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Ion-molecule Pairs in Solvolysis. Trapping of an Anthranyl Carbocation Molecule Pair by Solvent Water†

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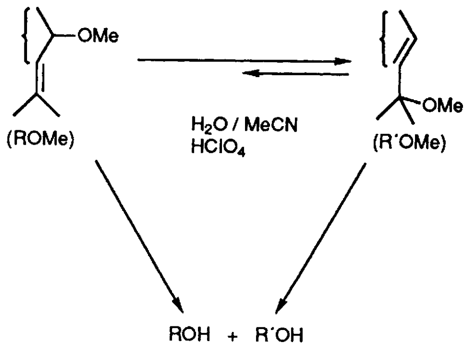
The specific acid-catalysed solvolysis of 9-benzylidene-10-methoxy-10-methyl-9,10-dihydroanthracene (**1**-OMe) in mixtures of water and acetonitrile proceeds mainly *via* a localized carbocation-molecule pair intermediate.

Ion pairs are well established intermediates in solvolysis reactions. Thus, contact (intimate) as well as solvent-separated ion pairs have been concluded to be intermediates in many reactions of substrates having negatively charged leaving groups.[1—6] However, the possible role of the analogous intermediates, *i.e.*, ion-molecule pairs, in heterolysis of substrates with uncharged leaving groups has received very little attention.[7—10]

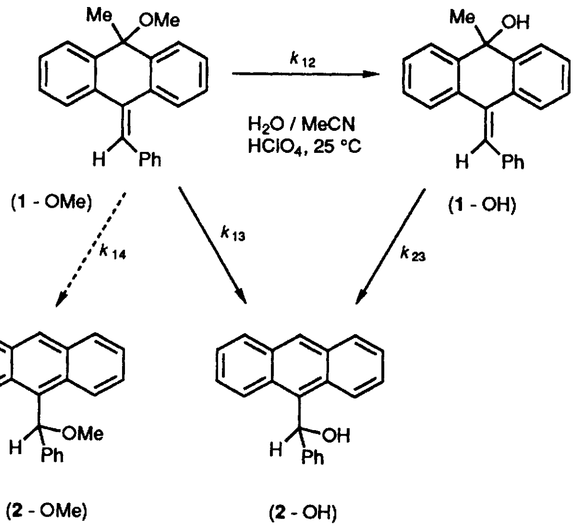
Recently, a specific acid-catalysed intramolecular allylic rearrangement was employed as an ion-molecule pair probe[10] (Scheme 1). Accordingly, the formation of the allylic isomer R'OMe along with the allylic alcohols ROH and R'OH was taken as evidence that the ion-molecule pair R^+OMeH is an intermediate with a significant lifetime.



Scheme 1

The present study employed a system (Scheme 2) in which the dissociation of the potential localized carbocation-molecule pair intermediate yields a 'free' solvent-equilibrated carbocation with the anthracene structure as the dominant resonance form. Since nucleophilic attack on the free carbocation is expected to yield only the anthracene derivative (**2**-OH), any unrearranged substitution product should arise from reaction of the carbocation-molecule pair and, accordingly, constitute evidence for such an intermediate.

The acid-catalysed ($HClO_4$) reaction of 9-benzylidene-10-methoxy-10-methyl-9,10-dihydroanthracene (**1**-OMe) in



Scheme 2

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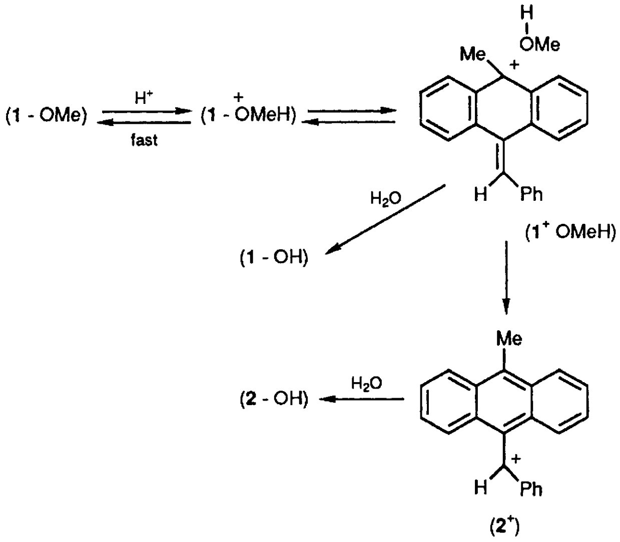
Table 1. Rate constants and rate ratios[a] for the acid-catalysed reactions of (**1**-OMe) and (**1**-OH) in water/acetonitrile and in water/methanol at 25.0 ± 0.1 °C.

Solvent	$10^6 k_{12}$ /s^{-1}	$10^6 k_{13}$ /s^{-1}	$10^6 k_{23}$ /s^{-1}	k_{12}/k_{13}	k_{14}[b] $/k_{13}$	k_{24}[b] $/k_{23}$	k_{21} $/k_{24}$[b]
25 vol% MeCN[c]	1000	110	20	9	—	—	—
50 vol% MeCN[d]	2820	350	55	8	—	—	—
50 vol% MeOH[e]	—	—	—	8	9	9	11

[a] Dimensionless ratio of second-order rate constants. [b] The rate constants k_{21} and k_{24} are the rate constants for conversion of alcohol (**1**-OH) to ether (**1**-OMe) and ether (**2**-OMe), respectively. [c] [HClO$_4$] = 0.6 mM, ionic strength 0.25 M (NaClO$_4$). [d] [HClO$_4$] = 1 mM, ionic strength 0.50 M (NaClO$_4$). [e] [HClO$_4$] = 0.2 mM.



Scheme 3

water/acetonitrile (25 or 50 vol% acetonitrile) at 25 °C was studied by a sampling HPLC procedure. The dominant product under kinetic control is (**1**-OH) (Table 1), only about 10% of the thermodynamically more stable 9-(1-hydroxybenzyl)-10-methylanthracene (**2**-OH) being formed. After a long reaction time all (**1**-OH) is converted to (**2**-OH). The acid-catalysed reaction of (**2**-OMe), on the other hand, yields (**2**-OH) as the sole product. The equilibrium constants [(**2**-OMe)]$_{eq}$/[(**1**-OMe)]$_{eq}$, [(**2**-OH)]$_{eq}$/[(**1**-OH)]$_{eq}$, and [(**2**-OMe)]$_{eq}$/[(**2**-OH)]$_{eq}$ have been measured in 50 vol% methanol in water as 550, 270, and 5.0, respectively.

Kinetic experiments with $HCO_2H-HCO_2^-$ buffers (ratio 2 : 1, [buffer] ≤0.4 M) in 25 vol% acetonitrile at constant ionic strength (KCl or NaClO$_4$) indicate that the reaction of (**1**-OMe) is specific-acid catalysed rather than general-acid catalysed.

The solvolysis of the alcohols (**1**-OH) and (**2**-OH) as well as of the ethers (**1**-OMe) and (**2**-OMe) may be studied in water–methanol mixtures. Reaction rate constants k_{21} and k_{24} for conversion of (**1**-OH) into (**1**-OMe) and (**2**-OMe), respectively, analogous to the reaction of (**1**-OMe) in Scheme 2 are introduced. The measured rate ratios k_{24}/k_{23} and k_{14}/k_{13} in 50 vol% methanol are similar (Table 1) in accord with partitioning from a common free carbocation. The results are consistent with the mechanistic model in Scheme 3.‡ The results indicate that the ion-molecule pair (**1**$^+$OMeH) has a significant lifetime; the dissociation to free carbocation is slower than nucleophilic attack by the solvent. The intermediates exhibit selectivity between different components of the solvent. The free ion (**2**$^+$) reacts nine times faster with a methanol than with a water molecule (Table 1). The ion-molecule pair shows a somewhat higher selectivity; (**1**$^+$OMeH) reacts thirteen times faster with ethanol than with water. The analogous intermediate (**1**$^+$OH$_2$) formed in reaction of (**1**-OH) discriminates between methanol and ethanol; methanol is 1.7 times more reactive than ethanol in water/methanol/ethanol (50/25/25 vol%).

Richard and Jencks have studied the selectivity toward alcohols of substituted 1-phenylethyl carbocations; an increasing reactivity of the carbocation is coupled with a decreasing selectivity.[2b] Thus, it was found for example that methanol reacts 220 times faster than water with the 1-[4-(dimethylamino)phenyl]ethyl carbocation but the 1-(4-methylphenyl)ethyl carbocation exhibits a rate ratio of only five. Other examples of low selectivities for carbocation reactions have been reported.[3—6] A value as low as k_{MeOH}/k_{H_2O} ~0.6 (ratio of second-order rate constants) has been reported for the reaction of the very short-lived carbocation-ion pair formed in the solvolysis of 9-(2-chloro-2-propyl)fluorene.[4]

Acid-catalysed (HClO$_4$) solvolysis in pure ethanol of the alcohol (**1**-OH) analogously yields the unrearranged ethyl ether as the dominant product under kinetic control. The rate ratio of anthranyl to anthracene product is about nine. Flynn and Bergson have studied the acid-catalysed ethanolysis of (**1**-OH) and did not note by their spectrophotometric technique that the anthranyl ether (**1**-OEt) is formed.[11] However, the strongly acidic conditions they used should have converted (**1**-OH) quickly to (**1**-OEt) which in a slower subsequent reaction continues to the final product, the anthracene derivative. Accordingly, the reported rate constants and activation parameters should refer to intermolecular rearrangement of the ethyl ether (**1**-OEt) and not to ethanolysis of (**1**-OH). The situation is presumably the same for the ethanolysis of the two other anthranyl derivatives that they have investigated.[11]

Observation of intramolecular rearrangement of (**1**-OMe) to (**2**-OMe) in water/acetonitrile would have been a further

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‡ One referee has pointed out that the intermediate that gives rise to product (**1**-OH) might be the conjugate acid of the substrate (**1**-OMeH)$^+$ instead of the ion-molecule pair. However, it is unreasonable that the tertiary species (**1**-OMeH)$^+$ undergoes an S_N2 reaction with solvent water at a rate that is nine times faster than its ionization to carbocation.

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indication for the ion-molecule pair. However, even at rather low water content of the solvent (10% vol%) only about 0.007 mol% of the rearrangement product (**2**-OMe) is formed (measured with a fluorescence HPLC detector). The reason that the intramolecular 1,5-rearrangement is insignificant is most likely the large distance which the methanol leaving group has to move. The distance is much shorter in the intramolecular allylic rearrangement.[10] Attempts are being made to trap the carbocation-molecule pair with other nucleophiles.

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