Table I. Rate Constants (in units of 10^{-9} cm³ molecule⁻¹ sec⁻¹) and Activation Energies for Exothermic Nucleophilic Displacement with CH₃Cl in the Gas Phase at 296°K

Nucleophile	$-\Delta H°_{298}$ kcal mol⁻¹	k_{exptl}[a]	k_{ADO}[b]	k_{exptl}/k_{ADO}	E_a,[c] kcal/mol⁻¹
H⁻	86 ± 1	2.5[d]	8.5	0.29	0.7 ± 0.2
NH₂⁻	66.1 ± 0.2	2.1[d]	2.4	0.88	0.1 ± 0.2
OH⁻	49 ± 1	1.9[d]	2.4	0.79	0.1 ± 0.2
F⁻	29 ± 8	1.8[d]	2.3	0.78	0.1 ± 0.2
C₂H⁻	62 ± 2	1.2	2.1	0.57	0.3 ± 0.1
CN⁻	30 ± 4 (15 ± 4)[e]	≤0.0004	2.0	≤0.0002	≥5

[a] Unless indicated otherwise, the accuracy is ±20%. [b] Calculated using the average dipole orientation theory, ref 6. The adjustable parameter, C = 0.21. [c] See footnote 8. The uncertainty in E_a reflects only the uncertainty in k_{exptl}. [d] Reference 5. Accuracy is ±30%. [e] Production of isocyanomethane.

Table II. Rate Constants (in units of 10^{-9} cm³ molecule⁻¹ sec⁻¹) and Activation Energies for Exothermic Nucleophilic Displacement Reactions with CH₃F in the Gas Phase at 296°K

Nucleophile	$-\Delta H°_{298}$, kcal mol⁻¹	k_{exptl}[a]	k_{ADO}[b]	k_{exptl}/k_{ADO}	E_a,[c] kcal mol⁻¹
H⁻	57 ± 8	0.015	7.6	0.0020	3.6 ± 0.1
NH₂⁻	37 ± 9	0.017	2.3	0.0074	2.9 ± 0.1
OH⁻	20 ± 8	0.024	2.2	0.011	2.6 ± 0.1
C₂H⁻	33 ± 9	≤0.0003	2.0	≤0.00015	≥5
CN⁻	1 ± 11 (−14 ± 11)[d]	≤0.0003	2.0	≤0.00015	≥5

[a] The accuracy is ±20%. [b] Calculated using the average dipole orientation theory, ref 6. The adjustable parameter C = 0.23. [c] See footnote 8. The uncertainty in E_a reflects only the uncertainty in k_{exptl}. [d] Production of isocyanomethane.

from the expected impurities in the reagent gases (CH₃Cl, SiF₄, and CH₃OCH₃ in the case of CH₃F and H₂O in the case of CH₃Cl) have been found to be negligible.

The reactions of H⁻, NH₂⁻, OH⁻, F⁻, and C₂H⁻ with CH₃Cl were all observed to proceed rapidly at essentially the theoretical capture rate[6,7] and consequently in the absence of any significant activation energy.[8] In contrast, the reaction with CN⁻ was observed to be surprisingly slow proceeding with a rate constant k_{exptl} ≲ $0.0002k_{capture}$. The formation of Cl⁻ is exothermic[9] in each case and was the only negative ion product observed. Although the neutral products were not identified, considerations of the energetics and mechanisms suggest that all the observed reactions correspond to nucleophilic displacement.[5]

(6) T. Su and M. T. Bowers, J. Chem. Phys., 58, 3027 (1973) and Int. J. Mass. Specrom. Ion Phys., 12, 347 (1973).

(7) The polarizabilities and permanent dipole moments of CH₃F and CH₃Cl were taken from E. W. Rothe and R. B. Bernstein, J. Chem. Phys., 31, 1619 (1959).

(8) The activation energy, E_a, is calculated from the relationship k_{exptl} = $k_{ADO}e^{-E_a/RT}$. It is assumed that the reaction would proceed at the capture rate in the absence of an activation energy. The neglect of steric effects in this simple model is justified for this series of reactions (except in the special case of the CN⁻ reactions) to the extent that most of the CH₃Cl reactions proceed at the capture rate, indicating the absence of such effects. However, since there are reasons other than an energy of activation which can cause an observed rate constant to be lower than the capture rate constant, the value of E_a determined from this model must be rigorously regarded as a maximum.

(9) The heats of formation of the neutral species were taken from J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, "Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Ions," NSRD-NBS 26, U. S. Government Printing Office, Washington, D. C., 1969. The heats of formation of H⁻, OH⁻, F⁻, and CN⁻ were taken from JANAF Thermochemical Tables, 2nd ed, Nat. Stand. Ref. Data Ser., Nat. Bur. Stand., No. 37 (1971). $\Delta H_f°_{298}$ (NH₂⁻) was taken from D. K. Bohme, R. S. Hemsworth, and H. W. Rundle, J. Chem. Phys., 59, 77 (1973) and $\Delta H_f°_{198}$ (C₂H⁻) = 71 ± 1 kcal/mol, unpublished results from this laboratory.

The reactions of H⁻, NH₂⁻, OH⁻, and C₂H⁻ with CH₃F were observed to be at least 100 times slower than the corresponding reactions with CH₃Cl. Indeed, for both the reactions of C₂H⁻ and CN⁻ the upper limit to k_{exptl} was measured to be 3 × 10^{-13} cm³ molecule⁻¹ sec⁻¹ which corresponds to an activation energy of 5 kcal mol⁻¹.[8] F⁻ was the only product observed in all of these reactions with CH₃F which again should correspond to nucleophilic displacement.[10]

The recent calculations of Dedieu and Veillard[1] and Bader, et al.,[2] allow a direct comparison with the experimental results for reactions 1 and 2. The low reactivity of CN⁻ toward CH₃F was predicted by Bader, et al.,[2] whose calculations yield an overall activation energy of 22 kcal mol⁻¹ for reaction 2. Such a large activation energy is not accessible to our room temperature measurements but the limit E_a ≳ 5 kcal mol⁻¹ for reaction 2 implied by our present result is consistent with the theoretical prediction. However, the large uncertainty in $\Delta H°_{298}$ for reaction 2 does not rule out the possibility that the reaction is in fact endothermic by more than 5 kcal mol⁻¹. This is certainly the case if the CN⁻ ion is constrained by the electrostatic interaction during the collision to produce isocyanomethane. The accord between theory and experiment is much more pronounced for reaction 1 for which the ab initio LCAO–MO–SCF calculations of Dedieu and Veillard[1] predict a barrier of 3.8 cal mol⁻¹ which is in remarkable agreement with the experimental value of 3.6 kcal mol⁻¹. Although this agreement may be fortuitous, the accord between theory and experiment generally for both SN2 reactions 1 and 2 is certainly very satisfying and should further encourage theoretical developments for reactions of this type. In particular, the origin of the energy barriers for the reaction of CN⁻ with CH₃Cl and of C₂H⁻ with CH₃F is especially intriguing.

(10) All other channels for the reactions of H⁻ and CN⁻ with CH₃F leading to the formation of F⁻ are endothermic. The presence of alternate channels for the C₂H⁻ reaction (several isomeric forms of CH₃C₂H are energetically accessible) would increase the lower limit to the activation energy deduced for the SN2 reaction. Both the NH₂⁻ and OH⁻ reactions have other channels leading to the formation of F⁻ which, within the uncertainty of $\Delta H°_{298}$, may be slightly exothermic but, as in the case of the CH₃Cl reactions,[5] are not likely to compete with the mechanistically simpler SN2 reaction.

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Detection of Neutral Products in Gas-Phase, Ion–Molecule Reactions

Sir:

Studies of ion–molecule reactions are relatively constrained, since, in contrast to most chemical investigations, the identity of only one of the products is usually determined.[1] In a majority of ion–molecule studies,

(1) In some cases, neutral products may be inferred on the basis of product ion identity and energetics. For example, see J. L. Beauchamp, Annu. Rev. Phys. Chem., 22, 527 (1971).

experimental technique focuses on ion (reactant and product) identities and relative concentrations as a function of experimental variables (pressure, time, ionization energy, etc.),[2] rather than on the elucidation of neutral products.[3]

We report a technique applicable to the identification of neutral products derived from ion–molecule reactions. This neutral detection technique entails the continuous initiation of ion–molecule reactions in a static system with periodic removal of ionic products, via attraction to plates and walls of the detection region. Then after an appropriate time, the neutral components of the reaction mixture are probed by mass spectrometric techniques. Both phases of this experimental procedure are carried out in a pulsed ion cyclotron resonance spectrometer.[4] The present apparatus permits creation of a static system in the analyzer region into which the desired reaction gases can be placed and in which pressures are monitored with a MKS Baratron capacitance manometer. Reaction in this gaseous mixture is initiated by switching on the electron beam to generate the appropriate reactant ion. Utilizing the trapped ion icr technique, the ion–molecule reaction of interest (e.g., $Cl^- + CH_3Br \rightarrow CH_3Cl + Br^-$) is followed by the disappearance of reactant ion (Cl^-) and the appearance of product ion (Br^-).[4,5] After a predetermined length of time,[6] the detection system (icr cell) is switched from negative ion to positive ion mode, and the icr performs as an analytical mass spectrometer to identify the species present in the reaction mixture. In favorable cases, the expected neutral product(s) will have unique positive ion peaks unobscured by the large excess of reactant gases. As might be inferred from the above description, an intricate set of control experiments is required in order to isolate the products

Figure 1. Sterechemical investigation of icn–molecule displacement reactions on cis- and trans-4-bromocyclohexanols. Solid lines represent reactions occurring with inversion, broken lines represent reactions occurring with retention at the carbon containing the halogen.

from the ion–molecule reaction as opposed to pyrolytic or radical reaction products.[7] Also, prepared mixtures of expected reactant–product gases have been run to confirm the detection limits of this technique.

In the study of nucleophilic displacement reactions of the form $X^- + RY \rightarrow Y^- + RX$, we have confirmed that the neutral product is indeed RX. Specifically, for the systems $F^- + CH_3Cl$, $F^- + CH_3Br$, and $Cl^- + CH_3Br$, the products CH_3F and CH_3Cl have unique parent–ion as well as product–ion peaks in the positive ion mass spectra of their representative reaction mixtures.[8,9] These are the neutral products expected, since they constitute the sole exothermic reaction channel for the respective product ion which is observed.[10]

Recognizing the utility of this procedure in identifying the neutral products of substitution reactions, an experiment was carried out to probe the mechanism of nucleophilic displacement reactions by examination of the stereochemistry at the reactive center.[11] Work on stereochemical determinations has recently been of general interest in mass spectrometry;[12] loss of H_2O from cyclohexanols has been investigated in detail and shown to be largely a cis 1,4-elimination process.[13] Detection of the neutrals resulting from the negative-ion displacement reaction of Cl^- on the cis- and trans-4-bromocyclohexanols (A and B in Figure 1) should reflect the stereochemistry at the halogen-containing

(2) J. E. Parker and R. S. Lehrle, Int. J. Mass Spectrom. Ion Phys., 7, 421 (1971); E. E. Ferguson, Advan. Electron. Electron Phys., 24 (1968); J. L. Franklin, Ed., "Ion Molecule Reactions," Plenum Press, New York, N. Y., 1972.

(3) This investigation is not the first attempt at the detection of neutral products of ion–molecule reactions. C. E. Melton, J. Chem. Phys., 45, 4414 (1966) and Int. J. Mass Spectrom. Ion Phys., 1, 353 (1968), has outlined modifications of a research mass spectrometer which allowed direct determination of ion–molecule neutral products (although the author noted the difficulty investigating negative ion systems). Also, K. O. Dyson, "Dynamic Mass Spectrometry, J. Price and J. Williams, Ed., Hayden & Son, London, 1970 and J. M. Lavigne, et al., Int. J. Mass Spectrom. Ion Phys., 6, 263 (1971), have presented techniques for determining neutral fragments and products. L. W. Sieck, et al., J. Chem. Phys., 53, 3336 (1970); ibid., 54, 3411 (1971), have used photoionization mass spectrometry and end product analysis of photolytic studies to delineate ion–molecule reactions by identification of ionic and neutral products. P. Ausloos, Progr. React. Kinet., 5, 113 (1970), gives a cogent justification for neutral analysis as well as a review of much of the area, particularly as applied to radiolysis chemistry.

(4) R. T. McIver, Jr., and R. C. Dunbar, Int. J. Mass. Spectrom. Ion Phys., 7, 471 (1971).

(5) The experimental system consists of an ion trap (cell) situated in a reaction chamber. The ion trap construction allows rapid equilibration of neutral gases between the ion trap and surrounding chamber, while retaining ions formed within the trap (likewise preventing entrance of any ions formed external to the trap). Although the pulsed icr mode limits ion production to a short period of each pulse sequence inside the ion trap,[4] ions are continuously generated outside the ion trap by electron capture from the filament (positioned external to an ion trap and giving continuous emission of electrons). These ions have the same identity as those trapped and detected in the icr cell and will have a probability of undergoing ion–molecule reactions before impinging and being neutralized at the walls of the reaction chamber. Therefore, neutral products are formed by many more ions than those trapped in the icr cell, consequently reducing the total reaction time by a factor of 10–15.

(6) Having previously determined the rate constants for the reaction and approximating the total ion production,[4] a reaction period corresponding to production of detectable quantity of neutral product may be calculated (usually 2–20 min).
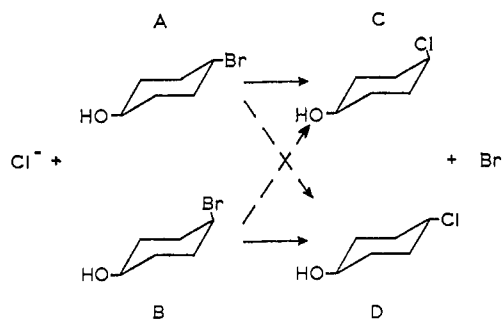
(7) C. A. Lieder and J. I. Brauman, submitted for publication.

(8) J. I. Brauman, W. N. Olmstead, and C. A. Lieder, J. Amer. Chem. Soc., 96, 4030 (1974).

(9) Neutral detection information can be attained from both the presence of m/e peaks and their concentration as a function of time.[4] For alkyl halide peaks, see J. L. Beauchamp, D. Holtz, S. D. Woodgate, and S. L. Patt, J. Amer. Chem. Soc., 94, 2798 (1972).

(10) J. L. Franklin, et al., "Ionization Potentials, Appearance Potentials, and Heats of Formation of Positive Ions," NSRDS-NBS 26 U. S. Government Printing Office, Washington, D. C., 1969, and D. R. Stull, E. F. Westrum, Jr., and G. C. Sinke, "The Chemical Thermodynamics of Organic Compounds," Wiley, New York, N. Y., 1969.

(11) S. Meyerson and A. W. Westhamp, Org. Mass Spectrom., 1, 659 (1968), and references therein.

(12) F. Cacace and M. Speranza, J. Amer. Chem. Soc., 94, 4447 (1972), have investigated the neutral products in a gas phase ion–molecule reaction involving the electrophilic attack of RT^+ on saturated carbon. For R = He, CH_4, and C_2H_5, predominant retention of configuration was found presumably proceeding through a three-center two-electron mechanism (commonly proposed for CH_5^+ structure, see G. A. Olah, et al., J. Amer. Chem. Soc., 93, 1251 (1971)). Although a powerful technique, this method may be limited by the existence of radioisotopes/radiolabel for the electrophile or nucleophile under study.

(13) M. M. Green, R. J. Cook, J. M. Schwab, and R. B. Roy, J. Amer. Chem. Soc., 92, 3076 (1970); M. M. Green and R. B. Roy, ibid., 92, 6368 (1970), and references therein. See also J. K. MacLeod and R. J. Wells, ibid., 95, 2387 (1973).

carbon.[14] Experiments and standardization on the compounds[15] in Figure 1 displayed the following results: A + Cl⁻ resulted in a percentage production of C (the "inverted" product) from A of 91 ± 14 (eight experimental runs); B + Cl⁻ resulted in a percentage production of D (the "inverted" product from B) of 86 ± 19 (seven experimental runs).[16] Therefore neutral detection of the distinguishable isomeric products indicates a nucleophilic displacement mechanism proceeding with predominant inversion of stereochemistry. Such a reaction mechanism corresponds to Walden inversion and backside attack[17] for the particular ion-molecule reactions depicted in Figure 1.

Neutral detection has allowed us to identify the products arising from ion–molecule reactions and has demonstrated the stereochemical pathway for a negative ion displacement reaction. With the increasing complexity of ion–molecule systems related to solution processes, mere identification of ionic species will often be inadequate to describe the total chemical reaction, thus the importance of neutral detection techniques. We suspect that icr detection will be but one of many methods utilized in the determination of mechanistic information retained in the neutral products of ion-molecule reactions.

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(14) The chloride-containing neutral product gives rise to a ratio of (parent − H₂O)⁺/(parent)⁺ positive mass peaks characteristic of cis or trans 1,4-stereochemistry.

(15) D. S. Noyce, B. N. Bastian, and R. S. Monson, *Tetrahedron Lett.*, 863 (1962); D. S. Noyce, B. N. Bastian, P. T. S. Lau, R. S. Monson, and B. Weinstein, *J. Org. Chem.* **34**, 1247 (1969).

(16) The predominant cis 1,4-elimination produces differences in the mass spectrum of the cis- and trans-4-chlorocyclohexanols which allows identification of the ion–molecule neutral product by monitoring the ratio of the (parent) ion peak/(parent − H₂O) ion peak, characteristic for cis Cl (C) and trans Cl (D) in Figure 1.

(17) J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill, New York, N. Y., 1962, Chapter 6.

(18) National Science Foundation Predoctoral Fellow.
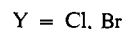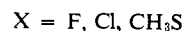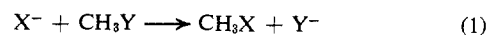
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Gas-Phase Nucleophilic Displacement Reactions

Sir:

Nucleophilic displacement is among the most widely studied of all chemical reactions. Structural changes[1] in nucleophile, leaving group, and substrate, as well as solvent effects[2] have been investigated extensively. Recent evidence, however, suggests that the medium can play a determining role in some ionic reactions[3] and thus leaves the analysis of other solution reactions in question. We report here the rates of some nucleo-

(1) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962.

(2) A. J. Parker, *Chem. Rev.*, **69**, 1 (1969).

(3) For example, see J. L. Beauchamp, *Annu. Rev. Phys. Chem.*, **22**, 527 (1971), for a recent discussion.

philic displacement reactions in the gas phase, eq 1.[4]

$$X^- + CH_3Y \longrightarrow CH_3X + Y^- \qquad (1)$$

$$X = F, Cl, CH_3S$$

$$Y = Cl, Br$$

The results show that nucleophilicity and leaving group ability cannot be treated as intrinsic properties. Indeed, nucleophilicity appears to depend on the specific substrate and leaving group ability to depend on the nucleophile.

Our experiments were conducted with the trapped ion, pulsed icr technique,[5] which permits observation of both reactant and product ions as a function of time.[6] Exclusive detection of a particular reaction channel was facilitated by initially ejecting undesired ions with one or two irradiating frequencies.[7] The anions utilized in this study were F⁻ from NF₃, Cl⁻ from CHCl₃, and CH₃S⁻ from CH₃SSCH₃. (CH₂S⁻ was eliminated by ion ejection.)

For each reaction, both reactant loss and product appearance were followed as a function of time. In all cases the total collision rate constant was also measured by the phase coherence method.[8a]

We believe that the reactions studied, eq 1, are nucleophilic displacement reactions for the following reasons. (a) They are clearly first order each in nucleophile and substrate. (b) In almost all cases, eq 1 is the only reasonable exothermic channel.[9] (c) When 1-chloro- and 1-bromoadamantane were used as substrates, they did not react. (d) Neutral detection in all cases examined showed only the expected product.[10] (e) In the 4-bromocyclohexanol system, neutral detection showed products with inversion of configuration.[10] Consequently, we believe that this gas-phase reaction corresponds closely to the analogous SN2 reaction in solution.

The results are shown in Table I. The rate differences are substantially larger than any differences in total collision rate constant (k_{coll} (exptl)) as measured independently by phase coherence decay studies.[8a] Also included in Table I are the rate constants calculated from the Gioumousis–Stevenson theory[8b] and from the modified ion–dipole theory of Su and Bowers.[8c] The rate constants observed do not appear to be well correlated with any simple property, including the exothermicity. Thus, when F⁻ reacts with a 1:1 mixture of methyl chloride and methyl bromide, Cl⁻ is produced

(4) Previous reports of similar reactions have appeared: (a) L. B, Young, E. Lee-Ruff, and D. K. Bohme, *J. Chem. Soc., Chem. Commun.*, 35 (1973); (b) D. K. Bohme and L. B. Young, *J. Amer. Chem. Soc.*, **92**, 7354 (1970).

(5) R. T. McIver, Jr., and R. C. Dunbar, *Int. J. Mass Spectrom. Ion Phys.*, **7**, 471 (1971).

(6) Pressures were measured with an MKS Baratron, and rate constants were calculated for the involved processes.

(7) For a similar experimental approach see J. I. Brauman, C. A. Lieder, and M. J. White, *J. Amer. Chem. Soc.*, **95**, 927 (1973).

(8) (a) C. A. Lieder, R. W. Wien, and R. T. McIver, Jr., *J. Chem. Phys.*, **56**, 5184 (1972); (b) G. Gioumousis and D. P. Stevenson, *J. Chem. Phys.*, **29**, 294 (1958); (c) T. Su and M. T. Bowers, *J. Chem. Phys.*, **58**, 3027 (1973); *Int. J. Mass Spectrom. Ion Phys.*, **12**, 347 (1973).

(9) Thermochemical data were obtained from D. R. Stull, E. F. Westrum, Jr., and G. C. Sinke, "The Chemical Thermodynamics of Organic Compounds," Wiley, New York, N. Y., 1969; S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968; J. L. Franklin, *et al.*, "Ionization Potentials, Appearance Potentials, and Heats of Formation of Positive Ions," NSRDS-NBS 26 U. S. Government Printing Office, Washington D. C., 1969.

(10) C. A. Lieder and J. I. Brauman, *J. Amer. Chem. Soc.*, **96**, 4028 (1974).