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Dissociation Energy of the HOOO Radical

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The dissociation of the hydrotrioxy (HOOO) radical to OH and O_2 has been studied theoretically using coupled-cluster methods. The calculated dissociation energy for the *trans*-HOOO isomer is 2.5 kcal mol^{-1} including zero-point corrections. The minimum energy path to dissociation has been explored and an exit barrier has been revealed, which may help to rationalize the apparent disagreement between theory and experiment on the magnitude of the bond energy.

Introduction

The hydrotrioxy (HOOO) radical has been proposed as an intermediate in several atmospheric, condensed phase, and surface processes.[1−5] Early theoretical predictions of the thermodynamic stability of the radical relative to OH + O_2 varied widely,[6,7] but in 1999 the HOOO species was observed experimentally through mass spectrometry and the neutralization-reionization of protonated ozone.[8] Recent calculations of the central OO bond energy in the *trans*-HOOO isomer have begun to cluster around 1 to 3 kcal mol^{-1},[9−14] significantly below the experimentally determined upper bound of 5.31 kcal mol^{-1}.[15] Though the infrared action experiment of ref 15 determines an upper limit to the dissociation energy, the difference between that upper limit and the true bond energy is expected to be small.[16] Much has been made of the discrepancies between theory and experiment for the HOOO radical,[12,13] not only for the bond energy, but also for the central OO bond distance. We have addressed the latter issue elsewhere;[17] in this work, we focus on the dissociation to OH + O_2.

The HEAT family of thermochemical protocols,[18−20] which are based on high-level ab initio calculations without empirical corrections, have been shown to provide heats of formation and dissociation energies to better than 0.25 kcal mol^{-1} (1 kJ mol^{-1}) accuracy in most cases.[18−21] In this work, such an approach has been employed to determine the dissociation energy of the *trans*-HOOO radical. To extend our understanding of the central OO bond, equation-of-motion coupled-cluster methods have been used to investigate the minimum energy path for the dissociation to OH + O_2. Standard single-reference coupled-cluster methods are not well-suited for the study of bond-breaking processes,[22] but the nature of equation-of-motion methods[23] is such that they can be applied with confidence to certain bond-breaking situations,[24] for example, the one discussed in this work.

Methods

A procedure similar to the HEAT protocol[18] was used to calculate the dissociation energy of the *trans*-HOOO radical, but as there are a few differences, our approach will be summarized here. The geometries[25] were optimized at the coupled cluster singles and doubles level with a perturbative treatment of triple excitations, CCSD(T),[26] employing an unrestricted Hartree-Fock, UHF, reference wave function. The cc-pVQZ[27] basis set from Dunning was used and all electrons were correlated. The largest contributions to the electronic energy are the UHF self-consistent field, UHF-SCF, energy and the CCSD(T) correlation energy, each extrapolated from calculations carried out with a series of core-polarized correlation-consistent basis sets which include diffuse functions, aug-cc-pCVXZ [X = T,Q,5].[27,28,63] A three-parameter exponential extrapolation[29] was used to approximate the UHF-SCF energy at the basis set limit, E_{HF}^{∞}. A two-parameter extrapolation[30] of the aug-cc-pCVXZ [X = Q,5] energies was used to determine the CCSD(T) correlation energy, $\Delta E_{CCSD(T)}^{\infty}$. To correct for deficiencies in the perturbative treatment of triple excitations, the difference in the extrapolated correlation energy at the coupled cluster singles, doubles, and triples level, CCSDT,[31−33] and the extrapolated CCSD(T) correlation energy was included, ΔE_{CCSDT}. The above two-parameter model was used in the extrapolations required for the CCSDT correction, but due to the cost of the full triples calculations, the smaller cc-pVXZ [X = T,Q][27] basis sets were used. The final correlation contribution included here was the difference in the coupled cluster singles, doubles, and triples energy with a perturbative treatment of quadruple excitations, CCSDT(Q),[34,35] and the CCSDT energy, both calculated with the cc-pVTZ basis set,[36] $\Delta E_{CCSDT(Q)}$. Core correlation effects were not included in the CCSDT or CCSDT(Q) corrections. The relativistic, diagonal Born-Oppenheimer, and spin-orbit corrections, ΔE_{rel}, ΔE_{DBOC}, and ΔE_{SO}, respectively, were included as discussed in ref 18. For the zero-point energy correction, ΔE_{ZPE}, the geometry optimizations[37] and anharmonic force field calculations were carried out at the CCSD(T) level with a triple-ζ contraction of the atomic natural orbitals basis set of Almlöf and Taylor,[38]

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TABLE 1: Contributions to D_0 for Dissociation of HOOO to OH + O_2 (both *trans* and *cis* isomers), and Dissociation of FOO to F + O_2, in kcal mol^{-1} [47]

	trans[a]	cis[b]	FOO[c]
E_{HF}^{∞}	−50.75	−48.13	−62.05
$\Delta E_{CCSD(T)}^{\infty}$	54.39	51.94	73.54
ΔE_{CCSDT}	0.34	0.27	0.37
$\Delta E_{CCSDT(Q)}$	1.39	1.14	2.13
ΔE_{rel}	−0.01	−0.01	0.00
ΔE_{DBOC}	0.03	0.04	−0.03
ΔE_{SO}[d]	−0.19	−0.19	−0.37
ΔE_{ZPE}	−2.74	−3.00	−1.30
D_0	2.47	2.06	12.28
D_0^{exp}	$\leq$5.31		11.90

[a] D_0^{exp} from ref 15. [b] No D_0^{exp} available. [c] D_0^{exp} from ref 48; error bar ±0.24 kcal mol^{-1}. [d] Values for O_2, OH, and F from ref 18.

ANO1 (4s3p2d1f/4s2p1d), and core electrons were excluded from the correlation treatment, (fc). A restricted open-shell Hartree-Fock, ROHF, reference wave function was used to avoid issues of spin contamination.[39]

The dissociation curve of *trans*-HOOO was investigated by calculating the minimum energy for fixed values of the central OO bond. The remaining internal coordinates were optimized utilizing gradients determined through finite difference of energies. A method originally presented by Stanton and Gauss[40,41] with some adjustments later made by Saeh and Stanton[42] was used to calculate the energies. In this approach, termed EOMIP-CCSD*, a noniteritive correction allows for the inclusion of some terms neglected in the traditional singles and doubles approximation of the equation-of-motion coupled-cluster method for ionized states, EOMIP-CCSD.[43] For the HOOO radical, the reference wave function used was that of the triplet HOOO anion, as it will properly dissociate to O_2 and the closed-shell species OH^-. By ejecting the appropriate electron a balanced treatment of the HOOO radical dissociating to the OH radical + O_2 may be obtained. Equation-of-motion methods for open-shell reference states are limited. The underutilized EOMIP-CCSD* approach was taken as it includes more dynamical correlation than the standard EOMIP-CCSD method. In addition to the constrained optimizations carried out to produce the dissociation curve, *trans*-HOOO and the dissociation products OH and O_2 were fully optimized.[44] In all EOMIP-CCSD* calculations reported here, the core electrons were not correlated, (fc). All calculations have been performed using the quantum chemical program package CFOUR (Coupled-Cluster techniques for Computational Chemistry);[45] those at the CCSDT(Q) level of theory were carried out with the string-based many-body suite MRCC[46] interfaced to CFOUR.

Discussion

The calculated dissociation energy, D_0, of the *trans*-HOOO radical is presented in Table 1, along with the corresponding values for *cis*-HOOO and the FOO radical for comparison. This theoretical value of 2.5 kcal mol^{-1} for the central OO bond energy of *trans*-HOOO is approximately 2.8 kcal mol^{-1} below the value inferred from the infrared action experiment (D_0^{exp} = 5.31 kcal mol^{-1}).[15] Such disagreement is unexpected considering the experimental approach and the theoretical methods used,[49] but there are a few aspects that should be addressed when dealing with this difficult system. The first issue is the presumed multireference character of and the proposed inability of single-reference methods to properly treat the HOOO radical. The second related issue is the large contribution of the quadruple excitations to the calculated bond energy of *trans*-HOOO ($\Delta E_{CCSDT(Q)}$ = 1.39 kcal mol^{-1}).[50] To address these potential problems, our thermochemical model was also applied to the isoelectronic radical FOO, which would presumably present similar difficulties concerning the electronic structure. The contribution of perturbative triples to the total atomization energy, %TAE[(T)], and the largest T_2 amplitude have proven useful as diagnostics of the multireference character of, or the effect of nondynamical correlation on, a species.[51] The high %TAE[(T)] values for *trans*-HOOO and FOO, 8 and 16% respectively, as well as the largest T_2 amplitudes, 0.06 and 0.16, suggest that these systems must be treated with care and highly correlated methods. While FOO appears to be the more troublesome of the two radicals with a %TAE[(T)] twice that of *trans*-HOOO, as well as the larger T_2 amplitude, the calculated energy for dissociation to F + O_2 is in quite good agreement with the experimental value (see Table 1 and ref 48). This would seem to indicate that our treatment of correlation is sufficient for these systems. In a study of hydrogen polyoxides, Denis and Ornellas[14] dealt with the issue of higher-order correlation in *trans*-HOOO through the use of an isodesmic reaction, which tends to cancel such effects.[21] On the basis of their calculated heat of formation for *trans*-HOOO ($\Delta_f H°_{298K}$ = 5.46 kcal mol^{-1}), the radical is approximately 3 kcal mol^{-1} less stable than indicated by the value derived from experimental data ($\Delta_f H°_{298K} \geq$ 2.51 kcal mol^{-1}),[52] a disagreement between theory and experiment that is comparable to that seen here.

Another issue encountered in the HOOO system is one not seen in the triatomic FOO system. It has been noted in ref 17 that due to a very low frequency torsional mode second-order vibrational perturbation theory, VPT2,[53] may not be appropriate for the prediction of fundamental frequencies for the HOOO radical. Work to apply an alternate treatment of the vibrational problem to this system is underway and will be the subject of a forthcoming paper. As VPT2 was used in the current calculation of the zero-point energies, the ΔE_{ZPE} contribution is a possible source of error in the determination of the dissociation energy, but it is not expected to be large enough to explain the difference between theory and experiment. Using zero-point energies based on the harmonic formula and fundamental frequencies for *trans*-HOOO[54,55] and the dissociation products, the correction to the dissociation energy is −2.33 kcal mol^{-1}. The difference between this and our VPT2 determination of the same correction, ΔE_{ZPE} = −2.74 kcal mol^{-1}, allows us to estimate the error in our calculated D_0 introduced by the use of VPT2 zero-point energies, less than 0.5 kcal mol^{-1}. The effects due to this error in the zero-point vibrational energy as well as residual correlation (discussed above) may not be negligible, but they cannot account for the nearly 3 kcal mol^{-1} discrepancy currently seen when comparing theoretically and experimentally determined values for D_0 of the *trans*-HOOO radical.

In constructing a minimum energy path for the dissociation of *trans*-HOOO to OH + O_2, a barrier was observed as shown in Figure 1. This is not the first time that a barrier has been found in theoretical studies of HOOO dissociation.[6,11,57,58] The magnitude of the exit barrier bears on the disagreement between the theoretical and experimentally inferred bond energies (see below), but the quality of this number is not as robust as the dissociation energy calculation summarized in Table 1. The treatment of dynamical correlation in the EOMIP-CCSD* calculations is not as good as that in the CCSD(T), CCSDT, and CCSDT(Q) calculations used for HOOO and the separated products, as seen in the fact that the electronic bond energy

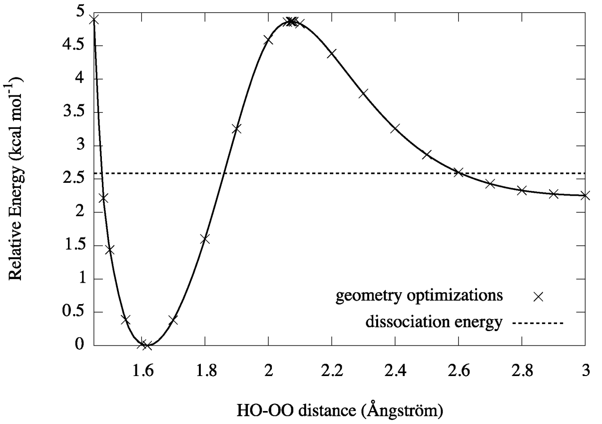

Figure 1. The EOMIP-CCSD*/cc-pVQZ (fc) minimum energy path for dissociation of *trans*-HOOO to OH + O_2.[56]

(D_e = 2.6 kcal mol^{-1}) obtained at the EOMIP-CCSD* level is about half that obtained at the highest level of calculation (D_e = 5.2 kcal mol^{-1}). However, the EOMIP-CCSD* method is capable of describing the bond dissociation better than the aforementioned single-reference approaches. What can be concluded is that there appears to be an exit barrier for unimolecular dissociation that it is approximately 3−5 kcal mol^{-1}; an estimate that is based on our calculated classical entrance barrier in qualitative agreement with some of those cited above[11,57]combined with our calculated dissociation energy. The presence of a barrier can be rationalized by the disruption of the favorable exchange interaction in the O_2 molecule when it is brought up to OH.

How is the barrier relevant to the discrepancy between experimental and theoretical determinations of D_0 in the *trans*-HOOO radical? In the infrared action experiment, the energy absorbed by a molecule through vibrational excitation, $h\nu_{IR}$, is known and exceeds that required to break the weakest bond within the molecule. Intramolecular redistribution of the energy leads to bond cleavage. The rotational and vibrational energy of the OH fragment, E_{int}(OH), is then measured through laser-induced fluorescence. The maximum energy observed in the OH fragment, E_{int}^{max} (OH), is taken to be the excess energy.[59] The difference in the energy of the photon absorbed and the maximum energy in the OH fragment is then the upper limit to the energy of the disrupted bond.[60]

$$h\nu_{IR} - E_{int}^{max}(OH) \geq D_0(HOOO) \qquad (1)$$

When a barrier exists in a unimolecular decomposition pathway, highly nonstatistical behavior can occur.[61,62] Calculations in ref 62 by Neumark and co-workers have shown that in the dissociation of acetyl radical to CH_3 and CO roughly 60% of the so-called impulsive energy (the energy difference between the transition state and the products) was carried off as translation. In the present case, where the transition state appears to sit 2−3 kcal mol^{-1} above the products, it would seem plausible that perhaps 2 kcal mol^{-1} could be carried off by translational degrees of freedom. This would tend to greatly offset the difference between the current theoretical D_0 of 2.5 kcal mol^{-1} and the experimental upper limit of ca. 5 kcal mol^{-1}.

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(25) The following equilibrium structural parameters were calculated at the UHF-CCSD(T)/cc-pVQZ level of theory. *trans*-HOOO: r_{HO} = 0.966 Å, $r_{centralOO}$ = 1.584 Å, $r_{terminalOO}$ = 1.226 Å, θ_{HOO} = 97.2°, θ_{OOO} = 109.8°. *cis*-HOOO: r_{HO} = 0.970 Å, $r_{centralOO}$ = 1.538 Å, $r_{terminalOO}$ = 1.244 Å, θ_{HOO} = 97.1°, θ_{OOO} = 111.7°. FOO: r_{FO} = 1.630 Å, r_{OO} = 1.190 Å, θ_{FOO} = 110.9°. OH: r_{OH} = 0.968 Å. O_2: r_{OO} = 1.206 Å.

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0.971 Å, $r_{\mathrm{centralOO}} = 1.605$ Å, $r_{\mathrm{terminalOO}} = 1.231$ Å, $\theta_{\mathrm{HOO}} = 96.9°$, $\theta_{\mathrm{OOO}} = 109.7°$. *cis*-HOOO: $r_{\mathrm{HO}} = 0.974$ Å, $r_{\mathrm{centralOO}} = 1.536$ Å, $r_{\mathrm{terminalOO}} = 1.253$ Å, $\theta_{\mathrm{HOO}} = 97.2°$, $\theta_{\mathrm{OOO}} = 111.6°$. FOO: $r_{\mathrm{FO}} = 1.641$ Å, $r_{\mathrm{OO}} = 1.196$ Å, $\theta_{\mathrm{FOO}} = 110.8°$. OH: $r_{\mathrm{OH}} = 0.972$ Å. O_2: $r_{\mathrm{OO}} = 1.213$ Å.

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