to reflux for 4 h. Evaporation and crystallization from dry toluene gave 87% of **10**: mp 255–260 °C; IR (Nujol) 1780 cm^{-1}; mass spectrum, *m/e* 259 (M$^+$).

Anal. Calcd for $C_{12}H_{15}O_4Cl$: C, 55.71; H, 5.80; Cl, 13.73. Found: C, 55.88; H, 5.78; Cl, 13.80.

5-Formyl-*cis,cis*-1,3,5-trimethylcyclohexane-1,3-dicarboxylic Anhydride (11). A modified Rosenmund reduction was used, following the procedure of Peters et al.[10] A slurry of Pd/C (10%, 20–30 mg) in 2 mL of acetone containing 0.1 mL of diisopropylethylamine was stirred 1 h under hydrogen. Acid chloride **10** (53 mg, 0.20 mmol) was added, and hydrogenation was continued for 2 h at 1 atm of H_2 and 25 °C. After filtration and evaporation, the residue was dissolved in ethyl acetate, and the resulting solution was washed with 1 N hydrochloric acid (3 × 10 mL) and water (4 × 10 mL). Drying and evaporation gave a solid which was recrystallized twice from toluene: 35%; mp 276–277 °C. The substance was obtained as a mixture of the free aldehyde **11** and an isomer which is assigned a cyclic 1,1-dilactone structure: IR (Nujol) 1795, 1760, 1720 cm^{-1}; mass spectrum, *m/e* 196 (M$^+$ – CO); ^{1}H NMR (250 MHz in $(CD_3)_2CO$–$CDCl_3$) δ 1.0–1.6 (m, 12 H), 2.55 (d, J = 15 Hz, 3 H), 7.57 (s, 0.6 H), 9.32 (s, 0.4 H).

Anal. Calcd for $C_{12}H_{16}O_4{\cdot}0.4H_2O$: C, 62.30; H, 7.26. Found: C, 62.23; H, 6.76.

5-Formyl-*cis,cis*-1,3,5-trimethyl-3-hydroxymethylcyclohexane-1-carboxylic Acid Lactone (8). A procedure nearly identical with that outlined above was employed with the acid chloride **7** by using a hydrogenation time of 24 h. Recrystallization of the reaction residue from water gave 60% of formyl lactone **8**: mp 156.5–158 °C; IR (Nujol) 1715 cm^{-1}; mass spectrum, *m/e* 182 (M$^+$ – CO); ^{1}H NMR ($CDCl_3$) δ 0.9–1.5 (m, 12 H), 1.80 (d, J = 17 Hz, 1 H), 2.4 (d, J = 14, 2 H), 4.0 (d, 2 H), 9.5 (s, 1 H).

Anal. Calcd for $C_{12}H_{18}O_3{\cdot}0.25H_2O$: C, 67.15; H, 8.62. Found: C, 67.20; H, 8.65.

Hydrogenation of **8** in acetic acid over platinum oxide containing a trace of ferrous chloride for 24 h at 1 atm of H_2 and 25 °C gave lactone alcohol after workup: 60%; mp 119–120 °C; IR (Nujol) 1710 cm^{-1}; mass spectrum, *m/e* 182 (M$^+$ – CH_2O); ^{1}H NMR ($CDCl_3$) δ 1.0–2.2 (m, 15 H), 3.3, 3.5 (2 d, J = 12 Hz, 2 H), 4.1 (br s, 2 H).

Determination of pK_a Values. Titration curves were determined at 25 °C with a Radiometer RTS822 automatic titration assembly with the glass electrode precalibrated against four standard buffers. All samples for titration were recrystallized twice and dried before analysis. The required *cis,cis*-1,3,5-cyclohexanetricarboxylic acid (**14**) was prepared by hydrogenation of 1,3,5-benzenetricarboxylic acid over Rh/C (5%) in water at 50 psi of H_2 for 40 h. Recrystallization from ethanol–toluene gave **14**, mp 219–220 °C (lit.[11] mp 218–219 °C). An extension of Martin's method[12] was used to obtain pK_a values from the titration curve by using pH values observed after addition of 0.5, 1.0, 1.5, 2.0, and 2.5 equiv of titrant.

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Registry No. 2, 79410-20-1; **2** (trimethyl ester), 79410-21-2; **2**·Na, 79410-22-3; **2**·2Na, 79410-23-4; **2**·3Na, 79410-24-5; **4**, 13987-76-3; **5**, 79420-96-5; **6**, 79410-25-6; **7**, 79410-26-7; **8**, 79410-27-8; **9**, 79410-28-9; **10**, 79410-29-0; **11**, 79410-30-3; **14**, 16526-68-4; **14**·3Na, 79410-31-4; **15**, 79410-32-5; 1,3,5-benzenetricarboxylic acid, 554-95-0.

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Regarding the Mechanism of the Carbonyl-Forming Elimination Reaction of Alkyl Nitrates

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The temperature dependence of k_H/k_D for the formation of benzaldehyde through base-catalyzed HNO_2 elimination from benzyl nitrate is indicative of a tunneling pathway of linear proton transfer. The same criterion applied to the uncatalyzed, gas-phase reaction reveals a cyclic transition state of nonlinear proton transfer. From these and other considerations it has been deduced that the base-catalyzed reaction is best formulated as a cyclic process of linear H transfer and is consistent with an $E_{CO}1cb$ rather than the $E_{CO}2$ mechanism previously claimed.

The base-catalyzed elimination reaction of alkyl nitrates, expressed by eq 1, has been the subject of a considerable

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

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 para substitution, and 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.

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

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 ($TS^{\ddagger}$).[5-13] This

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

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

[a] The decomposition of benzyl-α-*d* nitrate was carried out in sodium ethoxide/ethanol. After 30 min at the 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 techniques 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 reaction temperatures in this table. [c] Computed quantities: $[\Delta E_a]_D{}^H = 2.05 \pm 0.05$ kcal/mol; $A_H/A_D = 0.132 \pm 0.010$; correlation coefficient 0.9992.

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.

Results and Discussion

Base-Catalyzed Elimination of HNO_2. Benzyl-α-*d* nitrate (1) was synthesized in a sequence of reactions beginning with benzaldehyde plus $LiAlD_4$, 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, $C_6H_5CH(D) = 0$, and estimation of its deuterium content by means of the high-precision mass spectrometric 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 hydrogen transfer. The barrier width at the point of tunneling, estimated by means of a modified Bell–Caldin procedure,[12] is 1.32 Å (see Table II).

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 nitrite ion? Indeed, the putative $E_{CO}2$ mechanism is surely not acceptable when a tunneling pathway of proton transfer is shown to prevail, since an $E_{CO}2$ mechanism requires that the degree of nitrite ion departure in the TS[‡] 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.

Table II. Calculations[12] of Reaction Barrier Parameters from the Temperature Dependence of the Isotope Effect[a]

	ln (k_H/k_D)			
temp, °C	Arrhenius	quantum mechanical	difference	% difference
30	1.38 82	1.406 67	0.018 47	1.330 64
40	1.26 37	1.266 53	0.002 83	0.223 84
50	1.16 76	1.154 53	0.013 07	1.119 26
60	1.07 18	1.062 29	0.009 51	0.887 47
70	0.98 85	0.984 59	0.003 91	0.395 2

[a] Sum of variance = $\Sigma_i(\overline{x} - x_i)^2 = 0.000\,63$; E_H (classical) = 29 200 ± 10 cal/mol; E_D (classical) = 29 410 ± 10 cal/mol; E_H (quantum mechanical) = 21 800 cal/mol; $E_H(QM)/E_H(\text{classical}) = 0.747$; $E_D(\text{classical}) - E_H(\text{classical}) = 210$ cal/mol; $\Delta H°_{(\text{reaction})} = -5700 \pm 2000$ cal/mol; barrier width = 1.32 Å.

One possibility to be considered in explanation of these data is that base-catalyzed nitrate decomposition may be a cyclic process rather than the acyclic, concerted $E_{CO}2$ description previously advocated.

An argument in favor of this possibility is derived from the fact that the stronger and bulkier base, *tert*-butoxide, increases k_H/k_D,[4] presumably through increasing $[\Delta E_a]_D{}^H$ and decreasing A_H/A_D. Such facts have been previously identified [6,8,10,13] in cyclic processes as indications of a narrowing of the reaction barrier and consequent lowering of the level at which tunneling occurs, when a bulky group in the substrate is forcing together the reaction centers between which hydrogen is to be transferred linearly in a cyclic TS[‡] process. Such influences may also be regarded as an expression of the "corset" effect[19] of the *tert*-butyl group in strained, cyclic structures. Alternatively, the influence of the *tert*-butoxy group may be viewed as an example of the so-called Thorpe–Ingold scissors or gem effect[20] in cyclization processes.

On the other hand, the influence of the *tert*-butyl group in bringing about a narrowing of the barrier is not to be expected if the *tert*-butoxy anion was required to abstract the hydrogen in a direct, linear approach. Because of its great bulk (as well as greater basicity) compared to that of the ethoxy anion, the steric difficulty arising from the repulsive interactions involved in a direct encounter would logically tend to widen the barrier instead of the observed narrowing of the barrier.

Uncatalyzed Gas-Phase Thermal Elimination of HNO_2. The thermal decomposition of gaseous ethyl nitrate has been studied by Levy[21] in the temperature range of 161–201 °C under static conditions in a sealed glass bulb which emphasize biomolecular, induced decomposition and

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Table III. Temperature Independence of the Primary Hydrogen-Deuterium Isotope Effect for the Thermal Decomposition of Benzyl-α-*d* Nitrate[a]

temp, °C	$k_{\rm H}/k_{\rm D}$[b,c]	temp, °C	$k_{\rm H}/k_{\rm D}$[b,c]
217.8	1.427 ± 0.007	256.1	1.423 ± 0.009
237.9	1.404 ± 0.006	265.6	1.4335 ± 0.0002
222.5	1.404 ± 0.004	277.4	1.424 ± 0.009

[a] The pyrolysis reaction was carried out in a gold coil microreactor.[26] The substrate **1** was injected into the helium stream, and the product benzaldehyde was trapped in a capillary cooled to ~ −78 °C. The mass ratio measurements and calculations of $k_{\rm H}/k_{\rm D}$ were carried out as described in Table I. [b] See footnote *b* of Table I. Average $k_{\rm H}/k_{\rm D}$ = 1.42 ± 0.01.

wall effects. Under these circumstances it was found that a radical chain pathway prevailed which yielded very little acetaldehyde. The corresponding thermal decomposition of benzyl nitrates was not attempted. On the other hand, the uncatalyzed decomposition of benzyl nitrate at 90° in 90% aqueous ethanol has been reported[2] to produce largely (87%) benzaldehyde. Futhermore, the *p*-nitrobenzyl nitrate is decomposed to 100% aldehyde product under these conditions, while ethyl nitrate gives only 2% acetaldehyde at a rate which is only 10^{-8} as large as that of *p*-nitrobenzyl nitrate.

Against this background we undertook a study of the thermal decomposition of benzyl nitrate in the gas phase in a gold coil microreactor[22] which was designed to minimize wall-catalytic effects. Moreover, under extremely low concentrations (~10^{-6} mol/L) in a flowing (~50 mL/min) helium stream at relatively high temperatures, the reactants passing through the gold coil experienced contact with the thermostated heat source for a matter of seconds. These reaction circumstances tended to ensure a purely unimolecular mode of decomposition and minimum opportunity for radical chain reaction to occur, including the biomolecular, induced decomposition effects previously noted[21] for the ethyl nitrate thermolysis. As a confirmatory test of unimolecularity it was shown that doubling the concentration of reactant at a given flow rate of helium had no effect on the extent of reaction.

When **1** was thermolyzed under these conditions in the temperature range 218–278 °C, benzaldehyde was indeed found to be formed in good yields. The values of $k_{\rm H}/k_{\rm D}$, which were determined by mass ratio analysis[15] of the recovered benzaldehyde, proved to be nearly invariant with temperature and greater than 1.2, the highest value found for linear H transfer in model calculations carried out by Schneider and Stern[23] (see Table III). In this temperature range a reaction could conceivably give the appearance of having temperature-independent $k_{\rm H}/k_{\rm D}$ values because of a very small $[\Delta E_{\rm a}]_{\rm D}{}^{\rm H}$. However, the uncertainty inherent in these results can be expressed as follows: any temperature dependency of $k_{\rm H}/k_{\rm D}$ of greater than 50 cal/mol would have been within the limits of detectability in the range 218–278 °C in accordance with the established accuracy of the mass ratio analysis method employed. Thus, the value $k_{\rm H}/k_{\rm D}$ = 1.42 ± 0.01 is consonant with the conclusion that the mechanism of gas-phase elimination of HNO_2 from benzyl nitrate involves a cyclic mechanism of nonlinear H transfer, i.e., a bent TS‡. A close resemblance to the cis-elimination mechanism previously characterized[10] for the thermolysis of amine oxides in inert, noncoordinating solvents is therefore to be inferred, as shown in the comparison of TS‡ structures **2a** and **2b** in Figure 1.

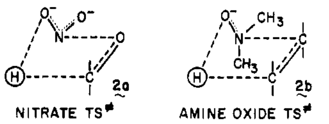

Figure 1. Comparison of nitrate and amine oxide thermolysis transition states.

Mechanism of the Base-Catalyzed Elimination of HNO_2. The argument previously advanced to support the proposed $E_{\rm CO}2$ elimination mechanism was based principally on the observations[1] of a large $k_{\rm H}/k_{\rm D}$ and a relatively large nitrogen isotope effect, k_{14}/k_{15}. The assumption made as the basis for this reasoning was that the observed isotope effects were characteristic of a synchronism[1] of hydrogen and nitrite bond breaking; i.e., in the rate-limiting step, both the C–H and O–N bonds were being broken. In other words, the respective, large values of both isotope effects were considered[1] to be indicative of a concerted process.

Since the kinetic deuterium isotope effect has now been shown to correlate with a tunneling mode of H transfer, synchronism of hydrogen and nitrite bond breaking is *not* an acceptable description of the elimination process here. Furthermore, there is abundant evidence of a very pronounced negative charge development at the benzylic carbon in the TS‡ (ρ = +3.40,[1] ρ = +3.89[3]). It must therefore be assumed that proton tunneling is responsible for this negative charge developing prior to the TS‡ for expulsion of a nitrite ion (always) at approximately the energy level at which the tunneling event occurs. In other words, the nitrite ion is "pushed off" at approximately the energy level of the carbanion generated by proton tunneling. To be even more specific as to the timing of events leading to the anionic TS‡, we must assume that the proton tunnels essentially without reversibility, since the resulting carbanion is forming at nearly the same energy level and more or less concomitantly with the "pushing off" of nitrite. We cannot envision any other reasonable circumstances under which both a proton tunneling isotope effect and a normal isotope effect for O–N bond cleavage could be observed for the same reaction.

It will be recalled that $k_{\rm H}/k_{\rm D}$ increases with increasing bulk of the alkoxide catalyst as well as with its reaction basicity (see Table IV). Since the magnitude of $k_{\rm H}/k_{\rm D}$ is inversely related to the energy level at which tunneling occurs, it will be recognized that such circumstances narrow the reaction barrier only when a cyclic mechanism of transfer is operative. Similar effects have been discussed earlier in this report as originating in the "coreset" effect,[19] which only *in a cyclic mechanism* can act to force together the reaction centers between which the hydrogen is transferred, the very factor involved in controlling barrier width.

It is also found[3] that $k_{\rm H}/k_{\rm D}$ increases directly with the positive Hammett σ value of a para substituent in benzyl nitrates. Apparently, the barrier width is narrowed by increasing electron withdrawal by the para substituent. This observation is again most readily understood if we assume a cyclic mechanism in which the centers involved in H transfer are located in the same molecule. Only under such circumstances can we picture the exercise of strong dipolar attractions between the electronegatively substituted benzene ring and the oxyanion centers of the nitrite moiety.

The finding[4] that the nitrogen isotope effect (k_{14}/k_{15}) *decreases* directly with increasing bulkiness and reaction basicity of the alkoxide catalyst and decreases, as well, with increased electron–withdrawal power of the para benzylic

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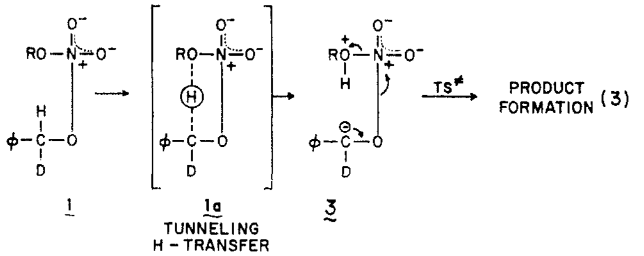
Table IV. Nitrogen and Primary Hydrogen-Deuterium Effects in the Carbonyl Elimination Reaction of Benzyl Nitrates with Base

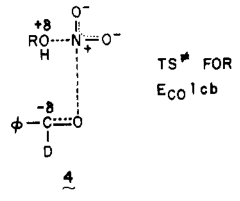
subst	ref	base/solvent	k_H/k_D[b]	k_{14}/k_{15}	% O-N bond cleavage in transition state
		Ethoxide in 90 vol %			
CH_3	3	$EtOH-H_2O$[a]	5.78 ± 0.23[e]	1.0226 ± 0.0012[e,g]	87[c]
H	3	$EtOH-H_2O$[2]	6.06 ± 0.24[e]	1.0195 ± 0.0007[e,g]	75[c]
Br	3	$EtOH-H_2O$[a]	6.40 ± 0.26[e]		
CF_3	3	$EtOH-H_2O$[a]	6.67 ± 0.27[e]	1.0160 ± 0.0005[e,g]	59[c]
NO_2	3	$EtOH-H_2O$[a]	8.12 ± 0.20[e]	1.0084 ± 0.0005[e,g]	20[c]
		Hydroxide in 40 vol %			
H	4	$EtOH-H_2O$		1.0207 ± 0.0004[f,g]	83[d]
H	4	ethoxide in EtOH	5.94 ± 0.20[f]	0.0182 ± 0.0006[f,g]	72[d]
H	4	t-BuO$^-$ in t-BuOH	6.41 ± 0.24[f]	1.0154 ± 0.0015[f]	58[d]

[a] The base solution was prepared from sodium ethoxide in ethanol by diluting with water so that the final solution was 90 vol % $EtOH-H_2O$. [b] The limits shown are the standard deviation. [c] The percent of O-N cleavage in the transition state was solved implicitly by an iteration method from the Bigeleisen expression:[30] $k_{14}/k_{15} = (M_{H*}/M_{L*})^{1/2}[1 + \Delta\mu G(\mu_{15}) - (\Delta\mu x^{1/2})]$. The percent O-N bond cleavage in the transition state = $(1 - X)\,100$ where $0 < X < 1$. $(M_{H*}/M_{L*})^{1/2} = 1.0048$ by using the cutoff approximation.[31] The O-N stretching vibration[32] of 860.6 cm^{-1} was used in evaluating the temperature-dependent term: $\Delta\mu = 7.6100 \times 10^{-2}$, $\mu_{15} = 4.1518$, and $G(\mu_{15}) = 0.275\,12$ (interpolated value).[33] [b] The Bigeleisen expression in footnote c was used in solving implicitly for the percent of O-N bond cleavage in the transition state. The following changes were required due to temperature change: $\Delta\mu = 7.3600 \times 10^{-2}$, $\mu_{15} = 4.0148$, and $G(\mu_{15}) = 0.269\,30$ (interpolated value).[33] [e] Reaction temperature 20.00 ± 0.03 °C. [f] Reaction temperature 30 °C. [g] Estimated maximum uncertainty based on the reproducibility of nitrite ion yields and rate constant values.

substituent, i.e., k_{14}/k_{15} varies inversely with k_H/k_D, requires somewhat lengthier consideration. The data in Table IV are the results of a program of calculations we have carried out on the basis of the assumption of N-O bond breaking in the TS‡. They do indeed show that the degree of bond breaking in the TS‡ diminishes with increasing electron withdrawal by the para substituent as well as with increasing bulkiness of the alkoxide catalyst. Thus, the narrower the barrier to H transfer and the lower the energy level of tunneling, the smaller the degree of N-O bond breaking in the product forming TS‡.

As deduced in the discussions above, the most attractive interpretation of all these results holds that a proton tunneling linearly between two centers in a cyclic array would leave behind a carbanion at the center with which it had lost affiliation. This is shown in eq 3 by the conversion of **1**, passing through **1a**, to **3**. In Figure 2, the solid line traces the reaction profile, indicating the shallow well of the carbanion **3** from which nitrite expulsion rises in passage over the nearly energy hill (TS‡) **4**. The narrowing of the reaction barrier, brought about by various circumstances discussed earlier, leads to a lower energy carbanion by virtue of tunneling at a lower level, as shown by the dashed-line profile in Figure 2. Such circumstances tend to bring the TS‡ for nitrite ion expulsion (as shown) closer to the reactant end of the reaction coordinate, thus lowering the degree of N-O bond breaking in the TS‡ and, consequently, diminishing k_{14}/k_{15}.





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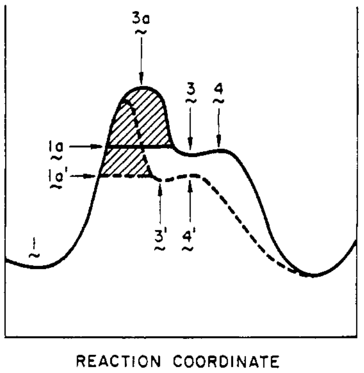

Figure 2. Reaction profile of eq 3 (where **3a** is the classical TS‡ at the top of the reaction barrier if tunneling had not occurred, **1a** is the configuration at the energy level of tunneling, and **3** is the carbanion saddle point preceding the TS‡ **4** leading to decomposition of **3**). The primed configurations, **1a′**, **3a′**, and **4′**, are the corresponding features of the reaction profile of a narrowed reaction barrier delineated by the dashed line.

Additional arguments to be considered in the interests of characterizing a cyclic TS‡ for the alkoxide-catalyzed reaction stem from the data in Table I. Not only do they confirm a tunnel correction but they also establish (since $A_H/A_D \leq 1.2$ and ≥ 0.7)[12] a linear path of H transfer between the carbon and oxygen centers in **1a**, in distinction to the uncatalyzed, gas-phase, thermal process (also) involving a cyclic but nonlinear (bent) geometry, **2b**. We should suppose that the catalytic alkoxide merely facilitates the cyclic H transfer that takes place in the uncatalyzed reaction at higher energy levels. Thus, to recapitulate what was stated earlier, the catalyst does not alter the essentially cyclic nature of the decomposition mechanism, as it would if it functioned in a direct hydrogen-abstraction step, a reaction feature rendered somewhat unlikely by the identification of a tunnel correction. The base or nucleophilic catalyst merely brings about a change in the geometry of the hydrogen-transfer step from bent to linear, rather than the profound change in mechanism that would be engendered by a conversion from the **2a** (pseudopericyclic)[25] TS‡ to the acyclic TS‡ organization of an $E_{CO}2$ process. This invocation of Ockham's razor[24] also allows for further understanding of the role of the catalyst and the manner in which it acts to lower the activation demand for reaction while bringing about the tunnel correction (as follows).

A reasonable explanation of the change from a bent to a linear TS‡ of H transfer induced by alkoxide ion catalysis derives from the fact that the oxygen centers of the nitrate are tied to their nitrogen by relatively short, dative bonds. The (uncatalyzed) planar, five-membered, cyclic TS‡ of linear H 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 a pentagonal, pseudopericyclic [25] TS‡ (**2a**). The role of the alkoxide ion catalyst therefore must entail prior coordination by the electrophilic 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 conditions, the distance of separation of C and O is exceedingly small, (ca. 1.3 Å), which creates the necessity for a tunnel correction in the subsequent H transfer.

Breslow[26] has declaimed against mechanistic decisions of Elcb character based on experimental criteria which do not clearly distinguish them from the E2 mechanism. Thornton,[27] going one step further, has developed criteria which allow one to predict the degree of bond making and breaking in an E2 TS‡, representing, in essence, a correlation of the degree of carbanion character in an E2 TS‡ with base strength. However, neither of these authors appears to have considered that the occurrence of a tunnel correction in an elimination process is a sufficient basis for the identification of an Elcb process.

The TS‡ for the analogous $E_{CO}1cb$ mechanism in the present instance (**4**) appears to be entirely consistent with the observed[1] lack of deuterium exchange, which has often troubled attempts to invoke a carbanion intermediate. Thus, it must only be assumed that the tunneling H transfer which leads to **4** establishes, more or less, the energy level at which **4** occurs. Such H transfer is therefore essentially irreversible, and the fact that it takes place in a cyclic mode also assures the exclusion of hydroxylic solvent otherwise capable of bringing about the exchange reaction. Cristol,[28] in fact, has recognized that the E1cb mechanism is favored in cyclic systems where the eliminated groups gave cis oreintations.

The mechanistic path proposed in eq 3 and illustrated by the reaction profile diagram of Figure 2 is not unprecedented. A good case in point is the ciné substitution reaction of aryl halides with strong base nucleophiles.[29] A large isotope effect ($k_H/k_D \approx 6$ at 30 °C)[29a] in this case 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 of comparable energy content. As in the alkoxide-catalyzed carbonyl-forming eliminating reaction of alkyl nitrates, we see here a nonconcerted carbanion process characterized by an isotope effect associated with irreversible H transfer, as well as a reaction TS‡ associated with C–X bond breaking.

Experimental Section

Benzyl-α-*d* alcohol was prepared from freshly distilled benzaldehyde (10 g, 0.94 mol) in anhydrous ethyl ether by reduction with 1.0 g of lithium aluminum deuteride (99%, Aldrich) in the usual manner. Gas chromatographic analysis showed only a very negligible (<0.2%) benzaldehyde peak: yield 9.5 g (95%); NMR (CCl_4) δ 7.2 (s, 5), 6.4 (m, 1), 6.25 (s, 1).

Benzyl-α-*d* chloride was prepared from 6.0 g of benzyl-α-*d* alcohol (0.055 mol) in a 50-mL flask equipped with magnetic stirring. To this was added 6.32 g 0.08 mol) dry pyridine followed by the dropwise addition of 9.5 g (0.08 mol) thionyl chloride under stirring and external cooling. After this addition was completed, the mixture was heated under reflux for 2 h, cooled, diluted with water, and extracted with ethyl ether. The ether layer was washed successively with 10% NaOH, 6 N HCl, and water to neutrality before being dried over anhydrous $MgSO_4$. The solvent was then stripped and the crude product used directly in the next step.

Benzyl-α-*d* Nitrate. To 20.0 g (0.118 mol) of $AgNO_3$ in 100 mL of dry, distilled acetonitrile (spectroscopic grade) was added a solution of the crude benzyl-α-*d* chloride (prepared as described above) in 25 mL of the same acetonitrile solvent. The mixture was allowed to stand in the dark at ambient temperature. It was then filtered to remove AgCl and the filtrate poured into ice–water. The product was extracted with two 50-mL portions of CH_2Cl_2, the combined extracts dried over $MgSO_4$, the solvent stripped in vacuo, and the residue vacuum distilled. Analysis of the distillate fractions by TLC revealed a mixture of benzyl nitrate and benzyl chloride. The pure benzyl nitrate was isolated via column chromatography on silica gel with hexane-chloroform (90:10) as the eluting solvent: IR (neat) 2150 (CD), 1600 and 1260 cm^{-1} (ONO_2).

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Registry No. Benzyl-α-*d* alcohol, 4546-45-6; benzyl-α-*d* chloride, 79449-94-8; benzyl-α-*d* nitrate, 76946-77-5.

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