Unimolecular Rearrangement of \textit{trans}-FONO to FNO$_2$. A Possible Model System for Atmospheric Nitrate Formation$^3$

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A high-level ab initio electronic structure study of the unimolecular rearrangement of \textit{trans}-FONO to fluoryl nitrate (FNO$_2$) is presented. The FO + NO $\rightarrow$ [FONO]$^*$ $\rightarrow$ 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 $\sigma$ 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 reaction.

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 \textit{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 $\rightarrow$ 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 peroxy radicals are known to oxidize$^3$ 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 peroxyxinate 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.
presented by Zhao et al. in a very recent paper 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 \( \tilde{A}^2 \) state of NO\(_2\), and correlates diabatically with \( F + \tilde{A}^2 \) 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–ONO bond breaking, and the adiabatic potential exhibits a transition state that separates the basins where \( ^2 \)B\(_2\)-like and \( ^2 \)A\(_1\)-like (near the FONO minimum and asymptotically, respectively) electronic structures (diabatic states |I\rangle and |II\rangle 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
is well outside those obtained for either ground- or excited-

other approaches. Significantly, the ONO bond angle (141.2

estimated (as compared to the more accurate methods), and the

tRHF reference function. The biradical nature of the transition

in all of the calculations except for CCSD when used with an

RHF reference function changes in the transition state region since they are

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

of this biradical system despite modest spin contamination,

Like the structures, the activation energies listed in Table 1

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 “dissocia-
tive” transition state is found. These results clearly support the

idea that the rearrangement barrier can be qualitatively under-

stood in terms of interacting diabatic states that asymptotically

correlate to different electronic states of NO2.

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 perform-

ing 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 and correlation energies with

the formula advocated by Helgaker et al. 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 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 FNO₂ 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 (B²B₂) electronic states of NO₂. 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 ex-

pressed 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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| TABLE 1: Geometrical Parameters (Å and deg), Imaginary Vibrational Frequencies (cm⁻¹) and Associated Intensities (km mol⁻¹) for the Transition State in the Rearrangement of trans-FONO to FNO₂. |
| --- | --- | --- | --- | --- | --- | --- | --- |
| level | rNO* | rNO | rFO | θNO | θONO* | ωimag | I | Eact |
| RCCSD/DZP | 1.1730 | 1.1891 | 2.0298 | 62.93 | 141.19 | 432i | 24 | 38 |
| UCCSD/DZP | 1.1964 | 1.2907 | 1.7619 | 45.89 | 119.71 | 1243i | 198 | 25 |
| RCCSD/T/DZP | 1.2149 | 1.2588 | 1.7804 | 46.60 | 123.23 | 1017i | 275 | 22 |
| UCCSD/T/DZP | 1.2022 | 1.2823 | 1.7417 | 46.10 | 121.92 | 1325i | 513 | 25 |
| RCCSD/T/DZP | 1.2132 | 1.2672 | 1.7564 | 46.34 | 122.57 | b | b | 21 |
| UCCSD/T/cc-pVTZ | 1.2014 | 1.2253 | 1.7265 | 46.23 | 126.26 | 905i | 330 | 25 |
| UCCSD/T/cc-pVQZ | 1.1892 | 1.2462 | 1.6927 | 45.84 | 124.57 | 1300i | 619 | 29 |
| MRAQCC/DZP | 1.2159 | 1.2906 | 1.7356 | 46.29 | 121.81 | 1204i | b | 20 |

The oxygen atom designated with an asterisk is that which is univalent. Not calculated.
References and Notes

In this work, reactions of ROO and NO in benzene were found to produce nitrates.
(17) Although feasible in aqueous solution, the stepwise fragmentation—recombination pathway is unlikely to be of any importance in the atmosphere, where the free alkoxy radicals can be scavenged by oxygen, and RO + O3 → RCHO + HO2 competes with the RO + NO2 + M → RONO2 + NO recombination pathway. In a polluted atmosphere, the concentrations of oxygen and nitrogen dioxide are measured 2 to be 5 × 1018 and 2 × 1010 cm−3, respectively, and the bimolecular rate constants for recombination of RO with NO2 and O3 are known [Wollenhaupt, M.; Crowley, J. N. J. Phys. Chem. A 2000, 104, 6429. Orlando, J. J.; Tyndall, G. S.; Wallington, T. J. Chem. Res. 2003, 103, 4657]. Using this information, the lifetime of an alkoxy radical with respect to NO2 recombination is estimated to be ca. 2 s, while that for recombination with O3 is 20 μs. That the lifetime of RO with respect to O3 recombination is 4 orders of magnitude less than that associated with recombination with NO2 suggests that the formation of nitrates via RO + NO reactions in the atmosphere must occur through a unimolecular transition state.
(28) In all cases, the barrier heights are calculated using structures of trans-FONO optimized at the same level of theory.
(32) Harmonic frequencies (in cm−1) for the transition state at the RCCSD(T)/cc-pVTZ level of theory are as follows: 1591, 956, 696, 300, and 906 (a′ symmetry); 290 (a′′); 10638, 10638. For trans-FONO, the values are 1776, 991, 810, 454 and 331 (a′); 222 (a′′). The optimized structure of trans-FONO at this level of theory is as follows: rONO = 1.160 Å, rNO2 = 1.483 Å, rON = 1.417 Å, θONO = 107.9°, and θON = 103.5°. The oxygen atom designated with an asterisk is that which is univalent.