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# Nucleofugalities of Neutral Leaving Groups in 80 % Aqueous Acetonitrile

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**Abstract:** Nucleofugalites of tetrahydrothiophene, dimethyl sulfide and differently substituted pyridines in 80 % aqueous acetonitrile have been derived from the $S_N1$ solvolysis rate constants of the corresponding X,Y-substituted benzhydryl derivatives (**1**–**10**). In solvolysis of sulfonium ions in 80 % aqueous acetonitrile, where acetonitrile is a good cation solvator, the solvation of the reactant ground state is an important rate determining variable since the positive charge is almost entirely located on the leaving group. As a consequence, reaction rates of sulfonium ions are more sensitive to the substrate structure in 80 % aqueous acetonitrile than in pure and aqueous alcohols, which are less efficient as cation solvators. In solvolysis of pyridinium ions the solvation of the reactant ground state is less important, since the positive charge is considerably distributed between the carbon at the reaction center and the leaving group. In such cases the important rate determining variable is solvation of the transition state. Slower reactions of pyridinium substrates progress over later, carbocation-like transition states in which the solvation is more important, so those substrates solvolyze slightly faster in aqueous acetonitrile than in methanol ($k_{80AN} > k_M$). Faster reactions proceed over earlier TS in which the solvation is diminished, so those substrates solvolyze somewhat faster in methanol than in aqueous acetonitrile ($k_{80AN} < k_M$).

**Keywords**: nucleofugality, reactivity, neutral leaving groups, solvolysis, aprotic solvent.

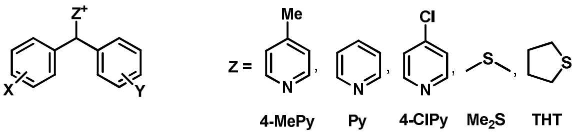
## INTRODUCTION

IT IS well known that solvents may have a strong influence on the rates of chemical reactions and chemical equilibria, and that the rate of a chemical reaction can be changed by several orders of magnitude only by changing the reaction medium.[1–3] Thus, through judicious choice of solvent, decisive acceleration or deceleration of a chemical reaction can be achieved.

Kinetic solvent effects on chemical reactions in different media are usually correlated in terms of "solvent polarity", which sums up all the specific and nonspecific interactions of the media with initial the reactant ground and transition state. Using hydrogen bonding as intermolecular interaction between the solvent molecules and solutes, the solvents used in $S_N1$ displacement reactions are usually classified as polar protic and polar aprotic (apolar aprotic solvents are not useful).[4] Polar protic solvents contain hydrogen atoms bound to electronegative elements as oxygen or nitrogen and they are usually good anion solvators. Solvents without the ability to form hydrogen bonds with the solute molecules are aprotic solvents. These solvents usually have dielectric constants larger than 30 and their molecules exhibit dipole moments larger than 2.00 *D*. The presence of a lone electron pair makes them good cation solvators and good electron-pair donor solvents. Beside acetonitrile, typical polar aprotic solvents are nitromethane, nitrobenzene, *N*,*N*-dimethylformamide, dimethyl sulfoxide, acetone, tetrahydrothiofen dioxide (sulfolane), cyclic ureas, *etc*.

In our previous works a very small variation of the rate of $S_N1$ reaction with solvent variation has been found for solvolyses of positively charged substrates (**1**–**10**) in polar protic solvents (pure and aqueous alcohols).[5–7] It is in accord with Hughes-Ingold rule that the non-creation of charge in the activation process in solvolysis reactions, as is in case with charged substrates, significantly reduces the influence of solvent polarity on rate. The pseudo first-order rate constants (*k*) for solvolysis of benzhydryldimethylsulfonium triflates,[5] benzhydryltetrahydothiophenium triflates,[6] and benzhydrylpyridinium perchlorates[7] were found to only slighty decrease with increasing solvent polarity due to more pronounced solvation effects in the reactant ground state than in the corresponding transition state.

In this work we have investigated the solvolytic reactivities of differently substituted positively charged benzhydrylium salts (**1**–**10**) in the mixture of water and polar aprotic solvent. Thus, examinations have been extended to solvolysis of benzhydryldimethylsulfonium, benzhydryltetrahydrothiophenium, and benzhydrylpyridinium salts (**1**–**10**) in 80 % aqueous acetontirile (*v*/*v*) at 25 °C. The main purpose of this work is to compare the results in aqueous acetonitrile with those obtained in pure and aqueous alcohols, and to establish how the differences in the substrate structures influence the relative rates in aqueous solvents with polar protic and polar nonprotic components, respectively.



**1** X = 4-OMe, Y = 4-OMe
**2** X = 4-OMe, Y = 4-OPh
**3** X = 4-OMe, Y = 4-Me
**4** X = 4-OMe, Y = H
**5** X = 4-Me, Y = 4-Me
**6** X = 4-Me, Y = H
**7** X = 4-F, Y = H
**8** X = H, Y = H
**9** X = 4-Cl, Y = H
**10** X = 3-Cl, Y = H

The rate of the heterolytic step in $S_N1$ solvolysis of charged substrates (**1**–**10**), similarly as that of neutral substrates, depends on the ability of a leaving group (here neutral leaving group) to depart from a substrate in a given solvent (nucleofugality) as well as on the ability of a carbocation moiety to leave a molecule (electrofugality).[8,9] These parameters have been related in the following special linear free energy relationship (LFER) [Eq. (1)] developed on solvolysis of benzhydryl derivates:

$$\log k\ (25\ ^\circ\mathrm{C}) = s_\mathrm{f}\,(E_\mathrm{f} + N_\mathrm{f}) \qquad (1)$$

in which: *k* is the first-order ionization rate constant, $s_\mathrm{f}$ is the nucleofuge-specific slope parameter, $N_\mathrm{f}$ is the nucleofugality, and $E_\mathrm{f}$ is the electrofugality parameter. $E_\mathrm{f}$ is an independent variable determined only with substituents on the benzhydryl system, whereas the nucleofuges are characterized with two parameters, $N_\mathrm{f}$ and $s_\mathrm{f}$, which are defined for the specific combination of a leaving group and a solvent.

Having in mind that the electrofugality is an independent variable in above equation (1), comparison of the nucleofuge specific parameters obtained in aqueous acetonitrile and in pure and aqueous alcoholic solvents can give valuable information about specific solvolytic behaviour of the substrates investigated.

# EXPERIMENTAL SECTION

## Substrate Preparation

All examined benzhydryldimethylsulfonium, benzhydryltetrahydrothiophenium, and benzhydrylpyridinium salts (**1**–**10**) were prepared according to the procedure described in References 5, 6 and 7.

## Kinetic Methods

Solvolysis rate constants of compounds (**1**–**10**) were measured titrimetrically by means of TIM 856 titration manager (Radiometer Analytical SAS Villeurbanne Cedex, France), using a Red Rod Ag|AgCl combined pH electrode. Typically, 20–50 mg of the substrate (**1**–**10**) was dissolved in 0.10–0.20 mL of dichloromethane, and injected into 80 % aqueous acetonitrile that was thermostated at the required temperature (±0.01 °C). The liberated dimethysulfonium triflates, tetrahydrothiophenium triflates, and pyridinium perchlorates were continuously titrated at pH ≈ 7 by using a 0.008 M or 0.016 M solution of sodium hydroxide in 80 % aqueous acetonitrile. Individual rate constants were obtained by the least-squares fitting of data to the first-order kinetic equation for three to four half-lives. The rate constants were averaged from at least three measurements.

# RESULTS AND DISCUSSION

The first-order solvolysis rates of X,Y-substituted benzhydryldimethylsulfonium, benzhydryltetrahydrothiophenium, and benzhydrylpyridinium salts (**1**–**10**) were measured titrimetrically in 80 % aqueous acetonitrile at 25 °C. In a few cases the rates were measured at least three different temperatures and extrapolated to 25 °C by using the Eyring equation. Details of kinetic measurements are given in Kinetic Methods of Experimental Section. The first-order rate constants (*k*) for solvolyses of differently substituted benzhydryldimethylsulfonium triflates (**6**–**10**-$Me_2S$), benzhydryltetrahydrothiophenium triflates (**6**–**10**-THT), and benzhydrylpyridinium perchlorates (**2**–**5**-4-ClPy, **1**–**4**-Py, **1**-4-MePy) in 80 % aqueous acetonitrile are presented in Table 1.

In order to calculate the nucleofugality ($N_\mathrm{f}$) and slope ($s_\mathrm{f}$) parameters for tetrahydrothiophene (THT), dimethyl sulfide ($Me_2S$), and substituted pyridine (4-ClPy, Py and 4-MePy) in 80 % aqueous acetonitrile, the logarithms of the first-order rate constants were plotted against reference electrofugalities determined earlier.[9] The plots of log *k* against $E_\mathrm{f}$ obtained for 80 % aqueous acetonitrile are given

**Table 1.** Solvolysis rate constants of X,Y-substituted benzhydryltetrahydrothiophenium (**6**–**10**-THT), benzhydryldimethylsulfonium (**6**–**10**-$Me_2S$), and benzhydrylpyridinium salts (**2**–**5**-4-ClPy, **1**–**4**-Py and **1**-4-MePy) in 80 % aqueous acetonitrile

| Compound | $E_\mathrm{f}$(a) | $t$ / °C | $k$ / $s^{-1}$ (b) |
|---|---|---|---|
| Z = 4-Methylpyridine (4-MePy) | | | |
| **1** X = 4-OMe, Y = 4′-OMe | 0.00 | 25 | (2.15 ± 0.03) × $10^{-4}$ |
| Z = Pyridine (Py) | | | |
| **1** X = 4-OMe, Y = 4′-OMe | 0.00 | 25 | (1.85 ± 0.04) × $10^{-3}$ |
| **2** X = 4-OMe, Y = 4′-OPh | −0.86 | 25 | (2.33 ± 0.06) × $10^{-4}$ |
| **3** X = 4-OMe, Y = 4′-Me | −1.32 | 25 | (6.89 ± 0.06) × $10^{-5}$ |
| **4** X = 4-OMe, Y = H | −2.09 | 25 | (1.28 ± 0.06) × $10^{-5}$ |
| Z = 4-Chloropyridine (4-ClPy) | | | |
| **2** X = 4-OMe, Y = 4′-OPh | −0.86 | 5 | (3.23 ± 0.02) × $10^{-4}$ |
| | | 10 | (6.40 ± 0.02) × $10^{-4}$ |
| | | 15 | (1.33 ± 0.04) × $10^{-4}$ |
| | | 25 | 4.92 × $10^{-3}$ (c,d) |
| **3** X = 4-OMe, Y = 4′-Me | −1.32 | 25 | (1.31 ± 0.10) × $10^{-3}$ |
| **4** X = 4-OMe, Y = H | −2.09 | 25 | (2.38 ± 0.04) × $10^{-4}$ |
| **5** X = 4-Me, Y = 4′-Me | −3.44 | 25 | (8.71 ± 0.04) × $10^{-6}$ |
| Z = Dimethyl sulfide ($Me_2S$) | | | |
| **6** X = 4-Me, Y = H | −4.68 | 5 | (6.11 ± 0.01) × $10^{-4}$ |
| | | 7 | (8.23 ± 0.06) × $10^{-4}$ |
| | | 10 | (1.35 ± 0.01) × $10^{-3}$ |
| | | 12 | (1.86 ± 0.02) × $10^{-3}$ |
| | | 15 | (3.05 ± 0.01) × $10^{-3}$ |
| | | 25 | 1.36 × $10^{-2}$ (c,e) |
| **7** X = 4-F, Y = H | −5.78 | 25 | (9.54 ± 0.10) × $10^{-4}$ |
| **8** X = H, Y = H | −6.05 | 25 | (6.51 ± 0.10) × $10^{-4}$ |
| **9** X = 4-Cl, Y = H | −6.52 | 25 | (2.76 ± 0.01) × $10^{-4}$ |
| **10** X = 3-Cl, Y = H | −7.74 | 25 | (1.72 ± 0.02) × $10^{-5}$ |
| Z = Tetrahydrothiophene (THT) | | | |
| **6** X = 4-Me, Y = H | −4.68 | 0.2 | (2.93 ± 0.03) × $10^{-4}$ |
| | | 5 | (6.95 ± 0.04) × $10^{-4}$ |
| | | 10 | (1.60 ± 0.03) × $10^{-3}$ |
| | | 25 | 1.75 × $10^{-2}$ (c,f) |
| **7** X = 4-F, Y = H | −5.78 | 25 | (1.41 ± 0.03) × $10^{-3}$ |
| **8** X = H, Y = H | −6.05 | 25 | (8.91 ± 0.03) × $10^{-4}$ |
| **9** X = 4-Cl, Y = H | −6.52 | 25 | (2.85 ± 0.04) × $10^{-4}$ |
| **10** X = 3-Cl, Y = H | −7.74 | 25 | (1.88 ± 0.01) × $10^{-5}$ |

(a) The electrofugality parameters $E_\mathrm{f}$ are taken from Ref. 9.

(b) Average rate constants from at least three runs performed at 25 °C. Errors are standard deviations.

(c) Extrapolated from data at different temperatures by using the Eyring equation.

(d) $\Delta H^‡$ = 91.9 ± 2.8 $kJmol^{-1}$, $\Delta S^‡$ = 19.2 ± 9.8 $JK^{-1}mol^{-1}$. Errors shown are standard errors.

(e) $\Delta H^‡$ = 105.1 ± 1.5 $kJmol^{-1}$, $\Delta S^‡$ = 71.9 ± 5.2 $JK^{-1}mol^{-1}$. Errors shown are standard errors.

(f) $\Delta H^‡$ = 109.2 ± 1.3 $kJmol^{-1}$, $\Delta S^‡$ = 87.5 ± 4.8 $JK^{-1}mol^{-1}$. Errors shown are standard errors.

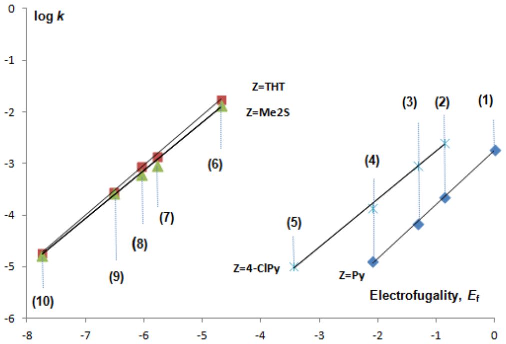


**Figure 1.** Plots of solvolysis rate constants log $k$ (25 °C) *vs.* the electrofugality parameters ($E_\mathrm{f}$)[9] of X,Y-substituted benzhydryltetrahydrothiophenium (**6**-**10**-THT), benzhydryldimethylsulfonium (**6**–**10**-$Me_2S$), benzhydryl-4-chloropyridinium (**2**–**5**-4-ClPy), and benzhydrylpyridinium (**1**–**4**-Py) ions in 80 % aqueous acetonitrile.

in Figure 1, whereas the extracted nucleofuge-specific parameters for tetrahydrothiophene, dimethyl sulfide, 4-chloropyridine, and pyridine in 80 % aqueous acetonitrile from the correlation lines ($R^2 > 0.99$) are given in Table 2. Nucleofugality of 4-methylpyridine in 80 % aqueous acetonitrile was obtained from a single rate constant of 4,4'-dimethoxybenzhydryl-4-methylpyridinium salts (**1**-4-MePy) and the average $s_\mathrm{f}$ value for pyridine (Py) and 4-chloropyridine (4-ClPy) in 80 % aqueous acetonitrile ($s_\mathrm{f}$ = 1.045) using Eq. (1). To compare the reactivities of the positively charged substrates (**1**–**10**) in protic solvents with those obtained in solvent with polar aprotic component, the nucleofuge specific parameters $N_\mathrm{f}$ and $s_\mathrm{f}$ for THT, $Me_2S$, 4-ClPy, Py, and 4-MePy in pure methanol obtained earlier[5–7] are also presented in Table 2.

The results presented in Tables 1 and 2 show that the decreasing trend of the reactivities of positively charged differently substituted benzhydryltetrahydrothiophenium, benzhydryldimethylsulfonium, and benzhydrylpyridinium salts (**1**–**10**) in 80 % aqueous acetonitrile is as follows: benzhydryltetrahydrothiophenium ions > benzhydryldimethylsulfonium ions > benzhydryl-4-chloropyridinium ions > benzhydrylpyridinium ions > benzhydryl-4-methylpyridinium ion. The same order of reactivities has been found in the series of aqueous and pure alcohols.[5–7] Again, the most important variable that determines the reactivity of charged substrates in aprotic solvent/water mixture, similarly as in aqueous and pure alcohols, is the solvation of the starting benzhydryl salts.

## Sulfonium Salts

Natural bond orbital (NBO) calculations in gas phase and in ethanol at B3LYP/6-311+G(2d,p) level of theory showed that the positive charge is almost completely (about 94 %

**Table 2.** Nucleofugality parameters $N_f$ and $s_f$ for tetrahydrothiophene (THT), dimethyl sulfide ($Me_2S$), 4-chloropyridine (4-ClPy), pyridine (Py), and 4-methylpyridine (4-MePy) in 80 % aqueous acetonitrile and pure methanol[5–7]

| Leaving group | 80 % aq. Acetonitrile | | Methanol | |
|---|---|---|---|---|
| | $N_f$ [(a)] | $s_f$ [(a)] | $N_f$ [(a)] | $s_f$ [(a)] |
| Tetrahydrothiophene (THT) | 2.87 ± 0.15 | 0.97 ± 0.06 | 2.81 ± 0.18[(c)] | 0.86 ± 0.04[(c)] |
| Dimethyl sulfide ($Me_2S$) | 2.64 ± 0.10 | 0.94 ± 0.05 | 2.78 ± 0.21[(d)] | 0.88 ± 0.05[(d)] |
| 4-Chloropyridine (4-ClPy) | −1.36 ± 0.16 | 1.05 ± 0.06 | −0.95 ± 0.03[(e)] | 1.24 ± 0.01[(e)] |
| Pyridine (Py) | −2.64 ± 0.14 | 1.04 ± 0.04 | −2.28 ± 0.17[(e)] | 1.18 ± 0.06[(e)] |
| 4-Methylpyridine (4-MePy) | −3.51[(b)] | 1.05[(b)] | −3.06[(e)] | 1.21[(e)] |

[(a)] Errors shown are standard errors.
[(b)] Calculated from the rate of 4,4'-dimethoxybenzhydryl-4-methylpyridinium salts (1-4-MePy) and the average sf value of pyridine (Py) and 4-chloropyridine (4-ClPy) in 80% aqueous acetonitrile (sf = 1.05) using Eq. (1).
[(c)] Data in pure methanol are taken from Ref. 6.
[(d)] Data in pure methanol are taken from Ref. 5.
[(e)] Data in pure methanol are taken from Ref. 7.

in ethanol)[6] located on the leaving group, so the demand for solvation in the reactant ground state is very important. However, the charge between the sulfur and the alkyl moiety is not equally distributed, but it is slightly lower on the sulfur of benzhydryltetrahydrothiophenium ion (0.80) than on the sulfur in benzhydryldimethylsulfonium ion (0.84), that is, the positive charge is somewhat more delocalized in the larger THT moiety. Because of less pronounced charge delocalization in $Me_2S$, the solvation of the reactant ground state in aqueous acetonitrile is more significant, hence the rates of all benzhydryldimethylsulfonium salts in 80 % aqueous acetonitrile are lower than the rates of the corresponding benzhydryltetrahydrothiophenium ions (Table 1). Higher reactivities of tetrahydrothiophenium ions than benzhydryldimethylsulfonium ions in solvolysis in pure and aqueous alcohols which are less efficient cation solvators, have earlier been attributed to lower intrinsic barriers.[6]

Because of somewhat more delocalized charge in the reactant ground state, tetrahydrothiophenium ions are less sensitive to the aprotic/protic solvent change than dimethylsulfonium salts. The ratios between the solvolysis rate constants of, for example, 4-fluorobenzhydryltetrahydrothiophenium (**7**-THT) and benzhydryltetrahydrothiophenium (**8**-THT) salts in 80 % aqueous acetonitrile and in 80 % aqueous ethanol[6] are 2.0 and 1.3, respectively whereas the ratios between the solvolysis rate constants of 4-fluorobenzhydryldimethylsulfonium (**7**-$Me_2S$) and benzhydryldimethylsulfonium (**8**-$Me_2S$) salts in the same solvents are 2.6 and 1.7,[5] respectively.

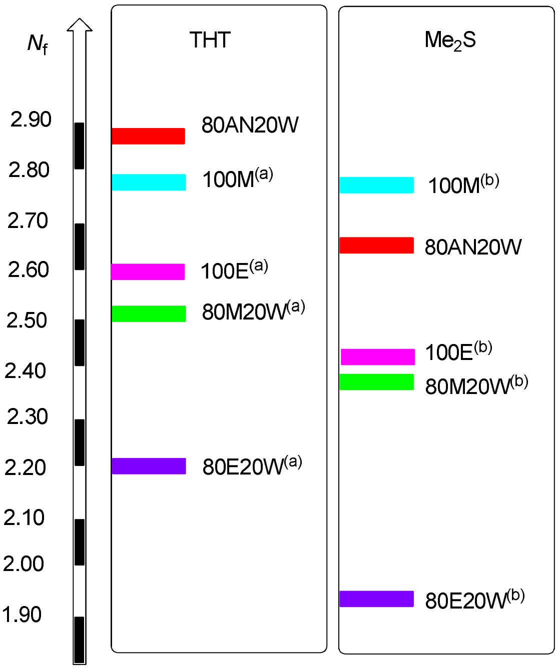


**Figure 2.** Nucleofugality parameter $N_f$ for tetrahydrothiophene (THT) and dimethyl sulfide ($Me_2S$) in various solvents (data for a and b are taken from Ref. 5 and 6, respectively).

All substituted benzhydryltetrahydrothiophenium and benzhydryldimethylsulfonium ions measured here solvolyze faster in 80 % aqueous acetonitrile than in 80 % aqueous ethanol and somewhat slower than in pure alcohols (absolute methanol and ethanol). However, it should be mentioned that according to rates predicted by equation (1), more reactive benzhydryltetrahydrothiophenium ions solvolyze faster in 80 % aqueous acetonitrile than in pure methanol. For example, the rate ratio for 4,4'-dimethoxylbenzhydryl derivate ($E_f$ = 0) of THT is $k_{80AN}/k_M$ = 2.33 ($k_{80AN} = 6.08 \times 10^2$ s$^{-1}$, $k_M = 2.61 \times 10^2$ s$^{-1}$). On the other hand, the rates of 4,4'-dimethoxylbenzhydryl derivative of $Me_2S$ in those two solvents are virtually the same ($k_{80AN}$ = $3.03 \times 10^2$ s$^{-1}$ *vs.* $k_M = 2.79 \times 10^2$ s$^{-1}$). Having in mind that more efficient stabilization of the reactant ground state diminishes the solvolysis rate, the above calculations indicate again that the stabilization of the reactant ground state by acetonitrile is less important in THT than in $Me_2S$. Similarly as the rate constants, $N_f$ values of tetrahydrothiophene in all examined polar protic solvents and 80 % aqueous acetonitrile, are slightly higher than $N_f$ values of dimethyl sulfide, indicating again that THT is somewhat better leaving group than $Me_2S$ in all solvents investigated (Table 2, Figure 2).

## Pyridinium Salts

Pyridine and its 4-substituted derivates (4-methylpyridine and 4-chloropyridine) are relatively poor leaving groups, similarly as *e.g.*, benzoate,[10] formate,[11,12] acetate,[11,12] isobutyrate,[11,12] and pivalate. [11,12] The electron-withdrawing substituents on the pyridine ring increase the rate of heterolysis step in 80 % aqueous acetonitrile similarly as in pure and aqueous alcohols,[7] so the $N_f$ value of 4-methylpyridine (4-MePy) is for about three units less than the $N_f$ value of 4-chloropyridine (4-ClPy). Benzhydrylpyridinium ions solvolyze slower than the corresponding benzhydrylsulfonium ions for about four to six orders of magnitude, depending on polarity of the solvents and also on the substituents on pyridine.[7]

Previous results obtained computationally in gas phase and in ethanol at MP2(fc)/6-31G(d) level of theory (solvent polarizable continuum model) showed that the positive charge in the reactant ground state of benzhydrylpyridinium ions is distributed between the nitrogen atom and the methine carbon atom in a way that only 66 % of the positive charge is located on the nitrogen atom.[13] It has also been shown that the charge distribution is almost invariant of the substituents on the benzhydryl group or pyridine moiety. This observation is completely different from that obtained with sulfonium salts (tetrahydrothiophenium and dimethylsulfonium) in which the positive charge is almost completely located on the leaving group.[6] Due to less positive charge on the heteroatom in the reactant ground state of pyridinium salts, the solvation effect of aprotic component of the aqueous solvent in the reactant ground state is less important for pyridinium salts than for sulfonium salts.

Because of the invariant charge distribution of the partial charges in the reactant ground state of beznhydrylpyridinium salts with changing electrofugality,[13] it can be approximated that the stabilizations by solvation in all the reactant ground states are similar. Thus, solvent effects of pyridinium salts come from different solvation of the transition state. To establish the effects of the solvent, it turned out again that it is advantageous to compare the ratios of the rate constants for various X,Y-substituted benzhydrylpyridinium salts in 80 % aqueous acetonitrile and pure methanol ($k_{80AN}/k_M$). Unlike sulfonium salt which all solvolyze faster in pure methanol than in 80 % aqueous acetonitrile, the ratio between the solvolysis rate constants of pyridinium ions in pure methanol and 80 % aq. acetontirile depend on absolute rate constants. The rate ratios $k_{80AN}/k_M$ obtained for some X,Y-substituted benzhydrylpyridinium ions are presented in Table 3 in which the rate constants in 80 % aqueous acetonitrile are presented in deccreasing order.

Table 3. Relative rate constants of some X,Y-substituted benzhydrylpyridinium ions in 80 % aqueous acetonitrile and pure methanol at 25 °C

| Substrate[(a)] | $k_{80AN}$ / $s^{-1}$ [(b)] | $k_{80AN}/k_M$[(c)] |
|---|---|---|
| **2**-4-ClPy | $4.92 \times 10^{-3}$ | 0.86 |
| **1**-Py | $1.85 \times 10^{-3}$ | 0.88 |
| **3**-4-ClPy | $1.31 \times 10^{-3}$ | 0.84 |
| **4**-4-ClPy | $2.38 \times 10^{-4}$ | 1.30 |
| **2**-Py | $2.33 \times 10^{-4}$ | 1.00 |
| **1**-4-MePy | $2.15 \times 10^{-4}$ | 1.09 |
| **3**-Py | $6.89 \times 10^{-5}$ | 1.52 |
| **4**-Py | $1.28 \times 10^{-5}$ | 1.69 |
| **5**-4-ClPy | $8.71 \times 10^{-6}$ | 2.50 |

(a) 4-ClPy = 4-chloropyridinium ion, Py = pyridinium ion, 4-MePy = 4-methylpyridinium ion.
(b) At 25 °C.
(c) Data for $k_M$ are taken from Ref. 7.

More reactive pyridinium substrates (**2**-4-ClPy, **1**-Py, and **3**-4-ClPy) solvolyze somewhat faster in pure methanol than in 80 % aq. acetontrile, while for the least reactive pyridinium salt the rate constants in 80 % aq. acetonitrile are higher than in pure methanol ($k_{AN}/k_M = 2.50$ for **5**-4-ClPy). This observation can be rationalized in terms of earlier and later transition state. Unlike the most reactive benzhydrylpyridinium substrates in which the charge distribution is similar in the reactant ground state and in early TS, in the later TS of the least reactive benzhydrylpyridinium substrates the transfer of the positive charge to the carbon atom is much more advanced. Therefore, the rate is enhanced in 80 % aq. acetonitrile in comparison to pure methanol due to more demand for solvation in the former. In the reaction that proceeds over early TS (solvolysis of more reactive pyridinium salts), the effect of solvation in TS is similar as the effect of solvation in the reactant ground state and the rate constants of more reactive pyridinium salts are similar in pure methanol and 80 % aq. acetonitrile.

The slopes of all log $k$ *vs.* $E_f$ correlation lines ($s_f$) obtained for tetrahydrothiofene, dimethyl sulfide and pyridine in 80 % aqueous acetonitrile (Table 2) are in the range of the $s_f$ values obtained for numerous substrates that solvolyze via $S_N1$ route ($s_f = 0.78-1.25$).[14] However, the values of the slope parameters obtained for pyridinium ions in

80 % aq. acetonitrile ($s_f$ = 1.05 for 4-ClPy and $s_f$ = 1.04 for Py) are considerably lower than the $s_f$ parameters obtained in pure and aqueous alcohols[7] ($s_f$ > 1.10; see Table 2 for pure methanol) while the values of the $s_f$ for THT and $Me_2S$ are higher in 80 % aqueous acetonitrile ($s_f$ = 0.97 and 0.94, respectively) than in pure and aqueous alcohols ($s_f$ is in the range of 0.86 to 0.89).[5,6] This observation can also be attributed to different importance of the solvation of the reactant ground state of sulfonium and pyidinium ions. In solvolysis of sulfonium ions in 80 % aq. acetonitrile, the solvation is very important because the positive charge is, as mentioned above, practically entirely located on the leaving group, so the reaction rates are more sensitive to the substrate structure than in alcohols. On the other hand, in pyridinium ions the positive charge is already delocalized in the reactant ground state, importance of solvation is diminished, and the solvolysis rates are less influenced with the substrate structure.

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