from the double bond of the vinyl monomer to the radical center of PhSe·.

The addition rate constant of PhSe· for each vinyl monomer is smaller than that of PhS· by a factor of ~10–50.[11,32] The lower reactivity of PhSe· is mainly attributed to the thermodynamic stability of PhSe· since the Kk_2 value for PhSe· is smaller than that of PhS·.[11,32] The ρ^+ value of PhSe· for substituted styrenes (−0.50) is more negative than that of PhS· (−0.26);[33] the polar nature of the transition state for PhSe· is greater than that of PhS·. The contribution of the polar effect to the actual rate, however, does not surpass that of the thermodynamic stability in the reactant.

Our findings for the reactivities of PhSe· and PhS· are compatible with the fact that the Se atom is less reactive than the S atom in the addition reaction with alkenes.[34] The polarization in the transition state of the Se atom addition reaction is presumed by Callear and Tyerman.[35] The bond dissociation energy data suggest that the selenium-centered radicals are in general more stable than the sulfur-centered radicals.[36]

Experimental Section

Commercially available diphenyl diselenide was purified by recrystallization. Vinyl monomers were used after distillation at reduced pressure. Carbon tetrachloride and hexane used as solvents were of spectrophotometric grade.

The flash experiments were made at room temperature controlled at 23 ± 1 °C. The flash apparatus was of standard design; half-duration and flash energy of xenon flash lamps (Xenon Corp. N-851 C) were ca. 10 μs and 150 J, respectively. The flash light in the range of 350–450 nm was selected by the use of appropriate light filters. Kinetic observations were made with a continuous monitor light source and photomultiplier detection. The oxygen concentrations of solutions were calculated from Henry's law by dissolving oxygen under partial pressure.[37]

Acknowledgment. I thank Professor M. Matsuda and Dr. M. Miyashita of Tohoku University for many helpful suggestions during the course of this study.

Registry No. Phenylseleno radical, 84065-55-4; α-methylstyrene, 98-83-9; styrene, 100-42-5; 4-vinylpyridine, 100-43-6; methyl methacrylate, 80-62-6; methacrylonitrile, 126-98-7; acrylonitrile, 107-13-1; isobutyl vinyl ether, 109-53-5; ethyl vinyl ether, 109-92-2; vinyl acetate, 108-05-4; *m*-chlorostyrene, 2039-85-2; *p*-bromostyrene, 2039-82-9; *p*-chlorostyrene, 1073-67-2; *m*-methylstyrene, 100-80-1; *p*-methylstyrene, 622-97-9; *p*-methoxystyrene, 637-69-4.

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Enlarged Deuterium Isotope Effects in Oxyanion-Catalyzed 1,3 Proton Transfer Competing with 1,2 Elimination as a Probe of a Common Tightly Hydrogen-Bonded Intermediate

Alf Thibblin

Contribution from the Institute of Chemistry, University of Uppsala, P.O. Box 531, S-751 21 Uppsala, Sweden. Received June 14, 1982

Abstract: The reaction of 1-(2-acetoxy-2-propyl)indene (**1**-h) or 1-(2-acetoxy-2-propyl)[1,3-$^{2}H_{2}$]indene (**1**-d) with *p*-NO_2PhO^- in methanol buffered with *p*-NO_2PhOH results in base-catalyzed 1,3 proton transfer, yielding 3-(2-acetoxy-2-propyl)indene (**2**-h) and 3-(2-acetoxy-2-propyl)[1,1-$^{2}H_{2}$]indene (**2**-d), respectively, in competition with base-promoted 1,2 elimination producing 1-isopropylideneindene (**3**-h) and 1-isopropylidene[3-^{2}H]indene (**3**-d), respectively. The overall deuterium isotope effect on the reaction of **1** was measured as $(k_{12}^{H} + k_{13}^{H})/(k_{12}^{D} + k_{13}^{D}) = 5.2$, which is composed of the rearrangement isotope effect $k_{12}^{H}/k_{12}^{D} = 12.2 \pm 1.0$ and the elimination isotope effect $k_{13}^{H}/k_{13}^{D} = 3.6$. The enlarged rearrangement isotope effect shows that the intramolecularity of the 1,3 proton-transfer reaction is substantial. The intramolecularity was determined as ca. 87% for [*p*-NO_2PhOH] = 0.24 M and ca. 80% for [*p*-NO_2PhOH] = 0.71 M by analyzing the ^{2}H content of the product **2**-d. The amplified isotope effect on the 1,3-prototropic shift together with the attenuated elimination isotope effect shows that the two reactions are coupled via at least one common intermediate, which is concluded to be a tightly hydrogen-bonded complex between the protonated base and the carbanion. An increase in basicity of the oxyanion favors elimination at the expense of rearrangement. Reaction of **2**-h and **2**-d predominantly give 1,4 elimination accompanied by a trace of competing 1,3 proton transfer. The isotope effect k_{23}^{H}/k_{23}^{D} was measured to 2.5; it is small owing to a large amount of internal return.

Tightly hydrogen-bonded carbanions are rather well-known intermediates in proton-transfer reactions, at least in nonpolar solvents.[1] A hydrogen-bonded complex between the conjugate acid of the proton-abstracting base and the carbanion is formed in the reaction. This intermediate can directly provide product (which, for example, may be a tautomer), initially undergo hydrogen exchange with the solvent or another hydrogen pool, or dissociate to a solvent-equilibrated carbanion. The latter behavior was found by Cram and co-workers when studying the 1,3 deuteron transfer of (−)-3-*tert*-butyl-1-methyl[1-^{2}H]indene in MeOK/MeOH.[2] The reaction was found to be <0.5% intramolecular and gives racemic product. Similarly, Ahlberg reported that 1-(2-hydroxy-2-propyl)indene rearranges intermolecularly in MeOK/MeOD.[3]

An increase in the collapse rate relative to dissociation of the initially formed intermediate, i.e., an increase in the intramo-

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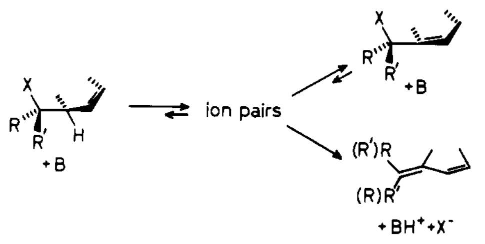
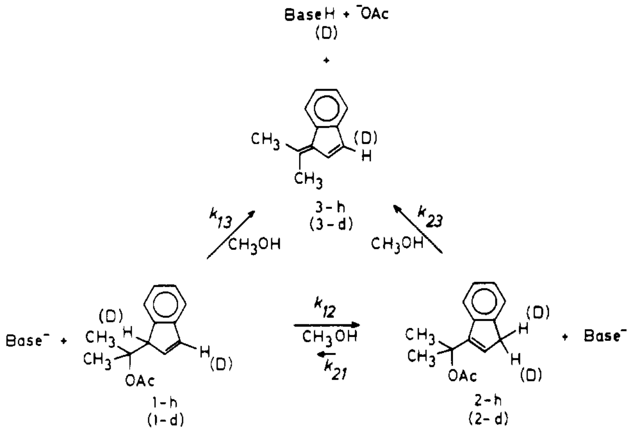
Scheme I



Scheme II



lecularity of the rearrangement, should be realized by decreasing the proton affinity of the base. Since the latter corresponds to a stronger conjugate acid, a faster reprotonation within the intermediate (i.e., to give the tautomer) would be expected.[4]

Only recently, during the last decade, has the intermediacy of tightly hydrogen-bonded carbanions in elimination reactions been discussed.[5-9] The existence of an intermediate that collapses to starting material with a rate larger or comparable to departure of the leaving group has been indicated by (i) a small kinetic deuterium isotope effect,[5-7] (ii) an anomalous temperature effect on the isotope effect,[7,9b] (iii) an anomalous temperature effect on the reaction rate,[8,9b] and (iv) a sizeable difference in kinetic chlorine isotope effect for protium- and deuterium-substituted substrates.[9]

The irreversible formation of ion pairs has been demonstrated by studying the competing reactions of elimination and 1,3 proton transfer according to Scheme I (B = tertiary amine).[6] Linear free energy relationships and observation of greatly enlarged rearrangement isotope effects coupled with attenuated elimination isotope effects for the two competing reactions constitute strong evidence that the reactions are connected via ion pairs. These reactions, which were studied in methanol, proceed via ammonium ion–indenyl anion ion pairs, leading to rearranged material with high intramolecularity.

Table I. Pseudo-First-Order Rate Constants for the Reactions of **1** and **2** in Methanol with p-NO_2PhONa[a] Buffered with p-NO_2PhOH at 30.00 ± 0.03 °C

substrate[b]	[p-NO_2PhOH], M	$10^9(k_{12}' + k_{13}')$, s^{-1}	$10^9 k_{12}'$, s^{-1}	$10^9 k_{13}'$, s^{-1}	$10^9 k_{23}'$, s^{-1}
1-h	0.245	1035	430	605	
1-d	0.245	194.7	34.2	160.5	
2-h	0.245				961
2-d	0.245				352
1-h	0.674	669.2	295.2	374.0	
1-d	0.674	126.0	25.0	101.0	
2-h	0.674				568.5
2-d	0.674				211.6

[a] 0.314 M. [b] 4.6 mM.

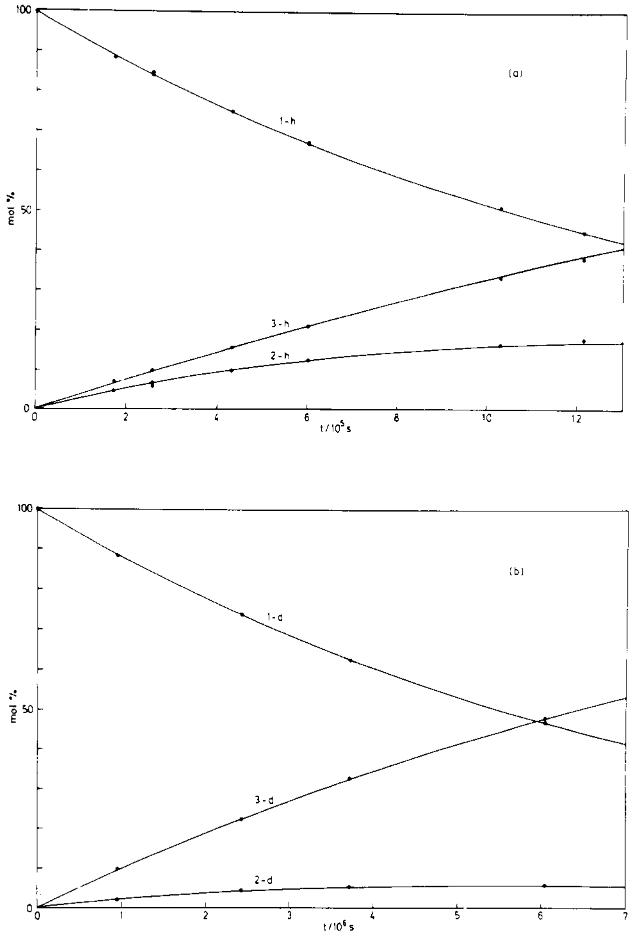


Figure 1. Time dependence of (a) **1**-h, **2**-h, and **3**-h and (b) **1**-d, **2**-d, and **3**-d in methanol with 0.314 M p-NO_2PhO^- buffered with 0.674 M p-NO_2PhOH at 30.00 ± 0.03 °C. The curves shown are computer simulated, and the points are the experimentally measured concentrations. Similar curves were obtained with 0.245 M p-NO_2PhOH.

The present work, which has employed the system of Scheme II and oxyanion bases, deals with the following questions: (i) Are the reactions coupled via a common tightly hydrogen-bonded intermediate of the type ArOH·C⁻? (ii) Is the 1,3 proton-transfer reaction intramolecular even with this type of base; i.e., how important is the role of electrostatic attraction in the ion pair to the intramolecularity? (iii) What is the relationship between base strength and intramolecularity?

Results

Reactions with p-NO_2PhO^-. The reaction of 1-(2-acetoxy-2-propyl)indene (**1**-h) with p-NO_2PhO^- in methanol in the presence

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Table II. Isotope Effects on the Pseudo-First-Order Rate Constants of Table I

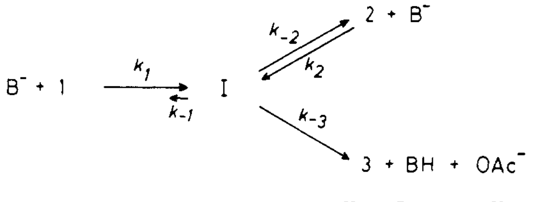
[p-NO_2PhOH], M	$\frac{(k_{12}' + k_{13}')^H}{(k_{12}' + k_{13}')^D}$	$\frac{(k_{12}')^H}{(k_{12}')^D}$	$\frac{(k_{13}')^H}{(k_{13}')^D}$	$\frac{(k_{23}')^H}{(k_{23}')^D}$
0.245	5.3 ± 0.2	12.6 ± 1.0	3.8 ± 0.2	2.7 ± 0.2
0.674	5.3 ± 0.2	11.8 ± 1.0	3.7 ± 0.2	2.7 ± 0.2

Table III. Approximative Second-Order Rate Constants and Isotope Effects for the Reactions of **1** and **2** with p-NO_2PhO^- with $K_{assoc} = 2.1$

substrate	$10^6 (k_{12} + k_{13})$, M^{-1} s^{-1}		$10^6 k_{12}$, M^{-1} s^{-1}		$10^6 k_{13}$, M^{-1} s^{-1}		$10^6 k_{23}$, M^{-1} s^{-1}	
1-h, **2**-h	4.0	5.2	1.8	12.2 ± 1.0^a	2.2	3.6	3.2	2.5
1-d, **2**-d	0.77		0.15		0.62		1.3	

^{a} The average value of $(k_{12}')^H/(k_{12}')^D$, cf. Table II.

Scheme III



of the conjugate acid (p-NO_2PhOH) provides the products 3-(2-acetoxy-2-propyl)indene (**2**-h) and 1-isopropylideneindene (**3**-h, Scheme II), the latter being the only product after long reaction time. The kinetics of the reaction of **1** as well as of **2** were studied by a calibrated sampling-quench high-performance liquid chromatography procedure (Table I and Figure 1). Relative to **1**-h, the corresponding [1,3-$^2H_2$] analogue **1**-d gives much less rearrangement under the same conditions, with only a small amount of 3-(2-acetoxy-2-propyl)[1,1-$^2H_2$]indene (**2**-d) being produced and 1-isopropylidene[3-^{2}H]indene (**3**-d) being the dominant product (Scheme II and Figure 1b). When **2**-h is the substrate, the main product is **3**-h; i.e., **1**-h is produced in a maximum concentration of <1 mol %. The amount of rearrangement obtained from **2**-d is even smaller.

The reactions follow the rate laws 1–3:

$$\frac{d[\mathbf{1}]}{dt} = -(k_{12}[ArO^-] + k_{13}[ArO^-] + k_{13}^{MeO}[MeO^-])[\mathbf{1}] + k_{21}[ArO^-][\mathbf{2}] = -(k_{12}' + k_{13}')[\mathbf{1}] + k_{21}'[\mathbf{2}] \quad (1)$$

$$\frac{d[\mathbf{2}]}{dt} = k_{12}[ArO^-][\mathbf{1}] - (k_{21}[ArO^-] + k_{23}[ArO^-] + k_{23}^{MeO}[MeO^-])[\mathbf{2}] = k_{12}'[\mathbf{1}] - (k_{21}' + k_{23}')[\mathbf{2}] \quad (2)$$

$$\frac{d[\mathbf{3}]}{dt} = (k_{13}[ArO^-] + k_{13}^{MeO}[MeO^-])[\mathbf{1}] + (k_{23}[ArO^-] + k_{23}^{MeO}[MeO^-])[\mathbf{2}] = k_{13}'[\mathbf{1}] + k_{23}'[\mathbf{2}] \quad (3)$$

The tautomeric equilibrium constant has been determined to be $[\mathbf{2}\text{-h}]_{eq}/[\mathbf{1}\text{-h}]_{eq} = 19.9 \pm 2.0$ at 30.00 ± 0.03 °C.[6f]

The concentration of added acid has to be rather high to suppress reaction with methoxide ion. The reported[10] pK_a of p-NO_2PhOH in methanol is 11.50, and that of MeOH 18.31, which gives the following equilibrium at low concentrations:

$$\frac{[ArOH][MeO^-]}{[ArO^-]} = 10^{-5.42} \quad (4)$$

The high concentration of buffer acid, however, introduces another problem, buffer association, as described by the equilibrium

$$ArOH + ArO^- \xrightleftharpoons{K_{assoc}} ArO^-{\cdot}HOAr \quad (5)$$

The value of K_{assoc} is estimated from the kinetics as 2.1 M^{-1}. It is concluded that the rate decrease at high concentration of ArOH is not due to a specific solvent effect since addition of $PhOCH_3$ does not affect the rate of the PhO^--promoted reaction.

The pseudo-first-order rate constants were determined by a simple computer simulation of the reactions (Figure 1) to yield the values recorded in Tables I and II. Since methoxide ion does not give any rearrangement, only elimination, the rate constants k_{12}' and k_{21}' refer to the p-nitrophenoxide-catalyzed reactions, while k_{13}' and k_{23}' include a small contribution from the methoxide-promoted elimination (eq 1–3). The ratios of k_{12}'/k_{13}' (Table I) at the two different acid concentrations are nearly equal, which shows that the contribution from $k^{MeO}[MeO^-]$ must be very small and, thus, that nearly all the elimination is derived from the ArO^--promoted reaction. The second-order rate constants are collected in Table III. Since the rearrangement reaction is affected solely by ArO^- (cf. eq 1–3), $k_{12}^H/k_{12}^D = (k_{12}')^H/(k_{12}')^D$.

The amount of protium incorporation in the tautomeric product was determined at buffer acid concentrations of 0.24 and 0.71 M, respectively; otherwise similar concentrations as in the kinetics runs were used. After the reaction was 15–23% completed, product **2** was separated from the starting material (**1**-d) and elimination product (**3**-d) and was analyzed by mass spectrometry. The incorporation of ^{1}H was determined as 13 and 20 atom %, respectively, the lower value referring to the experiment with the lower concentration of ArOH.

Reactions with PhO⁻. The stronger base PhO^- (pK_a = 14.46 in MeOH)[10] provides much less rearrangement. However, it is difficult to avoid the methoxide-promoted elimination in this case since the equilibrium constant (eq 6)[11] is so large that even a

$$K' = \frac{[PhOH][MeO^-]}{[PhO^-]} = 10^{-2.6} \quad (6)$$

concentration of 1.54 M in PhOH is not high enough to reduce $[MeO^-]$ to a kinetically insignificant level in a 0.287 M base solution. During these conditions, the maximum concentration of **2** is ca. 1% and <0.1% when starting from **1**-h and **1**-d, respectively.

An approximative rate constant $k_{12} + k_{13}$ (eq 1) can be obtained as the intercept from a plot of $k_1^{obsd}/[base]$ vs. 1/[PhOH]. Such a plot is curved, probably owing to buffer association effects. However, a linear regression using the concentration interval 0.08–0.2 M of phenol yielded $k_{12}^H + k_{13}^H = 1.1 \times 10^{-4}$ M^{-1} s^{-1} at 30.00 ± 0.03 °C. The slope of the plot gave pK' = 2.7.

Discussion

Mechanistic Implications of the Enlarged Isotope Effect k_{12}^H/k_{12}^D. The substantial isotope effect (5.2) measured for the total reaction of **1** with p-NO_2PhO^- and the unusually large isotope effect for the rearrangement reaction (k_{12}^H/k_{12}^D = 12.2) is plausibly interpretable in two different ways. One is that the rearrangement and elimination are separate reactions and that considerable proton tunneling contributes to the rate of the 1,3 proton-transfer reaction. The other alternative is a mechanism involving a common tightly hydrogen-bonded intermediate for the rearrangement and elimination (Scheme III). Evidence for the latter mechanism, e.g., linear free energy relationships and extreme deuterium isotope effects, has been reported for the present system using uncharged bases (tertiary amines).[6] Considerable tunneling was excluded by studies of a closely related model compound.[6f]

The consistency of the present results with the tightly hydrogen-bonded mechanism (Scheme III) is shown in the following. Application of the steady-state approximation yields eq 7–12,

$$k_{12} = k_1 \frac{k_{-2}}{k_{-1} + k_{-2} + k_{-3}} \quad (7)$$

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$$k_{13} = k_1 \frac{k_{-3}}{k_{-1} + k_{-2} + k_{-3}} \tag{8}$$

$$k_{23} = k_2 \frac{k_{-3}}{k_{-1} + k_{-2} + k_{-3}} \tag{9}$$

$$\frac{k_{12}{}^{\mathrm{H}}}{k_{12}{}^{\mathrm{D}}} = \frac{k_1{}^{\mathrm{H}}}{k_1{}^{\mathrm{D}}} \frac{k_{-2}{}^{\mathrm{H}}}{k_{-2}{}^{\mathrm{D}}} \frac{k_{-1}{}^{\mathrm{D}} + k_{-2}{}^{\mathrm{D}} + k_{-3}{}^{\mathrm{D}}}{k_{-1}{}^{\mathrm{H}} + k_{-2}{}^{\mathrm{H}} + k_{-3}{}^{\mathrm{H}}} \tag{10}$$

$$\frac{k_{13}{}^{\mathrm{H}}}{k_{13}{}^{\mathrm{D}}} = \frac{k_1{}^{\mathrm{H}}}{k_1{}^{\mathrm{D}}} \frac{k_{-3}{}^{\mathrm{H}}}{k_{-3}{}^{\mathrm{D}}} \frac{k_{-1}{}^{\mathrm{D}} + k_{-2}{}^{\mathrm{D}} + k_{-3}{}^{\mathrm{D}}}{k_{-1}{}^{\mathrm{H}} + k_{-2}{}^{\mathrm{H}} + k_{-3}{}^{\mathrm{H}}} \tag{11}$$

$$\frac{k_{23}{}^{\mathrm{H}}}{k_{23}{}^{\mathrm{D}}} = \frac{k_2{}^{\mathrm{H}}}{k_2{}^{\mathrm{D}}} \frac{k_{-3}{}^{\mathrm{H}}}{k_{-3}{}^{\mathrm{D}}} \frac{k_{-1}{}^{\mathrm{D}} + k_{-2}{}^{\mathrm{D}} + k_{-3}{}^{\mathrm{D}}}{k_{-1}{}^{\mathrm{H}} + k_{-2}{}^{\mathrm{H}} + k_{-3}{}^{\mathrm{H}}} \tag{12}$$

which relate the phenomenological and microscopic rate constants and isotope effects. As discussed in detail before,[6f,g] the isotope effect on k_{-3} is expected to be ca. 1 since the breaking of the carbon–hydrogen bond is largely completed upon formation of the hydrogen-bonded intermediate. On the other hand, k_1, k_2, k_{-1}, and k_{-2} all involve breaking or formation of carbon–hydrogen bonds and are expected to give normal isotope effects since carbon–hydrogen bonds in substrates having pK_a values close to another are broken or formed in these processes.[12] The implication of this reasoning is that the rearrangement isotope effect $k_{12}{}^{\mathrm{H}}/k_{12}{}^{\mathrm{D}}$ is equal to the ionization isotope effect $k_1{}^{\mathrm{H}}/k_1{}^{\mathrm{D}}$ multiplied by a factor larger than unity (eq 10). The competition between the elimination and the collapse of the tightly hydrogen-bonded intermediate to rearrangement product, which follows rate-limiting ionization, is thus the cause of the amplified rearrangement isotope effect. On the other hand, the isotope effects on the 1,2 and 1,4 elimination reactions are attenuated by multiplication of the ionization isotope effects by factors less than unity (eq 11 and 12) in accord with the experiments.[13]

The degree of amplification is determined by the relative amount of elimination. A small fraction of elimination ($k_{-2} \gg k_{-3}$) gives rise to a normal rearrangement isotope effect but a large attenuation of the elimination isotope effect. On the other hand, an enhanced fraction of elimination increases the amplification of the rearrangement isotope effect; the elimination isotope effect increases up to its maximum value, which equals the ionization isotope effect.

Reversibility of the ionization process has an attenuating effect on both the rearrangement and the elimination isotope effect. The following relationship can be derived from eq 8 and 9: $k_1{}^{\mathrm{H}}/k_1{}^{\mathrm{D}} \geq (k_{12}{}^{\mathrm{H}} + k_{13}{}^{\mathrm{H}})/(k_{12}{}^{\mathrm{D}} + k_{13}{}^{\mathrm{D}})$. The equality holds for irreversible ionization. The experimental value 5.2 for $(k_{12}{}^{\mathrm{H}} + k_{13}{}^{\mathrm{H}})/(k_{12}{}^{\mathrm{D}} + k_{13}{}^{\mathrm{D}})$ obtained with p-NO_2PhO^- is smaller than that obtained with MeO^- (6.5)[6d] and with, e.g., quinuclidine (Q) (7.1).[6f] The latter base has about the same thermodynamic basicity as p-NO_2PhO^- (Table IV). It is likely that the difference in ionization isotope effect with MeO^- and ArO^- is caused by a small amount of internal return and not to asymmetry of the transition state for proton transfer.[14]

Is the Ionization Assisted by Uncharged Bases? A Brønsted plot for the total reaction rate of **1**-h with MeO^-, PhO^-, and p-NO_2PhO^- has the slope $\beta = 0.53$, which is consistent with the large ionization isotope effects and implies an approximately half-transferred proton. The rate data for diazabicyclooctane (Dabco) and Q gives $\beta \approx 0.43$. It is not possible to include pyridine in the latter plot since the ionization is not irreversible with this base. As shown in Table IV, the nitrogen bases Dabco and Q react much faster than could be expected from their basicities (a factor of about 1600). This kinetic difference between the oxygen and nitrogen bases is likely caused, to some extent, by electrostatic stabilization of the rate-limiting ionization transition state by the development of positive charge on the proton-abstracting nitrogen of the amine. Solvation differences may also be of importance.[15] Moreover, it is possible that the "effective" size of the oxyanions is larger than that of the amines and therefore gives rise to steric hindrance to proton abstraction, which may account for a minor part of the rate difference.

Table IV. Rate Constants of Reaction of **1**-h with Some Tertiary Amines and Oxyanions in Methanol at 30 °C

base	pK_a	$10^6(k_{12} + k_{13})$, $M^{-1}\ s^{-1}$	k_{12}/k_{13}
pyridine	5.17[a]	0.573	14
Dabco[b]	9.22[c]	1060/2	5
Q[b]	11.45[c]	6290	1.3
p-NO_2PhO^-	11.50[d]	4.03	0.8
PhO^-	14.46[d]	112	≈0.04[e]
MeO^-	18.31[d]	16 000	<0.01

[a] In water, ref 18. [b] A factor of 2.5 has been used to convert the rate constants from 20 to 30 °C. [c] In water, ionic strength 1.0 M, ref 19. In *methanol*, the measured "pH" of a 0.07 M buffer solution with $[QH^+]/[Q] = 1$ was 0.04 "pH" unit higher than that of a similar buffer solution of p-NO_2PhOH. [d] Reference 10. [e] At [PhOH] = 1.54 M.

The basicity of the proton-abstracting base determines the ratio k_{12}/k_{13} (Table IV). Q and p-NO_2PhO^-, which have about the same thermodynamic basicity, yield similar ratios. As found in the reaction with MeO^-, because of the low acid strength of methanol, protonation to give rearrangement product does not compete successfully with departure of the leaving group. Severe steric hindrance also seems to increase the proportion of elimination,[6f,16] probably due to decreased stabilization of the intermediate complex.

Strength of the Hydrogen Bond. Ahlberg[3] and Cram[2] have reported that indenes undergo intermolecular 1,3 proton transfer in methanol. However, with tertiary amines as catalysts, the reaction is intramolecular.[6] Thus we have found, e.g., that **1** reacts with quinuclidine (Q) to give competing elimination and rearrangement at low buffer concentration with a rearrangement isotope effect of $k_{12}{}^{\mathrm{H}}/k_{12}{}^{\mathrm{D}} = 18.1 \pm 1.1$ and with an incorporation in the olefin **3**-d at "infinity" of 1 ± 4 atom % H.[6f]

The amplified rearrangement isotope effect of 12 found in this work shows that the intramolecularity must be high. This is confirmed by the mass spectrometric analyses. Somewhat more incorporation of protium was obtained with the higher concentration of the buffer acid, which is consistent with the somewhat smaller rearrangement isotope effect (Table II). Some incorporation (in **3**) has also been found with tertiary amines at high buffer–acid concentration.[6f]

The strength of the hydrogen bond in the tightly hydrogen-bonded carbanion intermediate is expected to be dependent on the acidity of the conjugate acid of the proton-abstracting base. Thus, decreasing the pK_a lowers the energy of the intermediate and may cause the lifetime to increase. However, the reprotonation (collapse) rate increases simultaneously, which has an opposite effect on the lifetime.

Kresge et al. have concluded that a tightly hydrogen-bonded intermediate is formed in the first step in the hydrogen-exchange reaction of phenylacetylene in water catalyzed by amines or hydroxide ion.[1c] The conclusion was based upon a kinetic deuterium isotope effect of 1 and a Brønsted plot with unit slope. The slow step of the reaction is thus breakage of the hydrogen bond followed by diffusion or rotation of a new hydrogen into hydrogen-bonding position. The final step, reprotonation of the carbanion, appears to be encounter controlled consistent with the localized electron

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(12) Owing to a secondary effect (**2**-d is dideuterated), $k_2{}^{\mathrm{H}}/k_2{}^{\mathrm{D}}$ should be somewhat larger than $k_1{}^{\mathrm{H}}/k_1{}^{\mathrm{D}}$. Accordingly, $k_{-2}{}^{\mathrm{H}}/k_{-2}{}^{\mathrm{D}}$ is expected to be somewhat smaller than $k_{-1}{}^{\mathrm{H}}/k_{-1}{}^{\mathrm{D}}$. Cf.: Alder, R. W.; Baker, R.; Brown, J. M. "Mechanism in Organic Chemistry"; Wiley-Interscience: New York, 1971; pp 18–20.

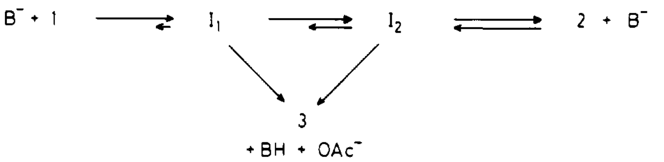
(13) Competition as the cause of extreme isotope effects has been generalized in ref 6g.

(14) (a) Melander, L. "Isotope Effects on Reaction Rates"; Ronald Press: New York, 1960; pp 24–32. (b) Westheimer, F. H. *Chem. Rev.* **1961**, *61*, 265–273.

(15) However, no significant difference between oxyanions and quinuclidines was found for an E1cB reaction with quinuclidinium ion as leaving group in H_2O/Me_2SO. Cf.: Gandler, J. R.; Jencks, W. P. *J. Am. Chem: Soc.* **1982**, *104*, 1937–1951.

(16) Thibblin, A., unpublished results.

Scheme IV



pair on the carbon. This localized charge is the cause of the strong hydrogen bond.

The present work shows that the charge on the carbanion does not need to be completely localized to give rise to a hydrogen bond of significant strength. The results seem to be the first evidence in a polar medium for a carbanion hydrogen bonded to an oxygen acid other than the one that originates from the conjugate base of the protic solvent.

Two-Intermediate Mechanism. The results suggest, after closer inspection of the data, that the rearrangement reaction proceeds via two tightly hydrogen-bonded intermediates (I_1 and I_2 in Scheme IV) that are *not* in equilibrium with each other; both give rise to elimination product. This is concluded from the fact that I_1, which is formed from **1**-h, gives about 55% of **3**-h, while I_2 collapses back to **2**-h with a rate faster than it eliminates, which is shown by the small isotope effect on the reaction of **2**.

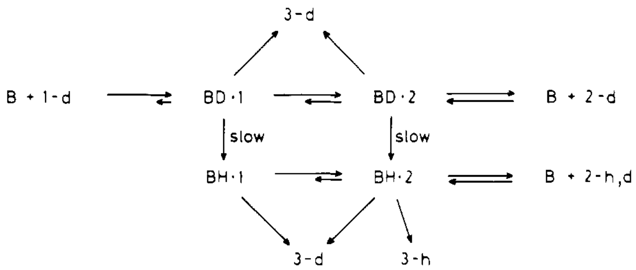
Another way to come to the same conclusion is to look at the ionization isotope effects. The one-intermediate mechanism (Scheme III) yields $(k_1^H/k_1^D)/(k_2^H/k_2^D) = (k_{13}^H/k_{13}^D)/(k_{23}^H/k_{23}^D) \approx 1.4$, which is higher than the expected value of 0.9. This anomaly can be removed by the two-intermediate mechanism. The ratio 0.9 was found in the irreversible E1cB reactions of **1** and **2** with NaOMe since the isotope effects were measured to $k_{13}^H/k_{13}^D = 6.5$ and $k_{23}^H/k_{23}^D = 7.6$.[6d,e] A value lower than unity is in accord with isotope effect theory.[12]

It seems reasonable that the two intermediates have the acid tightly hydrogen bonded to C1 and C3, respectively. We have previously concluded, on similar grounds, that the corresponding reactions with tertiary amines proceed in accord with Scheme IV.[6f] As long as the tightly hydrogen-bonded intermediates are in equilibrium with each other, the one-intermediate mechanism (Scheme III) is kinetically indistinguishable from the Scheme IV mechanism.

When I_1 is converted to I_2, the hydrogen bond to C1 is broken and the acid forms a new hydrogen bond to C2. In addition to stabilization by hydrogen bonding, the intermediates are plausibly stabilized electrostatically by interaction between a positively charged acid and the carbanion that increases the barrier to dissociation into "free" ions.[17] Hydrogen bonding to Q and p-NO_2PhO^- should be of similar strength since the basicities in methanol are about the same. Therefore, based upon the measured high intramolecularity with these two bases and the low one with methoxide, it is concluded that the dominant factor determining the stability of the intermediates toward dissociation is the pK_a of the catalyst.

In accord with the above conclusion, the term "E1cB ion-pair" mechanism might be somewhat confusing. Since hydrogen bonding is reasonably the dominant stabilizing factor for the intermediate in most reactions of E1cB ion-pair type, it is suggested that "E1cB-HBA" (a name first coined by Schlosser[5g] for lyate-promoted eliminations) is used as a collective name for elimination reaction mechanisms where a tightly hydrogen-bonded carbanion is formed, reversibly or irreversibly, and where the hydrogen-bonded acid (HBA) originates from the lyate ion or from another base, charged or uncharged.

Scheme V



Scheme V, where **2**-h,d represents 3-(2-acetoxy-2-propyl)[1-^{2}H]indene, seems to be the simplest mechanistic scheme that describes all experimental results with amine and oxyanion bases. The steps that are denoted as slow reasonably represent exchange of one acid molecule for another, not just exchange of the isotopic atoms. Some participation of a solvent-equilibrated carbanion is likely but not required to account for the results. However, it is also possible that a significant amount of a solvent-equilibrated carbanion is formed that mainly eliminates and only to a small extent is trapped by the buffer acid ArOH to provide **2**-h,d.

Work is in progress in this laboratory on the question of mechanism of the elimination from the tightly hydrogen-bonded carbanions. Is the elimination a one-step process and/or does the intermediate complex dissociate before departure of the leaving group?

Experimental Section

General Procedures. The ^{1}H NMR analyses were made with a JEOL FX 100 spectrometer equipped with a 5-mm dual probe (^{1}H, ^{13}C). The high-performance liquid chromatography analyses were carried out with a Hewlett Packard 1084B liquid chromatograph on a C8 reversed-phase column (4.6 × 130 mm). The mobile phase was a solution of 46 vol % ethanol in water. The kinetic runs were performed at constant temperature in a HETO 01 PT 623 thermostat. The temperature was measured with a calibrated mercury thermometer with an absolute accuracy of ±0.02 °C. Since the temperature of the bath did not deviate more than 0.01 °C from the average value, the absolute temperature was 20.00 ± 0.03 °C.

Materials. Methanol (Fluka for UV spectroscopy) stored over 0.3-nm molecular sieves was used as solvent without further purification. A stock solution of NaOMe was prepared by adding pure-cut pieces of sodium to methanol. The concentration was determined by titration of aliquots of this stock solution with 0.1 M HCl. Phenol (Merck p a) was distilled in a nitrogen atmosphere from Zn powder through a Vigreux column. The center cut was used to prepare reaction solutions by mixing appropriate amounts of phenol with NaOMe solution and methanol. Purification of p-NO_2PhOH was carried out by repeated recrystallization from toluene; mp 114.5–115 °C. The syntheses, purification, and deuterium content of the substrates have been reported previously.[6f] The purity was checked with HPLC.

Kinetics. A reaction flask equipped with a tight TFE septum was filled with 5 mL of base solution. After thermostating, 4 μL of pure **1** or 20 μL of a concentrated solution of **2** was injected with a syringe. During the run, aliquots (400 μL) were withdrawn with a syringe and rapidly transferred to a centrifuge tube containing 50 mL of ice–water and 200 μL of CH_3CCl_3. The mixture was shaken and centrifuged. The organic layer was transferred to a 1-mL vessel containing 500 μL of ethanol. This mixture was then analyzed by HPLC. The areas under the separated peaks of **1**, **2**, and **3** together with the relative extinction coefficients (response factors), which were determined by using several standard mixtures of **1**, **2**, and **3** prepared by weighing, gave the composition in mol %. A data point in Figure 1 is the average of data from three different injections from the same quench solution.

When studying the slow reactions with p-NO_2PhO^-, the reaction solution was distributed into small ampules, which were opened, diluted with ice–water, etc., and analyzed as above.

Search for D–H Exchange. The reaction of **1**-d was run in an ampule for 15 days at 30 °C (15 and 23% reaction, respectively). The concentrations at the beginning of the reaction were 0.01 M **1**-d, 0.329 M p-NO_2PhO^-, and 0.241 M or 0.713 M p-NO_2PhOH. The reaction mixture (10 mL) was quenched in the usual way and separated on a semipreparative C8 column (8 × 250 mm). The separated rearrangement product (**2**) was extracted from the ethanol–water solvent with carbon tetrachloride (spectrograde), concentrated by blowing a stream of dry nitrogen through the extract, and analyzed by mass spectroscopy

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(17) Association constants for singly charged ions in methanol are not large (e.g., K_{assoc} for $KClO_4$ is 11 at 25 °C), which means that, if hydrogen bonding is not considered, the ion-pair complex between the carbanion and the quinuclidinium ion (at a concentration of 0.002 M) is *destabilized* compared with the solvent equilibrated ions. Cf.: Conti, F.; Pistoia, G. *J. Phys. Chem.* **1968**, *72*, 2245–2248.

(18) Fasman, G. D., Ed. "Handbook of Biochemistry and Molecular Biology", 3rd ed.; CRC Press: Cleveland, OH, 1976; Vol. I, p 338.

(19) Alunni, S.; Jencks, W. P. *J. Am. Chem. Soc.* **1980**, *102*, 2052–2060.

(20 eV). The peak heights with m/e 217 and 218 were compared. In a control experiment, a mixture of **2**-h and **2**-d was analyzed on the mass spectrometer for the parent peaks m/e 216 and 218. The measured composition, after correction for the small natural abundance of m/e 218 in **2**-h, agreed with the correct value.

Evaluation of Rate Constants and Estimation of Errors. The rate constants of the reactions were evaluated by using a combination of manual treatment, which gave approximative values of $k_{12}' + k_{13}'$ and k_{23}' from plots of ln (mol % starting material) vs. time, and computer simulation. The latter method has been described in detail previously.[6f,g] When starting from pure **1**, the concentrations of **1**, **2**, and **3** are described by the following equations:

$$\text{mol \% } \mathbf{1} = ae^{-m_1t} + (100 - a)e^{-m_2t} \qquad \text{mol \% } \mathbf{2} = be^{-m_1t} - be^{-m_2t}$$

$$\text{mol \% } \mathbf{3} = 100 + ce^{-m_1t} - (100 + c)e^{-m_2t}$$

where

$$a = 100(k_{12}' + k_{13}' - m_2)/(m_1 - m_2)$$

$$b = 100k_{12}'/(m_2 - m_1)$$

$$m_1 = [(k_{12}' + k_{13}' + k_{21}' + k_{23}')^2/4 - k_{12}'k_{23}' - (k_{21}' + k_{23}')k_{13}']^{1/2} + \frac{1}{2}(k_{12}' + k_{13}' + k_{21}' + k_{23}')$$

$$m_2 = -[(k_{12}' + k_{13}' + k_{21}' + k_{23}')^2/4 - k_{12}k_{23} - (k_{21}' + k_{23}')k_{13}']^{1/2} + \frac{1}{2}(k_{12}' + k_{13}' + k_{21}' + k_{23}')$$

All estimated errors are considered to be maximum errors derived from maximum systematic errors and random errors. The maximum errors of the directly measured quantities were thus allowed to propagate as systematic errors into derived quantities, e.g., isotope effects.

Acknowledgment. I am indebted to Professor Heinz Koch for providing me with a preprint of ref 9b and to Professor Per Ahlberg for helpful discussions. The Swedish Natural Science Research Council has financially supported this work.

Registry No. **1**-h, 42271-88-5; **2**-h, 42447-90-5; D_2, 7782-39-0; p-NO_2PhO^-, 14609-74-6; PhO^-, 3229-70-7; MeO^-, 3315-60-4; Dabco, 280-57-9; Q, 100-76-5; pyridine, 110-86-1.

Low-Temperature and Time-Resolved Absorption Spectral Studies on the *sp*- and *ap*-2-(9-Fluorenyl)phenylnitrenes Generated from 1-Azatriptycene and 2-(9-Fluorenyl)phenyl Azide

Tadashi Sugawara, Nobuaki Nakashima, Keitaro Yoshihara, and Hiizu Iwamura*

Contribution from the Institute for Molecular Science, Myodaiji, Okazaki 444, Japan.

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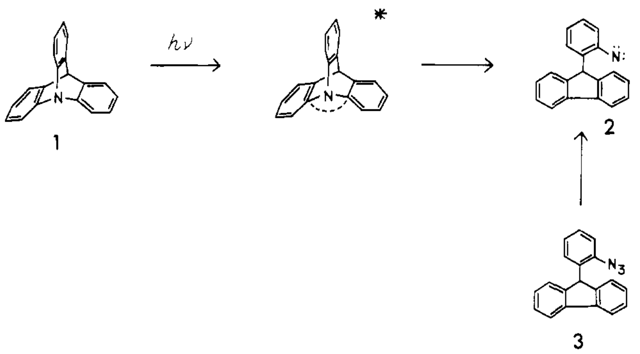
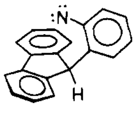
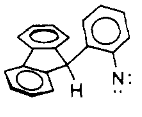
Abstract: Mechanistic details of the photorearrangement of 1-azatriptycene (**1**) have been disclosed by absorption spectroscopic studies on the irradiation of **1** and *o*- and *p*-(9-fluorenyl)phenyl azides (**3** and **4**). At 77 K, **1** developed on irradiation absorption peaks at 290, 302, and 340 nm, while **3** gave strong absorptions at 290, 302, and 314 nm, weak ones at 367 and 384 nm, and a broad band at 507 nm. By comparison with those of **4** and phenylnitrene in the literature, most of the absorptions were found to be due to *o*-(9-fluorenyl)phenylnitrene (**2**) except those at 340 nm from **1** and 507 nm from **3**. These were assigned to azanorcaradiene (**8**), which was presumed to be formed via the singlet **2** and could be considered a key intermediate for a number of the reaction products, and to quinone imine methide (**6**), respectively. The transient absorption spectra at room temperature were obtained after delay times of 100 and 450 ns. The time trace of the absorption intensities at 340 nm showed that **8** was formed by the sum of two kinetic processes with the rate constants of 4×10^6 and 1×10^6 s^{-1}. Addition of xenon (1.4 atm) suppressed the formation of **8**, while that of triplet **2** was kept almost constant. Combined with the observed rate of disappearance (1.2×10^8 s^{-1}) of **1**, a mechanistic scheme is proposed in which the singlet nitrene **2** is in equilibrium with the closed-shell valence isomer. An additional species should intervene before **8** is formed.

Contrary to the expected di-π-methane rearrangement[1] and the once postulated one-bond cleavage of the C–N bond,[2] 1-azatriptycene (**1**) undergoes photorearrangement in which direct bonding between two of the three benzene rings takes place with expulsion of the bridgehead nitrogen as a monocentric diradical species.[3] The intermediacy of this *o*-(9-fluorenyl)phenylnitrene (**2**) was indicated by the formation of the azepine derivatives and verified unambiguously by the detection of **2** in the triplet state by ESR spectra in matrices at 4 K. Nitrene **2** was independently generated by the photolysis of *o*-(9-fluorenyl)phenyl azide (**3**) in order to confirm the assignment. The observed field positions of **2** in ESR spectra derived from **1** and **3** were 6820 and 6837 G, respectively, showing the presence of slightly different conformations of **2**. Nitrene **2a** from **1** was considered to be in the *ap* conformation, while nitrene **2b** from **3** in the sp conformation, and the interconversion between them could be frozen out in matrices at a cryogenic temperature.[4] A slight difference in the product





2a



2b

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(1) (a) Hixson, S. S.; Mariano, P. S.; Zimmerman, H. E. *Chem. Rev.* **1973**, *73*, 531. (b) Zimmerman, H. E.; Viriot-Villaume, M.-L. *J. Am. Chem. Soc.* **1973**, *95*, 1274. (c) Zimmerman, H. E.; Amick, D. R. *Ibid.* **1973**, *95*, 3977. (d) Zimmerman, H. E.; Amick, D. R.; Hemetsberger, H. *Ibid.* **1973**, *95*, 4606.

(2) Wittig, G.; Steinhoff, G. *Liebigs Ann. Chem.* **1964**, *676*, 21.

(3) Sugawara, T.; Iwamura, H. *J. Am. Chem. Soc.* **1980**, *102*, 7134.

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