OXIDATIONS OF OLEFINS, ALCOHOLS, GLYCOLS AND OTHER ORGANIC COMPOUNDS, BY INORGANIC OXIDANTS SUCH AS CHROMIUM(VI), MANGANESE(VII), IODINE(VII), LEAD(IV), VANADIUM(V) AND HALOGENS, CONSIDERED IN THE LIGHT OF THE SELECTION RULES FOR ELECTROCYCLIC REACTIONS

J. S. LITTLER

Department of Organic Chemistry, The University, Bristol BS8 1TS

Abstract—A number of oxidations of organic functions by chromium(VI), manganese(VII), iodine(VII), lead (IV), vanadium(V) and halogens are considered in the light of the Zimmerman treatment of electrocyclic reactions. This treatment enables one to rationalise a number of experimental observations that are otherwise difficult to explain, e.g. that manganese(VII) *cis*-hydroxylates olefins but the isoelectronic chromium(VI) does not, that chromium(VI) oxidises alcohols but that iodine(VII) does not; that iodine(VII) and lead(IV) are good glycol fission reagents but that the other oxidants are not; that bromide adds *trans* rather than *cis* to a double bond. A number of other actual and hypothetical reactions are also considered, and it is demonstrated that selection rules play a significant part in determining the mechanisms of many of these reactions.

INTRODUCTION

THE Woodward-Hoffmann treatment of electrolytic reactions[1] has proved to be of major importance in certain fields of organic chemistry, and in consequence it would be highly desirable to extend it to reactions involving electrons in d-orbitals. The alternative treatment of Zimmerman,[2] using a topological approach to the orbital levels of the transition state, gives rise to the same predictions as the Woodward–Hoffmann treatment, and as it does not require knowledge of the molecular orbitals of the reagents or products, it seems to be easier to apply as a "rule of thumb" to systems containing d-electrons. It is of course essentially equivalent to Woodward and Hoffmann's generalised selection rules for pericyclic reactions using single atomic orbitals (ref. 1 p. 849).

The Zimmerman method requires the classification of the transition state as either "Hückel-like", in which all overlapping pairs of reacting orbitals are bonding (i.e. have the same sign of ψ), or "Möbius-like", in which one or an odd number of anti-bonding overlaps must occur. In a Hückel transition state $4n + 2$ electrons will form a closed shell (giving it stability), while $4n$ electrons are required for stable closed shells in a Möbius one. An "allowed" reaction may have either a Hückel or a Möbius-type transition state, provided that the correct number of electrons is available to stabilise that transition state.

This paper is an attempt to apply the Zimmerman treatment to a selection of oxidation processes which have not been discussed in Woodward and Hoffmann's recent exhaustive review article,[1] in order to see whether the treatment is correct in its predictions, and whether it can contribute to the understanding of the observed

mechanisms. If this purely qualitative treatment can correlate the observations it can be of use to the preparative chemist, and to the student of reaction kinetics; and it can also provide suggestions on which theoretical chemists can base more rigorous treatments.

DISCUSSION

A *The reacting orbitals.* The Zimmerman method requires us to select the reacting orbitals involved in each reaction. This is usually quite clear where the first-row elements are concerned, being the orbitals involved in the bonds being broken or made. When a transition metal complex is an oxidant the electrons enter the d-shell, so the reacting orbital must be the d-orbital they enter. It is necessary to classify this as either locally symmetric (σ-type) or antisymmetric (π-type) in order to know whether the transition state is of Möbius- or Hückel-type.

When chromium(VI) is reduced the initial product chromium(IV) is unstable, but it is generally considered to be an octahedral complex.[3] The d-electrons in the unexcited product must therefore be in a t_{2g} orbital (d_{xy}) which can overlap, in the reactions, using two adjacent lobes with opposite signs of the wavefunction. It can therefore be considered to be locally antisymmetric. In contrast manganese(VII) is reduced to tetrahedral manganese(V)[4] and the d-electrons must be in a $d_z{}^2$ orbital which will be locally symmetric whether one or both main lobes are involved in overlap with adjacent reacting orbitals. Iodine(VII) is reduced to iodine(V) (iodate), but here there are no vacant low-level d-orbitals to accommodate the electrons. Instead they behave as a "lone-pair",[5] occupying an orbital, with σ character, which will also be locally symmetric and which is directed along the three-fold axis of the IO_3^- pyramid. Lead(IV) is reduced to lead(II), which also has an "inert pair" of electrons in an orbital with much s character, which again is symmetric.[6]

Halogens, such as bromine, are reduced with fission of the Br—Br bond, so the reacting orbitals are clearly the sp orbitals which initially overlap to form that bond.

B *Oxidation of olefins.* We can now attempt to apply the above assumptions about the symmetries of the reacting orbitals to some specific cases. The well-known mechanism of oxidation of olefins by permanganate[7] clearly involves an electrocyclic process (1) involving six electrons and examination of the orbital overlap picture 2 or 3 shows that bonding interaction is possible all round the ring whether the $d_z{}^2$ orbital is parallel or perpendicular to the double bond. Hence this is a Hückel-type system satisfying the $4n + 2$ rule, and as such is allowed. The analogous oxidation by OsO_4 can be accounted for similarly.

A similar picture 4 can be drawn for the orbital overlap which would occur if chromium(VI) attacked by the same mechanism. Now not all overlapping orbitals are bonding, i.e. it is a Möbius-type system. As it does not satisfy the $4n$ rule it is "forbidden", and the reaction must find an alternative route. This in fact it does, by utilising an acyclic mechanism which is not subject to selection rules (5 → 6 → 7), (ref. 7, p. 140). At first sight it seems that a reaction (8) between periodate and olefins should be allowed; it is however well known that it does not occur unless permanganate is present as a catalyst.[8] The molecule produced by such a reaction would be the tetra-coordinated iodate complex 9 and as this would have 10 valency electrons it would be expected to have a structure like that of $IO_2F_2{}^-$, in which the lone pair occupies an equatorial position of a trigonal bipyramid (10). The lone-pair sp^3d orbital is therefore oriented in a direction most unfavourable for overlap with the other reacting orbitals

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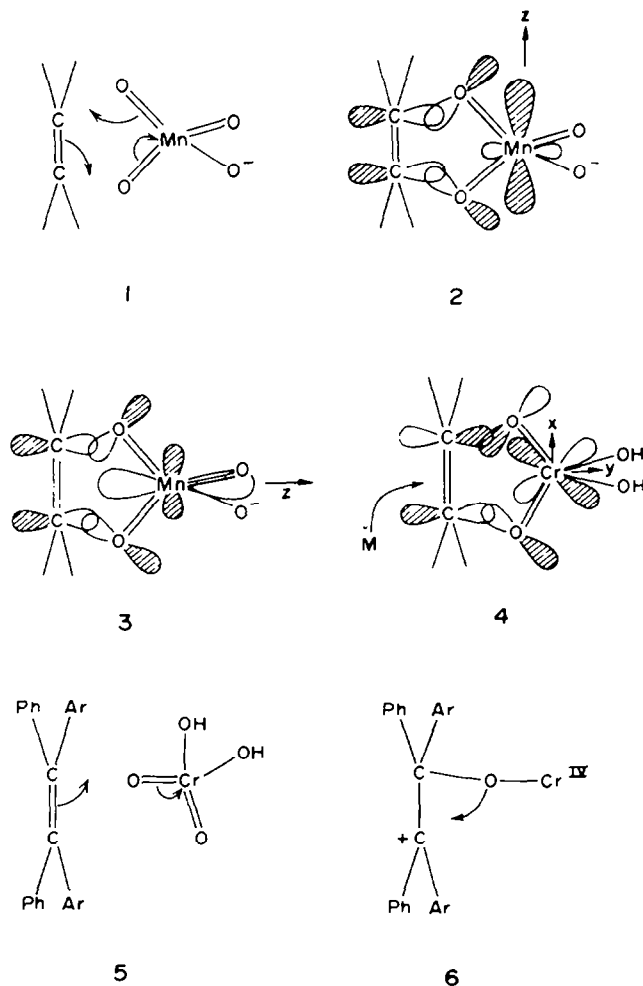
In orbital diagrams positive lobes are shaded. They are chosen to maximise the number of positive (bonding) overlaps between adjacent orbitals. Möbius-type systems are indicated by the letter M and an arrow indicating the antibonding overlap. Neither the orbitals nor the bond lengths are accurately drawn to scale. Axes are indicated in figs. 2, 3 and 4 but omitted elsewhere since the metal ions are drawn in the same orientations. Bonds are drawn in as conventional lines even when the orbitals which form them are involved in the reaction, as an aid to the visualisation of the geometry of the systems.

(11) and so no reaction occurs. The absence of reaction between diphenylselenone and *trans* stilbene $(k'' < 5 \times 10^{-4}$ mole l^{-1} sec^{-1} at 280° in sulpholane)[9] can be explained in the same way.

Lead tetra-acetate attacks olefins *via* the cation Pb(OAc)$_3{}^+$, (ref. 7, p. 336), Fig 12, and again a Hückel situation arises, this time with two electrons $(n = 0)$. In contrast, bromine, if it added *cis* to an olefin, would require a 4-electron Hückel-type transition

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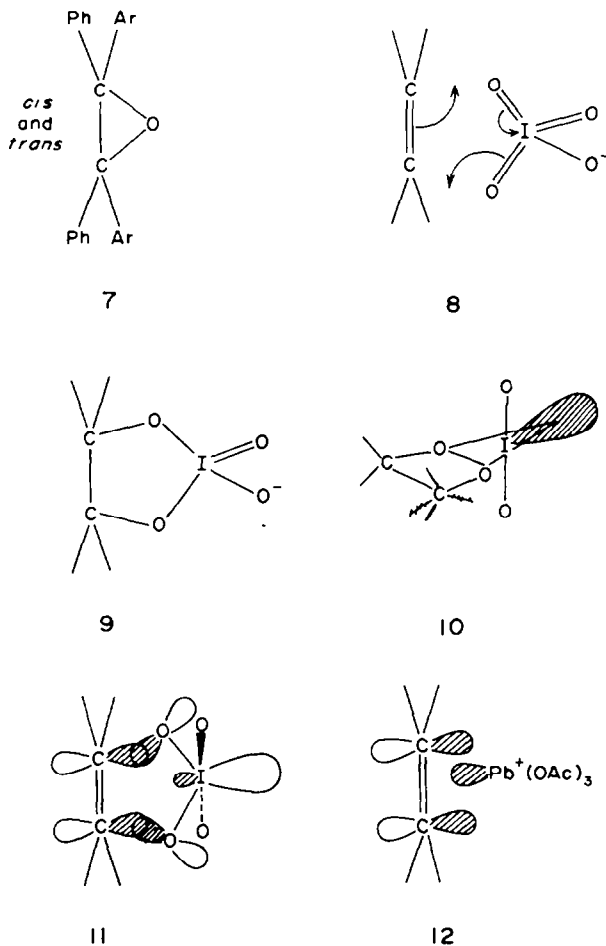
state, which is forbidden (13, 14), while the observed *trans* addition mechanism is either acyclic or involves a three membered ring transition state 15. like that of lead(IV).

It is clear that no "forbidden" paths are observed in these reactions. A brief treatment of additions to olefins of bromine, permanganate, and osmium tetroxide, by consideration of the lowest vacant orbital of the oxidant, comes to the same conclusions.[10]

C *Oxidation of alcohols.* The accepted electrocyclic mechanism of oxidation of alcohols by chromium(VI) (diagram 16), (ref. 7, p. 159), clearly involves 6 electrons, and the orbital picture 17 shows that this can be a Hückel-type system, i.e. this is an allowed process. An analogous mechanism (18) using periodic acid as an oxidant, would be forbidden because of the opposite local symmetry of the reacting orbital of iodate. It is significant that this process can be accomplished photochemically,[11] since thermally forbidden reactions are in general expected to be photochemically allowed.

Since the reacting orbitals of manganese(VII) and lead(IV) have the same local symmetry properties as that of iodine(VII) similar cyclic processes would also be
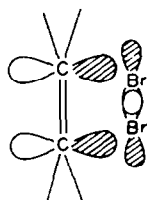
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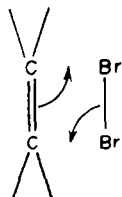
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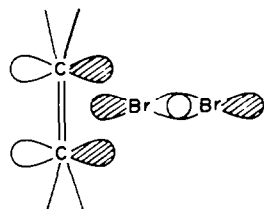
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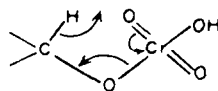
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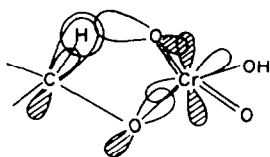
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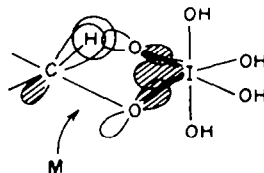
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forbidden. An alternative and at first sight attractive mechanism is represented by **19**; the corresponding orbital picture **20** shows that this is a forbidden Hückel-type system with $4n$-electrons, and in fact an acyclic mechanism is observed for oxidations by both manganese(VII) and lead(IV), (ref. 7, pp. 47, 284, and ref. 12).

Oxidation by bromine could proceed by the route **21**, the orbital picture **22** shows that this would be allowed. At present, however, the evidence is that an acyclic route is preferred (**23**).[12] This apparent exception may arise because the observed route can produce ionised and solvated HBr directly, while the electrocyclic route cannot. The bromine molecule may also be too large to allow effective orbital overlap. As the energy of ionisation and solvation must be a major part of the free energy of this particular process, the energetic advantages of the acyclic process may outweigh the advantages of the electrocyclic process.

D *Oxidation of α-glycols.* The Malaprade reaction (**24, 25**), (ref. 7, p. 373) is clearly an allowed electrocyclic process which may give rise directly to IO_3^- in the correct orientation, while the corresponding reaction with chromium(VI) is forbidden (**26**).
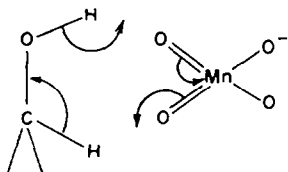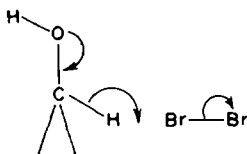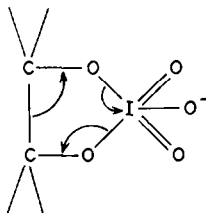
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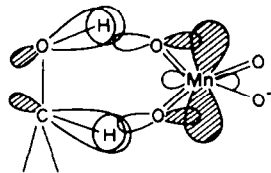
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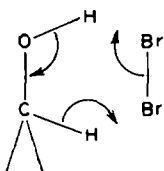
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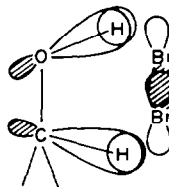
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This is in agreement with the observation that the preferred reaction of chromium(VI) is the independent oxidation of each CH—OH group to C=O (ref. 7, p. 170). This is of course not possible with di-tertiary glycols, which are oxidised by a cyclic mechanism which apparently violates the selection rule. One possible explanation is that the reaction may involve two one-equivalent steps (see below). As the amount of glycol cleavage is reduced when manganese(II) is added, and *trans* glycols can be attacked by an acyclic route, it is clear that the actual course of the reaction is not simple.[13]

Manganese(VII) reacts autocatalytically with di-tertiary glycols.[12] The formation of a cyclic complex will be difficult because of the slow exchange rate of the oxygen ligands, and although an electrocyclic process such as 27 would be allowed (Hückel-type, 10 electrons) it involves a large, possibly strained ring. Evidently indirect attack, e.g. *via* a manganese(III) glycol complex, is more favourable. A similar oxidation by bromine (28) would be forbidden (Hückel-type, 8 electrons); the reaction does not in fact occur.[12]
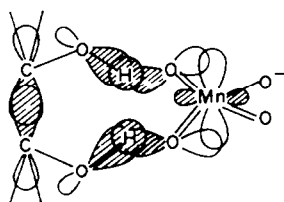
E *Other two-equivalent oxidations.* The Grob bis-decarboxylation 29 (ref. 7, p. 297), has been shown to be a non-concerted process. This is in agreement with the orbital
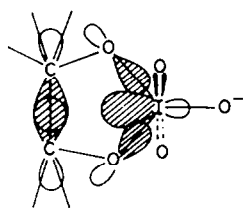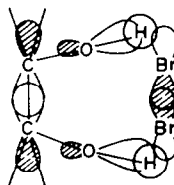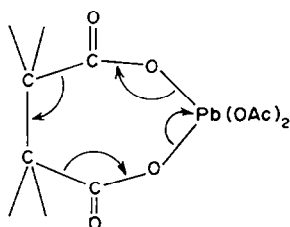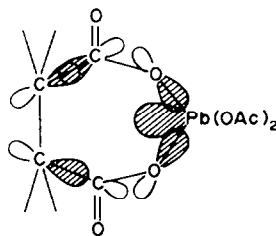
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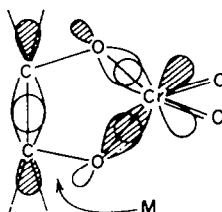
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picture **30**, which shows that a concerted mechanism would have an 8 electron Hückel transition state, and so be forbidden. A special case is the reaction **31** → **32**; the orbital picture **33** shows that this is an allowed Hückel-type process.

Mechanisms involving acetoxylation by lead(IV) apparently lead to ambiguities. For example in the acetoxylation of enols or phenols a 6e (5-membered ring) **34** or 8e (7 membered ring) **35** transition state can be written, and either Hückel or Möbius overlap is possible (Figs **36** to **39**), since the acetoxy group can behave either as an antarafacial or a suprafacial component. These various possibilities cannot be distinguished experimentally at present, but the fact that they exist may in part explain the versatility of lead(IV) as an oxidant.
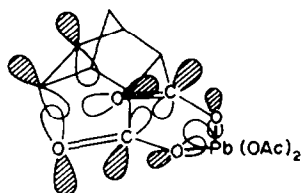
Halogens should be able to dehydrogenate hydrocarbons by an allowed electrocyclic process (**40**, **41**). In the case of bromine this would be endothermic, but it might be a possible mechanism for the high temperature dehydrogenation of hydrocarbons by iodine, a reaction which is usually assumed to involve free radicals.[14] The reaction
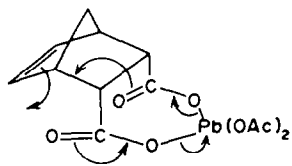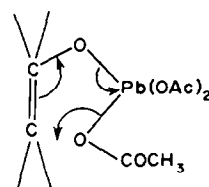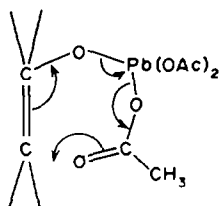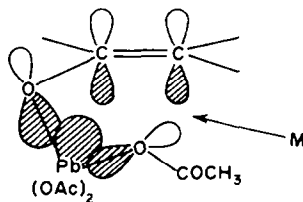
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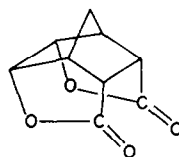
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would be expected to be more facile using chlorine, but it is evidently masked by the very rapid radical halogenation.

If the double-bond in the product is stabilised by being incorporated into an aromatic system, dehydrogenation of *cis* vicinal hydrogen atoms with bromine becomes thermodynamically possible. A number of examples of this reaction are known[15] e.g.
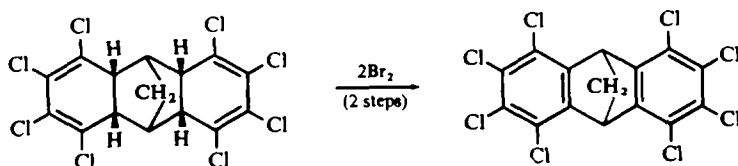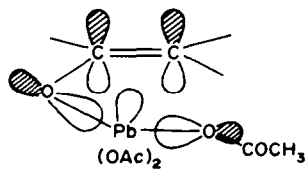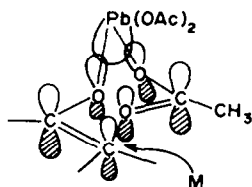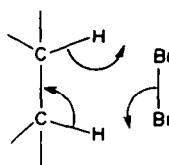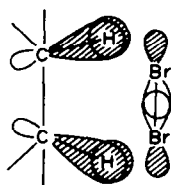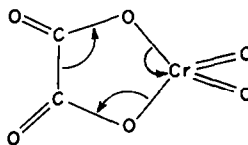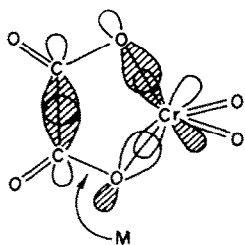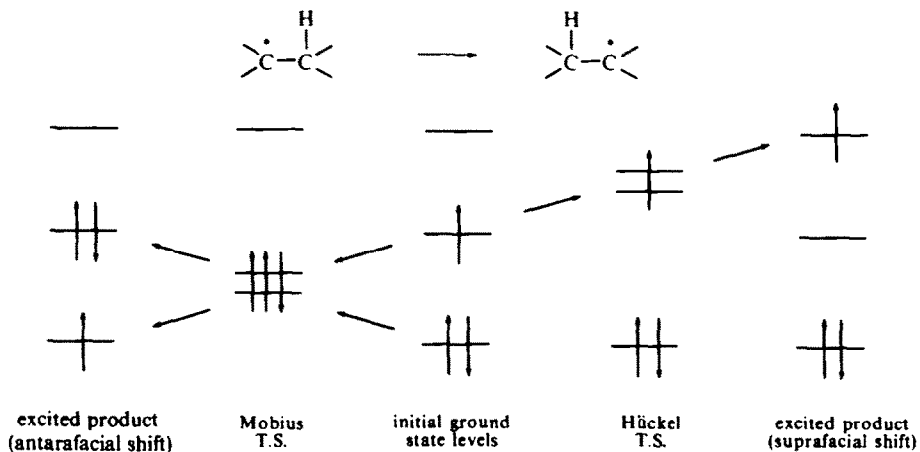
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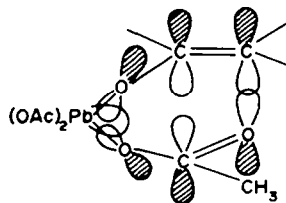
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As these reactions are carried out in non-polar solvents, and do not need a source of free radicals, they may well be electrocyclic processes.

Chromium(VI) does not oxidise oxalic acid by the obvious direct electrocyclic mechanism (42, 43), since the main path is second-order in oxalic acid.[16] On examination this route is found to be forbidden.
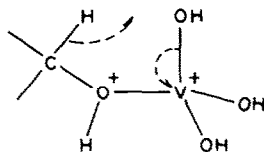
One-equivalent oxidants. In oxidations by one-equivalent oxidants such as vanadium(V) or cobalt(III) an odd number of electrons are involved, and so no electrocyclic processes can satisfy either the $4n$ or the $4n + 2$ rules. Consideration of the correlation diagram (below) for the simplest radical electrocyclic process, the 1,2-H-atom shift, suggests that ground-state radical starting materials can only give rise to excited state products, so that all thermal electrocyclic processes should be forbidden.

Conversely photochemical processes are allowed, since they can give rise directly to ground state products. This is in agreement with the observation that many one-equivalent oxidations have been found to be photosensitive (e.g. Fe(III) or Mn(III) with oxalic acid, Ce(IV) with alcohols) (ref. 7, pp. 274, 228).
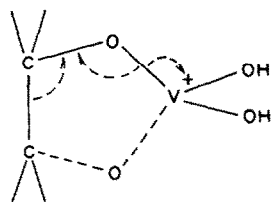
Thermal cyclic processes however do occur, e.g. (44) ref. 7, p. 198). Here the cyclic

excited product   Mobius   initial ground   Hückel   excited product
(antarafacial shift)   T.S.   state levels   T.S.   (suprafacial shift)

43   44

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process has the advantage that it generates a relatively stable radical R_2COH, but it is not essential, for if a more powerful oxidant such as Co^{3+} aq is used the less stable products $R_2CH-O\cdot$ or $R\cdot + RCHO$ are formed by an acyclic process (ref. 7, p. 202). The cyclic glycol fission process 45 also occurs, but it is thought that the ring is nonplanar (ref. 7, p. 204). In both these reactions cyclic geometry need not imply cyclic orbital overlap, so the selection rules which would appear to forbid these mechanisms need not apply.

CONCLUSIONS

It has been possible, using a minimum of general assumptions, to rationalise the behaviour of a number of oxidants which actually or potentially can act by electrocyclic mechanisms. A few exceptions have been found, but they can be accounted for from what is already known of the reactions in question. Clearly one would not expect the selection rules to be the sole determinant of the mechanisms of these reactions, but it is evident that they do exert a significant influence.

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