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Correlation of relative rates of chromyl chloride oxidation and chromic acid oxidation of acyclic alkenes versus alkene IPs and HOMOs[†]

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ABSTRACT: Plots of logarithms of relative reaction rates of chromyl chloride oxidation and of chromic acid oxidation of alkenes ($\log k_{\mathrm{rel}}$ values) versus alkene ionization potentials (IPs) and versus their highest occupied molecular orbital energy levels (HOMOs) demonstrate excellent correlations. Each plot has a similar appearance and shows a single line with a positive slope. The results indicate that the rate-determining step of each title reaction involves an electrophilic attack on the alkene π-bond without significant steric effects; this supports a proposed $2 + 3$ cycloaddition mechanism and disfavors a proposed stepwise $2 + 2$ cycloaddition mechanism. Comparison is made with other d^0 transition metal complexes that oxidize alkenes. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: chromyl chloride; chromic acid; alkene oxidation; relative reaction rates; ionization potentials (IPs); electrophilic addition; cycloadditon of alkenes; electronic effects versus steric effects

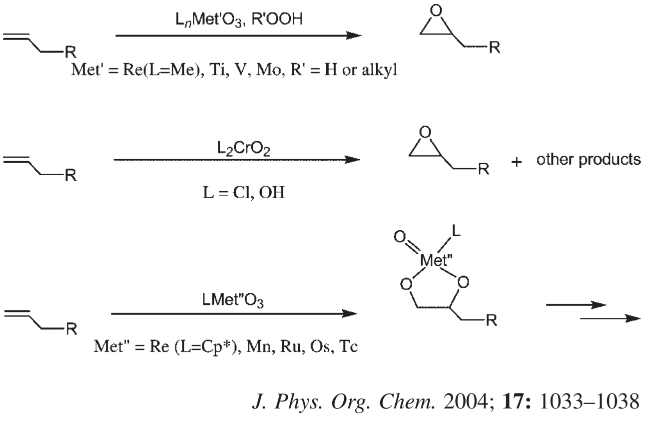
INTRODUCTION

We reported a method to differentiate the relative importance of electronic and steric effects in addition reactions of alkenes by correlating logarithms of relative reaction rates ($\log k_{\mathrm{rel}}$ values) versus the alkene ionization potentials (IPs) and versus their highest occupied molecular orbital energy levels (HOMOs) and applied this method to a variety of important addition reactions of alkenes.[1a–i] This technique offers synthetically valuable information about addition reactions to one alkene in the presence of another differently functionalized alkene and sometimes enables selection from among the proposed mechanisms.[1h–i] Therefore, it seems desirable to investigate reactions with great mechanistic and synthetic importance, in order to gather additional information about that reaction.

Oxidation of alkenes by transition metal oxo compounds has been an important topic in organic and organometallic chemistry for a long time.[2a–c] Intensive mechanistic studies have been carried out both theoretically[2d–t] and experimentally[2u–y] during the past decade. Among them, chromium(VI) compounds, such as CrO_2Cl_2 and H_2CrO_4, have been shown to be versatile oxidizing agents, and their reactions with alkenes yield epoxides commonly and other products depending on the reaction conditions.[2a–c,3–6] In this study, we use the above technique to explore chromyl chloride oxidation and chromic acid oxidation of alkenes, partly because of their importance in organic synthesis[2a–c,3,4] and partly because of interest in their mechanisms.[2a–c,5,6]

BACKGROUND

Interesting similarities and differences among reactions of alkenes with complexes of chromium(VI) versus those of other d^0 transition metals have been noted recently.[2k,p,5j,l] In oxidizing alkenes, complexes of Re(VII) (when $L = Me$),[2k] Ti(IV),[7] V(V),[8] Cr(VI)[5e] and Mo(VI)[9] each yields epoxides preferentially, while those of Re(VII) when $L = Cp^*$ ($= C_5Me_5$),[10] Mn(VII),[2a]



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Ru(VIII),[11] Os(VIII)[12] and Tc(VII)[13] each preferentially yields *cis*-dihydroxyalkanes.[2k]

The point has been made[2k,p] that in some epoxidations, $L_nMet'O_3$ does not react directly with the alkene, but with an additional oxygen source, which may be necessary to effect the reaction; in these cases, the addition proceeds by an indirect pathway.

Some of the above metals do not fit completely into either group Met′ or Met″. For example, it was noted[2p,w] that $MeReO_3$ compounds do not react directly with olefins,[2k] as do oxidizing compounds of Ti,[7] V[8] and Mo.[9] However, Cp^*ReO_3 is proposed to react with alkenes to give a $2+3$ addition product,[2w,10] as are the compounds of Mn,[2a] Ru,[11] Os[12] and Tc[13], but the former does not yield diols as the final product,[2w,10] as the later compounds do.[2a,11,12,13]

Another misfit is chromium. Chromyl chloride has been likened[2p] to other oxidizing metal complexes LMO_3, such as Os, Ru and Mn. Chromium fits Met′ in that it yields epoxides[2a–c,5e] as the others do; but it does not fit Met′ in that it does not require a peroxide to react with alkenes,[2a–c,5e] as the Os, Ru and Mn do.[2k,7,8,9] Chromium is like Met″ because its compounds react directly with the olefin[2a–c] in a proposed[5a–d] $2+3$ addition as do Os, Ru and Mn; but it is unlike Met″ because it does not give a diol as a product,[2a–c] as the others do.[2a,11,12,13]

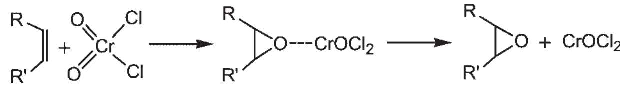
The above observations have spawned comparisons and contrasts of oxidation with chromium compounds versus those with compounds of Met″ (Re, Mn, Ru, Os and Tc).[2k,5e,j,l] As a result, proposals that these oxidations of alkenes proceed via $2+3$ reactions have been shared by many of these compounds, Cr,[5j,l] Os,[14] Re(L = Cp),[2j,k] Mn,[2p] Tc.[13]

There have been many experimental reports,[2q,u,v] theoretical reports,[2e,g–j,m–r,5j,l] and analyses[2s,v] favoring the $2+3$ mechanism over the $2+2$. Among these, density functional theory (DFT) calculations[2g–j,n–r,5j,l] predicted that the $2+2$ mechanism has a much higher activation energy than that of the $2+3$ mechanism in reactions of many such compounds, which led to the conclusion that the latter is more likely. In many[2g–j,n–r,5j,l] of the DFT calculations, the most stable point on the energy surface was the $2+3$ adduct,[2g–j,n–r,5j,l] which might be expected to hydrolyze to diols.[2n,5o] Owing to comparisons and concerns such as those noted above, questions linger as to (1) whether the $2+3$ mechanism or the $2+2$ mechanism is responsible for the products and (2) if the $2+3$ mechanism operates with chromium complexes, why the metalladioxylate intermediate would not yield diols as do complexes of the other metal Met″.

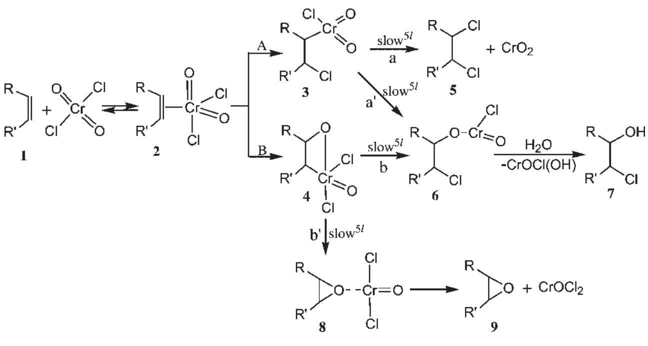
Oxidation using CrO_2Cl_2

The mechanism of chromyl chloride oxidation of alkenes has been investigated for decades.[2a–c,5] At least four[2a–c,5a–e,m,n] different mechanisms have been suggested for this reaction. The first suggestion was a ‘direct addition’ mechanism (Scheme 1),[2a–c] which was criticized due to its failure to explain all stereochemical aspects (such as the formation of the *cis*-chlorohydrin and the *cis*-dichloride) of chromyl chloride oxidation.[5e,i] Two other different mechanisms were then proposed: (1) the $2+2$ cycloaddition mechanism (Scheme 2)[2c,5e,i] and (2) the $2+3$ cycloaddition mechanism (Scheme 3).[5a–d] Recently, an ESR signal was observed in the oxidation of aryl substituted alkenes,[5m,n] and a diradical was proposed as the intermediate giving rise to this result. However, the stereospecificity of these reactions has been used to argue against radical intermediates in the C—O bond forming steps. In addition, the alkenes considered in this paper do not possess radical-stabilizing Ph substitutions. Therefore, in this study, we focus on the application of our results to the rate-determining steps of the mechanisms shown in Schemes 2 and 3.

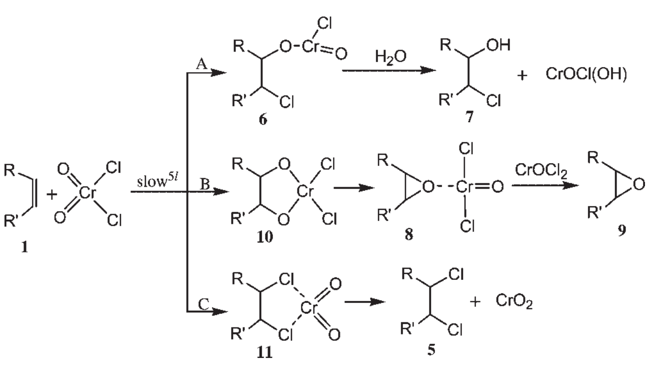
The main difference between the two proposed mechanisms shown in Schemes 2 and 3 is in their rate-determining steps and characteristics of their transition-state structures. In the $2+2$ mechanism (Scheme 2), the



Scheme 1. The direct addition mechanism for CrO_2Cl_2 oxidation of alkenes[2a–c,5l]



Scheme 2. The $2+2$ cycloaddition mechanism for CrO_2Cl_2 oxidation of alkenes[2c,5e,i,l]



Scheme 3. The $2+3$ cycloaddition mechanism for CrO_2Cl_2 oxidation of alkenes[5a–d,l]

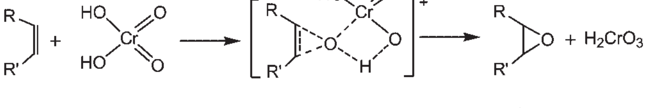
decompositions of intermediates **3** and **4** are proposed as rate-determining steps.[51] None of these transformations involves alkene π-electrons. In contrast, the $2+3$ mechanism (Scheme 3) requires a five-membered ring transition-state structure in the rate-determining formation of the intermediates and all involve breaking the alkene π-bond.

Oxidation using H_2CrO_4

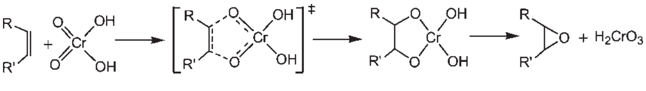
Chromic acid (H_2CrO_4) oxidation of alkenes produces epoxides or their higher oxidation level products.[2a,6b] A kinetic study of this reaction fostered a mechanism involving a three-membered transition-state structure (Scheme 4),[6b] similar to the 'direct addition mechanism' that was previously discarded for CrO_2Cl_2 oxidation of alkenes. Another proposed mechanism[2a,6b] for the H_2CrO_4 oxidation invoked a five-membered intermediate (Scheme 5). It is analogous to the $2+3$ mechanism for the chromyl chloride oxidation shown ($\mathbf{1} \rightarrow \mathbf{9}$) in Scheme 3 (path B). A major difference between these two proposed mechanisms for chromic acid oxidation of alkenes is that the former suggests a direct single-step formation of an epoxide (Scheme 4), while the latter requires formation of a five-membered intermediate between the reactants and the epoxide product (Scheme 5). In this study, we shall discuss its mechanisms through comparison with those of chromyl chloride oxidation of alkenes.

RESULTS AND DISCUSSION

Relative rates[5c] of chromyl chloride oxidation of alkenes, alkene IPs[15] and alkene HOMOs are shown in Table 1. Relative rates[6b] of chromic acid oxidation of alkenes, alkene IPs[15] and alkene HOMOs are shown in Table 2. Both reaction rates were determined by following the disappearance of the Cr(VI) oxidation reagents under pseudo-first-order conditions (large excess of alkene).[5c,6b] As in our previous studies,[1] cyclic alkenes and aryl alkenes are omitted in order to avoid complications due to ring strain or conjugation with the aryl group. Because the IP for compound 13 in Table 1 was not available in the literature, we calculated HOMOs for all alkenes to enable a check to be made using data for all compounds. The alkene HOMOs were calculated in the same manner as reported previously.[1a] Figures 1 and 2 show the similar correlations of $\log k_{\mathrm{rel}}$ values versus alkene IPs for chromyl chloride oxidation of alkenes and for chromic acid oxidation of alkenes, respectively. Each shows a single line with a positive slope and an excellent[16] correlation coefficient ($r_{\mathrm{all}} = 0.93$ in Fig. 1, $r_{\mathrm{all}} = 0.97$ in Fig. 2). The plots (not shown) of $\log k_{\mathrm{rel}}$ versus alkene HOMOs for both reactions are essentially analogous to Figs 1 and 2. They also have single lines with positive slopes and show excellent correlations ($r_{\mathrm{all}} = 0.94$ for the chromyl chloride oxidation and $r_{\mathrm{all}} = 0.95$ for the chromic acid oxidation). Correlation coefficients for all alkenes (r_{all} values) are calculated from individual values for the alkenes.

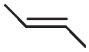
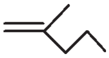
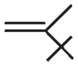
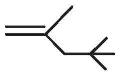
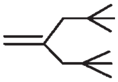
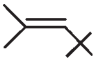
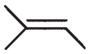
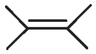


Scheme 4. The direct addition mechanism for H_2CrO_4 oxidation of alkenes[6b]



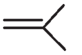
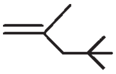
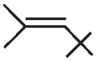
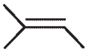
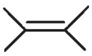
Scheme 5. The $2+3$ cycloaddition mechanism for H_2CrO_4 oxidation of alkenes[6b]

Table 1. IPs, HOMOs and relative rates of chromyl chloride (CrO_2Cl_2) oxidation of alkenes

No.	Alkene	IP (eV)[a]	HOMO (eV)	k_{rel}[b]
1		9.52	−9.94	1.22×10^2
2		9.51[c]	−9.95	88.0
3		9.48	−9.97	1.00×10^2
4		9.45	−9.96	5.36×10^2
5		9.43[c]	−9.95	77.0
6		9.12	−9.79	1.51×10^3
7		9.12	−9.78	1.38×10^3
8		9.08	−9.79	8.00×10^2
9		9.04	−9.77	1.48×10^3
10		9.04	−9.76	1.51×10^3
11		9.02	−9.75	1.05×10^3
12		8.91	−9.71	2.36×10^3
13			−9.78	7.54×10^2
14		8.83[d]	−9.64	1.38×10^5
15		8.68	−9.63	2.02×10^4
16		8.27	−9.49	3.91×10^5

[a] Ref. 15a, unless otherwise noted.
[b] Ref. 5c.
[c] Ref. 15b.
[d] Ref. 15c.

Table 2. IPs, HOMOs and relative rates of chromic acid (H_2CrO_4) oxidation of alkenes

No.	Alkene	IP (eV)[a]	HOMO (eV)	k_{rel}[b]
1		9.74	−9.97	32.3
2		9.63	−9.94	52.0
3		9.52	−9.94	75.5
4		9.48	−9.97	1.00×10^2
5		9.45	−9.96	68.7
6		9.44	−9.94	94.2
7		9.24	−9.80	2.48×10^2
8		9.12	−9.79	2.86×10^2
9		9.12	−9.78	1.89×10^2
10		9.04	−9.76	2.46×10^2
11		8.97	−9.75	2.78×10^2
12		8.91	−9.71	3.44×10^2
13		8.83[c]	−9.64	1.10×10^3
14		8.68	−9.63	3.13×10^3
15		8.27	−9.49	1.60×10^4

[a] Ref. 15a, unless otherwise noted.
[b] Ref. 6b.
[c] Ref. 15c.

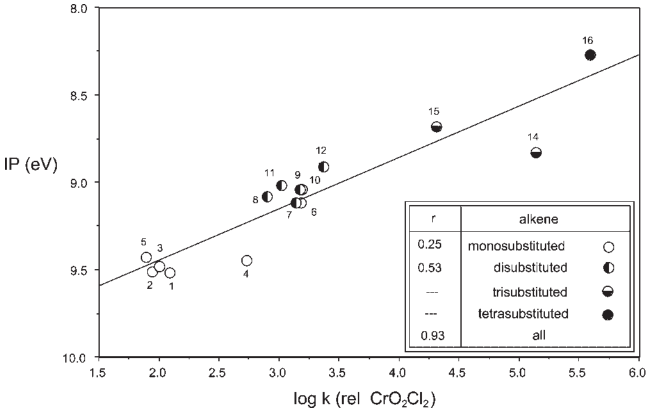


Figure 1. The plot of the log k_{rel} values for chromyl chloride oxidation of alkenes versus correspondent alkene IPs. Data are given in Table 1. Correlation coefficients (r values) are given in the legend for monosubstituted alkenes, for disubstituted alkenes and for all alkenes regardless of the degree of substitution about the double bond. The y-axis IP data are plotted in inverse order to facilitate comparison with the HOMO plots and previous studies

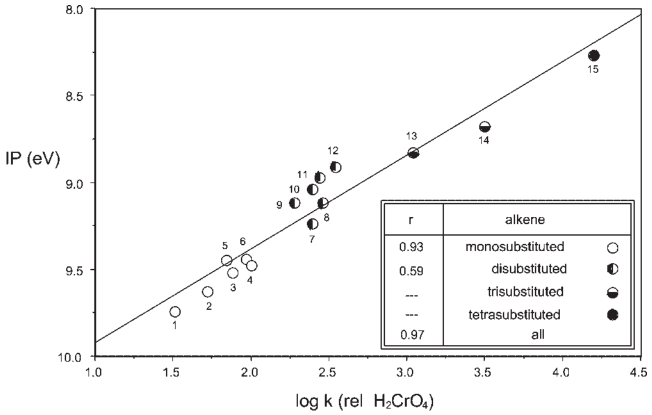


Figure 2. The plot of the log k_{rel} values for chromic acid oxidation of alkenes versus correspondent alkene IPs. Data are from Table 2

Steric effects and electronic effects

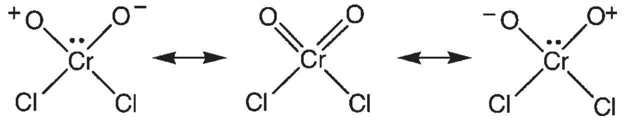
The excellent[16] correlation of log k_{rel} values versus alkene IPs and versus alkene HOMOs in each plot indicates that the rate-determining step of each reaction involves the alkene π-electrons. Each plot has a single line of correlation, regardless of the degree of alkene substitution, so there is no natural separation due to steric requirements of the alkenes, which has sometimes been observed in other additions to alkenes.[1a,b,d,g,h] This provides evidence that both chromyl chloride oxidation and chromic acid oxidation of alkenes are dependent more upon electronic effects than steric effects in their rate-determining steps.

All correlation lines in Figs 1 and 2 have positive slopes; in each reaction a lower IP (or a higher HOMO) corresponds to a greater reaction rate. Therefore, the rate-determining step, in chromyl chloride oxidation of alkenes and in chromic acid oxidation of alkenes, involves electrophilic attack upon the π-bond of the alkene. Electron-donating substituents in the alkene increase the rate of reaction using either reagent, and electron-withdrawing ones decrease it.

Differentiating between the proposed mechanisms

Many studies have attempted to differentiate between the $2+2$ mechanism versus the $2+3$ mechanism for chromyl chloride oxidation of alkenes.[5f,g,h,j,l] Some have favored the former mechanism,[5f,g,h] and have some favored the latter.[5j,l] The results of our current study indicate that the rate-determining step in the oxidation of alkenes, by using chromyl chloride or chromic acid, is an electrophilic attack upon the alkene π-bond. This disfavors the $2+2$ mechanism for chromyl chloride oxidation of alkenes, because in this mechanism (Scheme 2) the only electrophilic step is the formation of the chromyl chloride alkene complex ($\mathbf{1} \rightarrow \mathbf{2}$), which is generally agreed[2c,5i] not to be the rate-determining step, but a fast equilibrium. Neither of the two proposed[51] sets of rate-determining steps in the $2+2$ mechanism are viable possibilities, because they are not electrophilic processes involving the alkene π-bond; the formation of intermediates **3** and **4** from **2** (**2** → **3** and **2** → **4** in Scheme 2) are nucleophilic processes. The decomposition of these intermediates (**3** → **5**, **3** → **6**, **4** → **6** and **4** → **8** in Scheme 2) has no direct relationship to the alkene π-bond IPs and any mechanism with these as the rate-determining steps can be excluded. Ziegler's calculations[51] predicting that these are indeed the rate-determining steps excludes the $2+2$ mechanism (Scheme 2) in this reaction, in analog with calculations[2g–j,n–r] for other metal complex oxidations of alkenes using similar computational methods.

Our analysis that the rate-determining step is an electrophilic process involving attack upon the alkene π-bond supports the $2+3$ mechanism (Scheme 3). Electrophilic attack by the reactant CrO_2Cl_2 could be visualized by using one of its resonance structures in which an oxygen atom carries a positive charge.[5e]



Our investigations similarly indicate that the chromic acid oxidation of alkenes is also an electrophilic addition with a rate-determining step which involves the alkene π-electrons. The plot of $\log k_{rel}$ values versus alkene IPs for oxidation with H_2CrO_4 (Fig. 2) is essentially analogous to that of CrO_2Cl_2 (Fig. 1) with correlation coefficient $r_{all} = 0.97$. Our results are accommodated by either of the mechanisms in Scheme 4 or Scheme 5. One might argue to exclude the mechanism in Scheme 4 for the following reasons: (1) H_2CrO_4 is structurally similar to CrO_2Cl_2; (2) the two similar reagents might be expected to react in a similar manner; (3) an analogous mechanism for the CrO_2Cl_2 reagent was discarded and (4) a mechanism similar to that in Scheme 5 also agrees with the results obtained by using the reagent CrO_2Cl_2.

What explanations can be offered for the production of products other than diols? One possibility is that in the $2+2$ mechanism, the first step is actually the rate-determining step, although the results of Ziegler's study work against this. Another possibility is that the $2+3$ adduct reacts via a pathway other than hydrolysis to diols. This second possibility has been the subject of recent studies.[5m,n,o] The observation of an ESR signal in the reaction of the Cr(V) intermediate complex with CrO_2Cl_2: alkene $= 2{:}1$[5m,n,o] suggests that, for the $2+3$ adducts of CrO_2Cl_2 and of H_2CrO_4, instead of hydrolysis, perhaps an alternate reaction pathway involving diradicals is favored.

CONCLUSION

A single line in each correlation plot of $\log k_{rel}$ values versus alkene IPs (Figs 1 and 2) and versus alkene HOMOs ($r_{all} = 0.94$ and 0.95) for the oxidation of alkenes by using CrO_2Cl_2 and H_2CrO_4 demonstrates that (1) the rate-determining step of each reaction involves the alkene π-electrons and (2) these reactions are more dependent upon electronic effects than upon steric effects. Their positive slopes indicate that the rate-determining step in each reaction is an electrophilic addition. Our study supports the $2+3$ mechanism and disproves the $2+2$ mechanism with the rate-determining step that has been proposed for it.

Acknowledgement

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