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LETTERS

Mechanism of Gas-Phase Nucleophilic Displacement Reaction of NO_2^- with Ethyl Nitrate

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A mechanism for the gas-phase nucleophilic displacement reaction, $NO_2^- + C_2H_5ONO_2 \rightarrow NO_3^- + C_2H_5ONO_2$, has been postulated on the basis of the calculated stabilities of the $(NO_2^-{\cdot}C_2H_5ONO_2)$ complex. The potential-energy diagram for the reaction pathway is characterized by three minima. The relative yield of NO_3^- in mixtures with various bath gases has been examined with high-pressure mass spectrometry. The results indicate that the efficiency of NO_3^- production depends upon the nature of the third body.

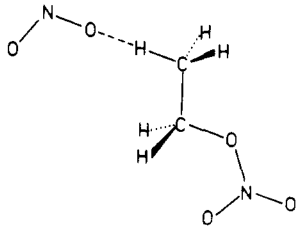
Introduction

Earlier studies[1] from this laboratory have provided data concerning NO_3^- production from ethyl nitrate by the following three-body reaction:

$$NO_2^- + C_2H_5ONO_2 \xrightarrow{M} NO_3^- + C_2H_5ONO, \quad \Delta H^\circ = -16 \text{ kcal/mol} \quad (1)$$

It has been experimentally found[1] that this reaction requires an activation energy close to 5 kcal/mol.

Semiempirical MINDO/3 calculations[1] indicated that reaction 1 probably proceeds by a nucleophilic displacement mechanism when NO_2^- directly attacks the α-carbon of the ethyl nitrate molecule, while the interaction of NO_2^- with an H atom of the CH_3 group favors the formation of a $NO_2^-{\cdot}C_2H_5ONO_2$ cluster (I). However, more recent INDO MO calculations,[2] performed for the $(NO_2^-{\cdot}C_2H_5ONO_2)$ complex, indicate that the bent structure II is more stable (by some 3.4 kcal/mol) than structure I. Since no energy barrier between I and II has been found,[3] it is likely that the initially formed structure I rearranges to form II.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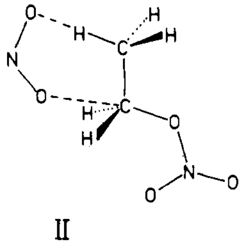
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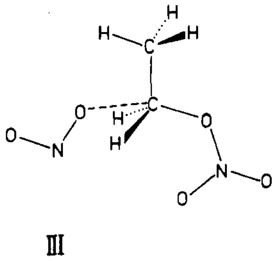
III

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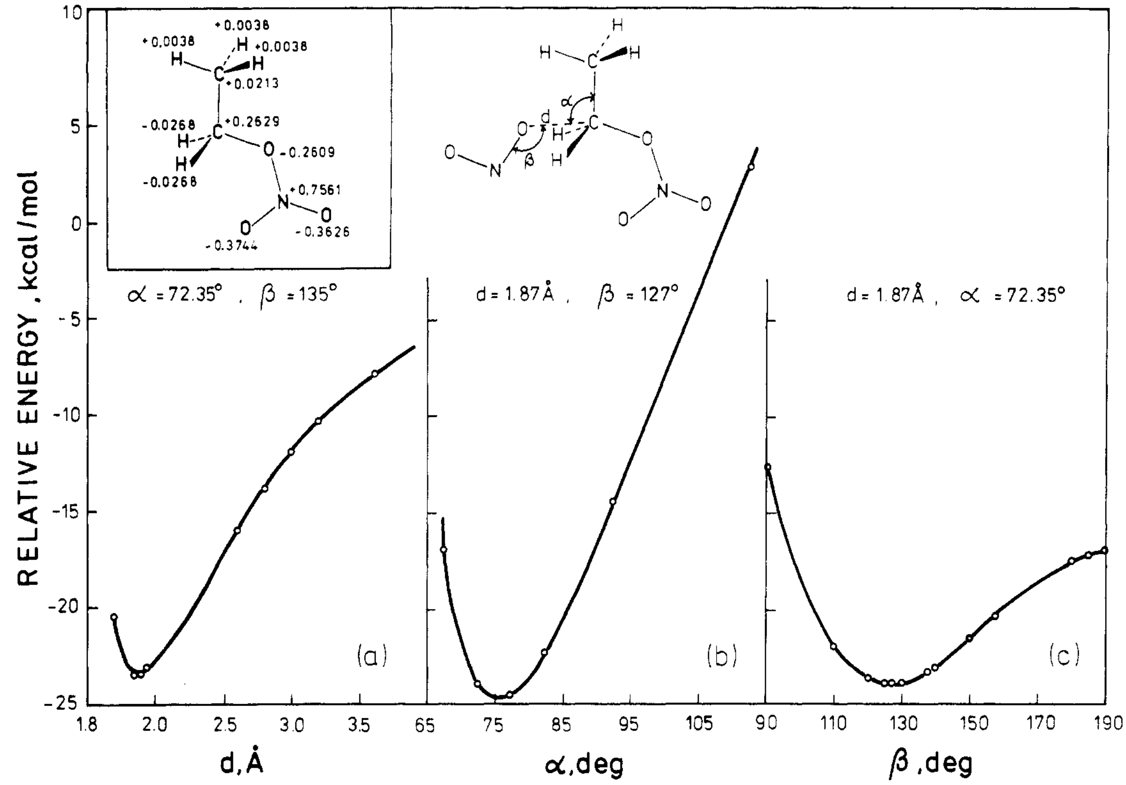


Figure 1. Relative energy of the ($NO_2^- \cdot C_2H_5ONO_2$) system as a function of parameters: (a) distance d, (b) angle α, and (c) angle β. Geometry is indicated in the figure. The insert shows the charge density on $C_2H_5ONO_2$. The data are obtained with the semiempirical INDO MO method.

In this report we show that the nucleophile's pathway leading to NO_3^- in the mechanism starting with interaction of NO_2^- with the methyl hydrogen of $C_2H_5ONO_2$ is characterized by a three-minimum-potential surface and that the relative yield of NO_3^- formation in reaction 1 is dependent on the nature of the third body, M. The proposed mechanism thus extends the one previously described.[1]

Experimental Section

The high-pressure mass spectrometer and relevant experimental details were described previously.[4,5] The ions were produced by bombardment of the gas mixtures $C_2H_5ONO_2$–M (where M = He, Ne, Ar, Kr, H_2, N_2, O_2, CO, CO_2, N_2O, CH_4, C_2H_6, C_3H_8, n-C_4H_{10}, and i-C_4H_{10}) with a 1-keV electron beam. The partial pressure of ethyl nitrate inside the reaction chamber was 0.02 torr, and the pressure of bath gas M was varied in the range from 0.2 to 2 torr. The temperature of mixtures was 367 ± 3 K.

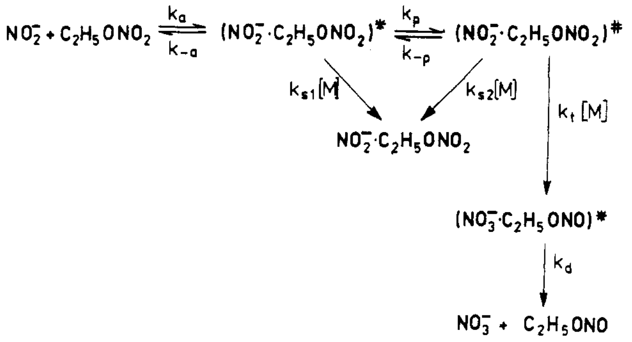
NO_2^- was produced by dissociative attachment of thermal electrons to $C_2H_5ONO_2$.[6]

Ethyl nitrate was from Dr. T. Schuchardt, Munchen, and was purified by the usual freeze–thaw cycle before use. All bath gases (commercially available products) were purified before use by passing them through a copper coil immersed in different cooling agents to remove traces of water.

Calculations

Semiempirical INDO MO calculations of the charge density on $C_2H_5ONO_2$ and the relative energy for the ($NO_2^- \cdot C_2H_5ONO_2$) system (structure III) were performed. The latter data were obtained for the parameters indicated in Figure 1, using the experimental geometry[7] for NO_2^- and the MNDO optimized geometry[2] for $C_2H_5ONO_2$. The optimized parameters for structure III are d = 1.87 Å, α = 75.4°, and β = 127°.

SCHEME I



Results and Discussion

The charge distribution from INDO MO calculations on the ethyl nitrate molecule is shown in the insert of Figure 1. It can be seen that a large fraction (~23%) of the positive charge is delocalized onto the C_2H_5 group and thus it seems likely that this positive end of the molecular dipole will orient to the NO_2^- ion in a capture collision between NO_2^- and $C_2H_5ONO_2$.

As NO_2^- approaches the methyl group hydrogens, formation of a hydrogen bonded structure like I is expected to occur. Since this structure is of lower stability than II and no energy barrier between structure I and II has been found, one may assume that the initially formed structure I rearranges to structure II.

If the nucleophilic displacement reaction could occur, the reacting system should attain such a point on the potential-energy surface at which the hydrogen bond ONO^-–$HCH_2CH_2ONO_2$ (in structure II) is ruptured. The present INDO MO calculations (in which the parameters d, α, and β were optimized, Figure 1) show that the resulting noncyclic structure III corresponds to an additional minimum on potential-energy surface of the (NO_2^-–$C_2H_5ONO_2$) system. The calculated total energy of structure III

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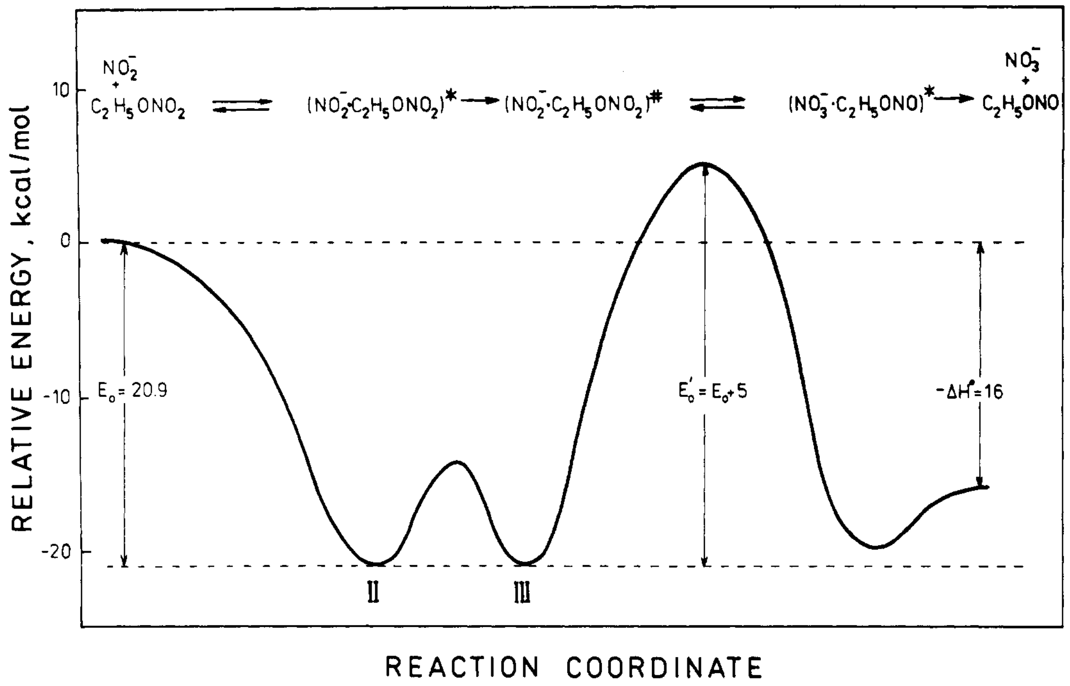

Figure 2. Potential-energy profile for the nucleophilic displacement reaction between NO_2^- and $C_2H_5ONO_2$. The energy of NO_2^-–$C_2H_5ONO_2$ at infinite separation (E_0) is based on the earlier obtained[2] energy attachment of $C_2H_5ONO_2$ to NO_2^- (20.9 kcal/mol). The barrier separating $(NO_2^-\cdot C_2H_5ONO_2)^*$ (structure II) and $(NO_2^-\cdot C_2H_5ONO_2)^‡$ (structure III) is found in this work (see text). The barrier height (E_0') between $(NO_2^-\cdot C_2H_5ONO_2)^‡$ and $(NO_3^-\cdot C_2H_5ONO)^*$ has been taken to be equal to E_0 plus measured activation energy for reaction 1. The ΔH^0 value corresponds to enthalpy change for reaction 1.

is close to that of II (the ion–molecule interaction energies obtained for structures II and III are 24.85 and 24.70 kcal/mol, respectively). The rearrangement II → III is associated with overcoming the small energy barrier the upper limit of which (6.9 kcal/mol, see Figure 1c) is calculated to be much lower than the total internal energy (~21 kcal/mol) of the $(NO_2^-\cdot C_2H_5ONO_2)$ complex at the temperature of our experiments. This suggests that under these conditions a rapid interconversion between structures II and III will occur.

The above considerations, together with the previously found[1] third-body dependence of reaction 1, suggest the mechanism shown in Scheme I for NO_3^- as well as the clustered ion $NO_2^-\cdot C_2H_5ONO_2$ formation.

The mechanism of the pathway leading to NO_3^- production by the reaction sequence which starts with the interaction of NO_2^- with the H atom of the CH_3 group may be represented by a potential-energy profile with three minima, as shown in Figure 2. The first and second minima are attributed to structures II and III, respectively, whereas the third one is assigned to a loosely bound complex $(NO_3^-\cdot C_2H_5ONO)^*$ that dissociates to NO_3^- and C_2H_5ONO.

The energy barrier (E_0') for the nucleophilic displacement of NO_3^- by NO_2^- at a carbon center is based primarily on our previous MINDO/3 calculations, which are probably valid in their qualitative details, and the experimentally found[1] activation energy for reaction 1. It should be added that potential-energy profiles with three minima (but without any positive barrier) have recently been proposed for nucleophilic displacement reactions of open shell anions PhN$^-\cdot$ and S$^-\cdot$ with different carbonyl compound molecules,[8,9] where the central minimum corresponds to a tetrahedral intermediate.

In the case of direct NO_2^- attack on the positively charged α-carbon of $C_2H_5ONO_2$ it seems likely that the $(NO_2^-\cdot C_2H_5ONO_2)$ complex structure initially takes a form similar to III, which also can interconvert with II or/and rearrange to the intermediate $(NO_3^-\cdot C_2H_5ONO)^*$ if the energy to cross the barrier toward products (i.e., NO_3^- + C_2H_5ONO) is sufficient. It should be mentioned that the structures where NO_2^- is bonded to the carbon of the CH_3 group or to the H atom of the CH_2 group were also examined and are calculated to be less stable than those I, II, and III, and one may expect that such unfavorable configurations, if formed, will relax to more stable structures like II or III.

The earlier work[1] showed experimentally (a) the stabilization of $(NO_2^-\cdot C_2H_5ONO_2)$ leading to the stable cluster $NO_2^-\cdot C_2H_5ONO_2$ and (b) the nucleophilic displacement at C_α producing NO_3^- are third-body dependent. Here we examined the influence of the third-body nature on these processes by experimental determination of the ratio $R = [NO_3^-]/([NO_2^-] + [NO_2^-\cdot C_2H_5ONO_2])$ in different bath gases.

Making a steady-state approximation for the complexes $(NO_2^-\cdot C_2H_5ONO_2)^*$, $(NO_2^-\cdot C_2H_5ONO_2)^‡$, and $(NO_3^-\cdot C_2H_5ONO)^*$ and, for simplicity, considering that $[NO_2^-]$ is proportional to $[(NO_2^-\cdot C_2H_5ONO_2)^*]$, i.e., $[NO_2^-] \approx \gamma\cdot[(NO_2^-\cdot C_2H_5ONO_2)^*]$, where γ is approximately independent of [M], one obtains

$$R = [NO_2^-]/([NO_2^-] + [NO_2^-\cdot C_2H_5ONO_2]) = (k_p k_t[M])/(k_{s1}[M] + k_{-a} - k_a[E]\delta)(k_{-+} + k_t[M] + k_{s2}[M]) + k_{s2}k_+[M] \quad (2)$$

where E = $C_2H_5ONO_2$. RRKM theory predicts[10] that at the temperatures of our experiments the interconversion II ⇄ III occurs very rapidly (the rate coefficient is some 10^{10} s^{-1} or higher). Hence, it is reasonable to assume that $k_{-p} >> (k_t[M] + k_{s2}[M])$, yielding

$$R^{-1}[M] \approx \sigma[M] + \frac{k_{-a} - k_a[E]\delta}{K_i k_t} \quad (3)$$

where $\sigma = (k_{s1}/K_i + k_{s2})/k_t$ represents the relative efficiency of collisional stabilization to activation of $(NO_2^-\cdot C_2H_5ONO_2)$ by M, and $K_i = k_p/k_{-p}$ is the equilibrium constant for the interconversion II ⇄ III.

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TABLE I: Relative Collisional Stabilization/Activation Efficiency Factors for Different Gases[a]

M	σ
He	2.30 ± 0.18
Ne	1.67 ± 0.17
Ar	1.30 ± 0.10
Kr	0.95 ± 0.11
H_2	2.27 ± 0.07
N_2	0.96 ± 0.17
O_2	1.22 ± 0.15
CO	2.17 ± 0.20
CO_2	2.16 ± 0.24
N_2O	1.43 ± 0.16
CH_4	1.72 ± 0.15
C_2H_6	2.07 ± 0.10
C_3H_8	2.07 ± 0.23
n-C_4H_{10}	2.45 ± 0.25
i-C_4H_{10}	2.47 ± 0.14

[a] The error in the σ values represents the confidence limits of linear regression coefficient determined for a confidence factor of 0.95.

Calculations[11] show that $K_i \approx 0.8$ at 367 K and is insensitive to the internal energy of intermediates II and III. This suggests that K_i remains practically constant in the pressure range used in our experiments and is the same for a variety of bath gases. Then a plot of $R^{-1}[M]$ vs. [M] at constant [E] should yield the σ value for any M.

Typical results are shown in Figure 3 and the σ values determined from this plot are listed in Table I. The errors reported represent the confidence limits of the linear regression coefficient determined for a confidence factor of 0.95. The main sources of error are pressure and ion current ratio measurements with uncertainties of ~1% and ~2.5%, respectively. This leads to ~3.5% uncertainty in $R^{-1}[M]$. It can be seen from Table I that σ depends upon the identity of M. Some implications for the effects of various third bodies in the stabilization (k_{s1}, k_{s2}) and activation (k_t) pathways of the intermediates II and III can be deduced from these data, in which one may distinguish two trends of σ variation with M. In the case of rare gases σ decreases with increasing atomic mass, while for alkanes it appears to increase with the molecular mass of hydrocarbon. The increase in σ in the latter case may be connected with an increase in the number of internal modes of M which can accept the excess internal energy of the intermediates II and III. On the other hand, in collisions of these intermediates with the monoatomic species, the excess internal energy is transfered into translational degrees of freedom of collider M. Studies of collisional stabilization of vibrationally excited ionic[12-15] and neutral[16,17] species by rare gases indicate that the stabilization efficiency of rare gases either does not depend on their mass[12,14,16,17] or increases with M.[13,15] Therefore it seems reasonable to asssume that the experimentally found trend of the decrease in σ with the mass of rare gas is caused by activation of $(NO_2^-{\cdot}C_2H_5ONO_2)$. This latter effect presumably arises from increasing with mass of M the contribution to collisional activation of such factors as: (a) the energy of the ion–neutral interaction which parallels the polarizability of the neutral species, (b) the density of states of the stretching mode $(NO_2^-{\cdot}C_2H_5ONO_2)$–M providing more effective energy transfer between colliding partners, and (c) translational energy transfer from M to the internal energy of the common complex $(NO_2^-{\cdot}C_2H_5ONO_2){\cdot}M$. It is obvious that increasing the energy of the system favors NO_3^- production over stabilization to $NO_2^-{\cdot}C_2H_5ONO_2$. Our results show that the competition of these two reaction channels is associated with a termolecular process dependent on the nature of the third body.

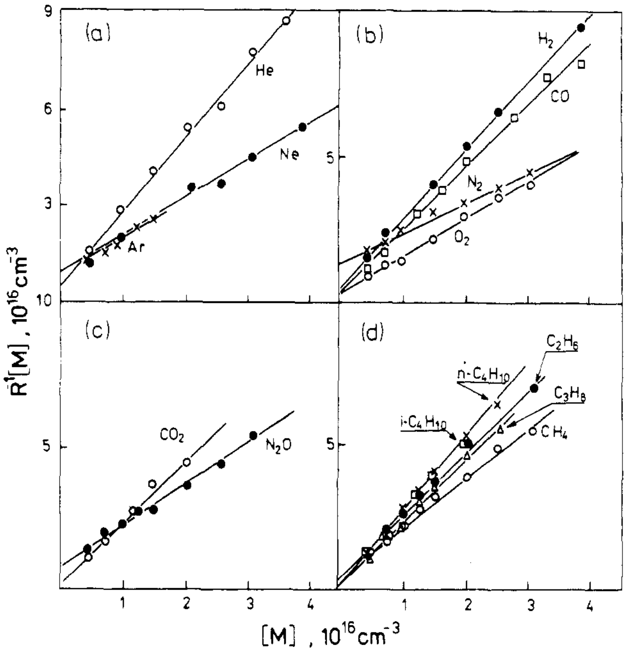

Figure 3. Variation of $R^{-1}[M]$ with concentration of collision gas M for different gases indicated in the figure.

Conclusions

The results of this work suggest that the gas-phase nucleophilic displacement reaction (1) probably occurs through a complex mechanism, as shown in Scheme I. The changes of potential energy of the reacting system $(NO_2^- + C_2H_5ONO_2)$ for this reaction pathway may be represented by a three well potential energy diagram, as illustrated in Figure 2. The first and second minima (Figure 2) may be attributed to structures II and III, respectively. The studies with various third bodies support the competition between two reaction channels: (a) formation of NO_3^- and (b) production of the clustered ion $NO_2^-{\cdot}C_2H_5ONO_2$, the competition depending upon the identity of the third body.

Registry No. He, 7440-59-7; Ne, 7440-01-9; Ar, 7440-37-1; Kr, 7439-90-9; H_2, 1333-74-0; N_2, 7727-37-9; O_2, 7782-44-7; CO, 630-08-0; CO_2, 124-38-9; N_2O, 16824-89-8; CH_4, 74-82-8; C_2H_6, 74-84-0; C_3H_8, 74-98-6; n-C_4H_{10}, 106-97-8; i-C_4H_{10}, 75-28-5.

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(11) The K_i value is calculated from the relationship $K_i \approx (1 - \Delta\epsilon_0/E_t)^{n-1}$ derived from the expression for the microcanonical rate constant (see ref 10a, Chapter 6). E_t, the total internal energy of $(NO_2^-{\cdot}C_2H_5ONO_2)$, is 21 kcal/mol. $\Delta\epsilon_0$, the difference between the energy barriers for forward (II → III) and reverse (III → II) pathways, is 0.15 kcal/mol. n, the number of internal degrees of freedom in $(NO_2^-{\cdot}C_2H_5ONO_2)$, is 35.

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