Microwave Absorption and Molecular Structure in Liquids. XXIII. The Dielectric Relaxation Times and Dipole Moments of Several Aryl Isocyanates and Related Compounds[1]

By Brian R. Jolliffe and Charles P. Smyth

Dielectric constant and loss measurements at wave lengths of 577 m. and 10.0, 3.22 and 1.25 cm. have been carried out at 20, 40 and 60° upon dilute benzene solutions of phenyl isocyanate, phenyl isothiocyanate, p-tolyl isocyanate, tolylene-2,4-diisocyanate, 1-naphthyl isocyanate and 2-biphenylene isocyanate. The densities, viscosities and refractive indices of the solutions have also been measured. The molecular dipole moments calculated from these data indicate that the direction of the bond from the ring to the linear isocyanate group is close to, if not coincident with, that of the axis of the group. The dielectric data have been used to construct arc plots, from which the dielectric relaxation times and their almost negligibly small distribution parameters have been calculated. The rather large molecular relaxation times resulting from the considerable protrusion of the polar group from the ring are found to vary in the expected manner with the direction of the molecular dipole relative to the molecular axes.

In previous papers of this series relaxation times of polar molecules have been measured both in the pure liquid and in solution in non-polar solvents, and the results discussed in terms of the viscosities of the liquids and the geometry of the molecules. In the present work, the influence of molecular shape on relaxation time has been investigated further in benzene solutions of phenyl isocyanate, p-tolyl isocyanate, tolylene-2,4-diisocyanate, 1-naphthyl isocyanate, 2-biphenylyl isocyanate and phenyl isothiocyanate.

Materials and Experimental Methods

The solutes were obtained from Brothers Chemical Company and Eastman Kodak Company. Preliminary measurements were made using the substances without purification, and final determinations were made with samples which had been distilled under reduced pressure. "C.P." grade benzene was used throughout the work without any further treatment after measurements of the static dielectric constant and loss in the microwave region had shown that, for use in these solutions, it was indistinguishable from benzene which had been distilled after drying with sodium hydride.

The techniques used for measuring ϵ', the dielectric constant, and ϵ'', the loss, at wave lengths of 1.25 and 3.22 cm. have been described in earlier papers,[2] as has the method by which ϵ_0, the "static" dielectric constant is measured at a wave length of 577 meters. The readings at 10.0 cm. were made with a resonant cavity apparatus constructed by Mr. D. A. Pitt.[3] At least three solutions of each substance were measured at each frequency at temperatures of 20, 40 and 60° in the concentration range 0.005 to 0.04 mole fraction. The slope a of the linear plot of ϵ' against the weight fraction was used as in previous work[4] to compute the position of points on Cole–Cole arc plots,[5] from which the critical wave length and relaxation time for each compound were obtained.

Table I shows the results obtained at the wave length λ_0 at which the measurement was carried out. The value at 577 m. wave length is the slope of the so-called static dielectric constant and the value at 5.89×10^{-5} cm. is the slope of the square of the refractive index for the sodium-D line. These data, together with the measured specific volumes of the solutions, have been used to calculate the

molecular dipole moments by means of the equation of Halverstadt and Kumler.[6] The moment values thus obtained are given in Table III, where, in the cases of the three substances previously measured, they are seen to agree with the literature values within the probable error of the latter. Table II gives the calculated critical wave lengths and the corresponding relaxation times and, in addition, the slopes of the straight lines obtained by plotting the measured viscosities of the solutions in centipoises against the mole fractions of the polar solutes. Table II also gives the heats of activation for dipole relaxation calculated from the slopes of the plots of the logarithm of the critical wave length against the reciprocal of the absolute temperature.

Discussion of Dipole Moments

Although the determination of the dipole moments of these compounds was incidental to the investigation of the molecular relaxation times, the moment values in Table III have some interest as evidence of structure and thus some significance in the interpretation of the values of the relaxation times. Electron diffraction[7] and microwave and infrared spectra[8,9] have shown the isocyanate and isothiocyanate groups to be linear with an angle 125° to 132° between the group axis and the R–N bond in CH_3NCO, $HNCO$, $HNCS$ and $DNCS$. Earlier dipole moment measurements on p-substituted phenyl isothiocyanates[10] showed the angle to be hardly distinguishable from 180° in these aromatic compounds, and the moment calculated for p-chlorophenyl isocyanate[11] on the assumption of complete linearity, that is, an angle of 180°, differed from the observed value by no more than the possible experimental error. The moment value 2.68 of p-tolyl isocyanate in Table III is indistinguishable from the sum of the phenyl isocyanate moment 2.29 in Table III and the toluene moment 0.37 in the vapor state and 0.4 in solution,[12] indicating an angle of 180°. Calculation of the moment of tolylene-2,4-diisocyanate as the vector sum

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(12) C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., New York, N. Y., 1955, p. 314.

TABLE I
Slopes for Dependence of Dielectric Constant and Loss upon Concentration

t, °C.	λ₀ (cm.)	a'	a"	a'	a"
		Phenyl isocyanate		Tolylene-2,4-diisocyanate	
20	577 m.	7.66	..	9.33	..
	10.0	6.48	2.54	7.33	3.32
	3.22	3.46	3.16	3.44	3.66
	1.25	1.59	1.94	1.82	2.22
	5.89 × 10⁻⁵	0.095	..	0.23	..
40	577 m.	6.98	..	8.53	..
	10.0	6.27	1.92	7.43	2.56
	3.22	4.02	2.94	4.36	3.56
	1.25	2.26	2.39	2.03	2.38
	5.89 × 10⁻⁵	0.12	..	0.27	..
60	577 m.	6.39	..	7.83	..
	10.0	5.95	1.28	7.07	2.08
	3.22	4.11	2.76	4.70	3.32
	1.25	2.66	2.50	2.03	2.54
	5.89 × 10⁻⁵	0.15	..	0.31	..
		Phenyl isothiocyanate		1-Naphthyl isocyanate	
20	577 m.	12.60	..	8.31	..
	10.0	9.52	5.20	6.55	3.22
	3.22	3.79	4.11	2.90	2.90
	1.25	2.16	2.14	1.70	1.84
	5.89 × 10⁻⁵	0.60	..	0.64	..
40	577 m.	11.27	..	7.62	..
	10.0	8.94	3.92	6.42	2.76
	3.22	4.43	4.15	3.40	2.85
	1.25	2.35	2.49	1.93	2.08
	5.89 × 10⁻⁵	0.61	..	0.79	..
60	577 m.	10.14	..	7.03	..
	10.0	8.55	3.07	6.15	2.01
	3.22	5.30	4.01	3.70	2.74
	1.25	2.75	2.68	2.00	2.20
	5.89 × 10⁻⁵	0.64	..	0.96	..
		p-Tolyl isocyanate		2-Biphenylene isocyanate	
20	577 m.	10.44	..	7.45	..
	10.0	7.83	4.45	4.90	3.30
	3.22	2.76	3.69	2.18	2.28
	1.25	1.41	1.93	1.46	1.29
	5.89 × 10⁻⁵	0.10	..	0.58	..
40	577 m.	9.52	..	6.80	..
	10.0	7.80	3.62	4.83	2.96
	3.22	3.23	3.68	2.69	2.51
	1.25	1.66	2.19	1.86	1.46
	5.89 × 10⁻⁵	0.15	..	0.63	..
60	577 m.	8.69	..	6.25	..
	10.0	7.24	2.64	4.68	2.26
	3.22	3.76	3.68	3.16	2.50
	1.25	1.82	2.43	1.95	1.60
	5.89 × 10⁻⁵	0.19	..	0.69	..

TABLE II
Slopes of Dependence of Viscosity on Concentration of Solute, Critical Wave Lengths and Relaxation Times

t, °C.	Δη/c.	λm (cm.)	τ(10⁻¹² sec.)	ΔH (kcal./mole)
		Phenyl isocyanate		
20	0.66	4.34	23.1	2.3
40	.58	3.45	18.4	
60	.48	2.69	14.3	
		Phenyl isothiocyanate		
20	1.34	6.48	34.5	2.3
40	1.10	5.17	27.5	
60	0.88	4.02	21.4	
		p-Tolyl isocyanate		
20	0.28	6.29	33.5	1.7
40	.26	5.34	28.4	
60	.22	4.41	23.5	
		Tolylene-2,4-diisocyanate		
20	0.98	5.32	28.3	2.4
40	.76	4.21	22.4	
60	.63	3.23	17.2	
		1-Naphthyl isocyanate		
20	1.84	5.92	31.5	1.8
40	1.41	4.92	26.2	
60	1.09	4.04	21.5	
		2-Biphenylyl isocyanate		
20	2.73	7.85	41.8	
40	2.02	6.49	34.5	
60	1.51	5.50	29.3	

TABLE III
Polarizations and Dipole Moments in Benzene Solution at 20°

Compound	Polarization (cc.) P∞	PE	μ(×10¹⁸) Present work	Lit.
Phenyl isocyanate	156.0	46.9	2.29	2.28[a]
Phenyl isothiocyanate	230.7	61.7	2.85	2.9[b]
p-Tolyl isocyanate	200.6	51.1	2.68	..
Tolylene-2,4-diisocyanate	204.9	72.9	2.52	..
1-Naphthyl isocyanate	187.5	76.2	2.32	2.30[a]
2-Biphenylyl isocyanate	184.9	85.1	2.19	..

[a] E. C. Cowley and J. R. Partington, J. Chem. Soc., 45 (1936). [b] C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., New York, N. Y., 1955, p. 314.

electronic charge from the nitrogen toward the ring could account for the observed decrease of moment from alkyl to aryl isocyanate and isothiocyanate. Such a shift of charge would give double-bond character to the bond between the group and the ring and widen the bond angle, though not necessarily to 180°. From these considerations of dipole moment, it appears a justifiable, though, perhaps, slightly approximate, assumption to treat the isocyanate and isothiocyanate moments as acting in the direction of the group's bond to the ring.

As in the cases of other 2-substituted biphenyls, the moment of 2-biphenylyl isocyanate is slightly lower than that of the phenyl compound, presumably because the small moment induced in the second ring opposes the isocyanate group moment.[14]

of the moments of phenyl isocyanate, 2.29, and p-tolyl isocyanate 2.68, with an angle of 120° between them resulting from the assumed linearity of the groups and bonds in the 2- and 4-positions gives a value of 2.62, but slightly larger than the observed 2.52. It has been suggested[13] that shift of

(13) C. P. Smyth, ref. 12, p. 318.

(14) G. C. Hampson and A. Weissberger, THIS JOURNAL, **58**, 2111 (1936).

Discussion of Relaxation Times

None of the compounds showed any considerable distribution of relaxation times, the values of α, the distribution parameter, never exceeding 0.05. The much larger relaxation time of phenyl isocyanate as compared to those of chlorobenzene, bromobenzene and the more polar nitrobenzene[15] gives evidence of the greater protrusion of the linear NCO group from the ring in a direction close to that of the bond from the ring to the group, as indicated by the previously discussed dipole moment values. The large increase in relaxation time from the isocyanate to the isothiocyanate (Table II) presumably results from the greater length of the protruding group and from the stronger intermolecular forces arising from the great polarizability of the sulfur atom and, to some extent, from the larger molecular dipole moment. The greater resistance to molecular motion is shown by the much higher values of $\Delta\eta/c$. The surprisingly large decrease in the values of $\Delta\eta/c$ for p-tolyl isocyanate as compared to phenyl isocyanate is qualitatively analogous to the decrease in viscosity from benzene to toluene,[15] but much greater than would be anticipated. Its explanation must await further measurements of this character. The considerable increase in the relaxation time of p-tolyl isocyanate over that of the phenyl compound parallels those observed for the corresponding chloro and nitro compounds, 19.5 for p-chlorotoluene[16] and 19 for p-nitrotoluene,[17] and results from a similar length-

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(16) A. J. Petro and C. P. Smyth, THIS JOURNAL, **79**, 6142 (1957).

(17) R. J. W. LeFèvre and E. P. A. Sullivan, *J. Chem. Soc.*, 3287 (1954).

ening of the molecular axis in which the dipole lies. The small decrease in relaxation time resulting from the attachment of a second isocyanate to the ring, in spite of an increase in molecular volume, dipole moment and $\Delta\eta/c$, may result from the fact that the molecular dipole is now at a considerable angle to the longest axis of the molecule, instead of being in it or nearly in it.

Although 1-naphthyl isocyanate has a larger molecular volume and much larger values of $\Delta\eta/c$ than p-tolyl isocyanate, its relaxation time is slightly shorter, as are those of 1-chloro- and 1-nitronaphthalene as compared to the corresponding toluenes. In all three cases, this presumably arises from the fact that the molecular axis in which the dipole lies is considerably longer in the substituted toluenes than in the 1-substituted naphthalenes. The longest relaxation times and the largest values of $\Delta\eta/c$ in Table II are found for the long molecule of 2-biphenylyl isocyanate, which has a moment component in the long axis of the molecule as well as perpendicular to it. The large value is consistent with the large size of the molecule and is slightly smaller than the value 42.5×10^{-12} reported[18] for 2-biphenylyl chloride at 23°, which it should exceed slightly because of the larger size of the isocyanate group. Since, however, the value for 2-biphenylyl chloride is obtained from a single measurement at a wave length far removed from the region of maximum absorption, one should merely expect it to be of the same order of magnitude as that of 2-biphenylyl isocyanate, as observed.

(18) E. Fischer, *Physik. Z.*, **40**, 645 (1939).

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Reactions of Methylene. 2. Ketene and Carbon Dioxide

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Flash irradiation of twin reaction vessels, one of which was filled with mixtures of ketene and ethylene and the other with mixtures of ketene and xenon or carbon dioxide or sulfur hexafluoride, showed only minor changes in the ratio of carbon monoxide yields from the two cells with flash intensity. No effect of radiation frequency on the relative yields was observed. It is concluded that the association reaction of methylene is unimportant, even under conditions of high radiation intensity and that the reaction of methylene with ketene is very fast. Methylene reacts with carbon dioxide about 2×10^{-2} as fast as with ketene, giving carbon monoxide and probably formaldehyde. It reacts to a slight extent also with sulfur hexafluoride. A large number of by-products of ketene decomposition have been identified. Formation of H_2 and C_2H_2 in the presence of CO_2 is strongly enhanced by increasing radiation intensity; that of CH_4, C_2H_6 and C_3H_8 is not. Formation of H_2 and C_2H_2 (and especially of H_2 in the presence of C_2H_4) is increased by radiation below 2300 Å., while that of the other by-products is not. Under steady irradiation the yields of by-products increase with decreasing pressure of ketene but are eliminated by the addition of oxygen. The significance of these findings is discussed.

The results of the first study[1] of the flash photochemical decomposition of ketene were interpreted as evidence for the occurrence of the association reaction of methylene. The original objective of the present experiments was a determination of the rate of this reaction by an adaptation of the rotating sector method[2] to the technique

(1) K. Knox, R. G. W. Norrish and G. Porter, *J. Chem. Soc.*, 1477 (1952).

(2) F. Briers, D. L. Chapman and E. Walters, *ibid.*, 562 (1926).

of flash photolysis.[3] While the work was in progress, evidence was accumulating for an extremely fast reaction of methylene with ketene,[4-6] implying the virtual absence of the association reaction. The present experiments support this conclusion and re-

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(4) G. B. Kistiakowsky and K. Sauer, THIS JOURNAL, **78**, 5699 (1956).

(5) G. B. Kistiakowsky and P. Kydd, *ibid.*, **79**, 4825 (1957).

(6) H. M. Frey and G. B. Kistiakowsky, *ibid.*, **79**, 6373 (1957).