

Contribution from Microwave Absorption to the Abnormally Large Differences between the Radio-Frequency and Visible-Frequency Polarizations of Several Metal Trisacetylacetonates

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Abstract: The dielectric relaxation behavior of the trisacetylacetonates of Al(III), Co(III), Fe(III), and Cr(III) in benzene solution has been investigated at 25 °C in the frequency range 0.002–135 GHz. These systems exhibit considerable absorption in the microwave region. The polarization change caused by absorption at frequencies below 135 GHz (4.5 cm^{-1}) explains ~36–45% of the observed differences of polarization between radio and visible frequencies ($P_{\text{RF}} - P_{\text{VF}}$). The inclusion of this polarization change, along with the previously reported changes of polarization caused by absorption in the regions 5–200 and 300–1600 cm^{-1} , accounts entirely for the abnormally large observed ($P_{\text{RF}} - P_{\text{VF}}$) values. The dielectric constants and losses, which follow Cole–Cole-type dispersions, are consistent with very short relaxation times, ~1–2 ps, indicative of associated processes of surprisingly high frequency. The origin of the microwave losses is discussed, the conclusion being that they are not relaxation losses of either rotating permanent dipoles or transitory multipole-induced dipoles. The balance of evidence, obtained from previous (vapor phase) polarization, X-ray, and far-infrared investigations, favors the microwave absorption as being connected with intramolecular motion(s), i.e., atomic polarization. For comparative purposes, the dielectric dispersion of the permanently dipolar compounds, acetylacetonone, H(acac), and tris(trifluoroacetylacetonato)aluminum(III), Al(acacF₃)₃, was also examined. The magnitude of the relaxation times found for H(acac) and Al(acacF₃)₃, 6.0 and 159 ps, respectively, is in accord with dipole orientation predominantly via molecular rotation. Dipole moments, as determined from the amplitude of the dispersion, were found to be 4.32 and 2.97 D for Al(acacF₃)₃ and H(acac), respectively, the latter value comparing with 3.0 D, the value obtained from gas-phase measurements.

The problem of accounting for the unusually large differences between the radio-frequency and visible-frequency polarizations, " $P_{\text{RF}} - P_{\text{VF}}$ " (ΔP_0^{VF}), of several metal acetylacetonates, for which the preponderance of experimental evidence favors the assignment of zero permanent dipole moments,^{1–14} has proven to be an intractable one. Since 1932, the origin of this "excess" polarization has been the concern of numerous publications^{1–10} which collectively have dealt with the following complexes of acetylacetonone: Be(acac)₂, Al(acac)₃, Co(acac)₃, Fe(acac)₃, Cr(acac)₃, Mn(acac)₃, Th(acac)₄, and Zr(acac)₄. The ΔP_0^{VF} values of these systems, ~30–86% of the P_{VF} values, correspond to apparent electric dipole moments of ~1.2–2.0 D at 25 °C.^{1–4}

A significant contribution to a resolution of this apparent anomaly has come from the far-infrared work of Angel¹⁵ and of Haigh et al.¹⁰ These authors demonstrated that the absorption exhibited by Be(acac)₂ and by the trisacetylacetonates of Al(III), Co(III), Fe(III), Cr(III), and Mn(III) in benzene solution in the region 5–200 cm^{-1} , together with that observed by Larsson and Eskilsson¹⁶ at 300–1600 cm^{-1} , explains ~50–60% of the observed differences. Since absorption above 1600 cm^{-1} is very unlikely to contribute substantially to the ΔP_0^{VF} values, the remaining

differences should be accountable in terms of absorption at frequencies lower than 5 cm^{-1} . Indeed, studies prior to the above investigations^{5,7,9} had shown that these systems do display microwave absorption not connected with polarization due to the ordering of permanent dipole moment components. However, two of these earlier investigations^{7,9} suffered from insufficient frequency coverage of the microwave absorption region (vide infra) while the third⁵ utilized observations made on only one dilute solution in the analysis of the dispersion. The present study was undertaken to better depict the microwave relaxation behavior. For this purpose, dielectric measurements on many solutions have been made over a wider frequency range than we previously employed,^{7,9} one of the measuring frequencies (4.5 cm^{-1}) being very close to the frequency of maximum absorption. It specifically deals with the trisacetylacetonates of Al(III), Co(III), Fe(III), and Cr(III) which presumably do not possess orientation polarization, yet have ~30–60 $\text{cm}^3\text{ mol}^{-1}$ of polarization not assignable as electronic polarization.^{1–4} Our primary objective was to obtain reliable values for the amount of this excess polarization undergoing dispersion below ~5 cm^{-1} . The latter are reported along with a discussion relating to the possible origin of the microwave absorption.

Experimental Section

Apparatus. Static dielectric constants, ϵ_0 , were measured at a radio frequency of 0.002 GHz and dielectric constants, ϵ' , and losses, ϵ'' , were determined at microwave frequencies of 135, 24.4, 9.25, and 2.00 GHz. The static dielectric constant apparatus which is capable of detecting changes in capacitance of ~0.002 pF has been previously described along with an associated error analysis.⁶ The 24.4- and 9.25-GHz measurements were made employing the standing-wave method.¹⁷ The error in ϵ'' has been found to be ± 0.00005 or $\pm 2\%$ (whichever is larger) and ± 0.0001 or $\pm 2\%$ (whichever is larger) at 9.25 and 24.4 GHz, respectively.⁷ The error in ϵ' has been estimated to be ~0.2% at both 9.25 and 24.4 GHz. The 135-GHz apparatus is essentially a microwave analogue of the Michelson optical interferometer.^{18,19} The error in the measured ϵ'' is ± 0.0001 or $\pm 2\%$ (whichever is larger), and that in ϵ' is less than 0.2%. The coaxial line resonant cavity method²⁰ was used for measure-

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Table I. Slopes, a' and a'' , for the Dependence of the Dielectric Constant and Loss of Solutions on Mole Fraction of Solute^a (25 °C)

ν (GHz)	Al(acac) ₃		Co(acac) ₃		Fe(acac) ₃		Cr(acac) ₃		H(acac)		Al(acacF ₃) ₃	
	a'	a''	a'	a''	a'	a''	a'	a''	a'	a''	a'	a''
135	2.58	0.400	2.69	0.357	3.14	0.941	2.76	0.560	1.64	2.85	1.67	0.49
24.4	3.16	0.325	3.20	0.246	4.08	0.638	3.35	0.357	6.31	4.14	2.10	1.01
9.25	3.25	0.243	3.37	0.158			3.56	0.228	10.96	3.73	2.43	2.77
2.00	3.50	0.100									11.40	9.31
0.00 ^b	3.60		3.52		4.77		3.82		12.40		27.67	

^aThe mole fractions of the most concentrated solutions examined were ~ 0.04 for the unsubstituted trisacetylacetonates. ^b a' at 0.002 GHz is referred to as a_0 in the body of the paper.

Table II. Infinite Frequency Intercepts, a_∞ , Critical Frequencies, $\bar{\nu}_m$, Relaxation Times, τ_0 , Distribution Parameters, α , Derivatives, β , of Specific Volume with Respect to Mole Fraction of Solute, and Dipole Moments, μ (25 °C)

	a_∞	$\bar{\nu}_m$ (cm ⁻¹)	τ_0 , ps	α	$-\beta$	μ , D
Al(acac) ₃	1.91	2.8 ^a	1.9	0.42	1.3555	
Co(acac) ₃	2.11	2.3 ^a	2.3	0.43	1.6658	
Fe(acac) ₃	1.10	4.8 ^a	1.1	0.39	1.6962	
Cr(acac) ₃	1.33	6.6 ^a	0.8	0.46	1.5665	
H(acac)	0.10	0.9	6.0	0.16		2.97 \pm 0.1, 3.03 ²²
Al(acacF ₃) ₃	1.70	0.03	159	0.18		4.32 \pm 0.04

^aResultant average of two independent determinations, each of which was in agreement to within 5%.

Table III. Molar Polarization Data (cm³) for Benzene Solutions at 25 °C^a

	this study			ΔP_0^{VF}		$\Delta P_0^{4.5}$		ΔP_0^{1600}	$\Delta P_0^{1600} + \Delta P_0^{4.5}$	$(\Delta P_0^{1600} + \Delta P_0^{4.5}) / \Delta P_0^{VF}$
	P_{RF}	$P_{4.5}$	P_{VF}	this study	previous study	$(P_{RF} - P_{4.5})$	calcd ^b			
Al(acac) ₃	131.9	116.9	91	40.9	43 41.8 (39.7)	15.0	14.4	24.5	39.2	0.95
Co(acac) ₃	134.5	122.3	99	35.5	31 30.0	12.2	14.0	16.6	29.7	0.92
Fe(acac) ₃	151.1	127.1	92	59.1	57 53.0 (55.1)	24.0	25.9	26.4	51.4	0.92
Cr(acac) ₃	138.8	123.2	95	43.8	43 40.0 (40.2)	15.6	16.2	24.0	39.9	0.96

^aThe ΔP_0^{VF} values in column 5 are the differences between the present P_{RF} results and literature P_{VF} values³ listed in column 4. The ΔP_0^{VF} values in columns 6 and 7 are solution values (25 °C) taken from ref 3-5, and those in parentheses are vapor-phase values obtained from measurements made at ~ 225 °C.² The $\Delta P_0^{4.5}$ values used in the sums given in column 12 are the average of those in columns 9 and 10. For the ratios in column 13, the values of ΔP_0^{VF} used are the means of the present and previously observed ones. Errors: radio-frequency and 4.5-cm⁻¹ polarization measurements (this study), ± 1.0 cm³ mol⁻¹; ($\Delta P_0^{1600} + \Delta P_0^{4.5}$) values, ± 5 cm³. ^bCalculated employing eq 2.

ments at 2 GHz, the errors in ϵ' and ϵ'' having been found to be ± 0.5 and $\pm 2\%$, respectively.¹⁸

A Lipkin bicapillary pycnometer was employed to measure densities. Duplicate density results differed by not more than 0.0001 g/cm³.

Materials. Reagent grade, thiophene-free benzene, obtained from the Fisher Scientific Co., was fractionally distilled over sodium and stored over Drierite, n_D^{20} 1.50111. Acetylacetone, obtained from the Aldrich Chemical Co., was used without further purification; n_D^{20} 1.4510. Tris(trifluoroacetylacetonato)aluminum(III), obtained from the Research Organic and Inorganic Chemical Co., was recrystallized from benzene-petroleum ether (low boiling) and dried under vacuum over Drierite, mp 120-121 °C. The unsubstituted trisacetylacetonates, obtained from the J. T. Baker Chemical Co., were purified by repeated crystallization from benzene-petroleum ether (bp 37-48 °C) and drying under vacuum over phosphorus pentoxide; mp 214.0-215.0, 182.5-184.0, 193.5-195.0, and 213.0-214.0 °C for Cr(acac)₃, Fe(acac)₃, Al(acac)₃, and Co(acac)₃, respectively.

Results and Discussion

Microwave Dispersion and Polarization. The values of the dielectric constant, ϵ' , and the loss, ϵ'' , were plotted against the mole fraction of solute in solution, f_2 , and slopes in the limit of zero concentration, a' and a'' , respectively, were obtained. The latter were fitted to Cole-Cole arcs²¹ to obtain the critical frequencies, $\bar{\nu}_m$, the corresponding mean relaxation times, τ_0 , the distribution coefficients, α , and the arc intercepts at infinite frequency, a_∞ . The values of these quantities are given in Tables I and II along with the limiting values of the slopes at zero concentration, β , for the dependence of specific volume, v , on mole fraction. For each substance investigated, five to eight benzene solutions were employed for the determination of a' , a'' , and β , the slopes being calculated by the method of least squares.

The τ_0 data listed for each of the unsubstituted trisacetylacetonates are the averages of those obtained from two deter-

minations (made on different sets of freshly prepared solutions), each of which was in agreement to within 5%. These values differ considerably with those from another study⁷ wherein the dispersion was examined solely in terms of dielectric losses obtained at only two microwave frequencies. The reported values (4-6 ps), which were calculated assuming a Debye-type absorption ($\alpha = 0$) are, at best, extreme upper limit estimates since the two measuring frequencies employed in the earlier work (9 and 25 GHz) are on the low-frequency side of the absorption maximum. This is clearly reflected in the loss data obtained at 135 GHz (Table I). In addition, the present study, which includes dielectric constant results along with loss observations at both lower and higher frequencies, shows that the dispersion curve is not a simple Debye-type one. Finally, the fact that the 135 GHz (4.5 cm⁻¹) measuring frequency is in the immediate neighborhood of the critical frequency enhances the reliability of the τ_0 and α parameters obtained for these systems. The relaxation times of the permanently dipolar compounds, acetylacetone, H(acac), and tris(trifluoroacetylacetonato)aluminum(III), Al(acacF₃)₃, will be referred to at a later point in the discussion.

The dipole moments listed in Table II were calculated from the total amplitude of the dispersion, i.e., $(a_0 - a_\infty)$, where $a_0 = a'$ at 0.002 GHz, employing the Debye equation modified for dilute solutions. The value obtained for H(acac), 2.97 \pm 0.1, compares with 3.0 D, the value obtained from gas-phase measurements.²² The value for Al(acacF₃)₃, 4.32 \pm 0.04, is believed to be particularly accurate owing to the favorable distribution of points along the arc, the a' value at 4.5 cm⁻¹, 1.67, being close to the infinite frequency intercept, 1.70.

Table III contains the presently measured radio-frequency (0.002 GHz) solute polarizations, P_{RF} , and the polarizations measured at the microwave frequency of 135 GHz (4.5 cm⁻¹), $P_{4.5}$. Also included are previously obtained visible-frequency

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(17300 cm⁻¹) values,³ P_{VF} , and observed P_{RF} and P_{VF} differences, designated as ΔP_0^{VF} . The present molar polarizations were generated by the Halverstadt-Kumler equation²³ which assumes the Clausius-Mossotti treatment of the internal field. The values of the dielectric constant and specific volume obtained by extrapolation to zero mole fraction, ϵ_1 and v_1 , respectively, were used in the calculations. In all cases, ϵ_1 and v_1 agreed with the standard values of 2.2727 and 1.1449 for pure dry benzene at 25 °C to within 0.01%. The P_{RF} and $P_{4.5}$ values at infinite dilution, deduced from the slopes, a_0 and $a'_{4.5}$, respectively, were checked by comparison with those calculated from the dielectric constant and specific volume for each concentration. No systematic variation of polarization with concentration was observed. This fact, together with the good least-squares linear fits of v , ϵ' , and ϵ'' vs. f_2 over the concentration range investigated for each of the compounds indicates normal behavior on the part of the solutions studied. The measured 4.5-cm⁻¹ polarizations listed in column 3 are in good agreement with those based on the Cole-Cole dispersion, viz., 117, 122, 125, and 122 cm³ for the Al(III), Co(III), Fe(III), and Cr(III) compounds, respectively, the latter being calculated using the $a'_{4.5}$ values deduced from the Cole-Cole parameters. The values of the polarization change which occurs below 4.5 cm⁻¹, $\Delta P_0^{4.5}$, listed in column 9, are the differences between the "individually measured" P_{RF} and $P_{4.5}$ polarizations (columns 2 and 3, respectively).

The calculated changes of polarization between the radio-frequency and the visible-frequency extremes caused by "absorption" at frequencies below 4.5 cm⁻¹ are tabulated in column 10. They were generated from the observed $a'_{4.5}$ data, $(d\epsilon'_{4.5}/df_2)_{f_2 \rightarrow 0}$, and the best-fit Cole-Cole parameters, α and τ_0 , the latter being obtained as previously described.²¹ In general, in the limit of infinite dilution, the amount of solute polarization undergoing dispersion below 4.5 cm⁻¹ is given in terms of the real part of the dielectric constant by the expression:

$$\Delta P_0^{4.5} = [3M_1v_1/(\epsilon_1 + 2)^2](a_0 - a'_{4.5}) \quad (1)$$

where a_0 and $a'_{4.5}$ are $(d\epsilon_0/df_2)_{f_2 \rightarrow 0}$ and $(d\epsilon'_{4.5}/df_2)_{f_2 \rightarrow 0}$, respectively, and M_1 , v_1 , and ϵ_1 are the molecular weight, specific volume, and dielectric constant of the nonabsorbing solvent (assumed to be independent of frequency), respectively. For the particular case of a Cole-Cole dispersion,²¹ eq 1 becomes:

$$\Delta P_0^{4.5} = \frac{3M_1v_1}{(\epsilon_1 + 2)^2} \left[\frac{a'_{4.5} \sin(\alpha\pi/2) + a'_{4.5}(\omega\tau_0)^{(1-\alpha)}}{\cos(\alpha\pi/2)} \right] \quad (2)$$

where ω is the angular frequency corresponding to 4.5 cm⁻¹. The term in brackets, which effectively determines the integrated intensity of the absorption in the specified frequency range, reduces to $a'_{4.5}\omega\tau_0$ for a Debye-type relaxation process. It is difficult to estimate the uncertainties in the $\Delta P_0^{4.5}$ values "as calculated from eq 2", but they are assessed at ± 3 cm³ (based on two independent determinations of the α and τ_0 parameters for each of the trisacetylacetonates). As seen from Table III, the calculated values are close to the observed differences; see column 9. This agreement is important in the context of the present work because it reflects the internal consistency of the dispersion and absorption data when fitted to the Cole-Cole equations for the frequency interval of chief concern, 0–4.5 cm⁻¹.

The ΔP_0^{1600} entries in column 11 are the "calculated" changes of polarization reported by Haigh et al.¹⁰ A few comments concerning these data which account for only ~50–60% of the observed ($P_{RF} - P_{VF}$) values are in order. Each ΔP_0^{1600} value reflects the sum of the individually calculated ΔP values associated with the optical absorption, $\alpha(\bar{\nu})$, spectra for three separate regions, 0–30, 30–200, and 200–1600 cm⁻¹, viz., $\Delta P_0^{1600} = \Delta P_0^{30} + \Delta P_0^{200} + \Delta P_0^{1600}$. The method employed for the calculation of the ΔP terms is based on the Kramers-Kronig relation²⁴ and involves the

determination of the area under the $\alpha(\bar{\nu})/\bar{\nu}^2$ vs. $\bar{\nu}$ curve (or the corresponding $\epsilon''(\bar{\nu})$ vs. $\ln \bar{\nu}$ curve) for each of the specified frequency regions.^{10,25} As pointed out by Haigh et al.,¹⁰ the ΔP_0^{1600} values do not include the contribution to the P_{RF} and P_{VF} differences ($P_{RF} - P_{VF}$) caused by absorption in the microwave region. This is due to the fact that for the lowest region, 0–30 cm⁻¹, the $\alpha(\bar{\nu})$ spectra were obtained from 5 to 25 cm⁻¹ and the reported ΔP_0^{30} values were generated (from the area under the $\alpha(\bar{\nu})/\bar{\nu}^2$ vs. $\bar{\nu}$ curve) by a simple extrapolation of the direct observations to $\bar{\nu} = 0$. When the microwave results (Table I) are included along with the losses corresponding to the $\alpha(\bar{\nu})$ spectra for the region¹⁰ 5–25 cm⁻¹, the contour of the $a''(\bar{\nu})$ vs. $\ln \bar{\nu}$ curves clearly shows that the ΔP_0^{30} values so obtained do not include the polarization change which occurs below ~4–5 cm⁻¹. This is reflected by the fact that simple addition of the $\Delta P_0^{4.5}$ data to the ΔP_0^{30} values previously reported¹⁰ yields the same result as obtained by integrating the complete $a''(\bar{\nu})$ vs. $\ln \bar{\nu}$ curve, the microwave portion being depicted in terms of the Cole-Cole form of the absorption curve. For example, the corrected ΔP_0^{30} value obtained for Al(acac)₃ by complete integration of the loss curve, i.e., 27.5 cm³ compared with 27.3 cm³ = ($\Delta P_0^{30} + \Delta P_0^{4.5}$), the reported value¹⁰ of ΔP_0^{30} (12.6 cm³) being used in the sum. The contribution from the microwave peak to the calculated polarization change, ΔP_0^{1600} , has therefore been included by direct addition, the $\Delta P_0^{4.5}$ values used in the sum ($\Delta P_0^{1600} + \Delta P_0^{4.5}$) being the average of those in columns 9 and 10; see column 12. The $\Delta P_0^{4.5}$ term proves to be a significant one, the proportion of the excess polarization associated with absorption at frequencies below 4.5 cm⁻¹, viz., $\Delta P_0^{4.5}/\Delta P_0^{VF}$ being 0.36, 0.41, 0.45, and 0.38 for the acetylacetonates of Al(III), Co(III), Fe(III), and Cr(III), respectively. Indeed, based on an estimate made employing microwave loss results obtained from measurements on one solution of Al(acac)₃,⁵ Haigh et al. had concluded that the effect of the microwave absorption is considerable for this system and, by inference, for all of the other acetylacetonates.¹⁰ In addition, Angel,¹⁵ using the same microwave data⁵ together with his far-infrared observations (10–250 cm⁻¹), estimated that a large portion (~32 cm³) of the excess polarization exhibited by Al(acac)₃ is associated with absorption in the low-frequency region between 0 and 120 cm⁻¹, the value of 32 cm³ being a lower-limit estimate. [In obtaining ΔP_0^{120} from the area under the $\epsilon''(\bar{\nu})$ vs. $\ln \bar{\nu}$ curve, the ϵ'' at the low-frequency end of this frequency region was taken to be zero at ~0.05 cm⁻¹, the result of linearly extrapolating the microwave losses observed at 1, 0.3, and 0.1 cm⁻¹. For Al(acac)₃, this procedure, which deletes the area under the extreme low-frequency wing associated with the Cole-Cole form of the absorption curve, has the effect of reducing the ΔP_0^{120} value by ~3 cm³.]

In summary, by including the $\Delta P_0^{4.5}$ data along with the calculated changes, ΔP_0^{1600} , previously obtained,¹⁰ it is possible to account for the large observed differences ($P_{RF} - P_{VF}$) as due to practically continuous absorption over a very wide frequency range; see column 13.

Origin of the Microwave Absorption. A great deal of evidence^{1–14} obtained from both structural and static polarization studies points to symmetrical (nonpolar) structures for the unsubstituted trisacetylacetonates being considered and consequently favors the assignment of the large ΔP_0^{VF} values to atomic polarization. The reader is referred to the literature for the relevant empirical data which requires zero permanent dipole moments for these molecules.^{1–4} The present data, taken in isolation, also support the absence of permanent polarity in these systems. In this regard, the following points are pertinent.

(1) The relaxation times displayed by the unsubstituted chelates are obviously too short to be associated with molecular rotation. The $\bar{\nu}$ corresponding to maximum absorption for relaxation governed by molecular rotational diffusion would certainly not be above ~0.04 cm⁻¹ ($\tau \sim 130$ ps) for these compounds.^{7,9} In contrast, the magnitude of the τ values found for the permanently dipolar molecules, H(acac) and Al(acacF₃)₃ (6.0 and 159 ps,

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respectively), is consistent with dipole orientation predominantly via molecular rotation⁹ (based on comparisons made with polar molecules of similar size and shape). Such a relaxation process would be anticipated for both these compounds since they should behave as essentially rigid dipoles. [H(acac) is mostly in the intramolecularly H-bonded enol form in benzene solution.²⁶] The τ values of the unsubstituted chelates are not even up to the value observed for the much smaller H(acac) molecule, let alone the value which would be expected for overall molecular rotation.

(2) Internal rotation can be eliminated as a possible relaxation mechanism because these molecules, even if they were permanently polar, lack the type of polar groupings capable of orienting in the applied field by internal rotation in the "usual" sense.

(3) A permanent moment of 1.1 D has been assigned to Al(acac)₃ by Nelson and White.²⁷ This value corresponds to the difference between the radio frequency and 29.7-cm⁻¹ polarizations observed for this compound (24.7 cm³), the latter being taken to be orientation polarization.²⁷ These workers have pictured the minimum potential energy configuration consistent with this moment as one in which the Al atom is displaced from the plane of the three C and two O atoms; i.e., each ring has two minima of potential energy vs. conformation. In addition, they interpreted the short relaxation times previously estimated for Al(acac)₃⁷ in terms of torsional jumps from one polar conformation to another. By implication, the other unsubstituted acetylacetonates were presumed to display the same relaxation mechanism. The temperature-independent static polarizations of these molecules argues against such an interpretation since inversion between two asymmetric conformations would result in a P_{RF} inversely proportional to temperature. Drops in static polarization of ~ 10 cm³ from 25 to 225 °C would be expected considering the differences ($P_{RF} - P_{29.7}$) observed for these systems by Haigh and Sutton.⁸ No such decreases have been observed. [The measured P_{RF} values in the gas phase² (~ 225 °C) and in solution³ (25 °C) agree to within 1–4 cm³ mol⁻¹.] Also, a refinement of the crystal structure of Fe(acac)₃ shows the six-membered rings to be completely planar.^{11,14} It is to be noted that while X-ray results obtained for the other trisacetylacetonates¹³ do not exclude the possibility that the metal atom may deviate from the plane of the chelate ring, the data do not require bent chelate rings.^{8,10} The general conclusion is that while these molecules do indeed possess considerable flexibility at the metal, any bending which might be present in the solid structure is due to crystal packing (steric) effects and not to double potential wells in the isolated molecule. In view of the foregoing discussion, it is concluded that the observed microwave losses are not relaxation losses involving permanent dipoles. Concerning other alternatives, the following should be noted.

(4) The losses are certainly not a reflection of long-wavelength tails of vibrational, infrared absorption bands. Not only do the measurements definitely establish the maximum absorption to be in the microwave region but, in addition, the losses at 24.4 and 9.3 GHz were previously shown to decrease with increase in temperature.^{5,7} An increase of the loss in the low-frequency tail would be expected for absorption from such a cause.²⁸

(5) The losses cannot be explained as arising from molecules (with nonpolar equilibrium configurations) excited in degenerate vibrational states. While such molecules have been shown to possess effective dipole moments²⁹ which can interact with uniform electric fields, the magnitude of the present absorption (associated with apparent moments of ~ 1.0 to 1.6 D) is much too great to be reconciled with such an effect. For example, the effective dipole moment connected with the vibrationally induced rotational absorption of PF₅ has been found to be 1.3×10^{-3} D.³⁰

(6) The molecular distortion or "collisional interaction" hypothesis³¹ (in which the dipole moment and relaxation time arise

from environmental conditions unique to the liquid state) has been suggested by Angel¹⁵ to account for the excess polarization and the microwave absorption exhibited by Al(acac)₃ in benzene solution. While it has been somewhat successful in explaining the small dielectric losses shown by benzene and several other nondipolar liquids,^{32,33} it is not tenable for the Al(acac)₃ system on several counts. In terms of this theory, the microwave absorption is caused by translational relaxation of temporary dipoles induced in polarizable molecules by molecular electric fields evoked by surrounding neighbors. If local molecular configurations unique to the dissolved state of Al(acac)₃ contribute to the static polarization, a large difference between the vapor and solution P_{RF} 's of this compound would be expected. For example, a contribution of ~ 25 cm³ to the solution P_{RF} of Al(acac)₃ (corresponding to an effective moment of 1.1 D) dispersing with a τ of 1.9 ps is consistent with the microwave loss data. A difference of this magnitude would have been easily detected. Actually, the P_{RF} 's in the gas phase² and in solution³ agree to within 3 cm³ for this compound. This same argument applies to the other unsubstituted chelates investigated. In no case are the unusually large P_{RF} values peculiar to the condensed phase;^{2,3} see Table III. In any event, the effective moment values (1.0 to 1.6 D) are simply too large to be realistically interpreted in terms of multipole-induced dipoles between collision partners. In fact, attempts to explain the microwave absorption of nondipolar liquids as having its origins in a quadrupole-induced dipole appearing in the molecules have been modestly successful only for cases where the effective dipole moments are very small, ~ 0.1 D.^{32,33} In addition, it has been shown that the extremely low microwave losses which might conceivably result from such intermolecular processes would be causally associated with accompanying collision-induced submillimeter absorption.³¹ While these systems do show absorption between 20 and 100 cm⁻¹, convincing arguments have been given by Haigh et al.¹⁰ showing that this absorption is due primarily to molecular vibrations, like that exhibited at higher frequencies.¹⁶

In summary, the balance of evidence is strongly in favor of the microwave loss being associated with intramolecular polarization not due to the ordering of permanent dipole moment components. Beyond this conclusion, little of an unequivocal nature can be said about the nature of the internal motions actually involved in the relaxation process. Consequently, the following discussion is to be taken in the latter vein.

The pertinent oscillation(s) would have to be of unusually low frequency. In this context, we speculate that vibrations of the rings, as units, relative to the remainder of the molecule may be responsible for the microwave dispersion. This speculation appears to be plausible on the following grounds. (1) X-ray,^{11–14} intramolecular ligand exchange,^{34–38} and far-infrared^{10,15} investigations show these chelates to possess a marked degree of flexibility. (2) It can be reasonably assumed that the lowest lying vibrations are bending modes of the rings about the metal atom as a center. The bonds to the metal atom are very polar in character and therefore relatively small force constants and large effective moment values can be anticipated for such motions. (3) The relaxational character of the absorption is consistent with a mechanism involving highly damped, low-frequency oscillators.^{39–43} As pointed out by Haigh

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and Sutton,⁸ very low-frequency bending modes of the large chelate rings about the O...O vector (controlled by a single-well potential function) would necessarily require movements of high amplitude on the part of the outer atoms and, therefore, could very well be heavily damped in solution. Such a collisionally damped process is compatible with both the temperature-independent ΔP_0^{VF} values and the previously observed decrease of loss with temperature.^{5,7}

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(Collision damping, while not affecting the polarizations at visible and radio frequencies, would greatly modify the form of the dispersion and absorption curves.^{8,9}) In conclusion, although a microwave dispersion of polarization associated with vibrational deformations is rather unusual, this speculation appears to best explain the dielectric behavior when the latter is contemplated in the light of previous observations, notably those from non-dielectric studies.

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Registry No. Al(acacF₃)₃, 14354-59-7; Cr(acac)₃, 21679-31-2; Fe(acac)₃, 14024-18-1; Al(acac)₃, 13963-57-0; Co(acac)₃, 21679-46-9; H(acac), 123-54-6.

Gas-Phase Organometallic Chemistry: Chain-Length Effects

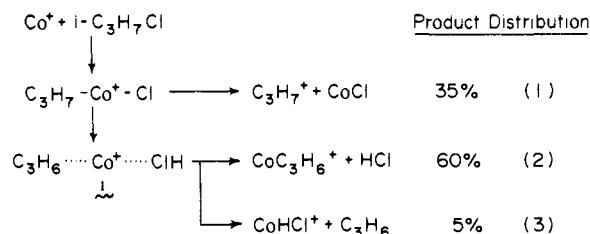
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Abstract: The gas-phase chemistry of Co⁺ with a series of 1-chloro normal alkanes and alcohols with the alkyl chain length varying from three to eight carbon atoms is presented. In the case of chloroalkanes, as the chain length increases, metal ion insertion into internal C-C bonds becomes preferred over that into the C-Cl bond which is the dominant site of insertion for smaller chloroalkanes. The cobalt ion exhibits a much richer chemistry with alcohols by inserting into almost every skeletal C-C bond. A model suggesting metal-carbon atom interactions via cyclic intermediates leading to insertion into C-C bonds at specific distances from the initial site of complexation is used to account for the observed products for alcohols. This may also occur to a lesser extent for the chloroalkanes. The order of preference for the metal insertion is also deduced from these experiments and is contrasted with that of the corresponding alkanes. Trends in the relative probabilities for H shifts from alkyl groups and chloro- and hydroxyalkyl groups are discussed, and H shifts other than β -H shifts are also suggested.

In the past several years a considerable number of studies concerning the chemistry/reactivity of metal and metal-containing ions with organic molecules have appeared in the literature. These studies, performed using ion cyclotron resonance (ICR) spectrometry,¹ Fourier transform mass spectrometry (FTMS),² and ion beam techniques³ have provided thermodynamic, kinetic, and mechanistic information concerning gas-phase organometallic chemistry.

In 1976, Allison and Ridge⁴ suggested a metal insertion/ β -H shift/competitive ligand loss reaction sequence for explaining the chemistry of gas-phase transition metal ions such as Fe⁺, Co⁺, and Ni⁺ with saturated, monofunctional organic molecules. For example, Co⁺ (which can be formed by electron impact on Co(CO)₃NO) reacts with 2-chloropropane⁵ by first inserting into



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the C-Cl bond. This intermediate can undergo charge transfer and fragment, or a β -H shift can occur, forming two ligands, propene and HCl. Subsequent dissociation of this complex accounts for the major fraction of the observed products.

This mechanism can be used to explain reported reactions such as dehydration of alcohols⁵ and dehydrohalogenation of alkyl halides.⁵ The mechanism can also be used to explain the chemistry of transition metal ions with most other organic molecules such as ketones^{1c,6} and alkanes.^{3a,7,8} In the case of small ketones,^{1c,6} each R-COR bond is the preferred site of metal insertion, while in the case of alkanes, insertion into C-C bonds and to a lesser extent, C-H bonds, appears to lead to the majority of the products.^{7,8}

Based on the chemistry reported to date, one may expect an ion such as Co⁺ to dehydrate all alcohols. In the case of 1-butanol,⁹ this was observed; however, insertion into C-C bonds also occurs. That is, 1-butanol exhibits both "alcohol-like" chemistry and "alkane-like" chemistry. There are other reported cases in which, as the alkyl chain length of a monofunctional organic molecule increases, reactions due to M⁺ insertion into C-C bonds of the alkyl chain occur in addition to insertion processes "typical" of the functional group. For example, in the chemistry of Fe⁺ with 2-pentanone, 20% of the products are due to insertion into a C-C bond^{1c} (Scheme I). Also, in the case of nitroalkanes,¹⁰ as the alkyl chain length increases, more reactions involving metal insertion into C-C bonds, i.e., away from the polar functional group, are observed.

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