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Reactions of 2-Substituted 1-Phenylethanones. 1. Nucleophilicity, Leaving Group Ability and Carbon Basicity of Cl^-, Br^-, SCN^- and $SeCN^-$ in Acetonitrile

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The reactions between some 2-substituted 1-phenylethanones (phenacyl compounds, ω-substituted acetophenones), $PhC(O)CH_2X$, and various ionic nucleophiles, Y^-, (X and Y = Cl, Br, SCN and SeCN) have been examined in acetonitrile. At 25.0 °C and for relatively short reaction times all the reactions proceed exclusively through nucleophilic attack at the methylene carbon atom and no formation of 2-isothiocyanato(2-isoselenocyanato)-substituted products could be observed.

For equal concentrations of reactants none of the reactions go to completion and equilibria are established. From the equilibrium constants it can be concluded that the carbon basicity order is $NCSe^- \geq NCS^- > Cl^- \gg Br^-$ toward the methylene carbon atom.

The reactions have been the subject of a kinetic study at 25.0 °C and all the reactions studied have been found to follow second order kinetics, first order in each of the reactants. The chloride ion, the bromide ion and the selenocyanate ion are approximately of the same nucleophilic strength and these ions are generally ten times more reactive than the thiocyanate ion toward the various substrates. The rates of reaction of the substrates suggest that the leaving group ability order is $Br^- \gg Cl^- > NCSe^- > NCS^-$.

As part of a program to study the effect of substituents upon the reactivity of alkyl halides toward nucleophilic species,[1] a kinetic study of 2-halo-1-phenylethanones (phenacyl halides, ω-haloacetophenones), $PhC(O)CH_2X$, was started. In this paper we want to report the results from a part of this study in which the thiocyanate ion, NCS^-, and the selenocyanate ion, $NCSe^-$, were used as the nucleophiles; eqn. 1.

$$PhC(O)CH_2X + Y^- \xrightarrow[25\ °C]{MeCN} PhC(O)CH_2Y + X^- \quad (1)$$

X = Cl and Br, Y = SCN and SeCN.

The reactions depicted by eqn. 1 were found to be clean substitution reactions toward the aliphatic carbon atom and no trace of isothiocyanato(isoselenocyanato)-substituted products could be detected. Some yellow coloration of the reaction mixtures could be observed only after 1 to 2 weeks at room temperature.

However, complications arose from the fact that none of the reactions studied were found to go to completion and the following equilibria were established, eqn. 2.

$$PhC(O)CH_2X + Y^- \underset{k_r}{\overset{k_f}{\rightleftharpoons}} PhC(O)CH_2Y + X^- \quad (2)$$

By suitable choice of the reactant concentrations both the forward and the reverse second-order rate constants, k_f and k_r, could be determined by following the rate of appearance or disappearance of the pseudohalide ions employing IR liquid cells.[2] The equilibrium constants, K, could be determined by the equilibrium concentrations of the reacting species and also by the ratio of the rate constants, k_f/k_r. The equilibrium constants could also be determined by NMR from more concentrated runs since the methylene protons in the various 2-substituted 1-phenylethanones are well-separated.

The purity of the reactions clearly indicated that 1-phenyl-2-thiocyanatoethanone, $PhC(O)CH_2SCN$, and 1-phenyl-2-selenocyanatoethanone, $PhC(O)CH_2SeCN$, could only yield the anticipated substitution products in the presence of thiocyanate and selenocyanate ions. By employing ^{13}C-pseudohalide ions and the IR technique,[2] the following reactions could also be examined kinetically, eqns. 3–5.

$$\mathrm{PhC(O)CH_2SCN + NCS \xrightarrow{k_f} PhC(O)CH_2SCN + NCS^-} \qquad (3)$$

$$\mathrm{PhC(O)CH_2SCN + NCSe^- \underset{k_r}{\overset{k_f}{\rightleftharpoons}} PhC(O)CH_2SeCN + NCS^-} \qquad (4)$$

$$\mathrm{PhC(O)CH_2SeCN + NCSe^- \xrightarrow{k_f} PhC(O)CH_2SeCN + NCSe^-} \qquad (5)$$

From the equilibrium constant for the reaction depicted by eqn. 4, the relative carbon basicity of the thiocyanate ion and the selenocyanate ion could be determined.

EXPERIMENTAL

Materials. Acetonitrile, Baker Analyzed Reagent, was purified as previously described[1] and flushed with dry nitrogen prior to use. Diethyl ether, petroleum ether and cyclohexane were dried with metallic sodium.

2-Chloro-1-phenylethanone and 2-bromo-1-phenylethanone were commercially available and were crystallized from ethanol, acetonitrile, diethyl ether and finally from light petroleum (40–60 °C) prior to use.

1-Phenyl-2-thiocyanatoethanone was prepared as described by Dykerhoff[3] and crystallized from ethanol and finally from cyclohexane. M.p. 76 °C (74 °C[3]).

1-Phenyl-2-selenocyanatoethanone was prepared from the corresponding bromo compound and 10 % excess of potassium selenocyanate, KSeCN, in ethanol at room temperature.[4] As soon as a yellow colour started to appear, the reaction mixture was poured into a large volume of water and the mixture set aside for 1 h in the refrigerator. The product was filtered off and crystallized several times from diethyl ether/light petroleum (40–60 °C) and finally from cyclohexane. M.p. 88 °C (85 °C[4]). Ethanol as suggested by Hofmann[4] as a crystallization agent was found to give a somewhat sticky product.

Tetraphenylarsonium, $\mathrm{Ph_4As^+}$, tetraphenylphosphonium, $\mathrm{Ph_4P^+}$, and bis(triphenylphosphine)iminium, $\mathrm{[(Ph_3P)_2N]^+}$, salts were used as the source of the nucleophiles. These salts were prepared and purified as previously described.[2,5] Only $\mathrm{[(Ph_3P)_2N]^+}$-salts, abbreviated $\mathrm{[PNP]^+}$-salts, were used as the source of the ^{13}C-pseudohalide ions. These compounds were prepared from potassium ^{13}C-cyanide,[5] 90.5 % enriched, used as received from British Oxygen Co. Ltd..

Determination of rate and equilibrium constants. In Table 1 are listed some IR, UV and NMR data for the 2-substituted 1-phenylethanones, RX, and the pseudohalide ions, X^-, employed in the present study. These data, except the IR data in the 1700 cm^{-1} region, column 3 in Table 1, formed the basis for the analytical methods applied in the present study for the determination of rate and equilibrium constants.

Table 1. IR, UV and NMR data for 1-phenyl-2-X-ethanones, (PhC(O)CH$_2$X), RX, and some anions, X^-, in acetonitrile.

RX,X^-	ν_{NCX}(cm^{-1})[a]	ν_{CO}(cm^{-1})[a]	λ_{max}(>300 nm)	δ_{CH_2} (Rel. TMS)[b]
RCl		1708(s), 1690(m)	~324(ε= 68)	4.95
RBr		1688(s), 1706(m)	324(ε=121)	4.65
RS^{12}CN	2159(m)[c]	1689(s), 1702(m)		4.85
S^{12}CN$^-$	2059(s)[d]			
RS^{13}CN	2116(m)			
S^{13}CN$^-$	2012(s)			
RSe^{12}CN	2161(m)[e]	1675(s), 1695(m)		4.90
Se^{12}CN$^-$	2068(s)[f]			
RSe^{13}CN	2111(m)			
Se^{13}CN$^-$	2023(s)			

[a] ±2 cm^{-1}. [b] ±0.01 ppm. [c] Peak height of RSCN in MeCN is 15 % of peak height due to NCS$^-$. [d] $A = 4.1 \times 10^4$ M^{-1} cm^{-2}, $\Delta\nu_{\frac{1}{2}} = 12$ cm^{-1}.[2] [e] Peak height of RSeCN is 11 % of peak height due to NCSe$^-$. [f] $A = 2.2 \times 10^4$ M^{-1} cm^{-2}, $\Delta\nu_{\frac{1}{2}} = 10$ cm^{-1}.[2]

The rate of the reaction between ionic chloride, Cl^-, and 2-bromo-1-phenylethanone, RBr, was determined by UV by following the rate of decrease in absorption at 324 nm. The rate of the reverse reaction, $RCl + Br^-$, could not be determined experimentally due to the low carbon basicity of the bromide ion. This rate constant, k_r, was therefore calculated from the equilibrium constant, K, determined independently by NMR, and the forward rate constant, k_f, by $k_r = k_f/K$. For reactions involving the bromide ion as nucleophile, this procedure was generally applied.

All the remaining rate constants were determined by the IR technique employing liquid cells by following the rate of appearance or/and disappearance of the pseudohalide ions in the 2000 – 2200 cm^{-1} region. For the reaction depicted by eqn. 4, the reaction between RSCN and ionic selenocyanate, $NCSe^-$, and for the reverse reaction, $RSeCN + NCS^-$, ^{13}C-pseudohalide ions had to be employed since $N^{12}CS^-$ and $N^{12}CSe^-$ absorb at 2059 and 2068 cm^{-1}, respectively, which are not sufficiently apart for accurate studies. Due to the low extinction coefficients of RSCN and RSeCN in the 2000 – 2200 cm^{-1} region the peaks due to these compounds did not interfere with the measurements in the concentration ranges used.

The concentration of the ionic nucleophiles was usually in the $(2-7) \times 10^{-3}$ M range, but for the slowest reactions, notably the reactions of RSCN, concentrations up to 2×10^{-2} M had to be used to avoid prolonged reaction times (see below). For some of the reactions both the effect of the cation, Ph_4As^+, Ph_4P^+ or $[PNP]^+$, and the concentration of the nucleophiles were examined and no dependence of rate constants upon cation or upon concentration was observed up to the maximum concentration employed, 2×10^{-2} M.

The rate constants were calculated from kinetic runs performed under both pseudo first-order and second-order conditions when experimentally possible, depending upon rate and equilibrium constants. When the pseudo first-order technique was used, the organic substrate and not the ionic nucleophile was the one in excess to avoid the concentration of the latter exceeding 2×10^{-2} M. (Examples: $RSCN + N^{13}CS^-$ and $RSCN + Cl^-$).

The linearity of the rate plots was generally satisfactory for several half-lives suggesting the reactions to be clean second-order reactions, first-order in each of the reactants. The only reactions deviating significantly from clean second-order kinetics when the reactions were followed for more than two half-lives were the slow reactions of 1-phenyl-2-thiocyanatoethanone, RSCN. For prolonged reaction times the reaction mixture turned slowly yellow and more thiocyanate ions were formed than calculated from the amount of consumed nucleophiles. The rate constants for the reactions of this substrate were therefore calculated from kinetic runs followed for only one to two half-lives. The equilibrium constants for reactions involving the thiocyanate ion were therefore calculated from more concentrated runs by the NMR technique or by IR after dilution.

The determination of equilibrium constants by NMR was performed on equilibrated solutions by comparison of peak heights due to the methylene protons. Concentrations up to 2×10^{-1} M were necessary to obtain reproducible results for equilibrium constants far from unity. (Reactions involving the bromide ion). In order to obtain sufficiently concentrated solutions of the anions only $[PNP]^+$-salts could be employed. In the calculations of the equilibrium constants the activity coefficients of the two competing anions were assumed to be the same.

Calculations. The reactions studied can be described with the following general equation, eqn. 6:

$$RA + B^- \underset{k_r}{\overset{k_f}{\rightleftharpoons}} RB + A^- \tag{6}$$

where k_f and k_r are the second-order rate constants for the forward and the reverse reaction, respectively. For equal start concentration of the reactants, a, the integrated rate equation is:

$$(2aK_r^{\frac{1}{2}})^{-1} \ln \frac{a - x(1 - K_r^{\frac{1}{2}})}{a - x(1 + K_r^{\frac{1}{2}})} = k_f t \tag{7}$$

where $K_r = k_r/k_f$ and x is the concentration of product at time t. For reactions where k_r is negligible compared with k_f, $K_r \ll 1$, the usual second-order rate equation can be applied, eqn. 8:

$$\frac{x}{a(a-x)} = k_f t \tag{8}$$

When $[RA]_0 = a$ and $[B^-]_0 = b$ and $a \neq b$, the following rate equation is valid, eqn. 9:

$$M^{-1} \ln \frac{2ab - x(a+b-M)}{2ab - x(a+b+M)} = k_f t \tag{9}$$

where $M = [(a-b)^2 + 4K_r]^{\frac{1}{2}}$ and $K_r = k_r/k_f$ as in eqn. 7.

For pseudo first-order reactions, $a \gg b$, eqn. 9 is reduced to:

$$Z^{-1} \ln \frac{2ab - x(a-Z)}{2ab - x(a+Z)} = k_f t \tag{10}$$

where $Z = (a^2 + 4abK_r)^{\frac{1}{2}}$.

For pseudo first-order reactions where the reactions are monitored by the rate of disappearance of the minor reactant, b, the rate equation is:

$$Z^{-1} \ln \frac{b(a+Z)+(b-x)(a-Z)}{b(a-Z)+(b-x)(a+Z)} = k_f t \tag{11}$$

where Z is as given above, eqn. 10, and $(b-x)$ is the concentration of the minor reactant at time t.

For the isotope exchange reactions, the reactions depicted by eqn. 3 and 5, $[RA]_0 = [B^-]_0 + [A^-]_0 = a$ for equal concentrations of reactants, eqn. 6. When the isotope purity of the applied ^{13}C-pseudohalide ions is 90.5 %, $[B^-]_0 = 0.905\ a$. Since K is necessarily unity, the following rate equation is obtained:

$$(2a)^{-1} \ln \frac{0.778a}{a-2.22x} = k_f t \tag{12}$$

where x denotes the concentration of products at time t.

When the progress of the reaction is followed by the rate of disappearance of the ^{13}C-pseudohalide ion, $(b-x)$, the integrated rate equation is:

$$(2a)^{-1} \ln \frac{0.778a}{2.22(b-x)-a} = k_f t \tag{13}$$

Instrumental. The UV measurements were performed with a Varian-Techtron UV-VIS Spectrofotometer, Model 635, employing matched 1 cm quartz cells. The IR measurements were performed with a Unicam SP 200 Infrared Spectrophotometer. IR liquid cells of 0.1 cm path-length were employed.

The reaction solutions were kept in a thermostated oil-bath at 25.0±0.1 °C. 4 to 8 aliquots were withdrawn periodically for each kinetic run.

The NMR measurements were performed at ≈27 °C on a JEOL NMR C-60 H Spectrometer. A Spin-decoupler JNM-SO 30 Counter was used to determine the resonance positions.

RESULTS

In Table 2 are listed the second-order rate constants, k_f, and the equilibrium constants, K, determined in the present study. The values for k_f and K are the average values from measurements performed at least in duplicate with varying concentrations of reactants. In column 4 in Table 2 are listed the calculated relative rate constants, k_f(rel), for each nucleophile reacting with the various substrates; the rate constant for the least reactive compound, RSCN, is unity.

As indicated in Table 2, several of the rate constants and especially some of the equilibrium constants have limited accuracy. Even though most of the equilibrium constants were determined in

Table 2. Second-order rate constants, k_f, relative rate constants, k_{rel}, (rate constants for RSCN reacting with each nucleophile are unity) and equilibrium constants, K, for the reactions between 2-substituted 1-phenylethanones, ($PhC(O)CH_2X$), RX, and various nucleophiles, Y^-, in acetonitrile at 25.0 °C.

RX	Y^-	$k_f/M^{-1}\,s^{-1}$	k_{rel}	K
RBr	$NCSe^-$	4.7 ± 0.9	1.3×10^4	$(6 \pm 3) \times 10^{2\,a}$
RCl	$NCSe^-$	$(2.2 \pm 0.2) \times 10^{-2}$	60	10 ± 2^{b}
RSeCN	$N^{13}CSe^-$	$(6.3 \pm 0.3) \times 10^{-3}$	18	1
RSCN	$N^{13}CSe^-$	$(3.7 \pm 0.3) \times 10^{-4}$	1	1.2 ± 0.1
RCl	Br^-	$\sim 8 \times 10^{-2\,c}$	~100	$(1.0 \pm 0.2) \times 10^{-2\,b}$
RSeCN	Br^-	$(6 \pm 3) \times 10^{-3}$	9	$(1.8 \pm 0.9) \times 10^{-3}$
RSCN	Br^-	$(7 \pm 2) \times 10^{-4\,c}$	1	$(1.1 \pm 0.3) \times 10^{-3}$
RBr	Cl^-	~ 8	$\sim 2.5 \times 10^4$	$(1.0 \pm 0.2) \times 10^{2\,a}$
RSeCN	Cl^-	$(2.6 \pm 0.2) \times 10^{-3}$	8	0.13 ± 0.01
RSCN	Cl^-	$(3.3 \pm 0.5) \times 10^{-4}$	1	0.2 ± 0.02
RBr	NCS^-	$(6.2 \pm 0.4) \pm 10^{-1}$	2.5×10^4	$(9 \pm 3) \times 10^{2\,a}$
RCl	NCS^-	$(1.9 \pm 0.2) \times 10^{-3}$	75	5 ± 1^{b}
RSeCN	$N^{13}CS^-$	$(3.1 \pm 0.3) \times 10^{-4}$	12	0.84 ± 0.1
RSCN	$N^{13}CS^-$	$(2.5 \pm 0.2) \times 10^{-5}$	1	1

[a] Calculated from K for the reverse reaction. [b] Determined only by NMR at 27 °C. [c] Calculated from K and k_r.

three independent ways; NMR, IR and, when possible, by the ratio of k_f and k_r, the experimental uncertainty was considerable for the equilibrium constants far from unity, *i.e.* for reactions involving the bromide ion. The equilibrium constants between 10 and 10^{-1}, however, are probably well within 20 %.

With the exception of the reactions of 2-bromo-1-phenylethanone, RBr, and the isotope exchange reactions, eqns. 3 and 5, all rate constants had to be calculated from rate equations in which the equilibrium constants were parameters, eqns. 7, 9, 10 and 11. The uncertainty in the equilibrium constants thus influenced the accuracy by which the rate constants could be determined. For the reactions of RBr, the simple second-order rate equation, eqn. 8, could be used with negligible error due to the low carbon basicity of the leaving group, the bromide ion. However, all reactions of this substrate were too rapid for both the UV and the IR techniques to allow the rate constants to be determined with high accuracy. (Half-lives from 30 to 300 s).

In none of the reactions studied, even after very long reaction times, could any formation of 2-isothiocyanato- and 2-isoselenocyanato-substituted products, $PhC(O)CH_2NCS$ and $PhC(O)CH_2NCSe$, respectively, be observed. Due to the large extinction coefficients of this class of compounds in the 2000–2200 cm^{-1} region,[6] it should have been possible to detect only trace amounts. No formation of elemental selenium or sulfur could be observed in any of the reactions.

All the 2-substituted 1-phenylethanones in the present study exhibited two strong absorptions in the 1700 cm^{-1} region. (Column 3 in Table 1). Due to the proximity of these peaks, they could not be used for the determination of rate and equilibrium constants. In the case of the chloro-substituted compound, the peak at the higher wavenumber has the highest intensity while the opposite is the case for the remaining three compounds. Apparently, the chloro-substituted compound exists predominantly in the *cis*-conformation while the 2-bromo-, 2-thiocyanato- and the 2-selenocyanato-1-phenylethanones prefer the *gauche*-conformation in acetonitrile. As has been pointed out by Jones and Spinner,[7] the *cis-gauche* equilibrium in 2-substituted 1-phenylethanones appears to be due to a complex interplay of electron-withdrawing effects and steric demands of the substituents.

DISCUSSION

2-Halo-1-phenylethanones, $PhC(O)CH_2X$ (X = Cl, Br and I), have long been known to be highly reactive toward nucleophilic species.[8–10] Actually, with some very few exceptions,[11] these compounds are generally regarded as considerably better alkylating agents than are all other alkyl halides.[12] In this study it is shown that even the thiocyanate ion and the selenocyanate ion can be easily displaced from the methylene carbon atom. Due to the facility by which this class of compound undergoes displacement reactions, the present study appears to be one of the very few studies on substitution reactions toward aliphatic carbon in which both the forward and the reverse rate constants together with equilibrium constants have been determined. The results therefore provide information on not only the nucleophilicity and the leaving group ability of the employed anions but also on their carbon basicity.[13] Data on basicity toward aliphatic carbon are most rare in the literature.[13–16]

In Table 3 are listed some ratios between the second-order rate constants for the various reactions studied. In Table 4 are listed some average nucleophilicities, average leaving group abilities and the carbon basicity of Br^-, Cl^-, $NCSe^-$ and NCS^-. These latter numbers are calculated from the data

Table 3. The ratio between second-order rate constants for various nucleophiles reacting with 2-substituted 1-phenylethanones, RX, in acetonitrile at 25.0 °C.

	$\frac{k_f(NCSe^-)}{k_f(NCS^-)}$	$\frac{k_f(NCSe^-)}{k_f(Cl^-)}$	$\frac{k_f(NCSe^-)}{k_f(Br^-)}$	$\frac{k_f(Br^-)}{k_f(Cl^-)}$
RBr	8	0.6		
RCl	11		~0.3	
RSeCN	20	2.5	~1.1	~2.3
RSCN	15	1.1	~0.5	~2.1

Table 4. The average nucleophilicity, the average leaving group ability and the carbon basicity of Br^-, Cl^-, $NCSe^-$ and NCS^- for reactions with 2-substituted 1-phenylethanones in acetonitrile at 25.0 °C. (Relative values to NCS^-.)

	Br^-	Cl^-	$NCSe^-$	NCS^-
Nucleophilicity [a]	15	7	10	1
L. group ability [b]	2×10^4	75	10	1
Carbon basicity [c]	1.4×10^{-3}	0.14	1.2	1

[a] Average values calculated from rate constants listed in Table 2 and rate ratios in Table 3. [b] Average values calculated from relative rate constants, k_{rel}, in Table 2, column 4. [c] Values from equilibrium constants, K, in Table 2.

in Tables 2 and 3 and are relative to the values for the thiocyanate ion.

The nucleophilicity of Br^-, Cl^-, $NCSe^-$ and NCS^-. The data in Tables 2 and 4 suggest that the bromide ion, the chloride ion and the selenocyanate ion are approximately of the same nucleophilic strength toward the methylene carbon atom in the various 2-substituted 1-phenylethanones. These ions appear to be about ten times as nucleophilic as is the thiocyanate ion. The same trend in reactivity has previously been observed for substitution reactions toward methyl iodide in acetonitrile.[17] None of the ions therefore seem to prefer the methylene carbon to the methyl carbon in methyl iodide to any significant extent.

The calculated rate ratios, listed in Table 3, indicate clearly that the effect of the leaving group upon the reactivity of the various ions is not pronounced, especially when taking into account that the reactivity of the various substrates spans over more than four powers of ten (column 4 in Table 2). Apparently, only when the leaving groups are very dissimilar *i.e.* the iodide ion and the tosylate ion,[18,19] may nucleophiles show significant preference for one or the other leaving group. In the present study all leaving groups, and thus all nucleophiles, are on the soft side of the scale[20] and the nucleophilicity of the various ions is not anticipated to be strongly dependent upon the leaving group. The data in Table 3, however, suggest that the selenocyanate ion favours slightly the selenocyanate ion as leaving group while the halide ions prefer slightly a halide ion as leaving group. This finding accords with the idea of maximum stabilization of the transition state in alkylation reactions when the entering and the leaving groups are similar.[18]

The leaving group ability of Br^-, Cl^-, $NCSe^-$ and NCS^-. The bromo-substituted compound is clearly the most reactive of the various ω-substituted 1-phenylethanones. The average rate ratio between RBr and RCl, ~300 (column 4 in Table 2 and Table 4), is considerable but is in no way exceptional for alkylation reactions in dipolar aprotic solvents.[21] In protic solvents considerably lower RBr/RCl ratios are generally observed which is predominantly due to the preferential solvation of the chloride ion which increases the leaving group ability of this ion in this class of solvent. In dipolar aprotic solvents, however, where the solvation of the chloride ion is negligible, large rate ratios between alkyl bromides and alkyl chlorides are observed which reflect the large difference in the bond energy of the carbon-bromine and of the carbon-chlorine bond.

The organic selenocyanate, RSeCN, reacts approximately 10 times as rapidly as does the corresponding thiocyanate, RSCN, with all the nucleophiles. Apparently, the weaker carbon-selenium bond is the cause of the higher reactivity of the selenocyanato-substituted compound. Several organic selenocyanates, RSeCN, are well-known to isomerize considerably more rapidly to the iso-substituted derivatives, RNCSe, than do the corresponding thiocyanates, RSCN ($R = Ph_2CH$ *etc.*).[22] The better leaving group ability of the selenocyanate ion from aliphatic carbon appears to be the probable cause of this observation.

The carbon basicity of Br^-, Cl^-, $NCSe^-$ and NCS^-. The bromide ion is clearly the least basic of the anions studied and this ion is about two orders of magnitude less basic than is the chloride ion. This observation agrees with the results by Parker[13] on the carbon basicity of the chloride ion and the bromide ion toward the butyl carbon atom in nitrobenzene at 80 °C and the methyl carbon atom in acetone at 25 °C. The basicity of the thiocyanate ion, however, toward the butyl carbon atom in nitrobenzene is reported by Parker[13] to be of the same order of magnitude as that of the bromide ion which is not in agreement with the results obtained in the present study; the thiocyanate ion and the selenocyanate ion being even more basic than the chloride ion.

The selenocyanate ion is slightly more basic than is the thiocyanate ion, even though the former ion is a considerably better leaving group. While the leaving group ability is a function of the energy of the bond to be broken and the solvation energy of the displaced ion, the carbon basicity is also a function of the nucleophilicity of the ion. Since the reactivity of nucleophilic species in substitution reactions toward aliphatic carbon is strongly dependent upon the polarizability of the nucleophile,[20] the carbon basicity is therefore also a function of the polarizability of the attacking nucleophile. The carbon basicity should therefore not parallel the hydrogen basicity to any significant extent when the nucleophilic atom is altered. This conclusion was arrived at by Bunnett[14] and Hine[16] several years ago. Since the nucleophilicity and the leaving group ability of nucleophilic species in substitution reactions toward aliphatic carbon is strongly dependent upon the structure of the transition state[1,20] which in turn is a function of the solvent[13] and the organic substrate,[1] it is obvious that no absolute order of carbon basicity of nucleophiles can be arrived at.

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