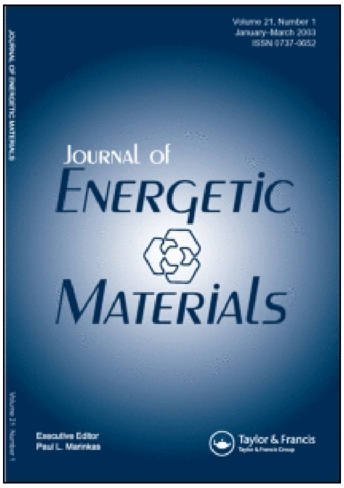

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DECOMPOSITION PATHWAYS LEADING TO HONO FOR NITROALKENES

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ABSTRACT

The reaction profiles for the dissociation of HONO from 1-nitro-2-methyl-1-propene have been examined for two distinct reaction pathways:

a. The unimolecular dissociation of HONO from the intermediate $CH_2=C(CH_3)CH=NOOH$ which in turn is formed by a unimolecular transfer of a hydrogen atom from the methyl group located cis to the nitro group in the parent molecule.

b. The unimolecular dissociation of HONO from the intermediate formed by a bimolecular transfer of a hydrogen atom between two parent molecules.

The overall activation enthalpies for the two processes are 62 and 50 kcal mol^{-1} respectively. The electronic nature of the transition states involved are discussed.

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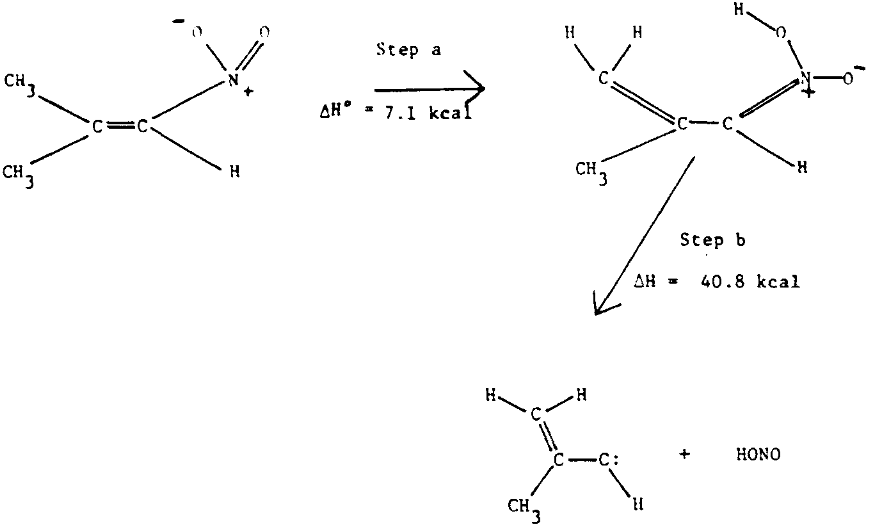
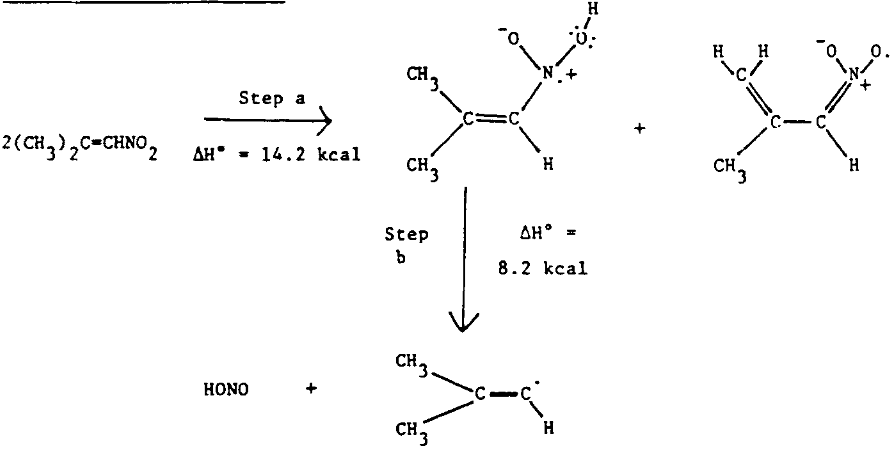
Mechanism 1 (Unimolecular)



Mechanism 2 (Bimolecular)



INTRODUCTION

There is presently a large interest in the kinetics and mechanisms operative in the thermal decomposition of nitrated derivatives of aliphatic hydrocarbons, alkenes, and aryl hydrocarbons.[1] Experimental studies primarily in the gas phase indicate that HONO is somehow involved as either a decomposition product[2] or as observable reaction intermediate.[3] Both of these alternatives have been suggested. The formation of HONO in the decomposition of nitromethane has been studied both experimentally[4] and theoretically.[5]

For the past several years this laboratory has been actively investigating possible mechanisms for the thermal decomposition of 2,4,6-trinitrotoluene (TNT) using 1-nitropropene as a model system.[6] These studies have been extended, for ancillary reasons, to include the related olefin 1-nitro-2-methyl-1-propene. In this latter case we have theoretically investigated the possible formation of HONO as a product of decomposition. We report the results of these studies here.

RESULTS AND DISCUSSION OF REACTANTS AND PRODUCTS

Two possible reaction mechanisms were examined. The reaction was viewed as the dissociation of HONO from a species which in turn was initially formed by the transfer of a hydrogen atom to the nitro group of the molecule. This latter process can occur by either a unimolecular or bimolecular pathway. Accordingly, two possible mechanisms can be operative.

Using the MNDO method of Dewar and co-workers,[7] semi-empirical molecular orbital calculations were carried out for the reactant and each of the products occurring in the above reactions and ΔH°_{298} calculated for each process. The results are shown in the above diagrams. Overall the first mechanism has ΔH° = 48 kcal mol^{-1} and for the second mechanism ΔH° = 22 kcal mol^{-1}. Thus on the basis of heat of reaction alone, thermodynamics favors the bimolecular process.

RESULTS AND DISCUSSION OF TRANSITION STATES

Transition states were located on the two potential surfaces for each of the two steps in each mechanism and enthalpies of activation were evaluated. The results are shown in Table 1. Entropies of activation were evaluated by performing a normal coordinate analysis of each transition state[7] and reactant, and calculating the requisite partition functions, thus enabling a calculation of the free energy of activation. These results are also tabulated at 298 K in Table 1. We also list the frequency calculated for the motion along the reaction coordinate for each barrier. Figures 1-4 depict the transition states found for each step in the two mechanisms.

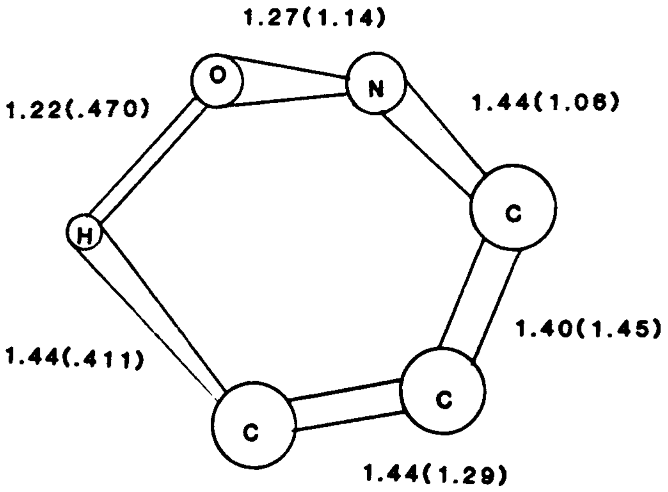


FIGURE 1
Transition State for the Unimolecular Hydrogen Atom Transfer in 1-Nitro 2-Methyl 1-Propene. Specified is the bond distance (bond order).

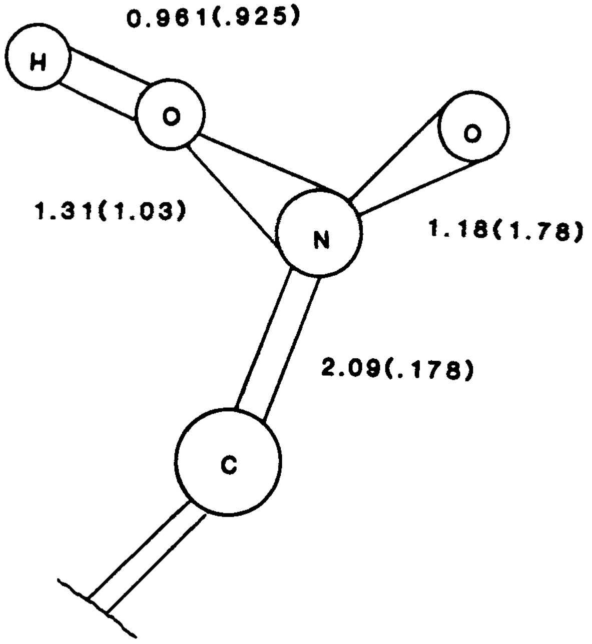


FIGURE 2
Transition State for HONO Dissociation from the aci 1-Nitro-2-Methyl-1-Propene. Specified is the bond distance (bond order).

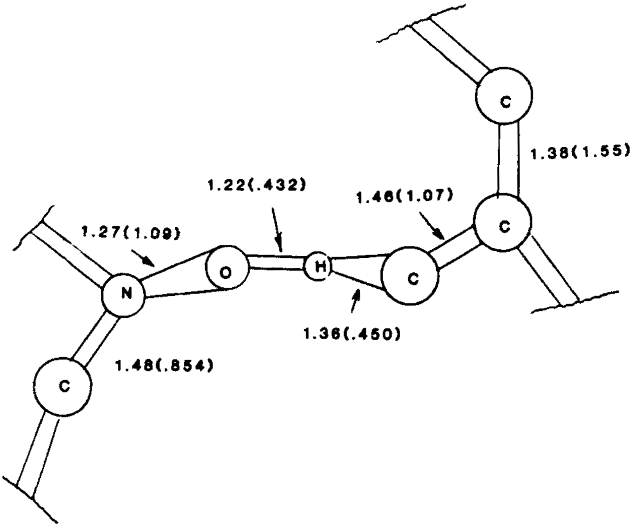


FIGURE 3
Transition State for the Bimolecular Hydrogen Atom Transfer in 1-Nitro-2-Methyl-1-Propene. Specified is the bond distance (bond order).

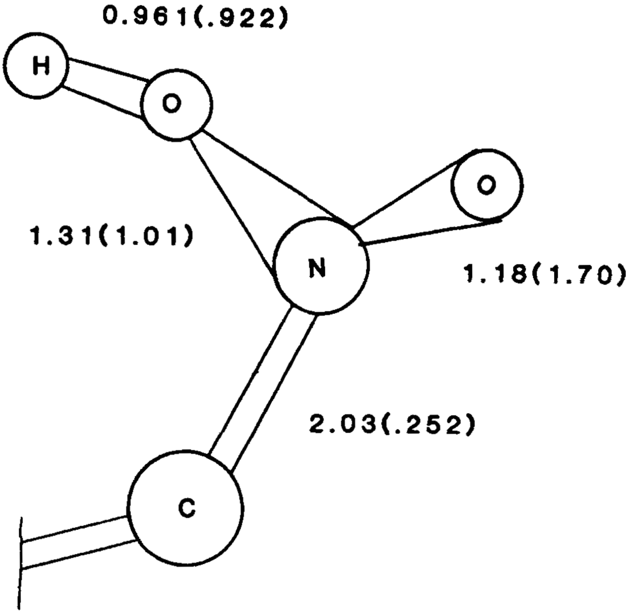


FIGURE 4
Transition State for HONO Dissociation from the Biomolecular Hydrogen Transfer Product. Only the geometry of the "business end" of the two molecules is shown. Specified is the bond distance (bond order).

TABLE 1

Activation Parameters*

Mechanism	$\Delta H^{\circ\dagger}$(kcal mol^{-1})	Frequency (cm^{-1})	$\Delta S^{\circ\dagger}$	ΔS°
1a	62.0	2749	-7.39(b)	-1.83(e)
1b	51.0	315	+6.48(c)	37.83(f)
2a	50.2	3837	-14.45(d)	-12.84(b)
2b	33.6	743	+1.07	44.73

*Temperature - 298 K; Entropy Units - Gibbs

a. These values are all based upon the results obtained from an UHF wave function.

b. These calculations employed the UHF wave functions. Vibrational analysis based upon the UHF result for 1-nitro-2-methyl-1-propene are deemed more reliable because of the absence of an anomalous low frequency contribution to the partition function. Such a contribution is present in the RHF result.

c. Low frequency contributions are present in both the reactant and transition state partition functions. We can expect some fortuitous cancellation leading to a somewhat more reliable result than is probably deserved.

d. This value is probably too high. A dominant low frequency mode was calculated for the transition state, reflecting the fact that this transition state calculated does not represent a perfect stationary point on the potential surface.

e. See c. The same type of cancellation will occur here.

f. The intermediate aci form contains a low frequency contribution which is absent in the product state, thus making this value too low. The actual result is probably 2-6 Gibbs higher.

The overall activation enthalapy for the unimolecular process is 62 kcal mol^{-1} while that of the bimolecular process is 50 kcal mol^{-1}. The origin of the barrier is similar in each case. In the first order mechanism, the largest barrier is associated with the hydrogen atom transfer step, 62 kcal

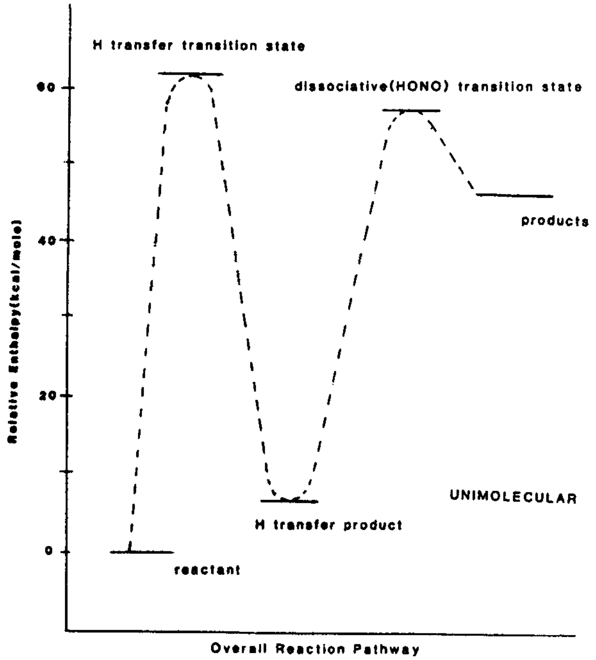


FIGURE 5
Reaction Pathway for Mechanism 1.

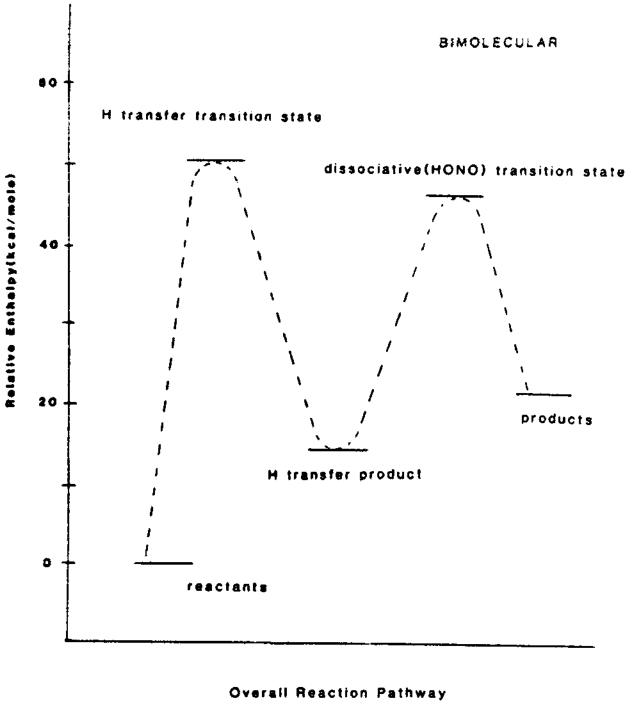


FIGURE 6
Reaction Pathway for Mechanism 2.

mol^{-1}, while the dissociative step possesses a barrier of 51 kcal mol^{-1}. The bimolecular hydrogen transfer process exhibits a 50 kcal mol^{-1} barrier, while dissociation of HONO from the resulting product shows a 34 kcal mol^{-1} barrier.

Let's consider the hydrogen transfer steps. The calculated barriers for the hydrogen atom transfer processes in the 1-nitro-1-propene system are 64 and 50 kcal/mole respectively[6] indicating that the H transfer processes in the two systems are energetically about the same. The replacement of the hydrogen atom in 1-nitro-1-propene by a methyl group to form 1-nitro-2-methyl-1-propene seems to have no effect on the hydrogen transfer process. It would be difficult to visualize the methyl group having an appreciable geometrical effect, and the results bear this out. Thus, in both systems, the bimolecular process is clearly favored. We must remember, however, that the bimolecular process was done via an unrestricted-Hartree-Fock (UHF) procedure, since the products are two radicals. MNDO-UHF results typically underestimate ΔH_f°'s by several kcal. However, this underestimation may be at least partially cancelled out by the tendency of MNDO to overestimate slightly activation enthalpies for hydrogen transfer reactions. On balance, the bimolecular process is still favored.

Now consider the HONO dissociation. In each mechanism the transition state associated with the HONO dissociation process appears to have about the same structure being characterized by a C-N bond distance of about 2.0 Å and a C-N bond order of approximately 0.2. The difference in activation energy for the dissociative processes (about 17 kcal mol^{-1}) is attributable to the markedly different skeletal structure of the two intermediates. They can be classically described as $(CH_3)_2C=CHNOOH$ in the bimolecular case and $CH_2=C(CH_3)CH=NOOH$ in the unimolecular case. The former structure seems to be able to lose a HONO fragment much more easily than the latter. In the unimolecular case the HONO fragment is bonded to the skeletal carbon atom via a partial double bond (bond order 1.53); thus, the HONO grouping is restricted to have its nitrogen atom coplanar with the first two carbon atoms of the molecule. In the bimolecular case the nitrogen atom of the HONO subunit is not constrained to coplanarity with the four carbon skeleton (CN bond order 0.84). Rotation can thus occur about the CN bond. This apparently constrains the choice of dissociation pathway available to the unimolecular reaction. Equally important, it requires more energy to break the partial double bond in the unimolecular case than to break the single bond present in the bimolecular case.

The transition states involved in the HONO dissociation steps are geometrically about the same for each mechanism. The energy maximum is reached when the HONO fragment is about 2 Å removed from the organic backbone of the species involved (see Figures 2 and 4). At this point the HONO portion of the intermediate already looks much like an isolated HONO molecule possessing both the O-N single bond and the N-O double bond. The origin of the energy maximum is not clear. Dissociation pathways of this type frequently exhibit a simple decrease of energy with distance and thus the reverse reaction shows no activation energy.[8] Factors such as hydrogen bonding between the oxygen atoms of HONO and other hydrogen atoms can be excluded on geometrical considerations.

The frequency associated with the motion along the reaction coordinate is relatively small for both pathways (unimolecular 315 cm^{-1}; bimolecular - 742 cm^{-1}). These frequencies indicate that the breaking of the C-N bond in both transition states does not require a great deal of energy.

Entropic considerations provide little, if any, basis for selection of one path over the other. The unimolecular mechanism gives rise to the larger overall increase in entropy, 36.0 Gibbs, versus 31.9 Gibbs for the bimolecular case. The larger difference arises in the hydrogen transfer step. Both lead to a decrease in entropy; however, the decrease is much larger in the bimolecular case as expected.

The entropies of activation for each step are shown in Table 1. Using these values the free energy of activation for the unimolecular and bimolecular hydrogen atom transfer steps are 64 and 55 kcal mol^{-1} (298K) respectively. Corresponding values for the HONO dissociation steps are 49 and 33 kcal mol^{-1}. The entropic contribution to these $\Delta G^{\circ\dagger}$ values is larger for the hydrogen atom transfer processes but still small relative to the whole.

It is difficult to find reasons for a large preference of one mechanism over the other. Small differences, both enthalpic and free energy-wise, indicate that the bimolecular mechanism seems to be preferable to the unimolecular process.

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8. The dissociation of NO_2 from an alphatic nitro compound is an example of this. The reaction $CH_3NO_2 \rightarrow CH_3 + NO_2$ shows this type of potential surface.