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Solvent Effect on the ET/S_N2 Competition in the Reaction of a Radical Anion with Some Benzyl Bromides[1]

Y. Huang and D. D. M. Wayner*

Steacie Institute for Molecular Sciences
National Research Council of Canada
Ottawa, Ontario, Canada K1A 0R6

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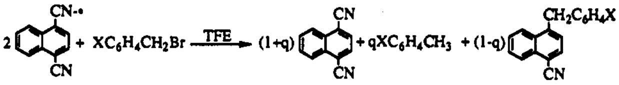
The possible role of electron transfer (ET) in the formal S_N2 substitution of alkyl bromides has been the subject of experimental and theoretical interest for a number of years.[2–8] Although there are numerous chemical examples representing the two limiting mechanisms, there have been no unequivocal reports of the observation of the transition from a predominantly ET-driven substitution reaction to a predominantly S_N2-driven reaction except for cases in which the steric demand of the reactants is altered. Experimentally, the relative contribution of ET in substitution reactions has been estimated by determining the rate constants for reaction of a substrate, RX (usually a halide), with a series radical anions which are believed to react by outer-sphere ET.[5,9] A plot of the rate constant versus the standard potential of the radical anion, $E°$, is then used to interpolate the expected ET rate for a given nucleophile. A reaction is assumed to proceed by direct substitution if the experimental rate constant is faster than that expected for outer-sphere ET. Using this approach, it has been shown that, in the absence of steric hindrance, substitution is generally faster than ET for a large variety of nucleophiles, including radical anions. For reactions of radical anions, the kinetic preference appears to be small. Thus, in the reaction of anthracene radical anion with optically active 2-octyl halide, only a small amount of inversion (ca. 10%) is observed.[2,10,11]

We now report data for the reaction of 1,4-dicyanonaphthalene (DCN) radical anion with a number of ring-substituted benzyl bromides in acetonitrile ($E°$ (DCN) = −1.257 V vs SCE) and *N,N*-dimethyl formamide (DMF, $E°$ (DCN) = −1.300 V vs SCE) which demonstrate a surprising influence of the solvent on the mechanism. The overall reaction is given in eq 1, where q is the fraction of the benzyl bromide that is reduced to the corresponding toluene. In this case, the products are either the corresponding



(1)

toluene or the α-aryl-4-cyano-1-methylnaphthalene. For the purposes of this communication, it is important to realize that the value of q does not reflect the competition between S_N2 and ET since the substitution products also can be obtained from the coupling of a benzyl radical with the radical anion.[2,5,10] The relationship between these values and the relative rates of the product-determining steps will be discussed in the full account of this work. The rate constants for the rate-determining step were determined by cyclic voltammetry (0.1 M tetrabutylammonium perchlorate, 3 mm glassy carbon disk electrode) using homogeneous redox catalysis and appropriate working curves (Table 1).[12,13] For both acetonitrile and DMF, a small amount (2–4 equiv based on DCN) of 2,2,2-trifluoroethanol (TFE) was added to the solution to ensure that all of the benzyl anions were converted to the corresponding toluene. The addition of this weak acid had no effect on the voltammogram of DCN. The values of q (Table 1) were determined independently by cyclic voltammetry as described by Pedersen[14] and by product studies (both methods agreed to within 5%).[15]

Table 1. Rate Constants for the Reaction of $DCN^{•-}$ with Some Substituted Benzyl Bromides[a]

	DMF		MeCN	
substituent	log(*k*)	*q*	log(*k*)	*q*
4-MeO	2.47	0.06	1.67	0.00
4-Me	2.42	0.10	1.80	0.01
4-*t*-Bu	2.32	0.12	1.97	0.05
H	2.40	0.38	2.20	0.30
4-Br	2.99	0.64	2.90	0.64
3-CN	3.91	0.84	3.94	0.88
4-CN	4.90	0.90	4.80	0.90
4-CF3	4.15	0.80		
3-CF3	3.49	0.90		

[a] Determined by homogeneous redox catalysis (refs 11, 12).

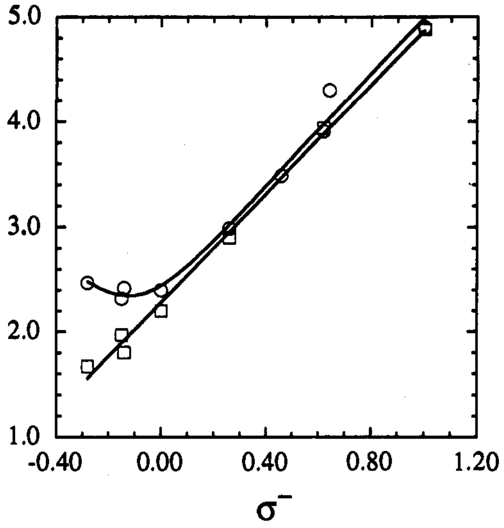


Figure 1. Hammett plot of log(k) versus σ^- for the reaction of $DCN^{•-}$ with some substituted benzyl bromides in acetonitrile (□) and DMF (○). The substituents used in acetonitrile were 4-MeO, 4-*t*-Bu, 4-Me, H, 4-Br, 3-CN, and 4-CN. In DMF, rate constants for the 3- and 4-CF_3 derivatives also are included.

We have assumed that the reaction between the radical anion and the benzyl bromide is rate limiting. A plot of log(k) versus σ^- for the reaction in acetonitrile is linear with a ρ value of 2.6 (Figure 1, r = 0.997 for seven points). This is predicted by Savéant's model for an outer-sphere dissociative electron-transfer

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[1] Issued as NRCC publication number 37229.

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[15] All of the bromides have been shown to be chemically stable in solution, even for the duration of the controlled potential experiments. The 4-methoxybenzyl bromide, which is the most reactive toward aventitious substitution or solvolysis, had a half-life of more than 14 h in the solvent/electrolyte solution which contained 5 equiv of TFE. Peak currents from the voltammograms of this bromide in both acetonitrile and DMF solvent systems were unchanged after 30 min (i.e., the duration of a typical cyclic voltammetric determination of a rate constant).

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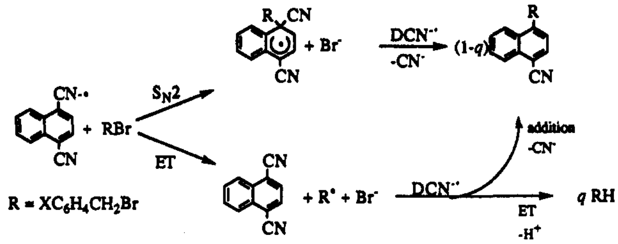
Scheme 1



process since the overall driving force depends on the change in the C–Br bond dissociation free energy.[16] Independent work by us[17] and by Savéant[18] has shown that electron-withdrawing substituents tend to weaken the C–Br bond in ring-substituted benzyl bromides. Using the experimentally determined bond energies and the solvent reorganization energy reported by Savéant for benzyl bromide,[18] a theoretical Hammett ρ value of 2.51 is obtained, in excellent agreement with the experimental value in acetonitrile. In DMF, a plot for the same reaction is significantly curved, suggesting a change of mechanism in this solvent as a function of the electron demand of the substituent.[19] The curved line drawn through the data points for DMF in Figure 1 was calculated for two competing processes with different Hammett parameters. This analysis gave two limiting Hammett slopes; one process with $\rho^- = 2.7$(i.e., the same as the ρ value in acetonitrile) and a second process with a ρ value of -2.1 ($r = 0.993$ for nine points). We interpret these results as the first unequivocal observation of the transition of a reaction between a radical anion and a primary alkyl halide from predominantly ET to predominantly S_N2 (Scheme 1). This is especially significant since the transition was induced without adjusting the steric requirements but simply by controlling the energetics of the electron transfer reaction. The difference in reactivity of the electron rich bromides in these solvents likely derives from a solvent effect on the S_N2 transition state rather than on the ET reaction since the rates for the electron-deficient bromides in both solvents are essentially the same. It also is apparent from Scheme 1 why the competition parameter, q, does not necessarily reflect the competion between ET and S_N2; the substitution product is derived from two different routes.

A number of additional observations support our conclusion. Firstly, when the driving force for electron transfer is increased by using 1,4-dicyanobenzene radical anion in DMF ($E° = -1.55$ V vs SCE), log(k) for the reaction with benzyl bromide, 4-methylbenzyl bromide, and 4-methoxybenzyl bromide is 4.56, 4.42, and 3.99, respectively. The inversion of the order of reactivity of the electron-rich benzyl bromides compared to $DCN^{\bullet-}$ (Table 1) is consistent with a change back to an ET-driven process. Secondly, the reaction of $DCN^{\bullet-}$ with benzyl tosylate gives only the substitution product, while with benzyl bromide the ratio of reduction to toluene versus substitution is ca. 4:6. This indicates that the benzyl radical is not an intermediate in the former reaction and that the radical anion is, indeed, capable of reacting by direct substitution. Finally, it is well established in the literature that the barrier for S_N2 substitution of benzyl bromides decreases with both electron-rich and electron-deficient substituents.[20,21] This implies that the kinetic trend for substitution versus ET will be in opposite directions for the electron-donating substituents. The observation that S_N2 reactions are generally faster in DMF than in acetonitrile (by ca. 5–50 times)[22] provides an explanation for why curvature is observed only in DMF.

This solvent effect is particularly remarkable since the two solvents are often used interchangeably for kinetic and mechanistic studies of electron-transfer and polar reactions. Our data suggest that further insights into the factors that control the rates of these two processes will be obtained from the study of solvent effects on the kinetics, an area which has not been fully exploited.

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(19) In principle, curvature also may indicate a change in the rate-limiting step. However, if one accepts that the first electron transfer is rate limiting for the more reactive bromides, it is more reasonable to propose that the curvature is a result of a change in mechanism. This is an important assumption since the derived rate constant, based on the observed catalytic currents, will be in error if the reaction of the radical anion with the bromide is faster than the subsequent reaction of the radical anion with the benzyl radical.

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