

vides us with the basic behavior observed in Figs. 2, 3 and 4 if we assume that the formate ion, too, reacts with the sulfate radical SO_4^- , as shown in the above propagation and termination reactions. In fact, since $G(\text{CO}_2)$ at complete formic acid ionization reaches a value of 680 at a $p\text{H}$ of 4.9 compared to 80 at a $p\text{H}$ of 0.5, the ratio $(k_4/2k_6)^{1/2}$ must be 8.5 times as great for the formate ion reactions as for the neutral molecule reactions. The higher carbon dioxide yields are therefore associated with a more efficient propagation reaction (greater k_4) or with a less efficient termination reaction (lower k_6).

Reaction 3, the conversion of the sulfate radical ion into a hydroxyl radical, need not be assumed in any of the present reactions. However, the inclusion of reaction 3 does not affect the kinetics of the decomposition reactions since hydroxyl radicals react efficiently with formic acid. In fact a point in favor of reaction 3 is that $G(\text{CO}_2)$ is lower in strong acid solutions than in weakly acid solutions. This result accords with the bisulfate inhibition of the photolytic decomposition of persulfuric acid observed by Tsao and Wilmarth.⁴

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY, PRINCETON, NEW JERSEY]

Microwave Absorption and Molecular Structure in Liquids. XXXVII. The Relaxation Times of Spherical Polar Molecules in Carbon Tetrachloride Solution^{1,2}

BY WORTH E. VAUGHAN,³ WILLIAM P. PURCELL⁴ AND CHARLES P. SMYTH

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Measurements of dielectric constant and loss of dilute solutions of five spherical polar molecules in carbon tetrachloride at temperatures between 20 and 60° have been carried out at various wave lengths between 1.25 and 50 cm. Measurements of dielectric constant alone were made at 577 m, and refractive indices were measured using the sodium d-line. Mutual viscosities were determined for seven polar solutes in carbon tetrachloride solution. The influence of solute size and rigidity on the relaxation times found is discussed. Dipole moments of two adamantane halides are reported.

In order to test the application of the Debye equation to a system where one would expect it to be valid, the dielectric behavior of solutions of spherical polar molecules in carbon tetrachloride was analyzed. Two approaches were considered. Since the macroscopic viscosities of the solutions are approximately equal at a given temperature, one might suppose that the internal friction coefficients as well would be independent of solute.⁵ In this case, at constant temperature, τ (the relaxation time) should vary as the molar volume from solute to solute. Alternatively, the internal friction factor could be replaced by the mutual viscosity η_m defined by Hill.⁶ If this is done, τ/η_m would be expected to vary as the molar volume.

Purification of Materials.—Carbon tetrachloride and the solutes were purified as shown in Table I. The substances investigated were obtained from (A) Matheson, Coleman and Bell, Inc., (B) Eastman Kodak Company, (C) Mr. Robert D. Nicholas, Princeton University. The authors express their appreciation to Mr. Nicholas for the preparation of adamantane bromide and adamantane chloride.

Experimental Results

The apparatus and various methods of measurement have been described previously.⁷⁻⁹ The slopes for dependence

(1) This research has been supported in part by the Office of Naval Research. Reproduction, translation, publication, use or disposal in whole or in part by or for the United States Government is permitted.

(2) This article represents a portion of the work submitted by Mr. W. E. Vaughan to the Graduate School of Princeton University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) National Science Foundation Fellow, 1957-1960.

(4) Allied Chemical Corporation Fellow, 1959-1960.

(5) C. P. Smyth, *Proc. Natl. Acad. Sci. U. S. A.*, **42**, 234 (1956).

(6) N. E. Hill, *Proc. Phys. Soc.*, **67B**, 149 (1954).

(7) H. L. Laquer and C. P. Smyth, *THIS JOURNAL*, **70**, 4097 (1948).

(8) W. M. Heston, Jr., A. D. Franklin, E. J. Hennelly and C. P. Smyth, *ibid.*, **72**, 3443 (1950).

(9) D. A. Pitt and C. P. Smyth, *J. Phys. Chem.*, **63**, 582 (1959).

TABLE I
PURIFICATION OF MATERIALS

Source	—B.p., °C.—		
	Obsd.	Lit.	
Carbon tetrachloride ^a	A	76.5	76.7 ^f
Fluorobenzene ^b	B	84	84.7 ^f
<i>t</i> -Amyl alcohol ^c	A	102	102.3 ^f
—M.p., °C.—			
<i>dl</i> -Camphor ^d	A	177	178.6 ^f
Adamantane chloride ^e	C	165	165 ^g
Adamantane bromide ^e	C	120	119-120 ^h

^a Fractionally distilled and stored over Drierite. ^b Dried over barium oxide and fractionally distilled. ^c Distilled and dried over anhydrous sodium sulfate. ^d Recrystallized from aqueous ethanol and sublimed. ^e Recrystallized from methanol at acetone-Dry Ice temperatures. ^f J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier Publishers, 1950. ^g H. Stetter, M. Schwarz and A. Hirschorn, *Chem. Ber.*, **92**, 1629 (1959). ^h S. Landa, S. Kriebel and E. Knoblock, *Chem. Listy*, **48**, 61 (1954).

of dielectric constants and losses upon mole fraction of solute are shown in Table II. The concentration range in mole fraction is given in parentheses for each set of solutions in Table II. Cole-Cole arc plots fit the data satisfactorily in every case.¹⁰ Values of a_∞ , the high frequency intercept, determined from the arc plot, α the distribution parameter, τ the relaxation time and V , the molar volume, are listed in Table III.

The percentage of monomer for solutions of *t*-amyl alcohol in carbon tetrachloride was determined in the concentration range 0.005 to 1 *M* at a temperature of 20°, using a Perkin-Elmer double beam infrared spectrophotometer with a lithium fluoride prism. The mole fraction equilibrium constant for dimer formation $K_x = \frac{X \text{ dimer}}{X^2 \text{ monomer}}$ was determined by the method of Liddel and Becker assuming a closed dimer.¹¹ Evidence for this assumption from nuclear magnetic resonance studies is given by Becker.¹² Smith and

(10) C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., New York, N. Y., 1955, p. 69.

(11) U. Liddel and E. D. Becker, *Spectrochim. Acta*, **10**, 70 (1958).

(12) E. Becker, U. Liddel and J. Shoolery, *J. Mol. Spec.*, **2**, 1 (1958).

TABLE II

SLOPES FOR DEPENDENCE OF DIELECTRIC CONSTANTS AND LOSSES OF CARBON TETRACHLORIDE SOLUTIONS UPON MOLE FRACTION OF SOLUTE

λ (cm.)	20°		40°		60°	
	a'	a''	a'	a''	a'	a''
<i>dl</i> -Camphor (0-0.05)						
57700	12.58		11.30		10.38	
50	12.56	0.51	11.50	0.40	10.35	0.33
25.0	12.50	1.30	11.46	0.93	10.28	0.66
10.0	12.10	2.73	11.24	2.07	10.04	1.50
3.22	8.52	6.08	8.39	4.87	8.32	3.86
1.253	3.24	5.35	3.55	5.10	3.87	4.72
Na D-line	0.00		0.00		0.00	
<i>t</i> -Amyl alcohol (0-0.03)						
57700	3.45		3.09		2.76	
10.0	3.38	0.20	2.95	0.30	2.73	0.12
3.22	3.10	.63	2.91	.49	2.63	.37
1.254	2.78	.98	2.56	.88	2.34	.74
Na D-line	-0.222		-0.224		-0.226	
Adamantane bromide (0-0.02)						
57700	8.89					
24.9	9.14	0.75				
10.0	8.05	2.65				
3.30	5.21	4.09				
1.20	1.64	1.81				
Na D-line	0.49					
Adamantane chloride (0-0.02)						
57700	8.25					
24.9	8.20	0.68				
10.0	7.42	1.97				
3.30	5.05	3.60				
1.20	1.84	2.02				
Na D-line	0.29					
Fluorobenzene (0-0.05)						
57700	2.77		2.42		2.19	
10.0	2.70	0.21	2.46	0.15	2.20	0.10
3.22	2.40	0.81	2.31	0.67	2.21	0.54
1.253	1.64	1.23	1.62	1.11	1.56	1.05
Na D-line	0.03		0.03		0.03	

Creitz favor an open dimer, with one hydroxyl group behaving as if it were not hydrogen-bonded.¹³ In this case the equilibrium constant obtained should be multiplied by two since two open dimers would then be indistinguishable from the closed dimer plus two monomers in the previous case as regards the infrared spectrum. Assuming a closed dimer the value obtained for *t*-amyl alcohol was $K_x = 5.9$. Solution concentrations for dielectric measurements were chosen so that a maximum of 0.5% alcohol would be present as dimer or polymer.

The dipole moments of adamantane bromide and adamantane chloride were measured at 20° with carbon tetrachloride as solvent. The Halverstadt-Kumler,¹⁴ Guggenheim¹⁵ and standard Debye methods were used to calculate the moments. The results are shown in Table IV, which indicates the method by appropriate initials and gives calculated values of the molar refraction R_D for the sodium D line, and the total induced polarization $P_E + A$ estimated from a_∞ , under P_∞ the total molar polarization at infinite dilution, and in the last two columns the moment values calculated from the polarization differences indicated.

(13) F. A. Smith and E. C. Creitz, *J. Research Natl. Bur. Standards*, **46**, No. 2, 145 (1951).

(14) I. F. Halverstadt and W. D. Kumler, *THIS JOURNAL*, **64**, 2988 (1942).

(15) E. A. Guggenheim, *Trans. Faraday Soc.*, **45**, 714 (1949).

TABLE III

RELAXATION TIMES AND OTHER QUANTITIES

t , °C.	a_∞	α	$\tau \times 10^{12}$ sec.	λ_a (cm.)	V (cc.)
Adamantane bromide					
20	1.08	0.00	19.1	3.60	156 ^a
Adamantane chloride					
20	1.11	0.00	15.9	3.00	152 ^a
Camphor					
20	0.05	0.03	11.0	2.07	153.1 ^b
40	.10	.05	8.6	1.63	154.6
60	.07	.04	7.0	1.32	156.1
Fluorobenzene					
20	0.03	0.07	5.3	1.00	93.9 ^c
40	.03	.05	4.8	0.91	96.3
60	.03	.01	4.4	0.83	99.2
<i>t</i> -Amyl alcohol					
20	0.44	0.16	2.97	0.56	109.0 ^c
40	.45	.11	2.67	.50	111.5
60	.46	.12	2.13	.40	114.1

^a Estimated from compounds of similar structure and known densities. ^b W. Klemm, W. Tilk and S. v. Müllenheim, *Z. anorg. allgem. Chem.*, **176**, 10 (1928). ^c J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier Publishers, 1950.

TABLE IV

DIPOLE MOMENTS ($\times 10^{18}$) OF ADAMANTANE CHLORIDE AND BROMIDE

	P_∞	Calculated from:	
		$(P_\infty - R_D)$	$(P_\infty - P_E + A)$
Chloride ($R_D = 46.7$, $P_E + A = 78.9$)			
D	177.8	2.51	2.18
H-K	177.5	2.51	2.18
G		2.53	
Bromide ($R_D = 49.6$, $P_E + A = 81.8$)			
D	183.7	2.54	2.21
H-K	188.8	2.59	2.27
G		2.59	

Discussion of Results

As shown by the data of Table III the distribution parameter α lies close to zero for all of these compounds except *t*-amyl alcohol, which can have both over-all molecular rotation and hydroxyl group rotation. If the relaxation times corresponding to the two processes are not very far apart, the result is an increase in α . The solutions measured were so dilute that, as indicated by the infrared absorption measurements, the concentration of associated molecules was too small to affect the dielectric measurements. Another factor which tends to increase the distribution for *t*-amyl alcohol is the possible rotation of the ethyl group which causes the molecule to assume different shapes with different relaxation times. The result is a distribution of relaxation times which shows up as a relatively large value for α . The adamantane halides show no distribution at all as would be expected in view of the nearly spherical shapes of these molecules. Fluorobenzene shows a slight distribution. It is ellipsoidal in shape, but its dipole moment lies along a molecular axis and, according to the Perrin theory,¹⁶ it should show one

(16) F. Perrin, *J. phys. radium*, **5**, 497 (1934).

relaxation time with no distribution. The small distribution commonly observed for such molecules presumably arises from variation of the internal friction coefficient according to the axis about which the molecule turns.

It is interesting to compare the values of a_∞ in Table III with a_D (the dielectric constant-mole fraction slope at the sodium D-line) in Table II. For camphor and fluorobenzene, these are close to one another, as one expects for rigid molecules whose atomic polarization should be small. That a_∞ is considerably larger than a_D for *t*-amyl alcohol is consistent with its non-rigidity, giving evidence of high frequency absorption by rotation of the hydroxyl group. It is surprising to note the large differences in these quantities for the adamantane halides which might be expected to have small atomic polarizations and for which no probable high frequency absorption mechanism can be postulated.

The adamantane halides and camphor have similar molar volumes but their relaxation times differ markedly. Furthermore, the relaxation time of fluorobenzene seems slightly small, considering its molar volume, relative to any of the first four compounds. In the series fluorobenzene, camphor, adamantane chloride, adamantane bromide, the molecular shape is that of an ellipsoid of rotation or approximately spherical shell with a protruding group, the protrusion of the group increasing from fluorobenzene to adamantane bromide. These protruding groups should affect the internal friction coefficients, while not having much effect on the molar volume. One might suppose that the internal friction coefficient increases with increasing protrusion of the polar group, which implies a corresponding increase in the relaxation time. A similar argument applies to the series fluorobenzene, chlorobenzene, bromobenzene, iodobenzene, nitrobenzene where the molar volumes increase slowly, but the relaxation times in carbon tetrachloride solution are 5.4(14°), 8.6(14°), 12.0(24°), 15.0(14°) and 15.2(20°), respectively.¹⁷ The small relaxation time shown by *t*-amyl alcohol would be expected if hydroxyl group rotation contributes appreciably, since the relaxation time of the hydroxyl group would be small.

In the absence of knowledge of the internal friction coefficient, it has been customary to examine the dependence of relaxation times upon the viscosity of the medium. For solutions, the mutual viscosity,⁶ which measures the solute-solvent viscous interaction, would seem to be a more reasonable quantity to employ.¹⁸ Although the use of mutual viscosity has not proved generally effective, values are given in Table V for the mutual viscosities η_m calculated by the Hill equation⁶ and the reduced relaxation times.

Another mutual viscosity η_m is the "properly averaged" mutual viscosity defined by

$$\eta_{12} = x_1^2\eta_1 + 2x_1x_2\eta_m + x_2^2\eta_2 \quad (1)$$

where η_{12} , η_1 and η_2 are the viscosities of solution, solvent and solute, respectively. This expression

(17) F. Buckley and A. A. Maryott, "Tables of Dielectric Dispersion Data for Pure Liquids and Dilute Solutions," NBS Circular 589 (1958).

(18) D. A. Pitt and C. P. Smyth, *THIS JOURNAL*, **81**, 783 (1959).

TABLE V

MUTUAL VISCOSITIES AND REDUCED RELAXATION TIMES				
Solute	t , °C.	η_m (cp.)	τ/η_m	τ/η_1
Carbon tetrachloride	20	0.970		
	40	.740		
	60	.586		
Camphor	20	2.16	5.1	11.3
	40	1.52	5.6	11.6
	60	1.13	6.2	11.9
Chlorobenzene	14	0.859	10.0	8.4
Fluorobenzene	20	.615	8.6	5.5
	40	.527	9.1	6.5
	60	.435	10.1	7.5
Pyridine	25	.797	9.8	8.6
<i>t</i> -Amyl alcohol	20	.696	4.3	3.1
	40	.529	5.0	3.6
	60	.416	5.1	3.6
<i>t</i> -Butyl chloride	20	.699	4.9	3.6
	40	.533	6.0	4.3
	60	.424	6.9	5.0
Chloroform	20	.508	9.8	5.2

is derived by considering a solution with x_1 mole-fraction of solvent and x_2 mole-fraction of solute. When a viscous interaction occurs between two molecules the probability that two solvent molecules are interacting is x_1^2 (giving a viscosity η_1), the probability that two solute molecules are interacting is x_2^2 (giving a viscosity η_2) and the probability that one solvent and one solute molecule are interacting is $2x_1x_2$ (giving the mutual viscosity η_m). The form of equation 1 is very similar to Hill's. In fact values of η_m calculated by both methods give essentially the same value. For example, for chlorobenzene in benzene, Hill's equation gives $\eta_m = 0.73$ while equation 1 gives $\eta_m = 0.72$. Similarly bromobenzene in benzene gives 0.90 and 0.89, respectively. Thus one might expect η_m to be a useful parameter apart from the theory of viscosity used by Hill in its derivation. Unfortunately, the use of η_m seems to offer no advantage over that of η_1 for the compounds studied.

Camphor, with the largest molar volume (see Table III) of the compounds in Table V has too small a value of τ/η_m , while τ/η_1 is consistent with the other compounds in the table. Chlorobenzene has slightly larger values of τ/η_m and τ/η_1 than fluorobenzene, as expected, but both are smaller than those for pyridine, which has a slightly smaller molecule. The values of τ/η_m and τ/η_1 for *t*-butyl chloride are small compared to chloroform. However, the more symmetrical molecule of *t*-butyl chloride might be expected to rotate more easily than that of chloroform, since it rotates in the solid state over a wide range of temperature, while the chloroform molecule does not.^{19,20} Since the values of τ calculated from the Debye equation are too large, replacing η_1 by η_m will lead to improved calculated values when $\eta_1 > \eta_m$ and worse when $\eta_m > \eta_1$. Thus improvement is obtained for all compounds studied except camphor. One should keep in mind, however, that the internal friction coefficient probably has a value considerably less than either the macroscopic or the mutual

(19) W. O. Baker and C. P. Smyth, *ibid.*, **61**, 2798 (1939).

(20) S. O. Morgan and H. H. Lowry, *J. Phys. Chem.*, **34**, 2385 (1930).

viscosity, which is one reason why calculated values of τ turn out too large when one uses η_l or η_m in the Debye equation.

The three different methods of calculating the dipole moment show excellent agreement for adamantane chloride and a small discrepancy between the Debye method and the other two for the bromide. The discrepancy is no larger than that frequently observed.¹⁴ The dipole moments of adamantane chloride and adamantane bromide calculated with the use of the refraction for the D-line are considerably larger than all of the values previously reported²¹ for alicyclic and ali-

phatic halides. When, however, values of the total induced polarization (electronic polarization + atomic polarization) estimated from a_∞ are used in the moment calculation, instead of the molar refraction for the sodium D line, the moment values obtained are close to those found for the branched-chain and cyclic chlorides and bromides, e.g., *t*-butyl chloride, 2.13; *t*-butyl bromide, 2.17; cyclopentyl bromide, 2.20; cyclohexyl chloride, 2.2; and cyclohexyl bromide, 2.2. These are slightly higher than the values found for the smaller chlorides and bromides, probably, because of inductive effects. The moment values for the two adamantane compounds are, therefore, what would be expected, but the reason for their high atomic polarization values is not apparent.

(21) C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., New York, N. Y., 1955, pp. 269, 274.

[CONTRIBUTION FROM THE RADIATION PHYSICS LABORATORY, ENGINEERING DEPT., E. I. DU PONT DE NEMOURS & COMPANY, WILMINGTON, DELAWARE]

Formation and Identification of Unique Radical Sites in Irradiated Amides

BY E. J. BURRELL, JR.

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The free radicals produced in each of ten N-substituted amides by irradiation with 2-Mev. electrons have been characterized by their e.p.r. spectra. A single species of radical is formed in each of nine of the amides. The $G(\text{radical})$ yield for N-(*n*-propyl)-propionamide is 4.7 ± 1.4 .

Introduction

Electron paramagnetic resonance (e.p.r.) spectroscopy can be a powerful tool in the characterization of free radical intermediates formed in radiation reactions. Because the concentration of these radicals is so low and their lifetimes so short, it has been necessary, in the first phase of such a characterization program, to accumulate the otherwise transient species in a frozen matrix. Although this accumulation of frozen free radicals gives rise to a strong e.p.r. signal, the observed e.p.r. spectrum may be influenced by the very matrix which stabilizes the radicals.¹

In some environments, however, the perturbation of the radical spectrum by the crystal lattice is small and the e.p.r. spectrum represents in a simple way the chemical structure of the radical. Ten members of the class of N-substituted amides, presented here, have e.p.r. spectra which characterize the radicals present. Three members of the class of quaternary ammonium halides previously discussed also show this behavior.² The e.p.r. spectrum of a single kind of radical formed in an irradiated solid has been observed in a number of other cases.³⁻⁶

Care must be taken that any anisotropic dipolar interaction of the unpaired electron be considered.⁷

(1) D. J. E. Ingram, "Free Radicals as Studied by Electron Spin Resonance," Academic Press, Inc., New York, N. Y., 1958, p. 117. See, however, H. Zeldes, G. T. Trammell, R. Livingston and R. W. Holmberg, *J. Chem. Phys.*, **32**, 618 (1960).

(2) E. J. Burrell, *J. Chem. Phys.*, **32**, 955 (1960).

(3) W. Gordy and C. G. McCormick, *THIS JOURNAL*, **78**, 3243 (1956); C. F. Luck and W. Gordy, *ibid.*, **78**, 3240 (1956).

(4) B. Smaller and M. S. Matheson, *J. Chem. Phys.*, **28**, 1169 (1958).

(5) R. H. Luebke and J. E. Willard, *THIS JOURNAL*, **81**, 761 (1959).

(6) R. G. Bennett, R. L. McCarthy, B. Nolin and J. Zimmerman, *J. Chem. Phys.*, **29**, 249 (1958).

It will be seen from the correlation of e.p.r. spectra with radical structure in examples reported here that anisotropic effects do not appear to interfere with the identification of the free radical structure.

Experimental

The N-substituted amides were synthesized for this study by members of the Carothers Laboratory, Textile Fibers Dept., E. I. du Pont de Nemours & Co. The fact that only one kind of radical is formed in nine of the amides is taken as a sufficient indication of purity. Two kinds of radicals appear in the other amide and probably represent two modes of decomposition rather than an impurity. Nuclear magnetic resonance analysis was used to confirm the molecular structure of each amide before irradiation.

Each amide was evacuated and sealed off at 10^{-5} mm. in a "Thermosil" (available from Thermal American Fused Quartz Co., Dover, New Jersey) quartz tube and irradiated at -80 or -195° with 2-Mev. electrons from the General Electric Resonant Transformer in this Laboratory. Neither color centers nor an e.p.r. signal was observed in the irradiated "Thermosil" quartz tube itself.

The e.p.r. spectra were obtained using a modified Varian V-4500 spectrometer.⁸ A quartz Dewar in the cylindrical e.p.r. cavity held the sample tube at -80° or -195° .

Computation of Predicted E.P.R. Spectra.—An I.B.M. 650 digital computer was programmed to compute the differential e.p.r. spectrum to be expected for a given model of the environment of the unpaired electron. The computer adjusted the hyperfine splitting and line-width parameters so as to give a least squares fit between the computed spectrum and the experimental spectrum. The computed e.p.r. spectra are shown in the figures with the corresponding experimental spectra. The detailed programming and computational techniques will appear shortly.

(7) H. M. McConnell, C. Heller, T. Cole and R. W. Fessenden, *THIS JOURNAL*, **82**, 766 (1960).

(8) R. G. Bennett, P. C. Hoell and R. P. Schwenker, *Rev. Sci. Instr.*, **29**, 659 (1958).