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Co-solvent effects on the indirect reduction of alkyl and benzyl halides: experimental evidence of a link between electron transfer and S_N1-like processes

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The influence of using water as co-solvent in *N*,*N*-dimethylformamide on the electron transfer process between electrochemically generated electron donors and alkyl and benzyl halides has been investigated. While the solvent effect in general is modest for primary alkyl halides and substituted benzyl chlorides, the reaction rate is enhanced substantially in the case of 2-bromo-2-methylpropane, 1-iodoadamantane, 4-methylbenzyl bromide and 4-methoxybenzyl bromide. For these compounds the results are interpreted as if the transition state possesses substantial carbonium ion character and that a shift from an electron transfer toward an S_N1-like pathway takes place as the water content is increased. The fact that the carbonium ion structure becomes even more pronounced when poor electron donors are employed may provide an explanation as to why a linear rather than the predicted quadratic free energy relationship is observed experimentally for the homogeneous reduction of 2-bromo-2-methylpropane.

It has been realized for a long time that the S_N1 and S_N2 mechanisms can be regarded as limiting cases for the aliphatic nucleophilic substitution reaction.[1] Later it was discovered that such reactions also may proceed *via* an electron transfer (ET) pathway[2] with varying degrees of electronic interaction between the electron donor and the acceptor in the transition state (TS).[3,4] In this manner, the link between S_N2 and ET could be established. In this paper our purpose is to describe the relationship between ET and S_N1-like pathways by clarifying to what extent the TSs of ET reactions possess carbonium ion character. This aspect would be of considerable importance for the further development and refinement of current ET theories,[5] where in most cases no specific attention is paid to the detailed structure of the TS.

The basic reaction scheme for the ET process between an electron donor, in this case a radical anion $A^{\bullet -}$, and an electron acceptor RX is shown below in eqns. (1)–(3).[6a,b] The rate-controlling first step is an ET from $A^{\bullet -}$ to RX [eqn. (1)] followed by a fast coupling reaction between the so-formed radical $R^{\bullet}$ and another molecule of $A^{\bullet -}$ to give the substitution product RA^- [eqn. (2)].† Eqn. (1) is depicted as a concerted mechanism, in which the cleavage of the R–X bond occurs simultaneously with the ET process, rather than a stepwise mechanism with formation of an intermediate radical anion $RX^{\bullet -}$.

$$A^{\bullet -} + RX \xrightarrow{k} A + R^{\bullet} + X^- \qquad (1)$$

$$A^{\bullet -} + R^{\bullet} \longrightarrow RA^- \qquad (2)$$

$$\text{Overall} \qquad 2A^{\bullet -} + RX \longrightarrow RA^- + A + X^- \qquad (3)$$

According to electrochemical investigations, this is true for the reduction process of most alkyl[7a] and benzyl halides.[7b] Interestingly, the existence of the radical anions of benzyl and 4-cyanobenzyl bromide has been inferred in a photochemical study[7c] because quantum yields smaller than 1 were found. However, a recent paper has questioned such interpretations by showing that even concerted processes may be endowed with low quantum yields.[7d]

The fundamental ET reaction [eqn. (1)] has been the subject of many papers but the issue of TS structure has been addressed only a few times and then with emphasis on its S_N2 character.[8] By now, it seems clear that the S_N2 process, in which the substitution products $RA^{\bullet}$ and X^- are formed in the first step between $A^{\bullet -}$ and RX, competes with the ET under appropriate conditions and for primary alkyl halides and in particular methyl halides it may even be the dominant pathway.[8d,e] ‡ The competition ratio of the two reaction pathways is dependent on the magnitude of the driving force, with the S_N2 reaction being favoured at low driving force. One interesting aspect neglected so far is whether the TS can attain carbonium ion character in a similar manner, especially for tertiary and benzylic substrates. In the limiting situation of the ET process shown in eqn. (4), an S_N1-like reaction, in terms of a complete dissociation of RX into R^+ and X^- prior to the ET and coupling reactions, might be envisioned.

$$R\text{–}X \underset{k_b}{\overset{k_f}{\rightleftharpoons}} R^+ + X^- \xrightarrow{A^{\bullet -}} A + R^{\bullet} + X^- \xrightarrow{A^{\bullet -}} A + RA^- + X^- \qquad (4)$$

Even though the heterolytic dissociation of the R–X bond is unlikely to occur for most substrates in aprotic solvents, the above mechanism has been observed for certain reactions involving compounds like 9-chloro-9-mesitylfluorene and 9-chloro-9-[α-(fluoren-9-ylidene)benzyl]fluorene in acetonitrile and triphenylmethyl chloride and bromide in tetrahydrofuran.[9] At least, this shows the potential of this particular aspect of ET reactions.

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† The radical anion $A^{\bullet -}$ is electrogenerated from the neutral compound A. The radical $R^{\bullet}$ formed in eqn. (1) may be further reduced by $A^{\bullet -}$ to R^- rather than being involved in the coupling reactions shown in eqn. (2). According to previous reports[6c] this reduction process should be taken into account for the benzyl halides investigated in the present paper. All carbanions formed are either protonated by residual water and/or the supporting electrolyte or react with RX in substitution or elimination reactions.

‡ According to calculations the interaction energy between the aromatic radical anions and alkyl halides in the TS of the ET process can also amount to several kcal mol^{-1}.[4b]

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One way to address the ET–S_N1 issue is to employ solvent effects in the description of TS structures. Such an approach takes advantage of the fact that an S_N1-like reaction is expected to be much more solvent dependent than the corresponding ET reaction where overall no charge is generated or consumed in the rate-controlling step. In practice, however, it is not a trivial task to carry out the experiments since it often implies the use of water or other protic solvents with the risk of introducing competing solvolysis and protonation processes. For instance, substrates such as triphenylmethyl bromide and 9-chloro-9-mesitylfluorene are hydrolysed and most radical anions easily become protonated in the presence of water.

In this paper, we selected as electron donors the radical anions of 1,4-dicyanobenzene (DCB), 1,4-dicyanonaphthalene (DCN) and 9,10-dicyanoanthracene (DCA), these being sufficiently weak bases to permit the use of different DMF–water solvent systems. Another prominent feature of the radical anions is that they have rather different electron-donating capabilities even though they exhibit similar solvation behaviours. The standard potentials E° of DCB (= −1.485 V *vs.* SCE), DCN (= −1.170 V *vs.* SCE) and DCA (= −0.740 V *vs.* SCE) show that a variation in the driving force of more than 0.7 eV can be accomplished. As electron acceptors a wide selection of primary, secondary and tertiary alkyl and benzyl halides was chosen providing the basis for carrying out a comparison of solvation behaviours: 1-bromobutane (**1**), 1-iodobutane (**2**), 1-iodo-2,2-dimethylpropane (**3**), 2-bromobutane (**4**), 2-bromo-2-methylpropane (**5**), 1-iodoadamantane (**6**), 4-cyanobenzyl bromide (**7**), benzyl bromide (**8**), 4-methylbenzyl bromide (**9**), 4-methoxybenzyl bromide (**10**), benzyl chloride (**11**), 4-methoxybenzyl chloride (**12**), 1-chloro-1-phenylethane (**13**) and 2-chloro-2-phenylpropane (**14**).

Experimental

Reagents

1-Bromobutane, 1-iodobutane, 1-iodo-2,2-dimethylpropane, 2-bromobutane, 2-bromo-2-methylpropane, 1-iodoadamantane,[10a] 4-cyanobenzyl bromide, benzyl bromide, 4-methylbenzyl bromide, benzyl chloride, 4-methoxybenzyl chloride, 1,4-dicyanobenzene, 1,4-dicyanonaphthalene[10b] and 9,10-dicyanoanthracene were commercially available or synthesized according to the references given. 1-Chloro-1-phenylethane, 2-chloro-2-phenylpropane and 4-methoxybenzyl bromide were prepared from the corresponding alcohols and gaseous HCl or HBr. The preparation of the supporting electrolyte, tetrabutylammonium tetrafluoroborate (Bu_4NBF_4), was carried out by standard procedures and the solvent, *N*,*N*-dimethylformamide (DMF), was obtained from Aczo. Water used as co-solvent in the DMF–0.1 M Bu_4NBF_4 solution was triply distilled.

Equipment

The rate constants *k* were determined using cyclic voltammetry or linear sweep voltammetry for the faster reactions ($k > 10$ M^{-1} s^{-1})[11a] and a dip-probe technique[11b] or a potentiostatic technique[11c] employing a rotating disk electrode for the slower reactions. The cyclic voltammetric cell was equipped with a working electrode made of glassy carbon and having a diameter of 1 mm, a reference electrode consisting of a silver wire in DMF–0.1 M Bu_4NBF_4 and a platinum counter electrode. In the potentiostatic and dip-probe techniques an H-cell was employed. Its cathodic compartment was equipped with either a rotating disk electrode (Metrohm 628–10, glassy carbon electrode of diameter = 3 mm) or a dip-probe (Ocean Optics, fiber-optic spectrometer S1000), the reference electrode and a platinum net. A carbon rod was positioned in the anodic compartment. The radical anions of DCB, DCN or DCA were generated electrochemically in a concentration range of 0.2–2 mM at the platinum net from the parent compounds in DMF–0.1 M Bu_4NBF_4 under an argon atmosphere. Degassed water was added in the desired amount and the oxidation current or the absorbance of the radical anion was measured as a function of time by means of the rotating disk electrode or the dip-probe in order to ensure that its stability was sufficiently high to proceed further. The substrate was then added in excess and the rate constant could be calculated from the pseudo first-order decay. A detailed description of the general procedures may be found in the references listed above. For almost all substrates studied hydrolysis presented no problem as the height of their reduction waves in linear sweep voltammetry was found to be largely unaffected by the presence of water. The only exception was 4-methoxybenzyl bromide, having a half-life of a few minutes in the DMF–water mixtures.

Results and discussions

In many instances, TS structures are better characterized if suitable configurations describing the reaction profile going from reactant state to the TS are introduced. This approach is much like the valence-bond configuration mixing model developed by Shaik and Pross, although product states are included therein in order to cover the entire reaction profile.[4a,12] In the present case, the three configurations shown below are selected, where configuration I describes the reactant state as well as its contribution to the TS structure and II and III correspond to radical (product) and carbonium ion TS contributions, respectively.

Reactant state I $A^{\bullet-}R^{\bullet\bullet}X$
Transition state I $A^{\bullet-}R^{\bullet\bullet}X$ II $A\,R^{\bullet}{:}X^{-}$ III $A^{\bullet-}R^{+}{:}X^{-}$

Admittedly, other configurations like $AR{:}^{-}X^{\bullet}$ might be included but since our purpose in this paper is to gain a qualitative insight we selected the most important configurations. Configuration II is generally considered to be the most significant contributor to the TS structure although configuration I should be taken into account as well in the case of an early TS.[4a] In relation to the discussion on the ET–S_N1 dichotomy, the inclusion of configuration III is an interesting point. Chemical systems having a TS structure with significant carbonium ion character could be considered as borderline cases representing a mechanistic link between ET and S_N1-like pathways.

In the further discussion, it would be essential to have an estimate of the heterolytic bond dissociation Gibbs energies of RX, ΔG°_{ion}, for the first step in eqn. (4), *i.e.* $R\text{–}X \rightleftharpoons R^+ + X^-$. Fortunately, ΔG°_{ion} can easily be deduced from a thermochemical cycle expressed in eqn. (5).[13] The parameters involved

$$\Delta G^\circ_{ion} \approx D_{RX} - TS^\circ_{X^\bullet} + F(E^\circ_{R^+/R^\bullet} - E^\circ_{X^\bullet/X^-}) \qquad (5)$$

are the homolytic bond dissociation energy of R–X, D_{RX}, the standard entropy of the halogen atom $X^\bullet$, $S^\circ_{X^\bullet}$, and the standard potentials of R^+, $E^\circ_{R^+/R^\bullet}$, and $X^\bullet$, $E^\circ_{X^\bullet/X^-}$. Relevant literature values[14]§ are gathered in Table 1 together with the calculated values of $\Delta G^\circ_{ion}(H_2O)$ and $\Delta G^\circ_{ion}(DMF)$ of compounds **1**–**14**.

As seen, ΔG°_{ion} is of a substantial magnitude for all sub-

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§ The values of $E^\circ_{R^+/R^\bullet}$ used in the calculations of ΔG°_{ion} (H_2O) and ΔG°_{ion}(DMF) were approximated by the half-wave potentials measured in acetonitrile.[14c–e] While this approach is reasonable as regards the thermodynamic significance of the voltammetric waves, it may seem more questionable to assume that the cation solvating abilities of the protophobic acetonitrile on one hand, and the much more protophilic water and DMF on the other hand, should be similar. However, since the solvent effect on R^+ compared with H^+ is much smaller due to the steric constraints at the ionic centre and charge delocalization effects and since the Gibbs energies of transfer of ammonium cations, $\Delta G_{tr,H_2O\rightarrow solvent}$, tabulated in ref. 14*g* are relatively small for the solvents in question (within a few kcal mol^{-1}), the validity of this approximation can be justified.

Table 1 Homolytic bond dissociation energy of the carbon–halogen bond, D_{RX}, standard entropy of $X^•$, $S^\circ_{X^•}$, standard potential of R^+, $E^\circ_{R^+/R^•}$, standard potential of $X^•$, $E^\circ_{X^•/X^-}$, and the heterolytic bond dissociation Gibbs energy of compounds **1**–**14**, ΔG°_{ion}

RX	D_{RX}[a]	$S^\circ_{X^•}$[b]	$E^\circ_{R^+/R^•}$[c]	$E^\circ_{X^•/X^-}$[d]	$\Delta G^\circ_{ion}(H_2O)$[e]	$\Delta G^\circ_{ion}(DMF)$[e,f]
1	70	41.8	<0.99	1.76	<40 42[g]	<49 51[g,h]
2	56	43.2	<0.99	1.11	<41 42[i]	<46 47[i,h]
3	56	43.2	<0.99[j]	1.11	<41 42[i]	<46 47[i,h]
4	73	41.8	0.47	1.76	31 27[k]	40 36[k,h]
5	70	41.8	0.09	1.76	19 11[l]	28 20[l,h]
6	59	43.2	0.09[m]	1.11	23	28
7	60	41.8	1.08	1.76	32	41
8	60	41.8	0.73	1.76	24	33
9	60	41.8	0.51	1.76	19	28
10	60	41.8	0.26	1.76	13	22
11	74	39.5	0.73	2.27	27	39
12	74	39.5	0.26	2.27	16	28
13	72	39.5	0.37	2.27	17	29
14	67	39.5	0.16	2.27	7	19

[a] In kcal mol^{-1}, ref. 14*a*. [b] In cal mol^{-1} K^{-1}, ref. 14*b*. [c] In V *vs*. SCE, refs. 14*c*–*e*. The listed values are half-wave potentials obtained in acetonitrile. [d] In V *vs* SCE, taken as an average of the data obtained in aqueous media in ref. 14*f*. [e] In kcal mol^{-1}. [f] $\Delta G^\circ_{ion}(DMF) \approx \Delta G^\circ_{ion}(H_2O) + \Delta G_{tr,H_2O\rightarrow DMF}$ (X^-), where the transfer Gibbs energies of the halide ions $\Delta G_{tr,H_2O\rightarrow DMF}$ (X^-) are from ref. 14*g*. [g] Ref. 14*h*, approximated by the value calculated for bromoethane. [h] Transformed to DMF using the values of $\Delta G_{tr,H_2O\rightarrow DMF}$ (X^-) given in ref. 14*g*. [i] Ref. 14*h*, approximated by the value calculated for iodoethane. [j] Assumed to be the same as for other primary systems. [k] Ref. 14*h*, approximated by the value calculated for 2-bromopropane. [l] Ref. 14*h*. [m] Approximated by the half-wave potential for the *tert*-butyl cation.

stances selected in this paper and $\Delta G^\circ_{ion}(H_2O) < \Delta G^\circ_{ion}(DMF)$ because of the better solvating properties of water with respect to the halide ions. The smallest $\Delta G^\circ_{ion}(H_2O)$ values in the range 7–23 kcal mol^{-1} are found for compounds such as 2-chloro-2-phenylpropane (**14**), 4-methoxybenzyl bromide (**10**), 4-methoxybenzyl chloride (**12**) and the tertiary alkyl halides, 2-bromo-2-methylpropane (**5**) and 1-iodoadamantane (**6**). On energetic grounds these compounds are therefore the most prominent candidates for developing carbonium ion character in the TS although the strong endergonic nature of the heterolytic processes should be emphasized.

From a kinetic point of view, the expected forward rate constant k_f for the S_N1-like process can be calculated easily from ΔG°_{ion} if the rate of the backward reaction of the pre-dissociation is assumed to be at the diffusion-controlled limit ($k_b \approx 10^{10}$ M^{-1} s^{-1}). For instance, ΔG°_{ion} values of 7, 13, 19 and 28 kcal mol^{-1} then correspond to k_f values of 6×10^4, 2, 7×10^{-5} and 10^{-11} s^{-1}, respectively. Considering the fact that the water content in the experiments carried out in this study never exceeded 20 vol% of the DMF–water mixtures and that the smallest value of $\Delta G^\circ_{ion}(DMF)$ in Table 1 is 19 kcal mol^{-1}, it seems plausible that for any of the substrates **1**–**14** the limiting S_N1-like pathway becomes too slow to occur.

The rate constants k of the ET reaction [eqn. (1)] involving different combinations of the selected electron donors $DCB^{•-}$, $DCN^{•-}$ and $DCA^{•-}$ and the substrates **1**–**14** were measured electrochemically for varying molar fractions of water, X_{H_2O}, in DMF. The results are summarized in Table 2. Moreover, relevant plots of log k/k_{DMF} *versus* X_{H_2O} are shown in Figs. 1–4 with k_{DMF} denoting the rate constant determined in the absence of water. None of the experiments gave any indication of a first-order rate-controlling step as would be expected if the reaction in eqn. (4) occurred. Rather the reaction rates were found to be dependent on the concentrations of both $A^{•-}$ and RX, consistent with the second-order ET reaction depicted in eqns. (1)–(3) and high ΔG°_{ion} values (see Table 1). Nevertheless, the solvation behaviour indicates that the TS structure is influenced substantially by the structure of the substrate. Without doubt the most notable feature of the results is the significant rate enhancement observed as a function of X_{H_2O} in the case of 2-bromo-2-methylpropane (**5**), 1-iodoadamantane (**6**), 4-methylbenzyl bromide (**9**) and 4-methoxybenzyl bromide (**10**), while essentially no solvent effect is observed for most of the remaining alkyl halides and benzyl halides. A detailed discussion of these behaviours is provided in the following within the framework of the configurations introduced above.

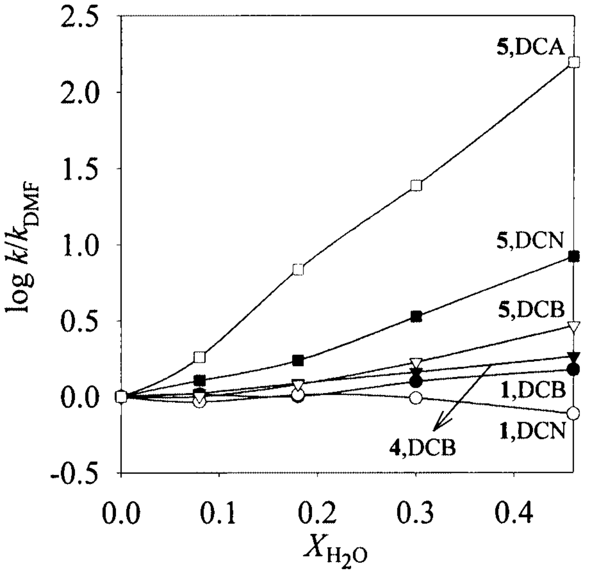

Fig. 1 Log k/k_{DMF} *versus* X_{H_2O} for the reaction between the radical anions of DCB, DCN or DCA and the alkyl bromides **1**, **4** and **5** in DMF–water mixtures.

Primary and secondary alkyl halides (1–4)

Figs. 1 and 2 show that the solvent effects on the rate constants are small for the reactions involving $DCB^{•-}$ and $DCN^{•-}$ as electron donors and 1-bromobutane (**1**), 1-iodobutane (**2**), 1-iodo-2,2-dimethylpropane (**3**) and 2-bromobutane (**4**) as electron acceptors which can be explained by TSs[4a] having greater contribution from configurations I and II, with only a small contribution from state III. This interpretation is in line with the large ΔG°_{ion} values calculated in Table 1 (31–49 kcal mol^{-1}). Interestingly, the presence of an S_N2 component in the reactions of the simple alkyl halides[8] is not reflected in a solvent effect, as the behaviour of **2** is the same as that of the sterically hindered **3** (*i.e.* neopentyl iodide). In other words, the major solvation sites in all cases are the electron donor in the reactant state and the developing halide in the TS; the solvent effect on those two states must be alike if it is to be consistent with the small influence exerted by water on the rate constants. The tendency of a slight increase in k for alkyl bromides and a decrease for alkyl iodides is in accordance with expectation since the larger iodide ion should be less stabilized by solvent inter-

Table 2 Rate constants k (M^{-1} s^{-1}) obtained for the reaction between radical anions of DCB, DCN or DCA and **1**–**14** at different molar fractions of water, X_{H_2O}, in DMF–0.1 M Bu_4NBF_4 at 20 °C. The measurements were carried out by cyclic voltammetry ($k > 10$ M^{-1} s^{-1}) or a potentiostatic method ($k < 10$ M^{-1} s^{-1}) unless otherwise noted. The estimated uncertainty on k is 10%

		k				
RX	A	X_{H_2O} = 0	0.08	0.18	0.30	0.46
1	DCB	0.28	0.29	0.28	0.35	0.42
1	DCN	3.9×10^{-3}	3.6×10^{-3}	4.0×10^{-3}	3.8×10^{-3}	3.0×10^{-3}
2	DCB	195	197	175	148	140
3	DCB	34	30	27	26	24
4	DCB	1.8	1.9	2.2	2.6	3.3
5	DCB	2.5	2.5	3.0	4.2	7.3
5	DCN	1.1×10^{-2}	1.4×10^{-2}	1.9×10^{-2}	3.7×10^{-2}	9.2×10^{-2}
5	DCA	1.6×10^{-4}	2.9×10^{-4}	1.1×10^{-3}	3.9×10^{-3}	2.5×10^{-2}
6	DCB	155	157	165	207	440
7	DCA	435	455	555	[a]	[a]
8	DCN	280[b]	300[b]	295[b]	310[b]	330[b]
8	DCA	1.4	1.9	2.1	2.4	4.2
9	DCN	270[b]	285[b]	370[b]	415[b]	495[b]
9	DCA	2.8[c]	3.2[c]	4.2[c]	6.5[c]	17[c]
10	DCA	5.3[c]	6.8[c]	11[c]	20[c]	49[c]
11	DCB	130	129	132	143	178
11	DCN	0.78	0.95	1.2	1.8	3.4
12	DCB	101	100	109	125	172
12	DCN	1.7	2.2	3.1	3.9	7.8
13	DCB	145	166	187	206	278
14	DCB	114	120	136	176	186

[a] Impossible to obtain in cyclic voltammetry due to the low solubility of DCA in the DMF–water mixture. [b] Measured by linear sweep voltammetry. [c] Measured by a dip-probe technique at a wavelength of 706 nm.

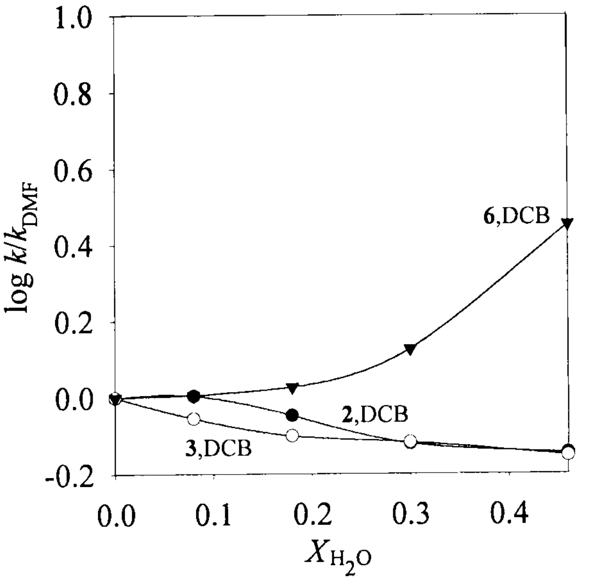

Fig. 2 Log k/k_{DMF} *versus* X_{H_2O} for the reaction between the radical anion of DCB and the alkyl iodides **2**, **3** and **6** in DMF–water mixtures.

actions, in terms of hydrogen bonding, than bromide. The decrease observed for the alkyl iodides is attributed to an increase in the solvent reorganization energy as the water content is raised. This effect more than compensates the concomitant increase in driving force resulting from the stabilization of iodide.

Tertiary alkyl halides (5, 6)

The characteristic feature of the reactions involving 2-bromo-2-methylpropane (**5**) and 1-iodoadamantane (**6**) compared with the simple alkyl halides **1**–**4** is the rate enhancement observed as a function of X_{H_2O} (see Figs. 1 and 2). Such remarkable behaviour is best understood in terms of the carbonium ion structure of the TS for tertiary substrates, thus underlining the importance of including configuration III in the description of the processes. The gradual changes observed in the plots might even be interpreted as if a smooth transition from an ET toward the S_N1-like pathway takes place for the tertiary compounds. Obviously, this interpretation is somewhat tentative because the contribution from the concomitant changes in the solvation energy of the TS structure should be accounted for as well, but certainly it is in accordance with the $\Delta G^{\circ}_{ion}(H_2O)$ values of 19–23 kcal mol^{-1} that are smaller than the corresponding $\Delta G^{\circ}_{ion}(DMF)$ values by 5–9 kcal mol^{-1}. The fact that the S_N2 process is important for most primary and secondary substrates, and unimportant for the tertiary alkyl halides, is not responsible for the solvent effects observed. This is clearly illustrated when the behaviour of the sterically hindered but primary **3** is compared with the behaviour of the tertiary **6**. In either case, the S_N2 reaction can be neglected but still the solvent effect is much more pronounced for **6** than for **3**. We believe that this specific result strengthens our argument concerning the development of carbonium ion character in the TS for tertiary alkyl halides.

Perhaps the most remarkable observation pertaining to the tertiary compounds is the dependency of log k/k_{DMF} on the driving force applied. The solvent effect becomes much more pronounced for 2-bromo-2-methylpropane (**5**) if the poorer electron donors $DCA^{\bullet-}$ ($E^{\circ}_{DCA} = -0.740$ V) and $DCN^{\bullet-}$ ($E^{\circ}_{DCN} = -1.170$ V) rather than $DCB^{\bullet-}$ ($E^{\circ}_{DCB} = -1.485$ V) are used. The log k/k_{DMF} values obtained at $X_{H_2O} = 0.46$ for the three donors are 2.19, 0.92 and 0.47, respectively. In comparison, the trend in log k/k_{DMF} values for the reaction between 1-bromobutane (**1**) and $DCN^{\bullet-}$ and $DCB^{\bullet-}$ is reversed with values of −0.11 and 0.18, respectively. Without doubt, the electron-donating/withdrawing abilities of the two reactants thus have a substantial influence on the TS structure of **5** in favour of configuration III at low driving force. Although the energy of reactant state I is lowered at low driving force, which moves the TS structurally in the direction of the product state II (Hammond effect), configuration III is also stabilized and this tends to move the TS toward this species (anti-Hammond effect). Thus, it is predicted that the overall effect on the TS structure of using a poorer electron donor is an increase in R–X bond breaking which ultimately might lead to a limiting S_N1-like situation as suggested by the trend observed in the data presented herein. Actually, the changes

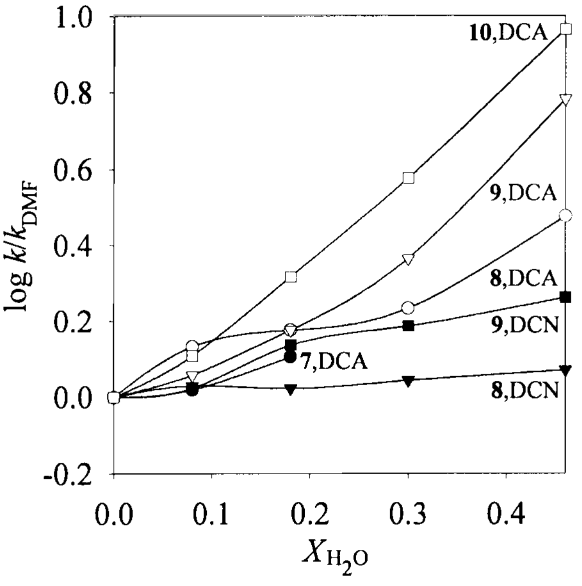

Fig. 3 Log k/k_{DMF} *versus* X_{H_2O} for the reaction between the radical anions of DCN or DCA and the benzyl bromides **7**–**10** in DMF–water mixtures.

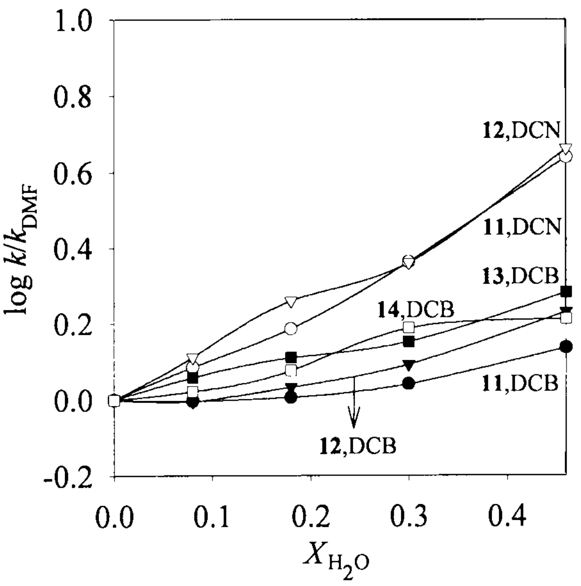

Fig. 4 Log k/k_{DMF} *versus* X_{H_2O} for the reaction between the radical anions of DCB or DCN and the benzyl chlorides **11**–**14** in DMF–water mixtures.

occurring in the TS structure as a function of driving force might be another important reason why[3a,5b] the experimentally obtained free energy relationship for the homogeneous reaction between a series of solution electron donors and **5** seems to be linear[8b] and not quadratic as predicted by the theory on dissociative ET reactions.[5a] The present investigation does not allow us to quantify the effect on the free energy plot of the increased carbonium character of the TS at low driving force exactly but at least it emphasizes the importance of paying attention to the specific structure of the TS for a given chemical system in the further refinement of current ET theories.

Benzyl bromides (7–10)

The electron-donating/withdrawing property of the *para*-substituent on benzyl bromide plays an important role for the overall solvation behaviour as shown in Fig. 3. Clearly, the reactions of 4-methylbenzyl bromide (**9**) and 4-methoxybenzyl bromide (**10**) with $DCA^{\cdot -}$ are more affected by the presence of water than the corresponding reactions of benzyl bromide (**8**) and in particular 4-cyanobenzyl bromide (**7**). In other words, the TS attains carbonium ion character in the former two cases because the electron-donating substituents lower the energy of configuration III. As seen in Table 1 the pertinent $\Delta G^{\circ}_{ion}(H_2O)$ values range from 13 to 32 kcal mol^{-1} in the series of compounds **7**–**10**. On the other hand, if the stronger electron donor $DCN^{\cdot -}$ is employed in the reactions with **8** and **9** the solvent effects observed are small. This behaviour is attributed to the occurrence of an earlier and more reactant-like TS, in which the contribution from configurations II and III is diminished at the expense of configuration I. The profound influence of the electron-donating abilities of the electron donor on the TS structure, which was also noted in the case of 2-bromo-2-methylpropane, emphasizes once more the important role of the driving force.

Benzyl chlorides (11–14)

The solvent effects depicted in Fig. 4 for the reactions between $DCB^{\cdot -}$ and benzyl chloride (**11**), 4-methoxybenzyl chloride (**12**), 1-chloro-1-phenylethane (**13**) and 2-chloro-2-phenylpropane (**14**) are all modest without any clear trend being present. Employing the poorer electron donor $DCN^{\cdot -}$ gives rise to a larger solvent effect as exemplified by the results obtained at X_{H_2O} = 0.46 for **11** (log k/k_{DMF} = 0.64), **12** (log k/k_{DMF} = 0.66) and **14** (log k/k_{DMF} = 0.87, where k_{DMF} = 0.9 M^{-1} s^{-1}). However, an interesting point is that the log k/k_{DMF} values are similar for all the substrates, albeit slightly higher for **14**, and this rules out any significant carbonium ion contribution. In addition, the S_N2 reaction can be excluded for the sterically hindered **14**.

The minor contribution of configuration III to the TS of the reactions of benzyl chlorides is quite surprising considering that the calculated $\Delta G^{\circ}_{ion}(H_2O)$ values for **12**–**14** of 7–17 kcal mol^{-1} are among the smallest values given in Table 1. The explanation of this phenomenon presumably lies in the presence of the strong carbon–chlorine bond which causes a radical anion character to predominate in the TS. The rate increase observed at low driving force as the water content is increased could be interpreted as the carbon–halogen bond in the radical anion being elongated somewhat with the negative charge located mainly on the halogen atom. However, complete cleavage of the carbon–chlorine bond does not occur, as shown in configuration II, since the solvent effect then would be larger. In that sense, the bond fragmentation that occurs in reduction of the benzyl chlorides might very well be a borderline case between the stepwise and concerted ET mechanism as has been described for a number of other chemical systems.[15] In our opinion, it therefore seems worthwhile to reconsider the previous assignment of these reactions to the concerted pathway.[16]

An interesting feature of the results pertaining to the benzyl halides emerges if the rate constants obtained for the different combinations of electron donors and acceptors are compared. Fig. 5 shows the relevant rate constants k_{DMF} for a given electron donor against the Hammett substituent constants σ^- for the series of benzyl bromides. The inset shows the corresponding development in the Hammett plot of 4-methoxybenzyl chloride and benzyl chloride as a function of driving force. As seen, there is a tendency for U-shaped plots to be observed at low driving force. In this context, it is noteworthy that a study of the reaction between $DCN^{\cdot -}$ and a series of substituted benzyl bromides revealed a remarkable solvent effect, where an U-shaped plot observed in DMF was replaced by a linear relationship in acetonitrile.[17] For nucleophilic substitution reactions involving anionic nucleophiles and substituted benzyl halides the observation of U-shaped Hammett plots is not unusual either.[18] Several explanations have been put forward to account for the curvature, *i.e.* a mechanism change, a change in the TS structure with differ-

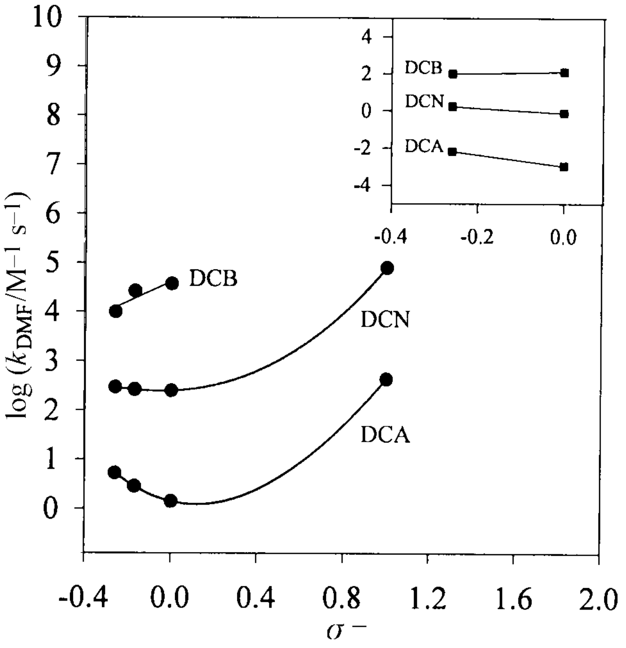

Fig. 5 Hammett plot of log k_{DMF} *versus* σ^- for the reaction between the radical anions of DCB, DCN or DCA and the benzyl bromides **7**–**10**. The rate data for DCB and DCN are taken from ref. 17. The inset is a Hammett plot of log k_{DMF} *versus* σ^- for the reaction between the radical anions of DCB, DCN or DCA and the benzyl chlorides **11** and **12**. For DCA log k_{DMF} is −2.96 and −2.17, respectively.

ing balance of bond formation and fragmentation as well as differing balance of polar and resonance effects exerted by the substituents. Also the valence-bond configuration mixing model has been employed in the interpretation of the phenomenon by including carbonium ion configurations in the description of S_N2 processes.[12b] In view of the results presented in this paper the carbonium ion structure of the TS may certainly play a role in the behaviour of ET reactions. The U-shaped plots are observed for the benzyl bromides only when a low driving force is applied, *i.e.* when DCA$^{\bullet-}$ and DCN$^{\bullet-}$ are used as electron donors and when configuration III is important. In this instance, an electron-donating group such as methoxy has a stabilizing influence on configuration III. When the driving force is increased by employing DCB$^{\bullet-}$ as electron donor, configuration III can be neglected which tends to straighten out the Hammett plot. On the other hand, this explanation cannot be employed for the corresponding development observed in the Hammett plot of 4-methoxybenzyl chloride and benzyl chloride since configuration III should be unimportant as inferred by the solvation data. Presumably, the changes occurring in the Hammett plot as a function of driving force are then merely a reflection of a substituent dependent variation in the intrinsic barriers due to the degree of carbon–chlorine bond elongation in the TS. A similar substituent effect has recently been found for the reduction processes of sulfides[19a] and disulfides.[19b] It should be noted that the contribution of a substantial S_N2 component for the reactions taking place at low driving force would also be in line with the above observations as suggested elsewhere.[17]

Conclusions

The present study illustrates the importance of including solvent effects in the description of ET reactions. In fact, the influence on the reaction rates may be so strong that the reactivity within seemingly similar reactions is reversed. For ET reactions involving tertiary alkyl halides and benzyl bromides carrying electron-donating groups the TS attains substantial carbonium structure as the water content is increased. For these substrates there seems to be a gradual shift from an ET toward an S_N1-like mechanism in which the heterolytic dissociation of the substrate to form a carbonium ion ultimately becomes the rate-controlling step. This interpretation also throws light on the puzzling experimental finding of a linear rather than the expected quadratic free energy relationship for the ET between a series of electron donors and 2-bromo-2-methylpropane in solution.[8b] A possible explanation of this phenomenon among others[5b] is related to the changes that occur in the TS structure as a function of the driving force, *i.e.* as the driving force is lowered, the carbonium ion character becomes more and more pronounced.

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