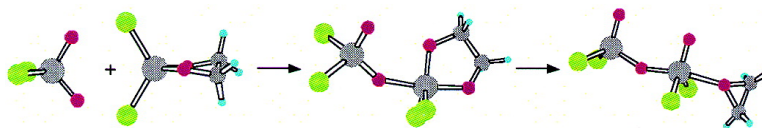


Mechanism of Chromyl Chloride Epoxidation

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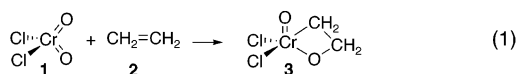
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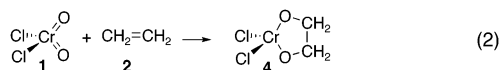
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Chromyl chloride, **1**, a classic oxidizing agent, reacts vigorously with alkenes, even at $-78\text{ }^{\circ}\text{C}$.¹ Hydrolysis of the amorphous product mixture yields epoxide and numerous side products including chlorohydrins and dichlorides. Cis diols, produced by the isoivalent osmium tetroxide and permanganate, are not observed.² The observation of chromyl chloride ethylene epoxidation is in seeming conflict with the fact that the reaction is endothermic by 26 kcal/mol in the gas phase.³ Further, the most stable species on the DFT potential surface⁶ can only logically produce diol upon hydrolysis. The experimental nonobservation of diol product, along with the preference for epoxidation rather than allylic oxidation, makes chromyl chloride reactivity unique and worth understanding.

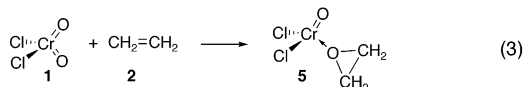
In 1977 Sharpless, Teranishi, and Bäckvall¹ proposed that alkene, **2**, epoxidation by chromyl chloride proceeds through a 2+2 pathway, forming an oxetane intermediate, **3**, which reductively eliminates the observed epoxide, eq 1.



This was proposed as an alternative to the classic Criegee 3+2 oxo pathway, eq 2, yielding the dioxylate, **4**, which is consistent with diol production, not epoxide formation.



A third possibility is the external attack of olefin to directly form a complexed epoxide, **5**, eq 3. Sharpless, Teranishi, and Bäckvall properly reasoned that this pathway should be disfavored as it represents a nucleophilic attack on the olefin by an electrophilic compound.



Energetic results for these intermediates using a range of electronic structure methodologies are collected in Table 1.⁷ Focusing on rows 1–6 of Table 1, it is clear that all density functional and hybrid methods do not give the same results. Formation of the dioxylate intermediate, **4**, ranges from being 27 kcal/mol exothermic (B3LYP) to being 5 kcal/mol endothermic (BLYP). All functionals, except LDA, find formation of the oxetane species, **3**, to be significantly endothermic. All functionals studied, except B3LYP, yield an epoxidation endothermicity roughly consistent with the upper experimental estimate.³ All functionals, except LDA, find the barrier for the 3+2 reaction between **1** and **2** to be greater than 15 kcal/mol.

Because there is no experimental data on the stability of any of the proposed intermediates, we have used the complete active space perturbation theory to second order (CASPT2) approach to obtain

Table 1. Chromyl Chloride Plus Ethylene Reaction Energetics, Relative to Chromyl Chloride and Ethylene^a

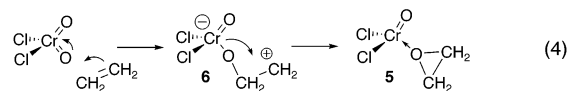
method	1+2 →4	1+2 →3	³ CrCl ₂ O +EO	1+2 →3 ⁵	1+2 →4 3+2 TS	1+2 →5 directTS	³ Cr ₂ Cl ₄ O ₃ +EO	7	7 →8TS
LDA ^{b,c}	-13	-3	36	3	2	21	-51	-	-4
BPW91 ^{d,e}	-1	18	32	12	18	34	-35	-22	18
BLYP ^{d,f}	5	23	37	15	20	35	-39	-21	17
PBE ^g	-4	14	32	9	15	30	-40	-30	11
HCTH147 ^h	-5	22	26	7	21	35	-37	-	21
B3LYP ⁱ	-27	18	9	-16	18	21	-43	-41	12
CASPT2	-17	24	26						
ZPE	4	3	1	3	2	2	2	4	1
-ΔS	11	11	3	9	12	10	9	21	20
ZPE + ΔH	3	3	1	3	2	2	2	5	2

^a kcal/mol ^b Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200. ^c Slater, J. C. *Phys. Rev.* **1951**, *81*, 385. ^d Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098–3100. ^e Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson K. A.; Pederson, M. R.; Fiolhais, C. *Phys. Rev. B* **1992**, *46*, 6671–6687. ^f Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785–789. ^g Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868. ^h Boese, A. D.; Doltsinis, N. L.; Handy, N. C.; Sprik, M. *J. Chem. Phys.* **2000**, *112*, 1670–1678. ⁱ Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652.

an independent reference point.¹² The results are provided in Table 1. CASPT2 predicts an epoxidation endothermicity consistent with the upper experimental estimate and predicts the oxetane species, **3**, to be endothermic, and the dioxylate, **4**, exothermic.

The only species below reactants on the potential surface is the experimentally unobserved **4**. Addition of zero-point effects and statistical thermodynamics does not change this conclusion for CASPT2, see Table 1. Comparison of columns 6 and 7 confirm the previous⁶ computational conclusion that the 3+2 pathway is energetically favored over direct approach of olefin; formation of the unobserved dioxylate, **4**, appears to be inevitable.

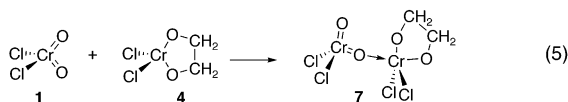
If epoxidation is significantly endothermic, how can chromyl chloride function as a vigorous epoxidizing agent? The answer to this question can be extracted from the structure of the direct addition saddlepoint, **6**. Rather than a conventional symmetric or near-symmetric approach of the olefin toward the oxygen, we find the saddlepoint to be quite asymmetric,¹³ consistent with the electronic rearrangement of eq 4.¹⁶



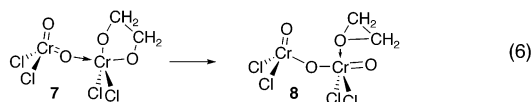
Although computed to be not competitive with the 3+2 pathway,¹⁸ this direct, carbocationic addition saddlepoint led us to suspect that the key to chromyl chloride epoxidation was a stabilization of **6**. However, neither CPCM continuum dichloromethane solvation¹⁹ nor explicit carbon tetrachloride coordination to the carbocationic center lowered the barrier significantly (less than 2 kcal/mol impact).

An alternative to carbocation stabilization is stabilization of the chromate portion of **6** by the delocalization of the negative charge

over a second equivalent of chromyl chloride. As presented in Table 1, column 8, reacting 2 equiv of chromyl chloride with ethylene to form $\text{Cr}_2\text{Cl}_4\text{O}_3$ plus epoxide is exothermic. Inclusion of the unfavorable three-body entropic term still yields an exoergic process. Further, merely docking a chromyl chloride adjacent to the dioxylate intermediate, **4**, leads spontaneously to a nearly trigonal bipyramidal dioxylate structure, **7**, that is energetically favored, column 9 of Table 1, see eq 5.



This adduct structure is connected to a dimeric epoxide adduct, **8**, through a low barrier, column 10 of Table 1, see eq 6.



We have also found a dimeric saddlepoint with the carbocationic center adjacent to a chloride, a pathway consistent with the formation of chlorohydrins. This zwitterionic model, **6**, is also consistent with the matrix observation²⁰ of aldehyde, which is likely formed through a carbocationic rearrangement. The model is also consistent with the observation of a Cr(V) ESR signal for the product of reacting chromyl chloride with aryl alkenes²¹ and the 2:1 metal-to-alkene product stoichiometry.

In summary, the epoxidation of alkenes by chromyl chloride, whether through a 3+2 pathway, a direct addition pathway, or possibly even through a 2+2 pathway, is thermodynamically driven by the formation of a dimeric Cr(V) product.

Acknowledgment. Helpful discussions with K. B. Sharpless, B. R. Bender, and C. J. Casewit are gratefully acknowledged.

Supporting Information Available: Total energies for each electronic structure model of each complex and the Cartesian coordinates of each structure (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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