The Nucleophilicity of the Cyanate Ion

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As pointed out by Norbury,[1] the cyanate ion has received little attention in inorganic as well as organic chemistry. Only recently, the property of the cyanate ion as a ligand in inorganic complexes has been examined (Ref. 2 and references therein).

The cyanate ion, belonging to the important class of molecules containing 16 valence electrons,[3] is a member of the pseudohalide group, although no information is available on the typical redox reaction

$$2NCO^- = (NCO)_2 + 2e$$

due to the non-existence of the dimeric oxidation product. The cyanate ion, potentially an ambident ion,[2] has most of the negative charge on the nitrogen end of the ion.[4,5] This causes the nitrogen end to be the reactive one, although the formation of oxygen-bonded cyanato complexes has been claimed.[2] With regard to the corresponding acid, HNCO, generally called "cyanic acid", the formation of a very small amount of isobutyl cyanate from the reaction between "cyanic acid" and diazoisobutane has been regarded as possible evidence for the presence of some hydrocyanic acid, HOCN, in "cyanic acid".[6] From alkyl halides, alkyl tosylates, or dialkyl sulfates, and ionic cyanates, only the corresponding alkyl isocyanates or the trimeric trialkyl isocyanurates are obtained, but this may be due to the facile isomerization of the first formed alkyl cyanates.[7] The ambident nature of the cyanate ion toward aliphatic carbon is thus neither proved nor disproved. Alkyl cyanates are usually made by decomposition of alkoxy thiatriazoles,[9] while aryl cyanates are formed from the corresponding phenolates and cyanogen bromide or chloride.[10] No cyanates have been detected from reactions of primary alkyl halides and silver isocyanate, while secondary alkyl halides and silver isocyanate yield the corresponding cyanates and isocyanates in almost equal amounts.[11]

To try to shed light on the reactivity of the cyanate ion, we have performed some kinetic studies on the reaction between methyl iodide and the cyanate ion in an aprotic solvent, acetonitrile, and a protic one, methanol. Due to the very low solubility of alkali cyanates in these solvents,[12] tetraphenylarsonium cyanate was used as the source of the ion in these solvents.[1,13] The reaction was followed in both solvents by UV spectroscopy, measuring the formation of the iodide ion,[14] and in acetonitrile by IR as well, measuring the disappearance of the peak at 2140 cm^{-1} due to ionic cyanate.[15]

In acetonitrile, the rate of reaction was examined in the $5 \times 10^{-2} - 2 \times 10^{-3}$ M region of both reactants, and the rate constant was found to increase steadily upon dilution in the $5 \times 10^{-2} - 1.5 \times 10^{-2}$ region, while for concentrations lower than 1.5×10^{-2}, no further increase in rate constant was observed, suggesting tetraphenylarsonium cyanate to be completely dissociated in dry acetonitrile for concentrations lower than 1.5×10^{-2} M. Rate constants, in acetonitrile, determined by both methods, agreed within 3 % and the logarithmic plots were completely linear up to $80 - 90$ % reaction, suggesting that isomerization of the possible intermediate, methyl cyanate, to methyl isocyanate, and the further trimerization of the latter, did not interfere with the kinetics. Likewise, in methanol, possible consecutive reactions were found not to interfere. The results, together with rate constants for some other nucleophiles, are collected in Table 1. The rate constants in methanol for the other nucleophiles are from Ref. 16, and for the cyanide ion in acetonitrile, from Ref. 14; otherwise, the data are from

Table 1. Rate constants at 25.0°C for nucleophiles reacting with methyl iodide in acetonitrile and methanol.

	$k_2(M^{-1} sec^{-1})$		$\dfrac{k_2(MeCN)}{k_2(MeOH)}$
	MeCN	MeOH	
OCN^-	1.7×10^{-2}	7.0×10^{-5}	2.4×10^2
N_3^-	2.45×10^{-1}	7.8×10^{-5}	3.4×10^3
NCS^-	2.06×10^{-2}	5.74×10^{-4}	36
$NCSe^-$	1.77×10^{-1}	9.13×10^{-3}	19
NC^-	26.5	6.45×10^{-4}	4.1×10^4
Cl^-	7.0×10^{-2}	3×10^{-6}	2.3×10^4
AcO^-	4.8×10^{-1}	2.7×10^{-6}	1.8×10^5
Ph_3As	2.4×10^{-5}	7.5×10^{-6}	3.2
Ph_3P	5.7×10^{-3}	6.6×10^{-2}	0.086
Et_3N	3.35×10^{-2}	5.95×10^{-4}	59

this work. The rate constants in acetonitrile for the ionic nucleophiles, selenocyanate, thiocyanate, and azide ion, were determined by the IR as well as the UV method as in the case of the cyanate ion, from runs where the initial concentrations of the nucleophile were in the 5×10^{-3} — 10^{-2} M region. The tetraphenylarsonium salts were used as source of the ions.

It is interesting to note that the reactivity of the cyanate ion is comparable with that of the other pseudohalide ions. In acetonitrile, a dipolar aprotic solvent, this ion is as reactive as the thiocyanate ion. The levelling effect of dipolar aprotic solvents on the reactivity of charged nucleophiles is well documented.[17]

The Edward equation,[18] relating reactivity of nucleophiles with hydrogen basicity and oxidation potential, often called the oxibase scale,[19] has been used with considerable success to predict oxidation potentials of nucleophiles. Some severe exceptions to the general application of this equation are known, however.[19,20] The high pK_a value of hydroisocyanic acid,[21] comparable with that of hydrazoic acid, and the rather equal nucleophilicity of these two ions with the same size and, most probably, the same nucleophilic atom, suggest that the oxidation potential of the cyanate ion is of the same order of magnitude as that of the azide ion. Interestingly, the same conclusion has been obtained from studies on charge-transfer-to-solvent bands of halide and pseudohalide ions.[22] A recently obtained value of the electron affinity of the cyanate ion [23] is comparable with that of the azide ion.[23]

Experimental. Acetonitrile, methanol, and the tetraphenylarsonium salts were purified as reported previously.[15,24] Triphenylarsine and triphenylphosphine were crystallized five times from ether. Triethylamine was distilled twice from sodium hydroxide pellets prior to use. Extreme care was exercised to exclude moisture during the preparation of the above-mentioned reagents and their solutions. Because of the rapid reaction between triphenylphosphine and oxygen in acetonitrile, oxygen was carefully excluded in this case. Methyl iodide was washed with a solution of potassium carbonate, then with water, and finally dried carefully over magnesium sulfate, distilled from silver wool and stored cold over silver wool in a black-painted bottle.

The UV measurements were performed with a Beckmann DB Spectrophotometer, using 0.1 cm quartz cells. The IR measurements were performed on an Unicam SP 200 Infrared Spectrophotometer using 0.1 cm liquid cells. The temperature during the experiments was $25 \pm 0.2°C$. The rate constants were reproducible to within 3 %.

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