X-Ray Photoelectron Spectroscopy of Chromium–Oxygen Systems

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X-Ray photoelectron spectroscopy has been used to study a series of chromium–oxygen compounds. It has been shown that the ionisation energy of the chromium $2p$ electrons is dependent primarily on the oxidation state of the chromium metal ion, but that small perturbations may be attributed to changes in crystal structure and hence the Madelung potential. Multiplet splitting in chromium(III) compounds contributes to peak widths, and the chemisorption of water and oxygen has a marked effect on the observed peak profiles. In addition such chemisorption apparently contributes to the build up of surface charge, thereby complicating the precise determination of binding energies.

WE report here a study in which *X*-ray photoelectron spectroscopy [1,2] has been used to monitor the behaviour of chromium and oxygen atoms in a series of chromium compounds. Several studies of chromium compounds have appeared in the literature.[3-8] For example, Hendrickson *et al.*[3] have reported values of the binding energy of the chromium $3p$ shell in a wide range of compounds including some oxides and several complexes. In an attempt to resolve the two expected oxygen lines in dichromate(VI) compounds, Brundle and Robin [4] investigated the spectrum of sodium dichromate(VI) but reported only a single peak. The very comprehensive paper by Carver *et al.*[5] discusses the bonding in several series of transition-metal compounds including some chromium oxides, halides, and complex salts. Attention in that paper was primarily focussed on the $3s$ photoelectron peak because of the greater degree of multiplet splitting [9-12] expected from it. The areas covered are quite extensive but somewhat disjointed and furthermore the several groups have used a variety of calibration processes that render direct comparison of the data difficult. This problem of energy standard is one of the unresolved problems in *X*-ray photoelectron spectroscopy,[13,14] and in this study

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[1] K. Siegbahn, C. Nordling, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, G. Johansson, T. Bergmark, S. E. Karlsson, I. Lindgren, and B. J. Lindberg, 'ESCA—Atomic, Molecular, and Solid-state Structure studied by means of Electron Spectroscopy,' Almqvist and Wiksell, Uppsala, 1967 (new edn., North Holland Publishing Co., Amsterdam, in the press).

[2] K. Siegbahn, C. Nordling, G. Johansson, J. Hedman, P. F. Hendén, K. Hamrin, U. Gelius, T. Bergmark, L. O. Werme, R. Manne, and Y. Baer, 'ESCA Applied to Free Molecules,' North Holland Publishing Co., Amsterdam, 1969.

[3] D. N. Hendrickson, J. M. Hollander, and W. L. Jolly, *Inorg. Chem.*, 1970, **9**, 162.

[4] C. R. Brundle and M. B. Robin, 'Determination of Organic Structures by Physical Methods,' eds. F. Nachod and G. Zuckerman, Academic Press, New York, 1971, vol. 3, p. 1.

[5] J. C. Carver, G. K. Schweitzer, and T. A. Carlson, *J. Chem. Phys.*, 1972, **57**, 973.

[6] R. Prins and T. Novakov, *Chem. Phys. Letters*, 1972, **16**, 86.

[7] M. V. Zeller and R. G. Hayes, *Chem. Phys. Letters*, 1971, **10**, 610.

[8] J. A. Connor, I. H. Hillier, V. R. Saunders, M. H. Wood, and M. Barber, *Mol. Phys.*, 1972, **24**, 497.

[9] C. S. Fadley and D. A. Shirley, *Phys. Rev. Letters*, 1968, **21**, 980.

[10] C. S. Fadley, D. A. Shirley, A. J. Freeman, P. S. Bagus, and J. V. Mallow, *Phys. Rev. Letters*, 1969, **23**, 1397.

[11] C. S. Fadley and D. A. Shirley, *Phys. Rev.*, 1970, **A2**, 1109.

[12] C. S. Fadley, 'Photoelectron Spectroscopy,' ed. D. A. Shirley, North Holland Publishing Co., Amsterdam, 1972.

[13] D. J. Hnatowich, J. Hindis, M. L. Perlman, and R. C. Ragaini, *J. Appl. Phys.*, 1971, **42**, 4883.

[14] P. Ascarelli and G. Missoni, *Faraday Discuss. Chem. Soc.*, 1973, **54**, 298.

we have used an internally consistent calibration method in an attempt to obtain a reliable set of data. Using this data it has been possible to assess more fully the effects of environment, oxidation number, and Madelung potential on the chromium and oxygen electron-binding energies within the series of chromium compounds studied.

As will be discussed below the technique of *X*-ray photoelectron spectroscopy is powerful in the resolution of problems of chemical structure and bonding, but great care is necessary in the interpretation of results since the technique is very sensitive to surface condition and it is easy to overlook the effects of low-level contamination and very small amounts of surface hydration.

EXPERIMENTAL

Materials and Reagents.—The chromate(III) compounds $LiCrO_2$ and $NaCrO_2$ were prepared by the reaction of the corresponding alkali-metal carbonate with Cr_2O_3 (Specpure grade) [equation (1); M = Li or Na]. The reaction

$$M_2CO_3 + Cr_2O_3 \longrightarrow 2MCrO_2 + CO_2\uparrow \qquad (1)$$

mixture was ground intimately using an agate mortar and pestle, and then compressed into pellet form. The pellet was placed in a nickel crucible and fired (at 973 K for $LiCrO_2$ and 1173 K for $NaCrO_2$) for 100 h in a stream of dry oxygen-free argon. The reaction product, which was dark green in both cases, was ground on cooling, and characterised by powder *X*-ray diffraction. All the lines in the diffraction pattern could be indexed on the basis of a hexagonal structure for both $LiCrO_2$ and $NaCrO_2$. The diffraction pattern given by the sample of $NaCrO_2$ used in this work was in excellent agreement with that reported previously by Gross *et al.*[15] Although lattice parameters are available for the hexagonal structure of $LiCrO_2$,[16] the diffraction pattern of this compound has not been reported previously and therefore the diffraction pattern given by the sample used in this work is shown in Table 1. The chromate(III) compound $CuCrO_2$ was prepared by heating a pelletised 1 : 1 $Cu_2O : Cr_2O_3$ reaction mixture at 1073 K for 48 h in a platinum crucible under a stream of dry oxygen-free argon. The dull green reaction product was characterised by powder *X*-ray diffraction; the diffraction pattern obtained was in good agreement with that reported by Stroupe.[17]

The oxide Cr_2O_3 was of Specpure grade purity (Johnson Matthey). The carbonates Li_2CO_3 and Na_2CO_3 were of AnalaR grade purity (B.D.H.). The chromate(VI) compounds Cs_2CrO_4, $Cs_2Cr_2O_7$, $Rb_2Cr_2O_7$, and Li_2CrO_4 were 99·9% pure reagents (Alfa Inorganics); those of K_2CrO_4, $K_2Cr_2O_7$, and $Na_2Cr_2O_7$ were AnalaR grade reagents (Hopkins and Williams). The compounds CrO_3 and Na_2CrO_4 were supplied by B.D.H.

X-*Ray Photoelectron Spectroscopic Measurements.*—Binding energies and chemical shifts were measured using a Vacuum Generators ESCA 2 *X*-ray photoelectron spectrometer with Al-K_α *X*-radiation (1486·6 eV). Samples were ground to a particle size of <50 μm and pressed into a gold-plated mesh. To compensate for charging effects a thin layer of gold was deposited on the surface of the sample, after insertion into the spectrometer, according to the method of Hnatowich *et al.*,[13] and binding energies were measured relative to the gold on the sample surface. In general, binding energies were measured relative to the gold $4f_{7/2}$ line, taken at 82·8 eV (see footnote in Table 2). For the caesium-containing compounds in which this line is obscured by the caesium $4d_{5/2}$ and $4d_{7/2}$ lines at *ca.* 80 eV, the gold $4f_{5/2}$ line at 86·4 eV was used. Observed binding energies, corrected for surface charging, for the electrons in the chromium species examined are listed in Table 2. The chromium $2p_{3/2}$, oxygen 1*s*, and the appropriate alkali-metal level binding energies are listed for all the compounds together with the peak width at half height, but the binding energies corresponding to other energy levels are only recorded where a peak was obtained with sufficient definition to permit accurate measurement. In general binding energies were measured (following deconvolution where necessary) by taking an average for the mid-point of the curve estimated from at least three positions up the peak. The values of the binding energies given in Table 2 are the result of several determinations on each compound.

TABLE 1

X-Ray diffraction pattern of $LiCrO_2$

d/nm	I/I_0	*h*	*k*	*l*
0·481	90	0	0	3
0·2472	50	1	0	1
0·2400	5	0	0	6
0·2370	10	0	1	2
0·2062	100	1	0	4
0·1895	15	0	1	5
0·1592	20	1	0	7
0·1464	30	0	1	8
0·1451	40	1	1	0
0·1388	20	1	1	3
0·1251	10	0	2	1
0·1240	3	1	1	6
0·1201	3	0	0	12
0·1186	10	0	2	4

Treatment of Hydrated Compounds.—The results from several preliminary experiments indicated that hydrated samples often gave spurious results. Furthermore, the adsorption of water on the surface of several supposedly anhydrous species also caused shifts in the photoelectron lines. Therefore, although in general care was taken to avoid hydrated compounds, it was necessary in certain cases to dehydrate the samples within the spectrometer to produce and maintain anhydrous surfaces from which reproducible results could be obtained. This was accomplished by controlled heating of the samples during which a simultaneous observation of the changing oxygen 1*s* peak profile allowed the removal of water to be monitored. In some cases complete removal of this residual absorbed water could not be accomplished without causing some sample degradation, but it was possible in these cases to extrapolate the position of the oxygen 1*s* peak. Thus, for example, the dichromate(VI) compounds could not be heated above *ca.* 430 K without causing decomposition, whereas the chromate(III) compounds could be heated to a considerably higher temperature. Details of the heating required are given in Table 2. As will be discussed below, this trace level of surface absorbed water appeared to have a dramatic effect on the degree to which surface-charge

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[15] P. Cross, G. L. Wilson, and W. A. Gutteridge, *J. Chem. Soc.* (*A*), 1970, 1908.

[16] W. Rüdorff and H. Becker, *Z. Naturforsch.*, 1954, **9***b*, 614.

[17] J. Stroupe, *J. Amer. Chem. Soc.*, 1949, **71**, 571.

build-up occurred. The O 1*s* peak was broadened to the high-binding-energy side by water adsorption and in general the peak due to the hydrate had a binding energy *ca.* 2 eV greater than that of the anhydrous compound. Therefore removal of water resulted in a marked sharpening of the O 1*s* response. Values for the oxygen 1*s* peak width at half height quoted in Table 2 are thus considered to be representative of the pure material, but it is possible that residual levels of surface contamination are still contributing to the widths.

RESULTS AND DISCUSSION

The chromium compounds studied can be divided into two groups, those containing chromium(VI) (namely some chromates, the dichromates, and CrO_3) in which the Cr $2p_{3/2}$ photoelectron peak occurred in the region 577—578 eV, and those containing chromium(III) (namely Cr_2O_3, $LiCrO_2$, $CuCrO_2$, and $NaCrO_2$) in which the Cr $2p_{3/2}$ peak occurred at *ca.* 575 eV.

TABLE 2

Binding energies/eV for elements in various chromium compounds [a]

	Chromium			Oxygen				
Compound	$2p_{3/2}$ (±0·2)	$2p_{3/2}$ peak width at half height	$2p_{1/2}$ (±0·2)	1*s* (±0·1)	1*s* peak width at half height	Other [b]	Surface charge (room temp.)	Comments
CrO_3	577·1	2·3	585·8	528·5	2·2		4·7	
Li_2CrO_4	578·6	1·7	587·8	529·1	2·2	Li(1*s*) 55·9(4·6)	0·3	Heated to 423 K to dehydrate in spectrometer
Na_2CrO_4	578·6	2·0	587·9	529·1	2·5	Na(2*s*) 62·0(2·8); Na(1*s*) 1 069·2 (2·5)	3·8	
K_2CrO_4	578·4	1·8	587·7	528·8	2·4	K($2p_{3/2}$) 291·4(1·9); K($2p_{1/2}$) 294·3	2·9	
Cs_2CrO_4	578·6	2·1	587·6	529·0	2·2	Cs($4d_{5/2}$) 74·3; Cs($4d_{3/2}$) 76·6; Cs($3d_{3/2}$) 723·3(2·3); Cs($3d_{1/2}$) 737·2(2·0)	4·2	
$CaCrO_4$	577·7	2·2	586·9	528·3	2·2	Ca($2p_{3/2}$) 345·1(2·6); Ca($2p_{1/2}$) 348·5	4·7	
$SrCrO_4$	578·4	2·2	587·4	528·9	2·7	Sr($3p_{3/2}$) 267·5(3·2); Sr($3p_{1/2}$) 278·2	4·5	
$BaCrO_4$	577·9	2·2	587·2	528·6	2·2	Ba($3d_{5/2}$)777·7(2·2); Ba($3d_{3/2}$)793·1(2·1)	7·5	
$Na_2Cr_2O_7$	578·2	2·0	587·3	528·8	2·7	Na(1*s*) 1069·4(2·7)	2·6	Heated to 323 K
$K_2Cr_2O_7$	578·2	2·3	587·6	528·8	3·7	K($2p_{3/2}$) 290·9(2·3); K($2p_{1/2}$) 293·5	3·0	Heated to 423 K
$Rb_2Cr_2O_7$	578·2	2·1	587·5	528·9	2·5	Rb($3p_{3/2}$) 236·1 (3·3); Rb($3p_{1/2}$) 245·1(3·0); Rb(3*s*) 319·6	3·4	
$Cs_2Cr_2O_7$	578·3	2·3	587·5	529·1	2·5	Cs($4d_{5/2}$) 73·9; Cs($4d_{3/2}$) 75·7; Cs($3d_{3/2}$) 722·7(2·4); Cs($3d_{1/2}$) 736·5(2·3)	5·5	
Cr_2O_3	575·6	3·0	585·3	529·3	*ca.* 2·2 [c]		4·2	Heated to 823 K to investigate surface charge
$LiCrO_2$	575·8	3·0	585·6	529·4	2·0	Li(1*s*) 54·4(3·2)	2·4	Spectrum recorded at 673 K
$NaCrO_2$	575·8	2·8	585·7	530·9	2·7	Na(2*s*) 62·8(2·8); Na(1*s*) 1071·2(3·2)	2·9 [d]	Spectrum recorded at 773 K
$CuCrO_2$	575·2	3·3	585·0	529·0	1·7	Cu($2p_{3/2}$) 931·1 (1·5); Cu($2p_{1/2}$) 951·1(2·0)	0·0	Spectrum recorded at 673 K

[a] Peak measured relative to gold evaporated onto the sample surface. Au $4f_{7/2}$ line taken at 82·8 eV.[13] Some workers claim that this value should be quoted as 84·0 eV, *e.g.* C. S. Fadley and D. A. Shirley, *J. Res. Nat. Bur. Stand.*, 1970, **14***A*, 543. [b] Li(1*s*) 55·9(4·6) indicates that the Li 1*s* peak binding energy was measured at 55·9 eV and the peak width at half height was 4·6 eV; similarly for the other peaks. [c] Sharpened to 1·7 eV at 823 K when Cr 2*p* doublet begins to sharpen (see text). [d] Very small charge on very fresh sample. Identical shifts were recorded at room temperature from foil which had been previously exposed to liquid sodium (see text).

Compounds of Chromium(VI).—In the chromate(VI) and dichromate(VI) compounds and CrO_3 the chromium ion has an essentially tetrahedrally co-ordinated structure, although the tetrahedron becomes quite distorted on progressing from CrO_4^{2-} to CrO_3 to $Cr_2O_7^{2-}$. The consequent variations in the Cr–O and Cr–Cr distances which accompany such distortions are known to have an effect on the soft *X*-ray band spectra.[18]

Chromates. In chromate(VI) compounds the oxygen atoms are involved in bonding to two different metal atoms but all the oxygen environments are equivalent. No significant shift in measured binding energy for oxygen and chromium was observed for the series of M_2CrO_4 compounds studied when M varied from Li to Cs. Thus, although the nature of the orthorhombic structure alters between Na_2CrO_4 and K_2CrO_4, the change in the associated Madelung potential is not sufficiently large to modify the measured binding energy.

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[18] D. W. Fisher, *J. Phys. Chem. Solids*, 1971, **32**, 2455.

For the chromates of general formula $MCrO_4$ (M = Ca, Sr, or Ba) on the other hand, no such regularity was observed and the Cr $2p_{3/2}$ binding energies occurred at 577·7, 578·4, and 577·9 eV for the Ca, Sr, and Ba salts respectively. $CaCrO_4$ has a tetragonal structure, $SrCrO_4$ is monoclinic, and $BaCrO_4$ has an orthorhombic lattice, and this more dramatic variation in structure type seems to be reflected in the measured binding energies *via* the Madelung potential of the complex salt.

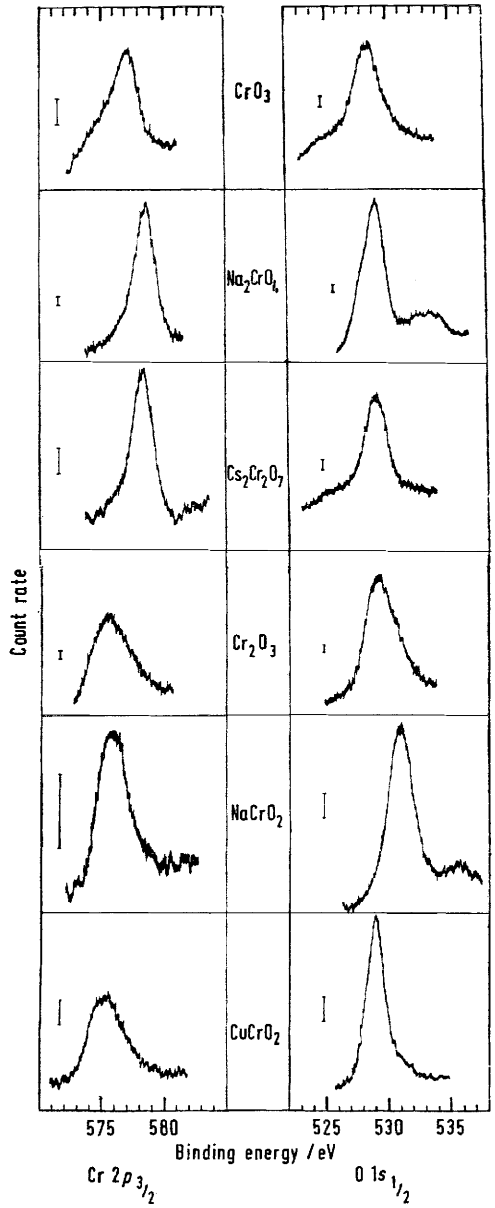

FIGURE 1 Chromium $2p_{3/2}$ and oxygen $1s_{1/2}$ peaks in various compounds: (I), 100 counts s^{-1}

Dichromates. The anhydrous caesium, rubidium, and potassium dichromate(VI) compounds crystallise as monoclinic structures in which the oxygen atoms form extremely distorted tetrahedra around the chromium atoms. As the unipositive cation decreases in size from caesium to lithium the structure type shows a progressive tendency towards hydrated forms. In this study we have tried to avoid hydrated compounds. Thus the compound $Li_2Cr_2O_7$, which was unobtainable in the anhydrous form, has been omitted and only the essentially anhydrous dichromate(VI) compounds are reported here. The spectra were very similar to those obtained for the chromate(VI) compounds and no discrete O 1*s* doublet was observed in agreement with previous observations.[4] There was however a suggestion of broadening in the O 1*s* peak compared with that in the chromate(VI) compounds and this may be due to the less symmetrical environment about each oxygen atom. Once again it is noteworthy that despite the change in structure type between Na and Cs in the dichromate(VI) series, the observed binding energies are remarkably constant.

Chromium trioxide. In CrO_3 the oxygen atoms form distorted tetrahedra around the chromium atoms and these tetrahedra link to form chains which are held together by van der Waals forces. Both the Cr–O and Cr–Cr distances are at variance with those observed in chromate(VI) compounds and this is reflected in the *X*-ray photoelectron spectrum. The Cr $2p_{3/2}$ peak was observed at a binding energy *ca.* 1·5 eV lower than those in the alkali-metal chromate(VI) compounds and its width at half height was the same as that measured for some of the dichromate(VI) compounds which have a distorted tetrahedral structure. The oxygen 1*s* peak, on the other hand was observed at 528·5 eV and its shape and width at half height is consistent with a structure in which the oxygen atoms are found in effectively one environment only.

The observed binding energies for the Cr $2p_{3/2}$ electrons in the alkali-metal chromate(VI) and dichromate(VI) compounds and CrO_3 are consistent with the view that the oxidation state of the metal atom decreases along the series M_2CrO_4 (578·6 eV), $M_2Cr_2O_7$ (578·2 eV), and CrO_3 (577·1 eV). This is in accord with solid-state diffuse-reflectance electronic-absorption spectra in which the electron-transfer bands show a small but definite shift to higher wavenumbers from M_2CrO_4 to $M_2Cr_2O_7$ to CrO_3 as chromium(VI) becomes progressively less oxidising.[19]

Compounds of Chromium(III).—In these compounds, namely Cr_2O_3 and the chromate(III) compounds of copper, lithium, and sodium, chromium has an essentially octahedrally co-ordinated structure. As can be seen from Table 2 the measured chromium 2*p* binding energies occur at *ca.* 2—3 eV lower than in chromium(VI) compounds. Whereas part of this shift may be due to the different co-ordination around the chromium atom in these compounds, it is undoubtedly true that the major contributing factor is the change in oxidation number.

Interestingly it may be observed that the oxygen 1*s* peaks from these compounds, which are considerably

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[19] G. C. Allen, D. W. Clack, and P. M. Tucker, unpublished work.

more covalent than the chromate(VI) and dichromate(VI) compounds, lie in general to higher binding energy than those in the Cr^{VI} compounds. Grossly this may be explained by the fact that in the chromate(III) compounds the co-ordination sphere of the oxygen atoms is composed of three chromium(III) ions and three unipositive metal ions, the combined effect of which is to reduce the electron density around the oxygen more effectively than that of the chromium(VI) ion in the chromate(VI) or dichromate(VI) compounds. However, this explanation may be an oversimplification in view of several seemingly contradictory facts which may be deduced from the values of the binding energies and peak widths given in Table 2. It is revealing for example to note that, in general, the chromium $2p_{3/2}$ peak widths are broader in these compounds than in the chromate(VI) and dichromate(VI) compounds. It is tempting to attribute this difference to the fact that the Cr^{VI} ion exists within a highly symmetrical environment in the chromate(VI) compounds, whereas in the corundum type structure of Cr_2O_3 or in the hexagonal structure of the chromate(III) compounds the Cr^{III} ion is not so symmetrically disposed. However, if this irregularity of environment is a major contributing factor in the determination of peak widths, it would be expected to apply to the oxygen peaks also, and until dehydration experiments enabled us to obtain accurate values this was thought to be the case (see below). Thus O 1*s* peak widths of up to 4·5 eV were observed in lithium and sodium chromate(III) compounds but this has subsequently been shown to be due to water absorption. In fact after dehydration the oxygen 1*s* peak in copper chromate(III) (which exhibits the greatest degree of structural distortion of the compounds investigated here) has the sharpest profile. Evidently other factors are involved in the Cr^{III} systems. These are now discussed.

Multiplet splitting and covalency effects. In the Cr^{VI} systems described above the relative peak widths of both chromium $2p_{3/2}$ and oxygen 1*s* electrons could be explained in terms of site symmetries and structural alterations. This is not the case with the Cr^{III} system where these factors may be overshadowed by multiplet splitting, which arises here because the chromium *d* shell contains unpaired electrons. This effect has been discussed in detail elsewhere (refs. 5, 9—12 and work cited therein); in general the magnitude of the multiplet splitting, $\Delta\varepsilon$, is greatest when both unfilled shells have the same principal quantum number. Furthermore, if the core vacancy is in an *s* shell, only two final states are possible, but *p*-shell holes will give rise to more complex final states. For this reason work designed to exhibit multiplet splittings [5,9-11] has primarily concerned the 3*s* level in chromium.

Multiplet splitting in the 2*p* shell is expected from calculations [9-11] to be much smaller than that in the 3*s* shell where $\Delta\varepsilon$ values of up to 6 eV have been observed. The effect of a smaller exchange interaction (between 2*p* and 3*d* electrons), combined with the greater complexity of the final states in the 2*p* hole case, means that *experimentally* each of the 2*p* spin–orbit levels will be broadened by up to 2 eV rather than being split into many components, since the resolving power of the *X*-ray photoelectron technique is not yet sufficiently high to observe the multiplets.

Although, in the chromate(III) compounds the chromium 2*p* peaks are broadened by multiplet splitting, the general widths of the oxygen peaks are narrower than in the chromium(VI) compounds and interestingly in the case of copper chromate(III) the copper $2p_{3/2}$ peak width of 1·5 eV is sharp in comparison to the Cr $2p_{3/2}$ peak (3·3 eV). This is a consequence of the fact that in this compound copper(I) has a full *d* shell and because of this d^{10} configuration does not exhibit multiplet splitting. This width of Cu $2p_{3/2}$ compares favourably with that of Cr $2p_{3/2}$ in the regular CrO_4^{2-} environment where the Cr^{VI} ion, electronic configuration d^0, also cannot exhibit splitting. A further small point worthy of note is that increasing covalency would be expected to reduce $\Delta\varepsilon$ values, since the more diffuse the valence electrons become the less strongly can they couple to the core electrons and hence the exchange interaction will be lessened. Furthermore antiferromagnetic behaviour would also be expected to produce lower $\Delta\varepsilon$ values because of the restriction imposed on the electron spins. As can be seen from Table 2, there is a small but significant sharpening of the Cr $2p_{3/2}$ peak in $LiCrO_2$ and $NaCrO_2$ when compared to $CuCrO_2$, which correlates with the magnetic properties of these compounds and the indication that $NaCrO_2$ is exceedingly covalent.[20]

From the foregoing discussion it can be seen that the binding energy and width of the Cr $2p_{3/2}$ and C 1*s* peaks may be explained satisfactorily by a consideration of oxidation number, ion environment, Madelung effects, and multiplet splittings. It has also been shown that the observed values are compatible with a consideration of the covalency of the Cr–O bond in chromate(III) compounds. There is, however, no simple explanation of the changes exhibited by the alkali-metal ion. Comparison of the peak positions of sodium in the chromate(VI) and dichromate(VI) compounds reveals a reasonably constant value as would be expected. However, when the chemical shifts of sodium and lithium in the chromate(VI) compounds are compared to those in the chromate(III) compounds an apparent inconsistency is revealed. It would be expected that in the covalent chromate(III) the alkali metal would have a lower binding energy than in the ionic chromate(VI) salts. This is indeed the case in the lithium series where the Li 1*s* peaks occur at 55·9 and 54·4 eV in the chromate(VI) and chromate(III) respectively, but in the sodium series the opposite is true (Na 1*s* at 62·0 and 62·8 eV). This is not a spurious result since the sodium 1*s* peak occurs at the same binding energy in the analogous ferrate(III) $NaFeO_2$,[21] and furthermore values for Na 1*s*, Cr $2p_{3/2}$,

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[20] A. J. Hooper, Ph.D. Thesis, University of Nottingham, 1971.

[21] G. C. Allen, M. T. Curtis, A. J. Hooper, and P. M. Tucker, unpublished work.

and O 1*s* were also found to be the same when recorded from a sample of sodium chromate(III) produced on a steel foil which had been previously exposed to liquid sodium.[22]

The explanation of these facts, or the reason for the high binding energy of oxygen in sodium chromate(III) is not clear. However, in view of the fact that in this work the values for the Cr 2*p* binding energy in the chromate(VI) compounds have shown that changes in crystal structure and concomitant Madelung effects can alter binding energies markedly, it may be hazardous to compare values obtained from different lattices. This is perhaps especially true when comparing results from highly ionic with those from highly covalent structures. In view of these apparent inconsistencies, further work aimed at understanding the bonding in these little understood MM′O$_2$ type compounds is proceeding and will be reported shortly.

Heating and the Effect of Water.—As mentioned in the Experimental section, heating was required in several cases to enable consistent data to be obtained. This was because the observed binding energies were altered by the presence of adsorbed species, particularly oxygen and water, in a manner that depended upon sample treatment; for example, exposure to air for long periods produced hydrated species.

Dichromium trioxide. This compound is known to have highly varying surface properties which depend at least partly on the degrees of non-stoicheiometry and hydration. In a series of elegant studies Zecchina *et al.*[23,24] investigated the i.r. spectra of α-Cr$_2$O$_3$ and from their work it can be shown that H$_2$O is chemisorbed at room temperature on Cr$_2$O$_3$ by a dissociative mechanism (producing surface OH groupings) and also by co-ordinative bonding, and these processes result in several types of interacting surface hydroxyl groups. Furthermore O$_2$ and CO are adsorbed on to Cr$_2$O$_3$ surfaces. The chemisorption of oxygen at room temperature is dissociative and oxygen atoms are linked to the surface through covalent double bonds. It has also been shown that highly active surface sites are produced by surface dehydration in which Cr^{3+} ions are present with different co-ordinative situations and, furthermore, at high temperatures (673 K) chromate-type groupings are formed and surface mobility promotes an equilibrium among the adsorbed species. Hence, from their work, which underlines the complexity of the Cr$_2$O$_3$ surface, it would be expected that the photoelectron spectrum resulting from the sample surface layers would exhibit variations which would be dependent upon the purity of the surface. This has been shown to be true. Consider the values presented in Table 3 and the spectra reproduced in Figure 2. It may be observed that the peak widths of both the chromium and oxygen photoelectron lines, particularly the latter, are dependent on the sample condition. Furthermore, it can be seen that the surface charge present on the sample is temperature dependent, and this dependency is fully reversible. Thus on heating a sample of Cr$_2$O$_3$ to *ca.* 850 K, the surface charge disappears but reappears as the sample is cooled.

TABLE 3

Variation of peak widths and surface charge for samples of Cr$_2$O$_3$ in different conditions

Cr$_2$O$_3$ Sample (Johnson Matthey, Specpure grade)	Peak width/eV Cr 2$p_{3/2}$	Peak width/eV O 1*s*	Surface charge/ eV
(1) Taken from bottle immediately seal broken	3·0	2·2	3·8
(2) Taken from bottle after several weeks	3·8	2·6	3·7
(3) Sample exposed to atmosphere for several months	4·5	Unresolved multiplet *ca.* 5·0	3·4
(4) Sample (2) heated to			
573 K	4·0	2·7	3·0
673 K	4·2	3·0	2·7
723 K	4·5	3·4	2·2
773 K	4·0	2·0	0·9
823 K	3·2	1·7	*ca.* 0·2

It is known that the surface charge on insulating samples contributes to the width of photoelectron lines because of the non-uniformity of the charges on adjacent particles, but it is not clear that this is the primary cause of the broadening in this case since the effect may

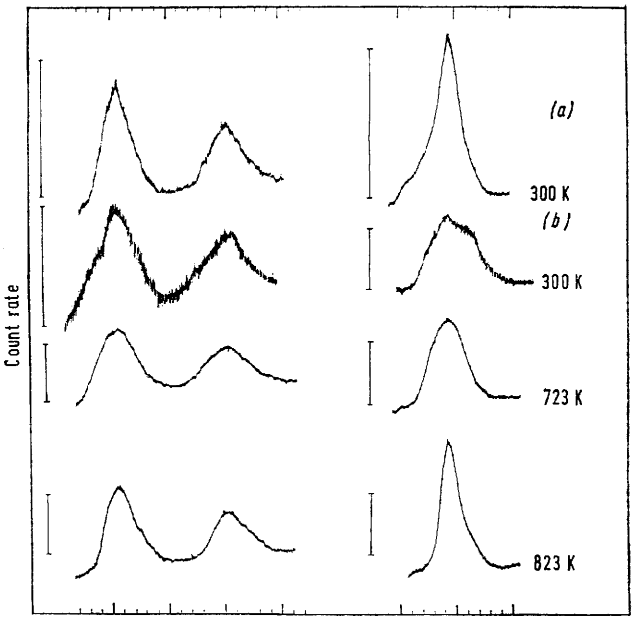

FIGURE 2 Effect of surface condition and temperature on spectra of Cr$_2$O$_3$: (*a*), fresh Specpure sample; (*b*), after several months exposure to the atmosphere; (I), 10^3 counts s^{-1}

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[22] A. J. Hooper and P. M. Tucker, unpublished work.

[23] A. Zecchina, S. Coluccia, E. Guglilminotti, and G. Ghiotti, *J. Phys. Chem.*, 1971, **75**, 2774.

[24] A. Zecchina, S. Coluccia, L. Cerruti, and E. Borello, *J. Phys. Chem.*, 1971, **75**, 2783.

be obscured by changes in the nature of the adsorbate surface. The results from the i.r. study [23,24] demonstrate the highly active nature of the Cr_2O_3 surface and it is more likely that this is the cause of the changing profiles. However, a monolayer of dichromium trioxide–chemisorbed species would contribute only about 15—20% of the total chromium and oxygen peak heights, and, in view of the large changes observed in the spectra reported here, the interaction occurring must involve considerably more than a monolayer. The fresh Specpure sample of Cr_2O_3, for example, exhibited relatively narrow profiles for both the Cr $2p_{3/2}$ and O 1*s* peaks but when this sample had been standing for only a few weeks in the re-stoppered bottle the peak widths had increased by *ca.* 20%. Further exposure to air produced an even more dramatic broadening as evidenced in the Figure.

The dissociative chemisorption of water discussed above has been shown [23] to proceed rapidly at partial pressures of considerably less than $0{\cdot}7 \times 10^2$ N m^{-2} at room temperature producing surface hydroxyl groups and above these pressures non-dissociative adsorption takes place. Such partial pressures are present in our laboratory and it is therefore hardly surprising that the photoelectron spectrum of Cr_2O_3 should change. The relatively sharp lines recorded from the freshly opened Specpure material, while perhaps not representative of absolutely pure Cr_2O_3, are undoubtedly better than those recorded after only a short exposure to air. Rapid formation of the various surface hydroxyl groups and the additional chemisorption of oxygen and carbon monoxide (always generated within ion-gauge monitored vacuum systems) causes the chromium ions to experience a less well defined potential due to different simultaneous adsorptions at the surface. The photoejected electrons thus have a larger energy spread and the linewidths of recorded peaks are greater. The oxygen 1*s* peak is also affected, being broadened to the high-binding-energy side by formation of the surface hydroxyl groups which have a binding energy of *ca.* 1 eV higher than lattice O^{2-} ions.[25]

It is interesting to note however that as a sample of Cr_2O_3 which has been exposed to air for only a short time (sample 2, Table 3) is heated within the spectrometer, the linewidths of both Cr 2*p* and O 1*s* peaks first increase and then collapse at *ca.* 800 K to a level comparable with the fresh Specpure sample. Zecchina *et al.*[23,24] showed that, under vacuum with liquid-nitrogen-cooled condensation traps, the surface of Cr_2O_3 which had become contaminated by hydroxyl-group formation would begin to be dehydrated above *ca.* 500 K. This onset of dehydration however left the surface with highly active Cr^{3+} sites and these tend to become saturated with adsorbed oxygen. Further heating to 700—800 K was shown to produce a surface which, although highly anhydrous and containing many active Cr^{3+} sites, remained partially covered by very mobile adsorbed oxygen. Our photoelectron spectra corroborate these findings. One may thus explain the initial broadening of the peak by the adsorption of oxygen following the onset of dehydration, and this effect may be exacerbated by thermal effects which would initially cause a more random surface. Then, as the surface becomes more highly dehydrated, and as desorption of oxygen proceeds, a more uniform condition will tend to prevail and this will result in peaks having better definition. It is thus suggested that the surface present at 800 K is fairly representative of pure Cr_2O_3 and as can be seen its spectrum compares favourably with that of the fresh material recorded at room temperature.

Zecchina *et al.*[24] suggested that at *ca.* 800 K there was evidence for chromate-type groupings being formed and for a high degree of surface mobility among the residual adsorbed species. In view of this it may be premature to claim that the spectrum recorded at this temperature is that of pure Cr_2O_3, particularly since the chemical shift of the oxygen 1*s* peak in chromates is similar to that in Cr_2O_3. Also, there is some evidence for a higher-oxidation-state chromium peak beginning to appear on the high-binding-energy side of the Cr 2*p* peak recorded from Cr_2O_3 at these temperatures. A peak in this position would be expected if chromate groupings were present and evidently much work remains to be done to characterise fully the nature of these complex oxide surfaces. Sufficient evidence has been presented here however to show that, unless care is taken, it is easy to record spectra from a completely unknown phase or compound rather than from the compound supposedly under investigation.

Sodium chromate(III). Similar difficulties were experienced when the chromate(III) compounds were investigated. These compounds are again typical of high-surface-area oxides in that there is a pronounced tendency to form surface hydroxyl groupings in a manner similar to Cr_2O_3. For example spectra obtained for $NaCrO_2$ under a variety of conditions are exhibited in Figure 3. O 1*s* Spectra obtained from two different samples of this chromate(III) at 300 K are shown at the top of the Figure. The first spectrum (*a*) was initially thought to be a composite triplet because of its width (4·5 eV). Such a triplet might be expected because in $NaCrO_2$ (which is isostructural with α-$NaFeO_2$ which was first investigated by Goldsztaub [26]) there are three non-equivalent pairs of oxygen atoms which are produced by the structural requirements of a distorted octahedral environment, but the observed broadening is due to surface adsorption and evidently the *X*-ray photoelectron technique is not sufficiently precise to reflect these small environmental variations. As can be seen in Figure 3 the oxygen 1*s* peak recorded from sample (*b*) at 300 K shows a clear doublet character. This sample had been exposed to air for several days, whereas the spectrum from sample (*a*) had been recorded shortly after preparation. Evidently the formation of surface

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[25] T. Robert, M. Bartel, and G. Offergeld, *Surface Sci.*, 1972, **33**, 123.

[26] M. S. Goldsztaub, *Compt. rend.*, 1933, **196**, 280.

hydroxyl groups is rapid in this case causing the higher-binding-energy peak.

As is demonstrated by reference to Figure 3, however, sodium chromate(III) may be dehydrated within the spectrometer by heating to 500—570 K at a pressure of about 10^{-6} N m^{-2}, when the spectrum shows a fairly broad oxygen response. Additional heating produces a further change which could be due to a degradation of the surface. Under this vacuum and at these temperatures sodium oxide (Na_2O) could be vaporised from the surface leaving Cr_2O_3. Some evidence for this explanation follows from the observed colour changes and the shift in the measured O 1*s* binding energy which follow further heating. This surface is very highly activated and immediately becomes saturated with chemisorbed water and oxygen upon exposure to air. Similar effects were observed with $LiCrO_2$, and studies on a series of $MM'O_2$ compounds are being undertaken to improve our understanding of the complex O 1*s* spectra.

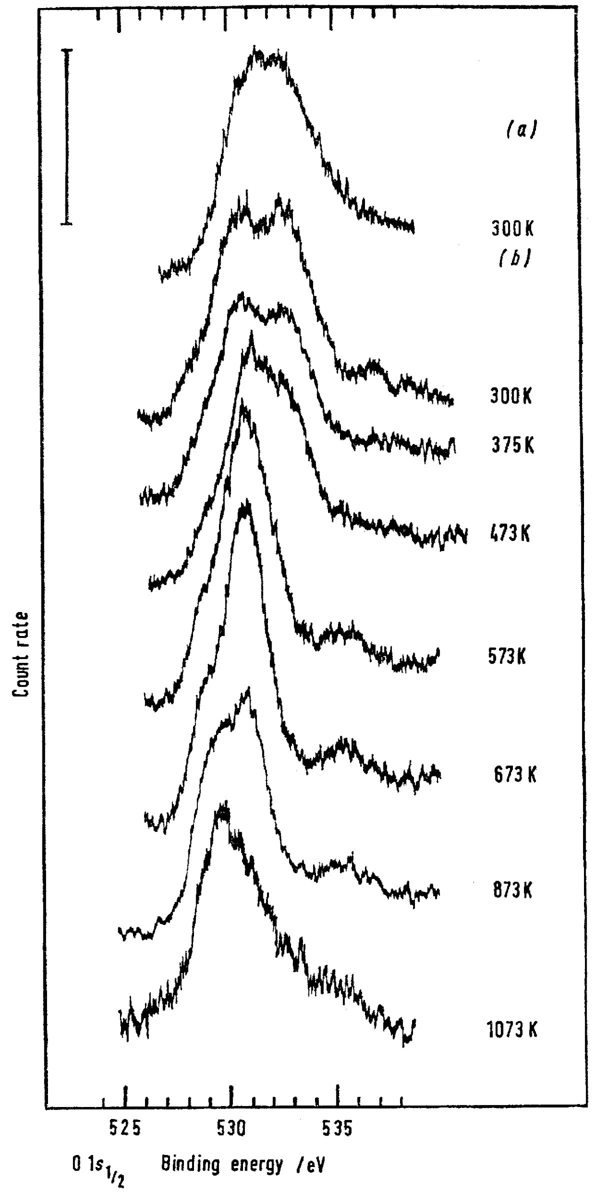

FIGURE 3 Effect of surface condition and temperature on the oxygen 1*s* peak recorded for $NaCrO_2$: (*a*), shortly after preparation; (*b*), after several days exposure to the atmosphere; (I), 10^3 counts s^{-1}

Other compounds. Table 2 lists the heating that was necessary on the other compounds measured. For example, moderate heating of several dichromate(VI) compounds and lithium chromate(VI) was required to obtain reproducible data; in all cases the dehydration was monitored by observation of the changing peak profiles and care was exercised to prevent degradation.

The Problem of Surface Charging on Hydrated Samples.—As mentioned above, one of the most important problems in the practical application of photoelectron spectroscopy to the study of insulators is the problem of surface charging. This charging occurs because photoelectrons leaving the sample are not completely replaced by electrons from the sample cage walls or from the *X*-ray window, and this results in apparently increased binding energies. The problem has been considered quite widely but as yet no single reliable method of determining the shift has been devised. Some workers[1,5,25] have used the carbon lines which result from the adsorption of residual hydrocarbon contamination remaining within the spectrometer, assuming that this very thin surface layer is in electrical equilibrium with the surface of the insulating sample. Other workers have used the carbon line emanating from adhesive tape on which the sample is sprinkled. In this case it assumed that the powder is in electrical equilibrium with the tape. However, as has been pointed out,[13] in both these methods the carbon 1*s* lines are due to substances of unknown and perhaps varying composition and it has not been demonstrated that electrical equilibrium exists, indeed the evidence is to the contrary. Hnatowich *et al.*[13] described the gold-decoration technique, suggesting that it could be demonstrated that the gold on the sample surface, which may be in the form of islands rather than a uniform layer, was in electrical equilibrium with the salts investigated. This method was used for consistency on the compounds investigated here, all of which are insulators except copper chromate(III), but the authors are not convinced that the method is foolproof; it is well known that the presence of surface layers on semiconductors can alter the underlying band levels and furthermore, in the presence of *X*-radiation, interfacial photovoltages can be generated when a metal is in contact with an insulator or a semiconductor. A better method would probably be to calibrate the binding energies of insulators by reference to their vacuum levels, as has been suggested,[14] since such a method does not rely on any assumptions about the coincidence of Fermi levels, attainment of electrical equilibrium, or changes in band levels.

The purpose of this discussion is not however to compare the relative merits of calibration processes but to point out a further complicating factor. This is the effect of adsorbed water. All the samples showed surface charging except copper chromate(III). It is interesting to observe that, in general, higher charges were recorded for compounds with larger cations. Since the smaller cation-containing species tend to crystallise as hydrates, it is tempting to conclude that the lower surface charge is due, at least in part, to a greater conductivity engendered by the presence of molecular water. Contrary to this supposition, however, are the observed facts concerning sodium chromate(III). Here a very freshly prepared sample had a small charge of *ca.* 0·3—0·5 eV. Such a sample will have a very low level of surface hydroxyl groups (see above). However, as the level of surface hydroxyl groups builds up, the surface charge appears to increase up to an equilibrium level of *ca.* 3 eV after several days exposure to air. Evidently other factors are involved, not least of which may be the fact that the adsorption of water on clean gold has been shown to change the work function by as much as 1 eV.[27] It may be that, in the case where insulating powders become contaminated with adsorbed moisture, the gold islands on the surface are no longer in electrical equilibrium with the sample. Similar changes in the observed surface charges were noted in several of the compounds studied, and, while no simple explanation is immediately forthcoming, such observations provide further impetus to the argument that an agreed method of calibrating binding energies in insulating samples is required, and such a method should not involve contaminating the sample surface.

CONCLUSION

X-Ray photoelectron spectroscopy has been used to study the bonding in a variety of chromium compounds. The binding energies of the chromium 2*p* electrons are dependent primarily on oxidation number but perturbations result from changes in structure and Madelung potential. Multiplet splitting in chromium(III) compounds contributes to peak widths and the chemisorption of water and oxygen has a marked effect on the observed peak profiles, and on the accuracy of determined binding energies.

[3/060 *Received, 11th January,* 1973]

[27] R. L. Wells and T. Fort, jun., *Surface Sci.*, 1972, **32**, 554.