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RELATIVE NUCLEOPHILICITIES OF "NAKED" ANIONS[1-4]

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The relative nucleophilicities of anions toward organic and inorganic substrates has been the subject of much research over the past several decades Although the relative nucleophilicities[5,6,7,8,9] vary considerably with substrate, the reactivities of nucleophilies toward a given substrate, e g , the saturated carbon atom in methylbromide, have been used to establish empirical reactivity scales Swain and Scott[10] developed a two parameter relationship with methylbromide as the substrate relative to water as a nucleophile Edwards[11] attempted to correlate the nucleophilicities relative to water to a four parameter equation based on both the polarizabilities and basicities of the anions Recently, Ritchie and Virtanen[12] correlated the reaction of each of several carbonium ion systems with a wide variety of anions using one empirical parameter In all of these scales the relative reactivities of the nucleophiles vary over several orders of magnitude In general solvation, bond strength in the product, charges on the nucleophile and substrate, and the "alpha effect" have been identified[7,8] as important variables related to nucleophilicity In addition, symbiotic effects between the nucleophile and the leaving group have been identified as an important factor bearing on relative nucleophilic strength[13] While Parker[14] has suggested that these effects are solvent dependent and should become less important in dipolar, aprotic solvents, Songstad and Engemyr[15] have shown that this symbiosis appears to be more important in dipolar aprotic solvents than in the protic counterparts At present, an absolute or inherent scale of nucleophile reactivity in solution has not as yet been developed

Bohme, Young and Lee-Ruff[16] have determined the nucleophilic reactivities of H^-, F^-, OH^- and NH_2^- toward CH_3Cl in the gas phase at 300°K These gas phase results indicate that the nucleophilic reactivity of the anions studied are approximately the same and do not correlate with the gas phase basicities This suggests that solvation of the anions is responsible for the large variations found in the reactivities of the anions in solution In a recent extention of these studies[17] the rate of reaction of CN^- was found to be surprisingly slow relative to the other anions Brauman, Olmstead, and Lieder[18] have shown that the relative reactivities of anions even in the gas phase depend on the substrate

Almost all the reported solution studies[5-9] on relative nucleophilicities have been performed in solvents with high dielectric constants (H_2O, $CH_3CH_2OH-H_2O$, etc) where the salts are usually dissociated but the ions are extensively solvated Some studies have been reported[5-7] in solvents with intermediate dielectric constants [DMF(37) and acetonitrile (39)] where anion solvation might be expected to be less extensive However, in the solvents with lower dielectric constants, the possibility of ion pairing increases, thus making it difficult to unambiguously interpret the data It has recently been reported that 18-crown-6 successfully solubilizes[2,3,4] potassium salts in acetonitrile producing extremely reactive anions ("naked" anions) presumeably because of the weak anion solvation forces in acetonitrile solutions and the complete dissociation of the electrolytes For example, the fluoride and acetate ions usually considered weak nucleophiles are powerful nucleophilies in acetonitrile [3,4] Conductance[19] studies on dilute solutions have demonstrated that these solutions contain primarily free ions In this communication, the relative reactivities of several "naked" anions toward benzyl tosylate in acetonitrile are reported and compared to other systems

The reaction of the anions with benzyl tosylate was followed by a conductance method similar to literature procedures[20,21] with a Beckman model RC-18A conductivity bridge The acetonitrile was Fisher reagent grade material which was refluxed over CaH_2 and distilled under nitrogen immediately before being transferred into a nitrogen purged dry box The 18-crown-6 was prepared and purified by a recent literature procedure [22] All the salt solutions studied were prepared in the dry box by dissolving weighed amounts of salt in a 0 1 M 18-crown-6 acetonitrile solution These solutions were transferred to the conductivity cell containing a sealed ampoule of benzyl tosylate prepared by the method of Kochi and Hammond [23] The cell was sealed by means of a ground glass joint and transferred to a water bath maintained at 30 00±0 05°C outside the dry box When the bridge reading was constant, the ampoule with the benzyl tosylate was broken by means of a special plunger device The plots of $\log(\Lambda_t-\Lambda_\infty)$ versus time were linear for at least the first 80% of the reaction The psuedo first order rate constants were obtained from the slope of these plots and converted to second order rate constants The products of the reactions have been isolated from preparative scale runs and unequivocally identified by NMR, IR and mass spectrometric techniques to be the products of simple displacement Infrared studies on the SCN^- solutions indicate that benzylthiocyanate appears to be the only product formed from that nucleophile

The rate constants shown in Table I have a total variation of less than a factor of 10 if SCN$^-$ is deleted If a statistical factor of two is applied to N$_3^-$ and CH$_3$COO$^-$ these rates vary by less than a factor of 5 These results are in direct contrast to the previously observed relative nucleophilicities (Table I) Furthermore, in these studies the halides appear to be nucleophiles with virtually identical reactivities, whereas the reactivities vary by a factor of 200 in water[5] and a factor of 20 in dimethylformamide[6,14] There appears to be a general leveling of the nucleophilicities of anions in acetonitrile Several reversals of the usual order of nucleophilicities may also be seen in Table I Quite surprisingly the "best" nucleophile is CH$_3$COO$^-$ (within experimental error) which is normally considered a very poor nucleophile, while SCN$^-$, one of the more potent nucleophiles in aqueous solution, is approximately 30 times slower than CH$_3$COO$^-$ Apparently, the reactivities of anions dissolved in acetonitrile do not vary appreciably, a situation reminiscent of most anions studied in the gas phase This would seem to indicate that variations in anion solvation in acetonitrile are not important factors in determining the relative reactivities These results tend to support the notion that "naked" anions in acetonitrile are solvated by much weaker forces than in protic solvents

Table I

Kinetic Data at 30 00±0 05 in Acetonitrile for the Reaction of "Naked" Anions with Benzyl Tosylate

Salt	Conc (Mx10^4)	-Slope^a (min^{-1}x10)	Correlation Coefficient	k^{b,c} (l mole^{-1}sec^{-1})	Relative Rates This Study	Relative Rates Swain and Scott
KN$_3$	5 22	2 53	0 990	1 07	10 0	20 0
	4 71	1 72	0 999	0 96		
	4 58	1 80	0 999	1 01		
KOAc	5 60	2 70	0 993	0 96	9 6	1 0
	3 95	2 45	0 999	0 92		
	5 07	1 56	0 997	0 96		
KCN	5 41	0 617	0 999	0 22	2 4	250 0
	6 17	0 542	0 998	0 21		
	7 98	0 949	0 998	0 26		
KF	3 32	0 381	0 975	0 15	1 4	0 2
	6 59	0 385	0 998	0 12		
KCl	5 53	0 693	0 999	0 12	1 3	2 0
	5 90	0 350	0 999	0 11		
	5 61	0 657	0 999	0 13		
	7 59	0 456	0 999	0 13		
KBr	6 74	0 456	0 998	0 13	1 3	16 0
	6 57	0 371	0 999	0 11		
	7 56	0 200	0 998	0 11		
KI	7 26	0 557	0 999	0 091	1 0	200 0
	7 02	0 256	0 999	0 084		
	7 75	0 240	0 999	0 088		
KSCN	5 59	0 0680	0 998	0 020	0 3	125 0
	5 89	0 0366	0 995	0 021		
	6 81	0 0979	0 999	0 020		

(a) The slope was obtained from the plot of log $(A_t - A_\infty)$ vs t

(b) The second order rate coefficients of Cl^-, Br^- and SCN^- toward n-Bu-I have previously been determined in CH_3CN taking into account ion pairing effects to be 4 0, 3 4 and 0 58 (x 10^{-3} $M^{-1}sec^{-1}$), respectively, which gives approximately the same order of nucleophilicity reported in this communication

(c) The second order rate coefficients of SCN^-, Br^- and N_3^-, Cl^- and AcO^- toward CH_3-OTs have been determined in CH_3CN by spectrophotometric procedures to be 2 3, 50, 25, 230 and 2600 (x 10^{-4} M^{-1} sec^{-1}), respectively The relative nucleophilicities determined from these rate constants are considerably different from the values reported in this communication.

While the relative nucleophilicities in acetonitrile are similar to those found in the gas phase, the absolute gas phase rates are approximately eleven orders of magnitude greater than those found for the anions in acetonitrile. This large difference in absolute rates is indicative of the moderating influence of the solvent on all the reactivities In fact Kabarle[24] has demonstrated that acetonitrile forms a stable adduct in the gas phase with halides ions and Coetzee and Sharpe[25] have shown that several anions in acetonitrile cause the C-H stretching frequencies of acetonitrile to shift to lower wavenumber values Consequently it can be concluded that the anions are solvated, but the differences in solvation in the series studied do not appreciably effect the relative kinetic properties of the anions

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