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REACTIONS OF AROMATIC RADICAL ANIONS. IX. COMPETITION STUDIES OF ELECTRON TRANSFER AND PROTON TRANSFER WITH SODIUM NAPHTHALENE

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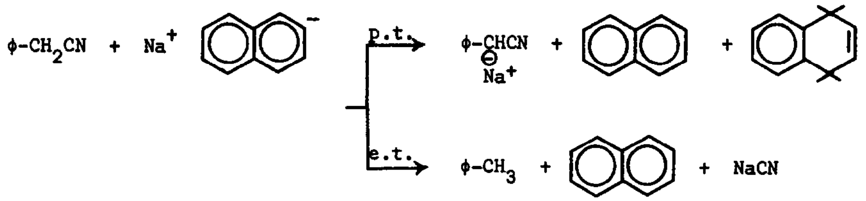
Aromatic radical anions react principally as reducing agents[1] or nucleophiles[1a,2] or combinations of these.[3] The factors affecting reaction path or partitioning have been in some cases identified,[1e,3b] but in the main are largely undefined. Understanding and control of the bifunctional reactivity of radical anions, while useful in itself for synthetic purposes, bears on related questions concerning other bifunctional reagents, notably anions. Accordingly, we have sought to identify and evaluate the critical factors determining partitioning in a competition study. We have now found it possible to systematically vary the yields of electron transfer and proton transfer products over a wide range.

Phenylacetonitrile was selected as a substrate that provides both acidic hydrogens and a reducible functionality. The reaction of phenylacetonitrile (0.5 M in tetrahydrofuran (THF)) with sodium naphthalene (0.5 M in THF) yields after water quenching the following products. naphthalene, dihydronaphthalene, toluene, phenylacetonitrile, sodium hydroxide and sodium cyanide. Small amounts of tetralin, phenylacetonitrile dimer and a dihydronaphthalene dimer are produced, but no phenethylamine, benzylated dihydronaphthalene or bibenzyl are observed. Material balances for the scheme shown in equation 1 are 95 ± 5%.



Ia

Ib

The phenylacetonitrile anion product of proton transfer (Ia) was established by quenching the reaction mixture with methyl iodide and analysing for α-methylphenylacetonitrile. Equally important, use of α,α-phenylacetonitrile-d_2 leads to dihydronaphthalene-d_2 as the product.

Suitable control experiments ensured that the nitriles were stable under the workup conditions. Proton transfer is thus uncomplicated and appears to follow the accepted mechanism for radical anion protonation.[2a,b]

Electron transfer is also uncomplicated, the major products (Ib) are toluene, naphthalene and sodium cyanide. In all cases yields of toluene determined by gas chromatography with internal standards and yields of sodium cyanide determined by titration of the aqueous extract agree within the experimental error of ± 1%. The absence of benzylated dihydronaphthalenes and amines suggest some differences in the mechanism of this reduction compared to that of benzyl chloride with sodium naphthalene and phenylacetonitrile with sodium in liquid ammonia

The importance of solvation and ion-pairing in radical anion chemistry is well documented.[4] Of particular importance to the current study contrasting reactivities have been observed for electron transfer[5] and proton transfer[6] reactions with single substrates as a function of ion pairing. For electron transfer of sodium naphthalene and naphthalene the reactivity order is free > loose > contact ion pairs,[5a] whereas for proton transfer to sodium naphthalene by water the order is contact ions> loose > free ions.[6a] Interestingly, in each case the range is approximately 2 order of magnitude. Accordingly, it was of interest to investigate the effect of changes in the state of ion-pairing on the competition between electron transfer and proton transfer reactions with the single substrate phenylacetonitrile.

Table I records the effect of select solvent changes on the competition reaction of sodium naphthalene and phenylacetonitrile

Table I

Effect of Solvent Variation on the Competition Between Electron Transfer and Proton Abstraction in the Reaction of Sodium Naphthalene and Phenylacetonitrile

Solvent System[a]	Ion Pairing State	% Electron Transfer[b]
THF-DEE	Tight[c]	6.4 ± 0.5
THF	Tight[d]	9.6 ± 0.9
THF-DME	Tight and Loose[d]	32.5 ± 2.0
THF-TG[e]	Glymated[f]	48.2 ± 3.2
THF-TG	Glymated[f]	19 6 ± 1.7

a) THF = tetrahydrofuran, DEE = diethylether, DME = dimethoxyethane, TG = tetraglyme. Radical anion solutions were prepared in THF and diluted with an equal volume of the second solvent unless otherwise noted

b) Proton transfer accounts for the remainder in all cases

c) This system provides tighter ion pairs than THF (Ref. 5b).

d) P. Chang, R. U. Slates and M Szwarc, J. Phys. Chem., 70, 3180 (1966).

e) Solutions were 0.4 M in tetraglyme and 0 4 M in sodium naphthalene.

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The important conclusion from these data is that electron transfer can be varied from a minor process (∿ 6%) to a major process (∿ 50%) by solvent variation. Moreover, the trend is in the direction that is anticipated from the kinetic studies of ion-pairing effects Thus solvent systems that favor loosening of the ion-pairs favor electron transfer. The only possible exception to this is the observation of decreasing electron transfer with increased addition of the complexing solvent tetraglyme These results have bearing on both mechanistic studies and synthetic applications of radical anions at high concentrations.

The detailed investigations of ion-pairing are for the most part determined for very dilute solutions ($<10^{-3}$ M)[4] Similarly, the kinetic studies relating the chemical reactivities in electron transfer and proton transfer reactions with ion-pairing are at these concentrations What is clear from the data in Table 1 is that although the same trends are observed at higher concentration the magnitude of the effect is considerably dampened. The opposing orders of reactivities imply an expected difference of 10^4 between electron transfer and proton transfer at the extremes of ion-pairing states Even with all the assumptions required in this estimate the observed value of 8 3 is sufficiently low to raise serious doubts about the extrapolation of data on ion-pairing and reactivity at low concentrations to preparative concentrations In view of the recent growing use of ion-pairing effects to account for disparate behavior[7] these findings mitigate for extreme caution in extrapolation[9]

While it is clear from this and other work that solvent, metal ion and temperature can affect the products at preparative scale concentrations it now appears that the defined ion-pairing state and reactivity relationship at low concentrations does not provide an adequate quantitative model What will be required will be similarly detailed studies of aggregation, ion-pairing and reactivity at the higher concentrations Our current studies focus on obtaining these data.

The quantitative caveat notwithstanding, the synthetic implications of these results are sufficiently clear to warrant exploitation. Radical anion reduction, when desired, can be favored by increasing cation solvation and disfavored, when not desired, by decreasing cation solvation. This suggests directions for the control of radical anion reactions which can be tested. Equally important, it raises the question of whether many anion reactions could be similarly directed.

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