

Acid-catalyzed solvolytic elimination (aromatization) of allylic ethers and alcohols

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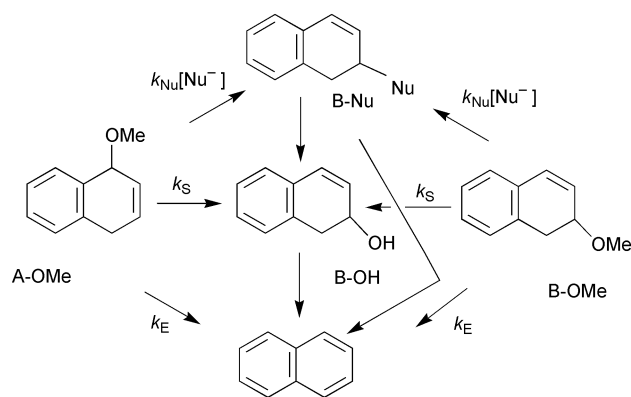
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Acid-catalyzed solvolysis of 1-methoxy-1-methyl-1,4-dihydronaphthalene (**1-OMe**) in 50 vol% acetonitrile in water yields exclusively the elimination product 1-methylnaphthalene (**3**). Neither intramolecular rearrangement giving 2-methoxy-4-methyl-1,2-dihydronaphthalene (**2-OMe**), nor nucleophilic substitution with water giving the corresponding alcohols (**1-OH**) or (**2-OH**), was observed. However, addition of the strongly nucleophilic azide ion gives rise to competing substitution. The **2-N₃** adduct rapidly loses HN₃, affording **3** as the final product. These results are consistent with a carbocation relatively stable towards trapping with nucleophiles, but which easily loses a hydron. This process has a rate constant of about $k_e = 6 \times 10^8 \text{ s}^{-1}$, which is more than an order of magnitude slower than the dehydration of the corresponding unsubstituted benzallylic carbocation (*J. Am. Chem. Soc.*, 1998, **120**, 6512). The heat of reaction of **1-OH** in 25 vol% glycerol in water, measured by microcalorimetry, is $\Delta H = -21.7 \pm 0.9 \text{ kcal mol}^{-1}$.

Introduction

We have recently reported on a mechanistic study of the acid-catalyzed solvolysis of **A-OMe** and **B-OMe**, and the corresponding alcohols (Scheme 1).¹ It was of interest to

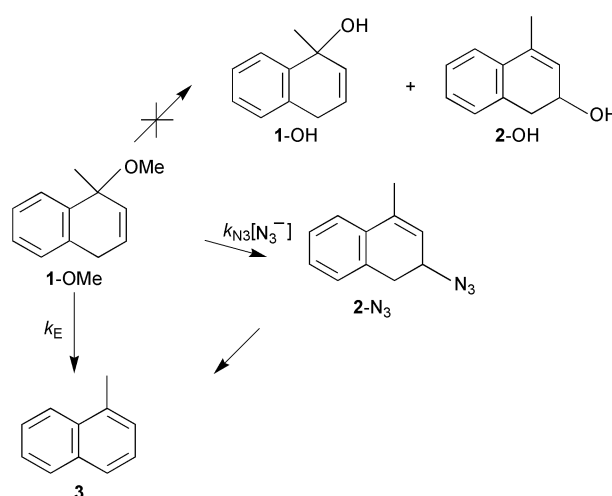


Scheme 1

study these reactions since they show very high elimination-to-substitution ratios, in contrast to most other solvolytic reactions, through relatively stable, solvent-equilibrated carbocations. Such carbocations generally yield mainly substitution products in nucleophilic solvents.²⁻⁴ The report clearly showed that the predominant elimination is attributable to the large thermodynamic stability of the naphthalene product and not to an unusually slow reaction of the carbocation with nucleophiles.¹

The studied reactions are of biochemical interest, since aromatic hydrates, such as naphthalene hydrates, are thought to be intermediates in the mammalian metabolism of aromatic hydrocarbons, along with arene oxides and dihydrodiols.⁵

We have now increased the stability of the benzallylic carbocation by introducing a methyl group in the 1-position (Scheme 2). The presence of the methyl group was expected to have a slight destabilizing effect on the elimination product, but should have only a very minor effect on the stability of the water adduct **2-OH**. Therefore, a somewhat larger substitution-to-elimination ratio was expected. The result, however, was the opposite, since no traces of the water adducts were found.



Scheme 2

Previous studies have shown that carbocation–molecule pairs are intermediates with significant lifetimes in some solvolytic reactions.⁶ It was therefore somewhat surprising to observe that there was no intramolecular rearrangement or formation of **A-OH** from **A-OMe** (Scheme 1). Such reactions might be more favoured with the methyl-substituted compound **1-OMe**, since we have found that the trapping of a localized tertiary carbocation with water is about one order of magnitude faster than its reaction to give aromatization.^{6f} The mechanistic details of these reactions are discussed within the present report.

Results

The acid-catalyzed solvolysis of 1-methoxy-1-methyl-1,4-dihydronaphthalene (**1-OMe**) in 50 vol% acetonitrile in water or in 25 vol% glycerol in water yields exclusively the elimination product 1-methylnaphthalene (**3**, Scheme 2). No traces of the rearranged ether product, 2-methoxy-4-methyl-1,2-dihydronaphthalene (**2-OMe**), or the alcohols, 1-hydroxy-1-methyl-1,4-dihydronaphthalene (**1-OH**) and 2-hydroxy-4-methyl-1,2-dihydronaphthalene (**2-OH**), were found. The kinetics of the reactions were studied either by a sampling high-performance

Table 1 Pseudo first-order and second-order rate constants for the acid-catalyzed reactions of **1-OMe** and **1-OH** at 25 °C

Solvent (method)	1-OMe		1-OH	
	$10^6 k_{\text{obs}}/\text{s}^{-1}$	$k_{\text{H}}/\text{M}^{-1} \text{s}^{-1}$	$10^6 k_{\text{obs}}/\text{s}^{-1}$	$k_{\text{H}}/\text{M}^{-1} \text{s}^{-1}$
MeCN-H ₂ O ^{a,b} (UV)	453	22.2	658	32.2
MeCN-H ₂ O ^{b,c} (UV)			8080	396
MeCN-H ₂ O ^{a,d} (MC)			24.2	33.4
MeCN-H ₂ O ^{a,e} 0.167 M NaN ₃ (HPLC)			521 (225 + 295)	176 (76 + 100)
Glycerol-H ₂ O ^{a,f} (MC)			278	3192

^a 50 vol% of the organic solvent component. ^b Substrate concentration 7 μM, 0.05 M acetate buffer, pH 4.69 before mixing with the organic solvent. ^c 25 vol% of the organic solvent component. ^d Substrate concentration 1.7 mM, 0.05 M acetate buffer, pH 6.14 before mixing with the organic solvent. ^e Substrate concentration 0.87 mM; buffered with 33 mM HN₃. The values given within brackets refer to substitution (k_{12}) and elimination (k_{13}), respectively (Scheme 3). ^f Substrate concentration 0.4 mM, 0.05 M phosphate buffer, pH 7.06 before mixing with the organic solvent.

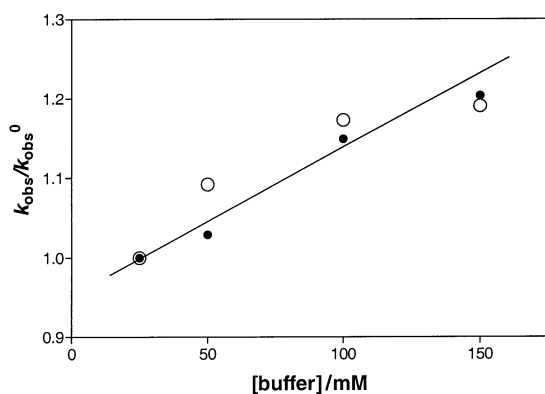


Fig. 1 Effect of acetic acid buffer (buffer ratio 9:1) on the rate of solvolysis of **1-OH** (○) and **1-OMe** (●) in 50 vol% methanol in water at 25 °C; 0.25 M sodium perchlorate added.

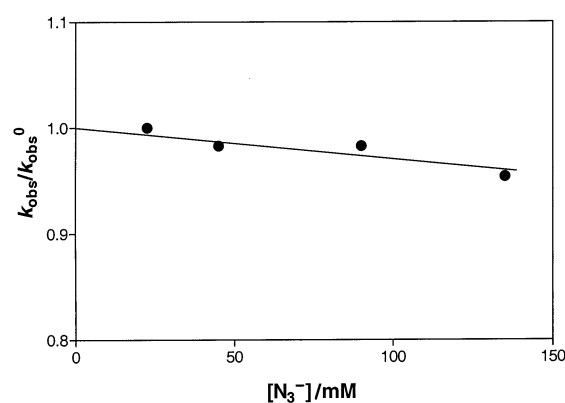


Fig. 2 Effect of sodium azide concentration on the rate of solvolysis of **1-OH** in 50 vol% acetonitrile in water at 25 °C. Ionic strength 0.20 M maintained with sodium perchlorate.

liquid chromatography procedure or by following the appearance of **3** as a function of time by UV spectrophotometry. The same methods were used to study the reactions of **1-OH**. This substrate also provides exclusively 1-methylnaphthalene (**3**). The measured rate constants are shown in Table 1.

There is a slight increase in the rate of the acid-catalyzed solvolysis of both **1-OH** and **1-OMe** with increasing acetate buffer concentration, in 50% aqueous acetonitrile as well as in 50% aqueous methanol (Fig. 1). This could be due to very weak buffer catalysis or to a specific medium effect of the acetate buffer. Alternatively, nucleophilic attack of the acetate ion on a reversibly-formed carbocation intermediate might explain the result. If there was a reaction of the carbocation with the acetate ion, it must be followed by a very fast breakdown of the acetate adduct(s), since no traces of such products were observed. However, we conclude that this is not the case, since there is no significant bimolecular reaction with the much stronger nucleophilic azide ion (Fig. 2).

Addition of azide ion gives rise to the substitution product **2-N₃** (Scheme 2), but no trace of **1-N₃** was observed. However, initially some **1-N₃** may be formed, since allylic azides are known to isomerize very rapidly (see Discussion section).

The azide adduct **2-N₃** is not stable, but rapidly reacts to give the elimination product **3** as the final product (Scheme 3).

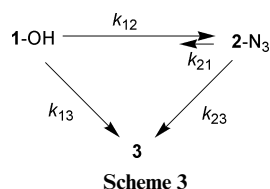


Fig. 3 shows the variation of the product composition as a function of time. The separate rate constants were obtained by computer simulation of the measured mol% versus time data.

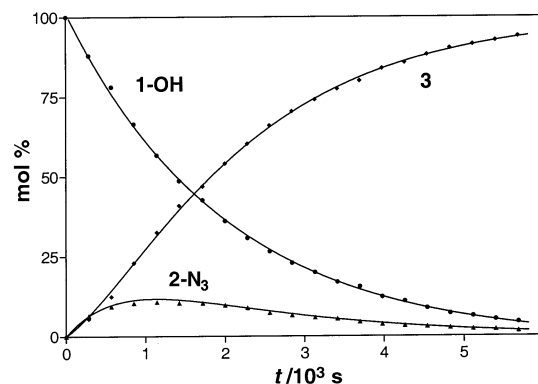


Fig. 3 The time dependence of the solvolysis reactions of **1-OH** (Scheme 3) in 50 vol% acetonitrile in water with 0.167 M NaN₃ added (buffered with 0.033 M HN₃) at 25 °C. The curves are computer simulated using eqns. (3)–(5).

The rate constant (k_{23}) of the decomposition of **2-N₃** was measured as $1.40 \times 10^{-3} \text{ s}^{-1}$.

The nucleophilic selectivity between azide ion and solvent water must be very large since, no trace of **2-OH** was detected in the solvolysis of **1-OH** or **1-OMe**, and no trace of **1-OH** was found in the reaction of **1-OMe**.

Calorimetric measurements

The acid-catalyzed reaction of **1-OH** has been studied by heat-flow microcalorimetry. The reaction was run in 50 vol% acetonitrile in water and in 25 vol% glycerol in water. The latter solvent mixture minimizes the possible disturbances from vaporization of trace amounts of the organic solvent component from the sealed reaction vial. A time period of 40–60 min after the initiation of the reaction was required for thermal equilibration (see Experimental section). The observed decrease

Table 2 Heat of reactions for the dehydration of **1-OH**, **A-OH**, and **B-OH** at 25 °C

Substrate	Solvent	$P_0^a/\mu\text{W}$	$\Delta H/\text{kcal mol}^{-1}$
1-OH ^b	MeCN–H ₂ O 1:1	9.2	-20.8 ± 1.1^d
1-OH ^c	Glycerol–H ₂ O 1:3	27.5	-21.7 ± 0.9^e
A-OH ^f	Glycerol–H ₂ O 1:3	20.0	-23.7 ± 0.4
B-OH ^f	Glycerol–H ₂ O 1:3	12.0	-18.4 ± 0.2

^a Heat flow at time zero (extrapolated). ^b Substrate concentration 1.7 mM. Acetate buffer 0.05 M, pH 6.14 (before mixing). ^c Substrate concentration 0.43 mM. Phosphate buffer 0.05 M, pH 7.06 (before mixing). ^d Standard deviation, average of 4 runs. ^e Standard deviation, average of 8 runs. ^f Ref. 1.

in heat flow after the equilibration period reflects the pseudo-first-order behaviour of the reaction. The measured rate constants agree with those obtained by the spectrophotometric technique (Table 1). The measured reaction enthalpies are given in Table 2, which also includes the data measured previously for the corresponding unsubstituted substrate **A-OH**.¹

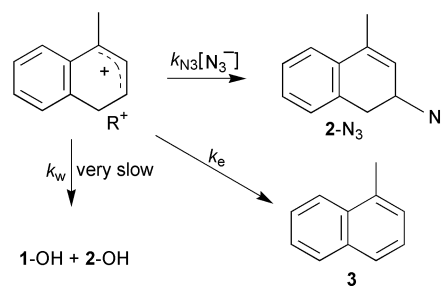
Discussion

The alcohol **1-OH** and the corresponding ether **1-OMe** are highly reactive. The fact that no alcohol products were found in the reaction of **1-OMe** indicates that external return is not of importance. Consistently, the alcohol reacts faster than the ether (Table 1) and it is 8 times more reactive than the unsubstituted alcohol **A-OH** (Scheme 1). It has been concluded that **A-OMe** and **B-OMe** undergo rate-limiting carbon–oxygen cleavage.¹ This indicates that **1-OH** and **1-OMe**, which give a more stable carbocation, react in the same manner.

Reaction with the strongly nucleophilic azide ion gives rise to the substitution product **2-N₃**. Moreover, the azide ion may also function as a general base ($pK_{\text{HN}_3} = 4.72$) providing the elimination product **3**. The experiments with added azide ion confirm that the formation of the benzallylic carbocation **R⁺** is rate-limiting, because there is no significant overall rate increase with 0.167 M N_3^- despite the fact that **2-N₃** is formed faster than **3** (Table 1, and Figs. 2 and 3). Thus, we can conclude that the slight increase in rate with increasing acetic acid buffer concentration is due to a medium effect and not to a one-step concerted elimination (and/or substitution) directly from the hydronated substrates or rate-limiting reaction *via* the carbocation intermediate.

The acid-catalyzed solvolysis of **1-OMe** is 10^5 times faster than the corresponding reaction of 2-methoxy-2-phenylpropane.⁷ The reactivity difference of the alcohols is even larger: **1-OH** is about 2×10^8 times more reactive than 2-hydroxy-2-phenylpropane (“cumyl alcohol”).⁷ This reflects the fact that the reactions of **1-OH** and **1-OMe** involve rate-limiting formation of the benzallylic carbocation, whilst the much less stable cumyl carbocation intermediate shows rate-limiting product formation. That the reaction of cumyl methyl ether, compared with cumyl alcohol, is about 2000 times faster is due to the fact that the predominant reaction of the carbocation intermediate is trapping by solvent water; the dehydration to give the elimination product is much slower, $k_{\text{E}}/k_{\text{S}} \sim 1 \times 10^{-3}$.⁷ This is in sharp contrast to the competition shown by the benzallylic carbocation **R⁺** (Scheme 4) where the trapping of **R⁺** by solvent water is at least 300 times slower than the dehydration to give the elimination product (*vide infra*).

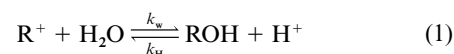
The much higher reactivity of **1-OMe** over that of the cumyl ether (10^5 times) can be attributed to enhanced resonance within the cyclic cation and the effect of a vinyl substituent.⁸ A comparison of the rate-limiting formation of the unsubstituted benzallylic carbocation with that of the noncyclic 1-phenylethyl carbocation shows an even larger reactivity difference ($\sim 10^8$ times). The effect of the vinyl substituent could be

**Scheme 4**

estimated by comparison with the rate constant measured for the corresponding substrate having a vinyl substituent instead of a methyl, *i.e.* 3-methoxy-3-phenylbutene. This substrate reacts about 21 times faster than the cumyl ether.⁹

Only one azide product (**2-N₃**) was observed in the solvolysis of **1-OMe** and **1-OH**. It is expected that nucleophilic attack on the α -carbon of the carbocation to give **1-N₃** should occur. However, this isomer is expected to be very short-lived, since allylic azides are known to isomerize very quickly. Accordingly, previous studies on solvolysis reactions of allylic substrates have reported only a single allylic azide product, the thermodynamically more stable isomer.^{1,10,11}

How stable is the benzallylic carbocation? The pK_{R} for the pseudo acid–base equilibrium for cation hydration [eqns. (1) and (2)] is a measure of the thermodynamic stability of a carbocation **R⁺**.



$$K_{\text{R}} = k_{\text{w}}/k_{\text{H}} = [\text{ROH}][\text{H}^+]/[\text{R}^+] \quad (2)$$

Values of $pK_{\text{R}} = -7.8$ and $pK_{\text{R}} \geq -6.3$ for the unsubstituted benzallylic carbocation to give **B-OH** and **A-OH**, respectively, have been reported.¹ An even larger pK_{R} (less negative) is expected for the methyl-substituted benzallylic carbocation. As a comparison, it should be noted that the 1-(4-methylphenyl)ethyl carbocation exhibits a very small thermodynamic stability of $pK_{\text{R}} = -12.8$, measured in 50 vol% 2,2,2-trifluoroethanol in water.⁴

How reactive is the benzallylic carbocation? There is no trapping by solvent water, so it is not possible to employ the “azide clock” method for measuring k_{w} . However, azide trapping can be used for measuring the rate constant (k_{e} , Scheme 4) of dehydration of the carbocation. The rate constant measured in this way is $k_{\text{e}} = 6 \times 10^8 \text{ s}^{-1}$, based upon the assumption that the azide trapping is diffusion-controlled (*vide infra*). It is 25 times smaller than the corresponding rate constant ($1.6 \times 10^{10} \text{ s}^{-1}$) for the deprotonation of the unsubstituted benzallylic carbocation.¹ This is reasonable, since it reflects the expected effects of the methyl group on the carbocation and the elimination product, which are stabilization and destabilization, respectively. The elimination rate constant of $1.6 \times 10^8 \text{ s}^{-1}$ is unusually large for a thermodynamically stable carbocation. For example, it is one order of magnitude larger than the rate constant for dehydration of the cumyl carbocation, which has a much lower thermodynamic stability.^{6f} The unusually fast hydron abstraction reflects the large thermodynamic stability of the elimination product **3** and suggests that the amount of hydron transfer in the transition state is small, corresponding to a very low Brønsted β value. The effect of general bases on the elimination-to-substitution ratio was reported to be insignificant for the unsubstituted substrate.¹ †

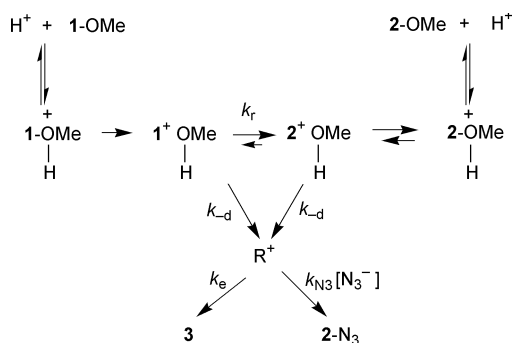
† A referee has raised a question about the fast dehydration of the cation with azide ion acting as a general base. If such a reaction is competitive with dehydration by the solvent, the derived rate constant of $k_{\text{e}} = 6 \times 10^8 \text{ s}^{-1}$ for the water reaction is an upper limit.

A lower limit for the trapping rate constant of the carbocation by solvent water could be estimated as $k_w \leq 2 \times 10^6 \text{ s}^{-1}$ based upon $k_w \leq k_d/300$ (no traces of **1-OH** and **2-OH** were observed, see Experimental section). The unsubstituted benzylic carbocation reacts with solvent water with $k_w \sim 1 \times 10^7 \text{ s}^{-1}$ (25 vol% acetonitrile in water).¹ Direct measurements of rate constants using flash photolysis have shown that carbocations with $k_w > 1 \times 10^5 \text{ s}^{-1}$ undergo diffusion-controlled reaction with azide ion in aqueous acetonitrile.¹²

The elimination product **3** is less stable than naphthalene. This is in accord with the about 2–3 kcal mol⁻¹ smaller reaction heat (Table 2). Moreover, the destabilization effect of the methyl group on the alcohol **2-OH** should be small. Therefore, we were surprised that no traces of alcohol products accompanies the elimination product **3**. We have no satisfactory explanation for this behaviour.

Ion–molecule pair intermediates

The results of the present work are consistent with a common solvent-equilibrated carbocation intermediate. The complex initially formed from the ether by carbon–oxygen cleavage is the ion–methanol pair, as indicated in Scheme 5. We have



Scheme 5

previously found indications in other systems for the intermediacy of ion–molecule pairs with significant lifetimes with methanol as the leaving group.^{6b,f,g} The failure to observe formation of **1-OH** and **2-OMe** from **1-OMe** (Scheme 2) is presumably due to an extensive delocalization of charge accompanying the cleavage of the carbon–oxygen bond. This delocalization is expected to influence the stability of the ion–molecule pair **1+OHMe** (Scheme 5), favouring diffusional separation by increasing the barrier for collapse of the ion–molecule pair back to covalent material, as well as increasing the barrier for direct substitution of the ion–molecule pair with a nucleophile, e.g. a water molecule.

This is in contrast to another aromatization reaction in which a highly delocalized carbocation is also produced.^{6f} The delocalization in this system was proposed to lag behind the rate-limiting cleavage of the carbon–oxygen bond.

Experimental

General procedures

NMR spectra were recorded at 25 °C with a Varian Unity 300 MHz spectrometer. Chemical shifts are indirectly referenced to TMS *via* the solvent signal (chloroform-*d*₁ 7.26 and 77.0 ppm). The high-performance liquid chromatography analyses were carried out with a Hewlett-Packard 1090 liquid chromatograph equipped with a diode-array detector on an Inertsil 5 ODS-2 (3 × 100 mm) reversed-phase column. The mobile phase was a solution of acetonitrile in water. The reactions were studied at constant temperature in a HETO 01 PT 623 thermostat bath. The pH was measured using a Radiometer PHM82 pH meter

with an Ingold micro glass electrode. The pH values given are those measured before mixing with the organic solvent.

The microcalorimetric experiments were carried out with a dual channel calorimeter (Thermometrics Thermal Activity Monitor 2277). The signals were recorded both on a two-channel potentiometric recorder and with a computer.

Materials

Merck silica gel 60 (240–400 mesh) was used for flash chromatography. Diethyl ether and tetrahydrofuran were distilled under nitrogen from sodium and benzophenone. Methanol and acetonitrile were of HPLC quality and HPLC UV gradient quality, respectively. All other chemicals used for the kinetic experiments were of reagent grade and used without further purification.

Syntheses

1-Hydroxy-1-methyl-1,4-dihydronaphthalene (1-OH). This was prepared by photooxygenation of 1-methyl-3,4-dihydronaphthalene, which was synthesized by methylation of α -tetralone, followed by reduction with sodium borohydride. The procedure has been described previously.¹³ The alcohol was purified by recrystallization from pentane.

1-Methoxy-1-methyl-1,4-dihydronaphthalene (1-OMe). A mixture of **1-OH** (0.18 g, 1.1 mmol), iodomethane (0.3 ml), and freshly prepared silver oxide (0.32 g, 1.4 mmol) in 2 ml of dichloromethane was stirred at room temperature for 20 h. The solution was diluted with 2 ml of pentane and directly added to an aluminium oxide column (activity grade II, basic). Elution with pentane followed by 20% diethylether–pentane gave 71 mg of the ether containing only a trace amount of 1-methylnaphthalene (**3**).

Kinetics and product studies

HPLC procedure. The reaction solutions were prepared by mixing acetonitrile or methanol with water at room temperature, *ca.* 22 °C. The reactions were initiated by addition of a few microliters of the substrate dissolved in acetonitrile to a 2 ml HPLC vial containing 1.2 ml of the thermostated reaction solution to give a final substrate concentration of about 1 mM. The reaction flask was sealed with a gas-tight PTFE septum and placed in a thermostated aluminium block in the HPLC apparatus. 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 *versus* time by means of a nonlinear regression computer program. Very good pseudo-first-order behaviour was observed for all the reactions studied.

The azide product **2-N₃** was not isolated but identified by its UV spectrum, which is similar to that of **B-N₃** (Scheme 1). The relative response factors of alcohol (**1-OH**) and 1-methylnaphthalene (**3**) were determined in a separate experiment. The relative response factor of **2-N₃** at 219 nm was assumed to be the same as that of **1-OH**. The separate rate constants for the reactions (Scheme 3 and Fig. 3) were evaluated by computer simulation based upon the product composition data, obtained from the HPLC peak areas and the relative response factors and the phenomenological reaction scheme (Scheme 3).

When starting from pure **1-OH**, the concentrations of **1-OH**, **2-N₃**, and **3** are described by the eqns. (3)–(5):¹⁴

$$\text{mol\% } \mathbf{1-OH} = ae^{-m_1 t} + (100 - a)e^{-m_2 t} \quad (3)$$

$$\text{mol\% } \mathbf{2-N_3} = be^{-m_1 t} - be^{-m_2 t} \quad (4)$$

$$\text{mol\% } \mathbf{3} = 100 - (\text{mol\% } \mathbf{1-OH}) - (\text{mol\% } \mathbf{2-N_3}) \quad (5)$$

where,

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

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

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

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

Microcalorimetric procedure. This technique has the advantage that both kinetic data and reaction heats are obtained from the same kinetic experiment. The reactions were run in parallel in the two channels, both composed of a sample compartment and a reference compartment. Glass vials (3 ml) were used as reaction and reference vessels. All four vessels were filled at the same time with 2.5 ml of premixed reaction solution (organic solvent and aqueous buffer). After this step, 20 μ l of substrate in acetonitrile was added to the two reaction vessels while 20 μ l of pure acetonitrile was added to the reference vessels. The vials were sealed with gas-tight PTFE septa and slowly introduced into the compartments of the instrument for about 15 min of pre-thermostating. They were then lowered further down into the detection chambers. The recording of the first-order heat-flow decay was started after a total equilibration time of 30–45 min. The reactions were followed for at least ten half-lives.

The microcalorimeter was statically calibrated after a kinetic experiment using the reaction solutions. The time constant of the instrument was found to be 140 s, *i.e.*, no correction for this parameter was necessary for calculation of the rate constants of the reaction heat decay.¹⁴ The rate constants were obtained from data of heat flow *versus* time by means of a nonlinear regression computer program. Very good first-order rate constants (k_{obs}) were measured. These agree well with those measured in the kinetics using the UV-spectrophotometric technique. (Table 1).

The extrapolated heat flow at time zero (P_0) was used for calculation of the reaction heat (ΔH) according to eqn. (6):

$$P_0 = \Delta H k_{\text{obs}} n \quad (6)$$

where n is the amount of substrate (mol) in the reaction vial.

The estimated errors are considered as 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.*, reaction rate constants.

Acknowledgements

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