Hydrocarbon Oxidation by High-Valent Group 6 Oxides

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Abstract: The results of a mechanistic study using ab initio theoretical methods are used to outline plausible mechanistic sequences for alkane, alcohol, and alkene oxidation by chromyl and molybdy1 chlorides. We suggest that the second o xo group is intimately involved in the reaction sequence. This spectator oxo group is suggested to play a central role in stabilizing critical intermediates in these reactions and may be important in other oxidation reactions of metal oxides (MnO₂⁻, OsO₄, RuO₄, and supported transition metal oxides).

I. Introduction

Chromic acid and related chromyl and molybdyl compounds form a class of versatile oxidizing agents capable of delivering oxygen atoms to most types of oxidizable organic groups. This versatility can be a drawback since specificity in reaction site is at times a desirable quality. An example of this is the product distribution for the oxidation of methylcyclopentane by chromyl chloride.

\[
\begin{align*}
\text{CH}_3 + \text{CrO}_2\text{Cl}_2 & \rightarrow \text{CHO} + \text{CH}_3\text{Cl} + \text{CH}_3\text{Cl} + \text{CH}_3\text{Cl}
\end{align*}
\]

Clearly this product mixture is neither synthetically useful nor mechanistically straightforward. Scheme I illustrates likely primary, secondary, and even higher-order reaction products of chromyl compounds reacting with a general alkane.

The likely primary processes a and b form alcohols (and alkyl chlorides if the oxidant is chromyl chloride). For example, propylbenzene reacts with chromyl chloride to form substantial 1-chloro-1-phenylpropane (eq 2).1,2

\[
\begin{align*}
\text{PhCH}_2\text{CH}_2\text{Cl} + \text{CrO}_2\text{Cl}_2 & \rightarrow \text{PhCH}_2\text{CH}_2\text{Cl} + \text{PhCH}_2\text{CH}_2\text{Cl}
\end{align*}
\]

whereas triphenylmethane forms predominantly triphenyl carbinol4 upon hydrolysis (eq 3). It is likely that alcohols and alkyl chlorides will be dehydrated under the reaction conditions4 as implied in path c of Scheme I. The olefins generated in situ can be subsequently oxidized as shown in path d of Scheme I. Alternatively, the alcohols may be oxidized to aldehydes and ketones as shown in path e of Scheme I. Finally, aldehydes can be oxidized by chromic acid to carboxylic acids as shown in path f of Scheme I and eventually to CO₂ and H₂O as shown in path g of Scheme I.

Out studies will concentrate on the energetics of chromyl chloride and molybdyl chloride oxidation of alkanes, alcohols, and alkenes. Section II provides a discussion of a significant mechanistic feature found to be common to each of the oxidation steps. Section III presents the results for alkane oxidation, Section IV, alcohol oxidation, and finally, Section V, the alkene oxidation. Some details of the theoretical calculations are presented in Section VI.

II. The Metal–Oxo Bond

The primary reaction step common to all of the reactions of chromyl chloride discussed in the sections that follow is the addition of either a σ or π bond across a Cr=O π bond. We find that these processes depend critically upon whether there is an

(61) For example, for I we estimate the following fundamental frequencies of vibration: NH stretch = 3120, NNH bend = 1434, NO stretch = 791, NN stretch = 1529, OH stretch = 3588, NNO bend = 593, NOH bend = 1265, and torsional = 1286 and 540 cm⁻¹. (62) Calculated by using the program THERMO written by A. K. Rappé.
extra (spectator) oxo group on the metal. Thus the $d^0$ or Cr(VI) complexes,

$$\text{(4)}$$

lead to a chemistry very different from that of the complex

$$\text{(5)}$$

which is also formally $d^0$ or Cr(VI). The reason for this has to do with the character of the metal–oxo bonds in (4) and (5).

Basically, this difference arises because the species in (4) can utilize two $\sigma$ bonds to the single oxygen, which, along with a $\sigma$ bond, leads to a strong triple bond. On the other hand, for (5) the two $\sigma$ orbitals are each used to form a $\pi$ bond to each of the two oxo groups. Thus, including the $\sigma$ bonds, both oxo groups are connected to the metal through double bonds.

A. Orbitals. In $\text{Cl}_2\text{CrO}_2$ we start with six valence electrons on the Cr of which two are involved in fairly ionic bonds to the two Cl ligands. This leaves four Cr electrons for the bonds in the two oxo groups.

In Figure 1 we show GVB orbitals for the dioxo species in (5). The CrO $\sigma$ bond of Figure 1a consists of two overlapping orbitals, each containing one electron. As this bond is stretched, one orbital (on the right) becomes an oxygen $p$ orbital oriented along the bond

$$(p_y),$$

while the other becomes a Cr $d$ orbital oriented along the bond ($d_{x^2}$). These two orbitals are spin paired to form the orbitals of a covalent $\pi$ bond.

The CrO $\pi$ bond of Figure 1b consists of a Cr $d\pi$ orbital ($d_{x^2}$) with one electron and an O $p\sigma$ orbital ($p_x$) with one electron paired to form a quite covalent $\pi$ bond.

Since the free oxygen atom starts with four electrons distributed among three $p$ orbitals and since the two $p$ orbitals in the $\pi$ bonds account for two electrons, there are two electrons remaining in the nonbonding $p$ orbital perpendicular to the CrO bond ($p_z$), as shown in Figure 1c.

Summarizing, the CrO bond is a rather covalent double bond involving two electrons in two $d$ orbitals on the Cr and electrons in two $p$ orbitals on the O (with the remaining two $p$ electrons on the oxygen in a nonbonding orbital). This is quite analogous to the CO bond of an aldehyde or ketone, as shown in Figure 2 (for formaldehyde). For comparison, as shown in Table 1, the bond dipoles for the Cr–O bond in $\text{Cl}_2\text{Cr}_2\text{O}_2$ and the C–O bond

in $\text{H}_2\text{CO}$.
of formaldehyde are $-1.24$ and $-2.74$ D, respectively.

The second CrO bond is identical with the one above, accounting for two more electrons in two additional Cr d orbitals. The remaining two electrons of the Cr are involved in somewhat ionic bonds to the Cl's as shown in Figure 3.

B. The Monooxo Complex. In Cl₂CrO, four of the six valence electrons on the Cr are used for partially ionic bonds to the four Cl ligands, leaving two electrons on the Cr for bonds to the oxo ligand.

In Figure 4 we show GVB orbitals of the Cr oxo bond of the monooxo species in (4a). Here (Figures 4b and 4c) we find that both $\sigma$ bonds of the Cr are used to make $\sigma$ bonds to the O. This uses up two electrons and two orbitals ($p_\sigma$ and $d_{\sigma}$) of the oxygen, leaving a doubly occupied $\sigma$ orbital ($p_\sigma$) on the oxygen. The remaining four electrons of the Cr are involved in partially ionic bonds to the four Cl's, leaving an empty $d_{\sigma}$ orbital pointing at the oxygen. The doubly occupied $p_\sigma$ orbital of the oxygen and the empty $d_{\sigma}$ orbital of the Cr lead to a donor-acceptor bond (or a Lewis acid–Lewis base bond much like that of BH$_3$–PH$_3$).

The result then is a triple bond between the Cr and oxygen (two $\pi$ bonds plus the donor–acceptor bond) involving two electrons from the Cr and four electrons from the oxygen. The net charge transfer is small so that the CrO bond is approximately neutral. The $\sigma$ bond dipole is $+5.10$ D (the $\sigma$ bond dipole of BH$_3$NH$_3$ is $+4.87$ D). Thus one should not draw the bond as

\[ \text{Cr} \equiv \text{O} \quad (6) \]

since this would imply an oxygen that has a plus charge. Yet one should not draw it as

\[ \text{Cr} = \text{O} \quad (7) \]

since this would imply a ketone-type double bond as found for the dioxo species. We will use the diagram

\[ \text{Cr} \equiv \text{O} \quad (8) \]

to indicate this bond where the two solid lines indicate covalent

\[ \sigma \] bonds and the dotted line represents a donor–acceptor $\sigma$ bond.

Thus, bonding in the monooxo complex is quite similar to that in carbon monoxide (see Figure 5) where there are two strong
Table II. Metal-Oxo Bond Strengths (kcal)

<table>
<thead>
<tr>
<th></th>
<th>Cr</th>
<th>Mo</th>
<th>difference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>51</td>
<td>82</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td>79</td>
<td>102</td>
<td>23</td>
</tr>
</tbody>
</table>

Figure 6. Geometric parameters for Cr and Mo monooxo and dioxo complexes. Bond angles in degrees; bond distances in angstroms. Underlined parameters were obtained from experiment or extrapolated from related molecules.

π bonds, each involving one π orbital from the C and one from the O plus a σ bond that is dominantly a doubly occupied π orbital on the oxygen. For comparison with the CrO σ bond dipole of +5.10 D for Cl₂CrO, the CO σ bond dipole of carbon monoxide is +4.34 D. The C 2π pair moves away from the oxygen to become the nonbonding orbital important in the Lewis base character of CO. In this case the CO π bonds are moderately ionic toward the O, but the shift of the C 2π pair behind the carbon leads to a nearly neutral charge distribution (the net dipole moment is calculated to be 0.17 D with the sign C←O). On the other hand, in CO₂ the two π orbitals of the C are used to make one π bond to each O, leading to two double bonds more like those in ketones. Thus the bonding in CO and CO₂ is analogous to that in Cl₂CrO and Cl₂CrO₂, respectively.

We should emphasize here that the rather neutral character of the Cr-oxo bonds is partly due to the presence of fairly ionic Cr-Cl bonds that pull charge from the Cr, making the Cr more electronnegative for its bonds to the oxoxygen. Replacing the Cl ligands with alkyl groups would lead to a more ionic Cr-oxo bond, leading to less triplet-bond character for the Cr-0 bond in (4a).

C. Comparison of Properties of Monooxo and Dioxo Bonds. The most important difference between metal-oxo double bonds and triple bonds is the bond energy. As tabulated in Table II, the triple bond is 31 kcal stronger than the double bond for Cr and 23 kcal stronger than that for Mo.

Some of the geometries are shown in Figure 6. Here we see that the bond length is nearly the same for the double and triple bonds, with differences on the order of 0.01 Å for both Cr and Mo. Experimental vibrational frequencies for several such compounds are tabulated in Table III where we see only small shifts in the M-O stretching frequencies (a systematic increase by about 30 cm⁻¹).

D. The Special Role of the Spectator Oxo Group. We will find in the following sections that the second oxo group of the dioxo species plays a special role in the chemistry of these systems. Consider, for example, the addition of an H₂ across the metal-oxo bond to form a hydroxyl hydride. In the case of the monooxo species, this process is quite endothermic, leading to ΔG = +71 kcal for

\[
\text{Cl}_2\text{CrO} + \text{H}_2 \rightarrow \text{Cl}_2\text{CrOH} + \text{H} \quad (9)
\]

The reason for this remarkable difference can be found by comparing the electronic structure in (10b) with that in (9a). In both cases there are four σ-bonded ligands [two Cl, one OH, and one H in (10b)] and an oxo bond. Thus, in (10b) the Cr can use both dσ orbitals to bond to a single oxygen, just as in (9a). The result is a triple metal-oxo bond, just as in Figure 3. Thus, in the reaction 10, the spectator oxo group (the one not involved in the bond) changes from a double bond to a triple bond, thereby stabilizing the product by ~31 kcal. That is, the spectator oxo group drives the reaction.

III. Oxidation of Alkanes by Chromyl Chloride

In order to provide a basis for discussion of reactions of chromyl chloride with alkanes, we will first consider the results of theoretical studies on the initial steps.
A. Theoretical Considerations. It is often assumed that addition of an alkane RH to chromyl chloride leads to the alkoxy hydroxide Cr(IV) species

\[
\text{Cl}_2\text{Cr}=\text{O} + RH \rightarrow \text{Cl}_2\text{Cr} \text{(OH)}_2 + R 
\]

(11)

However, we find that in all cases (see Figures 7-9) the presence of the spectator oxo group leads to addition across a single oxo bond

\[
\text{Cl}_2\text{Cr} \text{(OH)}_2 + RH \rightarrow \text{Cl}_2\text{Cr} \text{(OH)}_2 \text{(OH)}_2 + R 
\]

(12)

For R = H, this intermediate is stable with respect to decomposition (by ~6 kcal). On the other hand, if R is an alkyl group, the decomposition to form the radicals is favored in the gas phase [here the Cr species would be denoted as Cr(V)], with the energetics for (13)

\[
\text{Cl}_2\text{Cr} \rightarrow \text{Cl}_2 + \text{Cr} + \text{R} 
\]

(13)

approximately thermoneutral for R = CH₃ but increasingly exothermic for R = Et (ΔG = -7 kcal), R = i-Pr (ΔG = -11 kcal), and R = t-Bu (ΔG = -13 kcal). However, decomposition of (12b) to form alkyl chloride or alcohol is greatly more exothermic

\[
\text{Cl}_2\text{Cr} \rightarrow \text{Cl}_2 + \text{Cr} + \text{R} 
\]

(14)

with the alcohol favored (shown for ethane).

From Figure 7 we see that the dominant product of the reaction of chromyl with H₂ should be H₂O, whereas the reaction with alkenes RH should lead to alcohols. In both cases the Cr is left in the (formal) Cr(IV) state

\[
\text{Cr} \rightarrow \text{Cr} + \text{OH} \rightarrow \text{Cr} + \text{OH} + \text{R} 
\]

(15)

The major difference in the reaction with H₂ and RH is that via

decrease as one goes across a row of the periodic table and that the overlaps increase as one goes down a column. Table VI shows the σ and π bond overlaps for three complexes, verifying this effect.

B. Experiments. There is substantial evidence\textsuperscript{14} that chromyl compounds react with alkanes to initially form either alcohols, alkyl chlorides, or a stable complex,

$$\text{CrO}_2\text{Cl}_2 + \text{R-H} \rightarrow \text{R-OH} + \text{Cr(IV)}$$
$$\text{CrO}_2\text{Cl}_2 + \text{R-Cl} \rightarrow \text{Cr(IV)} + \text{R-Cl}$$

The initially formed products \(\text{R-OH}\) and \(\text{R-Cl}\) may undergo rapid secondary reactions leading to oxidation products attributable to alkene oxidation.\textsuperscript{12b} The stable complex undoubtedly undergoes a rapid secondary reaction leading to the first "observed" intermediate, the \(\text{Etard}\) complex, an insoluble hygroscopic brown solid that can be hydrolyzed under reducing conditions to directly form aldehydes and ketones.\textsuperscript{16} The product composition usually is diverse and very dependent on reaction conditions,\textsuperscript{1b} making detailed mechanistic study difficult. There is evidence for a Cr(V) intermediate\textsuperscript{5,6} and for the \(\text{Etard}\) complex having two Cr(IV) centers.\textsuperscript{7}

On the basis of the energetics described in Section III A, we propose a reaction scheme consistent with the experimental observations that consists of an initial addition of the \(\text{C-H}\) bond across one \(\text{Cr-O}\) bond forming an organometallic complex (reaction path a of Scheme II) that either reductively eliminates an alcohol (path b of Scheme II) or an alkyl chloride (path c of Scheme II) or reacts with a second \(\text{CrO}_2\text{Cl}_2\) molecule, initially forming a dative complex between the hydroxide and the second chromyl chloride (path d of Scheme II). This is followed by addition across a second \(\text{CH}\) bond, leading to a complex with a bridging carbene (path e of Scheme II) that can rearrange to a third dative complex consisting of a bridging water and a bridging carbonyl compound (path f of Scheme II), which is a feasible structure for the \(\text{Etard}\) complex.

We have concentrated on the initial reactions stressing factors that favor the reductive elimination pathways, since use of dilute solution or polymer supports will decrease the secondary reactions leading to \(\text{Etard}\) complex formation.

IV. Oxidation of Alcohols by Chromyl Chloride

In analogy to the alkane oxidation steps outlined in Section III, alcohols should be oxidized by chromyl chloride, the first steps being either addition across the \(\text{O-H}\) bond,

$$\text{R-OH} + \text{Cl}_2\text{CrCl_2} \rightarrow \text{Cl}_2\text{C}_2\text{H}_5\text{O}$$

or simple ligand substitution with a chloride,

$$\text{R-OH} + \text{Cl}_2\text{CrCl}_2 \rightarrow \text{RCl} + \text{Cl}_2\text{CrCl}_2$$

The energetics of these pathways for \(\text{C}_2\text{H}_5\text{OH}\) as the substrate are shown in Figure 11. The energetics suggest that chromyl chloride is a viable oxidizing reagent for water-insoluble alcohols and that if formed during alkane oxidation alcohols will subsequently be oxidized to aldehydes and ketones, explaining why they are generally not observed in hydrocarbon oxidation by chromyl chloride. The energetics for the molybdyl chloride oxidation of ethanol are shown in Figure 12. Again, the increased Mo bond strengths favor formation of the organometallic intermediate and disfavor the reductive elimination pathways.

V. Chromyl Chloride Oxidation of Alkenes

A novel aspect of olefin oxidation is the proposal\textsuperscript{9} of a metallacycle intermediate analogous to the metallohydrocarbon proposed for olefin metathesis (path a of Scheme III) that can decompose to form either a carbonyl compound (path b of Scheme III), an epoxide (path c of Scheme III), or the precursor to a chlorohydrin (path d of Scheme III). Experimentally, each of these products has been observed in alkene oxidation by chromyl chloride.\textsuperscript{7-9}
The energetics for the oxidation of ethylene by chromyl chloride are shown in Figure 13. These energetics confirm the proposal (Sharpless) that the metalloxyketane is a likely common precursor for all of the observed oxygen-containing products and rule out the direct addition reaction characteristic of oxidations by OsO₄ (path e of Scheme I).

It is noteworthy that CrO₂Cl₂ does not react to form significant diol products (diol is formed by hydrolysis of the initially formed epoxide), whereas for KMnO₄ the diol products are dominant without significant epoxide formation. This differential reactivity can be understood in terms of stabilization due to spectator oxo groups resulting from the differing number of valence electrons present. Starting from the respective metalloxyketane intermediates (where an arrow denotes a lone pair on the metal),

\[
\begin{align*}
1 & \quad \rightarrow & \quad 2 \\
3 & \quad \rightarrow & \quad 4 \\
5 & \quad \rightarrow & \quad 6
\end{align*}
\]

the difference is apparent. That is, for CrO₂Cl₂ the shift involves reaction with a strong metal-oxo triple bond, preventing (20), whereas for both KMnO₄ and OsO₄ the reaction is with an oxo double bond, leading to conversion of a spectator oxo into an oxo triple bond, thus enhancing (21) and (22) and driving the formation of species 4 and 6.

As discussed in Section III, a major difference between Cr and Mo compounds is the general increase in bond strength of 15 kcal per bond. This effect manifests itself in a strong relative disfavoring of any reductive elimination pathway for molybdenum (see Figure 14). For Mo and W, the C−C bond cleavage pathway will dominate the reductive elimination of epoxides or chlorohydrins, and it is very likely that it is through this pathway that MoO₃ and WO₃ are activated for metathesis on a polymer support.

The energetics for these processes are summarized in Figure 14 for molybdenum.

Under appropriately chosen operating conditions, olefins such as propene are allylically oxidized to carbonyls such as acrolein over...
supported MoO3 and WO3 catalysts. The addition across a C–H bond (as discussed in Section III) may be competitive with addition across the C–C π bond. Estimates of the energetics are presented in Figure 15 for Cl2CrO2, indicating that reaction across the C–C π bond should be kinetically favored over reaction across the C–H bond. The analogous reaction for molybdenum, as shown in Figure 16, should result in a more competitive situation. Experimentally, the products observed (C–C reaction vs. C–H reaction) are very dependent upon the reaction conditions.13-17 Imra7 has found that for nonstoichiometric MoO2 and WO3 the dominant product is the oxidative C–C bond cleavage product; that is, propene forms formaldehyde and acetaldehyde. Furthermore, San Filippo9 has found that chemisorbed chromyl chloride oxidatively cleaves the C–C double bond. The analogous reaction for molybdenum, as shown in Figure 15 for Cl2CrO2, indicating that reaction across the C–C π bond should be kinetically favored over reaction across the C–H bond. The analogous reaction for molybdenum, as shown in Figure 16, should result in a more competitive situation. Experimentally, the products observed (C–C reaction vs. C–H reaction) are very dependent upon the reaction conditions.13-17 Imra7 has found that for nonstoichiometric MoO2 and WO3 the dominant product is the oxidative C–C bond cleavage product; that is, propene forms formaldehyde and acetaldehyde. Furthermore, San Filippo9 has found that chemisorbed chromyl chloride oxidatively cleaves the C–C double bond.

Our interpretation of these results is that the true surface sites responsible for metathesis initiation C–C bond cleavage are as described in (23) with adjacent sites being needed to achieve quantitative yields of C–C bond cleavage through a process analogous to the bimolecular decomposition of homogeneous alkylidene complexes.18

VI. Theoretical Details
In all complexes we explicitly considered all electrons for Cr, Mo, C, O, and H atoms. The basis sets were all of the valence double χ or split valence type. As discussed by Rappé, Smedley, and Goddard,19 the d bases for the transition metals were optimized for the d6 configuration in order to yield a balanced description of the various s,d, d2, and d4 states. The specific basis sets used are selected from a new series of basis sets we have recently obtained for H–Ba and will be published separately.20

In the calculations reported here, the Cl atoms were described by using the SHC effective potential21 to replace the core electrons, and the basis set was contracted to minimal basis based on molecular calculations on TiCl4.

Two types of wave functions were utilized.

(a) GVB-PP (the generalized valence bond with perfect pairing restriction):22 In this wave function each correlated pair of electrons is described as a spin singlet state (φαφβ + φβφα).

(b) GVB-CI (generalized valence bond configuration interaction): Here a full configuration interaction is carried out among all configurations that can be formed from various occupationsof the GVB orbitals from the GVB-PP calculations.23,24 The GVB-PP level leaves out spin-coupling terms often important at saddle points for reactions; the GVB-CI allows general spin coupling and includes the simultaneous interpair correlation terms often essential for multiply bonded systems.

In the GVB-PP method, it is possible to select a specific subset of the electron pairs of a system to be correlated. In the calculations reported here, we have correlated all metal–ligand bond pairs except the metal–Cl bond pairs. In the nonmetal-containing compounds, only the two-electron pairs in the bonds are correlated.

As discussed previously,25 the following scheme for determining energetics for chemical processes is utilized. Using the GVB-CI method, we calculate the energy differences for reactions where the number and type of bonds are as similar as possible. To calculate the enthalpy changes at 0 K for these processes, one must add the differential zero-point corrections to the calculated energy differences. The resulting ΔHf,0 are combined with previously obtained ΔHf,0 for the other species in the idealized reactions to calculate ΔHf,0 for the molecules of interest. These ΔHf,0's are combined with vibrational frequencies (experimental, calculated, or estimated) and moments of inertia to obtain ΔH f,0 and S f,0. Finally, the ΔG,0 for the reactions of interest are calculated.

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Registry No. Cl2CrO2, 14977-61-8; Cl2MoO2, 13637-68-8; CH4, 74-82-8; C2H6, 74-84-0; C2H4OH, 64-17-5; C3H6, 74-85-1; C4H8, 115-07-1; H2, 1333-74-0.

(20) A. K. Rappé and W. A. Goddard III, manuscript in preparation.