Solute-Solvent Interactions. IV. Infrared Studies of Solvent Effects on Rotational Isomers of 1,2-Dichloroethane and 1,1,2,2-Tetrachloroethane

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Abstract: The influence of solvents on the C–Cl stretching absorption bands of the *trans* and *gauche* isomers of 1,2-dichloroethane and 1,1,2,2-tetrachloroethane was examined in terms of both relative frequency shifts and relative band intensities. The results indicate that the interaction of 1,2-dichloroethane with the solvents studied is mainly dielectric in nature. However, with 1,1,2,2-tetrachloroethane hydrogen bonding also becomes significant in proton-acceptor solvents, and it occurs with both isomers. A reasonably linear relationship exists between the relative intensities of the C–Cl stretching bands of the rotational isomers of each of these two solutes and the relative frequency shifts of the C–Cl stretching bands of *n*-propyl chloride or isobutyl chloride. This fact and also other evidence suggests that the main interaction responsible for the variation in relative stability of the two isomers in different solvents is dielectric in nature, and that the contribution of hydrogen bonding is less significant. It is speculated that the anomalous stabilization of the *gauche* isomer observed in aromatic solvents also is caused by an electrostatic rather than a hydrogen-bonding interaction.

Previous studies on rotational isomerism[3] showed that solvents affect the energy difference of rotational isomers. It was concluded[3-6] that this solvent influence is largely dielectric in nature, in that the energy decrease caused by an increase in the bulk dielectric constant of the solvent is more marked for the more polar isomer. One of the most typical examples studied is 1,2-dichloroethane (DCE). Thus Hallam and Ray[7] showed that the solvent shifts of the C–Cl stretching frequencies of DCE are greater for the more polar (*gauche*) isomer. Earlier, Mizushima, *et al.*,[4] had found that the intensity ratio of the Raman line at 754 cm^{-1} (assigned to the *trans* isomer) to that at 654 cm^{-1} (*gauche*) decreased from 5 to 1.2 as the dielectric constant of the solvent was increased from 2 (hexane) to 33 (methanol).

However, in benzene as solvent an anomalous result was obtained, in that the above Raman intensity ratio indicated a relatively larger number of *gauche* molecules than would be expected from the low dielectric constant of benzene. Dipole moment measurements[3,4,8] showed the same anomaly, and Kubo[8] inferred the formation of a 1:1 complex between DCE and benzene. However, Kuratani[9] reported that the infrared absorption frequencies of DCE are similar in benzene and in carbon tetrachloride, carbon disulfide, and acetonitrile, and therefore discounted such complex formation. On the other hand, Neckel and Volk[10] obtained infrared shifts for DCE on adding benzene, and believed that the *gauche* form is preferentially stabilized by hydrogen bonding with benzene. Nevertheless, no evidence was presented to rule out the possibility that the *trans* isomer may be involved in similar hydrogen bonding. Wada and Morino[11] also felt that a simple electrostatic model cannot account for the stabilization energy of DCE in benzene, and that some short-range interaction must be invoked. Recently, Chitoku and Higasi[12] concluded from dielectric relaxation measurements of DCE in several nonpolar solvents that the *gauche* form is preferentially stabilized in aromatic solvents by a weak interaction believed to involve hydrogen bonding.

The conclusions to be drawn from the above studies are that most, but not all, of the evidence points to a specific interaction of DCE with benzene, and that this interaction probably is more pronounced for the *gauche* isomer and tentatively has been attributed to hydrogen bonding, but that its exact nature is not clear.

In a previous paper[13] we have shown that while the solvent shifts of the C–Cl stretching frequencies of chlorinated hydrocarbons generally do depend upon the bulk dielectric constant of the solvent, an important contributing effect arises when the hydrogen atoms attached to the carbon of the C–Cl linkage have the ability to form hydrogen bonds with proton-acceptor solvents. In view of the unanswered questions summarized above, we have extended our work to a study of solvent effects on rotational isomerism. We have made further measurements with DCE, because intensity ratios for its rotational isomers have been reported for three solvents only.[7] In addition, we have carried out a similar study with 1,1,2,2-tetrachloroethane (TCE), which also exists in both *trans* and *gauche* forms,[14] and which should be considerably more effective than DCE as a hydrogen-bond donor. Furthermore, in benzene as solvent its dipole moment is anomalously high.[15] As in our previous paper, we refer

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Table I. Solvent Effects on the C–Cl Stretching Absorption Bands of 1,2-Dichloroethane

			T		G_1		G_2		Ratios of peak intensities	
			$\nu_{17,C-Cl}$ (*trans*)[b]		$\nu'_{17,C-Cl}$ (*gauche*)[b]		$\nu'_{5,C-Cl}$ (*gauche*)[b]			
	Solvent	ε[a]	ν, cm^{-1}	$10^3\Delta\nu/\nu$	ν, cm^{-1}	$10^3\Delta\nu/\nu$	ν, cm^{-1}	$10^3\Delta\nu/\nu$	A_T/A_{G_1}	A_T/A_{G_2}
	Vapor		727[c]		694[c]		669[c]			
1	*n*-Hexane	1.9			686.5	10.8	662.5	9.7		
2	Cyclohexane	2.0	716	15.1	686	11.5	662	10.5	8.2	13.5
3	Pentene	2.1	715	16.5	685.5	12.2	661	12.0	8.7	12.3
4	1,4-Dioxane	2.2	707	27.5	673.5	29.5	653.5	23.2	4.0	4.3
5	Carbon tetrachloride	2.2			685	13.0	660.5	12.7		
6	Benzene	2.3								
6′	Benzene-*d*	2.3	710.5	22.7	679	21.6	665.5	20.2	4.9	4.8
7	*p*-Xylene	2.3	710.5	22.7	680	20.2	657	17.9	5.8	5.4
8	Mesitylene	2.3	711	22.0			657.5	17.2		5.9
9	Tetrachloroethylene	2.3	714	17.9	685	13.0	660.5	12.7	7.9	9.9
10	Triethylamine	2.4			683.5	15.1	659	15.0		
11	Carbon disulfide	2.6	714	17.9	683.5	15.1	659	15.0	7.2	9.6
12	Diethyl ether	4.3	711	22.0	680	20.2	657.5	17.2	5.7	5.4
13	Ethyl acetate	6.0	709	24.8	673.5	29.5	654.5	21.7	3.6	3.6
14	Acetone	20.7	708	26.1	672	31.7	653	23.9	2.4	2.2
15	Acetonitrile	36.0	708	26.1	672	31.7	653	23.9	2.3	2.3
16	Nitromethane	36.7	707.5	26.8						

[a] Dielectric constant values for 20–25°, taken mainly from A. A. Maryott and E. R. Smith, "Table of Dielectric Constants of Pure Liquids," NBS Circular 514, 1951. [b] I. Nakagawa and S. Mizushima, *J. Chem. Phys.*, **21**, 2195 (1953). [c] S. Mizushima, T. Shimanouchi, I. Ichishima, and H. Kamiyama, *Rev. Universelle Mines*, **15**, 447 (1959).

Table II. Solvent Effects on the C–Cl Stretching Absorption Bands of 1,1,2,2-Tetrachloroethane

		T_1		G_1		T_2		G_2		Ratios of peak intensities	
		$\nu_{8,C-Cl}$ (*trans*)[a]		$\nu'_{16,C-Cl}$ (*gauche*)[a]		$\nu_{16,C-Cl}$ (*trans*)[a]		$\nu'_{4,C-Cl}$ (*gauche*)[a]			
	Solvent	ν, cm^{-1}	$10^3\Delta\nu/\nu$	ν, cm^{-1}	$10^3\Delta\nu/\nu$	ν, cm^{-1}	$10^3\Delta\nu/\nu$	ν, cm^{-1}	$10^3\Delta\nu/\nu$	A_{T_1}/A_{G_1}	A_{T_2}/A_{G_2}
	Vapor	761[a]		745[a]		722[a]		654[a]			
1	*n*-Hexane	758	3.9	739.5	7.4			651.5	3.8	0.81	
2	Cyclohexane	757.5[a]	4.6	739.5	7.4	717	6.9	651	4.6	0.77	1.07
3	Pentene	756.5	5.9	739	8.1	716	8.3	650.5	5.4	0.76	0.95
4	1,4-Dioxane	751	13.1	735	13.4	712.5	13.1	645.5	13.0	0.55	0.61
5	Carbon tetrachloride							650.5	5.4		
6	Benzene	753.5	9.9	737	10.7					0.55	
6′	Benzene-*d*	753.5	9.9	737	10.7	714.5	10.4	647	10.7	0.53	0.66
7	*p*-Xylene	753	10.5	737	10.7	714.5	10.4	647.5	9.9	0.62	0.67
8	Mesitylene	752.5	11.2	737	10.7	714.5	10.4	647.5	9.9	0.74	0.75
9	Tetrachloroethylene			738	9.4	716	8.3	650.5	5.4		0.99
10	Triethylamine							645	13.8		
11	Carbon disulfide	754.5	8.5	737	10.7	714.5	10.4	649	7.6	0.74	0.91
12	Diethyl ether			736.5	11.4	714	11.1	646	12.2	0.61	0.66
13	Ethyl acetate			737	10.7	714	11.1	645.5	13.0	0.42	0.57
14	Acetone	751.5	12.5	736.5	11.4	713.5	11.8	644.5	14.5	0.37	0.41
15	Acetonitrile			736.5	11.4	714.5	10.4	645	13.8		0.40
16	Nitromethane	753.5	9.9	737	10.7					0.34	

[a] Reference 14.

frequency shifts to those of *n*-propyl chloride as standard, rather than to those of the previously recommended[16] *cis*-dichloroethylene, because the interaction of the new reference compound with solvents is virtually completely electrostatic in nature, free of the hydrogen-bonding perturbations that affect *cis*-dichloroethylene.[13]

Experimental Section

Measurements were carried out as described before.[13] Transmittance values were reproducible to ±1%.

DCE (Fisher Certified Reagent) and TCE (Fisher Reagent Grade) were fractionally distilled from phosphorus pentoxide at atmospheric pressure. *p*-Xylene (Eastman White Label), mesitylene (Eastman Yellow Label), and pentene (Eastman Technical Grade) were dried over Linde 3A Molecular Sieves and then fractionally distilled at atmospheric pressure. Hexadeuteriobenzene (Merck) was used without further purification. Other solvents were the same as before.[13]

Results and Discussion

Tables I and II contain the observed C–Cl stretching frequencies of DCE and TCE, respectively, in wavenumber units, as well as the relative frequency shifts, $10^3\Delta\nu/\nu$, calculated on the basis of vapor-state frequencies. With TCE we made measurements on four bands, two for each rotational isomer. As reported before,[14] two additional bands of the *trans* isomer are very weak, and two of the *gauche* form are very close together. In addition to the ν_{C-Cl} values listed in our previous paper,[13] some complementary data for *n*-propyl chloride and isobutyl

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Table III. Solvent Effects on the C–Cl Stretching Frequencies of *n*-Propyl Chloride and Isobutyl Chloride

		n-Propyl chloride				Isobutyl chloride			
		ν_{C-Cl} (*trans*)		ν_{C-Cl} (*gauche*)		ν_{C-Cl} (*trans*)		ν_{C-Cl} (*gauche*)	
	Solvent	ν, cm^{-1}	$10^3\Delta\nu/\nu$	ν, cm^{-1}	$10^3\Delta\nu/\nu$	ν, cm^{-1}	$10^3\Delta\nu/\nu$	ν, cm^{-1}	$10^3\Delta\nu/\nu$
	Vapor	743[a]		660[a]		745.5[b]		698[b]	
3	Pentene	734	12.1	653.5	9.9	734	15.4	690.5	10.7
6	Benzene	725[c]	24.2			726.5[c]	25.3		
6′	Benzene-*d*	725	24.2	649	16.7	726.5	25.3	685	18.6
7	*p*-Xylene	726.5	22.2	650	15.1	728.5	22.8	686	17.2
8	Mesitylene	727	21.5	650.5	14.4	729.5	21.5		

[a] C. Komaki, I. Ichishima, K. Kuratani, T. Miyazawa, T. Shimanouchi, and S. Mizushima, *Bull. Chem. Soc. Japan*, **28**, 330 (1955). [b] Reference 7. [c] Reference 13.

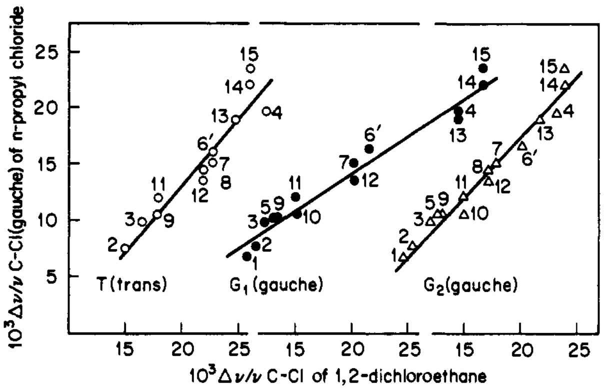

Figure 1. Relative frequency shifts of ν_{C-Cl} bands of 1,2-dichloroethane plotted against the corresponding shifts of *n*-propyl chloride; numbers of solvents refer to Table I.

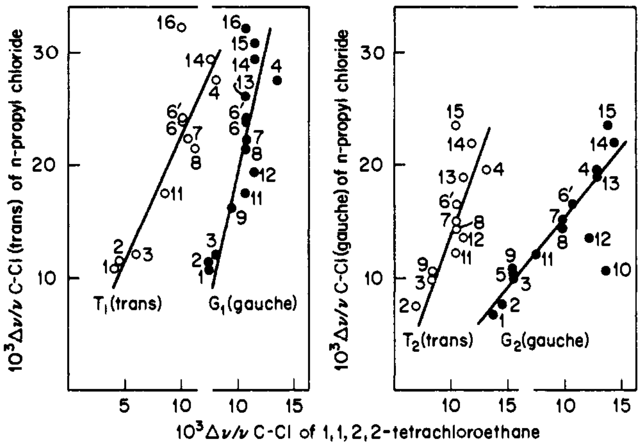

Figure 2. Relative frequency shifts of ν_{C-Cl} bands of 1,1,2,2-tetrachloroethane plotted against the corresponding shifts of *n*-propyl chloride; numbers of solvents refer to Table II.

chloride in pentene and in aromatic solvents are given in Table III; these two compounds give essentially the same results in all solvents studied when used as references.

In Figures 1 and 2 the relative frequency shifts of the C–Cl stretching vibration bands of the rotational isomers of DCE and TCE, respectively, are plotted against the corresponding shifts of *n*-propyl chloride as reference (modified Bellamy–Hallam–Williams plots[13]). The reasonable linearity obtained in Figure 1 for each of the three bands of DCE, even in solvents with strong hydrogen-bond acceptor properties, such as triethylamine and diethyl ether, shows that the interaction of this solute with solvents is largely dielectric in nature. On the other hand, Figure 2 shows that several points fall well off the straight lines for each of the four bands of TCE. This behavior is similar to that reported by us for other chlorinated hydrocarbons containing active hydrogen atoms,[13] and it indicates that TCE undergoes specific interactions with certain solvents. In the hydrogen-bond acceptor solvents triethylamine and diethyl ether, the main specific interaction undoubtedly is hydrogen bonding, and it involves both isomers of TCE.

Peak intensities were measured for both bands produced by each isomer, giving two corresponding sets of values for the ratio A_T/A_G for DCE and also for TCE. Those values that could be determined with reasonable accuracy are listed in Tables I and II. Because of some overlap of bands, and because the absorptivity indices of the two isomers may differ somewhat, these numbers only give an approximate indication of the relative populations of the two isomers. Two main facts emerge. First, for both DCE and TCE in most solvents, the relative population of the *gauche* isomer increases with increasing dielectric constant of the solvent, in agreement with previous conclusions for DCE[4,7,9] and TCE[14] in a limited number of solvents. Second, for both DCE and TCE in dioxane and in aromatic solvents, the relative population of the *gauche* isomer is greater than would be predicted on the basis of the bulk dielectric constants of these solvents, in agreement with previous results with DCE. Furthermore, this increase in the *gauche* population is approximately the same for DCE and TCE, which is an important result, because it provides an argument against the hypothesis discussed in the introductory section that hydrogen bonding is responsible for the relative stabilization of the *gauche* isomer of DCE in aromatic solvents. There are also other arguments against the hydrogen-bonding hypothesis. First, the C–Cl frequency shifts of *n*-propyl chloride and isobutyl chloride are adequately represented by the Kirkwood–Bauer–Magat treatment in all solvents studied, except again in dioxane and benzene[13] and other aromatic solvents (Table III). Clearly these two solutes also undergo a specific interaction with the solvents in question, although their hydrogen-bonding capacity is negligible. Second, the *gauche* isomer of both DCE and TCE is stabilized to a much greater extent by acetonitrile and nitromethane than by diethyl ether which is a much stronger hydrogen-bond acceptor but less polar than the first two solvents.

That the interaction responsible for the stabilization of

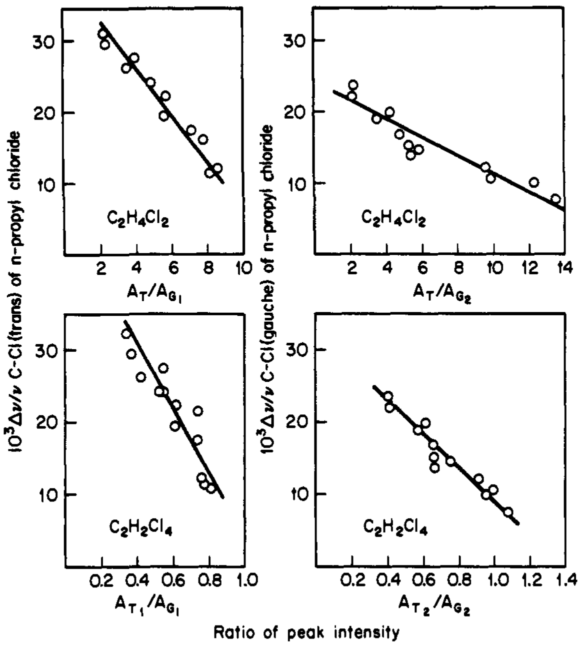

Figure 3. Correlation between the ratio of peak intensities of ν_{C-Cl} bands of rotational isomers of 1,2-dichloroethane or 1,1,2,2-tetrachloroethane and the relative frequency shift of ν_{C-Cl} band of *n*-propyl chloride.

the *gauche* isomer of DCE and of TCE may be largely electrostatic in nature is further suggested by the fact that a reasonably linear relationship exists between the intensity ratios A_T/A_G of both DCE and TCE and the relative frequency shifts of *n*-propyl chloride. Such plots are shown in Figure 3. We believe that the frequency shifts of the reference compound, *n*-propyl chloride, should be regarded as a measure of the "effective electrostatic polarity" of the solvent. It should be noted that for the aromatic solvents studied, all of which have the same bulk dielectric constant, this effective polarity increases in the order mesitylene < *p*-xylene < benzene (Table III), which is also the order of increasing stabilization of the *gauche* isomer, as measured by the intensity ratio (Tables I and II). These results are in harmony with previous observations that the dipole moments of DCE and TCE are larger in benzene than in *p*-xylene.[12,15] On the other hand, the order of hydrogen-bond acceptor power is the reverse of the above.[17]

It is noteworthy that the linear relationship between relative frequency shifts and intensity ratios holds reasonably well even for dioxane, benzene, and *p*-xylene as solvents, in which *n*-propyl chloride or isobutyl chloride gives anomalously large frequency shifts. As before,[13] we speculate that these solvents may be more polar locally than their macroscopic polarities would indicate. In agreement with the results of Mizushima, *et al.*,[4] the aliphatic double bond of pentene caused no anomaly.

We conclude that the interaction of DCE with all solvents studied is mainly electrostatic in nature. In the case of TCE hydrogen bonding occurs significantly with proton-acceptor solvents, and it involves both isomers. The relative populations of the two isomers appear to be influenced more markedly by electrostatic interactions than by hydrogen bonding.

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