

the rate picture is influenced by the capacities of the various media to solvate the reactants (as well as the activated complexes), and this factor has been discounted in this interpretation. It is generally accepted, however, that for qualitative purposes the change in the rate picture for a polar process as the solvent is changed is dominated by the capacity of the medium to contribute to the stabilization of the activated complex.¹⁰ It would be of considerable interest to test the responses of

(10) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, New York, 1953, p. 345.

other polar reactions of chlorine to the influence of medium changes as has been done in this investigation. Unfortunately, the number of such reactions, so far discovered, which are readily subject to kinetic study with carbon tetrachloride as the solvent and trifluoroacetic acid as catalyst and also with acetonitrile-nitromethane mixtures as the solvent are limited in number.

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Microwave Absorption and Molecular Structure in Liquids. XLVIII. The Dielectric Relaxation of Diphenyl Sulfide, Triphenylamine and Diphenylmethane^{1,2}

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The dielectric constants and losses at wave lengths of 1.20, 3.30, 10 and 25 cm. have been measured for diphenyl sulfide in benzene solution at 20° and in Nujol solution at 20, 40 and 60°; measurements being made in the latter case at 50 cm. also. Measurements have been made at wave lengths of 1.25 and 3.22 cm. on triphenylamine in benzene solution at 40° and on diphenylmethane, as the pure liquid, at 40 and 60°. Measurements of dielectric constant alone were made at a wave length of 575 m. and refractive indices were determined for the sodium D-line. Dielectric relaxation times and distribution parameters have been calculated from these data. The data obtained for diphenyl sulfide in benzene solution have been analyzed in terms of two relaxation times, the value of the relaxation time corresponding to the high frequency dispersion region being consistent with an intramolecular mechanism. The relaxation time of diphenyl sulfide in Nujol solution at 20° was observed to be about one tenth as large as would be expected if the molecule were completely rigid. Dipole orientation by intramolecular motion has been found to occur in the molecule of triphenylamine. The contribution to the dipole orientational mechanism of diphenylmethane by internal motion has been found to be somewhat smaller than previously believed. Dipole moment values of 0.22 and 0.43 *D* have been determined for diphenylmethane and triphenylamine, respectively.

The abnormally low dielectric relaxation time found for diphenyl ether⁴⁻⁷ has been attributed to intramolecular rotation of the phenyl rings with accompanying shift of pi electronic charge.⁸ Similarly low relaxation times found for diphenylmethane⁷ and diphenylamine⁹⁻¹¹ have suggested a similar relaxation mechanism for these molecules. To obtain further evidence as to possible mechanism, diphenylmethane, which had been impossible to measure accurately because of the smallness of its moment, was redetermined, and diphenyl sulfide and triphenylamine were measured to see if an intramolecular relaxation mechanism could be detected.

Experimental Methods

Apparatus.—The apparatus and the various methods of measurement have been described in previous papers.¹²⁻¹⁴

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(3) Esso Foundation Fellow, 1960-1961; National Science Foundation Summer Fellow, 1961.

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Purification of Materials.—Diphenyl sulfide, obtained from the Eastman Kodak Company, was fractionally distilled under reduced pressure and stored over Drierite. It gave a refractive index n_D^{20} 1.63411. Triphenylamine, obtained from the Aldrich Chemical Company, was recrystallized three times from a mixture of benzene and absolute ethanol. The resulting material, after recrystallization three times from ethyl ether, gave a melting point of 127.3–127.9°. Diphenylmethane, obtained from Matheson, Coleman and Bell, Inc., was fractionally distilled under reduced pressure and stored over Drierite. It gave a refractive index n_D^{20} 1.56831. Benzene, obtained from the Allied Chemical Corporation, was of the reagent grade, thiophene-free quality. It was used as received. Nujol, purchased from a local drug store, was treated as previously described.¹⁵

Experimental Results

The experimental results obtained from the solution studies were treated in the manner described in earlier papers.^{16,17} The slopes of the straight lines thus obtained, a' corresponding to ϵ' , and a'' corresponding to ϵ'' , were plotted in Cole-Cole arcs¹⁸ in the usual fashion¹⁶ to obtain the critical wave lengths, λ_m , the corresponding relaxation times, τ_0 , the distribution parameters, α , and the arc intercepts at infinite frequency, a_∞ . The values of these quantities are given in Tables I and III. The dipole moment calculated for triphenylamine from the 3.22 cm. dielectric constant and loss data by a method described previously¹⁹ is also included in Table III. The data obtained for di-

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phenylmethane, as the pure liquid, are listed in Tables II and IV. The concentration range in mole fraction of solute for the benzene solutions and in weight fraction for the Nujol solutions is given in parentheses for each set of solutions in Table I. The dipole moment calculated for diphenylmethane from the observed ϵ_0 and ϵ_∞ values by means of the Onsager equation²⁰ is also included in Table IV. The viscosity of the Nujol, as measured by Mr. J. E. Anderson in this Laboratory was 226.1 c.p.s. at 20°, 65.3 c.p.s. at 40° and 25.3 c.p.s. at 60°. The density of the Nujol, as measured by Mr. E. Forest in this Laboratory, was 0.8790 at 20°, 0.8678 at 40° and 0.8560 at 60°.

TABLE I

SLOPES FOR THE DEPENDENCE OF THE DIELECTRIC CONSTANT AND LOSS OF SOLUTIONS ON WEIGHT OR MOLE FRACTION OF SOLUTE

Wave length, (cm.)	-20°		-40°		-60°	
	a'	a''	a'	a''	a'	a''
Diphenyl sulfide-benzene (0-0.090)						
1.20	2.10	1.04				
3.30	3.28	1.11				
10	3.78	0.44				
25	3.91	0.19				
57500	3.97					
Diphenyl sulfide-Nujol (0-0.067)						
1.20	0.70	0.29	0.93	0.34	0.85	0.36
3.30	0.98	.29	0.99	.31	1.10	.29
10	1.15	.28	1.29	.24	1.30	.19
25	1.45	.22	1.50	.17	1.45	.12
50	1.50	.20	1.54	.12	1.48	.07
57500	1.67		1.55		1.45	
Triphenylamine-benzene (0-0.111)						
1.25			1.770	0.052		
3.22			1.778	0.042		
57500			1.784			

TABLE II

DIELECTRIC CONSTANTS AND LOSSES

Wave length, (cm.)	-40°		-60°	
	ϵ'	ϵ''	ϵ'	ϵ''
Diphenylmethane				
1.25	2.499	0.0148	2.475	0.0146
3.22	2.510	0.0168	2.482	0.0131
57500	2.526		2.493	

TABLE III

SLOPES a_D FOR THE DEPENDENCE OF THE SQUARE OF THE REFRACTIVE INDEX ON WEIGHT OR MOLE FRACTION OF SOLUTE, WITH INFINITE FREQUENCY INTERCEPTS, a_∞ , CRITICAL WAVE LENGTHS, λ_m , RELAXATION TIMES, τ_0 , DISTRIBUTION PARAMETERS, α , AND DIPOLE MOMENT, μ

t_i , °C.	a_D	a_∞	λ_m (cm.)	τ_0 (10^{-12} sec.)	α	μ ($\times 10^{18}$)
Diphenyl sulfide-benzene						
20	0.74	1.24	1.88	10.0	0.08	
Diphenyl sulfide-Nujol						
20		0.43	5.43	28.8	0.44	
40	0.33	.41	2.54	13.5	.36	
60		.39	1.71	9.1	.29	
Triphenylamine-benzene						
40	1.25	1.50	0.41	2	0.04	0.43

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TABLE IV

SQUARES, ϵ_D , OF REFRACTIVE INDEX, INFINITE FREQUENCY INTERCEPTS, ϵ_∞ , CRITICAL WAVE LENGTHS, λ_m , RELAXATION TIMES, τ_0 , DISTRIBUTION PARAMETER, α , AND DIPOLE MOMENT, μ

t_i , °C.	ϵ_D	ϵ_∞	λ_m (cm.)	τ_0 (10^{-12} sec.)	α	μ ($\times 10^{18}$)
Diphenylmethane						
40	2.4596	2.488	2.45	13	0.08	0.22
60	2.4319	2.460	1.35	7	0.08	0.22

Discussion of Results

Diphenyl Sulfide.—Although part of the dielectric relaxation of benzophenone has been shown to occur by over-all molecular rotation,²¹ the relaxation time, 16.4×10^{-12} sec., observed by Jackson and Powles²² for this molecule in benzene solution at 19° may be taken as a rough estimate of the relaxation time for a completely rigid diphenyl sulfide molecule, since the latter is of approximately the same size and shape as benzophenone and since the rigid fluorenone²⁷ molecule, which is similar in size, has a value 19.9×10^{-12} . The relaxation time, 10.0×10^{-12} sec., of diphenyl sulfide in dilute benzene solution at 20° is too low to be interpreted as due only to over-all molecular rotation and indicates some contribution to the relaxation of the molecule by an internal motion. Assuming the existence of two independent Debye-type mechanisms of relaxation for diphenyl sulfide, and using the method of analysis employed by Bergmann, Roberti and Smyth,²³ the relaxation times, τ_1 and τ_2 , associated with the over-all and the internal rotation, respectively, and the fractions, c_1 and c_2 , of the relaxation due to the two processes have been determined. The dielectric constant and loss data are then best fitted by $a_0 = 3.98$, $a_\infty = 1.02$, $c_1 = 0.59$, $\tau_1 = 16 \times 10^{-12}$ sec. and $\tau_2 = 4 \times 10^{-12}$ sec. The agreement between the calculated and the experimental a'' values is only fair. A better fit can be obtained for the loss data, at the expense of a slightly poorer fit for the dielectric constant data, by using $a_0 = 3.98$, $a_\infty = 1.19$, $c_1 = 0.52$, $\tau_1 = 16 \times 10^{-12}$ sec. and $\tau_2 = 4 \times 10^{-12}$ sec. The relaxation time for the over-all molecular rotation is in excellent agreement with that found for benzophenone.²² The value for internal rotation is close to the corresponding values found for diphenyl ether^{21,23} and diphenylamine.¹¹ The average of the c_2 values, 0.45, indicated by the two analyses is no more reliable than ± 10 per cent.

The lowering of the relaxation time of a non-rigid molecule below the value expected for a rigid molecule of similar size and shape is considerably enhanced in a highly viscous solvent. Diphenyl ether, for example, has a relaxation time in benzene solution⁴ one-fifth to one-sixth that of benzophenone,²² while in Nujol solution,⁷ its relaxation time, ca. 6×10^{-12} sec., is about one-fiftieth of the value, 295×10^{-12} sec., observed for benzophenone in a similar viscous paraffin oil.²² The same trends have

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been observed for diphenyl sulfide but to a lesser degree. The relaxation time of diphenyl sulfide in Nujol solution at 20° is 28.8×10^{-12} sec., or about one-tenth that which would be expected if the molecule were completely rigid. The relaxation times observed at 40 and 60° are also much too small to be interpreted as due only to over-all molecular rotation. A separation of the individual relaxation times of diphenyl sulfide in Nujol solution could not be effected because of the very small variation of α'' with frequency. However, the results of the Nujol measurements agree, at least qualitatively, with the conclusion reached from the analysis of the benzene data, *i.e.*, that an internal mechanism of relaxation accounts for a large part, 40 to 50 per cent. of the dipole orientation in diphenyl sulfide.

Triphenylamine.—The molecular dipole moment, $0.43 \pm 0.1 \times 10^{-18}$, in Table III is close to the values, 0.5 ± 0.1 and 0.45 , found by Mr. B. B. Howard and Dr. E. L. Grubb, respectively, in this Laboratory and to the mean, 0.49 , of three values, 0.26 ,²⁴ 0.55 ²⁵ and 0.65 ²⁶ reported in the literature.

Since the dipole moment is so small, the dielectric losses for the most concentrated solutions obtainable are very small, and the values of the relaxation time calculated from them are necessarily very approximate. The present determination, 2×10^{-12} sec. at 40°, and a value, 3×10^{-12} sec. at 40°, previously determined by Mr. B. B. Howard in this Laboratory should be less approximate than the value, 7×10^{-12} sec. at 20°, obtained in this Laboratory by Mr. W. S. Lovell and Dr. E. L. Grubb from measurements on more dilute solutions. All three of these values are much smaller than the relaxation times in benzene solution at 40°, 18.4 , 14.9 and 22.2×10^{-12} sec., found²⁷ for anthrone, fluorenone and phenanthrenequinone, respectively, which have molecules slightly smaller than that of triphenylamine. Indeed, the relaxation times of these three molecules for over-all molecular rotation should be lower than that of triphenylamine, since their molecular dipoles lie in the plane in which molecular rotation can occur most easily, which is not the case in triphenylamine. It, therefore, appears certain that a considerable part of the dielectric relaxation occurs through an intramolecular charge shift. It was concluded from previous dielectric measurements made in the frequency range, 3×10^4 to 10^8 cycles per second, that an inversion might be occurring in tribenzylamine,²⁸ where the relaxation time was fourteen times that of benzophenone. However, no evidence of molecular inversion was found²⁸ for triphenylphosphine, triphenylarsine and several sub-

stituted amines. It appears probable, therefore, that the intramolecular charge shift is similar to that occurring in diphenyl ether⁴ and diphenylamine,¹¹ but the amount of steric hindrance should be greater because of the presence of three rings instead of two attached to the central atom.

Diphenylmethane.—Diphenylmethane was found⁷ to have a short relaxation time, like that of diphenyl ether, but, as its dipole moment was small, the possible error in the determination of the relaxation time was large. It seemed desirable, therefore, to repeat the determination of the relaxation time with carefully dried material because of its considerable bearing upon the nature of the relaxation mechanism suggested for the molecules of the diphenyl ether-type. The fact that diphenylmethane can be measured as a pure liquid reduces the error in the determination of the relaxation time, but the comparison of the result with those for other pure liquids involves consideration of the effects of the different internal fields and liquid viscosities. These effects are roughly taken care of by calculating the so-called molecular or microscopic relaxation times,²⁹ τ_μ , and comparing the reduced relaxation times, the ratios of the molecular relaxation times to the viscosities, $\tau_\mu(10^{-12} \text{ sec.})/\eta(\text{c.p.s.})$, as shown in Table V. The values of the molar volume, V , are also given.

TABLE V
MOST PROBABLE AND REDUCED RELAXATION TIMES, AND
MOLAR VOLUMES AT 60°

	$\tau_\mu(10^{-12} \text{ sec.})$	τ_μ/η	$V(\text{cc.})$
Benzophenone ⁶	69	12	170
Diphenyl ether ²¹	3.9	2.2	164
Diphenylmethane	3.9 ^a	2.5	174
	τ^A	4.6	

^a Ref. 7. ^b Table IV.

The low polarity of the diphenylmethane molecule makes the data too approximate for a detailed analysis, but it is obvious in the present revised values, as well as in the results of the earlier measurements, that the observed relaxation time is too short to result entirely from rotation of the molecule as a whole. A considerable amount of the relaxation occurs by rotation of the molecule as a whole, because of its small fixed moment, but a considerable portion also must occur by an intramolecular mechanism. There are no unshared electron pairs on the central atom to shift into the attached phenyl groups as in diphenyl ether and the aryl amines to give mesomeric moments changing in size as the rings rotate, but hyperconjugation can give a very small shift of electronic charge in this direction and the consequent moment would change somewhat in size with ring rotation. The larger relaxation time found in the present work requires a smaller and more plausible role for the intramolecular mechanism than that previously suggested.

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