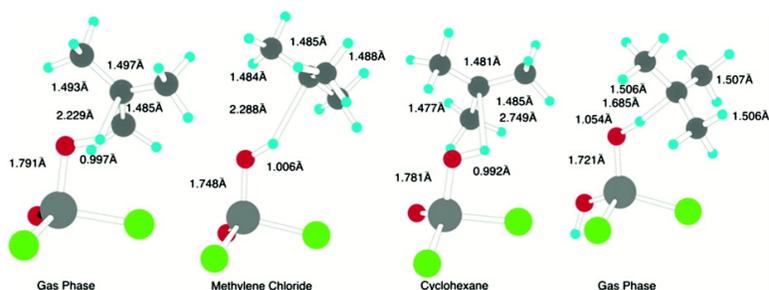


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Mechanism of Chromyl Chloride Alkane Oxidation

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In 1877, Étard reported the reaction of aryl alkanes with chromyl chloride to form a 1:2 complex in inert solvents.¹ This 1:2 Étard complex precipitates from solution, forming a brown amorphous material. Upon hydrolysis, aryl aldehyde is formed in ~90% yield. Saturated C–H bonds are also oxidized by CrCl₂O₂ via Étard complexes. C–H activation in solution seems to be in conflict with the fact that the reaction is endothermic in the gas phase² by 16 kcal/mol for the reaction of CrCl₂O₂ with toluene and by 11 kcal/mol for the reaction with propane.

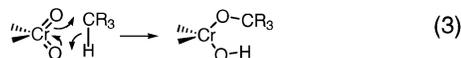
In his classic review,⁵ Wiberg suggested C–H bond activation occurred through carbocation formation, eq 1,



organic radical formation, eq 2,



or via a concerted addition, eq 3.



Wiberg favored the radical pathway given in eq 2 based on the observed kinetic isotope effect and relative reactivity of primary, secondary, and tertiary bonds. In a series of papers dating from the mid 1990s, Mayer, Cook, and Wang^{6,7} provided convincing experimental support for the radical pathway. Unfortunately, the experimentally observed activation energies are roughly 12 kcal/mol lower than theoretical estimates⁸ of radical pathway thermochemistry. For example, the observed activation energies⁶ for isobutane, cyclohexane, toluene, and cyclooctane are 21, 27, 16, and 19 kcal/mol, respectively, whereas the LANL2/BPW91⁹-computed reaction energies are 33, 37, 28, and 32 kcal/mol.

To determine if the ~12 kcal/mol discrepancy is due to the methodology used, we have computed the thermochemistry for isobutane hydrogen abstraction¹⁰ with two different basis sets, a range of density functionals, as well as the CASPT2¹⁵ wave function method. The results are summarized in Table 1. For this reaction, density functional methods are insensitive to the basis set, as well as to whether the wave function is spin restricted. Four of the functionals cluster at ~32 kcal/mol, while LDA (39 kcal/mol) and B3LYP (19 kcal/mol) differ significantly. The CASPT2 wave function approach yields 28 kcal/mol, 5 kcal/mol smaller than DFT. There is still a 7 kcal/mol discrepancy between the theoretical and experimental activation energetics.

Given the current interest in the catalytic activation of saturated hydrocarbons such as propane or methane, we have sought to unravel the discrepancies between observation and theory using

Table 1. Chromyl Chloride Plus Isobutane Reaction Energetics (kcal/mol)

method	vdz	sRvtz	sUvtz
LDA ^{a,b}	43	40	39
BPW91 ^{c,d}	36	34	32
BLYP ^{c,e}	35	33	32
PBE ^f	36	35	33
HCTH147 ^g	36	35	32
B3LYP ^h	23	21	19
CASPT2	27	28	
ZPE	-4		
-TΔS	3		
ZPE + ΔH	4		

^a Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200.
^b Slater, J. C. *Phys. Rev.* **1951**, *81*, 385. ^c Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098–3100. ^d Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Fiolhais, C. *Phys. Rev. B* **1992**, *46*, 6671–6687. ^e Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785–789. ^f Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868. ^g Boese, A. D.; Doltsinis, N. L.; Handy, N. C.; Sprick, M. *J. Chem. Phys.* **2000**, *112*, 1670–1678. ^h Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–52.

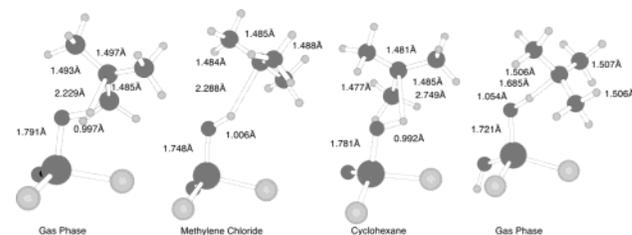


Figure 1. Molecular structures of the saddle point for the reaction between chromyl complexes and isobutane, in the gas phase and in solution, respectively.

LANL2/BPW91.⁹ For isobutane, this smaller basis approach obtains an abstraction energy of 33 kcal/mol, only 1 kcal/mol larger than the large basis all-electron methodology. An isobutane activation barrier of 29 kcal/mol is computed.

The C–C bond distances of the isobutane transition state, provided in Figure 1, are shorter than those of (CH₃)₃C[•] (1.500 Å) and slightly longer than those in (CH₃)₃C⁺ (1.472 Å). This suggests significant carbocation character in the organic fragment of the transition state. This means the saddlepoint has substantial zwitterionic character, rather than the previously invoked^{5,6} diradical character. We have previously suggested zwitterionic character in the alkene epoxidation saddlepoint.¹⁶ Zwitterionic character should be, and is, enhanced when the isobutane transition state is placed in an Onsager¹⁷ CH₂Cl₂ continuum solvent.¹⁸ There is a significant transition state structural reorganization, see Figure 1, and the barrier drops from 29 to 17 kcal/mol. Further, the transition state dipole moment increases from 9 to 20 D. Use of the smaller dielectric solvent, cyclohexane, results in a barrier drop of only 3 kcal/mol to 26 kcal/mol and a smaller dipole moment increase to 12 D. A mixed cyclohexane–CrCl₂O₂ solvent should have an intermediate dielectric constant.

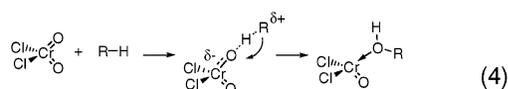
[†] Colorado State University.

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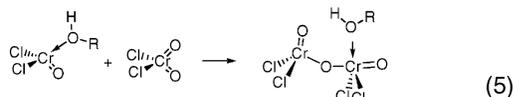
Zwitterionic character should also be enhanced by the addition of a second equivalent of CrCl_2O_2 .¹⁶ Formation of an alcohol adduct of $\text{Cr}_2\text{Cl}_4\text{O}_3$ with two Cr(V) sites is computed to be 25 kcal/mol exothermic.¹⁹ Following these observations, we examined the viability of a dimeric structure for CrCl_2O_2 . Other than a weak basis set superposition-induced complex with a binding energy of 0.6 kcal/mol, the only dimeric structure we find is computed to be 23 kcal/mol above two CrCl_2O_2 molecules.

We have investigated the reaction chemistry of the dimeric Cr(V) complex by modeling the simpler mononuclear complex, $\text{CrCl}_2(\text{O})\text{OH}$. $\text{CrCl}_2(\text{O})\text{OH}$ is computed to activate isobutane via the oxo ligand with a gas-phase barrier of 22 kcal/mol, 7 kcal/mol smaller than with CrCl_2O_2 .⁹ Reaction via $\text{CrCl}_2(\text{O})\text{OH}$ is computed to not be significantly solvent stabilized; the saddlepoint is lowered by less than 1 kcal/mol in dichloromethane. As shown in Figure 1, this transition state structure is consistent with radical abstraction; the C–C bond distances of 1.505–1.507 Å are longer those in $(\text{CH}_3)_3\text{C}^\bullet$.

Taken together, these observations suggest the following reaction scheme for alkane activation. The reaction sequence begins with an initial, rate-limiting, bimolecular reaction between CrCl_2O_2 and alkane, proceeding through a zwitterionic transition state, eq 4.



The high energy alcohol intermediate is subsequently trapped by CrCl_2O_2 , eq 5, forming a dinuclear complex with two Cr(V) sites.



One of the two Cr(V) sites reacts, in a kinetically invisible step, with an additional equivalent of alkane to generate two Cr(IV) sites.

This model is consistent with the observed first-order alkane and chromyl chloride kinetics, as well as with the radical clock results described by Wang and Mayer.⁷

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; 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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- (10) Geometry optimizations were carried out using LANL2 (ref 9) in g98 (ref 11) using 6-31g*/B3LYP or 6-31g*/BPW91. For reactants and intermediates, the choice of functional had little impact on the geometry, and the energetic consequence of a fixed geometry was ~ 1 kcal/mol. Energetics were obtained in MOLPRO 2002.3 (ref 12) using Ahlrichs vdz and vtz basis sets (ref 13) on Cr, augmented with an f function with an f exponent of 0.7; cc-pVTZ basis sets (ref 14) were used for the remaining elements. The CAS spaces in (electron,orbital) format were (12,12) for CrCl_2O_2 , (11,11) for $\text{CrCl}_2\text{O}_2\text{H}$, and (2,2) for C_6H_{10} . For each CASPT2 calculation, an eigenvalue shift of 0.3 was used. The functionals used ranged from the most popular, B3LYP, through a set of classic functionals (BPW91, BLYP, and LDA) and a functional popular in the solid-state physics community PBE, to a more modern functional, HCTH147.
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