oratories for technical assistance.

**Registry No.** **1**, 29707-62-8; **2**, 78183-91-2; **3**, 78109-48-5; **5a**, 78109-49-6; **5b**, 78183-92-3; **5b** benzhydryl ester, 70982-50-2; **5c**, 78109-50-9; **5d**, 78109-51-0; **6**, 78183-93-4.

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## Relative Nucleophilicities of Oxanions, Thianions, Carbanions, and Halide Ions in Dimethyl Sulfoxide Solution

*Summary:* Extrapolations of Brønsted-type plots have revealed that thiophenoxide ions are about $10^2$–$10^3$ times more nucleophilic toward alkyl halides in dimethyl sulfoxide solution than fluorenyl carbanions and $10^4$–$10^5$ times more nucleophilic than 2-naphthoxide ions of the same basicity.

*Sir:* The order of nucleophilicities of oxanions vs. thianions and of fluoride ion vs. chloride ion, as defined by relative rates of $S_N2$ reaction with alkyl halides, has long been a topic of interest and some controversy.[1,2] In hydroxylic solvents such as methanol the order is $RS^- > RO^-$ and $Cl^- > F^-$, and the high nucleophilicities of $RS^-$, $Cl^-$, and other highly polarizable anions ($Br^-$, $RSe^-$, $I^-$, etc.) have been attributed to the ability of their nonbonded electrons to initiate bonding at greater distances ("early transition states") and/or the availability of low-lying d orbitals[1b] or low-energy HOMO's.[1c] In dipolar nonhydroxylic solvents such as acetone or DMF, the order of nucleophilicities of halide ions is reversed, however.[2] This is true also in the gas phase where the order of nucleophilicities $F^-$, $CH_3O^- > CH_3S^- \gg Cl^- > CN^- > Br^-$ has been found, and the conclusion has been drawn that the high nucleophilicity of highly polarizable anions in solution is not an intrinsic factor but is instead an artifact caused by solvation.[3] This conclusion is supported by the observation of the same nucleophilicity order, i.e., $F^-$, $CH_3O^- > PhO^- > Cl^- > Br^-$, toward PrOTs in $Me_2SO$, although data allowing a direct comparison of oxanions and thianions are missing.[4]

In defining an order of relative nucleophilicities it is important, however, to compare anions of the same basicity. Although this is generally recognized, the necessary data are usually lacking. In hydroxylic solvents it is difficult because the range of basicities that can be measured is narrow (about 10 p*K* units). For example, weakly basic anions, such as halide ions, all have the same apparent basicity in $H_2O$ or MeOH, and strongly basic anions, such as carbanions or nitranions, cannot be generated in high enough concentration to permit rate studies to be made. In dipolar nonhydroxylic solvents, such as $Me_2SO$, anions of a much wider range of basicities can be studied (about 30 p*K* units). By placing remote substituents in the benzene rings in thiophenoxide ($PhS^-$), 2-naphthoxide ($2\text{-}NpO^-$), and 9-(carbomethoxy)fluorenyl ($9\text{-}CO_2Me\text{-}Fl^-$) anions, Brønsted-type plots can be obtained (e.g., Figure 1),[5] which allow such comparisons for nucleophilicities of thianions, carbanions, and oxanions. The present study shows that toward $PhCH_2Cl$, BuCl, and BuI the order of relative nucleophilicities in $Me_2SO$ solution is $ArS^- \gg 9\text{-}G\text{-}Fl^- > 2\text{-}NpO^-$ for anions of the same basicity.

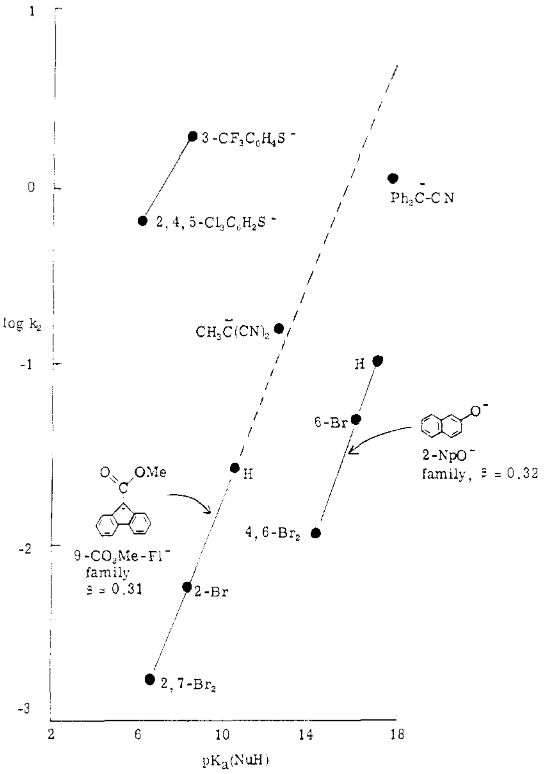

**Figure 1.** Brønsted-type plots for the reactions of thiophenoxide ions, 9-(carbomethoxy)fluorenyl carbanions ($9\text{-}CO_2Me\text{-}Fl^-$) and 2-naphthoxide ions ($2\text{-}NpO^-$) with $PhCH_2Cl$ in $Me_2SO$ solution at 25 °C.

Examination of Figure 1 shows that $9\text{-}CO_2Me\text{-}Fl^-$ carbanions reacting with $PhCH_2Cl$ in $Me_2SO$ solution exhibit essentially the same sensitivity to changes in basicity ($\beta_{Nu} = 0.31$) as do $2\text{-}NpO^-$ ions ($\beta_{Nu} = 0.32$). The fact that the points for $MeC(CN)_2^-$ and $Ph_2CCN^-$ carbanions fit near to the line for $9\text{-}CO_2Me\text{-}Fl^-$ anions supports our earlier conclusion that steric demands of $9\text{-}CO_2Me\text{-}Fl^-$ anions are low[5] and suggests that carbanion nucleophilicities do not vary much for carbanions of different structural types. The vertical gap between the two Brønsted lines corresponds to about a 25-fold greater nucleophilicity for carbanions vs. oxanions of equal basicity.

Most thiophenoxides react too rapidly with $PhCH_2Cl$ for the rates to be measured by our spectrophotometric method. We have observed, however, that the conjugate base of $2,4,5\text{-}Cl_3C_6H_2SH$ ($pK_a = 6.0$) reacts 318 times faster than the conjugate base of $9\text{-}CO_2Me\text{-}2,7\text{-}Br_2\text{-}FlH$ ($pK_a = 6.5$) and that the conjugate base of $3\text{-}CF_3C_6H_4SH$ ($pK_a = 8.1$) reacts 360 times faster than the conjugate base of 9-CN-FlH ($pK_a = 8.3$). It follows that, toward $PhCH_2Cl$ in $Me_2SO$, thiophenoxide ions are about $10^4$ times more nucleophilic than 2-naphthoxide ions of the same basicity (Figure 1).

Similar Brønsted-type plots have been made for these nucleophiles reacting with BuCl and/or BuI. The vertical

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Table I. Relative Nucleophilicities of 9-Substituted Fluorenyl Carbanions ($C^-$), 2-Naphthoxide Ions ($O^-$), and Thiophenoxide Ions ($S^-$) of the Same Basicity in $Me_2SO$ Solution at 25 °C[a]

| halide | $k^{C^-}/k^{O^-}$ | $k^{S^-}/k^{C^-}$ | $k^{S^-}/k^{O^-}$ |
|---|---|---|---|
| $PhCH_2Cl$ | 25 | 550 | 13 500 |
| BuCl | 4 | 3000 | 12 000 |
| BuI | 55 | 1300 | 72 000 |

[a] Derived from extrapolations using Brønsted-type plots (e.g., Figure 1). Detailed rate and $pK_a$ data for these reactions, together with reports of product studies, will be presented in the complete paper.

displacements from these Brønsted-type plots give the relative nucleophilicities of thiophenoxides, fluorenyl carbanions, and 2-naphthoxide ions, which are summarized in Table I.

Since the $\beta_{Nu}$ values vary slightly and the relative rates are substrate dependent (Table I), it is impossible to define exact relative nucleophilicities. It is clear, nevertheless, that thianions are far more nucleophilic in $Me_2SO$ than are carbanions or oxanions of the same basicity. Thiophenoxides are about $10^2$–$10^3$ times more nucleophilic than fluorenyl carbanions and $10^4$–$10^5$ times more nucleophilic than 2-naphthoxide ions, depending on the substrate.

The relatively high $k^{S^-}/k^{O^-}$ ratio toward alkyl halides in hydroxylic solvents[1] can be ascribed in part to the much stronger solvation of $O^-$ than $S^-$ through hydrogen bonding. If the difference in $pK_a$ values in $Me_2SO$ vs. $H_2O$ ($\Delta pK_a$) is taken as a measure of the relative loss of hydrogen bonding solvation energies in changing from $H_2O$ to $Me_2SO$, this amounts to about 4.4 kcal/mol for $PhS^-$ ($\Delta pK = 3.2^6$) and 9.5 kcal/mol for 2-$NpO^-$ ($\Delta pK_a = 6.9^6$). One would therefore expect 2-$NpO^-$ (or $PhO^-$) ions to become more nucleophilic, relative to $PhS^-$, in changing the medium from $H_2O$ (or MeOH) to $Me_2SO$, i.e., $k^{S^-}/k^{O^-}$ should decrease. This does not seem to occur, however, since in MeOH $k^{PhS^-}/k^{PhO^-} \simeq 10^4$ toward MeI,[7,8] which is about the same order of magnitude that we observe in $Me_2SO$ (Table I). Evidently, the decrease in $k^{S^-}/k^{O^-}$ in $Me_2SO$ caused by the absence of hydrogen bonding is counteracted by other factors that keep the ratio nearly constant in the two media.

The order of nucleophilicities, $F^- > Cl^-$, toward PrOTs in $Me_2SO$ cited above appears at first sight to be contrary to the $O^- < S^-$ order. There is evidence to indicate, however, that $F^-$ is a much stronger base in dipolar nonhydroxylic solvents than $Cl^-$.[9] The relative reactivities of $Cl^-$ and $Br^-$ toward PrOTs in $Me_2SO$, $k^{Cl^-}/k^{Br^-} = 6.6$,[4] correspond to that expected from their relative basicities.[10] Furthermore, fitting Parker's data for $Cl^-$ and $Br^-$ reacting with BuI in $Me_2SO$[2b] to our Brønsted line for the 9-$CO_2Me$-$Fl^-$ family ($\beta_{Nu} = 0.40$) indicates that a $Cl^-$ ion is about $10^4$ times more nucleophilic than a carbanion of the same basicity. This suggests that the higher nucleophilicity of anions derived from second (and higher) row elements vs. first row elements of the same basicity is a general phenomenon in solution and is an intrinsic property.

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**Registry No.** 9-$CO_2Me$-$Fl^-$, 12565-94-5; 2-$NpO^-$, 15147-55-4; $PhS^-$, 13133-62-5; $MeC(CN)_2^-$, 78232-00-5; $Ph_2CCN^-$, 18802-83-0; 2,4,5-$Cl_3C_6H_2S^-$, 78232-01-6; 9-$CO_2Me$-2,7-$Br_2$-$Fl^-$, 73838-70-7; 3-$CF_3C_6H_4S^-$, 78232-02-7; 9-CN-$Fl^-$, 40052-38-8; 6-Br-2-$NpO^-$, 78232-03-8; 4,6-$Br_2$-2-$NpO^-$, 78232-04-9; 2-Br-9-$CO_2Me$-$Fl^-$, 73838-71-8; $PhCH_2Cl$, 100-44-7; BuCl, 109-69-3; BuI, 542-69-8; 2-naphthol, 135-19-3; 9-(carbomethoxy)fluorene, 3002-30-0.

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## Tetraalkylammonium Trihydridocyanoborates. Versatile, Selective Reagents for Reductive Aminations in Nonpolar Media

*Summary:* Tetrabutylammonium cyanoborohydride or the combination of sodium cyanoborohydride with Aliquat 336 provides useful, convenient reagents for reductive amination of aldehydes and ketones in aprotic or protic media.

*Sir:* Trihydridocyanoborate (cyanoborohydride)[1] is well established as a mild, selective, acid-stable reducing agent for a variety of conversions including aldehydes and ketones to alcohols,[2] tosylhydrazones,[3] polar alkenes,[4] and alkyl halides[5] to hydrocarbons, and numerous carbon–nitrogen $\pi$-bond derivatives (imines, oximes, enamines) to amines.[2] This latter transformation has been particularly exploited as an excellent procedure for the reductive amination of aldehydes and ketones.[1,2,6] However, the commercially available sodium derivative suffers the limitation that solubility is restricted to a few polar protic ($H_2O$, low molecular weight alcohols), aprotic ($Me_2SO$, HMPA), or ether (THF, diglyme) solvents.[8] The reagent is almost totally insoluble and unreactive in most other useful solvents including $CH_2Cl_2$, $CHCl_3$, aromatic and aliphatic

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