Gas-phase Nucleophilicities of the Anions: H^-, F^-, OH^-, and NH_2^-

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Summary The nucleophilic reactivities of the anions H^-, F^-, OH^-, and NH_2^- for substitutions at CH_3Cl were determined quantitatively in the gas phase at 300 K using the flowing afterglow technique; comparisons are made with gas-phase basicities and solution nucleophilic reactivities.

THE current interest in intrinsic reactivities of organic anions motivated us to determine the gas-phase reactivity of some simple first-row nucleophiles. The flowing afterglow technique[1,2] was employed to investigate the kinetics at 300 K of nucleophilic substitution reactions of type (1),

$$X^- + CH_3Cl \rightarrow CH_3X + Cl^- \qquad (1)$$

where X^- may be H^-, NH_2^-, OH^-, or F^-. In such studies the thermalization of the anions prior to reaction is ensured by allowing the anions to undergo many thousands of collisions with inert buffer gas molecules prior to their entry into the reaction region. The experimental determination of the reaction rate constant under these conditions allows the calculation of reaction probabilities which are a direct measure of the intrinsic nucleophilicity of the anion, X^-.

Details of the experimental method and the associated data analysis have been fully described elsewhere.[1,2] Helium was used as the buffer gas at a pressure of *ca.* 0·4 Torr. Amide and hydride ions were generated by electron impact on ammonia, fluoride ion by 100 eV electron impact on fluorobenzene, and hydroxide ion by the hydrogen atom abstraction of oxide ion with ammonia.[2] The methyl chloride has a purity (liquid phase) of 99·5 mol %.

The experimental rate constants for nucleophilic substitution are summarized in the Table along with calculated values for the reaction probability, $P_{T,L}$, the ratio of the experimentally determined rate constant, k_{exp}, to the theoretical collision rate constant. The experimentally determined rate constants are believed to be accurate to ±30%. The relative accuracy should be ±10% or less The theoretical collision rate constant, k_T, is a sum of two terms:[4] k_L, the contribution due to the ion–induced dipole interaction, and k_D, the contribution due to an ion–dipole interaction as a result of which the dipole aligns itself or 'locks in' as the ion approaches. The true reaction probability is likely to have a value intermediate between P_T ($=k_{exp}/k_T$) and P_L ($=k_{exp}/k_L$) when $P_L < 1$ and intermediate between P_T and 1 when $P_L > 1$. A reaction probability $P_T =$ *ca.* 1 suggests that the dipole indeed 'locks in' as the ion approaches.

TABLE. *Rate constants and reaction probabilities for nucleophilic substitution with* CH_3Cl *in the gas phase at* 300 K.

	Rate constant, $k \times 10^9$ (cm^3 molecule^{-1} s^{-1})				Reaction probability	
Nucleophile	k_{exp}	k_L	k_D	k_T	P_L	P_T
H^-	2·5	5·0	17·4	19·9	0·50	0·13
F^-	1·8	1·3	4·6	5·9	1·4	0·31
OH^-	1·9	1·4	4·8	6·2	1·4	0·31
NH_2^-	2·1	1·4	4·9	6·3	1·5	0·33

The only negative-ion product observed in each of the reactions in the Table was Cl^-. Although the neutral products were not identified, the reaction channels should all correspond to nucleophilic substitution. Consideration of the energetics indicate that all other conceivable channels for the reactions of H^- and F^- with CH_3Cl are endothermic and will not proceed spontaneously at 300 K. One additional channel is exothermic, although considerably less exothermic than the nucleophilic substitution channel, for the reactions of both NH_2^- and OH^- with CH_3Cl, namely reactions (3) and (4). However, in both instances much

$$NH_2^- + CH_3Cl \rightarrow HCN + 2H_2 + Cl^- \quad (3)$$

$$OH^- + CH_3Cl \rightarrow CH_2O + H_2 + Cl^- \quad (4)$$

bond breaking and bond formation is involved. Such channels are not likely to compete effectively with mechanistically simpler channels.[5]

The results in the Table clearly establish that the nucleophiles H^-, F^-, OH^-, and NH_2^- all react extremely rapidly with CH_3Cl in the gas phase at 300 K, $k \geqslant 1 \cdot 8 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1} ($\geqslant 1 \cdot 1 \times 10^{12}$ l mol^{-1} s^{-1}). In all cases, nearly every collision leads to nucleophilic substitution; the probabilities for nucleophilic substitution are: $0 \cdot 5 > P(H^-) > 0 \cdot 1$, $1 > P(F^-) > 0 \cdot 3$, $1 > P(OH^-) > 0 \cdot 3$, and $1 > P(NH_2^-) > 0 \cdot 3$. Furthermore, since the nucleophilic substitution reactions in the gas phase proceed in the absence of solvent molecules and gegenions, these reaction probabilities identify intrinsic reactivity patterns. The results of this study, therefore, indicate that the intrinsic nucleophilic reactivities (based on the reaction probability, $P_{T,L}$, at 300 K) of H^-, F^-, OH^-, and NH_2^- towards CH_3Cl are all equal within the experimental errors and the uncertainties in the calculation of the theoretical collision rate constants.

In solution studies the actual rate constant for reaction, k_{exp}, is taken to be a measure of the nucleophilic reactivity of X^- and correlations are often made with the basicity of X^- in solution. The present results lead to an order of gas-phase nucleophilic reactivity based on k_{exp} of $H^- > NH_2^- \simeq OH^- \simeq F^-$. Earlier studies[3]† have revealed a gas-phase basicity order of $NH_2^- > H^- > OH^- > F^-$. Evidently, in the gas phase, the kinetic behaviour of X^- in reaction with CH_3Cl does not correlate with the basicity of X^-. For example, H^-, which is a stronger nucleophile than NH_2^- in the gas phase, has a lower gas-phase basicity than NH_2^-.

As was apparent from earlier gas-phase basicity studies,[6] solvation effects again seem to prevail over intrinsic reactivity patterns when the transition is made to solution. For instance, whereas the nucleophilicities of the fluoride and hydroxide ions are equal in the gas phase, the fluoride ion is about 25 times less reactive than the hydroxide ion in nucleophilic substitution of methyl chloride in aqueous solutions:[7] for OH^-, $k_{exp} = 1 \cdot 7 \times 10^{-5}$ l mol^{-1} s^{-1} and for F^-, $k_{exp} = 6 \cdot 5 \times 10^{-7}$ l mol^{-1} s^{-1}.

Work is now in progress to determine the gas-phase reactivity of these nucleophiles towards other substrates.

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† The reaction $OH^- + HF \rightarrow F^- + H_2O$ is exothermic by *ca.* 24 kcal mol^{-1}.

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