

CORRELATION OF THE IONIZATION POTENTIALS OF PSEUDO-AROMATIC METAL COMPLEXES WITH HAMMETT'S SUBSTITUENT CONSTANTS—II

CHROMIUM ACETYLACETONATES*

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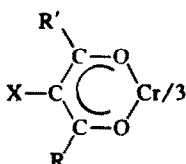
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Abstract—The first ionization potentials, E_1 , of substituted chromium(III) acetylacetonates are found to be a linear function of the sum of Hammett's σ_m and σ_p constants for substituents in various positions of the pseudo-aromatic rings, relative to the Cr atom. The equation for the regression is $E_1 = 7.40 + 0.380\Sigma\sigma \pm 0.02 \text{ eV}$, where 7.40 eV is the interpolated value for the tris-Cr chelate of malonaldehyde, and the slope of the correlation line is 0.380. From the value of the slope and other considerations, it is deduced that the ejected electron is an unpaired d_{xy} Cr electron in a $t_{2g}MO$.

We wish to report the second correlation of molecular ionization potentials of pseudo aromatic organometallic chelate compounds with a set of substituent constants. Recently, we have demonstrated that the ionization energies of the copper acetylacetonates¹ and many series of organic compounds² are linear functions, respectively, of Hammett's substituent constants³ and of Taft's inductive⁴ substituent constants, σ_I . This permits one to calculate by means of a simple single-parameter equation, to a good approximation, values of the ionization potentials of compounds which yield a low abundance of the primary cation radical, or are difficult to obtain in a purified state, or vaporize only with decomposition.

We show here that the ionization energies of substituted tris (β -keto enolate) complexes of Cr(III),



are a linear function of Hammett's substituent constants.³ The first ionization energy of these chelates corresponds

to the removal of an electron from the highest occupied molecular orbital,⁵ presumably from the π -system or one of the three unpaired electrons in the d_{xy} -type orbitals⁶ of Cr, remaining after formation of its hybrid d^2sp^3 orbitals.

It is quite obvious that electron releasing alkyl groups should increase the electron density of the heteroaromatic ring and thereby facilitate electron removal, whereas electron-withdrawing groups such as $-\text{NO}_2$ and $-\text{Cl}$ should increase the requisite ionization energy, as well as decrease the basicity and gas-phase proton affinity.⁷

It is seen from the position of the substituents in the above formulation that the appropriate substituent constants for R and R' should be the σ_m parameters derived originally for *meta* substituents on the benzene ring,³ and the corresponding σ_p constants for X. It should be noted that σ_m , like σ_I , is a measure of the inductive influence of a substituent.⁴ Table 1 presents the $\Sigma\sigma$ values (summed over all nine substituents in the three rings) together with the experimentally observed⁸ electron impact ionization potentials (E_1) for a series of the chromium (III) chelates. Despite contentions to the contrary for the copper⁹ and chromium¹⁰ acetylacetonates, a plot of the E_1 values vs $\Sigma\sigma$ results in an excellent straight line, the equation for which is:

$$E_{\text{Cr-R}} = E_{\text{Cr-H}} + a\Sigma\sigma \quad (1)$$

The slope, a , is found to be 0.380 eV and the value $E_{\text{Cr-H}}$,

*Part I should be considered as Ref. 1.

Table 1. Ring substituents and their corresponding $\Sigma\sigma$ values, along with experimental and calculated ionization potentials of various substituted acetylacetonatochromium(III) derivatives

Compound No.	Ring Substituents			E_1 (eV)	
	R-R and R' (all rings)	R-X (3 separate rings)	$\Sigma\sigma^a$	E_{exp}^{1b}	Eq. (2)
1	CH_3	H, H, H	-0.181	7.39	7.33
2	CH_3	H, H, NO_2	+0.60	7.61	7.63
3	CH_3	H, NO_2 , NO_2	+1.38	7.91	7.92
4	CH_3	NO_2 , NO_2 , NO_2	+2.15	8.22	8.22
5	CH_3	Cl, Cl, Cl	+0.49	— ^c	7.59
6	H	H, H, H	0	— ^c	7.40
7	<i>i</i> -Pr	H, H, H	-0.42	— ^c	7.24
8	<i>i</i> -Pr	NO_2 , NO_2 , NO_2	+1.91	— ^c	8.13

^a σ_m values from Ref. 3c; H = 0.0; Me = -0.03; from Ref. 24; *i*-Pr = -0.07;

^b σ_p values from Ref. 3a; H = 0.0; NO_2 = +0.778; Cl = +0.227. ^c E_1 values from

Ref. 8. ^cExperimental values not available.

which corresponds to the tris-Cr chelate of malonaldehyde, $\text{CH}_2(\text{CHO})_2$, is by interpolation 7.40 eV, and therefore we have

$$E_{\text{Cr-R}} = 7.40 + 0.380 \Sigma \sigma \pm 0.02 \text{ eV.} \quad (2)$$

This correlation ($r = 0.998$) indicates that the effect of substituents on the electron density in the chelate ring and at the Cr atom is primarily an inductive one, and lends support to the view that these chelates behave as heteroaromatic compounds.¹¹

In Table 1 we show a comparison between the experimentally obtained ionization energies and those values of E_i calculated by means of eqn (2). The agreement is seen to be very good. Also included in Table 1 are the interpolated E_i values for the tris-Cr malonaldehyde complex (cpd. 6) and the calculated E_i values for tris-diisopropylacetylacetonatochromium(III) (cpd. 7), tris-3, 5-diisopropyl-4-nitroacetylacetonatochromium(III) (cpd. 8), and the tris-4-chloroacetylacetonato complex (cpd. 5), for none of which experimental data are available†.

Although the a constant has units of energy (eV), it is analogous to the reaction constant, ρ , and reflects and susceptibility of the reaction site, the π -system or the $d_{xy}(t_{2g})$ chromium electron to substituent effects.

The a value of 0.380 obtained here may be compared to the corresponding a value of the E_i 's of the bisacetylacetonates of Cu(II) which was found¹ to be 1.00 and of alkylbenzenes¹² and alkylpyridines¹² which we have found to be 4.41 and 4.90 eV, respectively. Substitution of NO_2 for H in benzene leads to an increase of 0.68 eV (9.92-9.24),¹³ whereas replacement of the three p -H atoms of the Cr chelates by three p - NO_2 groups results in a raising of the E_i by 0.83 eV (8.22-7.39) or 0.28 eV/ NO_2 group. This fact, in addition to the much smaller a value for the Cr series compared to the Cu series and the benzene and pyridine series, indicates that the Cr chelates are considerably less sensitive to inductive effects than any of the latter.

The unpaired d_{xy} Cr electron, in a t_{2g} MO, is the one almost certainly expelled from its orbital, which was thought to be delocalized¹⁴ over the entire π -system, encompassing the Cr atom and all three chelate rings. Loss of the ionized electron by the π -system of the rings would be in accord with Barnum's HMO calculations¹⁵ and with the view expressed by Pearson *et al.*¹⁶ that ionization of acetylacetonates involves an orbital spread over the ligand. There is also evidence from NMR data on other paramagnetic acetylacetonates in which the spin density of the unpaired electron is delocalized and finds its way to an extent of around 10% into the spin density of the *para* H atoms, shifting the resonance frequency compared to the diamagnetic complexes.¹⁷ Since there are sixteen atoms in the 3-ring system of the Cr chelate, one might assume that approximately 5-6% of the spin density of the 3 unpaired t_{2g} electrons (d_{xy} , d_{xz} , d_{yz}) might reside at each of the atoms in the rings.

On the other hand, there is much stronger, indeed unequivocal, evidence that the site of electron loss is from an orbital largely dominated by the Cr atom⁸: the fact that the correlation is obtained with the appropriate *meta* and

para substituent constants, that all substituents in the rings were given equal weights, and that the only atom equidistant from all the substituents is the Cr atom; the fact that the a value is only one-thirteenth of that obtained¹² in the pyridine correlation (a perfectly analogous situation) indicates that the reaction site is relatively distant from the substituents and cannot therefore be the π -system (compare $a_i = 28.0^{2b}$ for R_2O : but 14.0^{2b} for $\text{R}_2\text{C} = \text{O}$., where the electron in both cases is lost from a non-bonding oxygen lone pair); the fact that substitution of Cr for the enol H atom of acetylacetonate ($E_i = 8.87 \text{ eV}$)¹⁶ lowers the E_i , whereas a higher value would be expected if a ligand electron were lost, since Cr^{3+} withdraws electron density from the ring.

Additional evidence that the metallic center is most certainly the site of electron loss can be adduced from the oxidation of metallocenes and metal arenes where the ferrocenium, nickelocenium and *bis*-benzene chromium cations are thought to have the positive center at the metal atom.¹⁸ This view is also supported by data and arguments for Cr chelates given by Lloyd¹⁹ and by Evans *et al.*,²⁰ and for Cu chelates by McGarvey²¹; and finally by the analogous reaction of photoionization of chlorophyll where, in the "photoelectric" or "photoionization" theory²² of photosynthesis, much evidence has been amassed²³ for the central Mg atom as the site of initial electron loss.

REFERENCES

- ¹B. W. Levitt and L. S. Levitt, *J. Coord. Chem.* **3**, 187 (1973); *Chem. & Ind.* 302 (1974).
- ^{2a}L. S. Levitt and B. W. Levitt, *Ibid.*, 990 (1970); ^bB. W. Levitt and L. S. Levitt, *Experientia* **26**, 1183 (1970); ^cB. W. Levitt and L. S. Levitt, *Israel J. Chem.* **9**, 71 (1971); ^dL. S. Levitt and B. W. Levitt, *J. Org. Chem.* **37**, 332 (1972); ^eB. W. Levitt and L. S. Levitt, *Israel J. Chem.* **9**, 711 (1971); ^fL. S. Levitt and B. W. Levitt, *Chem. & Ind.* 132 (1973); ^gL. S. Levitt and C. Párkányi, *Int. J. Sulf. Chem.*, **8**, 329 (1973); ^hL. S. Levitt, B. W. Levitt and C. Párkányi, *Tetrahedron* **28**, 3369 (1972); ⁱL. S. Levitt, *Chem. & Ind.* 637 (1973); ^jH. Widing and L. S. Levitt, *Tetrahedron* **30**, 611 (1974); ^kL. S. Levitt and B. W. Levitt, *Ibid.*, **29**, 941 (1973); ^lB. W. Levitt and L. S. Levitt, *Chem. & Ind.* 185 (1973); ^mB. W. Levitt, H. Widing and L. S. Levitt, *Can. J. Chem.* **51**, 3963 (1973); ⁿB. W. Levitt and L. S. Levitt, *Chem. & Ind.* 724 (1973); ^oB. W. Levitt, H. Widing and L. S. Levitt, *Ibid.*, 793 (1973).
- ^{3a}L. P. Hammett, *Physical Organic Chemistry* (2nd Edn.), p. 356, McGraw-Hill, New York, (1970); ^bJ. Hine, *Physical Organic Chemistry*, (2nd Edn.), p. 89, McGraw-Hill, New York, (1962); ^cD. H. McDaniel and H. C. Brown, *J. Org. Chem.* **23**, 420 (1958); ^dS. K. Dayal, S. Ehrenson and R. W. Taft, Jr., *J. Am. Chem. Soc.* **94**, 9113 (1972).
- ⁴R. W. Taft and I. C. Lewis, *Tetrahedron* **5**, 210 (1959).
- ⁵T. Koopmans, *Physica* **1**, 104 (1933); J. C. Lorquet, *Rev. Mod. Phys.* **32**, 312 (1960); R. S. Mulliken, *J. Chem. Phys.* **3**, 564 (1935); *Phys. Rev.* **74**, 736 (1948).
- ⁶J. E. Huheey, *Inorganic Chemistry* Chap. 8, Harper & Row, New York, (1972).
- ⁷L. S. Levitt and B. W. Levitt, *J. Phys. Chem.* **74**, 1812 (1970); *Tetrahedron* **27**, 3777 (1971).
- ⁸M. M. Bursey and P. F. Rogerson, *Inorg. Chem.* **9**, 676 (1970).
- ⁹H. F. Holtzclaw, Jr., L. Lintvedt, H. E. Baumgarten, R. G. Parker, M. M. Bursey and P. F. Rogerson, *J. Am. Chem. Soc.* **91**, 3774 (1969).
- ¹⁰G. M. Bancroft, C. Reichert, J. B. Westmore and H. D. Gesser, *Inorg. Chem.* **8**, 474 (1969).
- ¹¹J. P. Collman, R. A. Moss, H. Maltz and C. C. Heindel, *J. Am. Chem. Soc.* **83**, 531 (1961); R. H. Holm and F. A. Cotton, *Ibid.* **80**, 5658 (1958).
- ¹²L. S. Levitt, B. W. Levitt and C. Párkányi, unpublished work.
- ¹³K. Watanabe, T. Nakayama and J. Mottl, *J. Quant. Spect. Rad. Transfer*, **2**, 369 (1962).

†Not included in Table 1 is the value for the tris-trifluoromethyl substituted complex for which the calculated E_i value is 8.5 eV, whereas the value reported¹⁹ is 9.5 eV, which is a vertical E_i and was obtained by a different method (PES).

- ¹⁴A. A. Viček, *Prog. Inorg. Chem.* **5**, 370 (1963).
- ¹⁵D. W. Barnum, *J. Inorg. Nucl. Chem.* **21**, 221 (1961); **22**, 183 (1961). But see also E. A. Magnusson, K. A. Thomson and A. G. Wedd, *Chem. Comm.* 842 (1969).
- ¹⁶S. M. Schildcrout, R. G. Pearson and F. E. Stafford, *J. Am. Chem. Soc.* **90**, 4006 (1968).
- ¹⁷M. C. Day and J. Selbin, *Theoretical Inorganic Chemistry* (2nd Edn.), p. 436. Reinhold (1969).
- ¹⁸M. Cais and M. S. Lupin, *Adv. Organometallic Chem.* **8**, 211 (1970).
- ¹⁹D. R. Lloyd, *Chem. Comm.* 868 (1970); *Int. J. Mass Spectr. Ion Phys.* **4**, 500 (1970).
- ²⁰S. Evans, A. Hamnett and A. F. Orchard, *J. Coord. Chem.* **2**, 57 (1972).
- ²¹A. H. Maki and B. R. McGarvey, *J. Chem. Phys.* **29**, 31 (1958).
- ²²L. S. Levitt, *Science* **118**, 696 (1953).
- ²³L. S. Levitt, *Ibid.*, **120**, 33 (1954); *Bull. Amer. Phys. Soc. II*, **4**, 376 (1959); *J. Chem. Phys.* **28**, 515 (1958); *Experientia* **15**, 16 (1959); *Appl. Spectros* **14**, 161 (1960).
- ²⁴M. Charton, *J. Org. Chem.* **30**, 969 (1965).