828. *Structure and Reactivity of the Oxyanions of the Transition Metals. Part XV*. Mechanism of Oxidation by Chromate and Related Ions.*

By M. C. R. SYMONS.

Differences in the reactivity of chromate and periodate and related ions are discussed in terms of the biphilic character of these reagents.

EDWARDS and PEARSON [1] have recently enlarged upon the conclusion of Pearson *et al.*[2] that certain compounds commonly classified as nucleophilic are better classed as biphilic, since they are able, under appropriate conditions, to exhibit both electrophilic and nucleophilic character. They envisaged this duality as being seated at a single atom, such as the phosphorus of a tertiary phosphine.

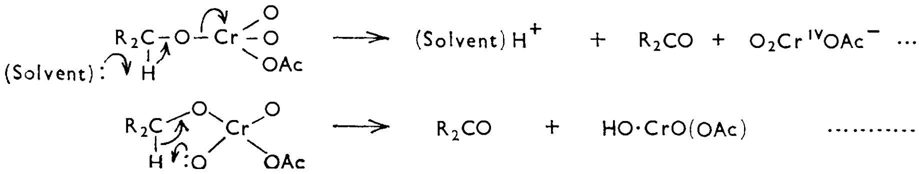
This concept can be conveniently extended to cover molecules that have nucleophilic and electrophilic properties centred on different atoms. A trivial example of such a biphilic reagent would be a carbonyl compound, the carbonyl carbon being electrophilic and the normal site for attack by nucleophiles, and the oxygen atom being nucleophilic and normally attacked by electrophiles. Similarly, one can discuss the reactivity of oxyions such as chromate or periodate in terms of the nucleophilicity of the four oxygen atoms and the electrophilic power of the central atom.

Rocek and Westheimer [3] have drawn attention to a major difference between the reactivity of acidified chromate and that of periodate and related oxidants towards alcohols and glycols. In these reactions the oxidants exhibit both nucleophilic and electrophilic reactivity, and one purpose of this paper is to suggest that an understanding of their different reactivities results from a consideration of the balance between these features.

Rocek [4] has suggested that the particular reactivity of chromate may be closely linked to the fact that quadrivalent chromium species are often paramagnetic, in contrast with quinquevalent iodine derivatives. This postulate is discussed in the light of the present theory.

Oxidation by Chromate.—In accord with the fact that, whilst primary and secondary alcohols are rapidly attacked by acidified solutions of chromate, tertiary alcohols are scarcely affected, it has been shown that tertiary glycols undergo carbon–carbon bond fission whilst those with α-hydrogen atoms are mainly oxidised to the corresponding carbonyl compounds. Such reactions with glycols, although unfamiliar, are in fact more favourable energetically than the " normal " fissions.[3]

There is good evidence that a necessary step prior to oxidation is the formation of alkyl



..... (1)

.... (2)

chromates,[5] or for glycols the corresponding cyclic esters if these are sterically likely.[3] Since monoalkyl chromates are relatively stable in the absence of light,[6,7] the reactive species are probably $RO\cdot CrO_2(OH)$,$RO\cdot CrO_2(OR)$, or, for oxidation in acetic acid,[3] $RO\cdot CrO_2(OAc)$. Inter- and intra-molecular modes of decomposition have frequently been

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* Part XIV, *J.*, 1962, 4411.

[1] Edwards and Pearson, *J. Amer. Chem. Soc.*, 1962, **84**, 16.

[2] Pearson, Cray, and Basolo, *J. Amer. Chem. Soc.*, 1960, **82**, 787.

[3] Rocek and Westheimer, *J. Amer. Chem. Soc.*, 1962, **84**, 2241.

[4] Rocek, *Tetrahedron Letters*, 1962, 136.

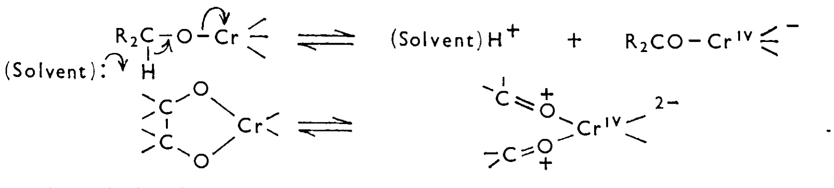
[5] Westheimer, *Chem. Rev.*, 1949, **45**, 419.

[6] Kläning, *Acta Chem. Scand.*, 1958, **12**, 576.

[7] Klaning and Symons, *J.*, 1960, 977.

postulated, examples being reactions (1) and (2), respectively. The role of the acetyl group is thus to enhance the electron-accepting power of chromium.

In this representation, the two electrons destined to become primarily $3d$ on chromium stem formally from the oxygen–chromium σ-bond, and the resulting quadrivalent chromium compound is only trico-ordinated. Since this is energetically unfavourable, we suggest a modification which takes account of the relatively strong π-bonding between oxygen and chromium.[8] Thus, even in the ground state of the ester there is considerable transfer of oxygen $2p(\pi)$ electrons into the e_g level. Attack by solvent can then be represented as a simple proton transfer (reaction 3). The complex represented as a quadrivalent chromium derivative can equally be represented as a sexivalent derivative, $\text{R}_2\ddot{\text{C}}^{-}\text{–OCr}\leqq$, a more satisfactory representation being one in which the four electrons involved are placed in π levels constructed from $2p(\pi)$ orbitals on carbon and oxygen, and the appropriate chromium $3d$ level. Such π bonding can only involve one of the oxygen $2p(\pi)$ levels and one of the chromium e_g pair. From these three atomic orbitals, three molecular orbitals can be constructed and the four π electrons will fill the two of lowest energy. There seems little likelihood that a triplet state will be involved, so that the suggestion [3] that paramagnetism may play an important role seems to be unfounded if this model is correct. This ambiguity of description often arises in transition-metal chemistry, and in general seems to be best resolved by application of molecular-orbital theory. The mechanistic significance is that solvolysis to give the carbonyl compound and tetraco-ordinated quadrivalent chromium may now proceed as a second step, thus avoiding the need to form an unstable trico-ordinated intermediate.



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Similarly, the process of glycol fission by chromate need not be treated as a simultaneous process leading to dico-ordinated chromium, but as an initial C–C bond fission to give an intermediate which, in one limit, can again be represented as a derivative of quadrivalent chromium, but which can in the other extreme be represented as a derivative of sexivalent chromium. On hydrolysis this will give the required products. It seems quite reasonable that this diketone derivative is unstable with respect to the original cyclic ester, in which case, provided an α-proton is available, the energetically favourable oxidation should be faster. Such an oxidation would presumably occur by a mechanism analogous to that suggested for monohydric alcohols.

Oxidation by Periodate.—Less is known about mechanisms of oxidation by periodate than by chromate, but certainly one major difference lies in the fact that oxyions such as chromate are able to accept electrons directly into low-lying d levels on the central metal atom, whereas periodate has no such capacity. This difference is clear-cut when chromate is compared with perchlorate or sulphate, since these ions react only as oxygen donors, but is less obvious for periodate because of its tendency to become octahedrally co-ordinated. However, there is no evidence, either in terms of reactivity or spectra, that the iodine of periodate can readily accept electrons as such.

There is some evidence that, in addition to water, which adds to give the ion $\text{IO}_2(\text{OH})_4^-$,[9] alcohols add to give esters such as $\text{IO}_2(\text{OR})_4^-$.[7] Certainly, if esters are formed as intermediates in the oxidation of alcohols and glycols, they are almost certain to be derivatives of penta- or hexa-co-ordinated iodine. Such esters are very sensitive to light,[7] but are relatively stable in the dark, in marked contrast with the corresponding glycollic esters.

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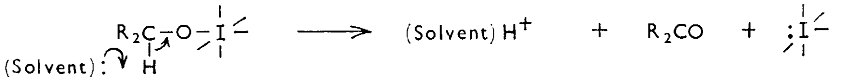
[8] Carrington and Symons, *J.*, 1960, 889.

[9] Keen and Symons, *Proc. Chem. Soc.*, 1960, 383.

A great deal has been written about glycol fission by periodate. We compare the probable paths for decomposition of periodate esters with those for chromate derivatives [reactions (3) and (4)]. Reaction (5) is less likely to be a two-stage process since the iodine, being octahedrally co-ordinated, has a very low electron-affinity, and there is no evidence that the $d(\pi)$ level has any tendency to accept electrons. The reaction, as a one-stage process, is thus mechanistically less satisfactory than the glycol fission in reaction (6). Furthermore, there is no evidence that iodate can expand its co-ordination shell so that reactions which give IO_3^- directly will be favoured.

It is concluded that the difference in reactivities of chromate and periodate has a twofold basis, namely that chromate, but not periodate, has low-lying acceptor *d* orbitals, and that esterification for chromate involves no change in co-ordination, whereas the iodine in periodate increases its co-ordination. These effects combine to lower the acidity of the α-protons in the periodate esters of primary and secondary alcohols relative to those of chromate but do not similarly modify the tendency towards glycol fission.



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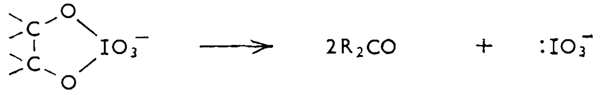

(6)

Relevance to Other Reactions.—These considerations, in addition to their possible significance to other oxidations, may also be relevant to the study of reductions. Thus, although none of the reactions under consideration is reversible, all processes, in reverse, provide reasonable pathways for the reduction of ketones to alcohols and glycols.

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