

Short Communications

The Selectivity of α -Naphthyl Radical in Reactions with Thiophenolate Ion, Diphenyl Disulfide and Aprotic Solvents

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The $S_{RN}1$ mechanism¹ (eqns. 1 to 3) can result in high yields of $Ar-Y$ only if the radical $Ar\cdot$ reacts selectively with the nucleophile Y^- (2). Bunnett and coworkers^{2,3} repeatedly cite the work of Bridger



and Russell⁴ regarding the exceedingly low reactivity of aryl radicals toward dimethyl sulfoxide (DMSO), a solvent commonly used in the $S_{RN}1$ reactions. We find it difficult to accept the validity of this assumption since the rate constants reported⁴ were values relative to the reaction with carbon tetrachloride. The rate constant ratio k_{DMSO}/k_{CCl_4} was 0.039.⁴ The absolute rate constant for the reaction of phenyl radical with CCl_4 , as solvent, has been determined to be equal to $3 \times 10^6 M^{-1} s^{-1}$ at 45 °C, which differs from the diffusion controlled rate under those conditions by a factor of $10^{3.5}$. The total absence of products arising from hydrogen abstraction by aryl radicals on solvents as reported by Bunnett and coworkers^{2,3} and in some cases by Pinson and Savéant,⁶ indicates a remarkable selectivity of aryl radicals for nucleophiles even in the presence of reactive solvents. For example, if the second order rate constant for reaction (4) is of the order of $10^5 M^{-1} s^{-1}$, the rate constant for reaction



(2) would have to be $10^{10} M^{-1} s^{-1}$ for 99.9% of the reaction to follow that pathway, providing the nucleophile concentration was 0.1 M.

Using the reaction of α -naphthyl radical with CBr_4 , which would be expected to be diffusion controlled in analogy to the data reported for phenyl radical⁵ as a standard we have determined the absolute rate constants for the reactions of the radical with DMSO, *N,N*-dimethylformamide (DMF), acetonitrile (AN), diphenyl disulfide (PhSSPh) and thiophenolate ion (PhS^-) at 20 °C. The source of the α -naphthyl radical was 1-naphthalenediazonium tetrafluoroborate which was reduced, either by iodide ion or electrolytically.* The rate constants are listed in Table 1. In the calculation of the absolute rate constants, eqn. (5) was used where κ was taken to be equal to unity⁸

$$k_{diff} = \kappa 4\pi a(D_A + D_B)N/10^3 \quad (5)$$

and the diffusion coefficients D_A and D_B were taken to be equal to $10^5 cm^2 s^{-1}$ in acetonitrile and adjusted according to the relative viscosities in the other solvents. The sum of the effective radii of reactants, a , was estimated to be equal to 4 Å.

* Deactivation of electrodes by aryl radicals is a serious problem during reduction of diazonium ions in voltammetric experiments but does not prevent electrolysis on a preparative scale.⁷

Table 1. Absolute rate constants for reactions of α -naphthyl radical at 20 °C.

Radical source ^a	Reactant/Solvent	$k/M^{-1} s^{-1}$
H	DMSO/DMSO	3×10^5
H	DMF/DMF	8×10^6
H	AN/AN	2.5×10^5
H	PhSSPh/DMSO	1.4×10^8
H	PhSSPh/AN	2×10^8
E	PhS^- /DMSO	1.7×10^8

^a From the reduction of 1-naphthalenediazonium tetrafluoroborate either homogeneously (H) by iodide ion or electrolytically (E).

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If we arbitrarily set 0.1 % yield of product derived from hydrogen abstraction reaction (4) as the limit where an analysis procedure should not fail to detect it, we arrive at the following rate constants necessary for reaction (2) to appear to be the exclusive pathway; 4.5×10^{10} (DMSO), 4.8×10^{10} (AN) and $1.0 \times 10^{12} \text{ M}^{-1} \text{ s}^{-1}$ (DMF). The rate constant that we observe for the reaction between α -naphthyl radical and PhS^- , $1.7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, suggests that the data reported by Pinson and Savéant for the reduction of 1-bromonaphthalene in DMSO in the presence of PhS^- are inconsistent with the involvement of the $S_{\text{RN}}1$ mechanism in the reaction which resulted in 100 % yield of α -naphthylthiophenyl ether.⁶ The rate constant for the reaction of the radical with PhSSPh is nearly identical to that for PhS^- and thus cannot account for the high yield either.

The results reported here cast some doubt on $S_{\text{RN}}1$ reactions which take place without concurrent hydrogen abstraction reactions from the solvent when reactions are conducted in DMSO or similar solvents. However, the results also provide strong evidence that α -naphthyl radical does react with PhS^- in DMSO giving NaSPh/NaH , the molar ratio of products, equal to 3.8 when the concentration of PhS^- was equal to 0.1 M. Thus, we do not dispute the occurrence of the $S_{\text{RN}}1$ mechanism but point out that the data in the literature are not entirely consistent with it. Detailed investigations along the lines of this study are in progress.

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