Acid-catalysed Intramolecular Allylic Rearrangement of Methyl Ethers in Aqueous Solvent. Evidence for the Intermediacy of Ion–Molecule Pairs in Solvolysis

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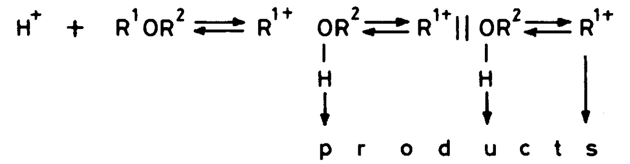
2-Methoxyisopropylideneindan (2-OMe) undergoes a facile acid-catalysed intramolecular allylic isomerization in 9.1 vol% acetonitrile in water producing 3-(1-methoxy-1-methyl)ethylindene (1-OMe), along with solvolysis yielding 3-(2-hydroxy-1-methylethyl)indene (1-OH) and 2-hydroxyisopropylideneindan (2-OH). The isomerization is 11 times slower than the formation of alcohols. The ether (1-OMe) also solvolyses, but more slowly, to give (1-OH) and trace amounts of (2-OH) and (2-OMe). This seems to be the first demonstration of a carbocation–molecule pair as intermediate in a heterolytic reaction in a highly aqueous solvent. Analysis of the kinetic data, in combination with results obtained from solvolysis of the corresponding chloride 3-(1-chloro-1-methylethyl)indene (1-Cl), suggests that the intramolecular rearrangement of the ethers may in fact have two discrete ion–molecule pairs in common with the solvolysis.

Carbocation ion pairs are well established intermediates in solvolysis reactions. Thus, both contact (or intimate) ion pairs and solvent-separated ion pairs, in which a solvent molecule has been inserted between the ions, have frequently been employed to rationalize the experimental results.[1–4] The possible role of the analogous intermediates that may be formed from substrates with neutral leaving groups, *i.e.*, ion–molecule pairs, has received very little attention.[5–7]

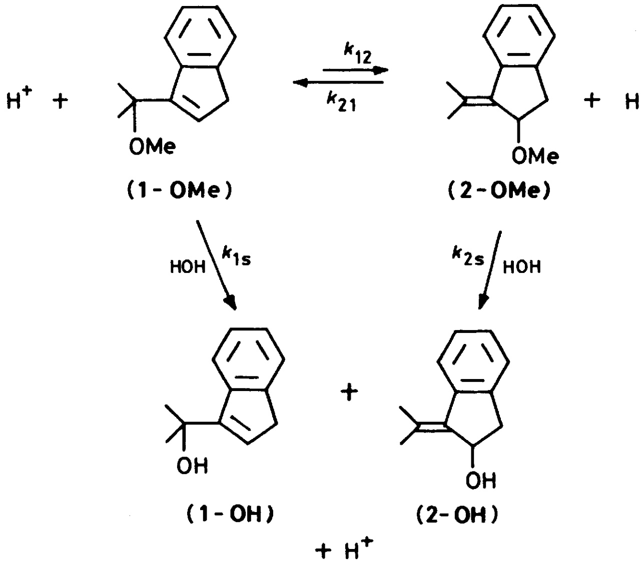
For example, the acid-catalysed heterolysis of an ether or alcohol may involve a contact ion–molecule pair, a free carbocation, and less likely, a solvent-separated ion–molecule pair.* All three intermediates may give products. The lifetime of these ion–molecule pairs is determined by the speed with which these species collapse to starting material, diffuse apart, and undergo a direct transformation to products. For example, if the contact ion–molecule pair collapses to covalent material in a shorter time than that required for a bond vibration ($< 10^{-13}$ s), it cannot be considered as an intermediate.[8] In such a case, it only constitutes an encounter complex for the reverse reaction.


$$H^+ + R^1OR^2 \rightleftharpoons R^{1+}\,\underset{H}{OR^2} \rightleftharpoons R^{1+}||\underset{H}{OR^2} \rightleftharpoons R^{1+} \longrightarrow \text{products}$$

In this paper, an intramolecular allylic rearrangement has been employed as an ion–molecule pair probe. The results constitute strong evidence that an allylic contact carbocation–molecule pair can exist in a highly aqueous medium. A completely consistent interpretation of all results requires introduction of another discrete contact ion–molecule pair which is not in equilibrium with the first, *i.e.*, the allylic isomerization makes use of two ion–molecule pair intermediates.

Results

The acid-catalysed ($HClO_4$) solvolysis of 2-methoxyisopropylideneindan (**2-OMe**) at a constant ionic strength of 0.75M ($NaClO_4$) in 10.3 mol % (25 vol %) acetonitrile in water at 35 °C produces the rearranged ether 3-(1-methoxy-1-methylethyl)indene (**1-OMe**) and the alcohols 3-(1-hydroxy-1-methylethyl)indene (**1-OH**) and 2-hydroxyisopropylideneindan (**2-OH**) (Scheme, Table). The corresponding reaction of the isomeric ether (**1-OMe**), which is considerably slower, yields (**1-OH**) as the dominant product, along with trace amounts of (**2-OMe**) and (**2-OH**). The reactions were also studied in 3.31 mol % (9.1 vol %) acetonitrile. The isomerization of the alcohols is much faster than that of the ethers and, after a long reaction time, (**1-OH**), which is the thermodynamically more stable of the alcohols, is the sole product besides trace amounts of the olefins 1-isopropylideneindene and 3-isopropenylindene. The ethers are quite unreactive in neutral solution.



Scheme.

The reactions of (**2-OMe**) as well as (**1-OMe**) were studied as a function of time by a sampling high-performance liquid chromatography (h.p.l.c.) procedure. The reactions follow the rate laws (1)—(3), where k_{1S} and k_{2S} denote the reaction rate constant of the disappearance of (**1-OMe**) and (**2-OMe**), respectively, to the alcohol products (**1-OH**) and (**2-OH**).

$$d[\textbf{(1-OMe)}]/dt = \{-(k_{12} + k_{1S})[\textbf{(1-OMe)}] + k_{21}[\textbf{(2-OMe)}]\}[H^+] \quad (1)$$

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* The interaction within a solvent-separated ion–molecule pair is presumably too weak to qualify it as a discrete intermediate.

Table. Rate constants for the acid-catalysed reactions of (**1-OMe**) and (**2-OMe**) in water–acetonitrile at 35.00 ± 0.03 °C[a]

mol % CH_3CN	$[HClO_4]$/mM	$10^6\ k_{1S}[H^+]/s^{-1}$	$10^6\ k_{12}[H^+]/s^{-1}$	k_{1S}/k_{12}	$10^6\ k_{2S}[H^+]/s^{-1}$	$10^6\ k_{21}[H^+]/s^{-1}$	k_{2S}/k_{21}
10.3[b]	2.4	5	0.1	~64	73	8	9
10.3[b]	4.8	14	0.2	~67	194	21	9
10.3[b,c]	7.2	24.1 ± 0.3	0.43 ± 0.14	56^{+10}_{-11}	314.7 ± 2.7	34.3 ± 1.7	9.2 ± 0.6
10.3[b,d]	7	17	1.1	~18	246	50	5
10.3[b,e]	7	18	0.3	~53	248	31	8
3.31[f]	8.7	77	0.7	~107	792	72	11

[a] [Substrate] 0.1 mM. [b] 25 vol %; ionic strength 0.75M maintained with $NaClO_4$. [c] Extra careful analysis; see Experimental section. [d] In the presence of 0.75M methanol. [e] In the presence of ethanol; the same volume as was added of methanol above (see Experimental section). [f] 9.1 vol %; ionic strength 0.91M maintained with $NaClO_4$.

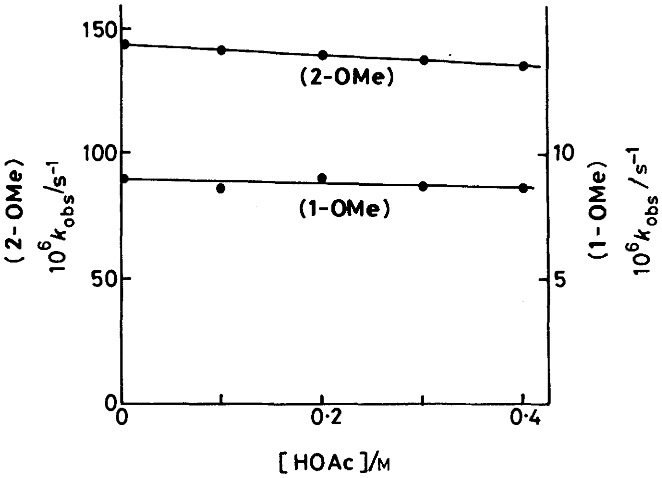


Figure. Observed rate constants for the reaction of (**1-OMe**) and (**2-OMe**) at different concentrations of acetic acid in 25 vol% acetonitrile in water at 25 °C buffered with 0.01M potassium hydrogen phthalate; ionic strength 0.75M, maintained with sodium perchlorate. The observed rate constants are corrected to pH 1.83

$$d[(\mathbf{2\text{-}OMe})]/dt = \{k_{12}[(\mathbf{1\text{-}OMe})] - (k_{21} + k_{2S})[(\mathbf{2\text{-}OMe})]\}[H^+] \quad (2)$$

$$d\{[(\mathbf{1\text{-}OH})] + [(\mathbf{2\text{-}OH})]\}/dt = \{k_{1S}[(\mathbf{1\text{-}OMe})] + k_{2S}[(\mathbf{2\text{-}OMe})]\}[H^+] \quad (3)$$

Only a trace of (**2-OMe**) is formed in the reaction of (**1-OMe**). Accordingly, in kinetic experiments starting with (**1-OMe**), equation (1) can be approximated by equation (1′). Furthermore, since k_{12} is much smaller than $k_{21} + k_{2S}$, a good approximation of equation (2) during the two half-lives for which the kinetics of the reaction of (**2-OMe**) was studied is equation (2′). Accordingly, the disappearance of (**2-OMe**) showed approximately pseudo-first-order behaviour. Accurate pseudo-first-order rate constants $k_{1S}[H^+]$, $k_{21}[H^+]$, and $k_{2S}[H^+]$ are obtained by computer simulation of the integrated expressions of equations (1)—(3). The results are collected in the Table.

$$d[(\mathbf{1\text{-}OMe})]/dt \approx -(k_{12} + k_{1S})[(\mathbf{1\text{-}OMe})][H^+] \quad (1')$$

$$d[(\mathbf{2\text{-}OMe})]/dt \approx -(k_{21} + k_{2S})[(\mathbf{2\text{-}OMe})][H^+] \quad (2')$$

Three concentrations of perchloric acid in 25 vol % acetonitrile were used for the kinetic studies. Plots of the observed rate constants $(k_{12} + k_{1S})\ [H^+]$ and $(k_{21} + k_{2S})\ [H^+]$ *versus* the concentration of perchloric acid are linear, as expected, but do not have zero intercepts. The reason is probably the high concentration of sodium perchlorate (0.75M), which may contain a small amount of a basic impurity. The slopes of the plots yield $(k_{12} + k_{1S}) = 4.0 \times 10^{-3}$ l mol^{-1} s^{-1} and $(k_{21} + k_{2S}) = 56 \times 10^{-3}$ l mol^{-1} s^{-1}. These values are 17 and 15% larger, respectively, than the values obtained at the acid concentration of 7.2mM (Table).

No significant change in reaction rate was found in the presence of up to 0.4M-acetic acid (Figure). This indicates that the acid catalysis is specific rather than general.

When some methanol or ethanol is added to the reaction solution, the rate of hydrolysis decreases (Table). The rate of (intra- and inter-molecular) rearrangement, on the other hand, increases substantially in the presence of methanol.

The very rapid reaction of 3-(1-chloro-1-methylethyl)indene (**1-Cl**) in 0.75M-methanol in 10.3 mol % acetonitrile in water produces the alcohols and the methyl ethers with a product ratio of [(**1-OMe**)]/[(**2-OMe**)] = 3.9 ± 0.1. This product ratio is equal to the rate ratio for formation of the two ethers since the ratio does not change with time and the equilibrium constant $K_{eq.} = [(\mathbf{1\text{-}OMe})]_{eq.}/[(\mathbf{2\text{-}OMe})]_{eq.}$ has a value of *ca.* 80 (entry 3 in Table).

Discussion

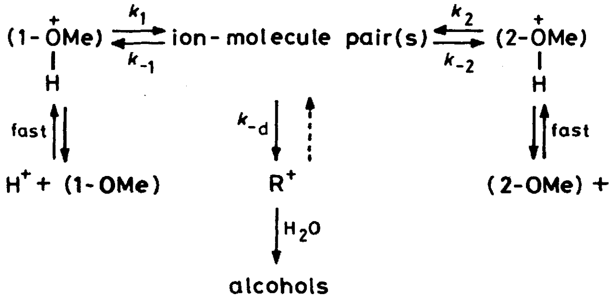
From the fact that no general acid catalysis was found (Figure), it is concluded that the protonated ethers, formed in fast pre-equilibria, are the reacting species. This is in accord with the high reactivity of the allylic carbocation formed in the solvolysis. Its reaction with solvent has a rate constant of *ca.* 4×10^9 s^{-1}.[3a] The addition of water and alcohols to carbocations usually shows general base catalysis. The catalysis has been found to be less important for less stable carbocations and disappears when the reaction with solvent and diffusion becomes competitive.[2c] In the reverse direction, this corresponds to specific acid catalysis of alcohol expulsion to form a short-lived carbocation intermediate.

The equilibrium constant of $K_{eq.} = k_{21}/k_{12} = 80^{+44}_{-23}$ (25 vol % acetonitrile in water) for the interconversion of the methyl ethers is considerably larger than that measured for the corresponding acetates (**1-OAc**) and (**2-OAc**) ($K_{eq.}$ 2.8).[3a] A large equilibrium constant has also been found for rearrangements of the alcohols (**1-OH**) and (**2-OH**).[3a] The reason for the smaller equilibrium constant for the acetates, the difference in equilibrium constants for the ethers and acetates corresponds to *ca.* 2 kcal mol^{-1}, is probably the fact that the acetoxy group is more bulky than the methoxy; this bulkiness causes a relative destabilization of (**1-OAc**).

The difference in thermodynamic stability, as expressed by the equilibrium constant, is not completely reflected in the reactivity of the ethers; (**2-OMe**) reacts *ca.* 14 times faster than (**1-OMe**) (Table) to give the rearrangement and solvolysis products.

Two mechanistic alternatives may be considered for the intramolecular allylic rearrangement that accompanies the solvolysis. Thus, the reaction may have a one-step concerted mechanism[9] or a stepwise ionic mechanism involving carbocation–molecule pair(s). The first alternative is not very likely since it involves nucleophilic attack of a positively charged oxygen atom on the other end of the allylic system. A positively charged oxygen atom is expected to be a very inefficient nucleophile and four-centred transition states are not very much favoured energetically.

The One-intermediate Mechanism.—The second alternative in which the bond with the leaving group is broken initially to form one or two rapidly equilibrating ion–molecule pair(s) followed by nucleophilic attack of the methanol leaving group still associated with the allylic system seems much more reasonable [equation (4)]. Allylic isomerizations with negatively charged 'leaving groups' under solvolytic conditions are generally discussed in terms of a mechanism of this type; the solvolysis and rearrangement are coupled *via* a common intermediate(s).[1,3,10]



(4)

The postulate of this type of mechanism combined with the observation of intramolecular rearrangement imply that the ion–molecule pair is not just an encounter complex for the reverse reaction but is a discrete intermediate with a significant lifetime. This lifetime makes it possible for the ion–molecule pair to choose between the two reaction paths and not just undergo diffusional separation (producing alcohols).

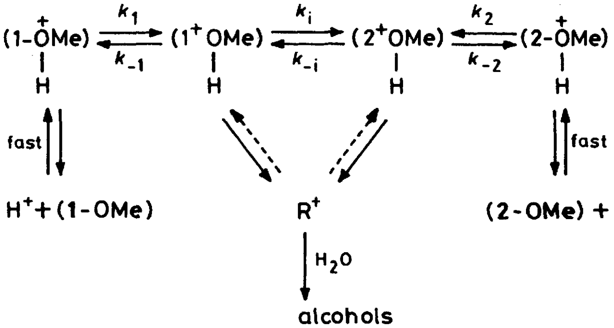
A 'solvated', *i.e.*, diffusionally equilibrated, methanol molecule has been found to be a 2.3 times better nucleophile than a solvent water molecule toward the allylic carbocation R^+.[3a] The methanol leaving group, before it has been diffusionally (solvent) equilibrated, should be several times more nucleophilic than a solvated methanol molecule. The expected high nucleophilicity of the methanol molecule of the ion–molecule pair should be reflected in a strong interaction between the carbocation centre and the oxygen of the methanol. Sneen and his co-workers have proposed the intermediacy of an ion–molecule pair for the hydrolysis of *p*-methoxybenzyldimethylsulphonium nitrate and considered, in a similar way, a strong interaction between the strongly nucleophilic dimethyl sulphide and the carbocation as responsible for the existence of an intermediate.[5]

Evidence has been found that an arenediazonium ion is dissociated to a carbocation–nitrogen molecule pair in low nucleophilic solvents before diffusion to a solvent-equilibrated carbocation.[7]

The dissociation of an ion–molecule pair to the solvent-equilibrated allylic carbocation R^+ may proceed *via* the solvent-separated ion–molecule pair. However, the interaction between the carbocation and the methanol molecule in this species, in contrast to a solvent-separated ion pair, should be very small. It is possible that the lifetime of the solvent-separated ion–molecule pair is less than the time required for a single bond vibration and, accordingly, the formation of R^+ from the contact ion–molecule pair becomes enforced concerted.[8] The tight pair may also proceed to alcohols by a one-step reaction. This process is predicted to be significant for a very unstable carbocation.

The amount of internal return, expressed as the ratios $k_{-1}/(k_{-2} + k_{-d})$ and $k_{-2}/(k_{-1} + k_{-d})$ [equation (4)], may be calculated from the rate ratios in the Table (25 vol % acetonitrile) as 0.11 and 0.016, respectively.

The Two-intermediate Mechanism.—Both the allylic ethers (**1-OMe**) and (**2-OMe**) are formed when the corresponding substrates (**1-Cl**), (**1-OH$_2^+$**), (**1-OAc**), or (**2-OAc**) are solvolysed in aqueous solution in the presence of methanol.[3a] The rate constant ratio of 3.9 ± 0.1 for formation of the two ethers from the chloride (**1-Cl**) (see Results section), which most likely solvolyses *via* a solvent-equilibrated carbocation, is equal to the collapse ratio k_{-1}/k_{-2} if the one-intermediate mechanism [equation (4)] is valid. However, a significantly larger value is obtained from the kinetic data of the Table, $k_{-1}/k_{-2} = (k_{21}/k_{2S})/(k_{12}/k_{1S}) = 6.1 \pm ^{1.6}_{1.5}$. Apparently, the one-intermediate mechanism cannot consistently account for all the results. The inconsistency is removed by extending the mechanistic model to include two discrete intermediates (equation (5)]. These are most likely of the contact carbocation–molecule type as discussed above, with the methanol molecule associated with C-1 and -3, respectively, of the allylic system.



(5)

Consistent with both the mechanistic schemes of equations (4) and (5) is the fact that the rate of rearrangement relative to solvolysis of (**2-OMe**) increases substantially in the presence of methanol (Table). Accordingly, the added methanol competes with water for reaction with the free carbocation R^+. In other words, the methanol increases the steady-state concentration of the tight intermediates which rapidly collapse and give rise to an enhanced amount of the rearrangement product.

The fact that the apparent collapse ratio is as small as *ca.* 4 [equation (4) and entry 4 in the Table yield $k_{-1}/k_{-2} \approx 18/5 \approx 4$] at 0.75M-methanol is a further support for the two-intermediate mechanism of equation (5). The value is significantly smaller than that measured without the addition of methanol. Since the main part of the methyl ethers at [MeOH] 0.75M is attributable to the methanol addition, *i.e.*, the reaction between R^+ and added methanol [which should give a product ratio of methyl ethers of 3.9 ± 0.1, as concluded from the reaction of (**1-Cl**)], the value of *ca.* 4 is quite consistent with the mechanistic scheme of equation (5). However, the mechanism of equation (6) requires the same apparent collapse ratio with and without addition of methanol.

It is not possible to estimate the amounts of collapse for the two-intermediate mechanism. Accordingly, the amounts of internal return may be larger than those calculated above for the one-intermediate mechanism.

The indication for two discrete ion–molecule pairs presented in this work is also a strong support for the conclusion that the uncatalysed isomerization of the analogous acetates (**1-OAc**) and (**2-OAc**) in 25 vol % acetonitrile in water have two discrete ion pairs in common with the solvolysis.[3]

The ethers give less rearrangement relative to alcohol formation than the acetates (ethers: $k_{12}/k_{1\mathrm{S}} = 0.02$ and $k_{21}/k_{2\mathrm{S}} = 0.11$; acetates: $k_{12}/k_{1\mathrm{S}} = 0.19$ and $k_{21}/k_{2\mathrm{S}} = 0.26$). Possible reasons for the difference are: (i) electrostatic stabilization of the ion-pair intermediate that increases the barrier to dissociation; (ii) a higher nucleophilic reactivity of the leaving group $^-$OAc;* (iii) the bifunctional nature of the acetate anion, which lowers the barrier for interconversion of the allylic ion pairs.

Electrostatic stabilization of tight carbanion ion pairs in proton-transfer reactions has been found to be of relatively small importance in highly aqueous media, the hydrogen bonding being the major stabilization factor.[11] The situation seems to be similar for the allylic carbocation intermediates studied; the contact ion-pair intermediates are not stabilized mainly by electrostatic interactions.

The bifunctional nature of the acetate anion may result in attack of the oxygen that has been part of the carbonyl group of the ester to give rearranged product. This may be a general way for bifunctional leaving groups to lower a high barrier of interconversion of allylic ion pairs. The above interpretation is consistent with the results of studies by Goering and his coworkers on the isomerization of oxygen-labelled *p*-nitrobenzoate esters.[10b]

Experimental

General Procedures.—H.p.l.c. analyses were carried out with a Hewlett–Packard 1084 B liquid chromatograph equipped with a variable-wavelength detector on a C8 reversed-phase column (3.0 × 200 mm). The mobile phase was a solution of methanol (or ethanol) in water. The relative extinction coefficients of the substrates and products have been reported previously.[3a] The reactions studied were performed at constant temperature in a HETO 01 PT 623 thermostat.

Materials.—The syntheses and purification of the substrates (**1-OMe**), (**2-OMe**), and (**1-Cl**) as well as the alcohols (**1-OH**) and (**2-OH**) and the olefins formed as minor products have been reported previously. Acetonitrile (Fluka; for u.v. spectroscopy) was used as solvent without further purification. Methanol and ethanol (0.5% water) were of spectroscopic quality. A stock solution of sodium perchlorate was prepared from perchloric acid and sodium hydroxide solution.

Kinetics.—The reaction solutions were prepared by mixing 3 (or 10) volumes of water solution of perchloric acid, ionic strength 1.00M maintained with $NaClO_4$, with one volume of acetonitrile at room temperature, *ca.* 22 °C. The methanol or ethanol present in some experiments was added to the reaction solution with a syringe (47 μl to 1.5 ml). The reactions were run in 1.5 ml h.p.l.c. flasks sealed with tight Teflon septa, which were placed in an aluminium block in the water thermostat with a temperature of 35.00 ± 0.03 °C. The reactions were initiated by rapid addition of the substrate (2 μl) dissolved in acetonitrile to give a final concentration of *ca.* 0.1mM. Portions of the reaction solution was transferred with a thermostatted syringe to another h.p.l.c. flask containing sodium hydrogen carbonate solution to neutralize the acid. Analysis by h.p.l.c. gave the mol % of the starting material and each product. Approximate rate contants of the disappearance of the substrate were obtained from plots of ln (mol % starting material) *versus* time. Computer simulation, using the approximate values as starting values for the calculation, yielded more accurate rate constants.[12]

For example, when starting from pure (**1-OMe**), the concentrations of (**2-OMe**) and alcohols are described by equations (6) and (7), where k' denotes the pseudo-first-order rate constant $k[\mathrm{H}^+]$ where relations (8)—(11) hold.

$$\text{mol \% } (\mathbf{1\text{-}OMe}) = a\,\mathrm{e}^{-m_1 t} + (100 - a)\mathrm{e}^{-m_2 t} \qquad (6)$$

$$\text{mol \% } (\mathbf{2\text{-}OMe}) = b\mathrm{e}^{-m_1 t} - b\,\mathrm{e}^{-m_2 t} \qquad (7)$$

$$a = 100\,(k'_{12} + k'_{1\mathrm{p}} - m_2)/(m_1 - m_2) \qquad (8)$$

$$b = 100\,k'_{12}/(m_2 - m_1) \qquad (9)$$

$$m_1 = [(k'_{12} + k'_{1\mathrm{S}} + k'_{21} + k'_{2\mathrm{S}})^2/4 - k'_{12}k'_{2\mathrm{S}} - (k'_{21} + k'_{2\mathrm{S}})\,k'_{1\mathrm{S}}]^{\frac{1}{2}} + \tfrac{1}{2}(k'_{12} + k'_{1\mathrm{S}} + k'_{21} + k'_{2\mathrm{S}}) \qquad (10)$$

$$m_2 = -[(k'_{12} + k'_{1\mathrm{S}} + k'_{21} + k'_{2\mathrm{S}})^2/4 - k'_{12}k'_{2\mathrm{S}} - (k'_{21} + k'_{2\mathrm{S}})\,k'_{1\mathrm{S}}]^{\frac{1}{2}} + \tfrac{1}{2}(k'_{12} + k'_{1\mathrm{S}} + k'_{21} + k'_{2\mathrm{S}}) \qquad (11)$$

The kinetic data at the acid concentration of 7.2mM were the object of an extra-careful analysis. An accurate determination of the small amount of (**2-OMe**) which is formed in kinetic runs starting from (**1-OMe**) was obtained in the following way. The reaction solution (4 ml) was shaken after an appropriate time with a mixture of ice–water (50 ml) and carbon tetrachloride (1 ml). After centrifugation, the organic phase was collected and the solvent evaporated. The residue was dissolved in acetonitrile (40 μl). Portions (5 μl) of this solution were analysed by h.p.l.c. at 290 nm to obtain a larger relative peak area from (**2-OMe**) than is obtained at 254 nm. The method was calibrated by analysing mixtures of (**1-OMe**) and (**2-OMe**) prepared from the pure substrates. For example, after 12% reaction the amount of (**1-OMe**) measured in this way was 0.10 ± 0.03 mol %.

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

Acknowledgements

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* The nucleophilic reactivity of solvated methanol toward R^+ is about half as large as that of solvated acetate anion.[3a]