454. *Correlation of Reaction Rates with Electronic Absorption Spectra for a Series of Trisoxalates of Tervalent Metals.*

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Simple crystal-field calculations of the contributions of the crystal-field stabilisation energy (CFSE) to the activation energy for a series of tris-oxalato-complexes of tervalent transition metals have been made by using values of the energy parameter Dq derived from absorption spectra. This has led to an " order of reactivity " which has been compared with the experimental results. Qualitative agreement has been found.

THE interpretation of the reactivity of octahedral complexes in terms of the electron population of the d-orbitals of the central metal has become possible through the use of simple crystal-field theory.[1] On this model, the octahedron is considered to react by one of two paths: (1) a dissociative path leading to a five-co-ordinate transition state, assumed, for the purposes of calculation, to be a tetragonal pyramid; or (2) an associative path giving a seven-co-ordinate transition state; in this case the model of Hush[2] has been used. The crystal-field stabilisation energy (CFSE) can be calculated for the original reactant and estimated for the transition state, on the assumption that the energy parameter Dq is unaltered. The difference in energy must be one of the terms contributing to the activation energy. It will not, however, be the only energy term, and hence the calculated activation energy will differ from that observed. To obtain agreement, the hydration energies, bond energies, etc., would have to be included.

If all these factors could be kept constant, it should be possible to predict an " order of reactivity " for a series of complexes of different metals with the same ligand. We have chosen to test the predictions on the series of trisoxalato-complexes of tervalent transition metals. This series consists of eight complexes that can be isolated and characterised, they are listed in Table 1.

TABLE 1.

Colours and magnetic moments for a series of trisoxalato-complexes of tervalent transition metals (Ox = oxalate).

Complex	Colour	Magnetic moment (B.M.)	Ref(s).	Complex	Colour	Magnetic moment (B.M.)	Ref(s).
VOx_3^{3-} ...	green	2·80	3	$CoOx_3^{3-}$ ...	green	0	7
$CrOx_3^{3-}$ ...	green	4·08	4	$RuOx_3^{3-}$ ...	green	2·13	8, 9
$MnOx_3^{3-}$ ...	red-violet	4·81, 4·96	5, 7	$RhOx_3^{3-}$ ...	orange	0	10
$FeOx_3^{3-}$ ...	green	5·98	6	$IrOx_3^{3-}$ ...	yellow	0	10

In such a series, the size and charge of the complex-ion are kept as constant as possible, so that energy terms depending on these factors should be almost constant throughout. Simple crystal-field arguments, however, neglect the possibility of covalent bonding between the central metal and the ligand. Such bonding will certainly occur. This is shown by the considerable decrease in the value of the Racah electron repulsion parameter (B) from that of the free ion.[11] The overall effect of some covalent bonding will be an

[1] Basolo and Pearson, " Mechanisms of Inorganic Reactions," Wiley, New York, 1958, p. 109.
[2] Hush, *Austral. J. Chem.*, 1962, **15**, 378.
[3] Figgis, Lewis, and Mabbs, *J.*, 1960, 2480.
[4] Rosenbohm, *Z. phys. Chem.*, 1919, **93**, 693.
[5] Goldenburg, *Trans. Faraday Soc.*, 1940, **36**, 847.
[6] Clark, Curtis, and Odell, *J.*, 1954, 63.
[7] Asmusson, " Magnetochemistry of Coordination Compounds," Jul. Gjellerups Forlag, Copenhagen, 1944, pp. 153 and 168.
[8] Dwyer and Sargeson, *J. Phys. Chem.*, 1956, **60**, 1331.
[9] Olliff and Odell, *J.*, 1964, 2467.
[10] Jørgensen, *Acta Chem. Scand.*, 1956, **10**, 518.
[11] Dunn, *J.*, 1959, 623.

increase in the observed value of Dq. If covalent bonding does occur, the energies associated with the making and breaking of the bonds will appear as contributions to the activation energy; the greater the degree of covalent bonding, the greater will be these contributions.

High values of Dq are usually associated with considerable electron delocalisation, *i.e.*, covalent bonding. Thus bond-making and -breaking contributions to the activation energy will be large when Dq is large.

<div align="center">EXPERIMENTAL</div>

The complexes were prepared by the standard methods in the literature (refs. in Table 1). Absorption spectra were obtained with a Shimadzu spectrophotometer.

<div align="center">RESULTS AND DISCUSSION</div>

Interpretation of the Ligand-field Spectra.—The d^4 *complexes* $MnOx_3^{3-}$. Trisoxalato-manganese(III) ions in solution undergo a rapid dissociation, to give finally the diaquo-bisoxalato-species.[12] This can be repressed by the addition of excess of free oxalate ion, when the predominant species is the red-purple trisoxalate. In agreement with Cartledge and Ericks,[12] a single broad maximum was found at *ca.* 500 mμ with a molar extinction coefficient (ε) of *ca.* 200. In the ground state the manganese ion will have the configuration $d_\epsilon^3 d_\gamma^1$ (^5E), and spin-allowed absorption will occur by excitation to the configuration $d_\epsilon^2 d_\gamma^2$ ($^5F_2$). The latter is the only excited state with maximum multiplicity. The energies of these levels have been given by Tanabe and Sugano[13] as:

$$d_\epsilon^3 d_\gamma^1 \ (^5E), \ -6Dq - 21B. \qquad d_\epsilon^2 d_\gamma^2 \ (^5F_2), \ 4Dq - 21B.$$

The excitation energy is thus $10Dq$, whence we can calculate $Dq = 2040$ cm.$^{-1}$.

A number of spin-forbidden transitions can be predicted but these have not been observed.

The d^6 *complexes*, $CoOx_3^{3-}$, $RhOx_3^{3-}$, *and* $IrOx_3^{3-}$. The absorption spectra of these compounds are as follows (where sh = shoulder).

	λ (mμ)	ν (cm.$^{-1}$)	ε		λ (mμ)	ν (cm.$^{-1}$)	ε
$CoOx_3^{3-}$	620	16,100	165	$RhOx_3^{3-}$	520	19,250	8
	420	23,800	218		398	25,100	290
$IrOx_3^{3}$	360	27,800	sh		330	30,300	sh

These d_6 complexes are analogous to the d^4 $MnOx_3^{3-}$ ion. They are all diamagnetic (or show weak temperature-independent paramagnetism)[7] in the ground state, and hence the configuration must be $d_\epsilon^6(^1A_1)$. The energy[13] of this state is $-24Dq - 16B + 8C$. Electron transitions will occur to the configuration $d_\epsilon^5 d_\gamma^1$, for which there are four states:

$$^3F_1, \ -14Dq - 16B + 5C. \qquad ^3F_2, \ -14Dq - 8B + 5C.$$
$$^1F_2, \ -14Dq + 7C. \qquad ^1F_1, \ -14Dq - 16B + 7C.$$

In two of the three spectra, two peaks having ε $\sim$200 are observed, and these can be attributed to the spin-allowed singlet transitions. The peaks will thus be separated by $16B$, giving the following values for B and Dq: $CoOx_3^{3-}$, $B = 480$ cm.$^{-1}$, $Dq = 1820$ cm.$^{-1}$; $RhOx_3^{3-}$, $B = 325$ cm.$^{-1}$, $Dq = 2650$ cm.$^{-1}$. As pointed out by Jørgensen,[10] Tanabe and Sugano's assumption of pure d orbitals is not really justified in these lower transition-series metals where paramagnetic resonance studies[14] have shown considerable mixing of the metal orbitals with ligand orbitals. However, it is probable that the values are of the correct order of magnitude. Using these values of B, and assuming a C/B ratio of 4·5, the value of Dq can be obtained.

The 520 mμ band (ε 8) in the spectrum of the rhodium complex will correspond to a

[12] Cartledge and Ericks, *J. Amer. Chem. Soc.*, 1936, **58**, 2065.
[13] Tanabe and Sugano, *J. Phys. Soc. Japan*, 1954, **9**, 753, 766.
[14] Griffiths and Owen, *Proc. Roy. Soc.*, 1954, *A*, **226**, 96.

transition to one of several possible triplet states, however, which triplet state is involved cannot be determined from the available data.

The iridium complex shows only one absorption band at 360 mμ. If a reasonable value * of 250 cm.$^{-1}$ is used for B, Dq can be calculated to be 2930 cm.$^{-1}$.

The d^5 *Complexes.* (a) $FeOx_3{}^{3-}$. The ground state is $d_\epsilon{}^3 d_\gamma{}^2$ ($^6A_1$) with energy $-35B$. Electron promotion to $d_\epsilon{}^2 d_\gamma{}^3$ involves the inversion of at least one spin, there being two quartet states ($^4F_1$ and $^4F_2$). Within the configuration $d_\epsilon{}^3 d_\gamma{}^2$ there will also be a number of further quartet levels ($^4F_2$, $^4E(2)$, $^4A_1$, $^4A_2$, $^4F_1$), the lowest of these being ^4E and $^4A_1$ with the same energy.

Parker [15] found only one absorption band attributable to the trisoxalato-ion, but Jørgensen [16] has found three bands at 10,700, 15,200, and 22,100 cm.$^{-1}$. Jørgensen's analysis [17] of these peaks gives: $Dq = 1370$ cm.$^{-1}$; $B = 740$ cm.$^{-1}$.

(b) $RuOx_3{}^{3-}$. The ground state in this complex has only one unpaired spin [8,9] corresponding to the configuration $d_\epsilon{}^5(^2F_2)$. Four absorption maxima are observed: 288 ($\epsilon_{corr.}$ 320); 375 ($\epsilon_{corr.}$ 350); 490 ($\epsilon_{corr.}$ 28); and 630 mμ ($\epsilon_{corr.}$ 11). The first two of these maxima can be interpreted [9] in terms of superimposition of spin-allowed bands, and the second two as spin-forbidden bands. On this basis we can calculate $Dq = 2870$ cm.$^{-1}$, and $B = 560$ cm.$^{-1}$.

The d^3 *complex*, $CrOx_3{}^{3-}$. Two peaks are observed at 565 mμ (17,700 cm.$^{-1}$) (ϵ 74) and 416 mμ (24,100 cm.$^{-1}$) (ϵ 98). The ground state is $d_\epsilon{}^3$ ($^4A_2$). Spin-allowed transitions occur from this state to the $^4F_2$ and $^4F_4$ levels of the $d_\epsilon{}^2 d_\gamma{}^1$ configuration, giving $Dq = 1770$ cm.$^{-1}$ and $B = 530$ cm.$^{-1}$.

The d^2 *complex*, $VOx_3{}^{3-}$. The vanadium complex was studied by Hartmann, Furlani, and Burger [18] who found two peaks at 16,300 and 23,500 cm.$^{-1}$. They interpreted the data in terms of octahedral symmetry with a trigonal perturbation. They have shown that the deviations from octahedral symmetry are small. On the assumption of complete octahedral symmetry, $Dq = 1810$ cm.$^{-1}$ and $B = 600$ cm.$^{-1}$.

The Dq and B values for all the complexes are summarised in Table 2.

TABLE 2.

Values of Dq and B for a series of trisoxalato-complexes of tervalent transition metals.

Complex	Dq (cm.$^{-1}$)	B (cm.$^{-1}$)	Complex	Dq (cm.$^{-1}$)	B (cm.$^{-1}$)
$MnOx_3{}^{3-}$	2040	—	$RhOx_3{}^{3-}$	2650	350
$FeOx_3{}^{3-}$	1370	740	$IrOx_3{}^{3-}$	2930	(250)
$RuOx_3{}^{3-}$	2870	560	$CrOx_3{}^{3-}$	1770	530
$CoOx_3{}^{3-}$	1820	500	$VOx_3{}^{3-}$	1810	600

Activation Energies.—Simple crystal-field arguments allow the calculation of crystal-field stabilisation energy (CFSE) differences between the ground state of the complex and postulated reaction intermediates,[1] from an initially octahedral complex. The form of the seven-fold intermediate has been the subject of calculations by Hush [2] who concludes that the most probable structure is one in which five ligands retain their normal positions, but positions 6 and 7 are out from the centres of two faces. It is also likely that these two bond lengths (R') will be different from the other five (R). For complexes of the oxalate type, this will mean some distortion of one oxalate group, which will be lessened if the bond length R' is increased from its normal value. Using the values of Dq obtained

* Ballhausen ("Introduction to Ligand Field Theory," McGraw-Hill, New York, 1962, pp. 277 and 281) has shown that B for $IrCl_6{}^{3-}$ is about 100 cm.$^{-1}$ less than for $RhCl_6{}^{3-}$ (180 and 290 cm.$^{-1}$). For $B = 200$ cm.$^{-1}$, $Dq = 2960$ cm.$^{-1}$ for $IrOx_3{}^{3-}$.

[15] Parker, *Trans. Faraday Soc.*, 1954, **50**, 1213.
[16] Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon, Oxford, 1962, p. 292.
[17] Ref. 16, p. 110.
[18] Hartmann, Furlani, and Burger, *Z. phys. Chem. (Frankfurt)*, 1956, **9**, 62; Hartmann and Furlani, *ibid.*, p. 162.

above, CFSE contributions to the activation energy can be calculated. These are shown in Table 3.

TABLE 3.

Contributions of the crystal-field stabilisation energy (CFSE) to the activation energy ($E^{\ddagger}$) for a series of trisoxalato-complexes of tervalent transition metals.

Complex	R'/R	CFSE contribution to $E^{\ddagger}$ (kcal. mole^{-1}) Associative path			Dissociative path	Complex	R'/R	CFSE contribution to $E^{\ddagger}$ (kcal. mole^{-1}) Associative path			Dissociative path
		1·0	1·25	1·50				1·0	1·25	1·50	
FeOx$_3$$^{3-}$		0	0	0	0	CrOx$_3$$^{3-}$		7·9	9·0	9·8	10·0
VOx$_3$$^{3-}$		−17·5	−3·5	−5·0	−5·8	CoOx$_3$$^{3-}$		16·1	18·6	20·1	20·5
MnOx$_3$$^{3-}$		−10·3	−16·0	−17·4	−18·0	RhOx$_3$$^{3-}$		23·6	27·0	29·4	29·9
RuOx$_3$$^{3-}$		−15·6	9·6	8·2	7·2	IrOx$_3$$^{3-}$		26·1	30·0	32·6	33·1

An approximate " order of reactivity " for the trisoxalates can be seen from this Table:

(Fast) Mn, V, Fe > Ru ∼ Cr > Co > Rh > Ir (Slow)

This order is independent of the mechanism. Because of the similarity in size and charge throughout the series of complexes chosen, energy terms depending on these two factors should be substantially constant, *e.g.*, hydration energies. The energies of bond-making and -breaking, however, will depend on the individual metals concerned and may cause variation from the order predicted.

Comparison with Experiment.—(a) *Carbon-14-labelled oxalate exchange.* These exchange reactions have been investigated with all the complexes except that of vanadium. There is rapid exchange for Fe [6] and Mn,[19] slow exchange for Cr,[20] Rh,[21] and Ir,[19] and decomposition before exchange for Ru [9] and Co.[22]

Of the cases where measurements were possible, the order found (Mn, Fe, Cr, Rh, Ir) is consistent with the order predicted. However, they are only strictly comparable if the reaction path is the same in all cases. The exchange of IrOx$_3$$^{3-}$ was found to be extremely slow (<1% in 30 days at 25°),[19] but the complexes of chromium [20] and rhodium [21] have been investigated in more detail. Both show evidence of mixed reaction-paths. The activation energy of the CrOx$_3$$^{3-}$ exchange has been determined as 13·3 kcal. mole^{-1} [20a] and 20 kcal. mole^{-1},[20b] while the RhOx$_3$$^{3-}$ exchange has an activation energy of about 24 kcal. mole^{-1}.[21]

(b) *Racemisation.* Octahedral trisoxalato-compounds are capable of forming *d*- and *l*-isomers. Complexes of V, Fe,[21,22] Mn,[22] and Ru [8] have not been resolved. Of the complexes that have been resolved, the racemisation of the Cr complex has $t_{\frac{1}{2}} = 20$ min.,[25] whereas for the racemisation of the Co complex the rate is *ca.* $\frac{1}{20}$ that of the Cr complex.[25] The Rh complex racemises [26,27] much more slowly than that of Cr, and the Ir complex is not racemised on boiling in aqueous solution for 1 hr.[28] Again the order is consistent with that predicted.

(c) *Aquation.* Aquation reactions of the general form:

$$MOx_3{}^{3-} + 2H_2O \longrightarrow MOx_2(H_2O)_2{}^- + Ox^{2-}$$

[19] Odell and Olliff, to be published.
[20] (a) Bishop, Llewellyn, Odell, Olliff, and Yih, *J.*, 1964, in the press; (b) Graziano and Harris, *J. Phys. Chem.*, 1959, **63**, 330.
[21] Barton and Harris, *Inorg. Chem.*, 1962, **1**, 251.
[22] Long, *J. Amer. Chem. Soc.*, 1941, **63**, 1353.
[23] Thomas, *J.*, 1921, **119**, 1140.
[24] Johnson, *Trans. Faraday Soc.*, 1935, **31**, 1612.
[25] Bushra and Johnson, *J.*, 1939, 1937.
[26] Jaeger and Thomas, *Proc. k. ned. Akad. Wetenschap*, 1916, **20**, 263; 1917, **21**, 157; *Ber.*, 1914, **47**, 1954.
[27] Odell, Olliff, and Seaton, to be published.
[28] Delepine, *Bull. Soc. Chim. (France)*, 1934, (v), **1**, 1256.

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are known to occur for a number of these compounds. Fast aquation occurs with the complexes of Mn [12] and Fe,[15] and slow aquation with those of Cr [20b,29] and Co.[29] The aquation of the Rh complex [21] is slower than that of the Cr complex.[20]

Conclusions.—The " order of reactivity " obtained from the simple crystal-field theory seems to give quite good qualitative agreement with the experimental results. The position of ruthenium in the series cannot be determined from the experimental results (although the non-resolution may be a hint).

The effect of bond-making and -breaking will be largest where Dq is large, *i.e.*, in the cases of ruthenium, rhodium, and iridium. Bond-making in the associative mechanism would lead to a gain in energy and a consequent compacting towards the low-energy end, while bond-breaking in the dissociative path would lead to loss of energy and consequent expansion towards the high-energy end. After allowance for these effects, it would appear that the activation energies in the two series will be comparable in magnitude. Activation energy would then not be a useful criterion for determining the mechanism, as pointed out elsewhere.[30]

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[29] Bunton, Carter, Llewellyn, Odell, and Yih, *J.,* 1964, in the press.
[30] Claridge, Odell, and Olliff, in the press.