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Extrusion of Alkenes from Rhenium(V) Diolates: Energetics and Mechanism

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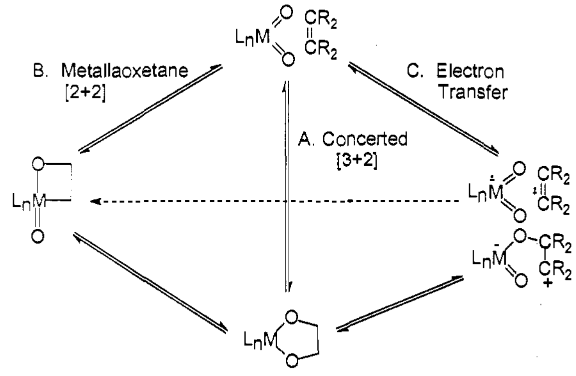
Abstract: The kinetics of extrusion of ethylene, 2-butene, and bicyclo[2.2.2]oct-2-ene from Cp*Re(O)(OCH(R)CH(R)O) (Cp* = η-$C_5(CH_3)_5$) are measured, as are the kinetics of oxidation of norbornene, norbornadiene, and *trans*-cyclooctene by Cp^*ReO_3. Activation parameters calculated from the data show that strain in the double bond has a large effect on the enthalpy of activation for alkene oxidation but little or no effect on the enthalpy of activation for alkene extrusion. Entropies of activation for alkene extrusion are less than zero. A secondary deuterium isotope effect of 1.3 at 99.5 °C is measured for extrusion of ethylene-d_4. Taken together, this data is inconsistent with a concerted mechanism for interaction of alkenes with Cp^*ReO_3 but consistent with a stepwise mechanism with a metallaoxetane intermediate.

Introduction

Oxidation of alkenes comprises several technologically and economically important transformations[1] that are catalyzed by a number of transition metal oxides. Understanding of the chemistry in this field is growing due to recent advances in synthetic and structural studies of high oxidation state organometallic compounds.[2] Reactivity of these species remains poorly understood; proposals have been put forward for mechanisms by which metal oxo units interact with C–C π bonds, but in many cases such hypotheses are untested by experiment and based on limited precedent.

A well-known example of such a mechanistic dilemma is the bishydroxylation of alkenes by OsO_4, $KMnO_4$, and related species (see Scheme 1). The original mechanistic proposal by Criegee, a concerted [3 + 2] cycloaddition (mechanism A),[3] has won wide acceptance by organic chemists,[4] in part due to the ease with which analogy can be drawn with other dipolar cycloadditions:[5] ozone, nitrones, carbonyl ylides, carbonyl oxides, nitrile oxides, and azides all undergo concerted [3 + 2] cycloadditions which show high stereoselectivities for syn addition to alkenes. Theoretical work[6,7] using both molecular orbital and molecular mechanics approaches has also suggested that such a hypothesis is consistent with calculations on species presumably lying on the reaction coordinate.

Scheme 1



However, there is to date no confirmed example of a pericyclic cycloaddition in which one of the members of the cyclic array of atoms is a transition metal. The prospect of discovering such an example has motivated much useful exploration, but to date, all examples for which conclusive evidence exists have proceeded by stepwise, nonpericyclic reorganizations.[8]

In 1977, Sharpless and co-workers suggested that this might be the case for osmylation.[9] They suggested that all known data could as easily be explained by a stepwise mechanism involving [2 + 2] cyclization to form a metallaoxetane (mechanism B) as by the concerted [3 + 2] mechanism. Since the appearance of this suggestion, extensive work has gone into seeking evidence of a metallaoxetane in osmylation[10,11] and into exploring the

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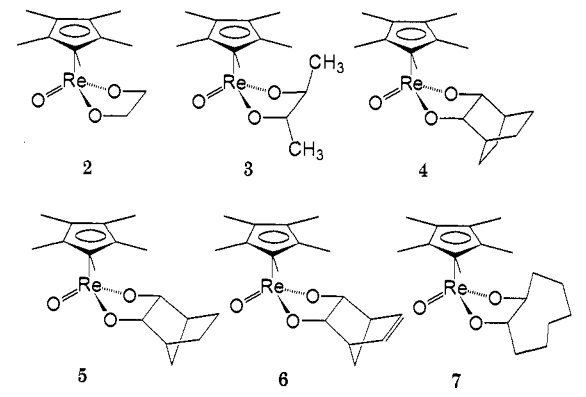
chemistry of metallaoxetanes in other systems.[12] The latter studies have suggested that metallaoxetanes may not engage in reactivity patterns required in oxidations,[13] but the structural differences with intermediates suggested for oxidations have left this question open. Further, theoretical work has indicated the feasibility of such a mechanism.[14] Precedent for formation of a metallacycle in this manner has been seen,[15] as has alkyl migration to an oxo ligand.[16]

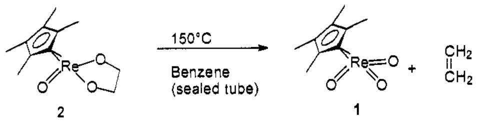
A final mechanism suggested by Kochi et al. (mechanism C)[17] involves initial electron transfer; the stereospecificity of osmylation demands that collapse of the odd-electron intermediates to either diolate or metallaoxetane be quite rapid.

We decided to explore the microscopic reverse of the alkene addition to metal oxides as a mechanistic model for osmylation in the expectation that several practical complications could be avoided. Several examples of cycloreversion of metal diolates have been reported, most notably for diolate complexes of rhenium.[18-22] These diolates are attractive objects for mechanistic study: many can be isolated as pure compounds; they do not exhibit the flexible coordination chemistry of osmium oxides; the cycloreversions proceed in nonpolar solvents; and the reactions are typically much slower than the very rapid osmylation reaction.

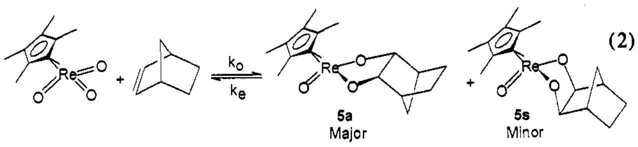
Chart 1



We chose to examine in detail an alkene extrusion first reported by Herrmann and co-workers (eq 1).[20] We made an initial discovery that this system is at a thermodynamic balance point (see eq 2);[23] this fact has allowed us to examine the energetics of both alkene extrusion and alkene oxidation as a function of substrate structure. This study is reported here.



(1)



(2)

Results

Preparation and Characterization of New Diolates. Compounds whose formation or fragmentation was studied are shown in Chart 1.

Preparation of ethanediolate **2** and butanediolate **3** was performed using the procedure of Herrmann et al.[20] Reaction of Cp^*ReO_3 with norbornene and norbornadiene has been reported previously.[23] Preparation of bicyclo[2.2.2]octane-2,3-diolate **4** was accomplished by a slight modification of the procedure for **2** and **3**, in which an excess of the diol was reacted with $Cp^*Re(O)Cl_2$ in the presence of pyridine. This produced predominantly *exo,anti*-**4**; assignment of structure was by analogy to **5** and **6**. A small amount (<2%) of a minor isomer was observed, as evidenced by a second Cp* signal in the ^{1}H NMR.

Reaction of Cp^*ReO_3 with a mixture of *cis*- and *trans*-cyclooctene led to formation of a new purple diolate. (An independent experiment with *cis*-cyclooctene led to no reaction.) This could be isolated by column chromatography. It was a single isomer as indicated by ^{13}C NMR: eight ring carbons plus the two for the Cp* ligand were evident. The trans stereochemistry was evident by the lack of symmetry in the ^{13}C NMR and by the presence of two different carbinol-type CH signals at δ 4.15 and 3.50 ppm in the ^{1}H NMR, consistent with one proton being syn and the other anti to the Cp* ring. Irradiation of the Cp* methyl signal at δ 1.72 ppm led to a slight nuclear Overhauser enhancement of signals at δ 3.50, 2.80, 2.68, and 1.5 ppm. This indicates these protons are in close proximity to the Cp* ligand. It is consistent with our earlier assignment of the structures of **5** and **6**. The major isomer of each had the carbinolic protons appearing at higher field; our assignment based on steric interaction placed the Cp* ring syn to the carbinolic protons.

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Table 1. Reaction Rates for Alkene Extrusion

diolate	alkene	T, K	10^5k_e, s^{-1}
2	ethylene	334.1	0.124
		339.1	0.262
		348.1	0.723
		356.5	2.06
		365.1	5.72
		372.2	12.5[a]
		378.0	21.6[b]
		378.1	17.6
		383.1	32.2
2-d_4	ethylene-d_4	372.2	9.48[a]
		378.0	17.6[b]
3	2-butene	349.1	0.042
		360.6	0.17
		372.6	0.61
		378.6	1.24
		389.9	4.74
		398.3	10.6
4	bicyclo[2.2.2]oct-2-ene	368.9	0.124
		372.6	0.126
		380.0	0.49
		382.2	0.60
		388.2	0.84
		396.2	2.26
		401.3	2.30
		401.3	5.33
		405.9	7.50

[a] Samples run side-by-side. [b] Samples run side-by-side.

Table 2. Equilibrium Constants for Formation of **4** from Bicyclo[2.2.2]oct-2-ene and Cp*ReO$_3$

T, K	[alkene], M	[**4**]/[Cp*ReO$_3$]	K_{eq}
378.0	0.188	0.046	0.246
378.0	0.322	0.080	0.249
382.2	0.204	0.047	0.230
387.2	0.188	0.031	0.164
387.2	0.322	0.047	0.147
397.3	0.188	0.022	0.118
397.3	0.322	0.041	0.127
401.6	0.780	0.10	0.128

Kinetics of Alkene Extrusion and Oxidation. Diolates **2**, **3**, and **4** were dissolved in C_6D_6 and sealed in NMR tubes under vacuum. They were heated to 60–130 °C; the kinetics of alkene extrusion were followed by periodic monitoring of the ^{1}H NMR signals for the Cp* ligand. The reactions were cleanly first order to at least four half lives.[24] Reaction rate constants (k_e is the first-order rate constant for extrusion) are summarized in Table 1. Measurement of the rate of reaction of **2**-d_4 led to estimation of a secondary deuterium isotope effect of 1.32 ± 0.06 at 99.1 °C. A separate determination at 104.8 °C gave a value of 1.23 ± 0.06.

Although preliminary studies indicated the equilibrium between **4** and its fragments strongly favored the latter, we wished to establish the thermodynamics of this process to gain a quantitative comparison to our earlier thermochemical results.[23] Reaction of a large excess of bicyclo[2.2.2]oct-2-ene with Cp*ReO$_3$ led to formation of small amounts of **4**; equilibrium constants as a function of temperature are shown in Table 2. This data allows calculation of $\Delta H° = -9.8 \pm 0.8$ kcal/mol and $\Delta S° = -28 \pm 4$ cal/(molK) for the oxidation of this alkene; a Van't Hoff plot is shown in Figure 1.

Oxidation of norbornadiene and *trans*-cyclooctene by Cp*ReO$_3$ were followed as pseudo-first-order reactions to at least four half-lives, where the alkene was present in excess (5–10 equiv). The observed pseudo-first-order rate constants and calculated second-order rate constants (k_o is the second-order rate constant for alkene oxidation) are in Table 3.

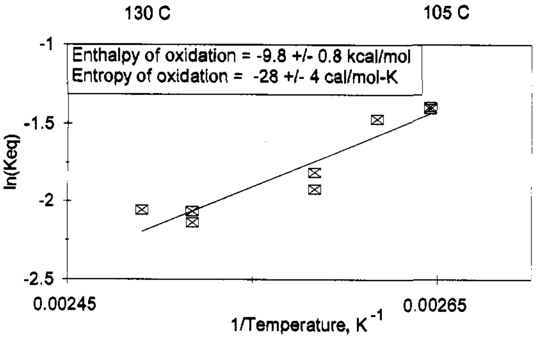

Figure 1. Van't Hoff Plot for oxidation of bicyclo[2.2.2]oct-2-ene: slope = 4920; intercept = −14.45; r^2 = 0.8901.

Table 3. Reaction Rates for Oxidation of Norbornadiene and *trans*-Cyclooctene

alkene	[alkene]$_{eq}$, M	T, K	10^5k_{obs}, s^{-1}	10^5k_o, M^{-1} s^{-1}
norbornadiene	0.292	370.4	2.10	7.20
	0.115	371.4	0.913	7.94
	0.167	382.0	2.50	15.0
	0.122	384.9	2.02	16.6
	0.245	385.0	2.95	12.1
	0.332	387.0	7.04	21.2
	0.134	393.9	4.15	31.0
	0.143	396.8	5.66	39.6
trans-cyclooctene	0.120	314	2.29	19.1
	0.148	322.3	4.72	30.0
	0.168	329.0	9.80	58.0
	0.23	338.1	20.0	87.0
	0.201	350.8	30.9	154
	0.308	350.9	49.0	159

Table 4. Reaction Rates for Equilibration of Cp*ReO$_3$ and Norbornene with **5**

[norbornene]$_{eq}$, M	T, K	10^5k_{obs}, s^{-1}	10^5k_o, M^{-1} s^{-1}	10^5k_e, s^{-1}
0.174	362.9	0.276	1.39	0.034
0.0924	370.4	0.234	1.86	0.062
0.149	370.4	0.368	2.02	0.067
0.2042	370.4	0.492	2.07	0.069
0.175	387.0	1.39	5.83	0.369
0.188	391.7	2.56	9.73	0.731
0.12	395.5	1.91	9.26	0.798
0.0747	395.5	1.74	10.8	0.932
0.347	399.6	6.70	15.0	1.49

Norbornene oxidation, as an equilibrium process, could be treated so as to yield both k_o and k_e from the pseudo-first-order rate of approach to equilibrium.[25] Because the equilibrium constant at each temperature ($K_{eq} = k_o/k_e$)[23] and the rate of approach to equilibrium ($k_{obs} = k_o$[norbornene] + k_e) were both known, the relevant rate constants may be determined. This data is summarized in Table 4.

Activation parameters for each process are summarized in Table 5. A representative Eyring plot is seen in Figure 2; others may be found in the supplementary material.

There is clearly a strain-induced acceleration of the alkene oxidations. In addition to the directly measured activation enthalpies, we can estimate ΔH^{*}_{o} for bicyclo[2.2.2]octene. Given $\Delta H° = -9.7$ kcal/mol and $\Delta H^{*}_{e} = 31.5$ kcal/mol, by difference, $\Delta H^{*}_{o} = 21.8$ kcal/mol. In a similar vein, if we assume the primary enthalpic difference between 2-butene and norbornene is the 5.7 kcal/mol of strain energy in the double bond, we can estimate $\Delta H° = -5.2$ kcal/mol for 2-butene and thus $\Delta H^{*}_{o} = 25.3$ kcal/mol. (A calculation based on the lower bound for $\Delta G° > 3.9$

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(24) Reaction of a large excess of bicyclo[2.2.2]oct-2-ene with Cp*ReO$_3$ led to formation of a small amount of **4**, but the measured equilibrium constant was small; see the subsequent discussion of thermodynamics. We conclude that where [**4**] < 0.1 M, the reaction can be treated as essentially an irreversible, first-order process, but cycloreversions of **4** were followed to only 3 half-lives.

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Table 5. Activation Parameters Measured for Alkene Oxidation and Extrusion

alkene	$\Delta H^{\ddagger}{}_{o}$[a]	$\Delta S^{\ddagger}{}_{o}$[a]	$\Delta H^{\ddagger}{}_{e}$[a]	$\Delta S^{\ddagger}{}_{e}$[a]	estimated strain in the double bond[b]
ethylene			28.0 ±0.4	−2.1 ±1.2	0
2-butene			30.5 ±0.5	−0.8 ±1.1	0
bicyclo[2.2.2]oct-2-ene			31.5 ±1.8	−0.9 ±4.7	4.3
norbornene	18.2 ±0.6	−30.0 ±1.8	29.1 ±0.5	−7.2 ±1.8	5.7
norbornadiene	16.8 ±0.9	−32.0 ±2.3			8.0
trans-cyclooctene	11.7 ±0.7	−38.4 ±2.1			9.0

[a] Units: $\Delta H^{\ddagger}$ in kcal/mol; $\Delta S^{\ddagger}$ in cal/(mol K). [b] Defined as the difference in total strain energy (in kcal/mol) between the alkene and the corresponding alkane. See ref 30.

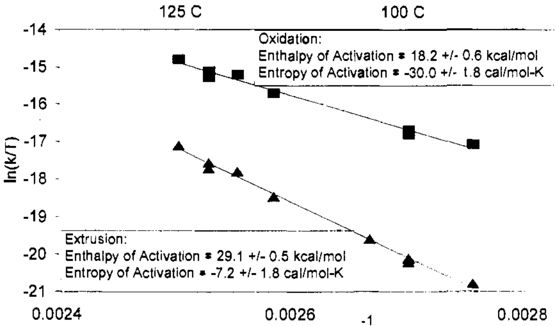


Figure 2. Eyring plots for the oxidation and extrusion of norbornene. For oxidation: slope = −9167; intercept = 8.05; r^2 = 0.9865. For extrusion: slope = −14673; intercept = 19.52; r^2 = 0.9949.

kcal/mol[26] and an assumed $\Delta S°$ of −25 cal/(molK) gives similar results.) A conservatively large estimate of uncertainties for both values of $\Delta H^{\ddagger}{}_{o}$ is ±3 kcal/mol. A similar process may be used to estimate other values which cannot be directly measured: relation of estimated strain energy in the double bond allows an estimate of $\Delta H°$ for norbornadiene and *trans*-cyclooctene, and by difference $\Delta H^{\ddagger}{}_{e}$ is calculated in each case. The weak link is the estimate of strain energy; relative values for the bicyclic alkenes are probably quite good, but estimation of the strain in *trans*-cyclooctene is more problematic.[27] These estimates are seen in Table 6.

Discussion

Each of the proposed mechanisms for osmylation is potentially applicable in this system (Scheme 2), and makes a number of predictions which our results test.

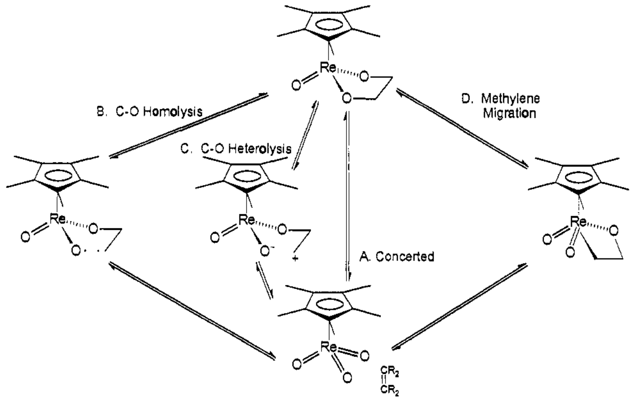
A. Concerted Process. In a concerted process, one predicts that increasing strain in the alkene will affect the enthalpy of activation for both cycloaddition and extrusion. In this mechanism, the cycloaddition causes rehybridization of the sp^2 carbons of the double bond to sp^3 in the diolate. A significant source of strain in those alkenes which undergo oxidation by Cp^*ReO_3 is structural constraint of the multiply bonded carbon atoms to geometries at odds with their sp^2 hybridization. At the transition state, this strain should be partially relieved. It will not be relieved totally due to the remaining C–C π interaction. One expects to see a lowering of the activation enthalpy[28] that is a substantial fraction of the overall change in strain energy. This has been observed in two cases that are generally accepted to be concerted cycloadditions.[29] Furthermore, the *opposite* effect should be seen in the extrusions: the increasing C–C π interaction at the transition state will result in higher activation enthalpy with increasing strain in the extruded alkene (see eq 3).

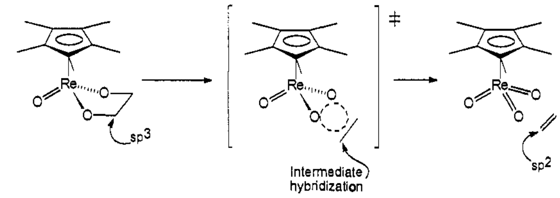
Table 6. Indirect Estimation of Activation Parameters for Unobserved Processes

alkene	estimated strain in the double bond[a]	estimated $\Delta H°$ for oxidation	calculated $\Delta H^{\ddagger}{}_{e}$ for cycloreversion
2-butene	0	−5.2	30.5[b]
bicyclo[2.2.2]oct-2-ene	4.3	−9.7[b]	31.5[b]
norbornene	5.7	−10.9[b]	29.1[b]
norbornadiene	8.0	−13.2	30.0
trans-cyclooctene	9.0	−14.2	26.1

[a] Difference between standard enthalpies of formation of alkene and the corresponding alkane, except for *trans*-cyclooctene, for which this is the difference between standard enthalpies of formation for *cis*- and *trans*-cyclooctene; see ref 30. All values are in kcal/mol. [b] Experimental value.

Scheme 2





(3)

Our observations are not consistent with the predictions arising from the concerted hypothesis. While there is the expected correlation of $\Delta H^{\ddagger}{}_{o}$ with the estimated strain energy in the double bond[30] (see Tables 5 and 6), the range of values for $\Delta H^{\ddagger}{}_{o}$ is as large as the range of strain energies. Conversely, extrusion of those alkenes which are electronically comparable (2-butene, bicyclo[2.2.2]octene, and norbornene) shows approximately the same activation enthalpy. Furthermore, reasonable estimates of $\Delta H^{\ddagger}{}_{e}$ for norbornadiene and *trans*-cyclooctene (which we are unable to observe directly) indicate that these values are no more than 30 kcal/mol and therefore similar to those values we can directly measure.

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(26) A sample with 2 M *trans*-2-butene and 0.03 M Cp^*ReO_3 showed no diolate after heating to 105 °C for one week. A detection limit of 1% gives $K_{eq} < 0.005$; $\Delta G° > 3.9$ kcal/mol.

(27) Estimates in the literature indicate a total strain energy of 16.5 kcal/mol, most of which arises from torsional deformation of the double bond (see ref 30). Cyclooctane has significant strain (10.2 kcal/mol), but this arises from interactions which are not present in *cis*- or *trans*-cyclooctene. We have taken the difference between the heats of formation of *cis*- and *trans*-cyclooctene (9.0 kcal/mol) as the strain due to the double bond. Even if *all* of the strain is relieved in forming the cyclooctanediolate, that leads to an estimated $\Delta H^{\ddagger}{}_{e}$ of 33.4 kcal/mol, far less than one predicts from the concerted mechanism.

(28) Strain has its greatest effect in enthalpy, due to the effect it has on bond strengths. Greenberg, A.; Liebman, J. F. *Strained Organic Molecules*; Academic Press: New York, 1978.

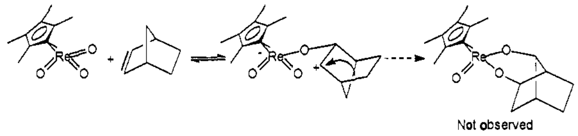
(29) (a) Epoxidation with peroxyacids: Shea, K. J.; Kim, J.-S. *J. Am. Chem. Soc.* **1992**, *114*, 3044–3051. (b) Cycloaddition of phenyl azide: Shea, K. J.; Kim, J.-S. *J. Am. Chem. Soc.* **1992**, *114*, 4846–4855.

(30) Strain in the double bond is defined as the difference in total strain between the alkene and the corresponding alkane. Allinger, N. L.; Sprague, J. T. *J. Am. Chem. Soc.* **1972**, *94*, 5734–5747.

If we wish to rationalize the data in terms of the concerted mechanism, we must demand that the transition state be structurally similar to the diolate: rehybridization of the alkene must be almost complete, or conversely, rehybridization of the diolate carbon has not begun. There are two strong arguments against this. First, it implies an early transition state for alkene extrusion. While this is consistent with the near-zero $\Delta S^{\ddagger}$ for unstrained alkene extrusion, the magnitude of $\Delta H^{\ddagger}$ is surprising and would suggest a violation of the Hammond postulate. More important is the magnitude of the secondary deuterium kinetic isotope effect (KIE) on ethylene extrusion. An early transition state with very little reorganization of bonding would demand a low KIE. However, our observed per-deuterium KIE (assuming a concerted mechanism) of 1.06–1.07 is of the same order of magnitude as that for the retro-Diels–Alder reaction.[31] From the point of view of the ethylene fragment, the transition state for a concerted extrusion would have to be as far toward product as that for the retro-Diels–Alder reaction. This attempt to reconcile the experimental data with the predictions of a concerted mechanism thus generates a fatal contradiction: in a cycloreversion there must be a significant change in bonding to the extruded alkene without any appreciable change in hybridization toward sp^2 carbon. We thus conclude that *in this system, cycloreversion cannot be a concerted process*; by the principle of microscopic reversibility, then, the alkene oxidations must involve stepwise formation of C–O bonds.

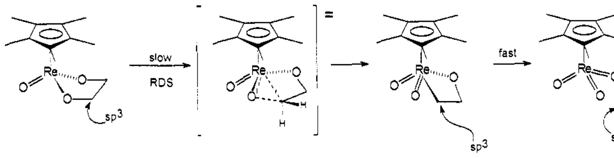
B. Electron Transfer/Homolytic CO Cleavage. If the interconversion of oxide with diolate involves an intermediate, what is this species? We can consider several candidates. The magnitude of $\Delta H^{\ddagger}$ for extrusion suggests homolysis of the C–O bond as an initial step (mechanism B, Scheme 2). This is the microscopic reverse of the Kochi proposal for osmylation. The biradical so formed would necessarily fragment to alkene rapidly, in order to maintain the stereochemical integrity shown by extrusion of 2-butene.[32] However, such a process is expected to have a large, positive $\Delta S^{\ddagger}$; for example, decomposition of cyclic azoalkanes typically shows $\Delta S^{\ddagger} \approx +5$ to $+15$ cal/(molK).[33] Furthermore, one expects increasing alkyl substitution at the reacting carbon to stabilize the intermediate radical and lower $\Delta H^{\ddagger}$. We observe behavior contrary to both of these predictions: any electronic effect favors extrusion of the less substituted ethylene from **2**, and all of the activation entropies for extrusion are zero or negative. In addition, the reported reduction potential of Cp*ReO$_3$ is incompatible with efficient electron transfer in the oxidation of the strained alkenes.[34]

C. Heterolytic Cleavage. One may also consider heterolytic C—O bond cleavage as an initial step in alkene extrusion; the alkene oxidation mechanism demanded by this proposal is attack of an *electrophilic* oxygen at the alkene. Such a process might be expected of a high oxidation state M═O system, although precedent is scarce. However, we again see evidence contrary to predictions made by this hypothesis. The electronic effect of alkyl substitution is predicted to be much larger[35] and again should lead to a *lower* $\Delta H^{\ddagger}$ with more substitution. Furthermore, had cationic character been generated at carbon in the norbornyl systems, a rapid rearrangement to a non-C_s symmetric cation should have been seen (see eq 4). This may depend on the rate at which the cation is either trapped by the second Re═O or extrudes alkene; these processes must both have activation barriers less than the estimated limit of 3 kcal/mol for the norbornyl rearrangement.[36]



(4)

D. Intermediacy of a Metallaoxetane. The mechanism which is consistent with all data is the stepwise process involving the metallaoxetane, where the migration of carbon between rhenium and oxygen is rate-limiting. The hybridization of the reacting carbons in the intermediate is sp^3, and since the strain associated with the sp^2 hybridization of the eventual product is not yet present at the transition state there should be little structural effect on the activation barrier (see eq 5). One expects that there will be a small amount of strain in the metallaoxetane, but the long Re–O and Re–C bonds will minimize this; estimates of ring strain in four-membered metallacycles have been in the 0–5 kcal/mol range,[37] and this will be largely invariant to alkene structure. There should be a steric effect due to increasing interaction with the Cp* methyl groups, and the larger activation enthalpy for extrusion of bicyclo[2.2.2]oct-2-ene may reflect such an effect. However, if the migrating group can "gear" with the methyl groups on the cyclopentadienyl ring, that effect may show up as a more negative entropy of activation (which indeed we see). On the other hand, the fact that we see little or no NOE effects between the Cp* methyl groups and the diolate ring suggests that there is little steric interaction at all. There should also be a small electronic effect which disfavors reaction of increasingly alkyl substituted carbon.[38]



(5)

One question this mechanism raises is whether one would expect to see a significant normal secondary kinetic isotope effect, since there is no net change in hybridization during the rate-determining step. It is worth pointing out that the migrating carbon has increased its coordination number in the transition state and thus achieved a *de facto* change in hybridization, albeit not necessarily one that will alter the overall strain in the molecule. A secondary

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(31) At 219 °C, this value for a retro-Diels–Alder reaction extruding ethylene is 1.17: Taagepara, M.; Thornton, E. R. *J. Am. Chem. Soc.* **1972**, *94*, 1168–1177. Corrected to 100 °C, this is estimated to be 1.06 per D. Independent experiments are consistent with this value (1.08 per D at 50 °C): Seltzer, S. *J. Am. Chem. Soc.* **1965**, *87*, 1534–1540.

(32) See ref 20; we used a 5:1 mixture of *threo*/*erythro* butanediol in making our diolate, and the butene mixture was formed in the same ratio. We have also prepared pure *erythro* butanediolate from the meso diol, and this gives only cis-2-butene: Gable, K. P. Unpublished results.

(33) Engel, P. S. *Chem Rev.* **1980**, *80*, 99–150.

(34) The reduction potential for Cp*ReO$_3$ has been measured as −1.72 V vs Ag/AgCl/3M KCl: Herrmann, W. A.; Kiprof, P.; Rypdal, K.; Tremmel, J.; Blom, R.; Alberto, R.; Behm, J.; Albach, R. W.; Bock, H.; Soulouki, B.; Mink, J.; Lichtenberger, D.; Gruhn, N. E. *J. Am. Chem. Soc.* **1991**, *113*, 6527–6537. Oxidation potentials for disubstituted alkenes are +2.05–2.26 V vs Ag/Ag$^+$: Fleischmann, M.; Pletcher, D. *Tetrahedron Lett.* **1968**, 6255–6258. This leads to a calculated $\Delta G°$ for electron transfer of more than 60 kcal/mol (based on $\Delta E° = 2.75$ V after correction for the different reference electrodes).

(35) For bromination of alkenes, $k_{\text{isobutene}}/k_{\text{ethylene}} = 5.5$: Ingold, C. K.; Ingold, E. H. *J. Chem. Soc.* **1931**, 2354–2368. For epoxidation with mCPBA, $k_{\text{2-butene}}/k_{\text{propene}} = k_{\text{propene}}/k_{\text{ethylene}} = 22$: Bartlett, P. D.; Sargent, G. D. *J. Am. Chem. Soc.* **1965**, *87*, 1297–1307. For addition of ArSCl to alkenes, $k_{cis\text{-2-butene}}/k_{\text{ethylene}} = 20.6$: Schmid, G. H.; Garratt, D. G. *Can. J. Chem.* **1973**, *51*, 2463–2468. For our case, $k_{\text{2-butene}}/k_{\text{ethylene}} = 0.048$ (373 K).

(36) (a) Yannoni, Y. S.; Macho, V.; Myhre, P. C. *J. Am. Chem. Soc.* **1982**, *104*, 907–909. (b) Olah, G. A.; White, A. M.; DeMember, J. R.; Commeyras, A. *J. Am. Chem. Soc.* **1970**, *92*, 4627–4640.

(37) (a) Moore, S. S.; DiCosimo, R.; Sowinski, A. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1981**, *103*, 948–949. (b) Sorensen, A. A.; Yang, G. K. *J. Am. Chem. Soc.* **1991**, *113*, 7061–7063.

(38) Substituent effects on alkyl migrations to coordinated CO have been rationalized in terms of decreasing M–C bond strength accelerating migration upon increasing alkyl substitution: Green, M.; Westlake, D. J. *J. Chem. Soc. A* **1971**, 367–371. The converse argument would apply in our case: increasing alkyl substitution destabilizes the M–C bond in the metallaoxetane and thus raises the activation enthalpy for extrusion.

isotope effect will arise primarily from changes in zero point energies for the ground and transition states.[39] Provided the deuterated compound has a lower ZPE, relative to the proteated compound, in the ground state than it has in the transition state, a normal KIE ($k_H > k_D$) is expected. Such a situation would arise from a change in C–H stretching and bending vibrations in the ground-state molecule to lower frequencies in the transition state.[40] Experimentally, such an isotope effect in 1,2-alkyl shifts has been observed in many organic examples[41] and several organometallic[42] rearrangements. Our observation would require a per-D KIE of 1.10–1.14; while this is larger than most of the effects seen in the cited methyl migrations, it is well within the accepted range of secondary deuterium KIEs.[39]

Although our data is consistent with the metallaoxetane mechanism, we must stress that there is as yet no positive evidence for the structure of the intermediate. We have delineated several important features of any proposed intermediate: at least one carbon is no longer bonded to oxygen, and carbon is not sp^2 hybridized nor is it particularly electron deficient. Confirmation of the metallaoxetane mechanism requires, for example, detailed analysis of substituent effects to define the symmetry of the transition state. These experiments are currently in progress.

Implications of This Work. Involvement of a metallaoxetane fits well with recent explorations of the reactivity of second- and third-row, d^0 M=X complexes (X = O, NR) with carbon–carbon multiple bonds. Formation of a metallacycle from alkynes is well-precedented.[43] Expansion of the four-membered metallacycle has less precedent, yet a similar process has been observed in one recent example.[44] Furthermore, this general reaction of an alkyl-to-oxo migration has been seen as well in two instances.[16]

One implication of this work is the need to consider more critically the common preference for the Criegee mechanism in osmylation. Despite significant differences in the ligand sphere, the similarities between Cp*ReO$_3$ and OsO$_4$ are striking. Both are third-row, d^0 transition metal oxo complexes; both undergo a stereospecific interaction with alkenes. Changing the metal and ligands will have several predictable effects on reactivity. First, an osmium oxo complex will have weaker M=O π interactions, which will thermodynamically favor the formation of diolate. According to the Hammond postulate, this should significantly decrease the transition state energy for the alkyl migration. (This would also occur for a putative concerted transition-state.) Replacement of Cp* by a fourth oxo ligand will likely decrease the net electron density at the metal and increase the oxidation potential. This should promote the migration of carbon from metal to oxygen[45] because this is where the fundamental redox chemistry occurs. Although the concerted process cannot be excluded in osmylation, the stepwise process we observe for rhenium must be energetically accessible for osmium.

Conclusion

We have demonstrated that strain in the double bond has a large effect on the energetics of alkenes reacting with Cp*ReO$_3$ but that there is little or no effect on the energetics of alkene extrusion. Taken in conjunction with the measured isotope effect, this data is inconsistent with a concerted [3 + 2] mechanism for interconversion of Cp*ReO$_3$ with diolates.

Experimental Section

General Methods. All reactions were performed using standard inert-atmosphere techniques in a nitrogen-filled glove box (Vacuum Atmospheres Co., HE 493) or on a double-manifold Schlenk line. Solvents were purified by vacuum distillation prior to use; ether, THF, and benzene were distilled from sodium benzophenone ketyl, and hexane was distilled from Na/K alloy. NMR spectra were obtained on either a Bruker AC300 (operating at 300.133 MHz for proton or 75.469 MHz for ^{13}C) or a Bruker AM400 (operating at 400.134 MHz for proton or 100.614 MHz for ^{13}C) spectrometer. All chemical shifts are referenced to residual protons in solvent and expressed in ppm downfield from tetramethylsilane. Infrared spectra were run on a Nicolet 510P spectrometer.

Cp*ReO$_3$ was made by a modification of published syntheses.[46] Cp*Re(O)(OCH$_2$CH$_2$O) and the analogous butanediolate were prepared according to published methods;[47] the d_4-ethanediolate was made by analogous procedures using ethylene glycol-*1,1,2,2-d$_4$* (98 atom % D) from Cambridge Isotopes Laboratories, Inc. Norbornene, norbornadiene, and bicyclo[2.2.2]octene were used as received from Aldrich. *trans*-Cyclooctene was prepared according to the method of Cope et al.[48] Elemental analyses were performed by Texas Analytical Laboratories.

(*exo*-Bicyclo[2.2.2]octane-2,3-diolato)(pentamethylcyclopentadienyl)(oxo) rhenium (4). *exo*-Bicyclo[2.2.2]octane-2,3-diol (100 mg, 0.70 mmol) and 50 mg of Cp*Re(O)Cl$_2$ (0.12 mmol) were dissolved in 3 mL of tetrahydrofuran. Pyridine (0.2 mL, 200 mg, 2.53 mmol) was added, and the mixture was stirred for 3 h. The dark-brown solution was reduced to a semisolid. Extraction of the residue with 1 mL of hexane, filtering, and removal of hexane gave 20 mg (0.04 mmol, 33% yield) of purple solid. ^{1}H NMR (C$_6$D$_6$): δ 1.20 (br d, J = 8 Hz, 2H), 1.48 (br s, 4H), 1.70 (s, 15H), 2.21 (br s, 2H), 2.32 (br d, J = 8 Hz, 2H), 4.10 (br s, 2H). ^{13}C NMR (C$_6$D$_6$): 11.0, 19.2, 24.9, 33.7, 92.0, 107.6. IR (CH$_2$Cl$_2$): 2938, 2870, 1439, 1190, 1120, 1062, 1010, 916 cm^{-1}. MS (EI): *m/e* 478 (M$^+$, ^{187}Re), 476 (M$^+$, ^{185}Re), 134. HRMS: 478.1520 (Calcd for C$_{18}$H$_{27}$O$_3$Re 478.1490).

(*exo*-Bicyclo[2.2.1]heptane-2,3-diolato)(pentamethylcyclopentadienyl)(oxo) rhenium (5). Cp*ReO$_3$ (50 mg, 0.14 mmol) and norbornene (0.68 g, 7.1 mmol) were dissolved in 3 mL of CHCl$_3$ and heated to reflux for 24 h. The CHCl$_3$ was removed *in vacuo* and the residue dissolved in 1 mL of hexane. The mixture was placed on a column of silica gel (0.5 × 5 cm^2) and chromatographed first with CHCl$_3$ (to remove unreacted Cp*ReO$_3$) and then with acetone. The purple diolate fraction was collected and solvent removed *in vacuo*. Lyophilization from benzene gave 30 mg of purple solid (0.06 mmol, 48%). Major isomer: ^{1}H NMR (C$_6$D$_6$): δ 0.95 (dtt, J = 10.4, 1.4, 1.4 Hz, 1H), 1.02 (ddd, J = 13.5, 6.5, 2.1 Hz, 2H), 1.28 (ddd, J = 13.5, 6.5, 3.2 Hz, 2H), 1.735 (s, 15H), 2.36 (dtt, J = 10.4, 1.5, 1.5 Hz, 1H), 2.62 (dddd, J = 3.2, 2.1, 1.5, 1.5 Hz, 2H), 4.05 (d, J = 1.5 Hz, 2H). ^{13}C NMR (C$_6$D$_6$): 10.93, 25.55, 32.03, 44.71, 99.00, 107.66. Minor isomer: ^{1}H NMR (C$_6$D$_6$): δ 0.77 (dtt, J = 10.4, 1.4, 1.4 Hz, 1H), 1.815 (s, 15H), 2.50 (m, 2H), 4.44 (d, J = 1.5

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Hz, 2H), other peaks obscured by major isomer. IR (CH_2Cl_2): 2965, 1456, 991, 918, 885, 787, 669 cm^{-1}. MS (EI): *m/e* 464 (M^+, ^{187}Re), 462 (M^+, ^{185}Re), 370, 367, 135, 134 (base peak), 119. HRMS: 464.1363 (Calcd for $C_{17}H_{25}O_3Re$ 464.1333). Anal. Calcd for $C_{17}H_{25}O_3Re$ (Found): C, 44.04 (43.96); H, 5.44 (5.49).

(*exo*-Bicyclo[2.2.1]hept-5-ene-2,3-diolato)(pentamethylcyclopentadienyl)(oxo) rhenium (6). Cp*ReO_3 (100 mg, 0.27 mmol) and norbornadiene (290 μL, 250 mg, 2.7 mmol) were dissolved in 5 mL of toluene. The solution was degassed on a vacuum line with three freeze–pump–thaw cycles and then heated to 110 °C under N_2 for 48 h. The reaction mixture was applied to a short column of silica gel (2 cm diameter × 6-cm long). Dichloromethane was used to elute hydrocarbons and Cp*ReO_3; acetone was then used to elute the purple diolate. Removal of solvent gave 60 mg (48%) of purple semisolid. NMR showed two isomers, but the material was analytically pure. Major product: ^1H NMR (C_6D_6): δ 1.723 (s, 15H), 1.80 (dtt, J = 9.4, 1.5, 1.5 Hz, 1H), 2.86 (dt, J = 9.4, 2 Hz, 1H), 3.02 (dddd, J = 2, 2, 1.5, 1.5 Hz, 2H), 4.44 (d, J = 1.5 Hz, 2H), 5.97 (dd, J = 2, 2 Hz, 2H). ^{13}C NMR (C_6D_6): 11.00, 43.20, 50.68, 95.69, 107.95, 139.11. Minor product: ^1H NMR (C_6D_6): δ 1.77 (s, 15H), 2.92 (ddd, J = 2.0, 2.0, 1.5 Hz, 2H), 3.66 (br d, J = 7.4 Hz, 1H), 4.91 (d, J = 2.0 Hz, 2H), 5.89 (dd, J = 2, 2 Hz, 2H). IR (CH_2Cl_2): 2924, 2855, 1466, 1451, 1030, 997, 989, 927, 890, 808, 652 cm^{-1}. MS (EI): *m/e* 462 (M^+, ^{187}Re), 460 (M^+, ^{185}Re), 396 (base peak), 394, 338, 336, 134, 119. HRMS: 462.1206 (Cacld for $C_{17}H_{23}O_3Re$ 462.1177). Anal. Calcd for $C_{17}H_{23}O_3Re$ (Found): C, 44.24 (44.16); H, 5.02 (5.10).

(*trans*-Cyclooctane-1,2-diolato)(pentamethylcyclopentadienyl)(oxo) rhenium (7). Cp*ReO_3 (50 mg, 0.14 mmol) was dissolved in 3 mL of $CHCl_3$; 0.4 mL of a 3:2 mixture of *trans*- and *cis*-cyclooctene (3.1 mmol) was added and the mixture heated to reflux for 2 h. Chromatography of the reaction mixture on silica gel (0.5 × 5 cm^2; $CHCl_3$ followed by acetone) gave 40 mg of purple oil (0.1 mmol, 75%). ^1H NMR (C_6D_6): δ 1.2–1.9 (m, 10H), 1.72 (s, 15H), 2.68 (m, 1H), 2.80 (m, 1H), 3.50 (dt, J = 4.0, 9.3 Hz, 1H), 4.18 (dt, J = 3.6, 9.3 Hz, 1H). ^{13}C NMR (C_6D_6): 107.5, 95.5, 94.5, 37.3, 36.1, 28.3, 28.2, 25.2, 24.9, 11.1. IR (CH_2Cl_2): 2924, 2855, 1466, 1457, 1030, 953, 934, 808, 673, 652 cm^{-1}. MS (EI): 480 (M^+, ^{187}Re), 478 (M^+, ^{185}Re), 371, 369, 367, 135, 134 (base peak). HRMS: 480.1676 (Cacld for $C_{18}H_{29}ReO_3$ 480.1647). Anal. Calcd for $C_{18}H_{29}ReO_3$ (Found): C, 45.08 (44.86); H, 6.09 (6.18).

Measurement of Kinetics. For cycloreversion of diolates, solutions of diolate were prepared under N_2 in C_6D_6 that were approximately 0.03 M. Samples were sealed in NMR tubes under vacuum. These were heated in a water/ethylene glycol bath thermostated to ±0.1 °C. Periodically, the sample tube was removed and cooled to 25 °C, and the NMR spectrum was recorded. A relaxation delay of 20–30 s was used to assure accurate integration. (T_1 relaxation times for the Cp* protons were measured to be approximately 4–7 s, using the inversion–recovery method.) Since neither intermediates nor byproducts were observed, it was assumed that the sum of diolate and trioxo signals was proportional to the initial concentration of diolate. Plotting ln([diolate]/[diolate] + [trioxo]) vs time gave linear plots with slope = $-k_{obs} = -k_e$.

For oxidation of strained alkenes, a solution of known concentration of Cp*ReO_3 (typically 0.02–0.03 M) in C_6D_6 was prepared. To this was added at least 5 equiv alkene; the sample was sealed under vacuum. The initial concentration of alkene was determined by NMR relative to Cp*ReO_3. Relaxation delays of up to 150 s were used to insure accurate integrations. Tubes were heated in a water/ethylene glycol bath thermostated to ±0.1 °C. Periodically, the tube was removed and the NMR spectrum measured. For oxidations which proceeded to completion, plotting ln([trioxo]/([trioxo] + [diolate])) versus time gave linear plots with slope = $-k_{obs}$, where now $k_{obs} = k_o$[alkene]. In the case of norbornene oxidation, the system was treated as a pseudo-first-order approach to equilibrium. Plotting $\ln\{([\text{trioxo}]_{init} - [\text{trioxo}]_{eq})/([\text{trioxo}]_{init} - [\text{trioxo}]_t)\}$ vs t gave slope = $-k_{obs}$, where $k_{obs} = k_o$[norbornene] + k_e.

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Supplementary Material Available: Eyring plots for alkene extrusion from **2**–**4** and for oxidation of norbornadiene and *trans*-cyclooctene (3 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.