tween the total gas and crosslinking yields and also the simultaneous increase in CH_4 yield in the glass-state at $-180°$, it is suggested that here an appreciable fraction ($G \simeq 0.9$) of the CH_4 is formed by a "molecular" primary process which involves neither $CH_3\cdot$ radicals nor polymer radicals as intermediates. Further discussion will be presented in a subsequent paper of this series.

Acknowledgment.—Miss D. McClung made the infrared measurements and P. C. Noble the mass spectrometer analyses. E. J. Lawton and J. S. Balwit assisted in the design of the gas measurement cell and provided the dosimetry. All irradiations were done by J. S. Balwit. In particular, the author is indebted to S. W. Kantor for providing unpublished infrared data on siloxanes.

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Microwave Absorption and Molecular Structure in Liquids. XXX. The Anomalous Dielectric Relaxation of Diphenyl Ether and Some Similar Molecules[1,2]

BY D. M. ROBERTI,[3] O. F. KALMAN AND C. P. SMYTH

RECEIVED NOVEMBER 25, 1959

Dielectric relaxation times have been determined for diphenylmethane, benzyl ether, bibenzyl and dibenzyl ether, as pure liquids, to be compared with previous values for diphenyl ether and benzophenone. All the measured compounds have relaxation times comparable to that for diphenyl ether, very low in comparison to that for benzophenone. In addition, the relaxation time of diphenyl ether measured in Nujol has been found to be relatively insensitive to viscosity and temperature. The results indicate that some form of intramolecular motion is responsible for the small relaxation time. Several previously proposed mechanisms are discussed.

The relaxation time of diphenyl ether in benzene was found by Fischer[4] to be 0.28×10^{-11} sec., a value seemingly much too small when compared with the value of 2.04×10^{-11} sec. for benzophenone, a molecule of approximately the same size and shape. The anomalously low relaxation time of diphenyl ether has interested a number of investigators, and the findings of Fischer have been approximately confirmed by measurements using other methods.[5,6]

The present research is an attempt to elucidate the problem by measuring the relaxation times of some molecules similar to diphenyl ether. In addition, measurements have been made on diphenyl ether in dilute solutions in Nujol.

Purification of Materials.—Diphenyl ether, obtained from Matheson, Coleman and Bell, Inc., was dried with calcium chloride and fractionally distilled under reduced pressure. It was crystallized slowly at 25–27° and a small portion poured off. The final product had a refractive index $n^{30.65}_{\mathrm{D}}$ 1.57596. Dibenzyl ether, obtained from Brothers Chemical Co. and distilled under reduced pressure, gave a density d^{20} 1.0424 and n^{20}_{D} 1.56264. Benzyl phenyl ether was synthesized according to the procedure of Peacock,[7] dried over calcium, fractionally distilled under reduced pressure and recrystallized from heptane. The final product had $d^{40} = 1.0518$ and a melting point of 36°. Diphenylmethane, from Matheson, Coleman and Bell, Inc., was fractionally distilled twice under reduced pressure, finally boiling at 114.5° at 6 mm. pressure, giving a d^{30} of 0.9971. Bibenzyl, obtained from Matheson, Coleman and Bell, Inc., was fractionally distilled, boiling at 270–271°, with a melting point of 51.2°.

Experimental Results

Dielectric constants, ϵ', and losses, ϵ'', at wave lengths of 1.25 and 3.22 cm. and the so-called static dielectric constant, ϵ_0, were measured over a range of temperatures by methods described or referred to in earlier papers of this series.[8] In the case of dibenzyl ether, measurements also were made at 10.0 cm. wave length. For some substances, measurements could not be made at lower temperatures because of high melting points. Densities were determined with a graduated pycnometer and viscosities with an Ostwald-Fenske viscometer. The values obtained for the liquid measurements at each temperature are given in Table I. For the solution measurements, Table II gives values of the slopes of the square of the refractive index, a_{D}, static dielectric constant, a_0, dielectric constant, a', and loss, a'', against the weight fraction of solute in solutions in Nujol made up from a specimen designated as Nujol (II).

From the dielectric constant data Cole–Cole arc plots were drawn and used to determine the critical wave lengths, λ_m, at which the loss is a maximum. Table III contains the values of the optical dielectric constants, ϵ_∞, the distribution parameters, α, and the critical wave lengths obtained from the arc plots. From the critical wave length, the macroscopic relaxation time, τ_M, is calculated according to the equation $\tau_M = \lambda_m/2\pi c$. To correct for the effect of dipole–dipole interaction in the liquid state, the Powles[9] internal field correction, found to be the most nearly correct form in a recent evaluation,[10] gives a molecular relaxation time, τ_μ. Values of τ_μ and of the dipole moments, μ, calculated from ϵ_0 and ϵ_∞ values by the Onsager equation are also

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(1) This research was supported in part by the United States Air Force through the Office of Scientific Research of the Air Research and Development Command and in part by the Office of Ordnance Research, U. S. Army. Reproduction, translation, publication, use or disposal in whole or in part by or for the United States Government is permitted.

(2) This paper represents a part of the work submitted by D. M. Roberti to the Graduate School of Princeton University in partial fulfillment of the requirements for the degree of Doctor of Philosophy. Portions of this paper were read before the American Chemical Society, Division of Physical Chemistry, Atlantic City, N. J., Sept. 16, 1959.

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(7) D. H. Peacock, *Proc. Chem. Soc.*, **30**, 247 (1914).

(8) R. S. Holland and C. P. Smyth, *J. Phys. Chem.*, **59**, 1088 (1955).

(9) J. G. Powles, *J. Chem. Phys.*, **21**, 633 (1953).

(10) R. C. Miller and C. P. Smyth, THIS JOURNAL, **79**, 3310 (1957).

TABLE I

DENSITIES, VISCOSITIES, DIELECTRIC CONSTANTS AND LOSSES

t, °C.	d	η	ϵ_0	1.25		3.22		10.0 cm.	
				ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''
				Diphenylmethane					
30	0.9971	2.575	2.540	2.510	0.0196	2.525	0.0156		
40	.9883	2.117	2.522	2.499	.0191	2.510	.0144		
60	.9682	1.538	2.488	2.472	.0197	2.481	.0121		
				Benzyl phenyl ether					
40	1.0518	3.989	3.748	2.797	0.243	2.986	0.382		
60	1.0306	2.453	3.609	2.809	0.321	3.069	0.393		
				Bibenzyl					
60	0.9585	1.896	2.484	2.454	0.0340	2.477	0.0357		
75	0.9470	1.480	2.514	2.445	0.0341	2.461	0.0311		
				Dibenzyl ether					
20	1.0424	5.507	3.821	2.785	0.285	3.028	0.460	3.559	0.461
40	1.0345	3.307	3.668	2.811	.358	3.109	.461	3.555	3.57
60	1.0049	2.199	3.532	2.845	.387	3.173	.431	3.489	.251

TABLE II

SLOPES (a) FOR DEPENDENCE OF DIELECTRIC CONSTANT AND LOSS ON WEIGHT FRACTION OF DIPHENYL ETHER IN NUJOL (II) AND VISCOSITY OF NUJOL (II)

t, °C.	η (c.p.s.)	a_D	a_0	1.25		3.22 cm.	
				a'	a''	a'	a''
20	210	0.216	1.02	0.683	0.204	0.910	0.146
40	60.4	.203	.943	.748	.180	.831	.118
60	23.8	.221	.907	.753	147	823	112

included in Table III. The dipole moments obtained by Reidinger,[11] 0.33 for diphenylmethane and 0.45 for bibenzyl, are somewhat higher than those found in this study. The values for the two ethers, 1.13 and 1.12, are to be compared with the vapor values for ethyl ether,[12] 1.16, and for diphenyl ether,[13] 1.16 and for diphenyl ether[13] 1.14. On the basis of these last two values it seems that the value 1.12 found for dibenzyl ether in this study is to be preferred to the value 1.38 found by Bergmann[14] by measurements in dilute benzene solutions at 21°.

For the solution measurements, values of a' and a'' were used similarly to construct the Cole–Cole arcs and from these critical wave lengths were calculated. In Table IV are given the slopes of the high-frequency dielectric constants, a_∞, values of α, λ_m, and τ, the atomic polarization, P_A, and the dipole moment, μ. Since there is no dipole–dipole interaction in dilute solution, there is no need for an internal field correction. The dipole moment, 0.96, found for diphenyl ether is somewhat lower than the vapor value[13] because of the high value found for the atomic polarization.

Discussion of Results

The observed apparent relaxation times are calculated from an absorption which may receive contributions from both molecular and intramolecular relaxation processes. The so-called "molecular relaxation time" may, therefore, be a composite quantity dependent upon two processes, one of which

TABLE III

OPTICAL DIELECTRIC CONSTANTS, DISTRIBUTION PARAMETERS, CRITICAL WAVE LENGTHS, RELAXATION TIMES AND DIPOLE MOMENTS

t, °C.	ϵ_∞	α	λ_m (cm.)	τ_M ($\times 10^{11}$ sec.)	τ_μ ($\times 10^{11}$ sec.)	μ ($\times 10^{18}$)
			Diphenylmethane			
30	2.485	0.18	1.23	0.65	0.65	0.26
40	2.471	.15	1.02	.54	.54	.26
60	2.442	.08	0.74	.39	.39	.26
			Benzyl phenyl ether			
40	2.615	0.23	5.9	3.1	2.8	1.13
60	2.565	.16	3.3	1.75	1.58	1.14
			Bibenzyl			
60	2.433	0.01	2.50	1.33	1.32	0.36
75	2.416	.00	1.97	1.05	1.04	0.34
			Dibenzyl ether			
20	2.69	0.06	5.19	2.76	2.58	1.12
40	2.66	.04	3.53	1.87	1.70	1.11
60	2.63	.02	2.49	1.32	1.21	1.11

TABLE IV

SLOPE FOR OPTICAL DIELECTRIC CONSTANT, a_∞, DISTRIBUTION PARAMETER, α, CRITICAL WAVE LENGTH, λ_μ, RELAXATION TIME, τ, ATOMIC POLARIZATION, P_A, AND DIPOLE MOMENT, μ, OF DIPHENYL ETHER IN NUJOL(II)

t, °C.	a_∞	α	λ_m (cm.)	τ ($\times 10^{11}$ sec.)	P_A (cc.)	μ ($\times 10^{18}$)
20	0.415	0.24	1.2	0.62	7	0.96
40	.440	.23	0.92	.49		
60	.455	.21	0.90	.48		

TABLE V

REDUCED RELAXATION TIMES AND MOLAR VOLUMES AT 60°, AND ACTIVATION ENERGIES

Pure liquids	τ_μ/η	V(cc.)	ΔH_ϵ (kcal.)	ΔH_V (kcal.)
Benzophenone	1.19	170	4.3	5.3
Diphenyl ether	0.23	164	1.9	3.8
Diphenylmethane	.25	174	2.7	3.4
Benzyl phenyl ether	.65	179	5.4	5.1
Bibenzyl	.70	190	3.0	3.8
Dibenzyl ether	.55	197	3.0	4.5

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[11] A. Reidinger, *Physik. Z.*, **39**, 380 (1938).

[12] C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., New York, N. Y., 1955, p. 298.

[13] *Ibid.*, p. 314.

[14] E. Bergmann, L. Engel and S. Sandor, *Z. physik. Chem.*, **10B**, 106 (1930).

may or may not predominate largely over the other. In order to compare the various molecules, it is desirable to reduce the relaxation times to a common viscosity, and, following Petro and Smyth,[15] the molecular relaxation times have been divided by the viscosities to give reduced relaxation times, τ_μ/η. These values, which should depend only on the size of the molecule, are listed for 60° in Table V. The values for diphenyl ether and benzophenone are listed for 60° in Table V. The values for diphenyl ether and benzophenone are from Calderwood and Smyth.[6] The values of the molar volume, V, also are given.

The reduced relaxation time of benzophenone may be taken as normal for a molecule of its size. The other molecules in the series are roughly the same in size, yet have much smaller values of reduced relaxation times. If a methylene group is taken to be approximately equivalent in size to an oxygen atom, then several of the molecules can be grouped in pairs. In one such pair, diphenyl ether and diphenylmethane, the slightly larger molar volume of the latter is reflected in a slightly larger reduced relaxation time. Fischer[4] felt that the low value for diphenyl ether might be due to orientation by internal motion of the molecule, associated with the presence of the oxygen atom, but there seems to be nothing anomalous about the relaxation times found for ethyl ether and decyl ether.[16] Furthermore, the low value found for diphenylmethane indicates that the anomaly is not peculiar to oxygen-containing molecules alone.

In comparing the second pair, benzyl phenyl ether and bibenzyl, a similar trend is seen, the slightly larger molar volume of the latter giving rise to a slightly larger reduced relaxation time. But while the molar volumes of the second pair are only slightly larger than the molar volumes of the first pair, the reduced relaxation times are considerably greater. Dibenzyl ether, while it has the largest molar volume of the group, has a reduced relaxation time intermediate between those of the first and second pairs.

The reduced relaxation time shown by benzophenone may be regarded as normal for molecular rotation. The lower values of reduced relaxation times shown by the other compounds must reflect the contribution of some other relaxation process, such as intramolecular rotation. The contribution of intramolecular motion of some kind is clearly indicated in the results of a recent study by G. W. Nederbragt[17] who found that linking the two rings of benzophenone together to form fluorenone had no effect on the relaxation time, while a similar linking of the diphenyl ether rings to give dibenzofuran increased the relaxation time four-fold, presumably by preventing rotation of the rings. In a similar experiment Maier[18] showed that preventing intramolecular motion by hydrogen bonding in 2-hydroxydiphenyl ether increased the relaxation time three-fold over that of the non-hydrogen-bonded 2-methyldiphenyl ether. An even more striking indication of the contribution of intramolecular rotation may be seen in the values for diphenyl ether in Nujol measured in this Laboratory and shown in Table IV. Although the viscosity of Nujol II at 20° is about 340 times that of benzene, the relaxation time of diphenyl ether in Nujol is not much larger than in benzene. Whereas Dieringer[5] found a relaxation time of 0.47–0.61, depending on concentration, for diphenyl ether in benzene at 21°, our results in Nujol at 20° show $\tau =$ 0.62. In sharp contrast, some measurements on benzophenone[19] at 19° show that the relaxation time goes from 1.64×10^{-11} sec. in benzene to 29.5×10^{-11} sec. in a paraffin oil of viscosity 197 c.p.s., slightly less viscous than Nujol II. The temperature dependence of the relaxation time of diphenyl ether in Nujol is also unusual. From previous work with Nujol solutions[20] one may make the conservative estimate that for a molecule of the size and shape of diphenyl ether, the relaxation time should decrease five-fold from 20 to 60°. As can be seen from Table IV, there is little change with temperature. Both these results emphasize the importance of an intramolecular rotation, which would be expected to be relatively insensitive to changes in viscosity and temperature.

Values of the distribution parameter, α, were found to be relatively large and much less sensitive to temperature than was found in previous work with Nujol,[20] again suggestive of an intramolecular orientation mechanism relatively independent of environment. Unfortunately, there are no other solution data with which one can compare the α values. The pure liquid results show the usual changes in α with temperature, but for these the relaxation time also changes with temperature.

In Table V are also listed the activation energies for dielectric relaxation, ΔH_ϵ, and for viscous flow, ΔH_V. The activation energies are of the order to be expected, that of ΔH_ϵ being lowest for diphenyl ether. As is usually found, ΔH_V is larger than ΔH_ϵ except for the case of benzyl phenyl ether. This anomalous result is unexplained.

It may at first appear that the low relaxation time process involves rotation of a polar group with a small group relaxation time. The smallest polar group of diphenyl ether which is capable of orienting by independent rotation is the phenoxy group, and the relaxation time for such a rotation should not be much smaller than that for toluene,[21] which has a reduced relaxation time of about 1. This rotation could not lower the observed relaxation time to the extent observed. Furthermore, the insertion of a methylene group into diphenyl ether and diphenylmethane should not triple the relaxation time, as is found.

It has been suggested previously[4] that the lowering of the relaxation time of diphenyl ether is caused by an inversion mechanism, similar to the "umbrella" inversion of ammonia. Such an inversion, however, if it were to occur, would take place at very low frequencies, and its effect would be to

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

(16) G. B. Rathmann, A. J. Curtis, P. L. McGeer and C. P. Smyth, *J. Chem. Phys.*, **25**, 413 (1956).

(17) G. W. Nederbragt, oral communication.

(18) W. Maier, *Archives des Sciences*, **12**, 20 (1959).

(19) W. Jackson and J. G. Powles, *Trans. Faraday Soc.*, **42A**, 101 (1946).

(20) O. F. Kalman and C. P. Smyth, THIS JOURNAL, **82**, 783 (1960).

(21) A. J. Petro and C. P. Smyth, *ibid.*, **79**, 6142 (1957).

raise, not lower, the relaxation time.[22] There is some evidence of the occurrence of such an inversion in tribenzylamine,[22] where the relaxation time is 14 times that of benzophenone. The lowering of the value for diphenyl ether, then, cannot be explained by an "inversion" mechanism.

Another mechanism has been proposed by Fischer,[23] who concludes that the small relaxation time must be at least an order of magnitude smaller than the relaxation time for molecular rotation. He considers that the "atomic dipole moment" due to the lone-pair electrons on the oxygen atom is modified bv resonance with the phenyl rings. As the phenyl rings rotate around their bonds to the oxygen atom, they move into orientations which permit more or less resonance and thus change both the direction and the size of the "atomic moment." A small rotation of the ring can produce a large orientational effect and might be responsible for small relaxation time. This mechanism cannot be reconciled with the small reduced relaxation time found for diphenylmethane and bibenzyl in this study, for these molecules have no lone-pair electrons. Some mechanism in which orientation occurs through varying degrees of resonance contributions, not necessarily involving lone pair electrons, is still not impossible, since a charge shift might occur in diphenylmethane and bibenzyl through hyperconjugation of the methylene groups. The intramolecular orientation process does not usually occur to the complete exclusion of the molecular orientation process. Rather, it gives rise to a second absorption region which may overlap and may obscure the absorption due to the slower molecular orientation. A future paper from this Laboratory[24] will examine these mechanisms in greater detail.

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[22] A. H. Price, *J. Phys. Chem.*, **62**, 773 (1958).

[23] E. Fischer, *Naturwissenchaften*, **43**, 153 (1956).

[24] K. Higasi and C. P. Smyth, to be published.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF KANSAS, LAWRENCE, KANSAS]

Solvent Effects on the Polarographic Reduction of Metal Ions. II. Nitrile Solvents

BY ROBERT C. LARSON AND REYNOLD T. IWAMOTO

RECEIVED DECEMBER 21, 1959

The ease of polarographic reduction of metal ions is greatest in benzonitrile, followed by phenylacetonitrile, acrylonitrile, propionitrile and acetonitrile, in that order. Comparison of polarographic half-wave potentials for the reduction of metal ions in the nitriles with infrared and chemical information on the interaction of nitriles with cations suggests a bridge mechanism for the reduction of metal ions in these solvents. The ease of reduction of metal ions in benzonitrile and acrylonitrile appears to be in a large measure due to the presence of a conjugated double bond system which facilitates electron transfer; ease of reduction in phenylacetonitrile appears to be due to the low dielectric constant (18.7) of this solvent.

In a previous communication,[1] the more positive (less reducing) $E_{1/2}$ values for the reduction of metal ions in benzonitrile as compared to those in acetonitrile were explained as being due to the delocalized electrons on the phenyl ring of benzonitrile facilitating electron transfer in the bridge mechanism for the reduction process. Three additional solvents, propionitrile, acrylonitrile and phenylacetonitrile, have been studied to elucidate more clearly the factors that influence polarographic $E_{1/2}$ values for metal ions in nitrile solvents.

Experimental

The polarographic technique, cells, instrumentation, supporting electrolyte and metal perchlorates have been described previously.[1]

Solvents.—Eastman practical grade solvents were purified as described. Propionitrile was fractionally distilled from phosphorus pentoxide with a three-foot column packed with glass helices. The middle fraction, b.p. 95–96° (735 mm.), was collected. Acrylonitrile was shaken intermittently with Molecular Sieve for two days and also fractionally distilled through the three-foot column, b.p. 78 ± 0.5° (735 mm.). Phenylacetonitrile was purified by fractional distillation at reduced pressure following passage through a column of highly activated alumina, b.p. 100° (*ca.* 8 mm.).

The water content of the polarographic solutions (containing supporting electrolyte and metal perchlorate) was determined by Karl Fischer titration to be *ca.* 0.01 *M*, which was essentially that found for the solvents.

Peak-type polarograms were obtained in several cases. Maximum suppressors, such as methyl red, sodium form of methyl red and Surfactol-100, were used to eliminate the peaks; they did not alter the shape or position of the polarographic waves.

Results

$E_{1/2}$ values for the polarographic reduction of metal ions are tabulated in Table I.

Discussion

The collection of $E_{1/2}$ values in Table I shows that the ease of polarographic reduction of metal ions is greatest in benzonitrile, followed by phenylacetonitrile, acrylonitrile, propionitrile and acetonitrile, in that order. Comparison of this order and the magnitudes of the differences in $E_{1/2}$ values with dielectric constants of the solvents: phenylacetonitrile (18.7), benzonitrile (25.2), propionitrile (27.2), acetonitrile (37.5) and acrylonitrile (38), indicates only partial correlation between dielectric constants of the solvents and the $E_{1/2}$ values for the metal ions in these solvents. The shift of half-wave potentials to less negative values going from acetonitrile to benzonitrile does not appear to be due to liquid junction effect, as such an effect would give constant shifts between solvents, which is not the case. Furthermore, the small difference (0.05 v.) in $E_{1/2}$ values for the weakly solvated barium ion between acetonitrile and benzonitrile suggests that liquid junction effect is small.

The ability of a nitrile to solvate an ion lies in the presence of the C≡N group. Participation of

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[1] R. C. Larson and R. T. Iwamoto, THIS JOURNAL, **82**, 3239 (1960).