[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Microwave Absorption and Molecular Structure in Liquids. XXVIII. The Dielectric Relaxation of Some Rigid Molecules in Viscous Solutions[1,2]

BY OTTO F. KALMAN AND CHARLES P. SMYTH

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The dielectric constants and losses at wave lengths of 1.25, 3.22, 10, 25 and 50 cm., and 300 m. have been measured for *d,l*-camphor, isoquinoline and 4-bromobiphenyl in solution in a viscous oil, and for acridine in the oil and in decalin at 20, 40 and 60°. The Cole–Cole arc plots have been used to calculate the most probable dielectric relaxation times for the solutions and their distribution parameters. The effect of viscosity on relaxation time increases from the slight viscosity dependence for the nearly spherical camphor molecule to a considerable dependence for the elongated molecules. Over this same range of molecular shape the activation energy for dielectric relaxation increases from a small value for the nearly spherical molecule to a value close to that for viscous flow for the elongated molecules. Where there is a possibility of more than one relaxation time for a molecule, the highly viscous solvent tends to increase the separation or distribution of the times.

Dielectric measurements have been carried out in the past upon solutions of polar molecules in solvents of different viscosities in order to investigate the relation between viscosity and dielectric relaxation time.[3] The measurements reported in the present paper have been carried out, in part, to extend our knowledge of this relationship by studying large solute molecules of known size, shape and dipole location in a very viscous solvent. The use of such a solvent in conjunction with large solute molecules tends to lower the frequencies of the dispersion region, thus making it possible to observe directly the region in which the dielectric constant values may be near that of the optical dielectric constant.

The ideal viscous solvent for purposes of study would be a pure compound composed of large rigid molecules, but, unfortunately, such a compound would be solid at the temperatures convenient for measurements and would probably decompose at higher temperatures. The viscous mixture of hydrocarbons sold under the trade name Nujol has been found convenient for use as a solvent. According to a private communication from the manufacturer, the samples employed in these measurements contained about 35% cycloparaffins. The estimated molecular weight based on empirical correlation diagrams[4,5] was 440. This is, at best, a rough average figure. The effective molecular weight probably is lowered by the motion of segments within the molecule.

Experimental Methods

The apparatus and the various methods of measurement have been described in previous papers.[6,7]

Purification of Materials.—*d,l*-Camphor, obtained from Matheson, Coleman and Bell Co., was crystallized from alcohol-water solution by W. E. Vaughan.

4-Bromobiphenyl, obtained from Brothers Chemical Co. was crystallized twice from absolute ethyl alcohol solution and dried under vacuum in an Abderhalden pistol. It formed white flaky crystals of m.p. 88.9–89.2°; lit.[8] m.p. 89–90°.

Isoquinoline, obtained from Eastman Kodak Co., was refluxed over barium oxide for several days and then fractionally distilled under vacuum; n_D (25.1°) 1.62239; lit.[9] 1.62233.

Acridine, obtained from Fisher Scientific Co., was crystallized from *n*-heptane solution and then from ethanol-water solution. It formed large rhombic crystals; m.p. 110.5–111.3°; lit.[10,11] 110–111°.

Nujol from Plough, Inc., was treated as previously described.[12]

Decalin, a mixture of *cis–trans* isomers, obtained from the Matheson, Coleman and Bell Co., Inc., was shaken with several portions of hot concentrated sulfuric acid, thoroughly washed with water and dried with Drierite and with calcium hydride. It was fractionally distilled; b.p. 191–192.8°; lit.[13] b.p. 191.7°.

Experimental Results

The experimental results were treated in the manner previously described,[6,7] except that the values of the dielectric constant ϵ', the loss ϵ'' and the square of the refractive index for the sodium-D line were plotted against the weight fraction of solute in the solution, instead of the mole fraction, because of the assortment of molecular weights in the solvent. The slopes of the straight lines thus obtained, a', corresponding to ϵ', and a'', corresponding to ϵ'', were plotted in Cole–Cole arcs[14] in the usual fashion[6,7] to obtain the critical wave lengths λ_m, the corresponding relaxation times τ, the distribution coefficients α and the arc intercepts at infinite frequency a_∞. The values of these quantities are given in Tables I and II. The concentration range in weight fraction is given in parentheses for each set of solutions in Table I. Table III gives the so-called static dielectric constants, measured at 300 meters, the viscosities, and the densities of the solvents. Two lots of Nujol, designated I and II, showed slight differences in values, too small to affect the values of the relaxation times.

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(2) This paper represents part of the work submitted by O. F. Kalman to the Graduate School of Princeton University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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TABLE I

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

Wave length, (cm.)	20°		40°		60°	
	a'	a''	a'	a''	a'	a''
	d,l-Camphor–Nujol (I) (0–0.0532)					
1.25	1.28	1.88	1.79	1.89	2.41	2.17
3.22	2.97	2.41	3.50	2.24	3.76	2.07
10	5.74	1.49	5.54	1.13	5.15	0.802
25	6.22	0.887	5.79	0.560	5.32	0.362
50	6.31	0.460	5.80	0.316	5.32	0.199
300 m.	6.28		5.76		5.33	
	4-Bromobiphenyl–Nujol (I) (0–0.0268)					
10	0.377	0.023	0.413	0.084	0.435	0.077
25	.392	.074	.439	.148	.502	.282
50	.436	.135	.555	.315	.790	.427
300 m.	1.51		1.41		1.31	
	Isoquinoline–Nujol (I) (0–0.0570)					
1.25	1.18	0.967	1.21	1.13	1.31	1.25
3.22	1.44	1.10	1.79	1.27	2.12	1.39
10	3.28	1.46	3.80	1.31	3.94	1.03
25	4.65	1.41	4.56	0.898	4.27	0.574
50	5.06	0.892	4.74	0.513	4.29	0.297
300 m.	5.60		4.83		4.38	
	Acridine–Nujol (II) (0–0.0223)					
3.22	0.698	0.121	0.735	0.21	0.790	0.284
10	.804	.160	0.963	.305	1.07	.456
25	.996	.337	1.305	.540	1.77	.613
50	1.17	.384	1.75	.525	2.11	.465
300 m.	2.79		2.59		2.38	
	Acridine–Decalin (0–0.0196)					
1.25	0.885	0.315	0.90	0.377	0.905	0.440
3.22	0.980	0.595	1.04	.734	1.18	.818
10	1.69	1.04	1.94	.909	2.14	.628
25	2.56	0.708	2.51	.432	2.34	.270
50	2.70	0.456	2.61	.282	2.38	.179
300 m.	2.86		2.60		2.46	

Discussion of Results

Contrary to the custom in the more recent papers of this series the Cole–Cole arc plots for each set of solutions are reproduced, because the points are so well distributed over the arc or so well grouped at one end as to establish the arcs as good representations of the data. For these data, therefore, the arc plot is a convenient, but not necessarily the only method of representing the distribution of relaxation times. The high frequency intercepts a_∞ of the arcs with the abscissa axis, corresponding to the optical dielectric constant, appear to be unusually accurate because of the favorable distribution of points along the curves, and their small separations from the points for a_D on the abscissa axis give further indication of this accuracy. Use of these points and densities measured for the two systems makes possible the calculation of the excess of the atomic polarization over that contained in the molar refraction for the sodium-D line. The values thus obtained, 2 cc. for 4-bromobiphenyl and 3.5 cc. for acridine, may be roughly corrected to total atomic polarization values, 4 cc. for 4-bromobiphenyl and 5–6 cc. for acridine, reasonable values for such molecules.

TABLE II

SLOPES FOR THE DEPENDENCE OF SQUARE OF REFRACTIVE INDEX a_D ON WEIGHT FRACTION, WITH INFINITE FREQUENCY INTERCEPTS a_∞, CRITICAL WAVE LENGTHS λ_m, RELAXATION TIMES τ AND DISTRIBUTION PARAMETERS α

t °C.	a_D	a_∞	λ_m(cm.)	τ(10^{-12}cm.)	α
	d,l-Camphor–Nujol (I)				
20	...	0.5	3.29	17.5	0.10
40	...	.5	2.41	12.8	.10
60	...	.5	1.75	9.3	.064
	4-Bromobiphenyl–Nujol (I)				
20	0.304	0.383	490	2580	0.082
40	.300	.400	150	797	.064
60	.266	.400	66	350	.031
	Isoquinoline–Nujol (I)				
20	0.316	0.44	8.78	46.5	0.30
40	.307	.50	4.73	25.1	.21
60	.300	.55	3.14	16.7	.16
	Acridine–Nujol (II)				
20	0.541	0.65	226	1200	0.402
40	0.578	.67	43	230	.308
60	...	.70	20	106	.152
	Acridine–Decalin				
20	0.583	0.80	10.5	55.5	0
40	0.552	.76	6.79	36.0	0
60	...	.73	4.84	25.7	0

TABLE III

STATIC DIELECTRIC CONSTANTS, VISCOSITIES AND DENSITIES OF SOLVENTS

t, °C.	ϵ_0	η (c.p.s.)	d(g./cm.^{3})
	Nujol (I)		
20	2.1999	211.0	0.8802
40	2.1585	61.1	.8662
60	2.1376	24.1	.8498
	Nujol (II)		
20	2.1815	210	0.8803
40	2.1603	60.4	.8675
60	2.1387	23.8	.8552
	Decalin		
20	2.1852	2.61	0.8874
40	2.1593	1.78	.8723
60	2.1328	1.31	.8576

In the arc plots for the isoquinoline–Nujol solutions, the 25 cm. point at 20° is considerably above the arc and that at 40° somewhat above. Deviations of this magnitude are usually attributable to exceptionally large experimental errors, but the wide distribution of the points for this system over the dispersion region makes possible the construction of Debye curves for a'' against the logarithm of the wave length, which indicate two maxima at 20°, merging to one wide maximum at 60°. These two maxima could be pictured as arising from dipole orientation by molecular rotation around the two short axes of the molecule, on the one hand, and around the one long axis on the other. However, the differences between the corresponding relaxation times are greater than would be expected according to the Perrin theory (see ref. 19) from the axial ratios of the molecules, which lead to the small differences in the two calculated values in

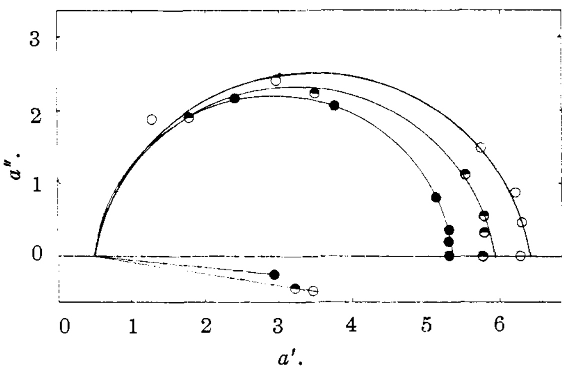

Fig. 1.—Arc plots of solutions of camphor in Nujol; ○, values at 20°; ◓, values at 40°; ●, values at 60°.

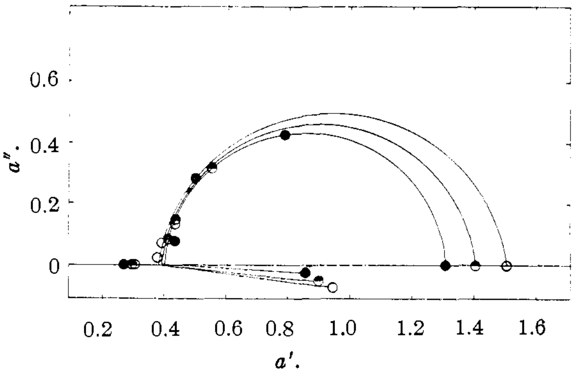

Fig. 2.—Arc plots for solutions of 4-bromobiphenyl in Nujol: ○, values at 20°; ◓, values at 40°; ●, values at 60°.

Table IV. Consequently, before further discussion, it seems better to seek confirmation of these results by measurements on other molecules of similar shape and dipole orientation.

The extent of the distribution of relaxation times is given empirically by the depression of the center of the semicircular plot as measured by $\alpha\pi/2$, the angle between the abscissa axis and the radius drawn to the center point from the a_∞ point. The accompanying figures and the values of α in Table II show that the distribution is small for the nearly spherical camphor molecule, for which the effect of viscosity on the relaxation time is small, and for 4-bromobiphenyl, for which the effect of viscosity is large. The dipole of this latter molecule lies in the long axis and its rotation around either of the two short axes should have about the same relaxation time as around the other. Only one relaxation should, therefore, be observed for this molecule. A similar absence of distribution of relaxation times has been observed by Mr. B. B. Howard for the molecule in heptane and in hexadecane solutions. The considerable distribution indicated for isoquinoline already has been shown to be representable in terms of the effects of the components of the molecular dipole along two molecular axes. The very large distribution indicated for acridine in Nujol is in sharp contrast to the small distribution for 4-bromobiphenyl and to the predictions of the Perrin theory, which requires only one relaxation time for both molecules because the molecular dipole lies in an axis of symmetry in each molecule. For acridine in decalin solution, the predicted absence of distribution is realized. Acridine has its molecular dipole in a short axis of the molecule, so that dipole orientation could occur by molecular rotation around a short axis or a long axis. It appears that the variable viscous molecular environment provided by Nujol enhances the effect of these differences and causes distribution.

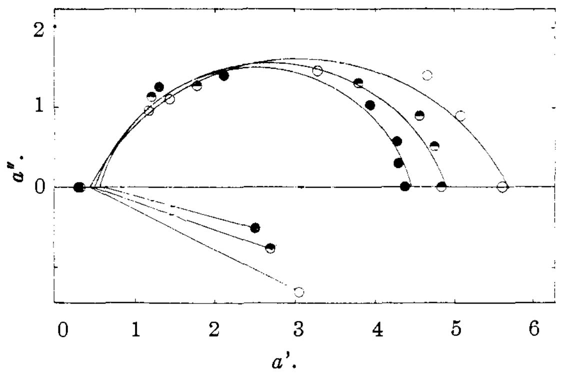

Fig. 3.—Arc plots for solutions of isoquinoline in Nujol: ○, values at 20°; ◓, values at 40°; ●, values at 60°.

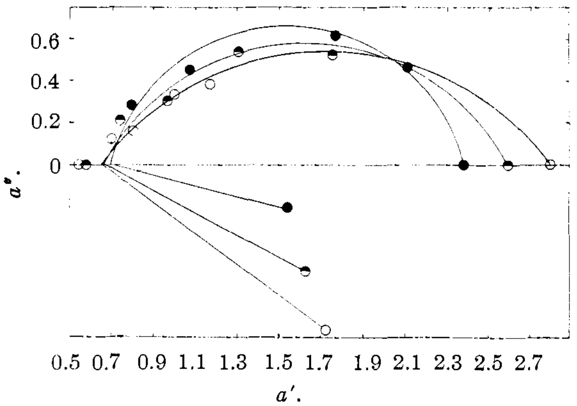

Fig. 4.—Arc plots for solutions of acridine in Nujol: ○, values at 20°; ◓, values at 40°; ●, values at 60°.

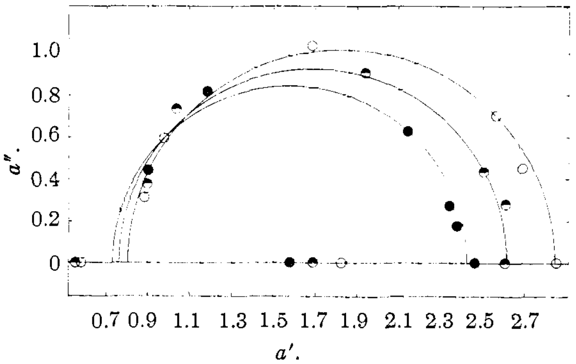

Fig. 5.—Arc plots for solutions of acridine in decalin: ○, values at 20°; ◓, values at 40°; ●, values at 60°.

It must be remembered that the Debye theory is based on the assumption that the dipolar molecule is a sphere surrounded by a uniform homogeneous fluid, an assumption made more realistic by Perrin by the treatment of the dipolar molecules as an ellipsoid. The large and considerably assorted molecules of Nujol provide a very different environment from the assumed. In the results of Table II, as has been generally observed, increase of temperature decreases the distribution, presumably, by increasing the microscopic uniformity of the liquid.

The relaxation times of camphor in solution in several different solvents having viscosities from 0.37 to 0.97 centipoise have been found[15] to range from 5.8 to 10.7×10^{-12} sec. at 20°, not paralleling the viscosities. The camphor molecule is somewhat spherical in shape, showing rotational freedom over a wide range of temperature in the crystalline solid.[16,17] The relaxation time 17.5 in Nujol solution at 20° (Table II) is only slightly larger, although the viscosity of Nujol is 211 c.p.s. at 20° and those of the Nujol solutions measured range down from this value only to 188 c.p.s. This is in accordance with many previous observations[3] that nearly spherical molecules can rotate with little dependence on the viscosity of the medium. The long molecule of 4-bromobiphenyl shows a relaxation time 148 times that of camphor at 20° because the orientation of its dipole by rotation involves the extensive displacement of neighboring molecules with consequent dependence on the viscosity of the liquid. The relaxation time decreases from 20 to 60° to 0.136 of its value, while the viscosity of the solvent decreases to 0.114 of this value over the same temperature range. The relaxation times of isoquinoline and camphor, which are much less dependent on viscosity, change much less with temperature. Acridine with its dipole in a short axis of a somewhat long molecule has a viscosity-dependent relaxation time, which decreases with rising temperature slightly more rapidly than the viscosity, both in Nujol and in decalin.

The effects of viscosity and molecular dimensions may be examined in terms of the equation of Fischer[18]

$$\tau = 4\pi\eta abcf/kT$$

where a, b and c are the semi-axes of an ellipsoidal molecule, η is taken, for purposes of the examination, as the macroscopic viscosity and f is a friction factor due to the geometry of the ellipsoid. The molecular dimensions have been obtained by measurements on Stuart–Briegleb models and used to calculate the axial ratios, from which the values of f are obtained by means of the tabulations of Budo, Fischer and Miyamoto.[19] The results are given in Table IV as the ratios of the calculated relaxation times to the experimentally observed values in Table II. For isoquinoline and α-chloronaphthalene, the equation gives two relaxation times, as shown.

As would be expected from previous observations,[3] the ratios are absurdly high for the nearly spherical molecules in the most viscous solvent and decrease to values only a little too high with increasing departure of the solute molecules from spherical shape and decreasing solvent viscosity. The tremendous discrepancies between theory and fact arise largely from the use of the macroscopic viscosity in the calculation instead of the unknown microscopic viscosity.[3]

TABLE IV

RATIOS OF CALCULATED AND EXPERIMENTAL RELAXATION TIMES

Nearly spherical molecules	20°	40°	60°
Nujol Solutions			
t-Butyl chloride	3870	1590	....
2,2-Dichloropropane	3020	1250	573
1,1,1-Trichloroethane	2330	950	421
Camphor	2110	782	394
Non-spherical molecules			
Isoquinoline	476	239	134
	418	210	117
α-Chloronaphthalene	188	100	55.3
	136	72.6	40
Elongated molecules			
Acridine	23.1	32.4	26.1
4-Bromobiphenyl	19.5	17.8	14.5
Heptane Solutions			
t-Butyl chloride	25	19	....
2,2-Dichloropropane	15.6	12.5	13.0
1,1,1-Trichloroethane	16.6	14.1	13.0
Camphor	10.5	9.9	8.9
α-Chloronaphthalene	4.4	3.9	3.8
Acridine (decalin)	6.2	6.1	5.9
4-Bromobiphenyl	2.09	1.97	1.84

Application of the concept of mutual viscosity[20] to the Nujol solutions shows its inadequacy for these data, which give too low and sometimes negative values for the mutual viscosity.[21] Meakins[22] concluded from measurements on a few molecules in different solvents that, when the solute molecule was at least three times as large as the solvent molecule, the solutions gave good agreement with Debye's simple equation, taking no account of molecular shape and using the macroscopic viscosity. This would be equivalent to using $f = 1$ and $a = b = c$ in Fischer's equation. Pitt and Smyth[7] found that a large flat porphyrazine molecule with its dipole in the long radius gave a relaxation time in benzene solution in rough agreement with that calculated by the simple Debye equation, while a similar molecule with dipole in the short axis gave a relaxation time considerably longer than that calculated by the Debye equation. These results indicate that the macroscopic viscosity has little meaning in the calculation of the absolute value of the relaxation time of a polar molecule unless it is surrounded by considerably smaller molecules. There is, however, a considerable parallelism between the magnitudes of the relaxation time and the viscosity in pure liquids.[3]

The free energies $\Delta F_\epsilon^{\ddagger}$, heats $\Delta H_\epsilon^{\ddagger}$ and entropies $\Delta S_\epsilon^{\ddagger}$ of activation for dielectric relaxation and the heat of activation ΔH_v for viscous flow,[23] calculated in the usual manner,[24] are given in Table V.

The increase in the $\Delta S_\epsilon^{\ddagger}$ values from the spherically shaped molecules toward the more elongated ones can be interpreted as due to increase in the

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TABLE V

ACTIVATION ENERGIES AND ENTROPIES IN NUJOL SOLUTIONS

Solute	$\Delta F_\epsilon^\ddagger$	$\Delta H_\epsilon^\ddagger$	$\Delta S_\epsilon^\ddagger$	ΔH_η	n
2,2-Dichloropropane[25]	1.77	1.60	−0.6	9.54	0.17
2,2-Dinitropropane[25]	2.20	1.99	−0.7	9.54	.20
d,l-Camphor	2.77	2.42	−1.2	10.5	.23
α-Chloronaphthalene[12]	3.50	3.63	0.5	9.54	.38
Isoquinoline	3.52	4.51	4.0	10.5	.43
4-Bromobiphenyl	5.61	9.00	11.5	10.5	.85
Acridine	5.17	11.0	19.8	10.2	1.1
Acridine (in decalin)	3.39	3.07	−1.1	3.35	0.92

disturbance of the surrounding molecules upon rotation of the elongated molecules. The changes in $\Delta S_\epsilon^\ddagger$ are consistent with this, except for acridine, which has a somewhat larger $\Delta S_\epsilon^\ddagger$ than 4-bromobiphenyl, and for α-chloronaphthalene, which has a very low value. Comparison with solution data for α-chloronaphthalene[12] in *n*-heptane shows that the increase in $\Delta S_\epsilon^\ddagger$ from heptane to Nujol solution is actually large, since the $\Delta S_\epsilon^\ddagger$ in heptane is very low, −4.0 e.u. Thus, the change in $\Delta S_\epsilon^\ddagger$ for α-chloronaphthalene from heptane to Nujol is +4.5 e.u., while for camphor it is 3.2 − 1.4 = 1.8 only. The $\Delta H_\epsilon^\ddagger$ values increase generally from the spherical molecules to the elongated ones, with 4-bromobiphenyl and acridine having values in the neighborhood of those for $\Delta H_\epsilon^\ddagger$. The ratio n of $\Delta H_\epsilon^\ddagger$ to $\Delta H_\eta^\ddagger$ in Table V goes from 0.16 to about 1.1 as the molecular shape changes. One may consider that only part of the forces acting in viscous flow hinder the dipole rotation and write $\Delta H_\epsilon^\ddagger = n\Delta H_\eta^\ddagger$. By using the rate equations for dielectric relaxation and viscous flow one can derive an empirical relationship $\tau = C\eta^n/T$, which satisfactorily represents the dependence of τ upon viscosity and temperature, C being a constant for each substance. This essentially empirical equation may be of value in the analysis of relaxation time data.

PRINCETON, NEW JERSEY

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF NORTHWESTERN UNIVERSITY]

Mechanism of Substitution Reactions of Complex Ions. XVI.[1] Exchange Reactions of Platinum(II) Complexes in Various Solvents[2]

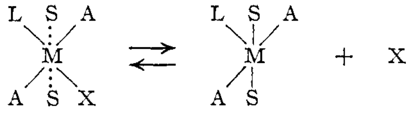
BY RALPH G. PEARSON, HARRY B. GRAY AND FRED BASOLO

RECEIVED JULY 24, 1959

The rate of chloride exchange of *trans*-Py(py)$_2$Cl$_2$ in a variety of solvents depends upon the properties of the solvent in a way consistent with strong interaction of the solvent and metal ion in the rate-determining step. Solvents with empty, or potentially empty, orbitals are particularly effective probably because of π-bonding to the platinum. The term *biphilic* reagent is proposed for substances which can simultaneously donate and accept electrons in substitution reactions.

Previous studies[3] on the substitution reactions of planar complexes of platinum(II) showed that a division of nucleophilic reagents (ligands) into two classes could be made. In one class were good reagents, whose reaction rates were high and depended on the concentration of the reagent; in the other class poor reagents with rates independent of concentration and, for a given complex ion, the same rate of reaction. This paper is a study of the mechanism of reaction of the latter class of reagents. As a typical example, chloride ion has been picked since, in a number of cases,[4] the exchange of chloride ion with chloro complex in aqueous solution goes by processes zero order in chloride ion.

A fairly detailed mechanism for the reaction sequence with poor reagents has been proposed.[5] In the absence of strong π-bonding groups, which might favor rearrangement to a trigonal bipyramid intermediate, the mechanism may be described as a "dissociation" with a five-coördinated intermediate which resembles a square pyramid. The mechanism thus assigns a heavy role to the solvent which is considered to occupy coördination sites above and below the square plane.[6] In dissociation of a labile group, two solvent molecules move in from a rather long bonding distance to a shorter one, thus helping to push off the leaving group, *viz.*



(1)

Such a process can serve as a path for chloride exchange with or without the intermediate formation of the solvated complex, MLA$_2$S.

In view of the participation of the solvent postulated in equation 1, a logical test is to study a chloride exchange reaction in a series of solvents to see whether a correlation exists between the coördinating properties of the solvent and the rate of exchange. The reaction selected was

$$trans\text{-Pt(pyridine)}_2\text{Cl}_2 + {}^*\text{Cl}^- \longrightarrow trans\text{-Pt(py)}_2{}^*\text{Cl}_2 + \text{Cl}^- \quad (2)$$

This complex was chosen because it is soluble in a wide variety of solvents although it is insoluble in water. The labeled chloride ion was added in the form of the quaternary salt, *n*-octadecylbenzyldimethylammonium[36] chloride, or as H^{36}Cl in a few

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[1] Previous paper in this series, R. G. Pearson, R. A. Munson and F. Basolo, THIS JOURNAL, **80**, 504 (1958).

[2] This investigation is partly supported by a grant from the U. S. Atomic Energy Commission under contract AT(11-1)-89-project No. 2.

[3] D. Banerjea, F. Basolo and R. G. Pearson, THIS JOURNAL, **79**, 4055 (1957).

[4] T. S. Elleman, J. W. Reishus and D. S. Martin, Jr., *ibid.*, **81**, 10 (1959).

[5] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, pp. 186–190. See also ref. 4, p. 17.

[6] Evidence for groups above and below the plane in "square" complexes is now extensive. See ref. 5, p. 186.