esses. When O_2 was in excess, oxidation to B_2O_3 and H_2 occurred, but when B_2H_6 was in excess, decomposition of B_2H_6 became important. Pyrolysis must become more rapid than the oxidation process under these conditions since some O_2 remained after the explosion. This type of decomposition of B_2H_6, initiated by another exothermic reaction, in this case the explosive oxidation of B_2H_6, has been observed previously. Gunn and Green[9] noted that the decomposition B_2H_6 was initiated by the explosive decomposition of stibine. The $H_2B_2O_3$ observed must arise from a reaction of O_2 with boroxine[10]

$$H_3B_3O_3(g) + \frac{1}{2}O_2(g) \longrightarrow$$
$$H_2B_2O_3(g) + \frac{1}{6}B_2H_6(g) + \frac{1}{3}B_2O_3(s) \quad (3)$$
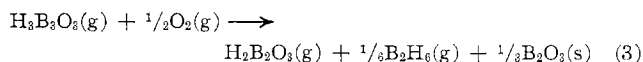
In most cases it was found that the presence of solid deposits produced on the wall of the reaction vessel did not notably affect the yield of $H_3B_3O_3$ obtained in a subsequent run in the same vessel. However, it was noted that a buildup of these deposits tended to inhibit initiation of the reaction by the electrical discharge.

This preparation of $H_3B_3O_3$ involving only the readily available B_2H_6 and O_2 as starting materials is more convenient than the high-temperature procedure or the use of B_5H_9 which is usually obtained by controlled pyrolysis of B_2H_6. Initiation of the reaction, using an electrical discharge rather than heat, avoids a complication due to the unpredictability of the explosion limits for these reactions. This method also affords an easy route to $H_2B_2O_3$ by reaction 3. Preferential isotopic labeling of the oxygen positions in $H_2B_2O_3$ is possible by using different isotopic species of oxygen in the initial preparation of $H_3B_3O_3$ and further reaction with labeled O_2 to obtain either H_2B_2-$^{16}O^{18}O_2$ or $H_2B_2^{18}O^{16}O_2$.

(9) S. R. Gunn and L. G. Green, *J. Phys. Chem.*, **65**, 779 (1961).
(10) L. Barton, S. K. Wason, and R. F. Porter, *ibid.*, **69**, 3160 (1965).

Electric Moments of Certain Substituted Tris(acetylacetonato)chromium(III) Compounds

BY ROBERT HENRY BROOK[1] AND HENRY FREISER

There has been considerable interest in recent years in the nature of the bonding in the chelate ring of β-diketones. Calvin and Wilson[2] explained the greater stability of Cu(II) chelates of β-diketones over those of salicylaldehydes in terms of the stabilizing influence

(1) NSF Undergraduate Research Participant 1963–1964.
(2) M. Calvin and K. W. Wilson, *J. Am. Chem. Soc.*, **67**, 2003 (1945).

of benzenoid resonance in the chelate ring. This view was strengthened by the determination, by X-ray crystallography,[3] of the planarity, C_{2v} symmetry, as well as of the 1.39-A distance of C–C atoms of the chelate ring of tris(acetylacetonato)iron(III). Cotton and Holm[4] have questioned the validity of the presence of "aromaticity" in these chelate rings on the basis of charge-transfer spectra and pmr measurements of a wide variety of acetylacetonates. Collman,[5] on the other hand, using arguments based on the chemical reactivity of acetylacetonates, considers that the term "quasiaromatic" applied to these chelate rings is important in the description of the chemical behavior of the acetylacetonate chelates.

Since the values of C–Cl and C–NO_2 group moments are sensitive to the nature of the carbon atom [C_{aliph}–Cl ($\mu = 1.93$ D.), C_{aliph}–NO_2 ($\mu = 3.2$ D.), C_{arom}–Cl ($\mu = 1.57$ D.), C_{arom}–NO_2 ($\mu = 4.0$ D.)],[6] this study was undertaken to shed further light on the nature of the chelate ring in tris(acetylacetonato)chromium(III).

In order to calculate the electric moment from dielectric polarization data obtained in solution, it is necessary to evaluate both the electronic and atomic polarizations. In most cases, where atomic polarization is relatively small, these two terms are combined and evaluated as the molar refraction at the Na D line.[7]

With compounds, such as the acetylacetone chelates, that have abnormally large atomic polarization values, solution measurements usually give meaningless results[8] when this procedure is followed.

In this work, we have attempted to overcome this problem in the following way. Reasoning that the atomic polarization of a closely related series of compounds would vary in a regular manner, we have assumed the induced polarization (the sum of electronic and atomic polarizations) values of the mono- and disubstituted chelates are evenly spaced between the values of the un- and trisubstituted chelates. Since the un- and trisubstituted chelates are symmetrical, their electric moments are considered to be zero so that their measured total dielectric polarizations are equal to their induced polarizations. Thus, with 6.5- and 25.0-cc/mole differences in total polarization between tris(acetylacetonato)chromium(III) and its trichloro and trinitro analogs, respectively, the induced polarizations of the mono- and disubstituted compounds are obtained by adding $\frac{1}{3}$ and $\frac{2}{3}$, respectively, of these differences to the induced polarization of the tris(acetylacetonato)chromium(III). Even in the case of the nitro series, where the increment is 8.25 cc/mole, the

(3) R. B. Roof, Jr., *Acta Cryst.*, **9**, 781 (1956).
(4) F. A. Cotton and R. H. Holm, *J. Am. Chem. Soc.*, **80**, 5660 (1960).
(5) J. P. Collman, R. A. Moss, S. D. Goldby, and W. S. Trahanovsky, *Chem. Ind.* (London), 1213 (1960); J. P. Collman, Advances in Chemistry Series, No. 37, American Chemical Society, Washington, D. C., 1963.
(6) These were taken from μ measurements in benzene for several typical alkyl or aryl compounds (compilation of dipole moments by L. R. Wesson, Laboratory for Insulation Research, Massachusetts Institute of Technology, 1946).
(7) C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., Inc., New York, N. Y., 1955.
(8) A. E. Finn, G. C. Hampson, and L. E. Sutton, *J. Chem. Soc.*, 1254 (1938); I. E. Coop and L. E. Sutton, *ibid.*, 1269 (1938).

maximum error likely to arise from this assumption (4.0 cc?) cannot affect the calculated value of the electric moment by more than approximately 0.02 D. The electric moments were then evaluated from the difference between the total and induced polarizations in the usual manner[7] (Table I).

TABLE I
DIELECTRIC POLARIZATION DATA IN BENZENE AT 30.0°

$10^3 f_2$	ϵ	d	P_2

Tris(acetylacetonato)chromium(III),
$P_E + P_A = 133$, $\mu = 0.00$ D.

$10^3 f_2$	ϵ	d	P_2
0.000	2.2627	0.86823	(133)
3.106	2.2731	0.87219	129.8
4.691	2.2784	0.87421	129.7
5.031	2.2811	0.87467	134.1
6.852	2.2899	0.87693	139.1

Bis(acetyacetonato)mono(3-chloroacetylacetonato)-chromium(III), $P_E + P_A = 131$, $\mu = 1.73$ D.

$10^3 f_2$	ϵ	d	P_2
0.000	2.2627	0.86823	(191)
2.135	2.2791	0.87156	197.5
3.738	2.2895	0.87423	187.9
4.232	2.2923	0.87463	188.2

Mono(acetylacetonato)bis(3-chloroacetylacetonato)-chromium(III), $P_E + P_A = 128$, $\mu = 1.65$ D.

$10^3 f_2$	ϵ	d	P_2
0.000	2.2627	0.86823	(182)
8.677	2.2684	0.86992	180.6
15.511	2.2724	0.87116	181.7
26.119	2.2898	0.87308	182.8

Tris(3-chloroacetylacetonato)chromium(III), $P_E + P_A = 126$

$10^3 f_2$	ϵ	d	P_2
0.000	2.2627	0.86823	(126)
10.978	2.2655	0.87064	126.5
21.881	2.2687	0.87280	131.0
33.629	2.2698	0.87523	121.7

Bis(acetylacetonato)mono(3-nitroacetylacetonato)-chromium(III), $P_E + P_A = 141$, $\mu = 3.99$ D.

$10^3 f_2$	ϵ	d	P_2
0.000	2.2627	0.86823	(462)
0.9015	2.2845	0.86970	442.6
1.418	2.2987	0.87054	460.1
2.015	2.3147	0.87148	465.2
2.731	2.3361	0.87263	479.5

Mono(acetylacetonato)bis(3-nitroacetylacetonato)-chromium(III), $P_E + P_A = 150$, $\mu = 3.97$ D.

$10^3 f_2$	ϵ	d	P_2
0.000	2.2627	0.86823	(466)
0.9682	2.2779	0.87019	473.1
1.492	2.3008	0.8711	467.9
1.969	2.3130	0.87205	466.9

Tris(3-nitroacetylacetonato)chromium(III), $P_E + P_A = 158$, $\mu = 0.00$ D.

$10^3 f_2$	ϵ	d	P_2
0.000	2.2627	0.86823	(158.2)
1.664	2.2698	0.87205	158.0
1.899	2.2703	0.87261	158.7
2.131	2.2718	0.87314	157.9

The value of the moment of the mononitrated chelate, 3.99 D., is much closer to the value observed when the nitro group is bonded to aromatic (or unsaturated) carbon atoms than to those for aliphatic carbon atoms. This is compatible with the hypothesis of aromatic or pseudo-aromatic character of the chelate rings. In the case of the monochlorinated chelate, however, the value found, 1.73 D., is intermediate between the values for the aliphatic and aromatic cases. This might suggest that a substituent capable of withdrawing electron density *via* conjugation can elicit a greater back π-bonding response from the metal ion that can a substituent which is electron donating *via* conjugative interaction. This highly speculative suggestion should be tested with a wider variety of substituted chelates.

The values of the moments of both pairs of mono- and disubstituted chelates are identical, within experimental error. This would be predicted on the basis of vector addition of the C–X (X = Cl or NO₂) moments and, hence, indicates that no significant interaction occurs across chelate rings between either two chloro or nitro groups. A more sensitive test of cross-chelate ring interaction would be to observe whether there would be any significant deviation from vector additivity in a disubstituted chelate having one electron-releasing (say Cl) and one electron-withdrawing (say NO₂) group.

Experimental Section

Materials.—The substituted chromium acetylacetonates were prepared and purified by Professor J. P. Collman. These were used without further treatment.

Measurements and Calculations.—The procedure used in this study has been previously described.[9] The measurements are summarized in Table I where the dielectric constants, ϵ, and the densities, d, of benzene solutions containing mole fraction f_2 of the substance indicated are given as well as the calculated value of the molar polarization, $P_E + P_A$, the sum of the electronic and atomic polarizations, which are calculated by linear extrapolation of the P_2 values between the unsubstituted and trisubstituted chelates. The dipole moment, μ, is calculated in the usual way.

(9) R. K. Keswani and H. Freiser, *J. Am. Chem. Soc.*, **71**, 218 (1949).

Complexes of Trichlorostannate(II) with Group Ib Metals

BY J. A. DILTS AND M. P. JOHNSON

There has been a considerable interest recently in the formation of metal complexes containing the $SnCl_3^-$ species as a ligand.[1] The majority of these complexes has involved second- and third-row transition metal ions with d⁶ and d⁸ electronic configurations. Of the

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