyclohexane	0.0314	25	4.1	0.00	1.42
	0.0314	55	3.2	0.00	1.43
Benzene	0.0221	25	7.1	0.03	1.57
	0.0221	55	4.8	0.09	1.53
<i>p</i> -Xylene	0.0311	25	8.5	0.09	1.50
	0.0311	55	5.2	0.08	1.51
Mesitylene	0.0346	25	9.6	0.02	1.43
	0.0346	55	5.6	0.08	1.49
<i>p</i> -Dioxane	0.0226	25	9.6	0.12	1.69
1,1,1,2-Tetrachloroethane					
Cyclohexane	0.0358	25	4.6	0.03	1.44
	0.0358	55	3.7	0.00	1.44
Benzene	0.0308	25	7.6	0.00	1.46
	0.0308	55	5.2	0.00	1.45
<i>p</i> -Xylene	0.0408	25	8.5	0.02	1.43
	0.0408	55	6.2	0.02	1.41
Mesitylene	0.0479	25	10.4	0.12	1.43
	0.0479	55	7.3	0.03	1.43
<i>p</i> -Dioxane	0.0257	25	13.7	0.04	1.53
1,1,2,2-Tetrachloroethane					
Cyclohexane	0.0248	25	5.6	0.06	1.59
	0.0248	55	4.0	0.09	1.60
Benzene	0.0213	25	10.4	0.05	1.71
	0.0213	55	7.0	0.09	1.71
<i>p</i> -Xylene	0.0266	25	13.4	0.08	1.74
	0.0266	55	8.0	0.12	1.71
Mesitylene	0.0300	25	19.7	0.12	1.65
	0.0300	55	11.7	0.08	1.63
<i>p</i> -Dioxane	0.0164	25	18.6	0.00	1.88
Pentachloroethane					
Cyclohexane	0.0489	25	6.6	0.00	1.07
	0.0489	55	4.9	0.00	1.03
Benzene	0.0425	25	12.7	0.08	1.07
	0.0425	55	7.7	0.06	1.15
<i>p</i> -Xylene	0.0587	25	15.4	0.08	1.17
	0.0587	55	9.5	0.08	1.13
Mesitylene	0.0674	25	21.7	0.10	1.11
	0.0674	55	16.7	0.09	1.09
<i>p</i> -Dioxane	0.0376	25	27.6	0.08	1.26

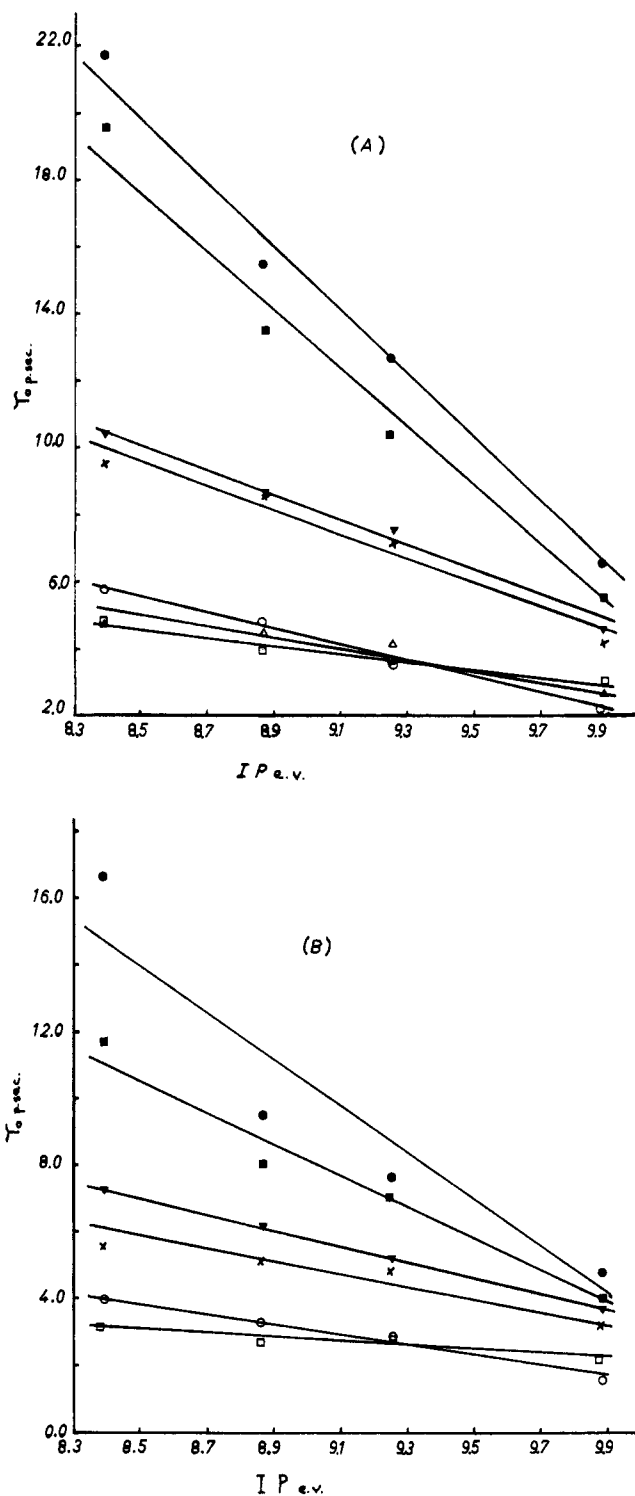


Figure 1. (A) Plot of the most probable relaxation time of the solute at 25° (1,2-dichloroethane at 20°) against the ionization potential of the solvent (cyclohexane, 9.88 eV; benzene, 9.25 eV; *p*-xylene, 8.86 eV; mesitylene, 8.39 eV: ●, pentachloroethane; ■, 1,1,2,2-tetrachloroethane; ▲, 1,1,1,2-tetrachloroethane; ×, 1,1,2-trichloroethane; □, 1,1,1-trichloroethane; ○, 1,2-dichloroethane; and △, 1,1-dichloroethane. (B) Similar to Figure 1A, but at 55°.

## Discussion

Small distribution parameters are obtained for almost all of the systems which have been examined (Table I), and the possibility of more than one contributing relaxation

**Table II.** Free Energy of Activation Differences,  $\Delta\Delta G_0^\ddagger$  (cal/mol), for Chloroethanes

Ethane solute	Benzene		<i>p</i> -Xylene		Mesitylene		<i>p</i> -Dioxane 25°
	25°	55°	25°	55°	25°	55°	
1,1-Dichloro-	280		310		340		470
1,2-Dichloro- <sup>a</sup>	300 <sup>a</sup>	380 <sup>b</sup>	490 <sup>a</sup>	470	590 <sup>a</sup>	600	710 <sup>a</sup>
1,1,1-Trichloro-	140	170	170	150	300	270	410
1,1,2-Trichloro-	320	320	430	320	500	370	500
1,1,1,2-Tetrachloro-	310	230	370	330	490	450	660
1,1,2,2-Tetrachloro-	370	370	520	450	750	710	720
Pentachloro-	390	300	500	430	710	800	850

<sup>a</sup> Refer to results at 20°. <sup>b</sup> Obtained from  $\tau_0$  in cyclohexane and benzene at 55 and 50°, respectively.

**Table III.** Effect of Solvent upon the Relaxation Time and Apparent Dipole Moment for Some Chloroethanes

Ethane solute	$\tau_{0B}/\tau_{0cyc}, 25^\circ$				$\Delta\mu/\mu_{cyc}, 25^\circ$			
	Benzene	<i>p</i> -Xylene	Mesitylene	<i>p</i> -Dioxane	Benzene	<i>p</i> -Xylene	Mesitylene	<i>p</i> -Dioxane
1,1-Dichloro-	1.60	1.68	1.76	2.20	-0.04	-0.03	-0.02	+0.02
1,2-Dichloro- <sup>a</sup>	1.67 <sup>a</sup>	2.29 <sup>a</sup>	2.76 <sup>a</sup>	3.29 <sup>a</sup>	+0.25 <sup>a</sup>	+0.08 <sup>a</sup>	+0.02 <sup>a</sup>	+0.25 <sup>a</sup>
1,1,1-Trichloro-	1.27	1.36	1.64	2.00	-0.01	-0.04	-0.04	+0.02
1,1,2-Trichloro-	1.72	2.05	2.32	2.32	+0.11	+0.06	+0.01	+0.19
1,1,1,2-Tetrachloro-	1.68	1.86	2.27	3.00	+0.01	-0.01	-0.01	+0.06
1,1,2,2-Tetrachloro-	1.86	2.39	3.52	3.32	+0.08	+0.09	+0.04	+0.18
Pentachloro-	1.92	2.33	3.29	4.18	0.00	+0.09	+0.04	+0.18

Solute	$\tau_{0B}/\tau_{0cyc}, 55^\circ$			$\Delta\mu/\mu_{cyc}, 55^\circ$		
	Benzene	<i>p</i> -Xylene	Mesitylene	Benzene	<i>p</i> -Xylene	Mesitylene
1,2-Dichloro-	1.81 <sup>b</sup>	2.06	2.50	+0.21 <sup>b</sup>	+0.07	+0.03
1,1,1-Trichloro-	1.30	1.25	1.50	-0.03	-0.01	-0.04
1,1,2-Trichloro-	1.50	1.62	1.75	+0.07	+0.06	+0.04
1,1,1,2-Tetrachloro-	1.41	1.66	1.98	+0.01	-0.02	-0.01
1,1,2,2-Tetrachloro-	1.75	2.00	2.93	+0.07	+0.07	+0.02
Pentachloro-	1.57	1.94	3.41	+0.12	+0.10	+0.06

<sup>a</sup> Refer to results at 20°. <sup>b</sup> Obtained from  $\tau_0$  in cyclohexane and benzene at 55 and 50°, respectively.

process in such cases must be considered. A contribution from an intramolecular process may be discarded for 1,1,1-trichloroethane, since there is no component moment perpendicular to the C-C axis, and for 1,1,1,2-tetra- and 1,1,2,2-tetrachloroethanes and pentachloroethane in view of their large potential barriers to internal rotation.<sup>6,17</sup> The fact that a plot of  $\tau_0$  (in cyclohexane) against volume for all the chloroethanes is approximately linear<sup>18</sup> is evidence against any appreciable contribution from an intramolecular process for 1,1-dichloro-, 1,2-dichloro-, and 1,1,2-trichloroethanes or from a discrete process originating from solute-solute interaction, which would hardly be a constant throughout the series. Furthermore, the distribution parameters show no trend with increased solute-solvent interaction (Table I) and are probably due to variations in local environment among the solute molecules, an effect which seems not uncommon for small polar molecules in nonpolar solvents.<sup>19</sup>

For the systems which have also been studied by Chitoku and Higasi<sup>5</sup> and Crossley and Walker<sup>6</sup> the agreement for the dipole moments is reasonable in view of the short relaxation times and the enhanced errors in the extrapolated  $\epsilon_\infty$  values. In general, we have used more dilute solutions than those of Crossley and Walker, and our relaxation times are somewhat shorter, the effect being most noticeable for the strong interactors 1,1,2,2-tetrachloroethane and pentachloroethane, indicating that solute-solute interaction is not negligible.

(17) A.-C. Tang and S.-Y. Chen, *Scientia* (Peking), **11**, 1491 (1962).

(18) J. Crossley and S. Walker, *J. Chem. Phys.*, **45**, 4733 (1966).

(19) J. Crossley, W. F. Hassell, and S. Walker, *Can. J. Chem.*, **46**, 2181 (1968).

For all the chloroethanes, with the exception of 1,1,2,2-tetrachloroethane, for which the relaxation time in mesitylene is longer than in *p*-dioxane, the relaxation times lengthen in the solvent order: cyclohexane < benzene < *p*-xylene < mesitylene < *p*-dioxane. The viscosities of the aromatic solvents (~0.6 cP) are less than those of cyclohexane, 0.9 cP, and *p*-dioxane, 1.2 cP at 25°. Thus, viscosity effects alone do not account for the relaxation behavior and, indeed, for such small nearly spherical molecules, especially 1,1,1-trichloroethane, the relaxation times might be almost independent of the macroscopic viscosity.<sup>20</sup> For the hydrocarbon solvents the relaxation time increases are comparable with their relative basicities,<sup>21,22</sup> indicating some type of donor-acceptor interaction where the aromatic solvents may act as proton acceptors. The basicities of the solvents should, to some extent, be reflected in their ionization potentials,<sup>23</sup> and these are plotted against the relaxation times for each ethane in Figure 1A and 1B. The linearity of these plots is comforting in that they confirm solute-solvent interactions as the major contributing factor in lengthening the relaxation times. However, no inference as to the specific nature of the interaction can be drawn solely on the basis of such a relationship. The ionization potential for *p*-

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(21) M. Tamres, *ibid.*, **74**, 3375 (1952).

(22) H. C. Brown and J. D. Brady, *ibid.*, **74**, 3570 (1952).

(23) V. J. Vendeneyev, L. V. Gurich, V. N. Kondratyev, V. A. Medvedev, and Ye. L. Frankevich, "Bond Energies, Ionization Potentials, and Electron Affinities," Edward Arnold Ltd., London, 1966.

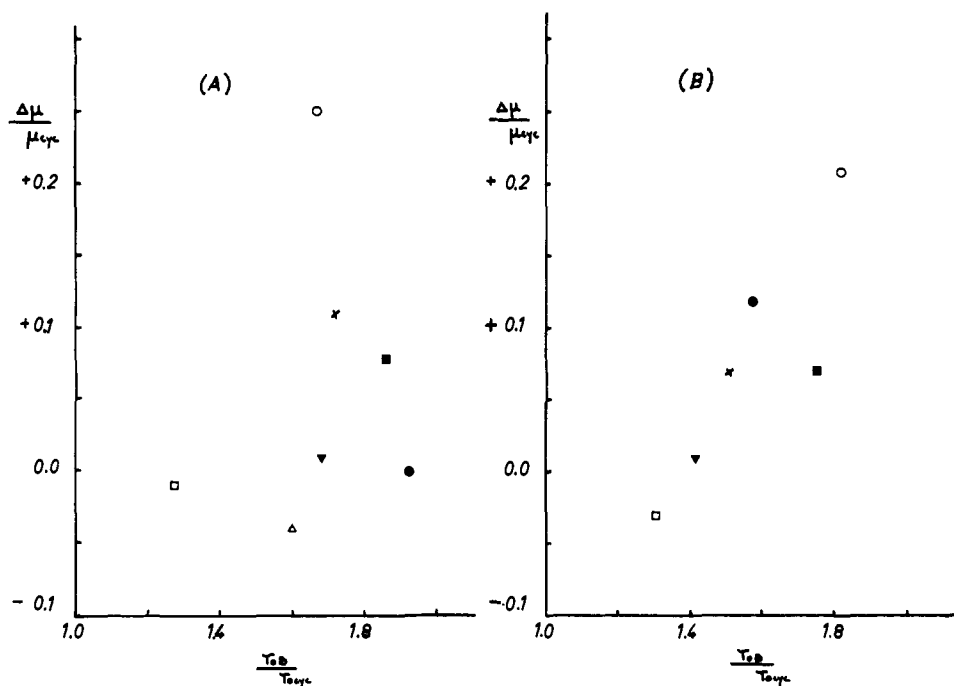


Figure 2. Plot of  $\Delta\mu/\mu_{cyc}$  against  $\tau_{0B}/\tau_{0cyc}$  for chloroethanes in benzene solution at (A) 25° (1,2-dichloroethane 20°) and (B) 55°. The solutes are identified as in Figure 1A.

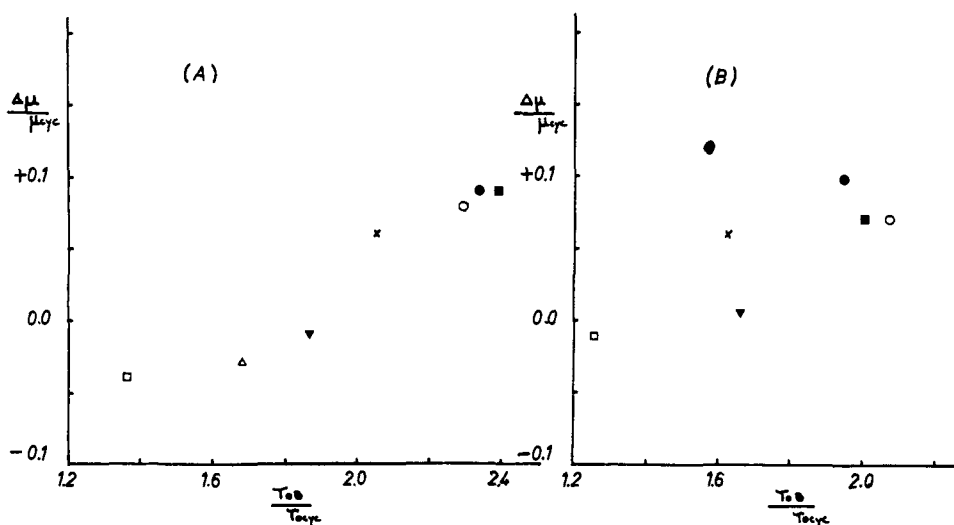


Figure 3. Plot of  $\Delta\mu/\mu_{cyc}$  against  $\tau_{0B}/\tau_{0cyc}$  for chloroethanes in *p*-xylene solution at (A) 25° (1,2-dichloroethane 20°) and (B) 55°. The solutes are identified as in Figure 1A.

dioxane is 9.52 eV, and the relaxation times in *p*-dioxane do not conform with the hydrocarbon solvent data, although the situation would be much improved if a viscosity correction were included. However, interaction with *p*-dioxane will involve the oxygen lone-pair electrons, not delocalized  $\pi$  electrons, and the systems are not completely analogous. For each ethane the degree of interaction with a solvent may be represented by  $\tau_{0B}/\tau_{0cyc}$ , where  $\tau_{0B}$  and  $\tau_{0cyc}$  are the most probable relaxation times in the potentially basic solvent and in the reference solvent cyclohexane, respectively. These ratios may be used in eq 2 to calculate the free energy of activation differences  $\Delta\Delta G_0^\ddagger$  for molecular relaxation. The values thus obtained are of the order expected for these systems and compare well with similar values obtained by nmr.<sup>24</sup>

(24) I. D. Kuntz, results to be published.

The relative interactions for the chloroethanes in a given solvent are compared with the dipole moment changes in Table III and Figures 2-5, in which  $\Delta\mu = \mu_B - \mu_{cyc}$ , where  $\mu_B$  and  $\mu_{cyc}$  refer to solvents in the same manner as  $\tau_{0B}$  and  $\tau_{0cyc}$ . The errors involved in these plots are necessarily large, but, apart from the *p*-dioxane results, there seems to be a clear increase in  $\Delta\mu/\mu_{cyc}$  for each solvent system with increasing interaction, and this solvent effect decreases in the order: benzene > *p*-xylene > mesitylene. It has been stated,<sup>3</sup> and confirmed by nmr<sup>24</sup> work on chloroethanes, that a methyl group in any molecule cannot form hydrogen bonds. Thus, the fact that the relaxation time for 1,1,1-trichloroethane increases in the solvent order cyclohexane < benzene < *p*-xylene < mesitylene < *p*-dioxane suggests that, though hydrogen bonding may be important in some of the other systems,

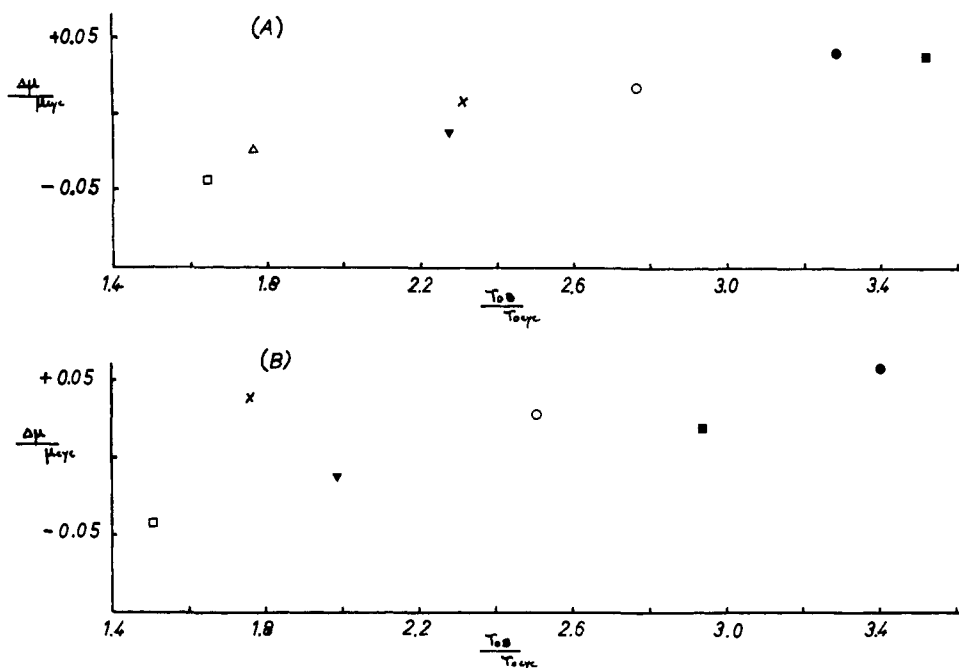


Figure 4. Plot of  $\Delta\mu/\mu_{cyc}$  against  $\tau_{0B}/\tau_{0cyc}$  for chloroethanes in mesitylene solution at (A) 25° (1,2-dichloroethane 20°) and (B) 55°. The solutes are identified as in Figure 1A.

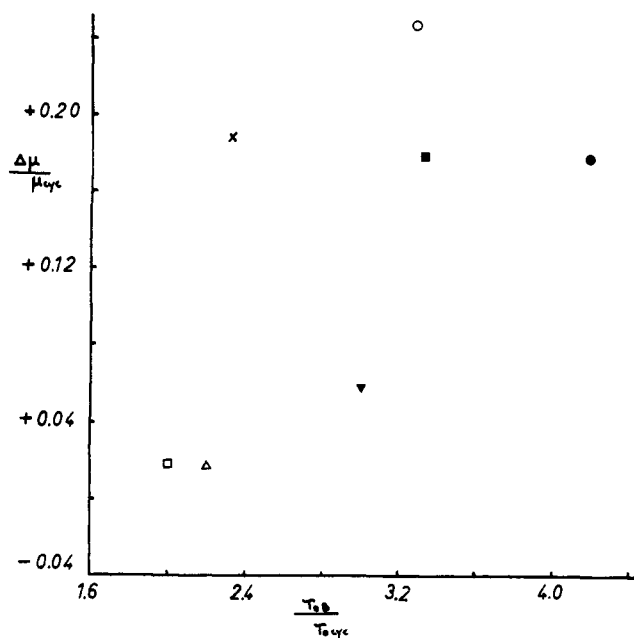


Figure 5. Plot of  $\Delta\mu/\mu_{cyc}$  against  $\tau_{0B}/\tau_{0cyc}$  for chloroethanes in *p*-dioxane solution at (A) 25° (1,2-dichloroethane 20°) and (B) 55°. The solutes are identified as in Figure 1A.

it is not the only contributing factor. Dipole-induced-dipole interaction is a strong possibility in such cases, and the effect may be compared with the behavior of trichlorofluoromethane, a molecule incapable of forming hydrogen bonds, which has a larger reduced relaxation time<sup>4</sup> in *p*-dioxane (5.7 psec) than in carbon tetrachloride (3.3 psec) at 20°. There is no clear relationship between the relative interaction strengths and the apparent dipole moments of

the ethanes, indicating that hydrogen bonding is more important than dipolar forces in many cases. The relative interactions for the solutes are, with the exception of 1,2-dichloroethane, as would be expected from the protonic nature of the hydrogen atoms within the molecules and show an order similar to that of the nmr chemical shifts for these solutes in a 10% solution of dimethyl sulfoxide in cyclohexane.<sup>25</sup> Proton magnetic resonance studies<sup>24,25</sup> indicate that 1,2-dichloroethane interacts with bases only to a slightly greater extent than 1,1,1-trichloroethane, and the results for the former (Tables II and III and Figures 2–5) are indeed surprising. Although very rough curves might be drawn in Figures 2–5, the complicating factors involved make it seem wiser to let the points alone indicate the general trend. Schneider<sup>7</sup> proposed the introduction of a volume term to account for the mean distance of approach between the interacting molecules. Crossley and Walker<sup>6</sup> found that such corrections yield more reasonable  $\tau_{0B}V/\tau_{0cyc}$  values for 1,2-dichloroethane, where  $V$  is the volume of the molecule, but they also indicate 1,1-dichloroethane to be a weaker interactor than 1,1,1-trichloroethane.

The relatively large  $\Delta\mu/\mu_{cyc}$  values for 1,2-dichloroethane have been interpreted in terms of an increased proportion of the polar *gauche* form relative to the nonpolar *trans* form.<sup>5</sup> This is often accounted for by the effect of increased dielectric constant on the electrostatic stabilization energy, causing the energy of the polar *gauche* form to decrease, relative to that of the nonpolar *trans* form. However, the dielectric constants of mesitylene and *p*-xylene are of the same order as that of benzene, but the dipole moments in the former solvents are less than in benzene. Furthermore, the dielectric constant of pure

(25) A. L. McClellan and S. W. Nicksic, *J. Phys. Chem.*, **69**, 446 (1965).

liquid 1,2-dichloroethane<sup>26</sup> at 25° is 10.16 and the dipole moment (1.88 D.) is not considerably different from the value in benzene solution. From Table I it is apparent that the dipole moment of this solute decreases in the same manner as those of 1,1,2,2-tetrachloroethane and 1,1,2-trichloroethane in the solvent order *p*-dioxane > benzene > *p*-xylene > mesitylene > cyclohexane. For 1,1,2,2-tetrachloroethane the potential barrier to internal rotation is large,<sup>17</sup> and the solvent effect would seem to be due to

(26) F. Buckley and A. A. Maryott, "Tables of Dielectric Dispersion Data for Pure Liquids and Dilute Solutions," National Bureau of Standards, Circular 589, Government Printing Office, Washington, D. C., 1958.

molecular interaction rather than any increased freedom for intramolecular rotation. From Figures 2–4, although the degree of interaction does appear to be anomalously large, the dipole moment changes for 1,2-dichloroethane are reasonable and suggest that they are not solely due to intramolecular effects.

In a specific solvent increasing molecular interaction appears to be accompanied by increased dipole moment changes for the chloroethane series. However, this effect decreases in the solvent order benzene > *p*-xylene > mesitylene, suggesting that the induced dipole moments decrease with increasing basicity or mean polarizability for these systems.

## Some Thermochemical Properties of Methyl Vinyl Ether, $\alpha$ -Chloroethyl Methyl Ether, and Iodomethyl Methyl Ether. Evidence for Nonbonded Electrostatic Interactions<sup>1</sup>

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**Abstract:** The entropies of methyl vinyl ether (MVE,  $S^{\circ}_{298} = 73.5$  gibbs/mole) and  $\alpha$ -chloroethyl methyl ether (CME,  $S^{\circ}_{298} = 82.4 \pm 2.1$  gibbs/mole) have been calculated, respectively, by statistical mechanical methods, and from the measured equilibrium constant,  $K_{\alpha}$ ,  $\text{CH}_3\text{OCHClCH}_3 \rightleftharpoons \text{HCl} + \text{CH}_3\text{OCH}=\text{CH}_2$  ( $\alpha$ ). In the latter measurement, HCl pressures were varied from 104.5 to 227.8 torr, and MVE from 28.57 to 213 torr.  $\log(K_{\alpha}/\text{atm}) = [(34.0 \pm 1.5)/4.576] - [(17.5 \pm 0.7)/\theta]$ , where  $\theta = 2.303RT$  in kilocalories/mole, and errors quoted are 95% confidence limits. Smoothing these values to  $\Delta H = 17.0$  kcal/mole by comparison with the similar equilibrium for ethyl vinyl ether leads to  $\Delta H_f^{\circ}_{298}(\text{CME}) = -65.2 \pm 1.2$  kcal/mole. The heat of formation of iodomethyl methyl ether ( $\Delta H_f^{\circ}_{298}(\text{IME}) = -29.3$  kcal/mole) was calculated from the equilibrium constant,  $K_{\text{eq}}$ , at 566°K for the system  $\text{CH}_3\text{OCH}_3 + \text{I}_2 \rightleftharpoons \text{HI} + \text{ICH}_2\text{OCH}_3$  (IME) and an assigned value for the entropy of the iodomethyl ether.  $\text{I}_2$  pressures were varied from 3.76 to 18.85 torr and dimethyl ether pressures from 39.62 to 592 torr. The temperature range was 515–631.6°K.  $S^{\circ}_{298}(\text{CME})$  was abnormally low by 1.9 gibbs/mole on comparison with isoelectronic *sec*-butyl chloride, and  $\Delta H_f^{\circ}(\text{CME})$  was abnormally stable by about 6.1 kcal/mole.  $\Delta H_f^{\circ}(\text{IME})$  showed a similar enhanced stability of about 3 kcal/mole. Both of these values are shown to be consistent with an electrostatic interaction of the halogens with the terminal methyl group arising from the alternate polarity of bond dipoles.

Data on the entropies and heat capacities of ethers are particularly scarce,<sup>2</sup> only those of dimethyl ether having been calculated<sup>3</sup> by the method of Pitzer and Gwinn<sup>4</sup> from a spectroscopic frequency assignment.

Entropies of other ethers have been estimated by group additivity methods<sup>2</sup> or else by an "isoelectronic replacement rule." The success of this rule depends on the observation that, at 298°K, replacement of the oxygen atom in an oxygen-containing compound by an isoelectronic group, here the methylene group, does not significantly alter the entropy, provided due account is

taken of any symmetry changes involved and the very small contribution of the H atoms. Table I shows that the rule is generally accurate within  $\pm 1$  gibbs/mole. The agreement is expectedly poor for the acids (and presumably esters), which have high OH (or OR) rotation barriers. The poor result for  $\text{H}_2\text{O}_2$  is due to the large difference in moments of inertia between  $\text{H}_2\text{O}_2$  and  $\text{C}_2\text{H}_6$ .

The external moment of inertia about the C–C axis in  $\text{C}_2\text{H}_6$  is three times larger than that about the O–O axis in  $\text{H}_2\text{O}_2$ . This is also approximately the case for the internal rotation, and correction for both of these effects amounts to about 2.5 gibbs/mole. A crude *a priori* estimate of the effect of losing two H atoms in a molecule can be made by assigning one C–H stretch at  $3000\text{ cm}^{-1}$  and two H–C–C deformations at about  $1000\text{ cm}^{-1}$ . At 300°K these amount to about 0.3 gibbs/mole per H atom, or 0.6 gibbs/mole for two H atoms, in good agreement with most of the  $\Delta S$  values shown.

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