Ion−Molecule Pairs in Leaving-Group-Promoted Solvolytic Elimination Reactions

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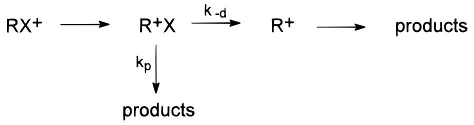
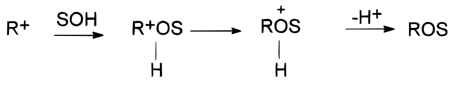
Solvolysis of 1-(1-methyl-1-phenylethyl)pyridinium cation (**1-P**$^+$) in 25 vol % acetonitrile in water at 60 °C provides the substitution product 2-hydroxy-2-phenylpropane (**1-OH**) and the elimination product 2-phenylpropene (**3**). The fraction of elimination is about half of that obtained with an acetate leaving group of similar basicity. The total rate of reaction is dependent on the basicity of the leaving group, 1-(1-methyl-1-(4-cyanophenyl)ethyl)pyridinium cation (**1-P-CN**$^+$) reacts 1100 times faster than **1-P**$^+$ which corresponds to a Brønsted parameter of $\beta_{lg} = -0.93$. Also the fraction of elimination is leaving-group dependent as expressed by a Brønsted parameter of $\beta = 0.12$ for the dehydronation of the ion−molecule pair by the leaving group. Addition of substituted pyridines has only a minor effect on the product ratio. The reactions are concluded to occur stepwise through a common carbocation intermediate of ion−molecule pair type. The overall kinetic deuterium isotope effects using the hexadeuteriated analogs were measured as $k_{obs}{}^{H}/k_{obs}{}^{D6} = 1.85 \pm 0.10$ (60 °C) with the pyridinium ion **1-P**$^+$and as $k_{obs}{}^{H}/k_{obs}{}^{D6} = 1.53 \pm 0.06$ (40 °C) with the 4-cyanopyridinium ion **1-P-CN**$^+$. The kinetic deuterium isotope effects on the elimination step (assuming the reaction from intermediate to alcohol is insensitive to isotopic substitution) were measured as $k_e{}^{H}/k_e{}^{D6} = 2.7 \pm 0.2$ for **1-P**$^+$ (60 °C) and 3.4 ± 0.2 for **1-P-CN**$^+$ (40 °C).

Introduction

We are interested in the role of ion−molecule pairs as intermediates in solvolytic elimination and substitution reactions.[1−10] Ion−molecule pairs are the initially formed complexes in stepwise solvolytic reactions of substrates with neutral leaving groups such as water, alcohols, thioethers, and amines (eq 1). Such encounter complexes also are formed when carbocations react with solvent in nucleophilic substitution reactions (eq 2). However, most often ion−molecule pairs have been ignored in discussions of reaction mechanisms. The "free", solvent-equilibrated carbocation generally has been considered to be the only intermediate in these reactions. Thus, reaction of the complex (k_p) has been assumed to be much slower than diffusional separation (k_{-d}) to free ions (eq 1). However, recent studies of some acid-catalyzed solvolysis reactions of ethers have revealed that the initially formed carbocationic intermediate is not just an encounter complex but an intermediate with a significant lifetime.[2,5−8] These reports include solvolysis of hydronated ethers in which an allylic rearrangement reaction[2] and an "aromatization" reaction,[5] respectively, were employed as ion−molecule pair probes.



$$\begin{tikzcd} RX^+ \arrow[r] & R^+X \arrow[r, "k_{-d}"] \arrow[d, "k_p"] & R^+ \arrow[r] & \text{products} \\ & \text{products} & & \end{tikzcd} \quad (1)$$



$$R^+ \xrightarrow{SOH} R^+\underset{\displaystyle\text{H}}{\underset{|}{\text{OS}}} \longrightarrow R\overset{+}{\underset{\displaystyle\text{H}}{\underset{|}{\text{OS}}}} \xrightarrow{-H^+} ROS \quad (2)$$

There seems to be only one previous report on the intermediacy of an ion−molecule pair in an elimination reaction in solution.[8] An irreversibly formed, very short-lived ion−molecule pair was concluded to be a common intermediate for the solvolytic elimination and substitution reactions of 9-(2-phenoxy-2-propyl)fluorene in acidic, highly aqueous media.[8] The mechanistic conclusions were based upon measured kinetic isotope effects and product compositions. Some of the results reported in the present paper have been communicated previously.[10]

Results

The solvolysis of 1-(1-methyl-1-phenylethyl)pyridinium (**1-P**$^+$) perchlorate or 1-(1-methyl-1-(4-cyanophenyl)ethyl)pyridinium (**1-P-CN**$^+$) perchlorate in 25 vol % acetonitrile in water provides the alcohol 2-hydroxy-2-phenylpropane (**1-OH**) and the alkene 2-phenylpropene (**3**, Scheme 1).

The kinetics of the reactions were studied by a sampling high-performance liquid chromatography procedure and, with **1-P-CN**$^+$ at 40 °C, by following the decrease in absorbance at 226 nm by UV spectrophotometry. The measured rate constants and reaction conditions are shown in Table 1. The effect of solvent on the total reaction rate is small but there is a significant effect on the elimination-to-substitution ratio k_E/k_S.

Addition of pyridine (17 mM) and 4-cyanopyridine (17 mM) to the reaction solutions of **1-P**$^+$ and **1-P-CN**$^+$, respectively, has no effect on total reaction rates. Small effects on the product compositions are observed. Owing to difficulties in accurately quantifying the amount of alcohol product **1-OH** in the presence of a large amount of pyridines, the reaction solutions in these product

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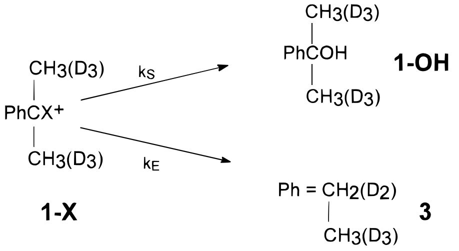
Scheme 1



1-P$^+$ (X = pyridine)

1-P-CN$^+$ (X = 4-cyanopyridine)

Table 1. Kinetic Data for the Solvolysis Reactions of 1-P$^+$ and 1-P-CN$^+$ and the Corresponding Deuteriated Compounds

substrate^a	temp, °C	$10^6(k_E + k_S)$,^{b} s^{-1}	$10^3 k_E/k_S$^{c}
	25 vol % Acetonitrile in Water		
1-P$^+$	60	1.79	27
d$_6$-1-P$^+$	60	0.97	10
1-P-CN$^+$	60	2030	11
d$_6$-1-P-CN$^+$	60	1422	3.0
1-OAc	60		66
1-OMe^d	60		4
1-P-CN$^+$	40	124.7	9
d$_6$-1-P-CN$^+$	40	81.3	2.6
	Methanol		
1-P$^+$	60		59
1-P-CN$^+$	40		8
	Ethanol		
1-P$^+$	60		99
1-P-CN$^+$	40		16

[a] Substrate concentration 3 mM. [b] Estimated maximum errors ±3% at 40 °C and ± 5% at 60 °C. [c] Estimated maximum error ± 1. [d] In acidic solution, reference 10.

Table 2. Nucleophilic Discrimination between Azide Anion and Methanol in 25 vol % Acetonitrile in Water at 40 °C

substrate^a	k_{N_3}/k_{MeOH}^{b}
1-P-CN$^+$	25
1-PNB	14
1-OAc	17

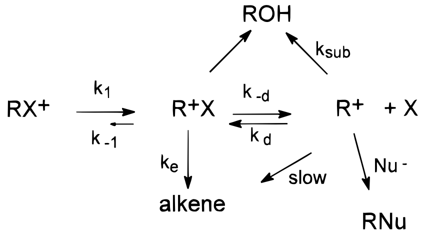
[a] Substrate concentration 3 mM. [b] Ratio of second-order rate constants (eq 3).

composition experiments contained a low concentration (0.48 M) of methanol. Thus, the amount of alkene **3** was compared with the amount of methyl ether product **1-OMe**. The measured product ratios of alkene **3** to substitution product **1-OMe** were 1.0 and 0.23 with **1-P$^+$** and **1-P-CN$^+$**, respectively, without pyridine addition and 1.0 and 0.27 with 0.40 M of pyridine or 0.36 M of 4-cyanopyridine added. Hydroxide anion (0.2 M) does not increase the rate of reaction of **1-P-CN$^+$** or increase the product ratio k_E/k_S (Table 1).

Azide anion does not increase the total reaction rate but gives rise to one further substitution product, 2-azido-2-phenylpropane (**1-N$_3$**). The nucleophilic discrimination between azide (0.25 M) and methanol (1.8 M), as expressed by ratios of second-order rate constants, was calculated from the measured product ratios by means of eq 3.

$$k_{N_3}/k_{MeOH} = ([\mathbf{1\text{-}N_3}]/[\mathbf{1\text{-}OMe}])([MeOH]/[N_3^-]) \quad (3)$$

Scheme 2



The data are collected in Table 2. The nucleophilic discrimination is larger for 4-cyanopyridine as leaving group than for 4-nitrobenzoate and acetate anions.

Discussion

The solvolysis of the cumyl derivatives **1-P$^+$** and **1-P-CN$^+$** in the aqueous solvent comprises S$_N$1−E1 reactions. The reactions are zero-order in nucleophile since no effect of added strong nucleophile, like azide anion, on the rate of disappearance of the substrates is observed. Furthermore, the elimination reactions are not solvent-promoted E2 reactions[11] since added hydroxide anion does not increase the rate of reaction of **1-P$^+$**[12] or **1-P-CN$^+$**, or increase the fraction of elimination.

The nature of the solvent has a very minor effect on the rate of solvolysis as expected for the solvolysis of substrates with neutral leaving groups. A logarithmic plot of the solvolysis rate of **1-P$^+$** versus the polarity (E_T) of the solvent has a slope of about zero.[12] This is in sharp contrast to cumyl derivatives with negatively charged leaving groups which show greatly enhanced solvolysis rates with increasing polarity of the solvent.

The difference in basicity of the leaving groups (pK_a = 5.17 and 1.90)[13] is reflected in the solvolysis rates; **1-P-CN$^+$** reacts about 1100 times faster than **1-P$^+$**. This corresponds to a Brønsted parameter of $\beta_{lg} = -0.93$.

It has been concluded that the solvolysis of cumyl halides and esters, which gives competing substitution and elimination, occurs by a branched mechanism with a common ion-pair intermediate.[14] The alkene is formed predominantly from the ion pair with the leaving group acting as the hydron-abstracting base. 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)$^+$.[15,16]

We conclude that the eliminations from **1-P$^+$** and **1-P-CN$^+$** occur in a similar manner; the basic pyridine leaving group abstracts a hydron within an ion−molecule pair (k_e, Scheme 2). The leaving group functions as a general base. The Brønsted parameter for the elimination from the ion−molecule pair calculated with the two pyridine leaving groups, assuming that the substitution reaction rate with the solvent is not affected, is $\beta = 0.12$ (Figure 1). The value is similar to that for catalysis by added substituted acetate anions ($\beta = 0.13$) reported for solvolysis of cumyl chloride.[14]

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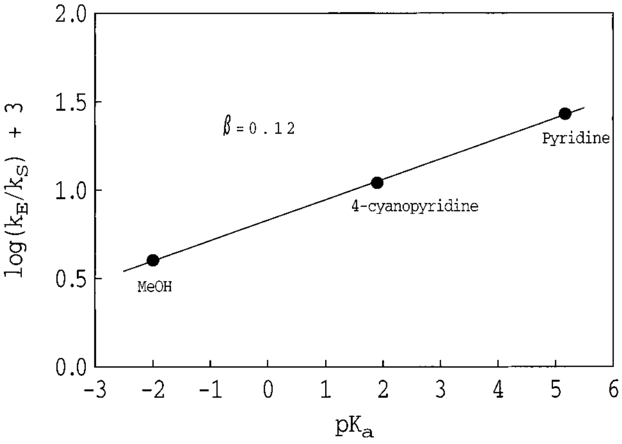

Figure 1. Brønsted plot for the dehydronation of the carbocation **1**$^+$ by the leaving group in 25 vol % acetonitrile in water at 60 °C. The pK_a values of the leaving groups refer to water.[13]

Addition of pyridine and 4-cyanopyridine, respectively, to the reaction solutions has only a minor effect on the elimination-to-substitution ratio. For example, 0.40 M pyridine does not increase significantly the alkene-to-ether ratio in a 0.48 M solution of methanol in 25 vol % acetonitrile in water. This indicates that formation (k_d) of the ion−molecule pair by diffusional association of the carbocation and pyridine is slow compared to the reaction of the carbocation with a nucleophilic solvent molecule (k_{sub}, Scheme 2). This result is not surprising since the unsubstituted cumyl carbocation is relatively short-lived; the lifetime is about 10^{-10} s in highly aqueous media.[17]

Bunton and co-workers have studied hydron transfer from relatively stable carbocations in 50 vol % acetonitrile−water.[18] They found that amines with little steric hindrance are efficient bases for the abstraction of a hydron from 1-ferrocenylalkyl carbocations. For example, acetate anion was found to have about the same reactivity as pyridine toward the carbocation. The more unstable cumyl carbocation intermediates exhibit similar reactivity differences, as concluded from the data of Table 1. Acetate anion in a cumyl ion pair gives about two times more alkene than pyridine in the cumyl ion−molecule pair. Thus, after correction for the statistical factor of two for the acetate anion, the bases show very similar reactivity.

It was found that steric hindrance is a more important factor in tertiary-amine promoted hydron-transfer from 1-ferrocenylalkyl carbocations than in ordinary hydron-transfer reactions.[18] Accordingly, it was concluded that the carbocation and the base are in close proximity in the transition state. Ion-dipole interactions in the encounter complex were suggested to be of importance. Such interactions are presumably responsible for the relative stability of the cumyl ion−molecule pairs as well as ion−molecule pairs in general formed in solvolysis reactions.

The nature of the solvent affects the competition between elimination and substitution. The elimination-to-substitution ratio k_E/k_S for **1-P**$^+$ increases in the solvent series 25 vol % acetonitrile in water, methanol, and ethanol (Table 1).

Table 3. Kinetic Deuterium Isotope Effects for the Reactions of 1-P$^+$ and 1-P-CN$^+$ in 25 vol % Acetonitrile in Water

substrate	temp, °C	$(k_E + k_S)^H/(k_E + k_S)^{D6}$	$(k_E/k_S)^H/(k_E/k_S)^{D6}$
1-P$^+$	60	1.85 ± 0.10	2.7 ± 0.2
1-P-CN$^+$	60	1.43 ± 0.10	3.5 ± 0.2
1-P-CN$^+$	40	1.53 ± 0.06	3.4 ± 0.2

The kinetic deuterium isotope effects on the elimination step k_e^H/k_e^{D6} can be approximated to the measured isotope effect $(k_E/k_S)^H/(k_E/k_S)^{D6}$ (Table 3) by assuming that the isotope effect on the formation of the alcohol is negligible. The isotope effect on k_e is composed of a primary kinetic isotope effect corresponding to the hydron transfer to the abstracting base (i.e., the leaving pyridine within the ion−molecule pair) and a small secondary isotope effect from the five nonreacting hydrogen atoms. The isotope effect on the elimination promoted by the pyridine leaving group ($k_e^H/k_e^{D6} = 2.7 \pm 0.2$) is smaller than with 4-cyanopyridine ($k_e^H/k_e^{D6} = 3.5 \pm 0.2$) and is in accord with an early transition state in which the extent of hydron transfer from the carbocation is relatively small. Consistently, the Brønsted parameter is small, $\beta = 0.12$.

The isotope effect on the total reaction rate of **1-P-CN**$^+$, $(k_E + k_S)^H/(k_E + k_S)^{D6} = 1.53 \pm 0.06$ at 40 °C (Table 3), is slightly larger than that measured for cumyl 4-nitrobenzoate **1-PNB** (1.40 ± 0.06 at 25 °C).[14] The isotope effect for **1-P**$^+$ is somewhat larger, 1.85 ± 0.10 at 60 °C (Table 3). The difference in magnitude for these three leaving groups may be attributed to a requirement for more hyperconjugative stabilization of the transition state of the rate-limiting ionization step with decreasing reactivity of the substrate. The maximal ionization isotope effect is $k^H/k^D = 1.15$ per deuterium at 25 °C,[19] i.e., $k^H/k^{D6} \leq 2.3$. A significant amount of internal return seems likely since solvation of the nucleophilic pyridine leaving group in the ion−molecule pair should be minor.

Our results are consistent wih the mechanism shown in Scheme 2. As discussed above, the elimination occurs mainly directly from the ion−molecule pair. The elimination from the "free" solvent-equilibrated carbocation is very slow as indicated by the very small elimination-to-substitution ratio for the acid-catalyzed solvolysis of the methyl ether **1-OMe** of $k_E/k_S = 4 \times 10^{-3}$ (Table 1).

The carbocationic intermediates show relatively low selectivity toward different nucleophiles (Table 2). A selectivity of $k_{N_3}/k_{HOH} = 42$ has been measured for cumyl chloride at 25 °C.[14] The value of $k_{N_3}/k_{MeOH} = 25$ for **1-P-CN**$^+$ (Table 2) combined with the value of $k_{MeOH}/k_{HOH} = 2.9$ measured previously for cumyl chloride[14] gives $k_{N_3}/k_{HOH} = 25 \times 2.9 = 74$. Thus, the reaction with solvent water (concentration 41.7 M) has a rate constant of about $k_{HOH}' = 5 \times 10^9 \times 41.7/74 = 3 \times 10^9$ s^{-1}. This is based upon the assumption that the reaction with azide anion is diffusion controlled with a rate constant of 5×10^9 M^{-1} s^{-1}.[20] The large rate constant for reaction of the intermediate with water as well as the different selectivities measured with different leaving groups (Table 2) indicate that a significant part of the substitution occurs at the ion−molecule pair stage. This should occur by a preas-

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sociation mechanism in which the azide ion is already present when the bond to the leaving group is cleaved (this is not explicitly indicated in Scheme 2).

Substituents on the phenyl group change the lifetime of the cumyl carbocation from about 10^{-7} s to about 10^{-13} s in highly aqueous media.[17] The longer lifetime corresponds to a solvent-equilibrated carbocation, and the shorter to an extremely short-lived ion pair that does not have a significant lifetime in the presence of an efficient nucleophile, i.e., an uncoupled concerted reaction or, if the nucleophile stabilizes the transition state, to a coupled concerted reaction.

Is there any other mechanistic alternative for the elimination reaction? A solvent-promoted E2 reaction should not be a reasonable mechanism because such a reaction should require an acidic β-hydron.[11] Moreover, a strong base, such as hydroxide anion, does not increase the reaction rate. A plausible mechanistic alternative is concerted pericyclic elimination. However, such a mechanism involves a four-centered transition state and this is not very favored energetically. The elimination reactions of cumyl derivatives with electron-withdrawing substituents on the phenyl group has been proposed to be of this type.[21] However, the results for these eliminations may be explained alternatively by an ion-pair mechanism which is supported by the measured values of the Hammett and Grunwald−Winstein parameters.[21]

Experimental Section

General Procedures. The high-performance liquid chromatography (HPLC) analyses were carried out with a liquid chromatograph equipped with a diode-array detector on a Asahipak ODP-50 reversed-phase column (5 μm, 4 × 150 mm). The mobile phase was a solution of acetonitrile in water. The reactions were studied at constant temperature in a water thermostat bath. The UV spectrophotometry was performed with a spectrophotometer equipped with an automatic cell changer kept at constant temperature with water from the thermostat bath.

Materials. Acetonitrile (Riedel de Haen or J. T. Baker) and methanol (J. T. Baker or Merck) were of HPLC grade and were used without further purification. All other chemicals were of reagent grade and were used without further purification.

2-Hydroxy-2-phenylpropane (**1-OH**) was purified by recrystallization of commercially available material (Aldrich) from pentane.

2-Phenylpropene (**3**) (Fluka) was purified by fractional distillation at reduced pressure.

1,1,1,3,3,3-($^2H_6$)-2-Hydroxy-2-phenylpropane (**d_6-1-OH**) was synthesized from 1,1,1,3,3,3-($^2H_6$)-acetone (Ciba, 99.5% ^2H) and phenylmagnesium bromide.[14]

1-(1-Methyl-1-phenylethyl)pyridinium (1-P$^+$) perchlorate was prepared from **1-Cl**[14] by a slight modification of a previously published method.[12] To dry pyridine (0.06 mol) and 1-methyl-1-phenylethyl chloride (0.02 mol) in dry nitromethane was added silver perchlorate (0.01 mol) dissolved in dry nitromethane (50 mL) with stirring over 40 min at −5 to 0 °C. The mixture was stirred further for 1 h, and then an additional portion of silver perchlorate (0.01 mol) in dry nitromethane (50 mL) was added in the same way. After stirring for 1 h, the silver salt was centrifuged off and ether added which resulted in a cloudy solution in which the product eventually precipitated out as a white solid. Recrystallization several times from acetonitrile−ether gave pure material in 10% yield: mp 126−128 °C (lit.[12] mp 124 °C).

1-(1-(1,1,1-($^2H_3$)-Methyl)-1-phenyl-2,2,2-($^2H_3$)ethyl)-pyridinium (d_6-1-P$^+$) perchlorate was prepared from **d_6-1-Cl**[14] as described above.

1-(1-Methyl-1-(4-cyanophenyl)ethyl)pyridinium (1-P-CN$^+$) perchlorate was prepared from **1-Cl** by the same method as used for **1-P$^+$**.

1-(1-(1,1,1-($^2H_3$)-Methyl)-1-(4-cyanophenyl)-2,2,2-($^2H_3$)-ethyl)pyridinium (d_6-1-P-CN$^+$) perchlorate was prepared from **d_6-1-Cl** as described above.

1-(1-Methyl-1-phenylethyl)acetate (1-OAc) was prepared by $ZnCl_2$-catalyzed acetylation of **1-OH** with acetic anhydride.[14]

1-(1-Methyl-1-phenylethyl)-4-nitrobenzoate (1-PNB) was prepared from **1-OH** and 4-nitrobenzoyl chloride in pyridine.[14]

Kinetics and Product Studies. The reaction solutions were prepared by mixing the organic solvent with water at room temperature, ca. 22 °C. The reaction vessel was a 2-mL HPLC flask, sealed with a gas-tight PTFE septum, which was placed in an aluminum block in the water thermostat bath. The reactions were initiated by fast addition of a few microlitres of the substrate dissolved in acetonitrile by means of a syringe. The concentration of the substrate in the reaction solution was usually 3 mM but in some experiments 0.3 mM. At appropriate intervals, samples were analyzed using the HPLC apparatus. The rate constants for the disappearance of the substrates were calculated from plots of substrate peak area, or substitution product area, versus time by means of a nonlinear regression computer program. Very good pseudo first-order behavior was seen for all of the reactions studied. The separate rate constants for the elimination and substitution reactions were calculated by combination of product composition data, obtained from the peak areas, and the relative response factors were determined in separate experiments, with the observed rate constants.

The relative response factors were measured for **1-OH** and **3** by analysis of mixtures of the two components prepared by weighing. The response factors for all other substitution products were assumed to be the same as that of **1-OH**. Experimental support for this assumption has been reported.

The kinetics of **1-P-CN$^+$** at 40 °C was also studied by following the decrease in absorbance at 226 nm using UV-spectrophotometry. The reactions, which were run in 3-mL quartz cells, were followed for at least 10 half-lives. The rate constants were calculated by means of a nonlinear regression computor program in which the measured infinity absorbance value was kept constant. Very good pseudo first-order behavior was observed.

The estimated errors are considered as maximum errors derived from maximum systematic errors and random errors.

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