Microwave Absorption and Molecular Structure in Liquids. LXXI. Polarity and Atomic Polarization in Three Metal Acetylacetonates

S. Dasgupta and C. P. Smyth

Contribution from the Frick Chemical Laboratory, Princeton University, Princeton, New Jersey. *Received May 18, 1967*

Abstract: The dielectric constants and losses of dilute benzene solutions of aluminum acetylacetonate, chromic acetylacetonate, and zirconium acetylacetonate have been measured at 2.2 mm and 1.25, 3.22, 10.01, and 57,500-cm wavelength. The data have been used to calculate small dielectric relaxation times, very large atomic polarizations, and apparent small dipole moment values. The most probable relaxation times are so small as to indicate that they are associated with intramolecular motion and not with the orientation of a permanent dipole by molecular rotation. It is, therefore, concluded that the small apparent dipole moment values probably arise from atomic polarization and not from permanent molecular moments, although the existence of small permanent moments is not completely excluded by the results. It appears that the atomic polarization of these compounds arises from absorption in the millimeter and centimeter wavelength region as well as from that in the infrared region, with which it is usually associated.

Investigations of the possible dipole moments of the metal acetylacetonates have led most investigators to the conclusion that the molecules possess zero dipole moments, but remarkably large atomic polarizations.[1-7] Large intramolecular dipoles should exist in these molecules, but the symmetry of the coordination structures points to mutual cancellation of these internal moments. As the situation has been excellently analyzed[2] and summarized[7] already, the discussion will not be repeated. However, because of the lack of complete certainty as to the absence of dipole moments and because of the abnormally high atomic polarizations, investigation of these compounds at microwave and millimeter wave frequencies has seemed highly desirable. Difficulty of purification and low solubility in nonpolar solvents have frequently made it difficult to obtain results sufficiently accurate to warrant firm conclusions. Indeed, the results of a series of measurements carried out by Dr. R. D. Nelson, Jr., in this laboratory some years ago have, for this reason, not been submitted for publication. The acetylacetonates selected for the present investigation were those of aluminum, $Al(C_5H_7O_2)_3$, chromium, $Cr(C_5H_7O_2)_3$, and zirconium, $Zr(C_5H_7O_2)_4$.

Experimental Section

Materials. Highly purified samples of aluminum and chromium acetylacetonates were given us by Professor Ernest N. DiCarlo of St. Joseph's College. Commercially obtained zirconium acetylacetonate was so impure as to be unusable. Professor George F. Wright of the University of Toronto very kindly prepared a sample of pure material for us.

Methods. The measurements of the dielectric constants ϵ' and dielectric loss ϵ'' were made at 0.22-, 1.25-, 3.22-, and 10.01-cm wavelengths. The static dielectric constant ϵ_0 was measured with the heterodyne-beat apparatus. The methods and the apparatus have been described previously.[8-12] The densities of the solutions at different temperatures were measured by means of a pycnometer.

Experimental Results

The dielectric constants ϵ' and losses ϵ'' measured at the wavelength λ_0 are given in Table I for the benzene solutions containing mole fraction c_2 of the metal acetylacetonate. These values have been used for Cole–Cole analysis[13] in an IBM 7094 computer to calculate the values of ϵ_∞, the infinite-frequency dielectric constant, τ_0, the most probable relaxation time, and α, the distribution parameter, which are listed in Table III. The total polarization P_{12} of each solution is calculated from the usual expression

$$P_{12} = \frac{c_1M_1 + c_2M_2}{d}\frac{\epsilon_0 - 1}{\epsilon_0 + 2}$$

where M_1, M_2 and c_1, c_2 are the molecular weights and mole fractions of the solvent and solute, d is the density of the solution, and ϵ_0 is the static dielectric constant of the solution given by the value of ϵ' at the 57,500-cm wavelength in Table I. The polarization P of the solute is obtained as $P = P_2 = (P_{12} - P_1)/c_2 + P_1$. The values of the electronic or optical polarization at infinite wavelengths, P_E, in Table II are those obtained by Finn, Hampson, and Sutton.[2] The infinite-frequency polarization of the solution is

$$P_{\infty 12} = \frac{c_1M_1 + c_2M_2}{d}\frac{\epsilon_\infty - 1}{\epsilon_\infty + 2}$$

and that for the solute is

$$P_\infty = P_{\infty 2} = (P_{\infty 12} - P_{\infty 1})/c_2 + P_{\infty 1}$$

where $P_{\infty 1}$, the infinite-frequency polarization for pure

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[1] J. W. Smith and W. R. Angus, *Proc. Roy. Soc.* (London), **A137**, 372 (1932).

[2] A. E. Finn, G. C. Hampson, and L. E. Sutton, *J. Chem. Soc.*, 1254 (1938).

[3] I. E. Coop and L. E. Sutton, *ibid.*, 1269 (1938).

[4] J. McQueen and J. W. Smith, *ibid.*, 1821 (1956).

[5] C. C. Meredith, L. Westland, and G. F. Wright, *J. Am. Chem. Soc.*, **79**, 2385 (1957).

[6] P. Podleschka, L. Westland, and G. F. Wright, *Can. J. Chem.*, **36**, 574 (1958).

[7] J. W. Smith, "Electric Dipole Moments," Butterworths Scientific Publications, London, 1955, pp 262-263, 276-279.

[8] S. K. Garg, H. Kilp, and C. P. Smyth, *J. Chem. Phys.*, **43**, 2341 (1965).

[9] W. M. Heston, E. J. Hennelly, and C. P. Smyth, *J. Am. Chem. Soc.*, **70**, 4093 (1948).

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

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

[12] G. L. Lewis and C. P. Smyth, *J. Chem. Phys.*, 7, 1085 (1939).

[13] K. S. Cole and R. H. Cole, *ibid.*, **9**, 341 (1941).

Table I. Dielectric Constants and Losses of Solutions in Benzene

Temp, °C	λ_0, cm	ϵ'	ϵ''
	Aluminum Acetylacetonate (c_2 = 0.0453)		
25.0	0.22	2.391	0.0153
	1.25	2.416	0.0192
	3.22	2.426	0.0110
	10.01	2.429	0.0048
	57,500	2.429	. . .
40.0	0.22	2.359	0.0183
	1.25	2.384	0.0136
	3.22	2.389	0.0092
	10.01	2.390	0.0043
	57,500	2.391	. . .
60.0	0.22	2.318	0.0187
	1.25	2.345	0.0123
	3.22	2.347	0.0064
	10.01	2.350	0.0030
	57,500	2.349	. . .
	Chromic Acetylacetonate (c_2 = 0.0210)		
25	0.22	2.340	0.0107
	1.25	2.348	0.0127
	3.22	2.356	0.0060
	10.01	2.358	0.0030
	57,500	2.359	. . .
40	0.22	2.308	0.0112
	1.25	2.319	0.0110
	3.22	2.322	0.0046
	10.01	2.324	0.0026
	57,500	2.324	. . .
60	0.22	2.262	0.0118
	1.25	2.275	0.0082
	3.22	2.279	0.0031
	10.01	2.280	0.0021
	57,500	2.280	. . .
	Zirconium Acetylacetonate (c_2 = 0.0131)		
25	0.22	2.323	0.0082
	1.25	2.333	0.0098
	3.22	2.338	0.0061
	10.01	2.340	0.0032
	57,500	2.342	. . .
40	0.22	2.296	0.0097
	1.25	2.306	0.0086
	3.22	2.309	0.0058
	10.01	2.313	0.0029
	57,500	2.314	. . .
60	0.22	2.254	0.0116
	1.25	2.266	0.0084
	3.22	2.271	0.0057
	10.01	2.274	0.0027
	57,500	2.274	. . .

Table II. Polarizations

			$P - P_E$		
Temp, °C	P_E	P	This work	Lit.	$P_\infty - P_E$
		Aluminum Acetylacetonate			
25	91.1[a]	132.87	41.8	42.9[a] 39.7[b]	27.6
40		132.54			
60		132.18			
		Chromic Acetylacetonate			
25	95.3[a]	135.26	40.0	42.2[a] 40.2[b]	21.3
40		134.79			
60		134.36			
		Zirconium Acetylacetonate			
25	123.5[a]	187.33	63.8	61.9[a]	39.4
40		186.95			
60		186.55			

[a] Reference 2. [b] Reference 3.

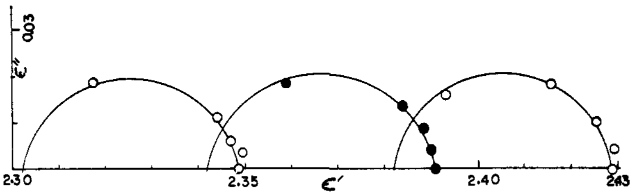

Figure 1. Arc plots for 0.0453 mole fraction of aluminum acetylacetonate solution in benzene at 25, 40, and 60°.

benzene, is taken to be identical with P_1, the low-frequency value.

Discussion of Results

There is a certain amount of *ad hoc* reasoning in the interpretation of these results. We have recently interpreted our results on a variety of siloxanes, the structures of most of which must have dipole moments, in terms of a small molecular moment, intramolecular dipole orientation, and large atomic polarization. The structures of the three metal acetylacetonates studied here appear to be symmetrical. X-Ray analysis has indicated the planarity of the six-membered rings in ferric acetylacetonate.[14] The preponderance of dipole moment evidence[1–4,7] indicates zero moment and very large atomic polarization. The total polarizations P in Table II show a slight decrease with rising temperature. Straight lines are obtained when P is plotted against $1/T$, and the slopes of these lines correspond to apparent moment values, 0.56 D. for aluminum acetylacetonate, 0.64 D. for chromic acetylacetonate, and 0.63 D. for zirconium acetylacetonate. However, the change of the polarization with temperature, in spite of its seeming regularity, is little, if any, larger than the possible experimental error, and nonpolar liquids sometimes show an apparent small variation of polarization with temperature. The values of $P - P_E$ in Table II are in excellent agreement with those in the literature, which have been taken to be P_A, the permanent moment being regarded as zero. If, however, $P_E + P_A = P_\infty$ is calculated from the values of ϵ_∞, the values obtained for $P_A = P_\infty - P_E$ are, as shown in Table II, considerably lower than those obtained as $P - P_E$. The difference would seem to indicate the existence of a molecular moment. The apparent dipole moment μ has been calculated by means of the Debye equation written in the form

$$\mu^2 = \frac{27kT}{4\pi N}\left(\frac{M_1c_1 + M_2c_2}{c_2d}\right)\frac{\epsilon_0 - \epsilon_\infty}{(\epsilon_0 + 2)(\epsilon_\infty + 2)}$$

where k is the gas constant per molecule; N, the number of molecules per mole; and T, the absolute temperature. The apparent dipole moments calculated by means of this equation are 0.90 D. for aluminum acetylacetonate, 1.02 D. for chromic acetylacetonate, and 1.18 D. for zirconium acetylacetonate.

The plots of ϵ'' against ϵ' give typical Cole–Cole arcs[13] (Figure 1), from which the ϵ_∞ and relaxation time values are obtained. The distribution parameter d is considerable in size, about the same for all three compounds, and unusual in that it increases with rising temperature instead of decreasing. The values of α are large enough to suggest a possibility of representing

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(14) R. B. Roof, Jr., *Acta Cryst.*, 9, 781 (1956).

Table III. Infinite-Frequency Dielectric Constants, Relaxation Times, and Distribution Parameters

Temp, °C	ϵ_∞	τ_0 (10^{-12} sec)	α
	Aluminum Acetylacetonate		
25	2.382	4.1	0.16
40	2.342	3.1	0.21
60	2.304	1.9	0.21
	Chromic Acetylacetonate		
25	2.324	3.1	0.14
40	2.288	2.5	0.22
60	2.246	1.5	0.22
	Zirconium Acetylacetonate		
25	2.317	4.4	0.14
40	2.288	3.6	0.21
60	2.248	2.9	0.24

the dielectric data in terms of two relaxation times,[15] τ_1 and τ_2, instead of τ_0 and α. When the data were computerized in these terms, a clearly best set of values was not obtained. The most probable approximations for the aluminum, chromium, and zirconium compounds were respectively about 10, 9, and 17 $\times$ 10^{-12} sec for τ_1 at 25°, and 2.0, 2.2, and 2.8 $\times$ 10^{-12} for τ_2, which was associated with a mechanism responsible for 50 to 90% of the relaxation at the different temperatures. Since our analysis does not give these values as unique solutions for τ_1 and τ_2, they are not included in Table III. The apparent values calculated for τ_1, although somewhat small for the molecules involved, could be associated with over-all molecular orientation. To the extent that they are credible, they suggest the possible existence of a permanent dipole moment in these molecules, as do the dubious moment values discussed earlier in this paper.

The relaxation times τ_0 are no more than 0.1–0.2 of what they would probably be if the molecules were orienting in the applied field by rotation of the whole molecule with a permanent dipole fixed in it. It would seem reasonable to conclude from this that the apparent dipole moments which have been calculated are not permanent molecular moments, but merely the result of induced intramolecular polarization, that is, atomic polarization, $P - P_\infty$, arising from microwave absorption and added to the already high atomic polarization, $P_\infty - P_E$, arising from infrared absorption. This is equivalent to saying that the atomic polarizations of these compounds arise from absorption in the millimeter and centimeter wavelength region as well as from infrared absorption, with which atomic polarization is normally associated. In summary, the results of the present paper do not exclude the possibility of the existence of permanent dipole moments in these three metal acetylacetonates. The most dependable evidence, however, seems in favor of an absence of permanent moment. In any event, the predominant cause of the observed dielectric relaxation is intramolecular motion, which is responsible for the atomic polarization.

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[15] K. Bergmann, D. M. Roberti, and C. P. Smyth, *J. Phys. Chem.*, **64**, 665 (1960).