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Reversible Oxidation of a Strained Alkene by Cp^*ReO_3

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Reactions of metal oxides with alkenes have wide application in organic chemistry.[1–4] The ability of a metal oxo complex to act as an oxidant is in part a function of the thermodynamics of the M=O bond. Little experimental evidence exists to describe the thermodynamics of this functional group.[5] Of particular interest is the magnitude of the π interaction; there is no estimate of this quantity for any metal oxo complex. Elucidation of the energetics of interaction of alkenes with metal oxides is crucial to the further understanding and utilization of these reactions, particularly in the design of new reagents. This paper reports the first such thermochemical analysis for the system alkene + Cp^*ReO_3 ($Cp^* = \eta^5\text{-}C_5(CH_3)_5$).[6]

Norbornene reacts with Cp^*ReO_3 (**I**) (C_6D_6, sealed tube) to form two new diolate complexes (eq 1) at temperatures between 90 and 125 °C. The major product is identified as the exo, anti isomer **IIa** on the basis of ^1H NMR evidence.[7] The upfield shift of H-2,3 (from 6.01 to 4.05 ppm) is consistent with formation of a carbinol from the C=C bond; the symmetry and approximate chemical environment of the rest of the bicyclo[2.2.1]heptane system is retained. The only coupling to H-2,3 observed is a 1.5-Hz W-type coupling to H-7a (0.95 ppm), confirmed by double resonance and 2-D COSY experiments. Assignment of this major isomer as having the Cp* ligand anti to the C-7 bridge is assumed on the basis of minimizing steric interactions.[8] Minor isomer **IIs** shows the same coupling behavior and so is assigned the exo, syn geometry.

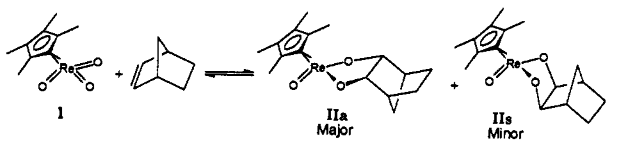

Table I. Equilibrium Constants for eq 1[a]

T, K	$[NB]_e$[b]	$[diolates]_e/[Cp^*ReO_3]_e$	K_{eq}, M^{-1}
362.9	0.174	5.61	32.2
370.4	0.109	3.57	32.7
370.4	0.241	10.2	41.3
382	0.199	2.85	14.3
387	0.175	2.70	15.4
391.7	0.188	2.61	13.8
395.5	0.113	1.46	12.9
395.5	0.0758	0.835	11.0
395.5	0.041	0.445	10.9
395.5	0.0175	0.190	10.9
399.6	0.347	3.69	10.6

[a] Initial concentration of rhenium complex ~0.018–0.03 mol L^{-1} in solvent C_6D_6. [b] Equilibrium concentration of norbornene, mol/L.

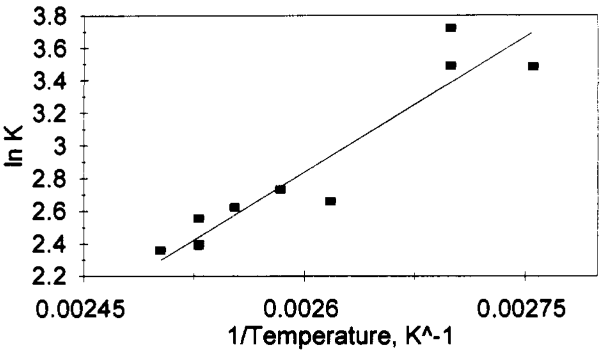

Figure 1. van't Hoff plot for eq 1 showing temperature dependence of K_{eq} between 90 and 125 °C. Slope ($= -\Delta H°/R$) = 5519, intercept = −11.5, $r^2 = 0.897$.

Even with a 10-fold or greater excess of norbornene, an equilibrium mixture of diolates and Cp^*ReO_3 results, and the mixture of diolates **IIa,s** may be isolated by chromatography on silica. The reverse reaction, fragmentation to form norbornene and Cp^*ReO_3, is observed when purified diolate is heated at 100 °C. Furthermore, measurement of the equilibrium constant at four different concentrations of norbornene leads to the same equilibrium constant (11.4 ± 1.5 at 122.4 °C). The temperature dependence of this equilibrium gives $\Delta H° = -10.9 \pm 0.9$ kcal/mol and $\Delta S° = -22.8 \pm 2.2$ eu (see Table I and Figure 1).

Norbornadiene reacts to completion to form **IIIa,s** at temperatures between 90 and 125 °C; at 110 °C, $K > 500\ M^{-1}$ and thus $\Delta G° < -4.5$ kcal/mol. Again two isomers are observed in approximately a 10:1 ratio, and NMR data suggest analogous structures for the major and minor isomers of **II**.[9] Clean fragmentation is not observed on heating the pure diolate, but slow decomposition to unidentified products is seen. Conversely, we confirm[6a,b] that no forward reaction is seen between Cp^*ReO_3 and excess ethylene (measured $[C_2H_4] = 2$ M); at 90 °C $K <$

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(7) Major isomer: ^1H NMR (C_6D_6) δ 0.95 (dtt, J = 10.4, 1.4, 1.4 Hz, 1 H, 1.02 (ddd, J = 13.5, 6.5, 2.1 Hz, 2 H), 1.28 (ddd, J = 13.5, 6.5, 3.2 Hz, 2 H), 1.735 (s, 15 H), 2.36 (dtt, J = 10.4, 1.5, 1.5 Hz, 1 H), 2.62 (dddd, J = 3.2, 2.1, 1.5, 1.5 Hz, 2 H), 4.05 (d, J = 1.5 Hz, 2 H); ^{13}C NMR (C_6D_6) δ 3.38, 10.93, 25.55, 44.71, 99.00, 107.66. Minor isomer: ^1H NMR (C_6D_6) δ 4.44 (d, J = 1.5 Hz, 2 H), 1.815 (s, 15 H), other peaks obscured by major isomer.

(8) Irradiation of the Cp* methyl groups in **IIa** showed no nuclear Overhauser enhancement of the norbornane protons for the major isomer; due to inability to resolve protons for the minor isomer, the analogous experiment was not performed. As pointed out by a referee, the lack of all four possible isomers in pure form means the assignment of structure is not proven beyond all doubt.

(9) Major product: ^1H NMR (C_6D_6) δ 1.723 (s, 15 H), 1.80 (dtt, J = 9.4, 1.5, 1.5 Hz, 1 H), 2.86 (dt, J = 9.4, 2 Hz, 1 H), 3.02 (dddd, J = 2, 2, 1.5, 1.5 Hz, 2 H), 4.44 (d, J = 1.5 Hz, 2 H), 5.97 (dd, J = 2, 2 Hz, 2 H); ^{13}C NMR (C_6D_6) δ 11.00, 43.20, 50.68, 95.69, 107.95, 139.11. Minor product: ^1H NMR (C_6D_6) δ 1.77 (s, 15 H), 2.92 (ddd, J = 2.0, 2.0, 1.5 Hz, 2 H), 3.66 (br d, J = 7.4 Hz, 1 H), 4.91 (d, J = 2.0 Hz, 2 H), 5.89 (dd, J = 2, 2 Hz, 2 H). Anal. Calcd for $C_{17}H_{23}O_3Re$ (Found): C, 44.24 (44.16); H, 5.02 (5.10).

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0.005 M^{-1} and $\Delta G° > 3.6$ kcal/mol. Ethylene extrusion from Cp*Re(O)(OCH$_2$CH$_2$O) (**IV**) is observed between 60 and 110 °C, as originally reported by Herrmann et al.[6a,b]

These results clearly show that this system is at a thermodynamic balance point. Unstrained alkenes are not oxidized by Cp*ReO$_3$,[10] but alkenes with even a small amount of strain are converted to diolates. The double bond strain energy in norbornene has been estimated as 5.7 kcal/mol.[11] Taking the "isolated bond" approach[12] and using strain energy, the expected electronic difference between ethylene and a disubstituted alkene,[13] and typical C—C, C=C, and C—O bond energies,[14] we estimate the Re-O π bond strength in Cp*ReO$_3$ (D(Re=O) − D(Re-O)) to be approximately 50 kcal/mol.[15] This estimate allows us to calculate that oxidation of ethylene should be thermoneutral or slightly exothermic, and therefore oxidation of unstrained alkenes with Cp*ReO$_3$ is disfavored only by entropy. The significance of this is that for a dioxo metal complex to be an effective bishydroxylation reagent, it must have a *weaker* M=O π interaction, as is expected for later metals (such as OsO$_4$) or those higher in the periodic table (such as MnO$_4^-$).

We are currently exploring how strain in these and other alkenes affects kinetic activation parameters in this system as a means of elucidating the energetics of the reaction pathway.

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Supplementary Material Available: Experimental procedures for preparation of **II** and **III**; derivation of ΔBDE for **II** and **I** (3 pages). Ordering information is given on any current masthead page.

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[10] Bicyclo[2.2.2]oct-2-ene forms only a small amount of diolate, while *trans*-cyclooctene reacts completely with Cp*ReO$_3$ at 90 °C. *cis*-Cyclooctene shows no reaction under these conditions. Gable, K. P., unpublished results.

[11] Double bond strain energy is defined as the difference in total strain energy between an alkene and its hydrogenated analog. Allinger, N. L.; Sprague, J. T. *J. Am. Chem. Soc.* **1972**, *94*, 5734–5747.

[12] Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*; 2rd ed.; Harper & Row: New York, 1981; pp 145–161.

[13] The isodesmic reaction $C_2H_4 + CH_3CH(OH)CH(OH)CH_3 \rightarrow HOCH_2CH_2OH +$ *cis*-$CH_3CH{=}CHCH_3$ has an estimated ΔH of +5.0 kcal/mol in the condensed phase. Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*; Chapman and Hall: New York, 1986. This should be the upper limit for ΔH_{rxn} in the absence of ring strain; we do not know the magnitude of steric effects but estimate that they are at most 1–2 kcal in favor of free norbornene. We thank a referee for bringing these effects to our attention.

[14] Gordon, A. J.; Ford, R. A. *The Chemist's Companion*; J. Wiley & Sons: New York, 1972; p 113.

[15] This includes the obviously incorrect approximation that the Re=O bond in **I** is the same as the Re=O bond in **II**, but such a discrepancy is likely to be minor compared to the overall bond strengths under discussion. Average M—O bond strength estimates for third-row metal oxides range from 127 kcal/mol for OsO$_4$ to 150 kcal/mol for MoO$_3$: see ref 5.