[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Microwave Absorption and Molecular Structure in Liquids. XV. The Critical Wave Lengths of Some Short-chain Aliphatic and Cyclic Ketones and of Phenyl Ether[1]

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The dielectric constants and losses of acetone, *n*-heptanone-2, *n*-heptanone-4, cyclohexanone, acetophenone, 2-acetonaphthone, benzophenone and phenyl ether have been measured at wave lengths of 1.24, 3.22 and 10.4 cm. at temperatures between 1 and 90°. The low frequency dielectric constants, refractive indices, densities and viscosities have also been measured. Cole and Cole arc plots have been drawn and used to calculate the critical wave lengths at which the loss is a maximum. The critical wave lengths and the ratios of critical wave length to viscosity are examined in their relations to molecular size and shape. The critical wave length of 2-acetonaphthone is larger and that of phenyl ether smaller than would be expected. As observed in previous work, marked changes in molecular shape may cause marked irregularities in the relations between molecular volume, critical wave length and viscosity.

This paper reports recent measurements carried out in extension of some investigations on ethers and ketones made some years ago and described in a recent paper[2] of this series. Acetone is measured as the first member of the ketone series. Although *n*-heptanone-2 was measured previously, repetition of the measurements, which are in satisfactory agreement with the results of the earlier work, make more exact a comparison between the unsymmetrical *n*-heptanone-2 and the symmetrical *n*-heptanone-4. Remeasurement of pure benzophenone gives better critical wave length values than those previously estimated from results at only two microwave frequencies. These and the values for the other cyclic ketones have been determined in the investigation of the dielectric relaxation of relatively rigid polar molecules. Phenyl ether has been measured because of the abnormally short relaxation time reported[3] for it in benzene solution.

Earlier papers[4,5] of this series have described the methods used in measuring the dielectric constants and losses of the liquids and in calculating the critical wave lengths from the results. The materials measured were obtained from the Brothers Chemical Co. or Matheson Coleman and Bell. Although the melting point of the benzophenone sample was 47.4°, 0.7–0.8° below the melting points of samples previously measured[2] in this Laboratory, the material appeared to be sufficiently pure to use without purification. The other materials were fractionally distilled or crystallized, usually after drying.

Experimental Results

The dielectric constants ϵ' and losses ϵ'' at the various wave lengths and temperatures used are given in Table I, together with the low frequency dielectric constant ϵ_0, measured on a bridge at 5 kc./sec., and a value for the dielectric constant at infinite frequency, ϵ_∞, calculated from measured refractive indices n_D by means of the equation

$$(\epsilon_\infty - 1)/(\epsilon_\infty + 2) = 1.05\,(n_D^2 - 1)/(n_D^2 + 2)$$

which includes an arbitrary increase of 5% in ϵ_∞ over n_D^2 to allow for atomic polarization. Table II shows the calculated values for the parameter α for the distribution of relaxation times, λ_m, the critical wave length, η, the viscosity, and the ratio, λ_m/η. The table also gives values of the dipole moment μ calculated from the values of ϵ_0 and ϵ_∞ by means of the Onsager equation.

TABLE I

DIELECTRIC CONSTANTS AND LOSSES

t, °C.		1.24 cm.		3.22 cm.		10.4 cm.		5 kc./sec.
	ϵ_∞	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ_0
				Acetone				
1	1.93	18.18	8.92	21.69	4.39	22.95	1.73	23.29
20	1.90	17.75	7.78	20.51	3.55	21.07	1.32	21.20
40	1.87	16.72	6.15	18.38	2.63	19.29	1.02	19.29
				n-Heptanone-2				
1	2.08	4.58	3.86	7.76	4.42	12.00	2.7	13.01
20	2.05	5.03	4.12	8.74	4.15	11.22	2.2	11.98
40	2.03	5.67	4.07	8.93	3.40	10.44	(0.90)	11.02
60	2.00	6.3	3.82	9.00	2.56	9.84	0.91	10.18
				n-Heptanone-4				
1	2.07	4.31	3.9	7.91	5.10	(11.43)	(3.62)	13.82
20	2.05	4.83	4.3	8.58	4.61	12.00	2.2	12.67
40	2.02	5.54	4.07	9.25	3.67	11.06	1.6	11.61
60	2.00	6.05	3.75	9.00	2.91	(9.82)	(0.92)	10.71
				Cyclohexanone				
1	2.21	5.55	5.06	10.76	6.39	...	..	17.01
20	2.18	6.84	5.28	11.67	5.72	...	..	16.00
40	2.15	7.33	5.26	11.92	4.65	14.1	2.1	14.99
60	2.13	7.94	5.16	11.81	3.65	13.4	2.0	13.99
				Acetophenone				
20	2.45	3.63	2.2	5.62	3.5	(12.8)	(6.1)	18.66
40	2.42	4.11	2.8	6.67	4.2	13.0	5.0	17.77
60	2.39	4.35	3.3	7.66	4.4	13.0	3.9	16.88
				Acetonaphthone-2				
60	2.65	3.43	0.60	3.65	1.16	4.73	2.49	13.03
70	2.63	3.42	.68	3.65	1.36	5.24	2.83	12.49
80	2.61	3.47	.78	3.83	1.57	5.63	3.29	12.15
90	2.59	3.47	.87	3.88	1.71	...	..	12.01
				Benzophenone				
60	2.64	3.37	0.95	3.82	1.91	6.21	3.92	10.91
70	2.63	3.38	1.10	3.91	2.10	6.96	3.86	10.54
80	2.61	3.38	1.22	4.24	2.33	7.51	3.56	10.23
90	2.60	3.39	1.33	4.44	2.52	...	..	9.99
				Phenyl ether				
40	2.57	3.17	0.397	3.43	0.295	3.56	0.123	3.61
60	2.54	3.18	.360	3.39	.222	3.46	.085	3.47
80	2.51	3.19	.312	3.31	.162	3.35	.061	3.35

Discussion of Results

The values of the dipole moment μ in Table II calculated by means of the Onsager equation show,

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[1] This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command under Contract No. AF18(600)1331. Reproduction, translation, publication, use or disposal in whole or in part by or for the United States Government is permitted.

[2] G. B. Rathmann, A. J. Curtis, P. L. McGeer and C. P. Smyth, *J. Chem. Phys.*, **24**, in press (1956).

[3] E. Fischer, *Z. Elektrochem.*, **53**, 16 (1949).

[4] W. M. Heston, Jr., E. J. Hennelly and C. P. Smyth, THIS JOURNAL, **70**, 4093 (1948).

[5] H. L. Laquer and C. P. Smyth, *ibid.*, **70**, 4097 (1948).

TABLE II

DISTRIBUTION COEFFICIENTS, CRITICAL WAVE LENGTHS, VISCOSITIES, RATIOS OF CRITICAL WAVE LENGTH AND VISCOSITY AND DIPOLE MOMENTS

t, °C.	α	λ_m, cm.	η	λ_m/η	$\mu \times 10^{18}$
		Acetone			
1	0.03	0.75	0.397	1.9	3.04
20	0	.63	.325	1.9	3.06
40	0	.52	.268	1.9	3.08
		n-Heptanone-2			
1	0.12	2.88	1.10	2.6	2.96
20	.07	2.04	0.807	2.5	2.97
40	.06	1.55	.624	2.5	2.99
60	.05	1.15	.500	2.3	3.00
		n-Heptanone-4			
1	0.09	3.26	0.98	3.3	3.06
20	.07	2.35	.736	3.2	3.07
40	.08	1.67	.571	2.9	3.08
60	.10	1.35	.460	2.9	3.09
		Cyclohexanone			
1	0.11	2.71	3.49	0.78	2.86
20	.11	1.95	2.25	.87	2.90
40	.11	1.55	1.55	.99	2.94
60	.10	1.23	1.12	1.1	2.97
		Acetophenone			
20	0.28	7.4	1.87	4.0	3.13
40	.25	6.0	1.31	4.6	3.20
60	.23	4.8	0.98	4.9	3.25
		2-Acetonaphthone			
60	0.09	31	4.13	7.5	3.03
70	.05	23	3.05	7.4	3.02
80	.07	19	2.45	7.7	3.04
90	.11	17	2.01	8.7	3.08
		Benzophenone			
60	0.04	13	4.19	3.0	2.83
70	.03	10	3.23	3.2	2.83
80	.04	8.3	2.62	3.2	2.83
90	.06	7.0	2.17	3.2	2.86
		Phenyl ether			
40	0.12	1.11	2.60	0.43	1.06
60	.08	0.84	1.78	.47	1.05
80	.05	0.68	1.31	.52	1.05

in general, about the same agreement with values obtained from vapor or solution measurements which is usually observed.[6] The small apparent increase with rising temperature is also usual.[7] Obviously, small differences in apparent moment between different molecules should have no structural significance attached to them. The very approximate values of the distribution parameter α are of the expected magnitude for the first five liquids in Table II, but appear rather small for molecules of such large size and irregular shape as those of the last three substances in the table.

In many of the previous papers of this series the Debye equation for the relaxation time of a liquid, $\tau = 4\pi\eta a^3/kT$, has been critically examined or used as a basis for discussion. Most of the molecules discussed in the present paper depart so much from spherical form that the radius a would seem to have no exact significance in their treatment. Since $\tau = \lambda_m/6\pi \times 10^{10}$, the ratio λ_m/η provides a rough basis for discussion of these molecules. Although, according to the above relationship, this ratio should decrease as the absolute temperature T increases, this is not generally the case for the values in Table II, where constancy is shown by acetone, a decrease by the two heptanones, and an increase by the other five liquids.

The molecule of acetone is somewhat similar in form to that of isopropyl bromide, the larger and more polarizable CH_2Br group in the latter replacing the CO in the former. The ratio of the critical wave length[8] 1.26 cm. at 1° to the viscosity[9] 0.597 centipoise of isopropyl bromide is 2.1, slightly larger than the ratio 1.9 for acetone in Table II as it should be.

The critical wave length values of *n*-heptanone-2 are lower than those found at the same temperatures in the previous measurements[2] by no more than the sum of the probable errors of the two sets of measurements. The slightly higher values found for *n*-heptanone-4 suggest the possibility that the location of the dipole at the center of the carbon chain makes segment orientation more difficult than it is when the dipole is near the end of the chain as in *n*-heptanone-2. However, it was concluded[10] that measurements on esters gave "no evidence of increase or decrease resulting from moving the molecular dipole from a location near the end of the molecule to one near the middle, although a small effect may well be obscured by the experimental errors." The values of the ratios for the heptanones are larger than those for acetone, but much less than the 2 to 1 relationship which might be predicted from the 137 cc. molar volumes of the heptanones at 1° as compared to 71.5 cc. for acetone. This may be due to a considerable amount of orientation of the heptanone molecules by rotation as extended rods around their long axes, as well as to a certain amount of segment orientation.

Cyclohexanone has a somewhat smaller molar volume, 101 cc. at 1°, than do the heptanones, a critical wave length of the same magnitude, and a viscosity about three times as large. The ratio of critical wave length to viscosity is, consequently, much smaller than those for the heptanones, indicating that the molecular rotation necessary for dipole orientation occurs much more readily than the combined rotational and translational motion involved in viscous flow. In dilute benzene solution, the measured[11] relaxation time corresponds to a critical wave length of 1.98 cm. and a ratio of critical wave length to viscosity of 3.0. The molecular model of cyclohexanone shows that the carbonyl oxygen does not protrude far beyond the hydrogens to cause much hindrance of rotation of

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[6] C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., Inc., New York, N. Y., 1955, pp. 290, 314.

[7] *Cf.* C. P. Smyth, ref. 6, p. 33.

[8] E. J. Hennelly, W. M. Heston, Jr., and C. P. Smyth, THIS JOURNAL, **70**, 4102 (1948).

[9] W. M. Heston, Jr., E. J. Hennelly and C. P. Smyth, *ibid.*, **72**, 2071 (1950).

[10] P. L. McGeer, A. J. Curtis, G. B. Rathmann and C. P. Smyth, *ibid.*, **74**, 3541 (1952).

[11] F. J. Cripwell and G. B. B. M. Sutherland, *Trans. Faraday Soc.*, **42A**, 149 (1946).

the fairly symmetrical structure. Similarly, cyclohexyl bromide has critical wave length values only 20 to 35% larger than those of *n*-hexyl bromide,[8] although its viscosity is more than twice as large.[9] A similar trend is evident in the four isomeric butyl bromides, which show an increase in viscosity[9] and a decrease in critical wave length[9] as the molecule changes from more or less linear to nearly spherical in form.

Although the molar volume of acetophenone, 117 cc. at 20°, is not much larger than that of cyclohexanone, 103 at 20°, and the viscosity is somewhat lower, the critical wave length and its ratio to viscosity are much larger. The greater difficulty of dipole orientation thus indicated may be attributed to the considerable protrusion of the CH_3CO group from the ring. In comparison with acetophenone, the critical wave length of 2-acetonaphthone is unexpectedly high, although the large naphthyl group should increase both critical wave length and viscosity. The molar volume of 2-acetonaphthone is about 30% higher, while the ratios of the critical wave length to the viscosity are almost twice as large. For 1-chloronaphthalene which is somewhat similar in shape and slightly smaller, the critical wave length[8] to viscosity[9] ratio is 3.7 at 1° and 3.3 at 55°. The molar volume of benzophenone, 170 cc. at 60°, is slightly larger than that of 2-acetonaphthone, 158, and the viscosity is nearly the same, but the critical wave length and its ratio to viscosity are much smaller, although they might be expected to be about the same. The ratio of the critical wave length to the viscosity is smaller for benzophenone than for acetophenone in spite of the larger size of the molecule. It would appear that, among these ketones, the behavior of 2-acetonaphthone is distinctly anomalous. It is evident that, as frequently observed before, marked changes in molecular shape cause marked irregularities in the relations between molecular volume, critical wave length and viscosity, but the relationships observed are consistent in order of magnitude.

The critical wave lengths found for phenyl ether are consistent with the value 0.53 cm. calculated from Fischer's relaxation time[3] determined by a thermal method in dilute benzene solution at 23°, which gives 0.85 for the ratio of critical wave length to viscosity. The phenyl ether molecule is very similar in size and shape to that of benzophenone, the molar volumes being 164 and 170 cc., respectively, at 60°. It is, therefore, surprising to find the critical wave lengths of phenyl ether only about one tenth and the ratios of critical wave length to viscosity only about one seventh of those for benzophenone. Fischer suggested that the low value for phenyl ether might be due to orientation by internal motion of the molecule, in particular, of the oxygen atom, which might occur in the other ethers as well. There appears, however, to be nothing markedly anomalous in the critical wave lengths found for ethyl ether,[2] 0.45 cm. at 20°, 0.90 cm. for butyl ether in dilute benzene solution,[3] and 6.5 cm. for decyl ether.[2] Also the values of the critical wave length to viscosity ratio are, for the pure liquid, half as large as those of cyclohexanone and, for the benzene solution, about the same size. Interpretation of the results for phenyl ether must wait upon the results of other measurements upon related substances.

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Reactions of Nitrate Esters. IV. Kinetics of Hydrazinolysis[1]

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In homogeneous systems, both the S_{NC} and S_{NX} type reactions of nitrate esters with hydrazine are first order with respect to the esters. The former is also first order in hydrazine, and solvent effects point to molecular hydrazine as the reactive nucleophile. The rate data for reduction (S_{NX}) indicate an apparently high order dependence on hydrazine concentration. Solvent effects suggest that $N_2H_3^-$ may be involved in the rate-determining step. Activation energies have been calculated for both processes. A heterogeneous reduction gives apparent zero-order kinetics, and there is evidence that diffusion of one reactant into the other is the rate-controlling process.

The hydrazinolysis of primary and secondary nitrate esters has been shown[2] to involve two major processes. Concentrated hydrazine solutions mainly effect a reduction of alkyl nitrates, *via* an initial displacement at nitrogen[3] (S_{NX} process),[4] resulting in the formation of nitrite ion, nitrogen, nitrous oxide, ammonia, hydrazoic acid and the alcohol corresponding to the ester. A displacement on carbon (S_{NC}),[4] yielding nitrate ion and substituted hydrazines, occurs to an increasing extent as more dilute hydrazine solutions are used. Aralkyl nitrates undergo this latter process predominantly in both concentrated and dilute hydrazine.[2]

A kinetic study of the two processes has been carried out in an attempt to ascertain whether differences in mechanism, other than the locus of attack, exist.

With alkyl nitrates, considerable reduction always occurs, even in dilute hydrazine solutions, and it has not been possible to isolate the S_{NC} reaction of these esters. With benzyl nitrate, on the other hand, the S_{NC} reaction occurs to the extent of more

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[1] Presented before the 128th National Meeting of the American Chemical Society, Minneapolis, Minn., September 1955.

[2] R. T. Merrow and R. W. Van Dolah, THIS JOURNAL, **76**, 4522 (1954).

[3] R. T. Merrow and R. W. Van Dolah, *ibid.*, **77**, 756 (1955).

[4] M. Anbar, I. Dostrovsky, D. Samuel and A. D. Yoffe, *J. Chem. Soc.*, 3603 (1954). The symbol S_{NC} is used to denote nucleophilic attack on the α-carbon atom of the alkyl group, and S_{NX} for nucleophilic attack on the central atom X of the oxy-acid (*e.g.*, X = N in nitrate or nitrite esters).