Ureas and amides as dipolar aprotic solvents in highly basic media. The dependence of kinetic basicity on solvent composition

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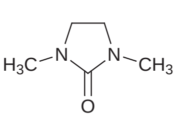
The basicity of dipolar aprotic solvent–water–HO⁻ systems with amides and ureas as the organic component has been studied kinetically because previous information is not available, excluding some H_- values measured for aqueous dimethylformamide (DMF) and tetramethylurea (TMU). It was found that the increase in basicity with the mole fraction of organic component is at least of the same magnitude as in aqueous dimethyl sulfoxide (DMSO). For instance, in the detritiation of chloroform-*t* the slopes of the plots $\log(k_2/\text{mol}^{-1}\ \text{dm}^3\ \text{s}^{-1})$ *vs.* x(urea) varied between 11.4–14.6 (as compared to 11.0 in aqueous DMSO) when TMU and cyclic ureas, 1,3-dimethylimidazolidin-2-one (DMI) and 1,3-dimethyl-3,4,5,6-tetrahydropyrimidin-2(1*H*)-one (DMPU), were used as the organic component in solvent mixture. In aqueous TMU acidity functions H_- were extrapolated from kinetic results using linear free energy correlations. Agreement with literature values was evident. This method was also used to extrapolate the H_- values in aqueous DMPU. On the basis of present work aqueous ureas can be recommended as solvents in highly basic media. The utility of amides, dimethylformamide and dimethylacetamide, is limited by their instability in basic water solutions.

Introduction

Water–dipolar aprotic solvent–HO⁻ systems are very useful highly basic media because their basicity can be changed gradually by increasing the amount of organic component in the solvent.[1a] As an additional advance, the solubility of organic compounds increases simultaneously. For instance, dimethyl sulfoxide (DMSO), sulfolane, acetonitrile, *N*,*N*-dimethylformamide (DMF), hexamethylphosphoric triamide (HMPA), pyridine, and tetramethylurea (TMU) have been used as the organic component and acidity functions, H_-, for these systems are available.[1a,2–7] The highest basicity is obtained in aqueous HMPA[6,8] but its suitability for use is reduced by its carcinogenic properties. Cyclic ureas, 1,3-dimethylimidazolidin-2-one (DMI, **I**) and 1,3-dimethyl-3,4,5,6-tetrahydropyrimidin-2(1*H*)-one (DMPU, **II**), which can replace HMPA as the solvent, have been studied intensively since the eighties.[9] However, information on the basicity of the water–cyclic urea (**I**) or (**II**)–HO⁻ system is not available. Therefore, we studied in this work the suitability of DMI and DMPU in highly basic media. The basicity of some acyclic amide and urea analogs, *N*,*N*-dimethylformamide $HCON(CH_3)_2$, *N*,*N*-dimethylacetamide (DMA) $CH_3CON(CH_3)_2$, and tetramethylurea $(CH_3)_2NCON(CH_3)_2$, was also studied for comparison.



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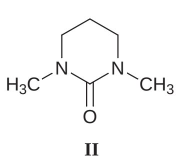

II

The amides and ureas mentioned above are sufficiently dipolar for water–aprotic solvent–HO⁻ mixtures with the following relative permittivities at 298 K: 37.60 (DMI),[10] 36.12 (DMPU),[10] 37.0 (DMF),[11] 37.78 (DMA)[11] and 23.45 (TMU).[11] Relative permittivities of aqueous TMU[12] and DMPU[13] decrease gradually from 78.39 to that of pure urea. In the density values of aqueous TMU,[12] DMPU,[13,14] DMF[15] and DMA[16] at 298.15 K a maximum is observed when the mole fraction of amide or urea is between 0.1 and 0.3, depending on the organic component. These maxima suggest[12] that water forms stable complexes with ureas and amides. The measured viscosities of aqueous TMU,[12] DMPU,[13] DMF[17] and DMA[16] are also in accordance with this complex formation as the maximum value is observed when the mole fraction of amide or urea is in the above mentioned range. Negative excess volumes of aqueous TMU,[12] DMI,[18] DMPU,[13,14] DMF[19] and DMA[16] reveal that interactions between water and amide (or urea) are more significant than water–water or amide–amide (or urea–urea) interactions. As a result of the complex formation between water and urea (or amide) desolvation of hydroxide ion may be exceptionally high when water is replaced by urea or amide. A considerable increase in basicity is thus expected in these solvents. The maxima in densities and viscosities are especially high in water–DMPU mixtures.[13,14] Consequently, a significant increase in basicity is expected with x(DMPU). Some values for the acidity function H_- have previously been measured for aqueous DMF[4] and aqueous TMU.[6]

In this work the basicities of different amide and urea systems were determined kinetically. The detritiation of carbon acids [eqns. (1) and (2)] was chosen as the model reaction in the measurements. Eqn. (3) can be obtained for the rate of

$$\text{RT} + \text{HO}^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{R}^-\cdot\text{TOH} \qquad (1)$$

$$\text{R}^-\cdot\text{TOH} \xrightarrow{k_2} \text{R}^- + \text{TOH} \qquad (2)$$

$$v = [k_1k_2/(k_{-1} + k_2)][\text{RT}][\text{HO}^-] = k_{\text{obs}}[\text{RT}][\text{HO}^-] \qquad (3)$$

detritiation by applying the steady state approximation to the hydrogen bonded complex $\text{R}^-\cdot\text{TOH}$.[16] In the detritiation of those carbon acids which produce localized carbanions $k_{-1} \gg k_2$ and consequently $k_{\text{obs}} = (k_1/k_{-1})k_2 = Kk_2$ in eqn. (3). When delocalized carbanions are formed in the detritiation $k_2 \gg k_{-1}$, which means that in eqn. (3) $k_{\text{obs}} = k_1$. Thus, depending on the mechanism of detritiation, the observed rate coefficient is proportional either to the equilibrium constant of the ionization reaction or to the rate coefficient of this ionization. Because both of these constants are dependent on the medium basicity, the measured log (k_{obs}/mol^{-1} dm^3 s^{-1}) values give information on changes in solvent basicity. As previously,[20] the detritiation of chloroform-*t* $CTCl_3$ (**1**) was chosen as the model reaction. To show that the order in basicity is independent of the carbon acid used in the kinetic measurements, the rate coefficients of the detritiation of 1,1,1-trifluoro-2-bromo-2-chloroethane $F_3CCBrClT$ (**2**, halotane-*t*) were determined in aqueous DMA and DMPU. In addition, 1,1-difluoro-2,2-dichloroethyl methyl ether $CH_3OCF_2CCl_2T$ (**3**, methoxyflurane-*t*) was submitted to kinetic studies in aqueous cyclic ureas to extend the measurements to mixtures with *x*(amide or urea) at least 0.5. In aqueous ureas some measurements were performed with acetophenone-*t* $PhCOCH_2T$ (**4**) as the model carbon acid.

In dilute aqueous solutions the HO^- promoted hydrolysis of amides[21,22] takes place with attack of the hydroxide ion on the acyl carbon. The reaction produces amines and carboxylate ions, lowering the hydroxide ion concentration in aqueous amide or urea. If this base-promoted reaction is significant, the utility of the amide (or urea)–water system as a highly basic medium is questionable. The instability of the dimethylformamide–water system containing hydroxide ion is evident on the basis of previous data.[23] If the instability has not been taken into account when kinetic measurements have been performed in aqueous DMF, the validity of rate coefficients is questionable due to the uncertainty of the hydroxide ion concentration of the solution. Therefore, we studied systematically the effect of the possible hydrolytic decomposition on hydroxide ion concentration in aqueous amide or urea.

Experimental

Materials

Dipolar aprotic solvents used in this work were TMU (Merck, 99%), DMI (Aldrich-Chemie, 98% and Fluka 99.5%), DMPU (Aldrich-Chemie, 98%), DMF (Merck 99.5%) and DMA (Fluka, 99%). The solvents were distilled at reduced pressure over calcium hydride. The middle fraction was collected. The products were stored in brown bottles to prevent possible photochemical decomposition reactions. Laboratory reverse-osmosis water was degassed before use. Mixtures of water with amides and ureas were prepared by weight.

The following tritiated carbon acids were used in kinetic measurements: chloroform, 1,1-difluoro-2,2-dichloroethyl methyl ether (methoxyflurane), 1,1,1-trifluoro-2-bromo-2-chloroethane (halotane) and acetophenone. The labelling of chloroform and acetophenone has been described previously.[24] Methoxyflurane and halothane were labelled by the same method.

Table 1 Hydrolytic decomposition of different amides and ureas in their mixtures with water at 298.15 K. The initial concentration of sodium hydroxide was 0.02 mol dm^{-3}

Amide or urea	*x* (amide or urea)	*k*/10^{-4} s^{-1}	Reference
DMF	0.076	9.9	23
	0.091	13.6	This work
	0.291	18.5	23
	0.303	19.2	This work
	0.499	5.8	This work
	0.536	6.1	23
	0.806	2.3	23
DMA	0.095	0.56	This work
	0.192	0.63	This work
	0.313	0.53	This work
	0.499	0.81	This work
DMI	0.100	0.015	This work
DMPU	0.100	0.0081	This work
TMU	0.100	0.0049	This work

Detritiation of carbon acids

The performance of kinetic measurements has been described previously.[20] In the reaction mixture the concentration of tetramethyl ammonium hydroxide was 0.011 mol dm^{-3}. The second order rate coefficients were found to be independent of hydroxide ion concentration. The base was added just before the reaction was started to exclude the possible decomposition of amide or urea. The detritiation of chloroform-*t* and acetophenone-*t* was studied at 298.15 K. With chloroform-*t* measurements were performed at four temperatures and the rate coefficients at 298.15 K were calculated on the basis of the Arrhenius equation. The detritiation of halotane-*t* and methoxyflurane-*t* was studied mainly at 278.15 K. In some mixtures measurements were performed at 3 or 4 temperatures.

Decomposition of aqueous amide and urea mixtures in basic solutions

The hydrolytic decomposition of amides and ureas was studied at 298.15 K in mixtures of *x*(amide or urea) ≈ 0.1. In water–DMF and water–DMA solvent mixtures the composition was also varied. In kinetic runs the concentration of sodium hydroxide was 0.02 mol dm^{-3}. The hydrolytic decomposition was followed with a Metrohm 644 conductometer equipped with a thermostated reaction cell. To prevent the absorption of carbon dioxide, nitrogen was passed over the solution during the reaction. As the hydrolytic decomposition of DMF and DMA was relatively fast, the progress of the reaction was followed directly in the reaction cell. For tetramethylurea and cyclic ureas 10 cm^3 samples were taken from the reaction mixture and quenched with 10 cm^3 of ice-cold water to stop the reaction. Hydroxide ion concentration in these samples was determined conductometrically by titrating with 2 mol dm^{-3} aqueous hydrogen chloride. In titration the acid solution was added with an Agla semimicro syringe. The consumption of aqueous hydrogen chloride was proportional to the progress of the reaction.

Results

Hydrolytic decomposition of ureas and amides

First-order rate coefficients for the hydrolytic decomposition of amides and ureas are given in Table 1. Dimethylformamide and dimethylacetamide were studied in several water–amide mixtures. The rate coefficients in aqueous DMF are in accordance with those of Buncel and Symons[23] (Table 1). A maximum is observed at *x*(DMF) ≈ 0.2. In aqueous DMA the dependence of rate coefficients on solvent composition remains obscure on the basis of present data.

The stability of aqueous TMU, DMI and DMPU was studied only in mixtures with *x*(organic component) = 0.1 (Table 1). The rate coefficients for the hydrolytic decomposition give half lives of 16 d (TMU), 5 d (DMI) and 10 d (DMPU) which are markedly higher than those for DMA (4 h) and DMF (9 min) in the same conditions.

Detritiation of different carbon acids in aqueous ureas or amides

Kinetic results for the detritiation of chloroform-*t* (**1**), halotane-*t* (**2**), methoxyflurane-*t* (**3**) and acetophenone-*t* (**4**) are presented in Table 2. In the detritiation of chloroform-*t* the measurements at 298.15 K could be extended to solutions with *x*(amide or urea) < 0.2. When the logarithms of the rate coefficients in water–DMPU and water–DMA mixtures are plotted against the mole fraction of organic component, a linear correlation is

Table 2 Second order rate coefficients for the detritiation of ST in water–amide and water–urea mixtures: (**1**) chloroform-*t*, (**2**) halotane-*t*, (**3**) methoxyflurane-*t* and (**4**) acetophenone-*t*. 0.011 mol dm^{-3} tetramethylammonium hydroxide has been used as the catalyst

ST	T/K	Amide or urea	x (amide or urea)	k_2/mol^{-1} dm^3 s^{-1}	α[c]
1	298.15	DMF	0.000	0.172[a]	
			0.0486	0.406 ± 0.005	
			0.0500	0.433 ± 0.013	
			0.0966	1.43 ± 0.03	
			0.157	6.50 ± 0.25	11.07 ± 0.10[d]
		DMA	0.000	0.172[a]	
			0.0483	0.583 ± 0.003	
			0.0952	1.87 ± 0.02	
			0.140	6.45 ± 0.17	11.3 ± 0.3
		TMU	0.000	0.172[a]	
			0.0273	0.324 ± 0.004	
			0.0492	0.596 ± 0.005	
			0.102	2.90 ± 0.18[b]	
			0.143	8.92 ± 0.20	
			0.188	33.6 ± 1.7[b]	12.32 ± 0.18
		DMI	0.000	0.172[a]	
			0.0149	0.202 ± 0.002	
			0.0267	0.265 ± 0.001	
			0.0495	0.483 ± 0.005	
			0.0512	0.565 ± 0.035[b]	
			0.0955	1.54 ± 0.12[b]	
			0.1009	1.64 ± 0.15[b]	
			0.142	5.21 ± 0.06	
			0.193	22.8 ± 0.5[b]	11.4 ± 0.3[d]
		DMPU	0.000	0.172[a]	
			0.0250	0.383 ± 0.005	
			0.0496	0.931 ± 0.006	
			0.0763	2.39 ± 0.03	
			0.0972	4.69 ± 0.01[b]	
			0.190	100 ± 4[b]	14.60 ± 0.13
2	278.15	DMA	0.000	0.0235 ± 0.0020[b]	
			0.0369	0.0572 ± 0.0013	
			0.0667	0.214 ± 0.004	
			0.0735	0.124 ± 0.001	
			0.109	0.680 ± 0.014	
			0.146	2.20 ± 0.08	
			0.154	2.65 ± 0.04	13.8 ± 0.4
		DMPU	0.000	0.0235 ± 0.0020[b]	
			0.0256	0.0856 ± 0.0015	
			0.0614	0.314 ± 0.003	
			0.0795	0.730 ± 0.013	
			0.111	2.72 ± 0.05	18.3 ± 0.5
3	278.15	DMI	0.000	0.000080 ± 0.000003[b]	
			0.0977	0.000348 ± 0.000005	
			0.192	0.00328 ± 0.00007	
			0.265	0.0160 ± 0.0002	
			0.387	0.187 ± 0.016[b]	
			0.488	2.22 ± 0.03	9.59 ± 0.18[d]
		DMPU	0.000	0.000080 ± 0.000003[b]	
			0.0966	0.000704 ± 0.000012	
			0.193	0.0055 ± 0.0006	
			0.262	0.0243 ± 0.0002	
			0.372	0.311 ± 0.010[b]	
			0.459	2.02 ± 0.05	
			0.503	5.0 ± 1.0	9.56 ± 0.05
4	298.15	TMU	0.000	0.00574[a]	
			0.0518	0.00669 ± 0.00005	
			0.112	0.01010 ± 0.00014	
			0.197	0.0224 ± 0.0003	
			0.377	0.119 ± 0.002	
			0.573	0.740 ± 0.005	4.043 ± 0.004[e]
		DMI	0.000	0.00574[a]	
			0.0529	0.00488 ± 0.00008	
			0.111	0.00690 ± 0.00007	
			0.192	0.0148 ± 0.0004	
			0.379	0.0981 ± 0.0017	
			0.570	0.682 ± 0.001	
			0.664	1.89 ± 0.02	4.41 ± 0.04[e]
		DMPU	0.000	0.00574[a]	
			0.0509	0.00926 ± 0.00006	
			0.101	0.0161 ± 0.0001	
			0.190	0.0352 ± 0.0005	
			0.375	0.255 ± 0.004	
			0.550	2.08 ± 0.02	4.62 ± 0.10

[a] See ref. 20. [b] Calculated from the measurements at different temperatures. [c] Slope of the plot log (k_2/mol^{-1} dm^3 s^{-1}) *vs.* x(amide or urea). [d] Points x(DMF) = x(DMI) = 0.000 are not included in the calculation of slopes. [e] Only the points with x(urea) higher than 0.1 are included in the calculation of slopes.

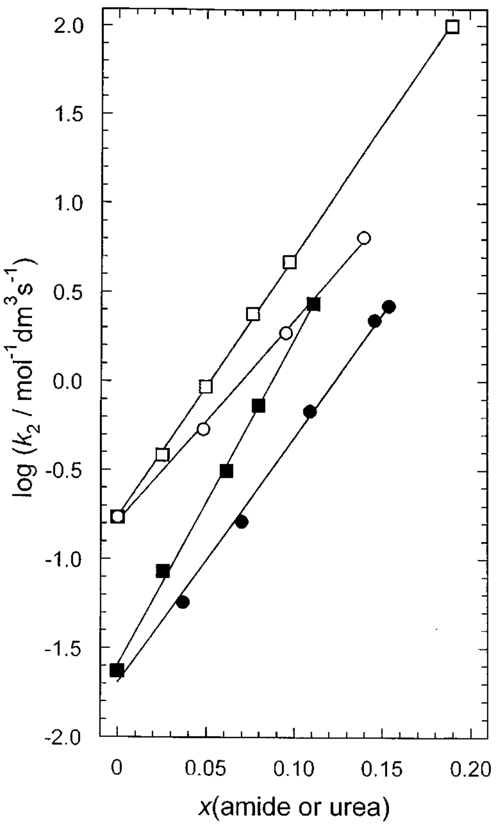

Fig. 1 Logarithms of the second-order rate coefficients in the detritiation of chloroform-*t* (**1**) at 298.15 K and halotane-*t* (**2**) at 278.15 K. Notations: Water–DMPU (square), water–DMA (circle), chloroform-*t* (open symbol), and halotane-*t* (solid symbol).

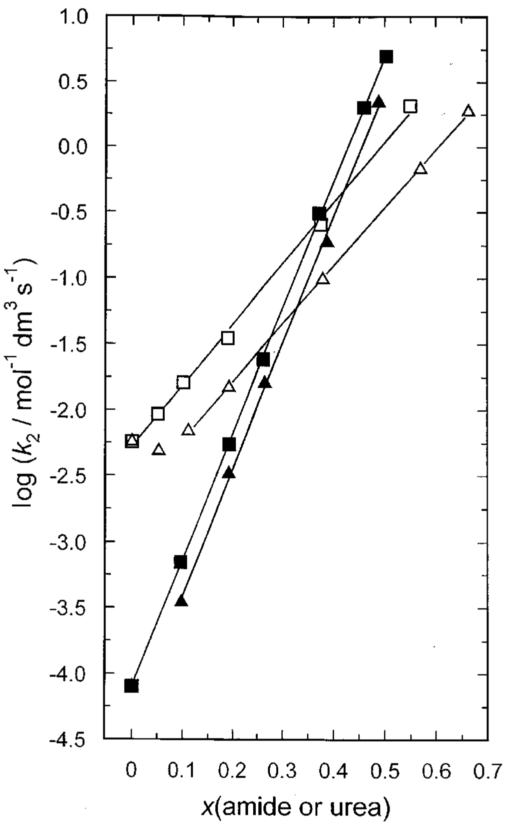

Fig. 2 Logarithms of the second-order rate coefficients in the detritiation of methoxyflurane-*t* (**3**) at 278.15 K and acetophenone-*t* (**4**) at 298.15 K. Notations: Water–DMPU (square), water–DMI (triangle), methoxyflurane-*t* (solid symbol), and acetophenone-*t* (open symbol).

observed (Fig. 1). In the detritiation of chloroform-*t* in water–DMF, water–TMU, and water–DMI mixtures a linear dependence also exists with the exception of the points x(DMF) = x(DMI) = 0.

The detritiation of halotane-*t* was studied at 278.15 K in aqueous DMA and DMPU. These measurements could be extended to mixtures with x(organic component) < 0.15. A linear correlation between logarithms of the rate coefficients and the mole fraction of urea or amide is evident also in this reaction (Fig. 1). The slopes of these plots, however, are markedly higher than the corresponding slopes in the detritiation of chloroform-*t*.

To extend the kinetic measurements to mixtures in which the mole fraction of urea is higher than above, the detritiation of methoxyflurane-*t* was studied in aqueous DMI and DMPU. At 278.15 K even mixtures with x(urea) ≈ 0.5 could be used in kinetic measurements. There is a linear correlation between log(k_2/mol^{-1} dm^3 s^{-1}) and x(urea) (Fig. 2) also in this range, except the point x(DMI) = 0. In addition, these two plots are parallel within experimental errors.

The detritiation of acetophenone-*t* was studied in aqueous ureas. These measurements could be extended even to mixtures with x(urea) > 0.5. As shown in Fig. 2, the plots of log(k_2/mol^{-1} dm^3 s^{-1}) *vs.* x(DMI or DMPU) are linear and parallel if in aqueous DMI the range x(DMI) < 0.1 is excluded. In aqueous tetramethylurea a linear correlation is also evident on the grounds of kinetic data in Table 2 when x(TMU) > 0.1.

Discussion

Stability of aqueous amides and ureas in basic solutions

Based on the kinetic results in Table 1, the stability of the water–amide or urea system containing sodium hydroxide as the base decreases in the order TMU > DMPU > DMI ≫ DMA > DMF. As the half lives of urea systems are at least several days, ureas are stable enough to be used as highly basic media. The situation is quite different with aqueous amides as their half lives in hydrolytic decomposition are of the magnitude of minutes or hours on the basis of the kinetic data in Table 1. If, for instance, aqueous dimethylformamide or dimethylacetamide are used in kinetic measurements, the base must be added to the reaction mixture just before the reaction is started to eliminate the decrease in hydroxide ion concentration. If, in addition, the reactions studied are relatively fast, the change in hydroxide ion concentration remains neglible during the reaction. Extrapolation to zero time can also be used as previously in the determination of the equilibrium basicity of aqueous DMF.[4]

Kinetic basicity of aqueous amides and ureas

As shown previously,[20] in aqueous dimethyl sulfoxide the logarithms of the rate coefficients for detritiation of different carbon acids depend linearly on the equilibrium basicity H_- of the solvent. Therefore, the slopes of the plots log(k_2/mol^{-1} dm^3 s^{-1}) *vs.* x(urea or amide) in Table 2 give also information on the increase in basicity. For the detritiation of chloroform-*t* these slopes vary between 11.07 and 14.60 with the highest slope in water–DMPU mixtures. In aqueous DMSO the corresponding slope is 11.0 ± 0.2 as obtained from previous kinetic data.[20] On the basis of the detritiation of chloroform-*t* it is obvious that in aqueous amide and urea systems the increase in basicity is slightly higher than in water–DMSO mixtures. From the previous data[8] the slope 21.3 ± 0.8 can be calculated for the detritiation of chloroform-*t* in aqueous HMPA. This indicates that in the water–HMPA system the increase in basicity with the mole fraction of the dipolar aprotic solvent is significantly higher than in aqueous DMPU. However, taking into account the issue of safety at work, aqueous DMPU is very capable of being used as the solvent in highly basic medium.

In the detritiation of halotane-*t* the slopes of the plots $\log(k_2/\text{mol}^{-1}\ \text{dm}^3\ \text{s}^{-1})$ *vs.* x(DMA or DMPU) are also presented in Table 2. In aqueous DMPU the slope is higher than in the corresponding DMA system by a factor of 1.33 which means that the increase in basicity is significantly higher in cyclic urea. In the detritiation of chloroform-*t* the corresponding factor 1.29 is equal within experimental error. Kinetic basicity seems thus to be independent of the carbon acid used in the measurements. In addition, the slopes in Table 2 reveal that the rate increase as a function of x(amide or urea) is much higher in the detritiation of halotane-*t* than in the detritiation of chloroform-*t*, the slopes differing by factors of 1.22 (DMA) and 1.25 (DMPU). The higher rate increase in the detritiation of halotane-*t* can be discussed in the terms of the Brønsted and Bjerrum eqn. (4) where $\gamma(\text{HO}^-)$, $\gamma(\text{ST})$ and $\gamma^{\ddagger}$ are the activity

$$k = k^0\{\gamma(\text{HO}^-)\gamma(\text{ST})/\gamma^{\ddagger}\} \qquad (4)$$

coefficients of hydroxide ion, substrate and transition state of the reaction as compared with that in water. In both reactions changes in activity coefficient of hydroxide ion are equal. In addition, solvent effects on neutral substrate, chloroform or halotane, can be excluded as compared to those of charged species, hydroxide ion and transition state of the reaction. The observed difference in the susceptibility to solvent basicity must be due to the changes in the activity coefficients of the transition states. It can be assumed that in the transition state of the detritiation of halotane-*t* the degree of triton transfer is higher than in the case of chloroform-*t* which means that in the detritiation of halotane-*t* the transition state is less hydroxide-ion-like than in the detritiation of chloroform-*t*. As changes in activity coefficients of hydroxide ion and transition state of the reaction with x(urea or amide) are parallel, they compensate for each other partially depending on the structure of the transition state. For halotane-*t* this compensation may be lower and therefore a higher increase in rate coefficients is expected.

In the detritiation of methoxyflurane-*t* the slopes of the plots $\log(k_2/\text{mol}^{-1}\ \text{dm}^3\ \text{s}^{-1})$ *vs.* x(urea), 9.59 ± 0.18 (DMI) and 9.56 ± 0.05 (DMPU) (Table 2) are equal within experimental errors and thus the increase in basicity is also equal. This result is well-founded because the cyclic ureas studied are structurally closely related. Therefore, at first sight, it seems surprising that in the detritiation of chloroform-*t* in aqueous DMI the slope of the plot $\log(k_2/\text{mol}^{-1}\ \text{dm}^3\ \text{s}^{-1})$ *vs.* x(urea) is lower than in aqueous DMPU: 14.60 (DMPU) and 11.4 (DMI). Kinetic measurements for the detritiation of chloroform-*t* have, however, mainly been performed in the range $x(\text{DMI}) = 0$–0.1 where the rate increase is exceptionally low also on grounds of kinetic results for methoxyflurane so that the point $x(\text{DMI}) = 0$ has been excluded in Fig. 2.

In the detritiation of the haloalkanes studied the susceptibility of reaction rate to solvent basicity can be compared, for instance, on the basis of kinetic data in aqueous DMPU (Table 2). The slopes of the plots (18.3, 14.60 and 9.56) decrease in the series halotane, chloroform and methoxyflurane. As discussed above, this means that the hydroxide ion like structure of the transition state increases in the same series.

To obtain additional information on the basicity of aqueous acyclic and cyclic ureas, the detritiation of acetophenone-*t* was studied in these solvent systems. As the susceptibility of this reaction to solvent basicity is relatively low the measurements could be extended even to a mole fraction of about 0.7. These results also indicate that the increase in basicity is similar in aqueous DMI and DMPU as the slopes of the plots $\log(k_2/\text{mol}^{-1}\ \text{dm}^3\ \text{s}^{-1})$ *vs.* x(DMI or DMPU), 4.41 ± 0.04 and 4.62 ± 0.10, are equal within experimental errors. In aqueous TMU the rate increase is slightly lower, as shown by the slope 4.043 ± 0.004. All these slopes are, however, significantly lower than in the detritiation of haloalkanes. This lower susceptibility to solvent basicity is mainly due to the hydroxide-ion-like transition state which means that the activity coefficient ratio $\gamma(\text{HO}^-)/\gamma^{\ddagger}$ in eqn. (4) increases only slightly with the mole fraction of organic component in the reaction mixture.[20] In aqueous DMI the rate coefficients even decrease slightly when $x(\text{DMI}) < 0.1$. Thus it is evident that in these mixtures changes in activity coefficients $\gamma(\text{ST})$ must be taken into account in addition to those of charged species in accordance with kinetic results in aqueous sulfolane.[25]

Estimation of equilibrium basicities from kinetic results

As seen above, changes in basicity of aqueous amides and ureas can be discussed solely on the basis of rate coefficients for detritiation reactions. If, however, comparison with equilibrium basicities H_- is desired, linear free energy correlations can be used for this purpose. In the following we discuss only the cases where deviations from the linearity of $\log(k_2/\text{mol}^{-1}\ \text{dm}^3\ \text{s}^{-1})$ *vs.* x(amide or urea) are not observed. In addition, since the detritiation of chloroform-*t* and halotane-*t* could be studied only in mixtures with a very low x(urea or amide), H_- values were not extrapolated from those data with the exception of chloroform-*t* in aqueous TMU. It has been observed previously[20] that in the detritiation of different carbon acids in aqueous DMSO the logarithms of rate coefficients depend linearly on both H_- and x(DMSO) of the solvent.[7] These linear free energy correlations can be applied also when the solvent system for the detritiation reaction is changed from aqueous DMSO to aqueous urea or amide.

The detritiation of chloroform-*t* in aqueous TMU is discussed first because equilibrium basicities of this system are available for comparison.[6] Using previous data[20] for the detritiation of chloroform-*t* in aqueous DMSO, relation (5) is obtained. From the kinetic data presented in Table 2 for the detritiation of chloroform-*t* in aqueous TMU the linear correlation (6) was observed. Eqns. (5) and (6) give the relation

$$\log(k_2/\text{mol}^{-1}\ \text{dm}^3\ \text{s}^{-1}) = (1.076 \pm 0.023)H_- - (13.73 \pm 0.29) \qquad (5)$$

$$\log(k_2/\text{mol}^{-1}\ \text{dm}^3\ \text{s}^{-1}) = (12.32 \pm 0.17)x(\text{TMU}) - (0.803 \pm 0.019) \qquad (6)$$

between x(TMU) and H_- of the solvent. Kinetic measurements for the detritiation of chloroform-*t* were performed only in mixtures with $x(\text{TMU}) < 0.188$ and the equilibrium basicities[6] have been determined after $x(\text{TMU}) > 0.1844$. Therefore, it is reasonable to extrapolate the H_- values from eqns. (5) and (6) to the mixture with $x(\text{TMU}) = 0.1844$ where equilibrium and kinetic measurements overlap. The H_- value 14.11 (Table 3) obtained by kinetic method is, within experimental errors, equal to the equilibrium H_- value 14.19 determined by Bowden and Prasannan.[6] Thus the method used in the present work seems to give reliable results.

For the detritiation of acetophenone-*t* the linear relationship (7) has been obtained in aqueous DMSO at 298.15 K.[20] From the kinetic results presented in Table 2 for the detritiation of acetophenone-*t* in aqueous DMPU the linear correlation (8) can be derived. The equality of eqns. (7) and (8) again gives a

$$\log(k_2/\text{mol}^{-1}\ \text{dm}^3\ \text{s}^{-1}) = (0.433 \pm 0.004)H_- - (7.48 \pm 0.06) \qquad (7)$$

$$\log(k_2/\text{mol}^{-1}\ \text{dm}^3\ \text{s}^{-1}) = (4.62 \pm 0.10)x(\text{DMPU}) - (2.27 \pm 0.03) \qquad (8)$$

relation between H_- and solvent composition. The H_- values shown in Table 3 were calculated in the mole fraction range 0–0.6 where kinetic measurements have been performed. These

Table 3 H_- values of aqueous TMU and DMPU calculated from kinetic results using a linear free energy correlation. For comparison, equilibrium basicities of aqueous TMU[6] and DMSO[7] are given in this table. The concentration of tetramethylammonium hydroxide is 0.011 mol dm^{-3}

Organic component	x(org. component)	H_-	Method
TMU	0.1844	14.19	Equilibrium[6]
	0.1844	14.11	Kinetic, detritiation of chloroform-*t*
DMPU	0.0	12.01	Kinetic, detritiation of acetophenone-*t*
	0.1	13.08	
	0.2	14.14	
	0.3	15.21	
	0.4	16.28	
	0.5	17.35	
	0.6	18.41	
DMPU	0.0	12.08	Kinetic, detritiation of methoxyflurane-*t*
	0.1	13.11	
	0.2	14.13	
	0.3	15.15	
	0.4	16.17	
	0.5	17.20	
DMSO	0.0	12.04	Equilibrium[7]
	0.1	13.04	
	0.2	14.24	
	0.3	15.37	
	0.4	16.34	
	0.5	17.44	
	0.6	18.49	

basicities, which refer to hydroxide ion concentration 0.011 mol dm^{-3}, can be compared with the equilibrium H_- values of aqueous DMSO[7] with the same hydroxide ion concentration (Table 3). The basicities of these two systems are almost equal.

$$\log (k_2/\text{mol}^{-1}\ \text{dm}^3\ \text{s}^{-1}) = (9.56 \pm 0.05)\, x(\text{DMPU}) - (4.094 \pm 0.015) \quad (9)$$

$$\log (k_2/\text{mol}^{-1}\ \text{dm}^3\ \text{s}^{-1}) = (0.936 \pm 0.012)H_- - (15.41 \pm 0.27) \quad (10)$$

Kinetic results for the detritiation of methoxyflurane-*t* in aqueous DMPU (Table 2) can also be used to extrapolate H_- values for this solvent system. At 278.15 K the free energy correlation (9) was found. Based on the kinetic results[26] for the detritiation of methoxyflurane-*t* in aqueous DMSO at 278.15 K, the linear correlation (10) is obtained. Again, the left sides in eqns. (9) and (10) are equal and thus a correlation between H_- and x(DMPU) is also obtained on the basis of these kinetic results. The calculated H_- values, given in Table 3, are almost equal with those obtained from the kinetic data for the detritiation of acetophenone-*t*. This agreement confirms the applicability of the extrapolation method.

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