Rozen's Epoxidation Reagent, CH₃CN-HOF: A Theoretical Study of Its Structure, Vibrational Spectroscopy, and Reaction Mechanism †

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Rozen's epoxidation reagent, CH₃CN-HOF, and a prototype epoxidation reaction employing it, have been subjected to an extensive ab initio and density functional study. Its anharmonic force field reveals a very strong red shift for the OH stretch and a strong blue shift for the HOF bend, in semiquantitative agreement with experiment. The very strong hydrogen bond (8.20 kcal/mol at the W1 level) not only serves to stabilize the reactant but also considerably lowers the barrier height for epoxidation of ethylene. Moreover, the reaction byproduct HF is found to act autocatalytically. The OH moiety acquires HO⁺ character in the transition state.

Our W1 benchmark data for the reaction profile allow the performance of various DFT functionals to be assessed. In general, "kinetics" functionals overestimate barrier heights, the BMK functional less so than the others. The B1B95 and TPSS33B95 meta-GGA functionals both perform very well, whereas general-purpose hybrid GGAs underestimate barrier heights. The simple PBE0 functional does reasonably well.

I. Introduction

Hypofluorous acid (HOF) was first synthesized by Studier and Appelman1 in 1971. It was, however, found to be a very unstable substance—at room temperature, decomposition of gaseous HOF to HF and 1/2 O₂ has a half-life of about 1 h, and the liquid has a tendency to explode at temperatures above −40 °C (in the presence of oxidizable material even at −78 °C).2

In 1986, Rozen and co-workers3 found a way both to stabilize the compound and to harness it as a synthetic reagent by complexation with acetonitrile. By bubbling an N₂ stream containing about 10% F₂ through an aqueous acetonitrile solution (10% H₂O), a CH₃CN-HOF complex is created that has a half-life of several hours at room temperature.

The great synthetic value of HOF results from its unique structure in which an oxygen atom is bonded to the only more electronegative element, fluorine, thus turning the oxygen into a strong electrophile. As such, HOF and CH₃CN-HOF are extremely powerful oxygenating and hydroxylating agents. CH₃CN-HOF can be used under very mild reaction conditions and can perform oxidative transformations of which other reagents are incapable. It will epoxidize any double bond, including very deactivated ones, rapidly and with high yields.4–7 It also efficiently oxidizes amines to nitro derivatives8–11 and transforms sulfides, even highly deactivated ones, into the corresponding sulfones.12,13 It is also useful for hydroxylation α to a carbonyl of many ketones, esters, and acids14,15 and many related transformations.16,17 Reactions are usually complete in a few minutes at temperatures ranging from 0 to 25 °C.

A number of mechanistic questions arise here, not only as to the mechanism of the reaction but also as to the role of CH₃CN: is it merely an otherwise inert reactant stabilizer, does it have a passive solvent role, or does it actively assist the reaction?

In an attempt to answer these questions, we carried out a computational study on the mechanism of a prototype reaction, namely epoxidation of the simplest olefin by CH₃CN-HOF:

\[
\text{H}_2\text{C}≡\text{CH}_2 + \text{HOF} \rightarrow \text{H}_2\text{C}≡\text{CH}_2 + \text{HF}
\]

To the best of our knowledge, this system has not previously been subjected to any theoretical studies, and available experimental data are very limited. In the present work, we will apply modern density functional theory (DFT) methods to the mechanism of this reaction and validate our DFT findings by means of high-accuracy ab initio calculations on the smaller systems. We will also consider the formation of alternative hydrogen bond networks (via the reaction products HF and/or F⁻). Finally, we will obtain DFT anharmonic force fields of the CH₃CN-HOF dimer and its monomers, in an effort to assist future spectroscopic studies on the dimer.

II. Computational Details

All DFT calculations were carried out using a locally modified version of Gaussian 03 Revision C.01.18 Initially, we employed the B97-1 hybrid GGA (generalized gradient approximation)
functional, which represents the Handy group reparametrization of Becke’s 1997 hybrid GGA. (This functional has 21% Hartree–Fock “exact” exchange.) B97-1 was previously shown to yield excellent performance for equilibrium properties in general,19,21 and for hydrogen bonds in particular.22

To give a realistic representation of the energetics and kinetics of the reaction, the DFT functional chosen should correctly reproduce both the reaction barriers and the hydrogen bond energies. As this combination is a rather difficult task for present-day DFT methods, we have considered a rather wide variety of functionals and validated them against benchmark ab initio calculations (see below). Our specific choices were to some extent motivated by our recent findings in a validation study on a number of late transition metal catalyzed reactions. Besides the B3LYP24,25 and PBE026 hybrid GGA functionals, we considered the following hybrid meta-GGA functionals:

- BMK (Boese–Martin for kinetics21)
- TPSS1KCIS, i.e., Tao–Perdew–Staroverov–Scuseria meta-GGA exchange22 with Krieger–Chen–Inaf–Savin meta-GGA correlation28 and 13% HF exchange, a combination proposed by Truhlar and co-workers29
- Becke’s B1B95 functional,30 which combines Becke’s meta-GGA correlation functional30 with Becke’s GGA exchange31 and 28% exact exchange
- BB1K, Truhlar’s kinetics variant32 (with 42% exact exchange) of the previous functional
- the mPW1B95 and mPWB1K functionals,33 which combine modified Perdew–Wang exchange34–36 with B95 correlation, and 31 and 44% exact exchange, respectively
- Truhlar’s very recent PW6B95 and PW6B6K functionals37
- the TPSS25B95 and TPSS33B95 functionals proposed by Quintal et al.,38 which are combinations of TPSS exchange with B95 correlation using 25 and 33% HF exchange, respectively
- the very recent M05 (Minnesota-2005) functional of Truhlar and co-workers.38

Jensen’s polarization consistent49–51 basis sets were used for all DFT calculations. Initial optimizations were carried out using the fairly small aug-pc1 basis set (which is of 3s2p1d+diffuse spd quality on first-row atoms). Further refinements employed the much more extensive aug-pc2 basis set, which is of 4s3p2d1f+diffuse spd quality. This large basis set was used not only to minimize basis set truncation error on the computed properties but also to reduce BSSE (basis set superposition error) on the H-bonded energies as far as possible. Finally, to check the basis set convergence, some single-point calculations were carried out using the aug-pc3 basis set, which is of 6s5p4d2f1g+diffuse spd+f quality.

Unless noted otherwise, geometries for the various species involved in this reaction were fully optimized at the respective levels of theory, and vibrational frequencies calculated to both characterize the stationary point and obtain zero-point vibrational energies (ZPVEs) and (rigid rotor-harmonic oscillator) thermal corrections. Subsequently, intrinsic reaction coordinate43,44 (IRC) calculations were carried out on the transition states to verify that the computed transition states were indeed saddle points between reactants and products. Solvation effects were approximated using a static isodensity surface polarized continuum model (IPCM)45 with acetonitrile as the solvent (ε = 36.64).

To validate the DFT calculations, selected reaction and association energies were also obtained by means of the W1 (Weizmann-1) ab initio computational thermochemistry protocol.46–48 Basically, W1 theory represents an extrapolation to the relativistic, infinite basis set, CCSD(T) limit: as documented elsewhere,46–48 errors in total atomization energies (TAEs) are typically in the kJ/mol range, and should therefore definitely be accurate enough for our purpose. We note that W1 theory has recently been used by several groups21,49,50 for generating benchmark data for parametrizing and validating DFT methods. The actual calculations were carried out by means of the MOLPRO 2002 electronic structure package51 and a driver script written in Perl.52

To facilitate future experimental spectroscopic studies on the CH3CN-HOF complex, we carried out an anharmonic force field study on this system. Following the approach first proposed by Schneider and Thiel,53 a full cubic and a semidiagonal quartic force field are obtained by central numerical differentiation (in rectilinear normal coordinates about the equilibrium geometry) of analytical second derivatives. The latter were obtained by means of locally modified versions of Gaussian 03;18 modified routines from CADPAC54 were used as the driver for the numerical differentiation routine. All the force fields have been analyzed by means of the SPECTRO55 and POLYAD56 rovibrational perturbation theory programs developed by the Handy and Martin groups, respectively. In all cases, when strong Fermi resonances lead to band origins perturbed more than about 2 cm⁻¹ from their second-order position, the deperturbed values are reported and resonance matrices diagonalized to obtain the true band origins. As second-order rovibrational perturbation theory leads to unphysical anharmonicities involving the very low-lying intermonomer vibrations in the complex, we have deleted all anharmonicity constants involving these three modes from the analysis.

III. Results and Discussion

A. Structure and Energetics of the CH3CN-HOF Complex. At the B97-1/aug-pc2 level of theory, we find the CH3CN-HOF complex to have C₂ symmetry. Its optimized structure is presented in Figure 1. The computed and experimentally derived equilibrium structural parameters of the complex and its constituent monomers are presented in Table 1, together with available experimental data. The latter include a spectroscopic rₑ geometry for the HOF molecule,57 an old rₑ,58 and a more recent approximate rₑ, structure59 for the acetonitrile molecule,58 and fairly crude X-ray diffraction data for the complex.2 (For a concise overview of the different geometry types, see Kuchitsu.60)

In general, agreement between the computed monomer geometries and the available rₑ data is very satisfactory, with computed values lying within or near experimental standard deviation bands. Larger deviations are found for the OF bond length, which is underestimated by 0.012 Å, and for the HOF angle, which is overestimated by 1.2°, although we note that the standard deviation on the experimental measurement is itself 0.5°. (It has been shown repeatedly (e.g., refs 61–63) that correlation effects in the OF bond represent a particular challenge for electronic structure methods in general and density functional theory in particular.) The large reported uncertainties in the crystallographic study of the CH3CN-HOF complex2 render any comparison with the computed data somewhat futile.
enthalpy of dissociation at 298 K of 3.63 kcal/mol. Assuming the difference between B97-1/aug-pc2 and W1 theory to be likewise transferable, our final best estimate is 3.57 kcal/mol. Agreement with the experimental value of Appelman et al.,67 3.42 ± 0.12 kcal/mol, is as good as we can reasonably expect. Even stronger hydrogen bonds are seen in the CH3CN-HF and CH2O-HF complexes (9.06 and 9.80 kcal/mol, respectively, at the W1 level). B97-1/aug-pc2 reproduces all of these rather well; single-point B97-1/aug-pc3 calculations at the B97-1/aug-pc2 geometry lower all the binding energies by 0.14–0.16 kcal/mol compared to aug-pc2, suggesting that the aug-pc2 basis set is sufficiently close to the basis set limit. (The aug-pc1 basis set is definitely inadequate.) Of the other functionals considered, PBE0, B3LYP, and TPSS33B95 all perform about as well as B97-1, whereas mPWB1K and BMK are somewhat inferior and B1B95 clearly understimates the hydrogen bond energies.

B. Vibrational Frequencies. Vibrational frequencies beyond the harmonic approximation were obtained by means of second-order rotation−vibration perturbation theory from a semidiagonal quartic force field obtained at the B97-1/aug-pc1 level and harmonic frequencies obtained at the B97-1/aug-pc2 level. This level of theory was shown previously68−70 to yield sufficiently reliable anharmonic vibrational frequencies for most purposes: sadly, large basis set CCSD(T) harmonic frequencies are not a practical option for the complex. As for the monomers, Breidung et al.71 and Peterson and co-workers66 previously obtained accurate CCSD(T) anharmonic force fields for HOF, whereas in a very recent study by Pouchan and co-workers72 on CH3CN, a B3LYP/cc-pVTZ anharmonic force field was combined with CCSD(T)/cc-pVTZ harmonic frequencies.

Calculated harmonic and fundamental frequencies of the free monomers and the CH3CN-HOF complex are presented in Table 4, together with the available experimental and selected ab initio data. For the monomers, harmonic frequencies are generally in good agreement with experiment or accurate ab initio values, except for the OF stretch in HOF and (to a lesser extent) the CN and CC stretching frequencies in CH3CN. (The aforementioned difficulties of DFT with describing OF bonds are seen here in amplified form.) As for the CN and CC stretches in CH3CN, one of the main consequences of the errors in these harmonic frequencies is that the observed υ1 + υ2 ≈ υ2 Fermi type 2 resonance is nearly absent in this computed spectrum.

As in the majority of hydrogen-bonded systems, the vibrational modes of the isolated monomers remain largely recognizable in the complex. A comparison of the vibrational modes of the complex to the corresponding modes of the isolated monomers (Table 4) reveals that spectral perturbations in the
TABLE 4: Harmonic and Fundamental Vibrational Frequencies (cm\(^{-1}\)) for Free and Complexed HOF and CH\(_3\)CN Molecules

<table>
<thead>
<tr>
<th>B97-1/aug-pc1</th>
<th>B97-1/aug-pc2</th>
<th>ab initio(^{e,f})</th>
<th>experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\omega)</td>
<td>(\nu)</td>
<td>(\omega)</td>
<td>(\nu)</td>
</tr>
<tr>
<td>3734.5</td>
<td>3546.5</td>
<td>3765.3</td>
<td>3582.5</td>
</tr>
<tr>
<td>1408.4</td>
<td>1367.2</td>
<td>1420.0</td>
<td>1380.0</td>
</tr>
<tr>
<td>971.0</td>
<td>951.0</td>
<td>1002.7</td>
<td>982.1</td>
</tr>
</tbody>
</table>

CH\(_3\)CN

| \(\omega\) | \(\nu\) | \(\omega\) | \(\nu\) | \(\omega\) | \(\nu\) | \(\omega\) | \(\nu\) | assignment |
|--------------|--------------|------------------|------------|
| 3047.4 | 2934.0 | 3044.4 | 2936.8 | 3065\(^{c}\) | 2970\(^c\) | 3044\(^d\) | 2954.1\(^e\) | CH\(_3\) (A\(_1\)) |
| 2359.7 | 2328.8 | 2355.5 | 2327.2 | 2297\(^c\) | 2247\(^c\) | 2294\(^d\) | 2266.3\(^e\) | CN (A\(_1\)) |
| 1391.7 | 1358.4 | 1404.4 | 1369.4 | 1413\(^{c}\) | 1376\(^e\) | 1418\(^d\) | 1385.0\(^e\) | CH\(_3\) deform. (A\(_1\)) |
| 932.9 | 926.0 | 1002.7 | 919.9 | 920\(^{c}\) | 913\(^e\) | 929\(^d\) | 920.2\(^e\) | CC (A\(_1\)) |
| 3132.2 | 2989.2 | 3121.0 | 2979.3 | 3149\(^d\) | 3053\(^{e}\) | 3135 | 3009\(^{e}\) | CH\(_3\) (E) |
| 1459.3 | 1429.6 | 1470.1 | 1438.7 | 1487\(^{d}\) | 1486\(^{e}\) | 1478\(^{d}\) | 1447.9\(^{e}\) | CH\(_3\) deform. (E) |
| 1049.7 | 1037.0 | 1056.3 | 1034.8 | 1061\(^{e}\) | 1038\(^{e}\) | 1062\(^{d}\) | 1040.8\(^{e}\) | CH\(_3\) rock (E) |
| 371.7 | 374.8 | 377.9 | 380.9 | 361\(^{e}\) | 364\(^{e}\) | 365\(^{d}\) | 362\(^{e}\) | CCN bend (E) |

**a**: QD=quasidegenerate. Experimental uncertainties are \(\pm 1\). **b**: Large basis set CCSD(T)+core-valence-\(\lambda\)-sca relativistic corrections, ref 66. **c**: Reference 77. **d**: Reference 78. **e**: CCSD(T)/cc-pVTZ, ref 72. **f**: Reference 79. **g**: In Fermi resonance with HOF bend overtone at 2861.2 cm\(^{-1}\); deperturbed bond origins at 3254.6 and 2904.8 cm\(^{-1}\), respectively, and \(W = 261.7\) cm\(^{-1}\). **h**: In Fermi resonance with HOF bend overtone at 2861.4 cm\(^{-1}\); deperturbed bond origins at 3276.1 and 2901.9 cm\(^{-1}\), respectively, and \(W = 259.2\) cm\(^{-1}\). **i**: In Fermi resonance with HOF bend overtone at 2866 cm\(^{-1}\); deperturbed bond origins at 3203 and 2915 cm\(^{-1}\), respectively, and \(W = 255.1\) cm\(^{-1}\). **j**: In argon/helium matrix, ref 67.

CH\(_3\)CN moiety are rather small (less than 20 cm\(^{-1}\)), whereas much stronger shifts are seen in the FOH moiety. Specifically, the O–H stretching vibration is red-shifted by 248 cm\(^{-1}\), and the FOH bending mode exhibits a blue shift of 86 cm\(^{-1}\). The blue shift for the FOH bending mode is in very good agreement with that found experimentally by Appelman et al., but these authors report an extremely large red shift of almost 350 cm\(^{-1}\) in the OH stretch that is only in semiquantitative agreement with our calculations. The OH red shift in the complex causes narrowing of the Fermi resonance gap, the Fermi resonance with HOF bend overtone at 2861.2 cm\(^{-1}\); deperturbed bond origins at 3254.6 and 2904.8 cm\(^{-1}\), respectively, and \(W = 261.7\) cm\(^{-1}\). In Fermi resonance with HOF bend overtone at 2861.4 cm\(^{-1}\); deperturbed bond origins at 3276.1 and 2901.9 cm\(^{-1}\), respectively, and \(W = 259.2\) cm\(^{-1}\). In Fermi resonance with HOF bend overtone at 2866 cm\(^{-1}\); deperturbed bond origins at 3203 and 2915 cm\(^{-1}\), respectively, and \(W = 255.1\) cm\(^{-1}\). In argon/helium matrix, ref 67.

For HOF, comparison between experimental gas-phase and noble gas matrix IR spectra from different sources\(^{25,73}\) leads to conflicting conclusions: although matrix red shifts of only 1–6 cm\(^{-1}\) were found by Appelman et al., one of the researchers involved in refs 2 and 67 reports a red shift of 25 cm\(^{-1}\) for the OH mode in Table 15 of his Ph.D. thesis.\(^{73}\) (Appelman et al.\(^{75}\) found a matrix red shift of 41 cm\(^{-1}\) in \(N\_2\).) Comparison between B97-1/aug-pc2 harmonic frequency calculations on HOF in the gas phase and using a PCM model\(^{24}\) with argon as the “solvent” reveals a large computed red shift of 67 cm\(^{-1}\); literature evidence\(^{76}\) suggests that medium shifts calculated using the PCM model are semiquantitative at best, yet the calculation would seem to indicate a significant red shift.

We therefore carried out an anharmonic force field calculation for the entire complex at the PCM-B97-1/aug-pc1 level. The results (Table 4) suggest a red shift of about 53 cm\(^{-1}\) on the unperturbed HO stretch; narrowing of the Fermi resonance gap, and the resulting increased perturbation, reduce the matrix shift to about 47 cm\(^{-1}\). Our computed HOF stretching frequency in Ar matrix, 3251 cm\(^{-1}\), is actually in rather good agreement (perhaps to some extent fortuitously) with the experimental observation at 3230 cm\(^{-1}\).

Appelman et al. also report a strong and broad band at 2860 cm\(^{-1}\), which shifts to 2113 cm\(^{-1}\) upon deuteration. On the basis of our calculations, we assign these bands to the overtone of the HOF viz. DOF bend (calculated at 2904 and 2134 cm\(^{-1}\), respectively, in the gas phase at the B97-1/aug-pc2 level, and at 2866 and 2140 cm\(^{-1}\), respectively, in PCM argon at the B97-1/aug-pc1 level).

Dunkelberg\(^{73}\) reports an even larger red shift, to 3141 cm\(^{-1}\), in CH\(_3\)CN at \(-150^\circ\)C; at the PCM-B97-1/aug-pc1 level, we find a deperturbed fundamental at 2953 cm\(^{-1}\) (very close to the HOF overtone at 2916 cm\(^{-1}\)) and a perturbed fundamental at 3053 cm\(^{-1}\). Once again, PCM reproduces this medium effect qualitatively but not quantitatively.

C. Mechanism and Kinetics for the Epoxidation Reaction.

At the B97-1/aug-pc2 level and in the gas phase, the epoxidation of ethylene by free HOF is calculated to be exothermic by \(\Delta E_e = -68.6\) kcal/mol and exergonic by \(\Delta G_{298} = -65.8\) kcal/mol. The former value is in very good agreement with our W1 result, \(\Delta E_e = -71.00\) kcal/mol. With CH\(_3\)CN-HOF as the reactant, the reaction is likewise highly exothermic (\(\Delta E_e = -69.8\) kcal/mol, \(\Delta G_{298} = -66.0\) kcal/mol).
The epoxidation transition state structure in both cases, bare HOF and CH$_3$CN-HOF, is displayed in Figure 2. In both cases, $\tau$(O–F) is stretched by over 0.3 Å compared to the reactant, but $\tau$(C==C) is elongated by only 0.04 Å, and $\tau$(C–O) of about 2 Å likewise indicates no epoxide bonds have been formed yet. This relatively “early" transition state is consistent with the Hammond postulate and the very exothermic character of the reaction. According to the APT charge distribution, the HOF moiety acquires HO$^+$ F$^-$ character in the transition state, with partial charges of +0.86 and −0.86 e, respectively, without CH$_3$CN and +0.90 and −0.94 e, respectively, with hydrogen-bonded CH$_3$CN.

The strongly polar character of the transition state also expresses itself in the rather slow basis set convergence for the barrier height: it still increases by 0.44 kcal/mol between aug-pc2 and aug-pc3 basis sets, compared to −0.10 kcal/mol for the overall reaction energy. (The aug-pc1 basis set is clearly woefully inadequate.)

Reproduction of reaction barrier heights continues to be an Achilles heel of density functional theory, and indeed the B97-1/aug-pc2 barrier is too low, relative to the W1 value, by 4.45 kcal/mol, of which only 10% can be attributed to basis set incompleteness. Various “kinetics” functionals such as PW6B6K, BB1K, and mPW1B1K seriously (6–10 kcal/mol) overestimate the barrier, the BMK functional less so (3 kcal/mol). The relatively good performance of PW6B95 for the barrier (and even better one of the very recent M05 functional are marred by 10 kcal/mol errors in the overall reaction energy. The simple PBE0 functional puts in a fairly creditable performance, and B1B95 reproduces the barrier height almost exactly and TPSS33B95 only slightly overestimates it. TPSS25B95, TPSS1K CIS, and mPW1B95 all underestimate the barrier height.

We were unable to carry out W1 calculations for the reaction with CH$_3$CN-HOF, but we can assume that the most reliable results would be obtained from functionals that can handle well both the H-bond energies and the barrier in the absence of CH$_3$CN. It is thus encouraging that B1B95/aug-pc2 and TPSS33B95/aug-pc2 yield nearly identical results for the barrier heights, even with the limitations of the former in describing the hydrogen bonds. Qualitatively, all functionals show that complexation to CH$_3$CN lowers the barrier height by 3–4 kcal/mol, and that the already highly exothermic reaction becomes slightly more so, due to the stronger H-bond energy of C$_2$H$_5$OHF compared to CH$_3$CN-HOF. Consideration of continuum solvent effects further lowers the barriers by 5–7 kcal/mol. (We note that continuum solvent models are not a substitute for explicitly considering the hydrogen bond; as can be seen in Table 5, in the absence of an explicit CH$_3$CN hydrogen bond acceptor, exaggerated solvent effects are found that lead to chemically meaningless negative barrier heights.)

One potential alternative reaction pathway involves first formation of methyl cyanide N-oxide (aka methyl fulminate) HOF + CH$_3$CN $\rightarrow$ HF + CH$_3$CNO, followed by epoxidation by the fulminate, CH$_3$CNO + HC$_2$=CH$_2$ $\rightarrow$ C$_2$H$_4$OF + CH$_3$CN. Even at the B97-1/aug-pc2 level (where reaction barriers will be underestimated), we found both steps to have unrealistically high barriers, $\Delta G_{298}^{e}$ = 41.32 and 57.19 kcal/mol, respectively.

D. Alternative Hydrogen Bond Assisted Transition State?

To investigate possible involvement of other H-bond donors/acceptors in the reaction process, we sought transition states involving F$^-$ and HF, rather than CH$_3$CN, in the H-bond acceptor role. Optimization at the B97-1/aug-pc2 level led to the structures presented in Figure 3. HF may initially be present in the reaction mixture as a product of the in-situ generation of C$_2$H$_4$OF + HF, followed by epoxidation by hydrogen-bonded CH$_3$CN, and is of course generated as a byproduct of the epoxidation reaction. Acetonitrile can act as a weak base, and thus some F$^-$ could be present in equilibrium with HF. (However, at the B97-1/aug-pc2 level, the already highly exothermic reaction is of course generated as a byproduct of the epoxidation reaction. Acetonitrile can act as a weak base, and thus some F$^-$ could be present in equilibrium with HF.)

| TABLE 5: DFT and W1 Energetics (kcal/mol) for the Epoxidation Reaction |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| Energy Difference (kcal/mol) | $\Delta G^e$ | $\Delta G^e_{298}$ | $\Delta G^e_{298}$(sol) | $\Delta E$ |
| HOF             | 6.77            | 5.36            | 71.29            | 75.09          |
| B97-1/aug-pc1   | 10.66           | 5.76            | 69.79            | 73.93          |
| B97-1/aug-pc2   | 11.06           | 6.91            | 69.91            | 80.22          |
| B97-1/aug-pc3   | 12.36           | 8.38            | 74.37            | 78.38          |
| B1B95/aug-pc2   | 14.71           | 8.32            | 72.22            | 84.16          |
| B1B95/aug-pc3   | 16.57           | 8.38            | 74.32            | 84.14          |
| PBE0/aug-pc2    | 18.89           | 8.34            | 74.48            | 84.14          |
| TPSS25B95/aug-pc2 | 24.22         | 8.38            | 74.48            | 84.14          |
| TPSS33B95/aug-pc2 | 24.24         | 8.38            | 74.48            | 84.14          |
| M05/aug-pc2     | 24.24           | 8.38            | 74.48            | 84.14          |
| W1              | 24.24           | 8.38            | 74.48            | 84.14          |

* Single point calculation at B97-1/aug-pc2 geometry.  
* Single point calculation at B1B95/aug-pc2 geometry.
“earlier” than for the CH3CN complex.) It thus appears that the reaction is accelerated autocatalytically by its own reaction byproducts.

Once again, the B1B95 and TPSS33B95 functionals yield barriers in excellent agreement with each other, whereas B97-1 is systematically too low.

IV. Conclusions

In Rozen’s epoxidation reagent, a strong hydrogen bond is formed between HOF and CH3CN. This hydrogen bond not only stabilizes the reactant but also significantly lowers the epoxidation reaction barrier. The HOF moiety acquires HO+ character in the transition state. Furthermore, the reaction byproduct, HF, can autocatalytically accelerate the reaction.

Our W1 benchmark data for the reaction profile allow the performance of various DFT functionals to be assessed. In general, “kinetics” functionals exhibit overestimate barrier heights, BMK less so than the others. The B1B95 and TPSS33B95 meta-GGA functionals both perform very well, whereas general-purpose hybrid GGA’s underestimate barrier heights. The simple PBE0 functional does reasonably well. In terms of the preferred percentage of Hartree–Fock exchange, this reaction, which has a very polar transition state, seems to take a middle position between main group hydrogen transfer reactions (which prefer elevated HF exchange percentages in the 40–45% range\(^2,21\)) and late transition metal catalyzed reactions (which prefer more typical HF exchange percentages in the 20–25% range\(^2,11\)).

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