to *N*-alkylpyridone could be detected under our pyrolysis conditions. These results categorically exclude the intermediacy of the pyridone in our elimination reaction.

We then investigated the relationship between substituents on the pyridine ring and the competition between Hoffman and Saytzeff elimination. The product distributions for a series of 2-octyl pyridyl ethers are listed in Table I. For analysis purposes, we have also included values for the basicity of the pyridine corresponding to that portion of the ether substrate.[6] In order to consider our results in terms that would more directly correspond to a linear free-energy relationship, a plot of the log of the ratio of 1-octene to 2-octene vs. pyridine basicity is shown in Figure 1. The correlation suggested by this plot (*r* = 0.984) is also shown. The deviation observed for **6** (6-*tert*-butyl substituent) suggests the onset of a steric effect that promotes production of anomalously large amounts of terminal olefin.[7] Interestingly, little or no steric effect is observed with a 6-trimethylsilyl substituent.[8]

This kind of correlation has superficial analogy in the work of Bartsch et al. on bimolecular eliminations in solution, where the production of 1-butene in eliminations from 2-iodobutane was correlated with base strength.[9] They found that stronger bases gave more terminal olefin and that steric effects were only important in extremely hindered bases. We must, however, note that there is an important difference between our reaction and those results. In our systems there is a simultaneous change of both base and leaving group. Since increased basicity corresponds to reduced nucleofugality (leaving-group ability), the observation of increased 1-octene with increased base strength could equally well be correlated with decreased nucleofugality.[10]

To decide whether our product selectivity correlated to basicity or nucleofugality we sought a set of substrates that would allow the separation of these two effects. We reasoned that an amine substituent at either the 4 or 6 position of the pyridine ring would greatly increase pyridine basicity while having little or no destabilizing effect on the aryloxide leaving group.[11] Thus, a correlation based on basicity would predict substantially increased terminal olefin production, while leaving-group considerations would suggest little or no effect on product distribution. We therefore synthesized and pyrolyzed compounds **2a**, **3a**, and **5a** where X = N(CH₃)₂ instead of H.

We found that the product distributions from **2a**, **3a**, and **5a** were identical (±1%) with those for **2**, **3**, and **5** respectively; i.e., the 4-N(CH₃)₂ group has no effect on the distribution of pyrolysis products. We interpret this to indicate a transition state involving very little N–H bond formation but a great deal of C–O bond cleavage. Clearly, increased partial positive charge on the carbon skeleton as the leaving group improves provides an explanation for

the trend in olefin regiochemistry. We have also observed somewhat enhanced rates of pyrolysis with the electron-poor pyridines (e.g., 6-Br) and with increased alkyl substitution in the alkyl fragment,[12] both of which are consistent with this model.

Further experiments are underway to assess the scope and limits of product control in this reaction and to identify candidates for synthetically useful regiochemical control in such an elimination.

(6) Basicity values are for the gas-phase basicity of each compound's pyridine fragment (H instead of alkoxy) and are (except for 5) from: Aue, D. H.; Webb, H. M.; Bowers, M. T.; Liotta, C. L.; Alexander, C. J.; Hopkins, H. P. *J. Am. Chem. Soc.* **1976**, *98*, 854. The basicity of 5 was measured by Ms. Naomi Lev using standard ICR techniques.

(7) For a discussion of hindered pyridine bases in bimolecular eliminations see: Brown, H. C.; Nakagawa, M. *J. Am. Chem. Soc.* **1956**, *78*, 2197.

(8) Compare to: Bott, G.; Field, L. D.; Sternhell, S. *J. Am. Chem. Soc.* **1980**, *102*, 5618.

(9) Bartsch, R. A.; Read, R. A.; Larsen, D. T.; Roberts, D. K.; Scott, K. J.; Cho, B. R. *J. Am. Chem. Soc.* **1979**, *101*, 1176 and references therein.

(10) This observation has been made for bimolecular eliminations in solution; cf.: Bartsch, R. A.; Bunnett, J. F. *J. Am. Chem. Soc.* **1969**, *91*, 1376.

(11) 4-N(CH₃)₂ increases pyridine basicity by ca. 15 kcal/mol⁶ while amine substitution at the 3 position of a phenol does little to affect its basicity (Pross, A.; Radom, L.; Taft, R. W. *J. Org. Chem.* **1980**, *45*, 818).

(12) Specifically, we compared the reactivity of the *n*-octyl, 2-octyl, and *tert*-butyl ethers under a standard set of reaction conditions.

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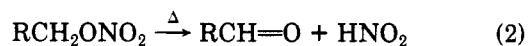*Cleveland, Ohio 44106*
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The Transition State in the Carbonyl-Forming Elimination Reaction of Alkyl Nitrates

Summary: The title reaction, now found to involve proton tunneling with base catalysis and a cyclic, nonlinear proton transfer in the uncatalyzed gas-phase process, cannot have (as previously formulated) an $E_{CO}2$ mechanism.

Sir: The base-catalyzed elimination reaction of alkyl nitrates, expressed by eq 1, had been the subject of a con-

$$RCH_2ONO_2 + Y^- \rightarrow RCH{=}O + NO_2^- + YH \quad (1)$$

siderable number of studies[1-4] which have led to its formulation as a concerted $E_{CO}2$ process. The postulated mechanism has been based on the results of measurements (with benzyl nitrates) of the primary hydrogen–deuterium isotope effects (k_H/k_D) as a function of base, solvent composition, and para substitution, the nitrogen isotope effect (k_{14}/k_{15}) as a function of base strength and parasubstitution, and the occurrence of a minute degree of deuterium exchange in unreacted substrate. In all cases each of the isotope effects were determined at a single temperature in the range of 20–30 °C. Moreover, the reactivity parameters of the uncatalyzed decomposition reaction which takes place in the absence of solvent according to eq 2 have neither been measured nor taken into consideration.

$$RCH_2ONO_2 \xrightarrow{\Delta} RCH{=}O + HNO_2 \quad (2)$$

(1) Buncel, E.; Bourns, A. N. *Can. J. Chem.* **1960**, *38*, 2457.
(2) Baker, J. W.; Heggs, T. G. *J. Chem. Soc.* **1955**, 616.
(3) Smith, P. J.; Pollack, C. A.; Bourns, A. N. *Can. J. Chem.* **1975**, *53*, 1319.
(4) Pollack, C. A.; Smith, P. J. *Can. J. Chem.* **1971**, *49*, 3856.

Table I. Temperature Dependence on the Primary Hydrogen–Deuterium Isotope Effect for Decomposition of Benzyl-α-d Nitrate by Sodium Ethoxide[a]

temp, °C	k_H/k_D[b]
30.0	4.01
40.0	3.54
50.0	3.21
60.0	2.92
70.0	2.69

Computed Quantities (coeff of correl = 0.9992)
$[\Delta E_a]_D{}^H = 2.05 \pm 0.05$ kcal/mol
$A_H/A_D = 0.132 \pm 0.010$

[a] The decomposition of benzyl-α-d nitrate was carried out in sodium ethoxide/ethanol. After 30 min at reaction temperature the mixture was worked up and the benzaldehyde/benzaldehyde-α-d product was isolated by preparative GLC methods. [b] For the intramolecular competitive decomposition of benzyl-α-d nitrate, the primary hydrogen–deuterium isotope effect may be expressed as $k_H/k_D = M_D/M_H$. By use of the mass spectrometric equipment and technique previously developed in these laboratories and applied generally for high-precision mass ratio measurements,[15,16] the parent ions M_H and M_D of benzaldehyde and benzaldehyde-α-d were monitored at 106 and 107 amu, respectively. An ionizing voltage of 70 eV was employed. Corrections were made for contributions by the peaks M_{H+1} and M_{D-1} to the mass ratio, M_D/M_H. At least 20 000 measurements were averaged to arrive at the k_H/k_D values reported for *each* of the reaction temperatures in this table.

The temperature dependence of k_H/k_D constitutes a mechanistic criterion which has been shown to be of particular value in sorting out the structural properties of hydrogen-transfer reaction transition states (TS‡).[5-13] This criterion has now been applied to elucidate the features of the carbonyl-elimination mechanism, both in the base-catalyzed and uncatalyzed (gas phase) versions, for comparison with the corresponding features[14] of the E2 and related olefin-forming elimination reactions.

Benzyl-α-d nitrate (1) was synthesized in a sequence of reactions beginning with benzaldehyde and LiAlD$_4$, proceeding through benzyl-α-d chloride and final reaction with AgNO$_3$. This preparation, after analysis of its deuterium content, was subjected to reaction in the prescribed manner[1] with sodium ethoxide in ethanol at five temperatures in the range of 30–70 °C. The magnitude of k_H/k_D at each temperature (see Table I) was obtained after quantitative recovery of the product, $C_6H_5CH(D) = O$, and estimation of its deuterium content by means of the high-precision mass spectroscopic technique previously developed and applied in these laboratories.[15-18]

The Arrhenius parameters of the isotope effect derived from these results, $[\Delta E_a]_D{}^H = 2.05$ kcal/mol and $A_H/A_D = 0.13$, are clearly indicative[12] of a tunneling mode of

Table II. Temperature Independence of the Primary Hydrogen–Deuterium Isotope Effect for Thermal Decomposition of Benzyl-α-d Nitrate[a,b]

temp, °C	k_H/k_D[c]
217.8	1.427 ± 0.007
237.9	1.404 ± 0.006
222.5	1.404 ± 0.004
256.1	1.423 ± 0.009
265.6	1.4335 ± 0.0002
277.4	1.424 ± 0.009

ave 1.42 ± 0.01

[a] The pyrolysis reaction was carried out in the gold coil microreactor.[22] The substrate 1 was injected into the helium stream and the product benzaldehyde was trapped in a capillary cooled to ca. -78 °C. The mass ratio measurements and calculations of k_H/k_D were carried out as described in Table I. [b] The concentration of substrate in the helium stream passing through the reaction zone was usually of the order of 2×10^{-4} M/L. Since the percent yield of benzaldehyde was found to be independent of the concentration of substrate, it was concluded that the uncatalyzed thermolysis reaction was a unimolecular process. [c] See footnote b of Table I.

Figure 1. Comparison of nitrate and amine oxide thermolysis transition states.

hydrogen transfer. The barrier width at the point of tunneling, estimated by means of a modified Bell–Caldin procedure,[12] is ~ 0.9 Å. The finding of a tunneling pathway in which the reaction centers between which the hydrogen is transferred are very close together is not consistent with the previously accepted[1-4] $E_{CO}2$ mechanism. How can such an event as the tunneling of a proton be timed to synchronize with the nontunneling elimination of nitrate ion? Indeed, the putative $E_{CO}2$ mechanism is surely not acceptable when a tunneling pathway of proton transfer is shown to prevail, since $E_{CO}2$ requires the degree of nitrite ion departure in the TS‡ to be identical with the degree of proton transfer in the TS‡. In fact, it is highly questionable to discuss the properties of a TS‡ for the quantum-mechanical phenomenon we recognize as proton tunneling.

In an effort to formulate an alternative to the $E_{CO}2$ mechanism of the reaction, we undertook a study of the uncatalyzed decomposition of alkyl nitrates through application of the same KIE criterion applied (above) to the alkoxide-catalyzed process. When 1 was thermolyzed in the gold-coil microreactor[19] at very high dilution in a helium stream, the unimolecular (see Table II) formation of benzaldehyde was found to take place readily in the temperature range 208–277 °C. The values k_H/k_D, determined by mass ratio analysis of the recovered benzaldehyde, proved to be invariant with temperature (see Table II) and greater than the maximum $(A_H/A_D = 1.2)^{20}$ value for linear hydrogen transfer. A close resemblance to the cyclic cis-elimination mechanism previously characterized[10] for the thermolysis of amine oxides is therefore to be inferred, as shown in the comparison of TS‡ structures 2a and 2b in Figure 1.

Not only do the data in Table I confirm a tunnel correction in the alkoxide-catalyzed reaction but they also

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(13) Kwart, H.; Janssen, J. W. A. M. *J. Org. Chem.* **1977**, *42*, 1530.
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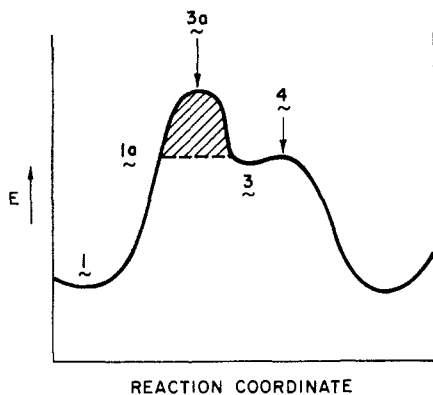(15) Kwart, H.; Stanulonis, J. J. *J. Am. Chem. Soc.* **1976**, *98*, 4009.
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Figure 2. Reaction profile of eq 3, where **3a** is the classical TS‡ at the top of the reaction barrier if tunneling had not occurred, **1a** is the configuration at the energy level of tunneling, and **3** is the carbanion saddle point preceding the TS‡ **4** leading to decomposition of **3**.

establish a linear mode of hydrogen transfer between the carbon and oxygen centers, in distinction to the uncatalyzed process involving a cyclic, nonlinear (bent) one. Invoking Ockham's razor,[21] the most consistent explanation of the course of the catalyzed decomposition reaction would suppose that the catalytic species facilitates the cyclic hydrogen transfer that takes place in the uncatalyzed reaction. That is to say, the simplest assumption is that the catalyzed linear hydrogen-transfer process of tunneling occurs between reaction centers in a similarly structured molecular arrangement.

A reasonable explanation of the change from a bent to a linear TS‡ of hydrogen transfer induced by alkoxide ion catalysis stems from the fact that the (formally) oxyanion centers of the nitrate are tied to their nitrogen by relatively short, dative bonds. An uncatalyzed planar, five-membered, cyclic TS‡ of linear hydrogen transfer is not possible since in a structure of this nature neither of the tightly bound oxygens can be aligned in a coaxial C···H···O relationship similar to that shown in **1a**, eq 3. The abstraction
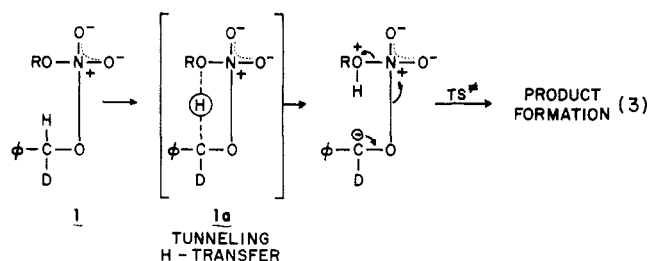
of hydrogen must be effected angularly by a nonbonding oxygen orbital in what could be a pentagonal, pseudo-pericyclic[22] TS‡, **2a**. The role of the alkoxide ion catalyst, therefore, must entail prior coordination by the electro-

philic nitrate nitrogen and the formation of a longer, covalent N–O bond. This brings the alkoxide oxygen into the required coaxial C···H···O relationship shown in **1a**. However, under these circumstances the distance of separation of C and O is exceedingly small, which creates the necessity for a tunnel correction in the subsequent hydrogen-transfer event. It can also be anticipated that a large degree of electron withdrawal at the benzylic carbon induced by para-substituent effects will bring about an even shorter distance between the hydrogen-transfer centers and thus a narrowing of the reaction barrier. The report[3] of an increase in k_H/k_D with increasing electron withdrawal by para substituents is in good accord with this analysis.

When these considerations are coupled with the strong indications ($p = +3.40$,[1] $p = +3.89$[3]) of a pronounced negative charge development at the benzylic carbon, the mechanism proposed in eq 3 emerges as the most attractive means of correlating *all* the mechanistic evidence. As illustrated in the reaction profile (Figure 2), the carbanion intermediate **3** arises via proton tunneling in **1**. The reaction progresses from this saddle point (**3**) to a TS‡ (**4**)
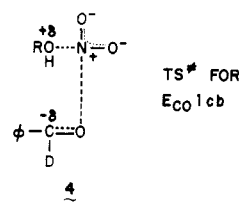
for nitrite ion departure at *nearly the same energy level*. The mechanistic path proposed in eq 3 and illustrated in Figure 2 is well precedented. Elimination reactions of this or even greater degrees of complexity are familiar in carbanion-mediated reactions. A good case in point is the cine substitution reaction of aryl halides with strong base.[23] Here a large KIE ($k_H/k_D \simeq 6$ at –30 °C)[23a] is associated with a process where the essentially irreversible formation of a well-characterized carbanion intermediate, the subsequent expulsion of the leaving group, and the attack of the nucleophile on the benzyne intermediate (all) occur via a series of transition states at comparable energy levels.[23b]

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