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Unimolecular Rearrangement of *trans*-FONO to FNO_2. A Possible Model System for Atmospheric Nitrate Formation[†]

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A high-level ab initio electronic structure study of the unimolecular rearrangement of *trans*-FONO to fluoryl nitrate (FNO_2) is presented. The FO + NO → [FONO]* → FNO_2 reaction is found to proceed through a tight transition state with a calculated height of 22(3) kcal mol^{-1}. The isomerization process is described qualitatively in terms of a two-state diabatic model that involves the fluorine atom and the ground and first excited σ states of NO_2.

This report is concerned with the reaction between the nitric oxide (NO) and fluorine oxide (FO) radicals as a model system for the atmospherically important combination of NO with peroxy (HOO and, especially, ROO) radicals. In all cases, there is a reactive ROONO complex that features both cis and trans minima on the potential energy surface. In the case of HOONO, the cis isomer has an internal hydrogen bond, which clearly is not present in FONO and ROONO. Hence, the FO + NO model system studied here is more qualitatively similar to the combination of alkylperoxy radicals with NO than it is to the isoelectronic HOO + NO reaction. With an eye toward the objective of studying the detailed quantum dynamics of this class of reaction, the FO + NO reaction

$$\begin{aligned} FO + NO &\rightarrow F + NO_2 \\ &\rightarrow FNO_2 \end{aligned} \tag{1}$$

is especially attractive as a model system since it has but six internal degrees of freedom. The principal result of this paper is to report a *unimolecular* mechanism for isomerization of the FONO intermediate formed by reaction of FO + NO to nitryl fluoride (FNO_2), as well as some qualitative discussion about this transition state as well as benchmark calculations that should be useful for guiding studies of the analogous alkylperoxynitrite (ROONO) isomerizations. While we believe that the findings of this research are of sufficient generality to provide insight into the atmospherically ROO + NO → $RONO_2$ reaction, the isomerization of FONO discussed below is interesting in its own right.

Oxidations of nitric oxide to nitrogen dioxide and nitrates are of considerable atmospheric importance.[1,2] Automotive nitric oxide emissions are the principal factor driving air pollution in cities,[3,4] and organic peroxyl radicals are known to oxidize[5] NO to NO_2, which subsequently produces tropospheric ozone.[6] Although most of the NO is oxidized in the manner described above, some collisions ultimately lead to formation of organic nitrates ($RONO_2$).[7,8,9] Smog chamber studies[9] at atmospheric pressure as well as laboratory flow tube studies[10,11] demonstrate that the amount of organic nitrate increases with the size of the alkyl group on ROO.[12] The nitrate yield also increases with gas pressure and decreasing temperature. Although atmospheric methyl nitrate and ethyl nitrate are believed to be of marine origin,[13,14,15] ROO + NO radical−radical reactions are thought to be the most important source of larger alkyl nitrates in the atmosphere.[3,16]

Negative activation energies that have been observed[10,11] for ROO + NO reactions strongly imply the involvement of an ROONO intermediate, which tends to subsequently fragment to RO + NO_2. The means by which nitrates are formed is less clear. The simplest means by which this can occur is by a stepwise fragmentation−recombination process, but this is probably not a tenable pathway in the atmosphere.[17] Unimolecular mechanisms are harder to envision, but so-called "dissociative transition states" for isomerization of HOONO have been presented in the literature,[18] where the peroxy bond is lengthened to ca. 2.5−3 Å. In this work, we show that there is a third feature on the potential energy surface that links the peroxynitrite intermediate to nitrates, namely a tight transition state with considerably more modest lengthening of the peroxy bond. It should be noted that a similar transition state has been

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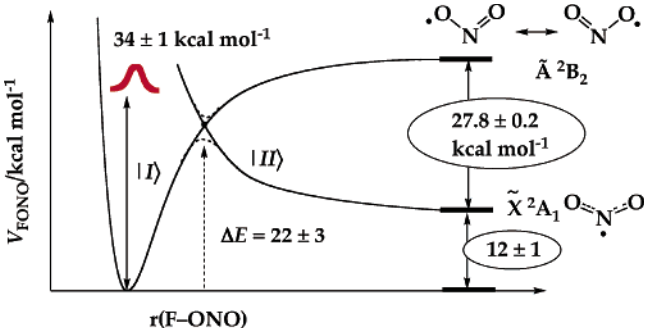

Figure 1. Schematic representation of the two-state diabatic model that rationalizes the nature of the F−O stretching potential in *trans*-FONO.

presented by Zhao et al. in a very recent paper[19] for HOO + NO. However, these authors refer to it as the transition state for breaking of the peroxy bond, and do not explicitly note its role in unimolecular isomerization.

The physical basis for the tight unimolecular barrier can be understood in several ways. As also pointed out by Zhao et al., as the F−ONO bond of FONO (or the O−O bond in HOONO or ROONO) is extended, the electronic structure of the intermediate is reminiscent of a biradical complex involving F and the *excited* $\tilde{A}^2B_2$ state of NO_2, and correlates diabatically with F + $\tilde{A}^2B_2$ NO_2 at infinite separation. This excited state of NO_2 is known to lie 27.8 kcal mol^{-1} above the ground state.[20] The diabatic potential that separates to the ground state of NO_2, while strongly attractive as the F approaches NO_2 in the vicinity of the C_2 rotation axis, is repulsive as F approaches along a direction consistent with the NOF bond angle in *trans*-FONO due to strong electronic repulsion. Hence, the dominant diabatic state necessarily changes along the reaction coordinate for F−O bond breaking, and the adiabatic potential exhibits a transition state that separates the basins where "$^2B_2$-like" and "$^2A_1$-like" (near the FONO minimum and asymptotically, respectively) electronic structures (diabatic states |I⟩ and |II⟩ in Figure 1) dominate. After crossing the barrier in the outward direction, the exiting fluorine (or OH or OR, in the case of HOONO or ROONO complexes) now experiences an attractive interaction to the nitrogen atom; the minimum energy pathway leads down from the transition state to the nitrate minimum. It is important to point out that the barrier in question serves as the transition state for fragmentation (as recognized by Zhao et al.) as well as isomerization. A contour plot of the surface, as described by an analytical model potential, is shown in Figure 2, where the bifunctional nature of the transition state should be clear.

If such a qualitative characterization has any merit, then such a transition state should satisfy the following criteria: (1) the wave function should change rapidly in the vicinity of the transition state; (2) the ONO bond angle in the transition state should be intermediate between those found in the ground and excited states of NO_2; (3) the electronic structure of the complex should have fairly appreciable biradical character. The remainder of this report is devoted to a summary of our computational findings with regard to these criteria, and to an exploration of what level of theory is required to obtain an adequate description of the transition state.

Calculations were performed with various coupled-cluster approaches, and two basis sets: the correlation-consistent cc-pVTZ basis of Dunning[21] and the DZP basis set described in ref 22. Most of the coupled-cluster calculations, which used the CCSD,[23] CCSD(T),[24] and full CCSDT[25] methods, were based on restricted Hartree−Fock (RHF) reference functions. However, a spin-polarized (unrestricted) UHF reference was also used in some calculations because of the biradical nature of the transition state. In addition, the multireference averaged quadratic coupled-cluster approach[26] was also used to locate the transition state in conjunction with the DZP basis set. This method is closely related to the multireference averaged coupled-pair functional method of Gdanitz and Ahlrichs,[27] and is most appropriately viewed as a multireference configuration interaction calculation in which the size-consistency correction is treated self-consistently. Most important for the present purpose, it is a true multireference approach (it is based on a zeroth-order wave function obtained from a multiconfigurational self-consistent field calculation) and represents a benchmark against which the quality of the standard coupled-cluster methods can be judged.

Transition state structures calculated at several levels of theory are presented in Table 1, along with activation energies relative to *trans*-FONO,[28] imaginary harmonic frequencies that correspond to the reaction coordinate, and associated infrared intensities. Much can be learned from the calculations in the DZP basis, which is small enough to allow the (rather extensive) CCSDT and MRAQCC calculations to be performed. It is

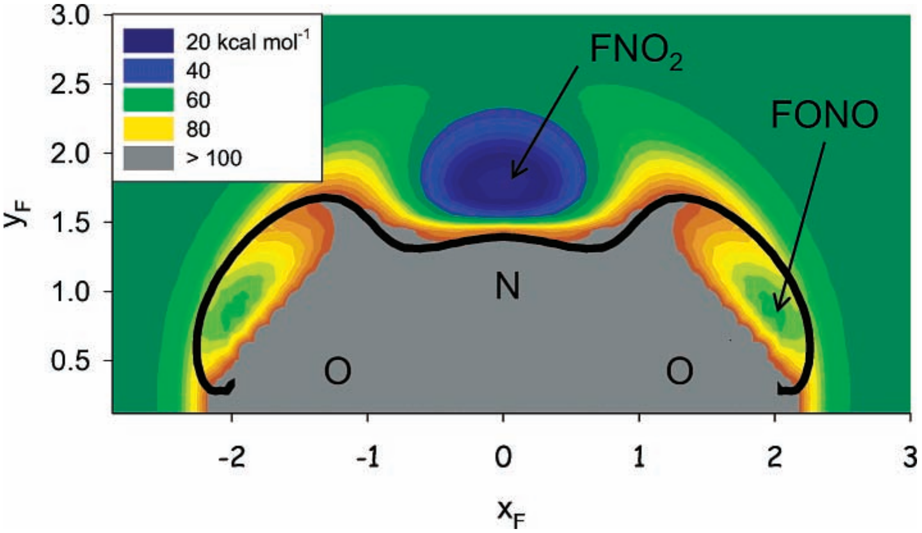

Figure 2. Contour map of the lowest energy diabatic surface, plotted as a function of the Cartesian coordinates of the F atom with the NO_2 geometry constrained to its configuration at the transition state, the two NO bond lengths are 1.19 and 1.25 Å, and θ = 125°. The thick solid line represents the points at which the two diabatic surfaces cross.

TABLE 1: Geometrical Parameters (Å and deg), Imaginary Vibrational Frequencies (cm^{-1}) and Associated Intensities (km mol^{-1}), and Barrier Heights (kcal mol^{-1}) for the Transition State in the Rearrangement of *trans*-FONO to FNO_2.

level	$r_{\mathrm{NO}^*}{}^{a}$	r_{NO}	r_{FO}	θ_{FNO}	θ_{ONO^*}	ω_{imag}	I	E_{act}
RCCSD/DZP	1.1730	1.1891	2.0298	62.93	141.19	432*i*	24	38
UCCSD/DZP	1.1964	1.2907	1.7619	45.89	119.71	1243*i*	198	25
RCCSD(T)/DZP	1.2149	1.2588	1.7804	46.60	123.23	1017*i*	275	22
UCCSD(T)/DZP	1.2022	1.2823	1.7417	46.10	121.92	1325*i*	513	25
RCCSDT/DZP	1.2132	1.2672	1.7564	46.34	122.57	*b*	*b*	21
RCCSD(T)/PVTZ	1.2014	1.2253	1.7265	46.23	126.26	905*i*	330	25
UCCSD(T)/PVTZ	1.1892	1.2462	1.6927	45.84	124.57	1300*i*	619	29
MRAQCC/DZP	1.2159	1.2906	1.7356	46.29	121.81	1204*i*	*b*	20

[a] The oxygen atom designated with an asterisk is that which is univalent. [b] Not calculated.

striking that quite similar transition state structures are obtained in all of the calculations except for CCSD when used with an RHF reference function. The biradical nature of the transition state is reflected in the relatively large magnitude of the largest T_2 excitation amplitude in the RHF calculations, and this demand is such that the CCSD method is clearly not sufficient to treat this system properly. The F−O distance is significantly overestimated (as compared to the more accurate methods), and the bond angles are also quite different from those given by the other approaches. Significantly, the ONO bond angle (141.2°) is well outside those obtained for either ground- or excited-state NO_2 (134.1 and 101.0°, respectively, at the same level of theory). However, when triple excitations are included in the CCSD(T) model or the full CCSDT approach, the RHF-based calculations give structures similar to those found in the UHF-based calculations and, more important, that obtained with MRAQCC with the same basis set. The results suggest that UHF-based CC calculations provide a rather good description of this biradical system despite modest spin contamination, which is in line with conclusions based on a study of *p*-benzyne,[29] which is essentially a pure biradical.

When the basis set is expanded from DZP to cc-pVTZ, the predictable shortening of internuclear distances is observed. Nonetheless, the structures of the transition state do not change in a qualitative way; the F−O distances are lowered from roughly 1.75 to 1.70 Å, the FON bond angle stays about the same, and the ONO bond angle increases slightly. It is difficult to judge whether the UCCSD(T) or RCCSD(T) structures obtained with the cc-pVTZ is more reliable, but differences between them are not large.

The imaginary frequencies associated with the reaction coordinate are relatively large in magnitude, indicating a rather sharp transition state. Within the simple diabatic model described above that can be used to understand this reaction, these results are consistent with a rather weakly avoided crossing. The infrared intensities, although clearly of no importance in a spectroscopic sense, are an indication of how rapidly the wave function changes in the transition state region since they are proportional to the square of the dipole moment derivative. Indeed, quite large values are found for all calculations except for RCCSD with the DZP basis, where a much more “dissociative” transition state is found. These results clearly support the idea that the rearrangement barrier can be qualitatively understood in terms of interacting diabatic states that asymptotically correlate to different electronic states of NO_2.

Like the structures, the activation energies listed in Table 1 exhibit a relatively consistent behavior for all approaches except CCSD when an RHF reference function is used. Calculated barriers with the DZP basis at the other levels of theory range from 20 kcal mol^{-1} [MRAQCC] to 25 kcal mol^{-1} [UCCSD(T)]. It is notable that the RCCSD(T) barrier obtained is closer to the MRAQCC result than is the UCCSD(T) result. Extension of the basis from DZP to cc-pVTZ acts to increase the barrier by a few kcal mol^{-1}. If one applies a correction to the RCCSD(T)/cc-pVTZ barrier of −2 kcal mol^{-1} (the difference between RCCSD(T) and MRAQCC barriers with the DZP basis, an estimate of 23 kcal mol^{-1} is obtained. Finally, using the UCCSD(T) structures obtained with the cc-pVTZ basis set, the effects of further basis set extension were assessed by performing additional RCCSD(T) single-point calculations with the cc-pVQZ and cc-pV5Z basis sets. Extrapolation of the SCF energy with the usual exponential ansatz[30] and correlation energies with the formula advocated by Helgaker et al.[31] gives an estimate of 24.4 kcal mol^{-1} for the RCCSD(T) barrier height in the basis set limit. Taken as a whole, the calculations summarized above suggest that the barrier height is 22 ± 3 kcal mol^{-1}. The zero-point vibrational correction calculated from the RCCSD(T)/cc-pVTZ harmonic frequencies[32] of *trans*-FONO and the transition state lowers the barrier by an additional kcal mol^{-1}.

The results of this paper confirm that there is indeed a tight transition state that separates *trans*-FONO and FNO_2 on the potential energy surface. Evidence is consistent with a qualitative model involving interacting diabatic states that correlate *trans*-FONO asymptotically to the fluorine atom and the ground and excited ($\tilde{B}\,^2B_2$) electronic states of NO_2. In other work, we have developed an analytic potential energy surface for the FO + NO reaction, which is parametrized solely on the basis of quadratic and cubic force fields of the minimum energy structures and their energy differences. The potential is expressed in a diabatic basis, with the adiabatic states obtained by diagonalization of a 2 × 2 Hamiltonian. This model potential gives a transition state structure and activation energy in good agreement with the full ab initio calculations, even though no property of the transition state was used in its parametrization. This is yet further evidence that the qualitative model discussed here contains the essential physics of the problem.

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