estimating the nine fundamental vibrational frequencies using model compounds.[61] The zero-point corrections in kcal/mol are as follows: I (20.2), II (20.2), III (20.0), IV (20.2), V (19.5), VI (19.5), VII (21.4), VIII (21.1), and IX (18.9). These vibrational frequencies and the rotational constants were used to estimate the $C_p(T)$ in order to convert ΔH(0 K) to ΔH(298 K). The enthalpy corrections[62] in kcal/mol were as follows: I (2.7), II (2.6), III (2.6), IV (2.6), V (2.7), VI (2.7), VII (2.5), VIII (2.5), and IX (3.0).

Acknowledgment. We wish to thank Dr. Anthony K. Rappé for aid and helpful discussions. We are also grateful for partial support of this work by a contract from the U.S. Department of Energy (Contract No. DE-AM03-76SF00767; Project Agreement No. DE-AT03-80ER10608).

Registry No. I, 81407-93-4; III, 81390-26-3; V, 67615-78-5; VII, 63831-72-1; VIII, 63831-71-0.

---

[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.

[63] Foner, S. N.; Hudson, R. L. *J. Chem. Phys.* **1978**, *68*, 3162.

Hydrocarbon Oxidation by High-Valent Group 6 Oxides

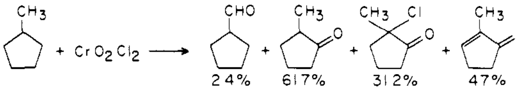
Anthony K. Rappé† and William A. Goddard, III*

Contribution No. 6511 from the Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125. *Received August 20, 1981*

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 molybdyl chlorides. We suggest that the second oxo 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 (MnO_4^{2-}, OsO_4, RuO_4, and supported transition metal oxides).

I. Introduction

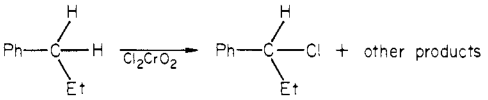
Chromic acid and related chromyl and molybdyl compounds form a class of versatile oxidizing agents[1] capable of delivering oxygen atoms to most types of oxidizable organic groups. This versatility can be a drawback since specificity in reaction site is at times a desirable quality. An example of this is the product distribution for the oxidation of methylcyclopentane by chromyl chloride[2]



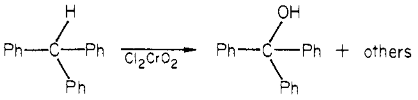
(1)

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),[1b,3]



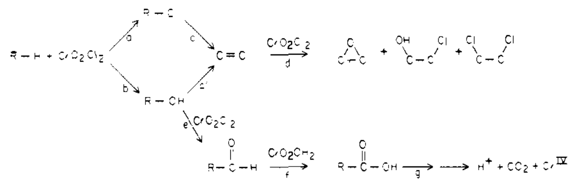
(2)



(3)

whereas triphenylmethane forms predominantly triphenyl carbinol[4] upon hydrolysis (eq 3). It is likely that alcohols and alkyl chlorides will be dehydrated under the reaction conditions[1c] 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 CO_2 and H_2O as shown in path g of Scheme I.

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

---

† Bantrell Fellow, 1980-1981. Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523.

[1] (a) W. H. Hartford and M. Darrin, *Chem. Rev.*, **58**, 1-61 (1958); (b) K. B. Wiberg, "Oxidation in Organic Chemistry", Part A, Academic Press, New York, 1965, pp. 69-184; (c) F. Freeman, *Rev. React. Species Chem. React.*, **1**, 37-64 (1973).

[2] V. Psemetschi, I. Necsoiu, M. Rentea, and C. D. Nenitzescu, *Rev. Roum. Chim.*, **14**, 1567-1574 (1969).

[3] L. M. Stephenson, J. Egnatchik, and D. R. Speth, *J. Org. Chem.*, **44**, 346-349 (1979)

[4] I. Necsoiu, V. Przemetchi, A. Ghenciulescu, C. N. Rentea, and C. D. Nenitzescu, *Tetrahedron*, **22**, 3037-3045 (1966).

0002-7863/82/1504-3287$01.25/0

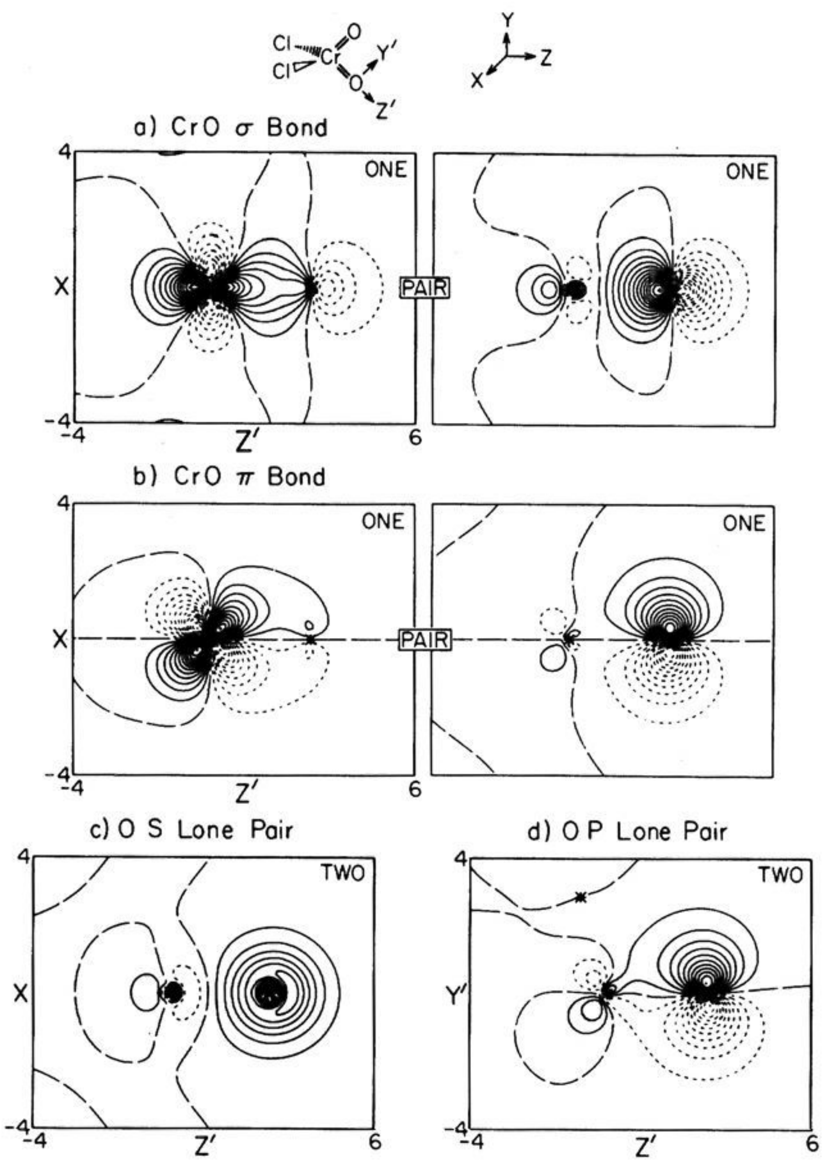
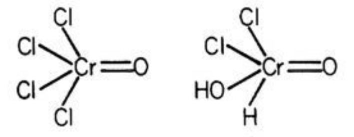


Figure 1. GVB orbitals for one CrO bond of Cl_2CrO_2. Long dashes indicate zero amplitude; the spacing between contours is 0.05 au; the same convention is used in all plots.

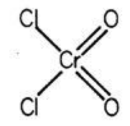
extra (spectator) oxo group on the metal. Thus the d^0 or Cr(VI) complexes



a b

(4)

lead to a chemistry very different from that of the complex



(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 dπ bonds to the single oxygen, which, along with a σ bond, leads to a strong *triple bond*. On the other hand, for (5) the two dπ orbitals are each used to form a π bond to each of the two oxo groups. Thus, including the σ bonds, both oxo groups are connected to the metal through *double bonds*. This interpretation was derived from examination of the ab initio orbitals from ab initio generalized valence bond (GVB) calculations (details in Section VI). Note that the GVB orbitals are unique. Unlike the case with molecular orbitals, one cannot mix occupied orbitals without increasing the total energy of the system.

A. Orbitals. In Cl_2CrO_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.

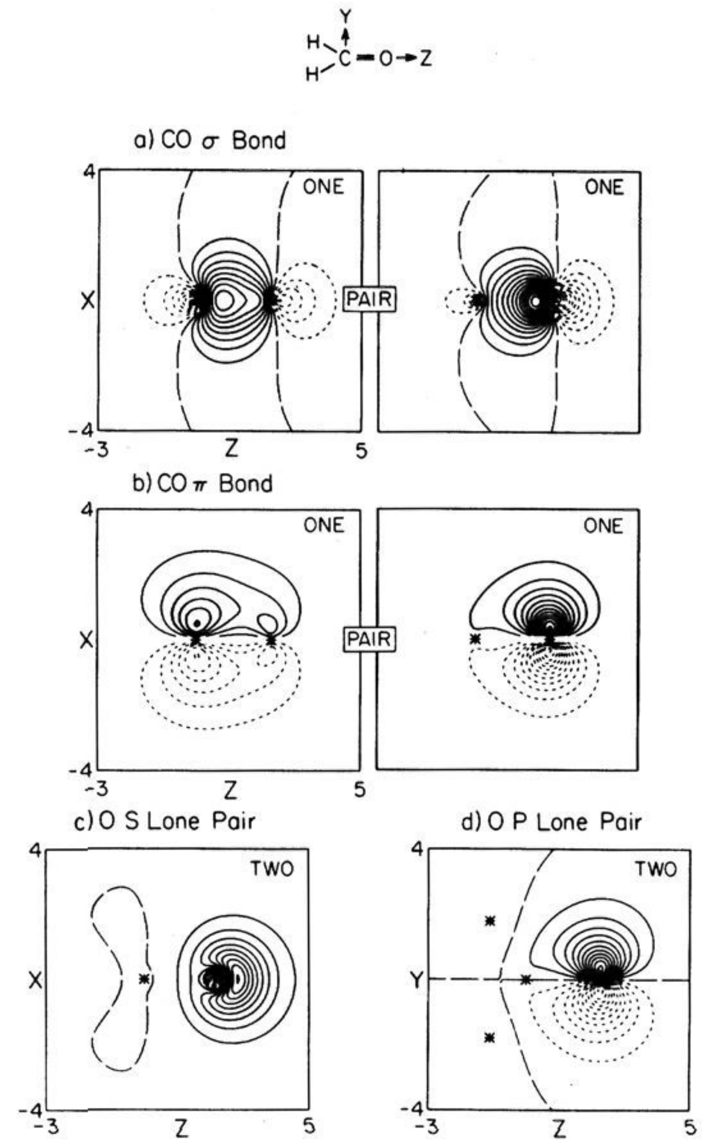
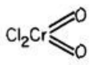


Figure 2. GVB orbitals for the CO bond of H_2CO.

Table I. Bond Dipoles (in Debye) for Various Molecules

	bond	dipole
	Cr–O σ bond	−1.1097
	Cr–O π bond	−0.1324
	Cr–O total bond	−1.2424
$H_2C{=}O$	C–O σ bond	−1.3509
	C–O π bond	−1.3848
	C–O total bond	−2.7354
H_3B---NH_3	B–N σ bond	+4.8688
$Cl_4Cr{\equiv}O$	Cr–O σ bond	+5.0990
	Cr–O π bond	−0.4613
	Cr–O total bond	+4.1766
$C{\equiv}O$	C–O σ bond	+4.3398
	C–O π bond	−2.5822
	C–O total bond[a]	−0.8245

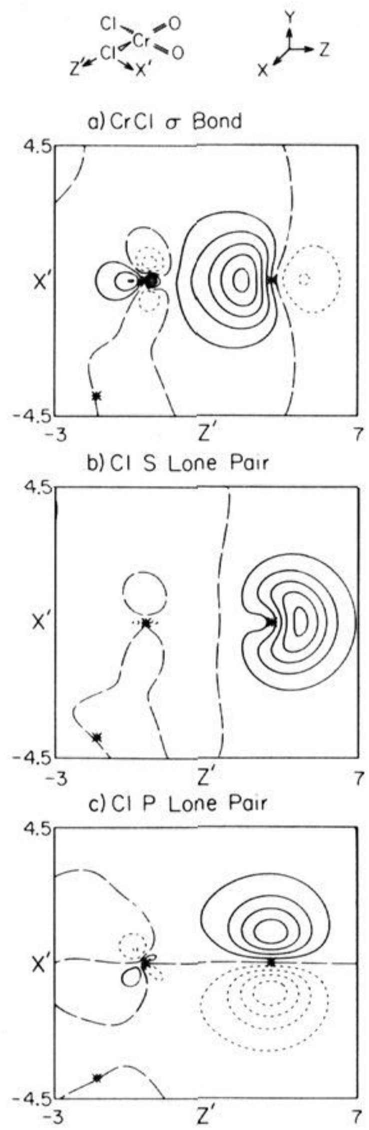
[a] This does not include the carbon and oxygen 2s lone pairs. The total dipole moment calculated for CO is −0.17 D.

In Figure 1 we show GVB orbitals for the dioxo species in (5). The CrO σ 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_z), while the other becomes a Cr d orbital oriented along the bond (d_{z^2}). These two orbitals are spin paired to form the orbitals of a covalent σ bond.

The CrO π bond of Figure 1b consists of a Cr dπ orbital (d_{xz}) with one electron and an O pπ orbital (p_x) with one electron paired to form a quite covalent π bond.

Since the free oxygen atom starts with four electrons distributed among three p orbitals and since the two p orbitals in the σ and π bonds account for two electrons, there are two electrons remaining in the nonbonding p orbital perpendicular to the CrO bond (p_y), 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 I, the bond dipoles for the Cr=O bond in Cl_2CrO_2 and the C=O bond



a) CrCl σ Bond

b) Cl S Lone Pair

c) Cl P Lone Pair

Figure 3. GVB orbitals for the Cr–Cl bond of Cl_2CrO_2. In addition, there is a Cl p_y-like orbital analogous to the Cl p_x-like orbital shown in part c.

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 Cl_4CrO, 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 monoxo species in (4a). Here (Figures 4b and 4c) we find that both dπ orbitals of the Cr are used to make π bonds to the O. This uses up two electrons and two orbitals (p_x and dp_y) of the oxygen, leaving a doubly occupied σ orbital (p_z) 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_{z^2} orbital pointing at the oxygen. The doubly occupied p_z orbital of the oxyygen and the empty d_{z^2} 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 π 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 σ bond dipole is +5.10 D (the σ bond dipole of BH_3NH_3 is +4.87 D). Thus one should not draw the bond as

$$\mathrm{Cr{\equiv}O} \tag{6}$$

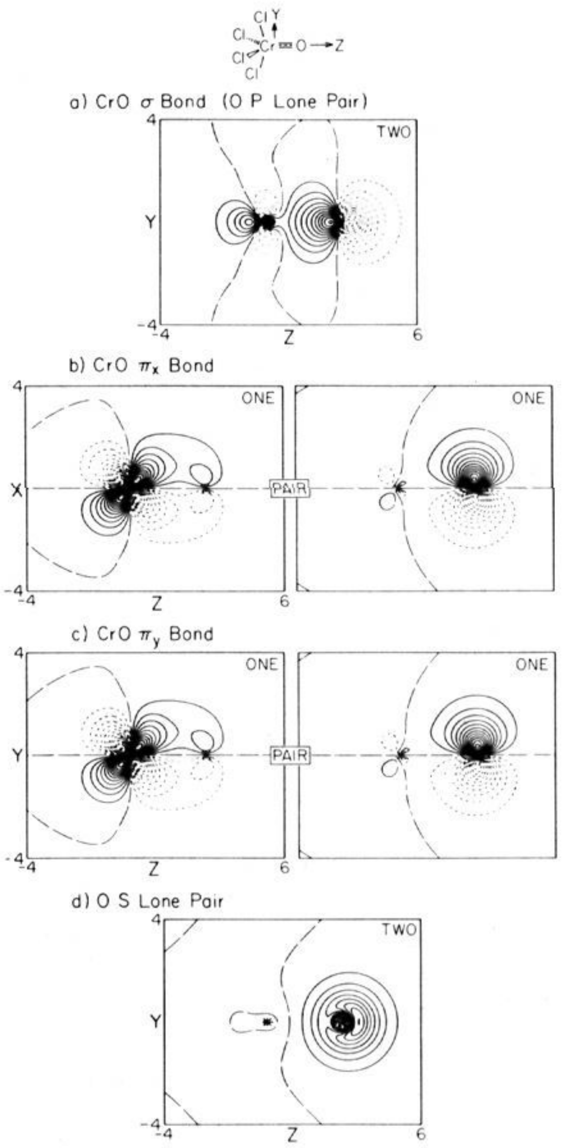
since this would imply an oxygen that has a plus charge. Yet one should not draw it as

$$\mathrm{Cr{=}O} \tag{7}$$

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

$$\mathrm{Cr}\overset{\cdots}{=}\mathrm{O} \tag{8}$$

to indicate this bond where the two solid lines indicate covalent (π) bonds and the dotted line represents a donor–acceptor σ bond.



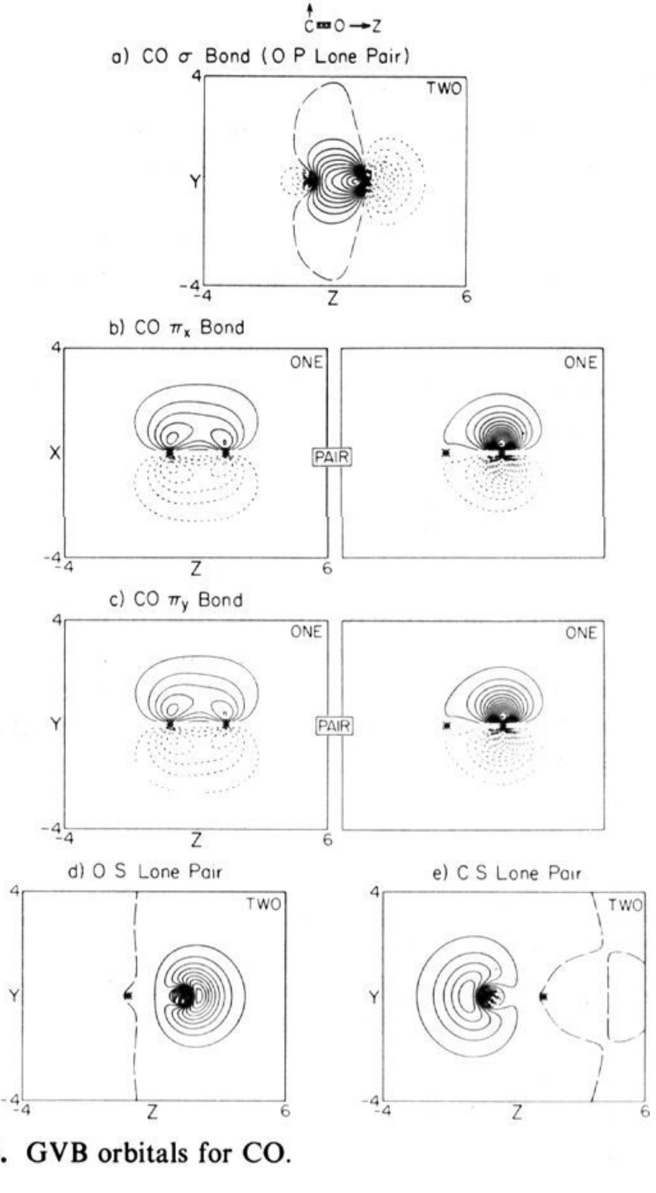
a) CrO σ Bond (O P Lone Pair)

b) CrO π_x Bond

c) CrO π_y Bond

d) O S Lone Pair

Figure 4. GVB orbitals for the CrO bond of Cl_4CrO.



a) CO σ Bond (O P Lone Pair)

b) CO π_x Bond

c) CO π_y Bond

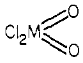
d) O S Lone Pair

e) C S Lone Pair

Figure 5. GVB orbitals for CO.

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)

			difference
Cr	51	82	31
Mo	79	102	23

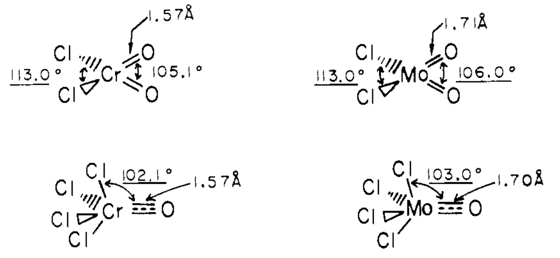


Figure 6. Geometric parameters for Cr and Mo monooxo and dioxo complexes. Bond angles in degrees; bond distances in angströms. Underlined parameters were obtained from experiment or extrapolated from related molecules.

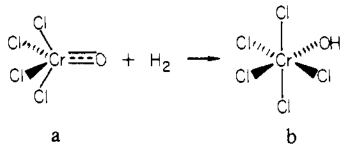
π bonds, each involving one pπ orbital from the C and one from the O plus a σ bond that is dominantly a doubly occupied p orbital on the oxygen. For comparison with the CrO σ bond dipole of +5.10 D for Cl_4CrO, the CO σ bond dipole of carbon monoxide is +4.34 D. The C 2s pair moves away from the oxygen 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 2s 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 CO_2 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 CO_2 is analogous to that in Cl_4CrO and Cl_2CrO_2, 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 electronegative for its bonds to the oxygens. Replacing the Cl ligands with alkyl groups would lead to a more ionic Cr–oxygen bond, leading to less triplet-bond character for the Cr–O 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.

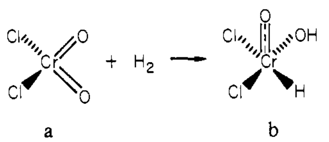
Some of the geometries are shown in Figure 6. Here we see that the bond length is nearly the same for the double and triple bonds, with differences on the order of 0.01 Å for both Cr and Mo. Experimental vibrational frequencies for several such compounds are tabulated in Table III where we see only small 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 H_2 across the metal–oxo bond to form a hydroxyl hydride. In the case of the monooxo species, this process is quite *endothermic*, leading to $\Delta G = +71$ kcal for



(9)

However, for the dioxo species, this process is *exothermic*, with $\Delta G = -7$ kcal for



(10)

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 dπ 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.

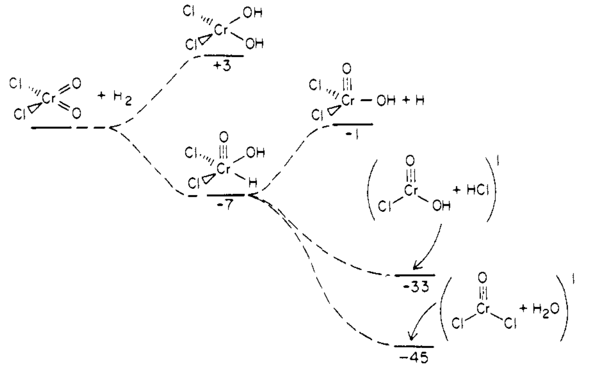


Figure 7. Energetics (ΔG_{300}) of the reaction of H_2 with Cl_2CrO_2. The units are kcal/mol for Figures 7–16.

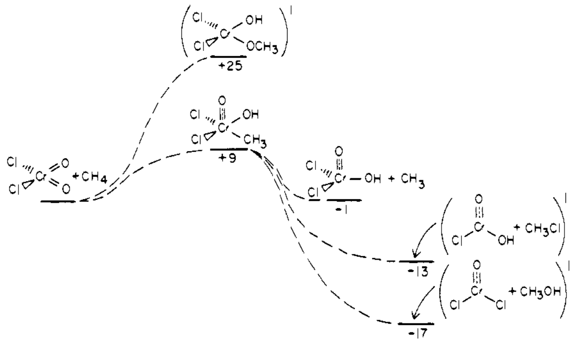


Figure 8. Energetics (ΔG_{300}) of the reaction of CH_4 with Cl_2CrO_2.

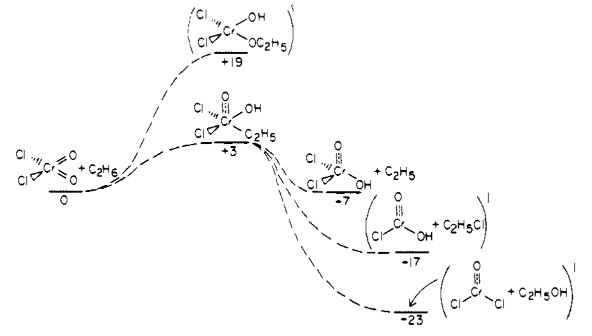
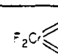
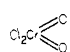
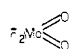
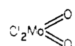
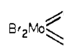


Figure 9. Energetics (ΔG_{300}) of the reaction of C_2H_6 with Cl_2CrO_2.

III. Oxidation of Alkanes by Chromyl Chloride

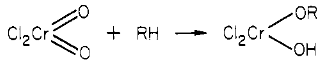
In order to provide a basis for discussion of reactions of chromyl chloride with alkanes, we will first consider the results of theoretical studies on the initial steps.

Table III. M–O Vibrational Frequencies (cm^{-1}) of Gaseous MO_2X_2 and MOX_4 Complexes[a]

complex				change[b]
 	1016 asym 1006 sym	$F_4Cr{=}O$		
 	994 asym 984	$Cl_4Cr{=}O$		
 	1009 987	$F_4Mo{=}O$	1030	+32
 	994 sym 972 sym	$Cl_4Mo{=}O$	1015	+32
 	991 sym 969 asym	$Br_4Mo{=}O$	998	+18

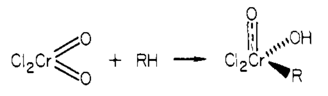
[a] B. G. Ward and F. E. Stafford, *Inorg. Chem.*, 7, 2569 (1968). [b] Comparing the value for $X_4M{=}O$ with the average value for X_2MO_2.

A. Theoretical Considerations. It is often assumed that addition of an alkane RH to chromyl chloride leads to the alkoxy hydroxide Cr(IV) species



(11)

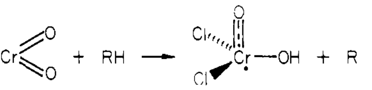
However, we find that in all cases (see Figures 7–9) the presence of the spectator oxo group leads to addition across a single oxo bond



b

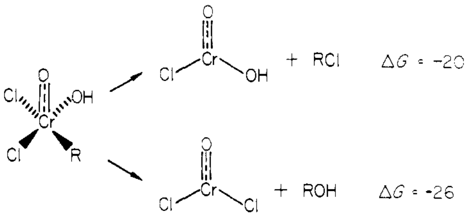
(12)

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)



(13)

approximately thermoneutral for R = CH_3 but increasingly exothermic for R = Et ($\Delta G = -7$ kcal), R = *i*-Pr ($\Delta G = -11$ kcal), and R = *t*-Bu (ΔG) −13 kcal). However, decomposition of (12b) to form alkyl chloride or alcohol is greatly more exothermic

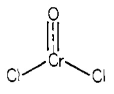


(14)

(15)

with the alcohol favored (shown for ethane).

From Figure 7 we see that the dominant product of the reaction of chromyl with H_2 should be H_2O, whereas the reaction with alkenes RH should lead to alcohols. In both cases the Cr is left in the (formal) Cr(IV) state



The major difference in the reaction with H_2 and RH is that via (13) the latter case should lead to a large concentration of Cr(V) plus alkyl radical. [We suggest, however, that this Cr(V) intermediate (which has been observed and implicated in the mechanism[3,5,6]) is not an *essential* feature of the reaction mechanism.]

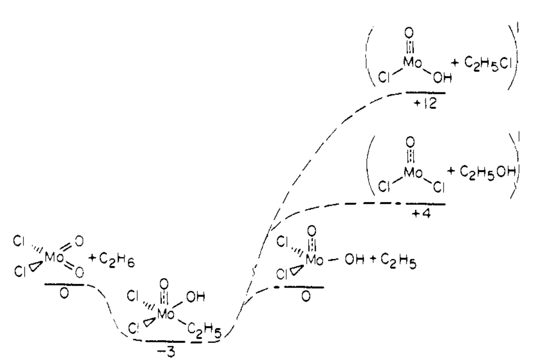


Figure 10. Energetics (ΔG_{300}) of the reaction of C_2H_6 with Cl_2MoO_2.

Table IV. Trends in Bond Strength (kcal/mol) within the Same Row

molecule	bond strength	diff from Ti to Cr
$(Cl)_2Ti{-}O$	140[b]	−89
$(Cl_2)(O)Cr{-}O$	51[b]	
$(Cl)_2Ti{-}CH_2$	78[b]	−30
$(Cl_2)(O)Cr{-}CH_2$	48[b]	
Ti-(O-*t*-Bu)$_4$	104[a]	
V-(O-*t*-Bu)$_4$	90[a]	−32
Cr-(O-*t*-Bu)$_4$	72[a]	

[a] V. I. Tel'noi and I. B. Rabinovich, *Russ. Chem. Rev.* (*Engl. Transl.*), 46, 689–705 (1977). [b] Theoretical calculations; ref 25.

Table V. Trends in Bond Strength (kcal/mol) within the Same Column

		difference	
molecule	bond strength	1st to 2nd	2nd to 3rd
$(Cl_2)(O)Cr{-}O$	51[b]	28	
$(Cl_2)(O)Mo{-}O$	79[b]		
$(Cl_2)(O)Cr{-}CH_2$	48[b]	23	
$(Cl_2)(O)Mo{-}CH_2$	71[b]		
Ti-(O-*i*-C_3H_7)$_4$	106[a]		
Zr-(O-*i*-C_3H_7)$_4$	126[a]	20	4
Hf-(O-*i*-C_3H_7)$_4$	130[a]		

[a] See footnote *a*, Table IV. [b] Theoretical calculations; ref 25.

Table VI. GVB Orbital Overlaps for Metal-Alkylidene Bonds

molecule	σ bond	π bond
$(Cl)_2Ti{-}CH_2$	0.74	0.41
$(Cl_2)(O)Cr{-}CH_2$	0.60	0.39
$(Cl)_2(O)Mo{-}CH_2$	0.74	0.53

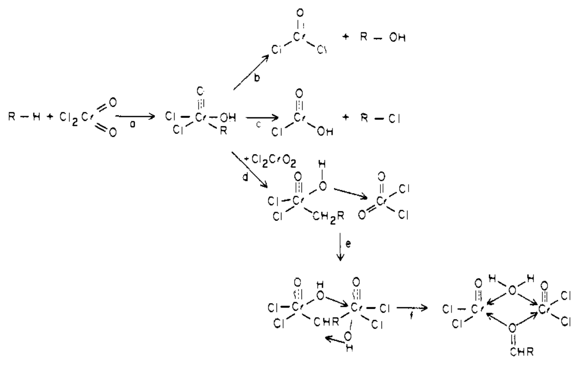
A major difference between Cr and Mo compounds is the general increase in bond strength of 10–20 kcal per bond. This effect will manifest itself in that oxidation of alkanes by molybdyl compounds (e.g., see Figures 8 and 10) should result in a smaller barrier, a smaller concentration of alkyl radicals and Mo(V) species, and less alkyl chloride or alcohol production with an enhanced direct formation of an Étard complex (vide infra), since the final rearrangement will be the only reductive elimination step in the pathway. As discussed previously,[6] the origin of this dramatic difference is the increased bond strengths in Mo complexes and a futher increase for W compounds. This is due to the general trend that transition metal ligand bond strengths decrease as one moves across the periodic table from the left to the right and increase as one moves down a column. Examples of this are shown in Tables IV and V. This suggests that the orbital overlaps between the ligand orbitals and the metal orbitals

---

(5) I. P. Gragerov and M. P. Ponomarchuk, *J. Org. Chem. USSR* (*Engl. Transl.*), 3, 440–445 (1967); **5**, 1125 (1969).

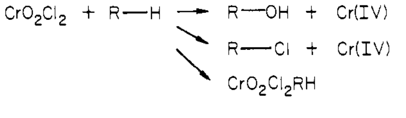
(6) A preliminary account of this work has been published; see A. K. Rappé and W. A. Goddard III, *Nature* (*London*), **285**, 311–312 (1980); *J. Am. Chem. Soc.*, **102**, 5114–5115 (1980). For additional details, see A. K. Rappé, Ph.D. Thesis, California Institute of Technology, October 1980.

Scheme II



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[1-4] that chromyl compounds react with alkanes to initially form either alcohols, alkyl chlorides, or a stable complex,



$$\mathrm{CrO_2Cl_2 + R{-}H} \begin{array}{l} \rightarrow \mathrm{R{-}OH + Cr(IV)} \\ \searrow \mathrm{R{-}Cl + Cr(IV)} \\ \searrow \mathrm{CrO_2Cl_2RH} \end{array} \quad (16)$$

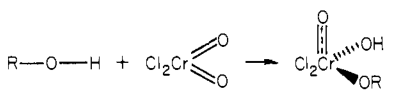
The initially formed products R–OH and R–Cl may undergo rapid secondary reactions leading to oxidation products attributable to alkene oxidation.[1b,c] The stable complex undoubtedly undergoes a rapid secondary reaction leading to the first "observed" intermediate, the Étard complex, an insoluble hygroscopic brown solid that can be hydrolyzed under reducing conditions to directly form aldehydes and ketones.[1c] The product composition usually is diverse and very dependent on reaction conditions,[1b] making detailed mechanistic study difficult. There is evidence for a Cr(V) intermediate[3,5,6] and for the Étard complex having two Cr(IV) centers.[1]

On the basis of the energetics described in Section IIIA, we propose a reaction scheme consistent with the experimental observations that consists of an initial addition of the C–H bond across *one* Cr–O π 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 CrO_2Cl_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 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 Étard complex.

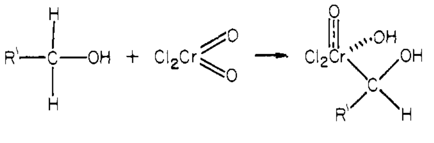
We have concentrated on the initial reactions stressing factors that favor the reductive elimination pathways, since use of dilute solution or polymer supports will decrease the secondary reactions leading to Étard complex formation.

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 O–H bond,


(17)

addition across a C–H bond (the α bond most likely),


(18)

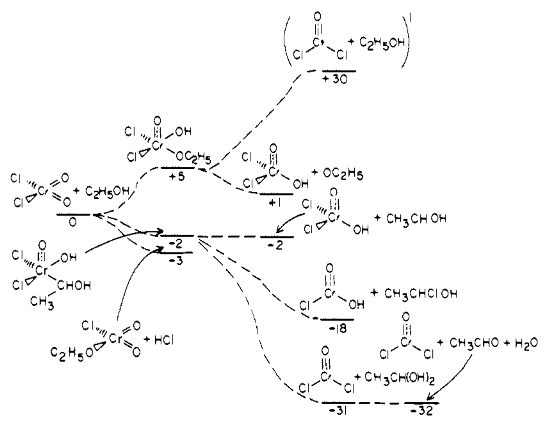


Figure 11. Energetics (ΔG_{300}) for the reaction of C_2H_5OH with Cl_2CrO_2.

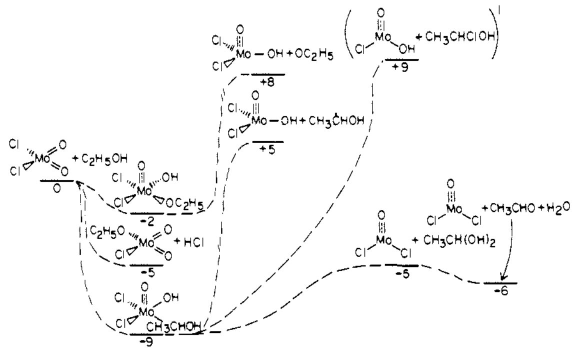
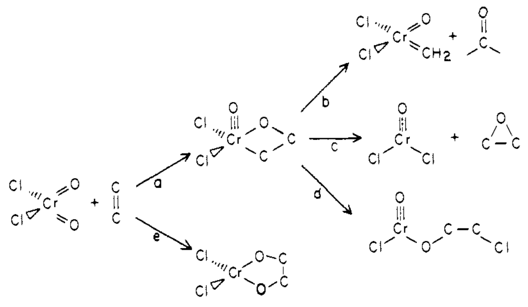
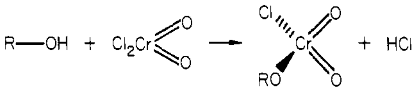


Figure 12. Energetics (ΔG_{300}) for the reaction of C_2H_5OH with Cl_2MoO_2.

Scheme III



or simple ligand substitution with a chloride,


(19)

The energetics of these pathways for C_2H_5OH 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[8] of a metallocycle intermediate analogous to the metallocyclobutane 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.[7-9]

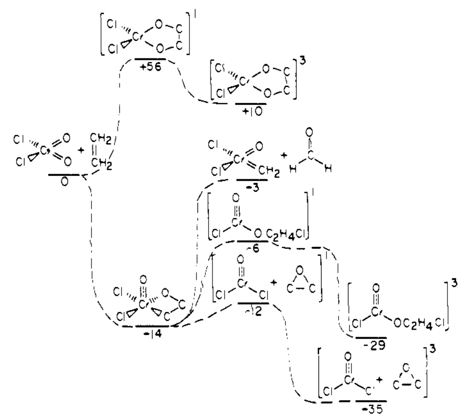
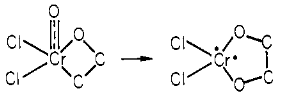


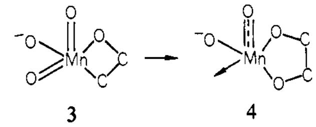
Figure 13. Energetics (ΔG_{300}) for the reaction of C_2H_4 with Cl_2CrO_2.

The energetics for the oxidation of ethylene by chromyl chloride are shown in Figure 13. These energetics confirm the proposal (Sharpless[8]) that the metallocyclooxetane is a likely common precursor for all of the observed oxygen-containing products and rule out the direct addition reaction characteristic of oxidations by OsO_4 (path e of Scheme III).

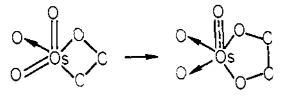
It is noteworthy that CrO_2Cl_2 does *not* react to form significant diol products (diol is formed by hydrolysis of the initially formed epoxide[8]), whereas for $KMnO_4$[10] and OsO_4[11] the diol products are dominant without significant epoxide formation. This differential reactivity can be understood in terms of stabilization due to spectator oxo groups resulting from the differing number of valence electrons present. Starting from the respective metallocyclooxetane intermediates (where an arrow denotes a lone pair on the metal),



1 2 (20)



3 4 (21)



5 6 (22)

the difference is apparent. That is, for CrO_2Cl_2 the shift involves reaction with a strong metal–oxo triple bond, preventing (20), whereas for both $KMnO_2$ and OsO_4 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**.

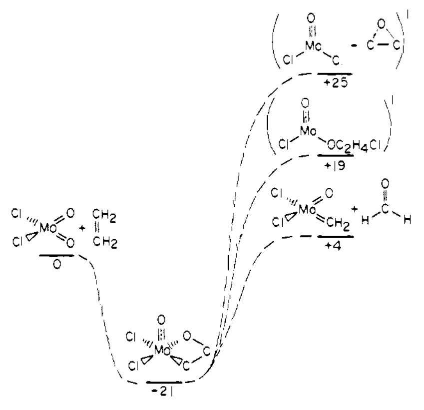


Figure 14. Energetics (ΔG_{300}) for the reaction of C_2H_4 with Cl_2MoO_2.

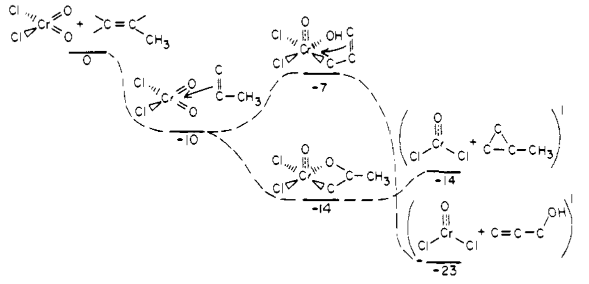


Figure 15. Energetics (ΔG_{300}) for the reaction of propene with Cl_2CrO_2.

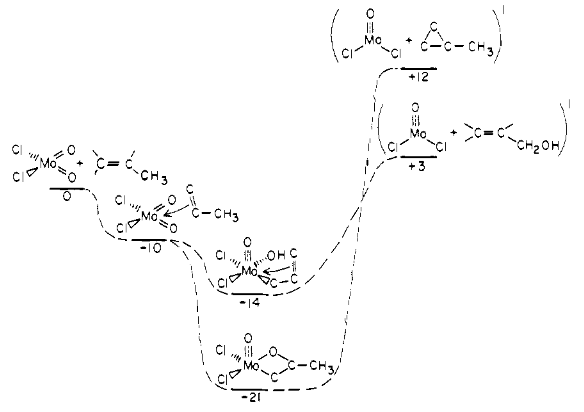
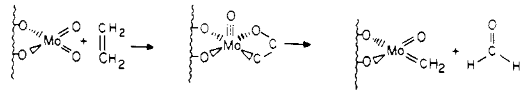


Figure 16. Energetics (ΔG_{300}) for the reaction of propene with Cl_2MoO_2.

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 MoO_3 and WO_3 are activated for metathesis on a polymer support[12]



(23)

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

Under appropriately chosen operating conditions, olefins such as propene are allylicly oxidized to carbonyls such as acrolein over

---

[7] (a) F. Freeman, C. R. Armstead, M. G. Essig, E. L. Karchefski, C. J. Kojima, V. C. Manopoli, and A. H. Wickman, *J. Chem. Soc., Chem. Commun.*, 65 (1980); (b) R. A. Walton, *Prog. Inorg. Chem.*, **16**, 1–226 (1972).

[8] K. B. Sharpless, A. Y. Teranishi, and J. E. Bäckvall, *J. Am. Chem. Soc.*, **99**, 3120–3128 (1977).

[9] J. San Filippo, Jr., and C. Chern, *J. Org. Chem.*, **42**, 2182–2183 (1977).

[10] (a) R. Stewart, "Oxidation in Organic Chemistry", Part A, K. B. Wiberg, Ed., Academic Press, New York, 1965, pp 1–68; (b) H. O. House, "Modern Synthetic Reactions", Benjamin, Menlo Park, California, 1972, pp 257–291; (c) D. M. Walba, M. D. Wand, and M. C. Wilkes, *J. Am. Chem. Soc.*, **101**, 4398–4399 (1979); (d) J. E. Baldwin, M. L. Crossley, and E. M. Lehtonen, *J. Chem. Soc., Chem. Comm.*, 918–920 (1979); (e) E. Klein and W. Rojahn, *Tetrahedron*, **21**, 2353–2358 (1965).

[11] (a) M. Schröder, *Chem. Rev.*, **80**, 107–213 (1980); (b) K. B. Sharpless, C. A. Chong, and K. J. Oshima, *J. Org. Chem.*, **41**, 177–179 (1976); (c) E. Herranz and K. B. Sharpless, *ibid.*, **43**, 2544–2548 (1978); (d) E. Herranz, S. A. Biller, and K. B. Sharpless, *J. Am. Chem. Soc.*, **100**, 3596–3598 (1978); (e) E. Herranz and K. B. Sharpless, *J. Org. Chem.*, **45**, 2710–2713 (1980).

[12] (a) E. A. Lombardo, M. Lo Jacono, and W. K. Hall, *J. Catal.*, **64**, 150–162 (1980); (b) R. H. Grubbs and S. J. Swetnick, *J. Mol. Catal.*, **8**, 25–36 (1980).

supported MoO_3 and WO_3 catalysts.[13] 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 Cl_2CrO_2, 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] Imra[17] has found that for nonstoichiometric MoO_3 and WO_3 the dominant product is the oxidative C–C bond cleavage product; that is, propene forms formaldehyde and acetaldehyde. Furthermore, San Filippo[9] 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 d^6 configuration in order to yield a balanced description of the various s^1d^5, s^2d^4, and d^6 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]

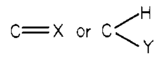
In the calculations reported here, the Cl atoms were described by using the SHC effective potential[21] to replace the core electrons, and the basis set was contracted to minimal basis based on molecular calculations on $TiCl_4$.

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 $(\phi_a\phi_b + \phi_b\phi_a)$.

(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 $\Delta H_{f,0}$ are combined with previously obtained $\Delta H_{f,0}$ for the other species in the idealized reactions to calculate $\Delta H_{f,0}$'s for the molecules of interest. These $\Delta H_{f,0}$'s are combined with vibrational frequencies (experimental, calculated, or estimated) and moments of inertia to obtain $\Delta H_{f,300}$ and S_{300}. Finally, the $\Delta G_{r,300}$ for the reactions of interest are calculated.

Acknowledgment. This research was supported mainly by the National Science Foundation (Grant No. CHE-80-17774) and made use of the Dreyfus-NSF Theoretical Chemistry Computer at Caltech, which was funded through grants from the Camille and Henry Dreyfus Foundation, the National Science Foundation (Grant No. CHE-78-20235), and the Sloan Fund of the California Institute of Technology. Partial computing support of this work was also provided by a grant from the National Resource for Computation in Chemistry (NRCC), and acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support. We wish to thank Fred Tebbe for helpful discussions.

Registry No. Cl_2CrO_2, 14977-61-8; Cl_2MoO_2, 13637-68-8; CH_4, 74-82-8; C_2H_6, 74-84-0; C_2H_5OH, 64-17-5; C_2H_4, 74-85-1; C_3H_6, 115-07-1; H_2, 1333-74-0.

---

(13) L. D. Krenze and G. W. Keulks, *J. Catal.*, **61**, 316–325 (1980); **64**, 295–302 (1980).

(14) S. De Rossi, E. Iguchi, M. Schiavello, and R. J. D. Tilley, *J. Catal.*, **61**, 256–263 (1980).

(15) P. E. Dai and J. H. Lundsford, *J. Catal.*, **64**, 173–183 (1980).

(16) J. Engelhardt, *J. Catal.*, **62**, 243–252 (1980).

(17) L. Imra and K. F. Wedemeyer, U.S. Patent No. 3946081.

(18) R. R. Schrock, S. Rocklage, J. Wengrovious, G. Rupprecht, and J. Fellmann, *J. Mol. Catal.*, **8**, 73–83 (1980).

(19) A. K. Rappé, T. A. Smedley, and W. A. Goddard III, *J. Phys. Chem.*, **85**, 2607–2611 (1981).

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

(21) A. K. Rappé, T. A. Smedley, and W. A. Goddard III, *J. Phys. Chem.*, **85**, 1662–1666 (1981).

(22) F. W. Bobrowicz and W. A. Goddard III, In "Modern Theoretical Chemistry: Methods of Electronic Structure Theory", Vol. 3, H. F. Schaefer III, Ed., Plenum Press, New York, 1977, Chapter 4, pp 79–127.

(23) C. J. Casewit and W. A. Goddard III, *J. Am. Chem. Soc.*, **102**, 4057–4062 (1980).

(24) J. H. Davis, W. A. Goddard III, and L. B. Harding, *J. Am. Chem. Soc.*, **99**, 2919–2925 (1977).

(25) A. K. Rappé and W. A. Goddard III, In "Potential Energy Surfaces and Dynamics Calculations", D. G. Truhlar, Ed., Plenum Press, New York, 1981, pp 661–684.