

for the analogous molecular reaction, eq 3.

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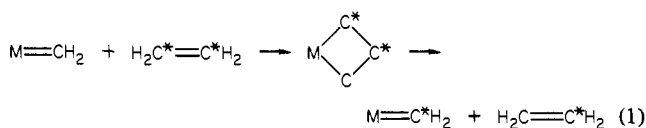
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Mechanism of Metathesis and Epoxidation in Chromium and Molybdenum Complexes Containing Methyl-Oxo Bonds

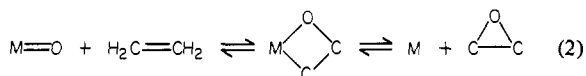
Sir:

Transition-metal metallocycle complexes are recognized as crucial intermediates in a variety of homogeneous and heterogeneous catalytic processes. There is no doubt that metallocycles¹ are intermediates in such reactions as olefin metathesis,² epoxidation,³ and deepoxidation;⁴ however, even a qualitative understanding of the energetics of their formation and decomposition is lacking. In this communication, we use the results of ab initio theoretical studies to examine the thermochemistry and mechanism for epoxidation and metathesis of olefins by Cr and Mo complexes. As described below, the theoretical calculations are ab initio (including the core electrons of the Cr and Mo), using a good basis set and including electron correlation [generalized valence bond (GVB) and configuration interaction (CI)].

Consider Scheme I. If X is a carbene (and M = Mo or W), the energetics are of relevance to the Herrison-Chauvin mechanism² for olefin metathesis (eq 1). If X is an oxo group, the



energetics are relevant for olefin epoxidation and deepoxidation. Indeed, Sharpless and co-workers have suggested that olefin epoxidation by chromyl chloride³ (Cl_2CrO_2) might occur by the forward reaction (eq 2) and that deepoxidation⁴ might occur by the reverse reaction.



Using energy changes from extensive ab initio calculations and estimated zero-point vibrational energies, we obtained ΔH for these steps at 0 K. Using standard methods⁵ and analogy to similar systems, we estimated the ΔS for 25 °C and corrected ΔH from

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(3) K. B. Sharpless, A. Y. Teranishi, and J. E. Bäckvall, *J. Am. Chem. Soc.*, **99**, 3120 (1977).

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Scheme I

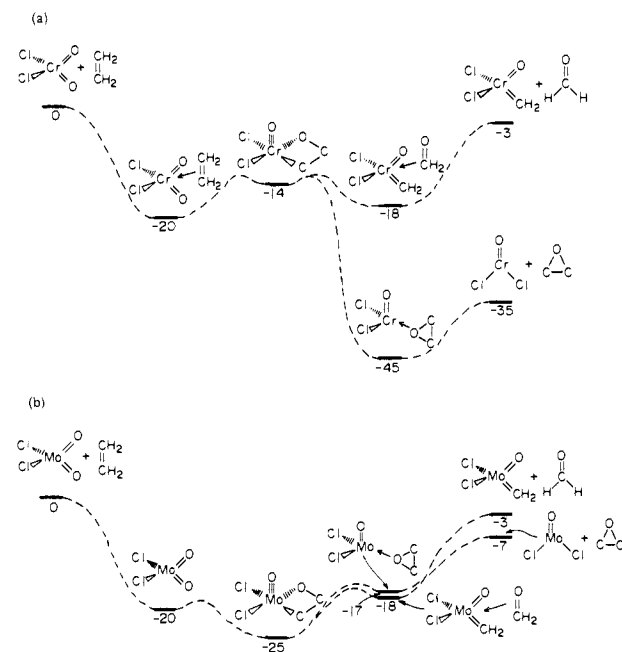
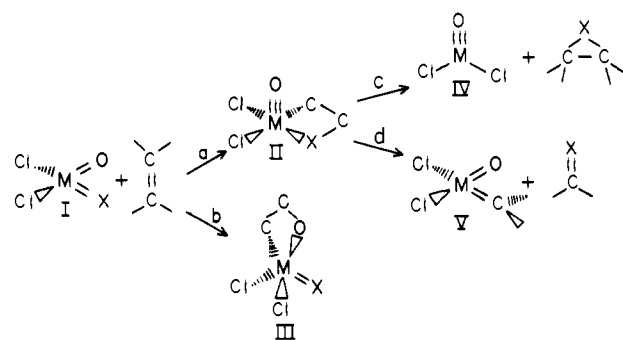


Figure 1. Schematic potential curves for (a) the reaction of Cl_2CrO_2 with C_2H_4 and (b) the reaction of Cl_2MoO_2 with C_2H_4 (energy in kcal/mol).

0 K to 25 °C to obtain ΔG at 25 °C (most reactions are run at this temperature or lower).

The energetics⁶ of these two processes for Cr are shown in Figures 1a and 2a, and relevant observations are described below. First, the metal-oxo bond is very different for $\text{Cl}_2\text{R}_2\text{CrO}$ and Cl_2CrO_2 . We find that the metal-oxygen bond of Cl_4CrO (and the metallocyclic species II) is essentially a triple bond (analogous to the bond in $\text{C}\equiv\text{O}$) whereas the metal-oxygen bonds in Cl_2CrO_2 are double bonds (analogous to the $\text{C}=\text{O}$ bond in $\text{O}=\text{C}=\text{O}$ or a ketone). The origins of this effect will be discussed in detail elsewhere, but basically, $\text{Cl}_4\text{Cr}=\text{O}$ has available two low-lying, singly occupied d orbitals that can participate in π bonds to the same oxygen whereas in Cl_2CrO_2 the corresponding orbitals are each involved in a single π bond to different oxygens. The result is that the oxo bond in $\text{Cl}_4\text{Cr}=\text{O}$ is 31 kcal stronger than an oxo bond in Cl_2CrO_2 (82 vs. 51 kcal, respectively). Similarly, the oxo bond in the metallocycle II is a triple bond, and hence the second oxo group in I is not a spectator but actually drives the formation of the metallocycle. Secondly, bond energies for the oxo bond in Cl_2CrO_2 and the carbene bond in $\text{Cl}_2\text{CrOCH}_2$ are similar⁷ (51 and 48 kcal, respectively), thus explaining the extraordinary

(6) (a) The relevant heats of formation at 300 K are $\text{Cl}_2\text{CrO}_2 = -123.9$,¹⁰ $\text{Cl}_2\text{OCrCH}_2 = -87.7$, $\text{Cl}_2\text{OCrC}_2\text{H}_4\text{O} = -137.9$, $\text{Cl}_2\text{OCrC}_3\text{H}_6 = -98.4$, and $\text{Cl}_2\text{CrO} = -132.5$ kcal/mol. The energetics for the π complexes were estimated from related experimental energetics. (b) The energetics for the Cl_2MoO_2 , $\text{Cl}_2\text{MoOCH}_2$, and related compounds are estimated from Cl_2MoO_2 and relevant chromium compounds.

(7) This should be compared with the 6-kcal difference in bond energy between $\text{H}_2\text{C}=\text{O}$ and $\text{H}_2\text{C}=\text{CH}_2$ (179 and 173 kcal, respectively).

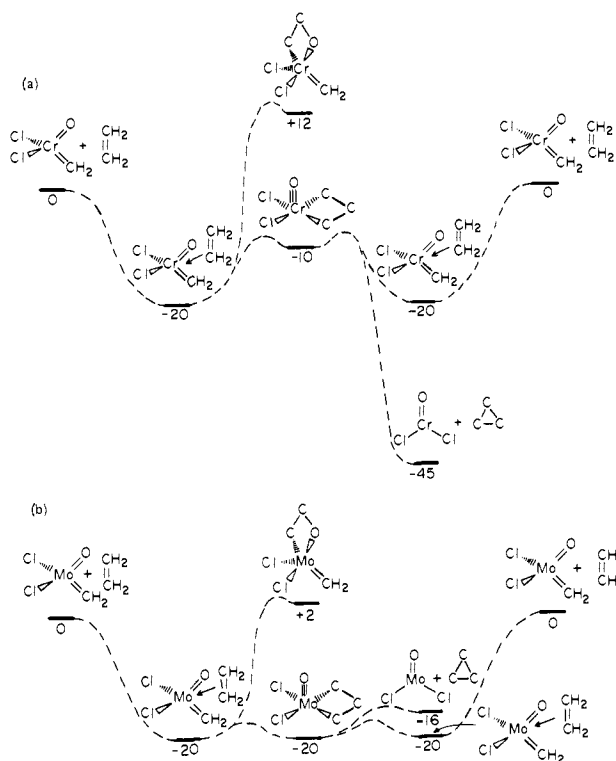


Figure 2. Schematic potential curves for (a) the reaction of $\text{Cl}_2\text{Cr}(\text{O})(\text{CH}_2)$ with C_2H_4 and (b) the reaction of $\text{Cl}_2\text{Mo}(\text{O})(\text{CH}_2)$ with C_2H_4 (energy in kcal/mol).

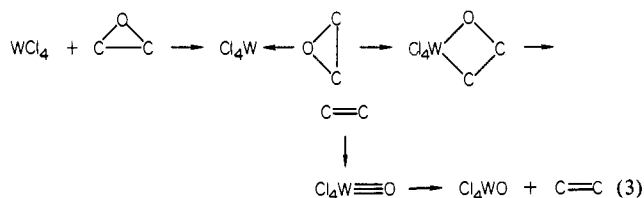
similarity between the two reactions in Figures 1a and 2a.

For Mo, the energies^{6b} change as indicated in Figures 1b and 2b, clearly dictating a different chemistry for the molybdenum analogues of Figures 1a and 2a. For example, chromium will epoxidize olefins but should not metathesize olefins (or even produce substantial C-C bond cleavage products) due to the energetic dominance of the reductive elimination pathway c of Scheme I. In contrast, for molybdenum (and tungsten), C-C bond cleavage is competitive with reductive elimination due to the relative disfavor of the reductive elimination pathway for Mo (and W). The origin of this dramatic difference is the increased σ bond strengths in the Mo compounds (~ 15 kcal/bond). An obvious prediction is that Cl_2MoO_2 will react with olefins to form substantial C-C bond cleavage products (or decomposition through an alternate pathway involving chlorine).

In considering the role of Cl_2OMCH_2 in metathesis, we must consider the competition of the side reaction b in Scheme I, forming species III with $\text{X} = \text{CH}_2$. As shown in Figure 2, this pathway is energetically inaccessible.

Experiments by Muetterties^{2b} lead to indirect support of these ideas. He finds that $\text{WCl}_6/\text{C}_2\text{H}_5\text{AlCl}_2$ is catalytically inactive for olefin metathesis (a system where Cl_4WCH_2 has been implicated^{2c}) unless catalytic amounts of oxygen are present in the reaction mixture. Our conclusion is that Cl_2WOCH_2 is the active catalyst for stable W(VI) olefin metathesis catalysts and that a spectator oxo bond is intimately involved in the catalytic process. In addition, Sharpless et al.³ find that chromyl chloride leads only to epoxidation of olefins,⁸ and they have suggested a mechanism essentially identical with that supported by our calculations. Finally, Sharpless and co-workers⁴ have developed a synthetically useful deepoxidation process involving the reaction of W(IV) with epoxides, forming the corresponding olefin (and Cl_4WO). We find that this reaction (eq 3) is driven by the formation of a very strong W-O triple bond.

Computational details are as follows. The basis in the Cr was obtained by optimizing primitive Gaussians so as to have four functions describe each of the 1s, 2p, and 3d atomic orbitals and



two functions describe each of the 2s, 3s, 4s, 3p, and 4p orbitals. The basis was contracted to a split-valence basis (minimal basis for the core orbitals, two contracted basis functions for the 4s, 4p, and 3d orbitals). The oxygen and carbon atoms were described with an analogous basis, but d functions were included on O or C bonded to a metal. The Cl core orbitals were replaced with an effective potential, and the 3s and 3p orbitals were described with a minimum-valence basis.

It was found that uncorrelated wave functions (Hartree-Fock) lead to an extremely bad description of the metal-oxo bond (errors of 150 kcal for species II). Thus, all calculations were carried out with fully correlated metal-oxo bonds. This involved GVB calculations with three correlated pairs per oxygen. In addition, the M-C and M-O bonds of the metalocycle were correlated. Other bonds (C_2H_4 and H_2CO) were correlated so that all processes involved the same level of correlation along the reaction path. After the GVB orbitals were solved, a CI was carried out within the occupied GVB orbitals (GVB-CI).⁹

Summary. Using accurate ab initio methods, we have calculated bond energies and reaction enthalpies for several processes possibly involved in metathesis and epoxidation. These results allow a clearer understanding of the mechanisms and suggest that in activating metal chlorides it is essential to have spectator metal-oxo bonds.

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Resolution of Underivatized Amino Acids by Reversed-Phase Chromatography

Sir:

Enantiomers can be separated by liquid chromatography by using either a chiral support or a chiral mobile phase. The potential of the latter approach has only recently begun to be realized.^{1,2}

We report the separation of underivatized amino acid enantiomers by liquid chromatography using a chiral mobile phase and a reversed-phase column. The chiral eluant is a dilute aqueous solution of L-proline (0.017 M) and copper acetate (0.008 M), which can form diastereomeric complexes with the D and L enantiomers of amino acids. Resolution is ascribed to differences in stability and polarity of these diastereomeric species.

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(8) There are side reactions that result in incorporation of chlorine.