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ION–MOLECULE PAIRS AS INTERMEDIATES IN SOLVOLYSIS. CATALYSIS BY THE PYRIDINE LEAVING GROUP ON THE ELIMINATION REACTION

ALF THIBBLIN* AND HARVINDER SIDHU

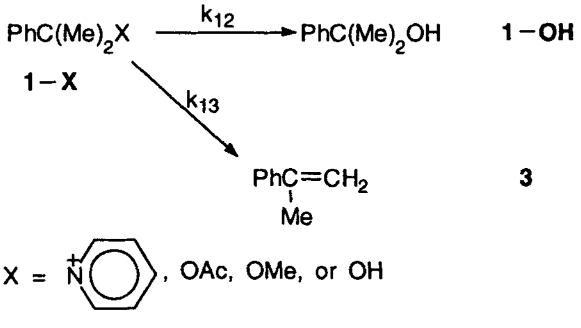
Institute of Chemistry, University of Uppsala, P.O. Box 531, S-751 21 Uppsala, Sweden

Solvolysis of the 1-(1-methyl-1-phenylethyl)pyridinium cation (1-P$^+$) in 25% (v/v) acetonitrile in water at 60 °C provides the alcohol 2-hydroxy-2-phenylpropane (1-OH) as the main product along with the alkene 2-phenylpropene (3). The formation of the elimination product 3 is promoted by the leaving pyridine. Thus, eight times more 3 is obtained from 1-P$^+$ than from the protonated ether 1-OMeH$^+$. Hydron abstraction by the leaving pyridine is only two times less efficient than with AcO$^-$ as leaving group. The results indicate that the ion–molecule pair 1^+–P has a significant lifetime. The elimination product is formed mainly from the ion – molecule pair. The free carbocation yields almost exclusively the substitution product.

The first process in a stepwise solvolysis reaction of a substrate with a neutral leaving group is ionization to a carbocation–molecule pair. This complex has generally been ignored in discussions of reaction mechanisms. The 'free,' diffusionally-equilibrated carbocation has been considered to be the only intermediate in these reactions. Thus, diffusional separation has been assumed to be much faster than reaction (or collapse) of the ion–molecule pair. However, there are a few reports in the literature that suggest that the ion–molecule pair is not just an encounter complex but may be an intermediate with a significant lifetime.[1–5] For example, a 1,3-rearrangement reaction[2] and an 'aromatization' reaction[5] have been employed as probes for the intermediacy of ion–molecule pairs. Ion–neutral complexes have also been suggested to be common intermediates in gas-phase reactions.[6]

This paper reports results which strongly suggest that the elimination of pyridine from the 1-(1-methyl-1-phenylethyl)pyridinium cation (**1-P**$^+$) involves an ion–molecule pair as intermediate. There seems to be no previous report on the role of ion–molecule pairs in elimination reactions.

The reactions of **1-X** [X = (pyridine)$^+$ or OAc] and the acid-catalysed reactions of **1-OMe** and **1-OH** have been followed by a sampling high-performance liquid chromatography (HPLC) procedure (Scheme 1). The reaction conditions and the results are given in Table 1. The acid-catalysed reaction of **1-OMe** is accompanied by some conversion of the alcohol **1-OH** into the alkene 2-phenylpropene (**3**). The rate constants for **1-OMe** presented in Table 1 are corrected for this conversion by the same procedure as has been described previously.[7] The solvolysis of **1-P**$^+$ is much slower than that of **1-OAc**. The rate of the former reaction, as expected for heterolysis of a substrate with an uncharged leaving group, is not very sensitive to solvent polarity.[8,9]



Scheme 1

The results clearly show that the substrates with the basic leaving groups pyridine and AcO$^-$ yield much more elimination than the substrate with the leaving group MeOH. Accordingly, the elimination and substitution reactions do not have a free carbocation as a common intermediate. We conclude that the basic

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[*] Author for correspondence.

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Table 1. Rate constants for the reactions of **1-P**$^+$, **1-OAc**, **1-OMe** and **1-OH** in 25% (v/v) acetonitrile in water at 60 °C

Substrate	pK_{HX}^{b}	[HClO$_4$] (mM)	$10^4(k_{12}+k_{13})$ (s^{-1})	$10^3 k_{13}/k_{12}$
1-P^{+a}	5.2		0.001	30 ± 1
1-OAc	4.8		2.2	59 ± 1
1-OMe	−2.2	3	2.3	4 ± 1
1-OH	−1.7	3	0.01	

^{a}With ClO$_4^-$ as anion; substrate concentration, 3 mM.
^{b}The pK_a of the protonated leaving group in water at 25 °C.[12]

leaving groups abstract a hydron within an ion–molecule pair and an ion pair,[7] respectively. Elimination promoted by the negatively charged leaving group at the stage of the contact ion pair has been suggested before.[7,10,11] For example, it has been concluded that reaction via the ion pair is the main route to elimination product in solvolysis in highly aqueous media even for such a relatively stable carbocation as Ph$_2$C(Me)$^+$.[11] Diffusional separation yields the free carbocation which almost exclusively yields the substitution product **1-OH.**[7] The following mechanistic scheme is consistent with the data for **1-P**$^+$:

$$\begin{tikzcd}
\mathbf{1\text{-}P}^+ \arrow[r, shift left, "k_1"] & \mathbf{1}^+\mathbf{-P} \arrow[l, shift left, "k_{-1}"] \arrow[r, "k_2"] \arrow[d, "k_3"] & \mathbf{1\text{-}OH} \\
 & \mathbf{3} &
\end{tikzcd}$$

The reaction of the ion–molecule pair **1**$^+$**–P** to **1-OH**, represented by rate constant k_2, occurs presumably mainly via diffusional separation followed by reaction with water and only to a small extent by direct attack of solvent water on the ion–molecule pair.

The leaving acetate anion is twice as efficient at promoting elimination than pyridine (Table 1). Pyridine has approximately the same basicity as acetate anion and is for this reason expected to yield a similar amount of alkene product [pyridine is 0·4 pK_a units more basic than acetate anion in water, however, pyridine is *less* basic than AcO$^-$ in 50% (v/v) acetonitrile in water[13]]. The difference in elimination reactivity of **1**$^+$**–P** and **1**$^+$**–OAc** is presumably due to the negative charge of the acetate anion, which may decrease the rate of dissociation of the ion pair. The solvation change of the acetate anion that accompanies the separation should cost more in free energy than that of the leaving pyridine. Another factor which may be of importance is the bifunctional nature of acetate anion, which may decrease the energy of the elimination transition state.

A rough Brønsted β_{lg} value of 0·12 can be estimated for the reaction from intermediate to alkene from the data of **1-P**$^+$ and **1-OMe** by assuming that the rates of formation of **1-OH** from **1**$^+$**–P** and **1**$^+$**–OMeH** are similar. The small value of β indicates an early transition state for the hydron transfer, i.e. a small degree of hydron transfer in the elimination transition state. The value is in good agreement with the Brønsted value of $\beta = 0{\cdot}13$ that was measured for the dehydronation of the carbocation intermediate formed in solvolysis of **1-Cl** at 25 °C with substituted acetate anions.[7] Bunton *et al.*[13] have found that added anions are efficient in promoting elimination from ferrocenyl carbocations in 50% (v/v) acetonitrile in water.

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