Experimental and Computational Study of the [2 + 2] Dissociation of Rhenaoxetanes in the Gas Phase

Xiangyang Zhang,* Sanja Narancic, and Peter Chen*

Laboratorium für Organische Chemie, Eidgenössiche Technische Hochschule (ETH), Zürich, Switzerland

Received April 13, 2005

Summary: Energy-resolved collision-induced dissociation cross-section measurements are applied to the reaction by which a rhenium diolate complex loses an aldehyde to produce a rhenium carbene. The measured threshold as well as ab initio calculations indicate that the diolate has rearranged to a metallaoxetane, from which the [2 + 2] dissociation occurs. The measured activation energy is in good agreement with the computed values.

We report an experimental determination of the activation energy for the [2 + 2] dissociation of a rhenaoxetane to a carbene complex and an aldehyde by measurement of energy-resolved collision-induced dissociation (CID) cross-sections. The longstanding controversy concerning [3 + 2][1] versus [2 + 2][2] mechanisms in high-valent oxo complexes related to metal-mediated oxidation chemistry has spawned a large literature of experimental[3] and computational[4] studies from which a recent consensus concluded that [2 + 2] mechanisms were unlikely to play an important role under the specific reaction conditions. Nevertheless, the original logic derived from CrO_2Cl_2-mediated oxidations, further supported by hints from metathesis chemistry, led us to seek conditions under which [2 + 2] mechanisms may be favored. We have recently reported experimental[5] and computational[6] evidence for just such a significant [2 + 2] pathway in the dissociation of Re(V) diolate complexes isoelectronic with the Os(VI) diolates produced in the asymmetric dihydroxylation reaction.[7] The observed products indicate a rearrangement to the metallaoxetane followed by cleavage of an aldehyde, producing a metathesis-competent carbene complex. We furthermore presented a qualitative theoretical argument in which the specific structural requirements for a favorable [2 + 2] mechanism were detailed. The reported work, however, was based on the observation of reaction products, identified by their *m/z* ratio under standardized conditions. Quantitative predictions from DFT and ab initio calculations could be confirmed only qualitatively. The present work ameliorates this deficiency by presenting quantitative measurements that may be directly compared to calculations and, furthermore, identifies the dissociating species unambiguously as the rhenaoxetane produced by rearrangement of the rhenium diolate precursor. In the larger context, this work represents a step toward relieving the deplorable paucity of reliable bond energies and activation barriers for “interesting” medium-to-large organometallic species.[8]

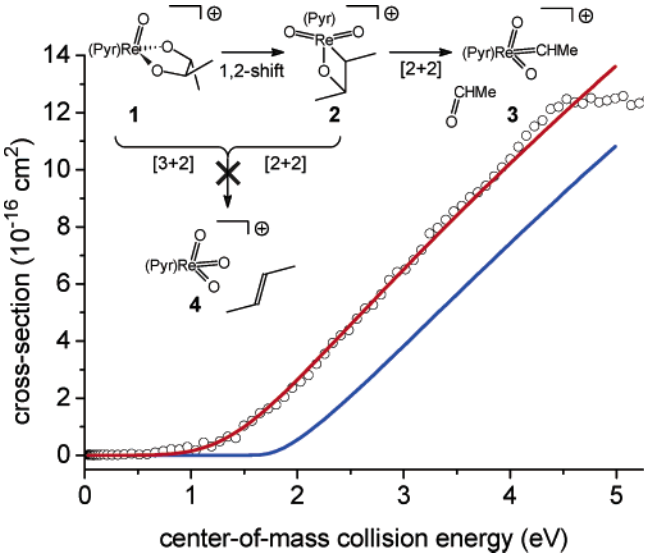

Figure 1. Relative energy-resolved reaction cross-section, $\sigma(E)/\sigma_0$, for the dissociation of *m/z* 370 to *m/z* 326 upon collision with xenon. The red line shows the fit to the experimental points for energies between 0 and 4.5 eV, which yields $E_0 = 1.05 \pm 0.1$ eV and $n = 1.75$. The blue line shows the unconvoluted cross-section at 0 K.

Electrospray ionization tandem mass spectrometric (ESI-MS/MS) studies on the reactions of the (pyridine)((2*R*,3*R*)-(−)-butanediolato)ReO cation (**1**) were carried out as previously described.[9] Complex **1**, with *m/z* 370, was prepared in the rf 24-pole region of the modified Finnigan MAT TSQ-700 mass spectrometer, mass-selected in the first quadrupole, and subjected to CID with xenon in the octopole.[10] The intensity of the sole CID product, **3** at *m/z* 326, was monitored through the

---

* To whom correspondence should be addressed. E-mail: chen@org.chem.ethz.ch (P.C.).

[1] Böseken, J. *Recl. Trav. Chim. Pays-Bas* **1922**, *41*, 199. Criegee, R. *Liebigs Ann. Chem.* **1936**, *522*, 75. Criegee, R. *Angew. Chem.* **1937**, *50*, 153. Criegee, R. *Angew. Chem.* **1938**, *51*, 519. Criegee, R.; Marchand, B.; Wannowias, H. *Liebigs Ann. Chem.* **1942**, *550*, 99.

[2] Sharpless, K. B.; Teranishi, A. Y.; Bäckvall, J. E. *J. Am. Chem. Soc.* **1977**, *99*, 3120.

[3] DelMonte, A. J.; Haller, J.; Houk, K. N.; Sharpless, K. B.; Singleton, D. A.; Thomas, A. A. *J. Am. Chem. Soc.* **1997**, *119*, 9907 and references therein.

[4] For a review of the extensive computational literature, see: Deubel, D. V.; Frenking, G. *Acc. Chem. Res.* **2003**, *36*, 645.

[5] Chen, X.; Zhang, X.; Chen, P. *Angew. Chem., Int. Ed.* **2003**, *42*, 3798. Zhang, X.; Chen, X.; Chen, P. *Organometallics* **2004**, *23*, 3437.

[6] Narancic, S.; Chen, P. *Organometallics* **2005**, *24*, 10.

[7] Sharpless, K. B. *Angew. Chem., Int. Ed.* **2002**, *41*, 2024.

[8] A comprehensive review can be found in: Marks, T. J. In *Bonding Energetics in Organometallic Compounds*; ACS Symposium Series 428; American Chemical Society: Washington DC, 1990; pp 1–17.

[9] The diolate complex from the reaction of anhydrous (2*R*,3*R*)-(−)-butanediol (*trans*-diol) and $[(Pyr)_4ReO_2]^+[BPh_4]^-$ in CH_2Cl_2 was electrosprayed as described in ref 5. The ESI-MS/MS spectra can be seen in the Supporting Information.

10.1021/om0502842 CCC: $30.25 © 2005 American Chemical Society
Publication on Web 05/17/2005

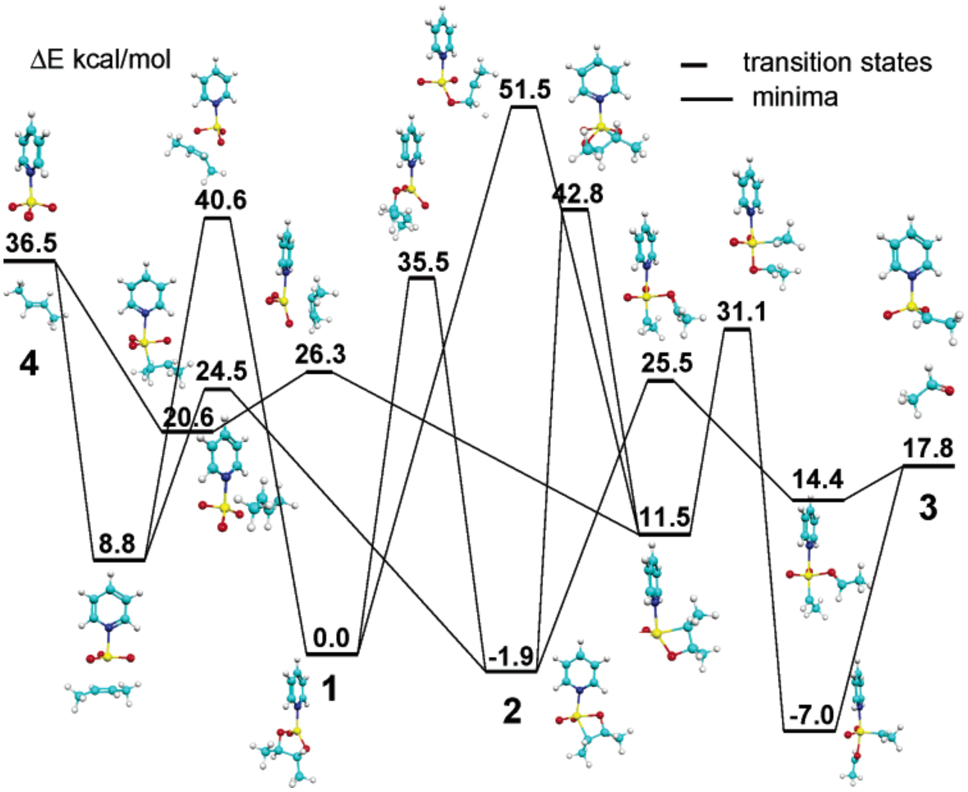

Figure 2. Energies, relative to **1**, at the CCSD/TZP//BP86/TZP level for **1**–**4** and other relevant isomers and transition states.

second quadrupole and is shown in Figure 1. Of the several diolate complexes previously characterized, **1** was chosen to avoid technical difficulties arising from multiple product channels which occur for many of the other analogues. The energy-resolved CID cross-sections were recorded with the first quadrupole in rfd mode to obtain a narrower kinetic energy distribution for the selected ion (see the Supporting Information). The energy-resolved cross-sections were deconvoluted using the program CRUNCH (version D1), developed by Armentrout and co-workers,[11] with the internal energy of the ions set to the 70 °C manifold temperature to which the ions were thermalized in the rf 24-pole region[12] (3–10 mTorr Ar). CRUNCH models the cross-section according to the equation

$$\sigma(E) = \left(\frac{n\sigma_0}{E}\right)\sum_i g_i \int_{E_0 - E_i}^{E} [1 - \exp(-k(\epsilon + E_i)\tau)](E - \epsilon)^{n-1}\, d\epsilon$$

where $\sigma(E)$ is the cross-section as a function of the center-of-mass collision energy E, σ_0 is a scaling factor, E_0 is the threshold energy for reaction, E_i is the internal energy of a given vibrational state with a relative population g_i, n is an adjustable parameter, k is (the computed) energy-dependent RRKM rate, and τ is the residence time in the collision cell. The RRKM calculation in the deconvolution requires the frequencies for the reactant ion as well as those for the transition state. The optimized structures and frequencies were computed at the BP86/TZP level of theory using the ADF 2000.02 (Amsterdam Density Functional) package[13] or Gaussian 2003[14] on Quant-X Alpha (Compaq Unix Tru64 5.3), HP Superdome with 64 PA8600 processors (HP/UX), and AMD Athlon (Red Hat Linux 7.1) machines.

Final single-point energies at each critical point, recomputed using the ab initio CCSD/TZP method, are shown in Figure 2. Details of the calculations can be found in the Supporting Information. Correction of ΔE to ΔG was not done in this case; our prior work[6] showed, unsurprisingly, that only the relative energies of the asymptotic dissociation products are significantly affected by explicit inclusion of entropy. The shift should moreover be dominated by translational entropy and therefore remain largely insensitive to structural differences between isomers. For the RRKM part of the CRUNCH fit, torsional vibrations, e.g. rotation of the pyridine ligand, were replaced by adiabatic free rotors with the corresponding moments of inertia. The remaining frequencies were treated as harmonic but were scaled by 0.9.

The CRUNCH fit to the experimental data points, using the DFT computed frequencies for the starting ions and transition state, produces $E_0 = 1.05 \pm 0.1$ eV and $n = 1.75$. The experimental threshold energy, $E_0 =$

---

[10] The measurement was done at 240, 180, 118, and 58 μTorr of xenon and then extrapolated to zero pressure.

[11] Armentrout, P. B. *Thermochemical Measurements by Guided Ion Beam Mass Spectrometry*; JAI Press: Greenwich, CT, 1992; Vol. 1. Rodgers, M. T.; Armentrout, P. B. *J. Phys. Chem. A* **1997**, *101*, 1238 and references therein.

[12] Gerlich, D. In *State-Selected and State-to-State Ion–Molecule Reaction Dynamics*; Ng, C. Y., Baer, M., Eds.; Wiley: New York, 1992; Part 1, pp 1–176.

[13] te Velde, G.; Bickelhaupt, F. M.; Baerends, E. J.; Guerra, C. F.; van Gisbergen, S. J. A.; Snijders, J. G.; Ziegler, T. *J. Comput. Chem.* **2001**, *22*, 931.

[14] Pople, J. A., et al. *Gaussian 03*, Revision C.02; Gaussian, Inc., Pittsburgh, PA, 2003.

24.2 ± 2.3 kcal/mol, can be directly compared to the CCSD/TZP//BP86/TZP energies. There is a good match of the measured threshold, E_0, to the activation energy for [2 + 2] cleavage of **2** to **3** and acetaldehyde (via the intermediate σ complex) for which $E_a = 25.5 + 1.9 = 27.4$ kcal/mol. In comparison to the unsubstituted case, we see that alkyl substitution selectively lowers the computed transition states for [2 + 2] cleavage relative to all other transition states, consistent with our previous experimental observations.[5] While there are very few benchmarks for the accuracy of ab initio energies for medium-to-large organometallic complexes, and even fewer for complexes with 5d-block metals,[15] it is unlikely that the experimental threshold could correspond to any other process, given that the experiment specifically monitored the conversion of *m*/*z* 370 into *m*/*z* 326. The species monitored at *m*/*z* 370 must necessarily be **2** and not **1**, because the rate-limiting transition state for the process **1** → **3** is the transition state for the 1,2 shift, **1** → **2**, which is computed to show an activation energy of 35.5 kcal/mol. Indirectly, this confirms the computed result that **2** lies lower in energy than does **1**. If one considers that it was the diolate complex that was electrosprayed from solution and that one of the two original pyridine ligands was removed by collisions in the source and rf 24-pole ion guide prior to mass selection of the ion at *m*/*z* 370, one can imagine that there was more than ample opportunity for the ion at *m*/*z* 370 to isomerize to the lower energy structure. An isomerization to the more stable isomer prior to selection (and removal of any **3** produced already in the rf 24-pole region by the first quadrupole), followed by the [2 + 2] dissociation of **2** to produce **3,** is the only consistent interpretation of the energy dependence of the experimental reaction cross-sections.

We report a quantitative study of the first unambiguous [2 + 2] reaction involving high-valent metal oxo complexes in the 5d block. The measurement of the energy-resolved reaction cross-section produces an activation energy in good agreement with the computed value at the CCSD level of theory, lending credibility to theoretical modeling of the other less accessible parts of the potential surface.

Acknowledgment. Assistance in the setup and operation of the instrument by Rolf Dietiker is acknowledged. This project has been supported financially by the ETH Zürich, the Swiss National Science Foundation, and the Robert Gnehm Foundation.

Supporting Information Available: Text, tables, and figures giving the details of the computation, as well as the experimental measurements, fits, and the complete ref 14. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0502842

---

(15) For example, relativistic effects on thermochemical predictions are large and are only approximately treated by effective core potentials. Pyykkö, P. *Chem. Rev.* **1988**, *88*, 563. Suzumura, T.; Nakajima, T.; Hirao, K. *Int. J. Quantum Chem.* **1999**, *75*, 757. Liu, W.; Franke, R. *J. Comput. Chem.* **2002**, *23*, 564. Koseki, S.; Ishihara, Y.; Fedorov, D.; Umeda, H.; Schmidt, M. W.; Gordon, M. S. *J. Phys. Chem. A* **2004**, *108*, 4707.