627. *Structure and Reactivity of the Oxyanions of Transition Metals. Part XI.* Ultraviolet Spectra of Monosubstituted Chromate Ions.*

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The preparation of dilute solutions of chromates, $RO\cdot CrO_3^-$, where R is alkyl, substituted alkyl, or acyl, is described, and their ultraviolet spectra are compared with those deduced from formation constants for these esters, together with spectra of aqueous-alcoholic solutions containing acid chromate in addition to the monoesters. Characteristic changes in the energy and intensity of the second band in the ultraviolet spectra as the group R is varied are correlated with σ^* values for these groups, and hence a qualitative interpretation of the spectra is offered.

CONVERSION of chromate (CrO_4^{2-}) of symmetry T_d into mono-derivatives ($X\cdot CrO_3^-$) of symmetry C_{3v} results in marked changes in the ultraviolet spectra, those for all $X\cdot CrO_3^-$ ions being qualitatively similar to each other, but characteristically different from that of chromate [1,2,3] (cf. Fig. 1).

The spectra of monochromate esters presented earlier were deduced indirectly from calculated equilibrium constants, and the spectra of solutions containing considerable amounts of acid chromate.[2] Such measurements have now been extended to other monoalkyl and monoacyl chromates; the calculated spectra are now compared with experimental spectra of solutions containing chromium exclusively as the monosubstituted chromate.

Our aim was to test the applicability of an orbital-level scheme proposed [3] to account for the spectra of XMO_3 molecules having C_{3v} symmetry.[3] Our interest in the nature of these transitions arises in part from the photo-sensitivity of monochromate esters.[4,5]

EXPERIMENTAL

Materials.—Water was redistilled from alkaline permanganate. Alcohols were dried before distillation: methanol with magnesium; ethanol, propanol, propan-2-ol, and t-butyl alcohol with calcium; and 1,3-dichloropropan-2-ol, ethylene chlorohydrin and methylcellosolve (2-methoxyethanol) with sodium carbonate. The water content of acetic acid was determined by Karl Fischer titration, and the water then removed by mixing the acid with the calculated amount of acetic anhydride and storing the whole for 72 hr. at room temperature. Other materials were Merck's "p. A." or "für Chromatographie." Ammonium dichromate was Merck's "puriss."

Spectra in Anhydrous Solvents.—The solutions listed in Table 1 were prepared by dissolving ammonium dichromate in the anhydrous solvent, the reaction $(NH_4)_2Cr_2O_7 + 2ROH \longrightarrow 2NH_4\cdot RCrO_4 + H_2O$ occurring. These solutions were diluted to give suitable optical densities and it was established that Beer's law held in the 2×10^{-3} to 10^{-4}M-region. This means that, in contrast with solutions of chromate in dilute aqueous acids, the concentration of dichromate is always small in this concentration range. Chromate concentrations were estimated spectrophotometrically after dilution with aqueous sodium hydroxide. The extinction coefficient at 373 mμ was taken as 4830, and it was established that under these conditions the esters were completely hydrolysed to sodium chromate.

Solutions in anhydrous unsubstituted alcohols were stable for several days at room temperature, as judged from their absorption spectra. For other solvents it was necessary to extrapolate to zero time of the spectrophotometric measurements because of slow decomposition, so that these results are less accurate.

Measurements were made with a Beckman DU spectrophotometer whose cell compartment

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* Part X, *J.*, 1960, 973.

[1] Helmholz, Brennen, and Wolfsberg, *J. Chem. Phys.*, 1955, **23**, 853.

[2] Kläning, *Acta Chem. Scand.*, 1957, **11**, 1313; 1958, **12**, 576.

[3] Bailey, Carrington, Lott, and Symons, *J.*, 1960, 290.

[4] Kläning, *Acta Chem. Scand.*, 1958, **12**, 807; 1959, **13**, 2152.

[5] Kläning and Symons, *J.*, 1960, 977.

was thermostatically controlled at 25° ± 0·1°. The procedure for estimating esterification equilibria was as described previously.[2]

Results are given in Table 1, and typical spectra are shown in Fig. 1. Extinction coefficients are based on a molar extinction coefficient of 1530 for acid chromate at 350 mμ. To allow for overlap between the bands the following procedure was adopted: it was assumed that the first and the second band are symmetrical, that the third band contributes little at the peak of the second, that the first band has a maximum at 22,500 cm.$^{-1}$ in all cases, and that overlap of this with the second band does not extend below 22,000 cm.$^{-1}$. After subtraction of the first band, the maximum for the second was obtained by the method of mid-points, and the intensity was calculated by using the equation: $f = 4{\cdot}33 \times 10^{-9}\int \varepsilon d\nu$. Unfortunately, resolution of the first band was such that subtle changes in this band would not have been observed.

FIG. 1. *Ultraviolet spectra of* (a) CrO_4^{2-} *in* H_2O, (b) $Bu^tO{\cdot}CrO_3^-$ *in* Bu^tOH, (c) $Pr^iO{\cdot}CrO_3^-$ *in* Pr^iOH, (d) $MeO{\cdot}CrO_3^-$ *in* MeOH, (e) $HCrO_4^-$ *in* H_2O, *and* (f) $AcO{\cdot}CrO_3^-$ *in* AcOH.

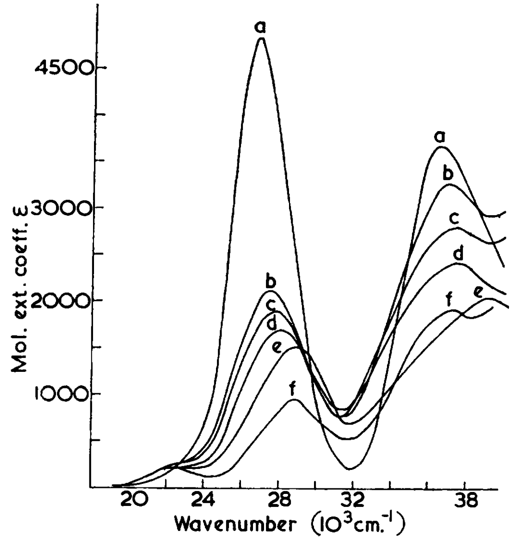


FIG. 2. *Correlation of the energies of maxima of the second band with their transition probabilities. (Key in Table* 1.)

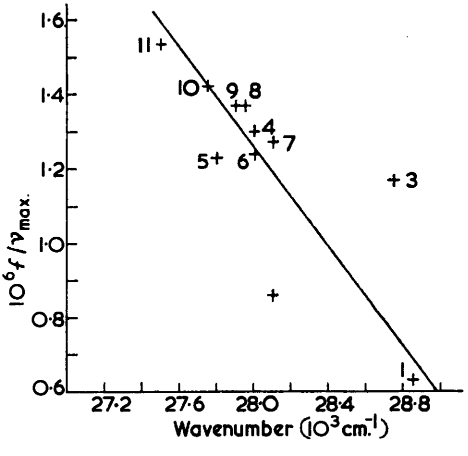


FIG. 3. *Correlation of transition probabilities for the second band with substituent constant σ.* (Key in Table* 1.)

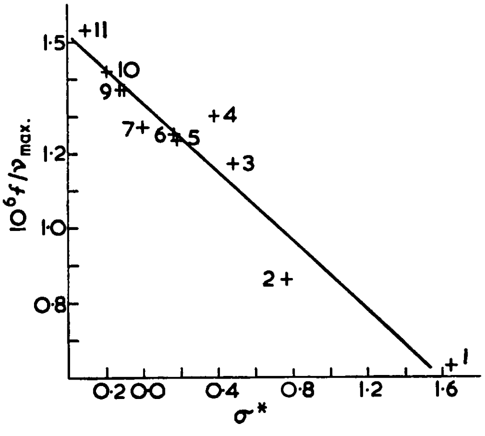
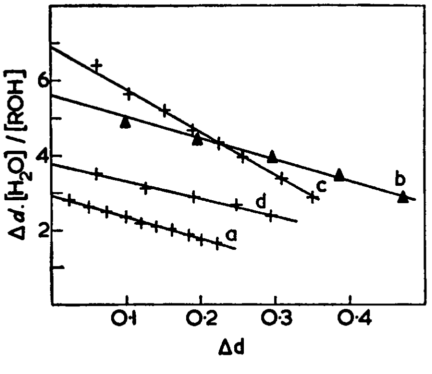


FIG. 4. *Plot of* $\Delta d[H_2O]/[ROH]$ *against* Δd *for potassium dichromate in aqueous solutions containing* (a) *ethylene chlorohydrin*, (b) *t-butanol*, (c) *ethylene glycol*, *and* (d) *acetic acid*.



In Fig. 2 absorption maxima of the second bands are compared with their transition probabilities. The upward trend of the latter with decreasing energy is clear, although the results for acid chromate and 1,3-dichloropropan-2-ol are rather poorly correlated. Variation of the σ^* value for R,[6] with the transition probability is shown in Fig. 3: correlation with $\nu_{max.}$ is similar but a straight-line law is less well obeyed.

TABLE 1. *Ultraviolet spectra of mono-derivatives of chromates,* $RO{\cdot}CrO_3^-$ *in solvent* ROH.

$\nu_{max.}$ and $\varepsilon_{max.}$ are the band maxima (cm.$^{-1}$) and extinction coefficients derived from solutions of $(NH_4)_2Cr_2O_7$ in these solvents, $\nu_{max.}$ (calc.)and $\varepsilon_{max.}$ (calc.) those derived from K_E the equilibrium constant for $ROH + HCrO_4^- \rightleftharpoons RO{\cdot}CrO_3^- + H_2O$. f is the experimental oscillator strength for the first and second bands calculated from equation 1: σ^* is a measure of the electron-withdrawing power of R, taken from ref. 13.

No.	Solvent	$\nu_{max.}$	$\nu_{max.}$ (calc.)	$10^2 f$	$10^6 f/\nu_{max.}$	$\varepsilon_{max.}$	$\varepsilon_{max.}$ (calc.)	σ^*	K_E
1	AcOH	22,500		0·354	0·157	190		1·65	4·5
		28,850	28,900	1·82	0·633	945	810		
		37,300				1930			
2	$(CH_2Cl)_2CH{\cdot}OH$	22,500		0·353	0·157	200			
		28,100		2·41	0·857	1320		0·77 [a]	—
		—				—			
3	H_2O	22,500		0·352	0·157	200			
		28,750		3·37	1·17	1530		0·49	
		38,900				2060			
4	$CH_2Cl{\cdot}CH_2{\cdot}OH$	22,500		0·359	0·160	210		0·385	5·9
		28,000	28,000	3·64	1·30	1720	1770		
		37,200				2630			
5	$(CH_2{\cdot}OH)_2$	22,500		0·363	0·161	220			
		27,800	27,900	3·43	1·23	1760	1770	0·20	11·8
		37,000				2450			
6	$MeO{\cdot}CH_2{\cdot}CH_2{\cdot}OH$	22,500		0·376	0·167	220			
		28,000		3·59	1·24	1740		0·186	—
		37,200				2560			
7	MeOH	22,500		0·365	0·162	210			
		28,100	28,000	3·56	1·27	1700	1790	0·000	4·7
		37,400				2430			
8	EtOH	22,500		0·377	0·167	220			
		27,950	27,650	3·84	1·37	1820	1930	0·100	6·9
		37,250				2630			
9	Pr^nOH	22,500		0·406	0·180	225			
		27,900	27,650	3·82	1·37	1830	1930	0·115	9·7
		37,200				2600			
10	Pr^iOH	22,500		0·398	0·177	220			
		27,750	27,550	3·92	1·42	1910	2020	−0·190	8·3
		37,300				2810			
11	Bu^tOH	22,500		0·376	0·167	220			
		27,500	27,400	4·20	1·53	2120	2030	−0·300	5·8
		37,000				3280			

[a] Estimated by analogy from data for a series of related compounds given in ref. 13.

TABLE 2. *Isosbestic points* (mμ) *for* $(NH_4)_2Cr_2O_7$ *in aqueous alcohols.*

[ROH] (M)	Bu^t		Pr^iOH		[ROH] (M)	Bu^t		Pr^iOH	
2	318	338	321	341	8	316	341	321	342
4	318	340	323	341	100%	320	339	323	340
6	316	341	321	342					

These results are self-consistent and thus support the view that monoesters $RO{\cdot}CrO_3^-$ are formed from the ammonium salt in anhydrous solvents: $Cr_2O_7^{2-} + 2ROH \longrightarrow 2RO{\cdot}CrO_3^- + H_2O$, and that little, if any $HCrO_4^-$ is present. Further support for this comes from the fact that good isosbestic points were found for the spectra of solutions prepared from ammonium dichromate, water, and various alcohols (see Table 2). It is unlikely that diesters $(RO)_2CrO_2$ were formed under these conditions, but their absence was confirmed by extracting the solutions with iso-octane.

Spectra in Aqueous Solvents.—Equilibria of the type, $ROH + HCrO_4^- \rightleftharpoons ROCrO_3^- + H_2O$, were studied spectrophotometrically, as described previously,[2] by measuring the difference,

[6] Taft in Newman's " Steric Effects in Organic Chemistry," Wiley and Sons, Inc., New York, 1956.

Δd, in optical density between that of aqueous acid chromate and that of the same concentration of $\mathrm{Cr^{VI}}$ in a given solvent mixture. By neglecting activity coefficients, the relation

$$\Delta d[\mathrm{H_2O}]/[\mathrm{ROH}] = \Delta\varepsilon \,.\, K_{\mathrm{E}}l[\mathrm{Cr^{VI}}] - K_{\mathrm{E}}\Delta d \quad . \quad . \quad . \quad . \quad . \quad (1)$$

can be derived,[2] where Δd is the difference between the extinction coefficients of $\mathrm{HCrO_4^-}$ and $\mathrm{RO{\cdot}CrO_3^-}$ at the wavelength used. The optical length of the cell, l, was 10 cm., and the concentrations of water, alcohol, and total $\mathrm{Cr^{VI}}$ were in the regions 30—55M, 0—5M, and 10^{-4}M respectively. The results are shown in Fig. 4 as a plot of $\Delta d[\mathrm{H_2O}]/[\mathrm{ROH}]$ against Δd. K_{E} was calculated from the slopes of these plots, and the results are given in Table 1.

From measurements of Δd at various wavelengths, absorption spectra of the monoesters $\mathrm{RO{\cdot}CrO_3^-}$ were constructed. These were all closely similar to those shown in Fig. 1, confirming the postulate that these are pure spectra of the monoesters. Wavelengths at which Δd was zero are listed in Table 2.

DISCUSSION

Electron-spin resonance studies of ions such as manganate ($\mathrm{MnO_4^{2-}}$), hypomanganate ($\mathrm{MnO_4^{3-}}$), and ferrate ($\mathrm{FeO_4^{2-}}$) have established, apparently without ambiguity, that the first excited level for closed-shell ions such as chromate is doubly degenerate,[7] and hence that the first intense band can be described as $t_1 \longrightarrow e$.[8] The t_1 orbital is non-bonding on oxygen and the e orbital is π-antibonding, but is probably largely localised as the $d\gamma$-orbital of the central metal.[9]

On going from closed-shell $\mathrm{MO_4}$ ions to $\mathrm{XMO_3}$ the symmetry is lowered from T_d to C_{3v}, and the t_1 level is split into a doublet ($4e$) and a singlet (a_2).[1,8] The first excited level remains a doublet ($5e$), although its energy, relative to that in $\mathrm{MO_4}$ may be altered. The a_2 level involves only non-bonding electrons on oxygen, whereas the $4e$ level involves, in addition, non-bonding electrons on X.

There are thus two allowed transitions in place of the $t_1 \longrightarrow e$ transition of $\mathrm{MO_4}$, and our problem is to decide which of the transitions $a_2 \longrightarrow 5e$ and $4e \longrightarrow 5e$ lies lower.

In an earlier analysis[3] based on calculations of oscillator strengths similar to those of Ballhausen and Lier,[10] it was concluded that the relatively weak long-wavelength band corresponded to the $4e \longrightarrow 5e$ transition and the second stronger band to the $a_2 \longrightarrow 5e$ transition. The key relation, that

$$f \,.\, \mathrm{MO_3X} = f \,.\, \mathrm{MO_4} \times \tfrac{1}{3} \times \frac{\nu^1}{\nu}$$

(where f is the oscillator strength and ν^1 and ν are the transition energies for $\mathrm{MO_3X}$ and $\mathrm{MO_4}$) required by this theory for the $a_2 \longrightarrow e$ transition, was in satisfactory agreement with experiment only if data for the second band were used.

However, the whole basis of these calculations is now thought to be in error[11] and we have therefore turned to other methods for making an assignment.

From a chemical viewpoint it seems reasonable to suggest that, provided the electron-affinity of X differs sufficiently from that of oxygen, one of the two bands should involve electron-transfer primarily from X and the other from oxygen. In that case we conclude that, for the esters described above, which have approximate C_{3v} symmetry in the chromophore, transitions from RO should require greater energy than those from oxygen and that only the former transitions should be markedly dependent on the electron-affinity of R, shifting to shorter wavelengths as the electron-affinity of R increases. A similar trend is expected for the transition from halogen in halogenochromate ions on going down the Periodic Table. Further, as the electron-affinity of R increases and the amount of π-bonding to the oxygen of the RO group decreases, so the oscillator strength for any

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[7] Carrington, Ingram, Lott, Schonland, and Symons, *Proc. Roy. Soc.*, 1960, *A*, **254**, 101.

[8] Carrington and Symons, *J.*, 1960, 889.

[9] Schonland, *Proc. Roy. Soc.*, 1960, *A*, **254**, 111.

[10] Ballhausen and Lier, *J. Mol. Spectroscopy*, 1958, **2**, 342.

[11] Carrington and Schonland, *Mol. Phys.*, 1960, **3**, 331.

charge-transfer transition from this group will decrease, tending to zero as the amount of π-bonding decreases.

All these properties are found for the second band. In Fig. 2 the trend to smaller transition probabilities with increase in energy is shown, and in Fig. 3 the relation between transition probability and the σ^* values for the substituents is given. Since σ^* is a measure of the inductive effect of these groups,[6] this shows that, as the electron-attracting power of R increases so the transition probability decreases; and the energy also increases regularly.

In contrast, the first band is relatively insensitive to changes in R, as would be expected, on our simple picture, for a transition from the oxide ligands. We conclude, therefore, that the first band is $a_2 \longrightarrow 5e$, and the second $4e \longrightarrow 5e$.

These qualitative arguments are only reasonable provided the alkyl-oxygen is sufficiently different from the remaining three oxygens to warrant clear-cut differentiation between transitions involving non-bonding electrons on alkyl-oxygen and those involving the remainder. However, one cannot so readily justify any such differentiation between the three remaining oxide ligands of the monoesters, and the four ligands of the parent ion. It therefore seems probable that the low-intensity band which is invariably found in the 22,000 cm.$^{-1}$ region for mono-derivatives of chromate arises from the very weak band found by Teltow [12] on the long-wavelength edge of the first intense bands in the spectra of crystals containing CrO_4^{2-} and MnO_4^-. This band is presumably the ${}^1T_1 \longleftarrow {}^1A_1$ component of the $t_1 \longrightarrow e$ transition of these ions, which is forbidden by the electric-dipole selection rules. In C_{3v} symmetry, the $a_2 \longrightarrow e$ transition is ${}^1E \longleftarrow {}^1A_1$, and the $e \longrightarrow e$ transition has as allowed components ${}^1A_1 \longleftarrow {}^1A_1$ and ${}^1E \longleftarrow {}^1A_1$. Detailed calculations by Carrington [13] suggest that the intensity of the first band in the spectra of mono-derivatives of chromates is derived by a process of "borrowing" from the second transition, since both transitions have ${}^1E \longleftarrow {}^1A_1$ components.

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[12] Teltow, *Z. phys. Chem.*, 1938, *B*, **40**, 397; 1939, *B*, **43**, 198.
[13] Carrington, unpublished work.