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Formation and Reactions of Negative Ions Relevant to Chemical Ionization Mass Spectrometry. I. CI Mass Spectra of Organic Compounds Produced by F^- Reactions

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A systematic study of the negative-ion chemical ionization mass spectra produced by the reaction of F^- with a wide variety of organic compounds has been accomplished. A time-of-flight mass spectrometer fitted with a modified high pressure ion source was employed for these experiments. The F^- reagent ion was generated from CF_3H or NF_3, typically at an ion source pressure of 100 μm. In pure NF_3, F^- is the major ion formed and constitutes more than 90% of the total ion intensity. While F^- is also the major primary ion formed in pure CF_3H, it undergoes rapid ion-molecule reactions at elevated source pressures, yielding $(HF)_nF^-$ (n = 1–3) ions, which makes CF_3H less suitable as a chemical ionization reagent gas. Among the organic compounds investigated were carboxylic acids, ketones, aldehydes, esters, alcohols, phenols, halides, nitriles, nitrobenzene, ethers, amines and hydrocarbons. An intense $(M - 1)^-$ ion was observed in the F^- chemical ionization mass spectra of carboxylic acids, ketones, aldehydes and phenols. Alcohols yield only $(M + F)^-$ ions upon reaction with F^-. A weaker $(M + F)^-$ ion was also detected in the F^- chemical ionization spectra of carboxylic acids, aldehydes, ketones and nitriles. The F^- chemical ionization mass spectra of esters, halides, nitriles, nitrobenzene and ethers are characterized primarily by the ions, $RCOO^-$, X^-, CN^-, NO_2^-, and OR^-, respectively. In addition, esters show a very weak $(M - 1)^-$ ion (except formates). In the F^- chemical ionization spectra of some aliphatic alkanes and o-xylene, a very weak $(M + F)^-$ ion was observed. Amines and aliphatic alkenes exhibit only insignificant fragment ions under similar conditions, while aromatic hydrocarbons, such as benzene and toluene are not reactive at all with the F^- ion. The mechanisms of the various reactions mentioned are discussed, and several experimental complications are noted. In still other studies, the effects of varying several experimental parameters, including source pressure, relative proportions of the reagent and analyte, and other ion source parameters, on the observed chemical ionization mass spectra were also investigated. In a mixture of NF_3 and n-butanol, for example, the ratio of the intensities of the ions characteristic of the alcohol to that of the $(HF)_nF^-$ ion was found to decrease with increasing sample pressure, with increasing NF_3 pressure, and with increasing electron energy. No significant effects on the spectra were observed to result from variation of the source repeller field or the source temperature. The addition of argon to the source as a potential moderator did not alter the F^- chemical ionization spectrum significantly, but the use of oxygen appears to inhibit formation of the $(HF)_nF^-$ cluster ion. The advantages of using F^- as a chemical ionization reagent are discussed, and comparisons are made with other reagent ions.

Introduction

Interest in the development and applications of negative-ion chemical ionization (NICI) mass spectrometry has expanded rapidly in the past ten years, as clearly indicated by the attendance at the present and other recent symposia (*1*) con-

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cerned with this topic. The number of publications appearing in the chemical literature which deal with NICI mass spectrometry has also increased significantly during this time period. Several current comprehensive reviews (*2-4*) have surveyed these publications. In spite of the increasing activity in this field of research, however, relatively few negative ions have yet been investigated as chemical ionization reagents. This is illustrated by the listing shown in Table 1. This situation is due to the lack of established methods for generating usable quantities of many types of negative ions, and to the uncertainties which currently prevail in the understanding of gas phase negative ion chemistry.

In the present paper, we report the results of a systematic study of the reactions of the fluoride negative ion, F^-, with a variety of organic molecules, which are representative of different functional group classes. The F^- ion was selected for investigation as a NICI reagent ion for several reasons. First, it was expected that F^- could be readily produced in large abundance by electron impact on molecules such as CH_3F and NF_3. The appearance potential of F^- from NF_3 is very near 0 eV (*11*), and previous experiments in our laboratory have demonstrated that the rate coefficient for attachment of near-thermal electrons to NF_3, yielding F^-, was very large (*12*). Also, F^- is the only ionic product observed from low energy electron attachment to NF_3. Secondly, the proton affinity of F^- is relatively high, 1548 KJ/mole, which is just between the proton affinities of OH^-, (1632 KJ/mole) and Cl^- (1393 KJ/mole) (*2*). The anionic nucleophilicity of F^- also lies between that of OH^- and Cl^-, which have previously been utilized in NICI studies (see Table 1). These considerations suggest that F^- should be reactive with a number of organic molecules. Still another feature of F^- as a NICI reagent ion is that fluorine is monoisotopic, so that if F^- associates with a particular molecule, only one $(M + 19)^-$ product ion will be observed, since no isotope peaks can be formed. Thus the F^- NICI mass spectra should be simpler and more readily interpreted than those resulting from reactions of other halide negative ions.

The experimental procedures employed and the results obtained in this investigation are described in the following sections.

Experimental

The instrument utilized for the experiments reported herein is a Bendix Model 12-101 time-of-flight mass spectrometer equipped with a 100 cm. drift tube. The mass spectrometer is fitted with a specially designed, high pressure ion source, which was developed by Chang and Tiernan (*13*). Figure 1 shows a schematic diagram of the ion source and the focusing lens system. The source, which was constructed from a solid copper block, is actually an open cylinder with an inside diameter of 1.91 cm and a length of 1 cm. A gas inlet orifice, 0.64 cm in diameter, was cut into the side of the block. An electron entrance plate (EEP) and an ion exit plate (IEP) are utilized to seal the top and the bottom of the source cylinder. Both plates were identically manufactured from stainless steel, and are cone-shaped, with a 0.05 cm diameter orifice at the cone apex. A −6V dc potential is applied continuously to the electron entrance plate as a repeller potential. This facilitates removal of ions from the source. The ion exit plate is maintained at ground potential. Both plates can be used to monitor the electron beam current if desired, by suitable connections. A coiled tungsten wire filament is located about 1 cm from the electron entrance plate. In order to collimate the electron beam, a beam-focusing cylinder, which was constructed from 90% transparent rhenium mesh screen, is used to surround the filament. Use of the transparent wire mesh permits efficient pumping of neutral gas from the filament region. This focusing cylinder and one end of the fila-

Table 1. Negative ions used as chemical ionization mass spectrometry reagents in studies reported to date.

Reagent ion	Source gases	Type of ion source used	Typical total source pressure, torr	Reference
H^-	H_2	Electron impact	1	*(2)*
O^-	N_2O/N_2	Electron impact	0.3-0.5	*(5)*
O_2^-	$N_2O/N_2/O_2$	Electron impact	0.3-0.5	*(2)*
O_2^-	O_2, H_2/O_2	Townsend discharge	1	*(6,7)*
O_2^-	Air	Atmosphere pressure ionization	Atmospheric pressure	*(8)*
Cl^-	CH_2Cl_2	Electron impact	1	*(9)*
OH^-	N_2O/H_2, N_2O/CH_4	Electron impact	1-3	*(10)*
CH_3O^-	CH_3ONO/CH_4	Electron impact	1	*(7)*

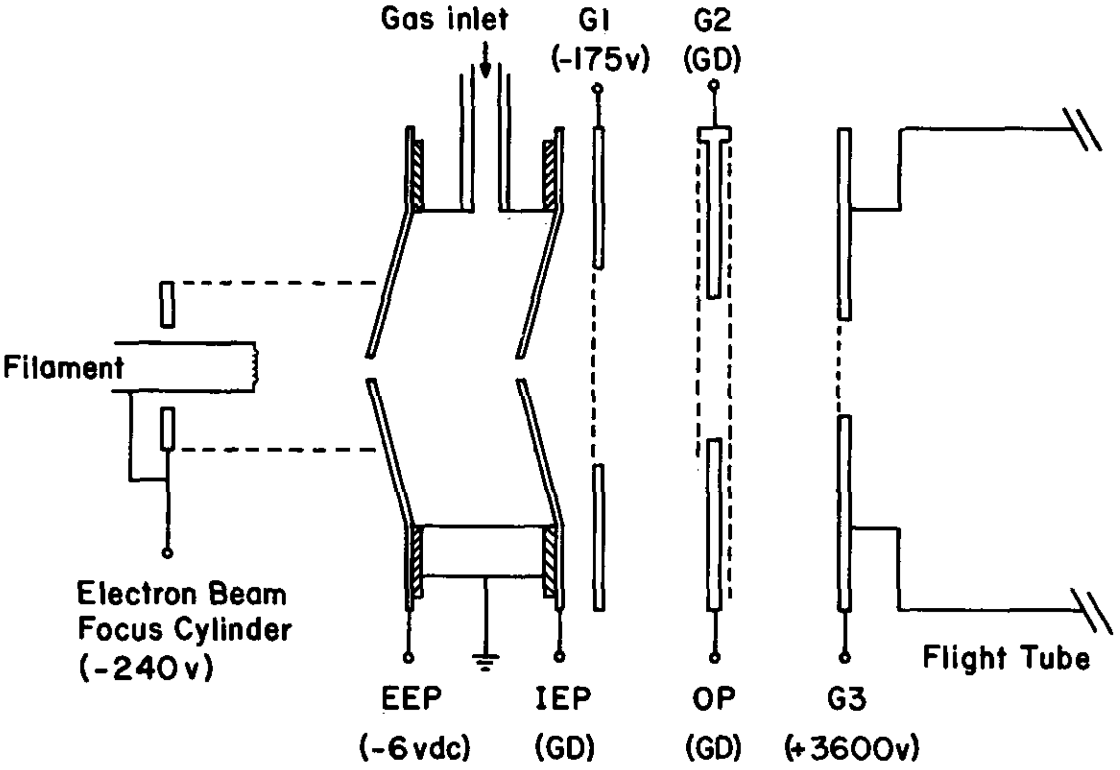


FIGURE 1. Schematic diagram of high pressure ion source developed for a time-of-flight mass spectrometer.

ment are maintained at a negative potential of −240 V.

The filament is mounted in such a way that the electron beam path coincides with the ion axis. This arrangement differs from that used in most conventional ion sources, in which, the electron beam typically enters the side of the source chamber at an angle of 90° to the direction of ion extraction. With the latter configuration, ions formed in the region just above the ion exit aperture are more likely to be extracted and detected. At lower source pressure this conventional configuration functions well, since ions are formed uniformly along the electron path. However, as the source pressure is increased, the penetrating power of the electron beam decreases rapidly. Thus, only a few ions are formed in the region near the exit aperture. With our new source design, all primary ions are formed along the electron beam path (which is coaxial with the ion extraction path) and are therefore produced in the region directly adjacent to the ion exit aperture. At higher pressures in the source, these primary ions then react with other molecules in the same region to form the secondary product ions. As noted earlier, a repeller field is applied to drive ions thus formed through the ion exit aperture, which increases the number of ions reaching the detector on any given pulse cycle.

The ion source of the mass spectrometer is housed inside a T-shaped stainless tube which was fabricated for this purpose and which is connected directly to the drift tube of the mass spectrometer. This housing incorporates a high speed pumping port, to which a 4-in. oil diffusion pumping system is directly attached via a flexible 10-cm stainless steel bellows. For the source exit aperture currently used, this is adequate to maintain a pressure differential of about 1000:1 between the source interior and the surrounding region. This differential pumping reduces collisions between ions and neutrals outside the source region to a significant extent. The drift tube region is pumped by the standard pumping system which consists of a 4-in. mercury diffusion pump, a Bendix combined liquid nitrogen trap and Freon-cooled baffle, and a Welch forepump. The pressure is monitored by a Philips-type cold-cathode ionization gauge (Veeco) which measures pressures as low as 2×10^{-6} mm Hg.

The sample inlet system is an all-metal dual reservoir system, containing two 1-liter stainless steel expansion tanks. Each reservoir is connected to the ion source via a variable gas leak, in one case, a Granville-Phillips Series 213 motor-driven variable leak, and in the other, a Granville-Phillips Series 203 manually adjusted leak. Additions to the sample inlet system were constructed recently to permit introduction of multi-component reagent mixtures and gas samples, and to allow coupling of a gas chromatograph (GC) to the mass spectrometer. These additional inlet sections are also controlled by Granville-Phillips Series 203 manually adjusted leaks, and permit introduction of condensed phase samples from an inlet tube. The latter is a U-shaped 1/4-in. ID glass tube with one end sealed by a septum, and the other end connected to a Whitey SS-2RS4 metric valve, which controls the molecular flow of the sample vapor. This tube was installed near the source-housing flange in order to reduce condensation in the inlet to a minimum. A MKS Baratron pressure sensor head (type 77-H-1) is attached to the source housing to measure the ion source pressure directly. All tubing used for interconnections in this system is 1.27 cm diameter stainless steel tubing. Swagelok tube fittings are used for all couplings. A variety of values are also used in the system. The sample inlet system and the pressure reference side of the MKS sensor are pumped by means of a CVC type PMCS-2B diffusion pump, backed by a Welch 1400B forepump.

A Hewlett-Packard 2116C computer with 16-bit word length and 24K core memory was used for data acquisition. Since the analog electrometer used for the recording of negative ions is not electrically isolated, the signals from the multiplier cannot be directly input into the computer. Instead, the output signal of the amplifier is further amplified by a Keithley Instrument Type 109 pulse amplifier with 50 ohms input resistance and 20 DB gain. The amplified signal is then transmitted to a scan converter (Pacific Instrument), which is built into the oscilloscope. The computer directly accepts the signal from the scan converter. This procedure introduces some noise, and reduces detection sensitivity considerably, but permits direct computer acquisition of the data. Four channels are used to establish communication between the computer and the TOF mass spectrometer. The first channel transmits a signal from the Y axis of the oscilloscope to the computer for the ion intensity. The second channel transmits a signal from the X axis of the oscilloscope to the computer for a ramp voltage. The third channel transmits the junction voltage of a thermocouple used for temperature measurement. The fourth channel carries a relay message to the computer. These analog signals are converted into digital signals by the A/D converter of the computer. The digital signals are then processed by the computer using previously designed software developed in our laboratory.

Negative ion mass spectra were recorded with the TOF mass spectrometer, normally under the following conditions: accelerating voltage, 3.6 kV; primary electron beam voltage, 240 eV; ion source envelope pressure, approximately 5×10^{-6} mm Hg; source temperature, 70-120°C; and the emission current (which is the current measured at the electron entrance plate) was adjusted to obtain maximum ion intensity. Usually, the latter was varied from several tenths milliampere to about 10 mA. The source pressure was monitored by an MKS Baratron Type 77-H-1 pressure sensor head. The sample pressure was maintained at a constant value, usually between 0.5 and 10 μm and the total pressure was maintained at 100 μm (with the reagent gas added).

Fluoroform used in these studies was obtained from Matheson Gas Products, East Rutherford, N.J., and was specified to be approximately 99.9% pure. NF_3 was obtained from Air Products and Chemicals Inc., Allentown, Pa., with a reported purity of 99.92% minimum. All organic compounds studied were obtained from commercial suppliers and were used without further purification.

Results and Discussion

Formation of the Primary F^- Ion Reactant with Fluoroform as the Reagent Gas

Spectrum of Pure CHF_3 Under NICI Conditions. In principle, the F^- ion can be produced from several gaseous fluoride compounds by electron impact. The appearance potential of F^- from fluoroform (CHF_3) is about 9.3 eV (*11*). Thus initially the latter molecule was selected as the reactant source molecule. The NICI mass spectrum of CHF_3 at a pressure of 0.1 torr and a temperature of 100°C is shown in Table 2. It can be seen that electron impact on CHF_3 at relatively high source pressure yields very small amounts of F^-, and large abundances of various cluster ions. Apparently this is due to the rapid association reaction of the F^- ion with one or more HF molecules, to form cluster ions of the type, $[(HF)_nF]^-$, where n = 1-3 (*14*). There are two possible sources for the HF molecules. One possibility is the proton transfer reaction between F^- and the fluoroform molecule, in which CF_3^- is also formed [Eq. (1)].

$$F^- + CHF_3 \rightarrow CF_3^- + HF \qquad (1)$$

Table 2. NICI mass spectrum of fluoroform obtained at 100°C and 0.1 μm ion source pressure.

m/e	Ion	Relative intensity, %
19	F^-	—
39	$(HF)F^-$	19.2
59	$(HF)_2F^-$	100.0
69	CF_3^-	6.9
79	$(HF)_3F^-$	23.8
85	CF_3O^-	24.7
89	$(CHF_3)F^-/(CF_3)^-(HF)$	8.0
105	$(CF_3O)\ (HF)^-$	8.3
109	$(CHF_3)\ (HF)^-$	11.5
128	$(CF_2)\ (CF_3O)^-$	9.5
135	$C_2F_5O^-$	10.3

The other possibility is a reaction of F radicals, generated in the initial electron impact event, with hydrogen-containing impurities (RH) resident within the ion source [Eqs. (2) and (3)].

$$CHF_3 + e \rightarrow F^- + 2F + CH \qquad (2)$$

$$F + RH \rightarrow HF + R \qquad (3)$$

The enthalpy of reaction (1) is on the order of −56.5 kcal/mole, and this process is therefore substantially exothermic. For many RH reactants, reaction (3) would also be highly exothermic.

Trace quantities of O_2^- or O^- ions inside the source could react with fluoroform molecules to yield the observed m/e 85 peak corresponding to the $(M - H + O)^-$ ion in the NICI spectrum shown in Table 2. The m/e 89 ion could be formed either by clustering between fluoroform and F^-, or by clustering between HF and CF_3^-. As shown in Table 2, both the m/e 105 and the m/e 109 ions can be explained on the basis of clustering of HF with the m/e 85 and 89 ions. There are also relatively small amounts of m/e 128 and m/e 135 in the NICI spectrum. It is tentatively assumed that the former ion is $C_3F_4O^-$, while the latter ion is apparently $C_2F_5O^-$, which probably arises from HC_2F_5 or other such impurities in the fluoroform.

Temperature Effects on the NICI Spectrum of CHF_3. The relative abundances of ions observed in the fluoroform NICI mass spectrum were found to be temperature-dependent. The variation in the relative intensities was studied over a temperature range of 70 to 230°C, at a total source pressure of 0.1 μm. It was observed that the relative intensity of m/e 39 increases with increasing source temperature, while the intensities of m/e 59 and 79 decrease, as do those of the m/e 105 and 109 ions. It seems apparent that at higher source temperatures the formation of the larger cluster ions in fluoroform is less favored. This is consistent with the increased relative intensity of the m/e 69 ions as the temperature is increased.

A trace quantity of n-butanol (about 0.5 μm) was injected into the ion source which also contained fluoroform at a pressure of 0.1 μm. Molecular, or quasi-molecular ions, such as $(M - 1)^-$ and $(M + F)^-$, were not observed in the NICI spectrum under these conditions. The failure to observe such ions possibly indicates that the reaction rate of F^- with n-butanol is much slower than that of F^- with neutrals such as HF.

Formation of Primary F^- Ion Reactant with NF_3 as the Reagent Gas

Spectrum of Pure NF_3 Under NICI Conditions. Owing to the very low intensity of the primary F^- ion observed in the fluoroform NICI spectrum, a second reagent gas, NF_3, was tested as a source of F^-. The NICI spectrum of NF_3 at a total pressure of 0.1 μm shows that the m/e 19, F^- is the major peak, with only a trace quantity of m/e 39, HF_2^-. Again, the HF molecule with which F^- clusters here is probably formed from hydrogen-containing impurities in the source, by a mechanism similar to that described previously.

NICI Spectrum of n-Butanol Obtained with NF_3 Reagent Gas. Table 3 shows the NICI spectrum of n-butanol obtained with NF_3 reagent gas at a total pressure of 100 μm and at a temperature of 70°C. About 0.5 μm of n-butanol was injected into the source with the NF_3 for this experiment. The ions at m/e 19, 39, and 59 are presumably formed as described earlier. The m/e 93 likely originates from the direct attachment of F^- to the n-butanol sample molecule, and the m/e 113 is then formed by clustering of an HF molecule with the $(M + F)^-$ ion. Apparently, F^- undergoes competing reactions with the n-butanol and HF molecules. Several additional experiments were therefore conducted in which various experimental parameters were varied, in an attempt to maximize the intensity of the $(M + F)^-$ product.

Effects of Varying Experimental Conditions on the NICI Spectrum of n-Butanol Obtained with NF_3 Reagent. Variation of the Total Pressure of NF_3. At an electron energy of 240 eV, and a source temperature of about 70°C, the rela-

Table 3. NICI spectrum of n-butanol (0.5 μm) obtained with NF_3 reagent gas at a total pressure of 100 μm

m/e	Ions	Relative intensity, %
19	F^-	47.7
39	$(HF)F^-$	100.0
59	$(HF)_2F^-$	64.5
93	$(M + F)^-$	10.8
113	$(HF)\ (M + F)^-$	3.2

Table 4. Ratio of relative intensities of *m/e* 39 to 93 in the NICI spectrum of NF_3-*n*-butanol at various pressures of NF_3.

P_{NF_3}, μm	Relative intensity, %		Ratio I_{39}/I_{93}
	I_{39}	I_{93}	
30	8.4	7.4	1.1
40	25.0	19.9	1.3
60	31.2	8.3	3.8
80	59.8	10.2	5.9
100	100.0	10.8	9.3
120	31.3	2.8	11.2

tive intensities of *m/e* 39, $(HF)F^-$, and *m/e* 93, $(C_4H_9OH)F^-$, in the NICI spectrum of an *n*-buta nol-NF_3 mixture were observed at various total ion source pressures over the range from 40 to 120 μm. The observed intensities and the ratio of these are shown in Table 4. The *n*-butanol sample in these experiments was maintained at a constant pressure of 0.5 μm. It can be seen from Table 4 that the ratio of the relative intensity of *m/e* 39 to that of *m/e* 93 increases as the pressure of NF_3 increases. This indicates that at higher pressures the preferred reaction is the association reaction of F^- with HF. The *m/e* 93 ion is formed via a second-order reaction, in which F^- ions are first produced from NF_3, and then cluster with *n*-butanol molecules. The $(HF)F^-$ product ions, on the other hand, are formed by a reaction which is at least third-order. Probably, the F radical, produced by electron impact on NF_3, abstracts a hydrogen atom from an *n*-butanol molecule or other hydrogen-containing impurities to form an HF molecule, which then clusters with F^-. Thus, the observed intensity of the $(HF)F^-$ ion varies as the third power of the pressure. At higher pressures, the reaction forming $(HF)F^-$ is thus more favorable than that forming $(M + F)^-$. Thus, in order to observe a distinct quasimolecular anion in the F^- NICI mass spectrum, such as *m/e* 93 in this example, the total source pressure has to be kept relatively low. However, the pressure cannot be lower than 30 μm, or this product is not observed, owing to the characteristics of the ion source employed in the present studies.

VARIATION OF THE ELECTRON ENERGY. The electron energy is another parameter of considerable importance in NICI experiments. When the electron energy was lowered to 40 eV, while all other parameters were kept constant for the present gaseous system, the reaction leading to formation of the $(M + F)^-$ ion was found to be favored. The ratio of *m/e* 39 to *m/e* 93 was found to decrease abruptly as the electron energy was reduced from 240 V to 40 V. A possible explanation is that the production of F radicals is enhanced significantly at higher electron energies. The F radicals thus formed react, in turn, with *n*-butanol to form more HF molecules. Thus, F^- collisions with HF molecules are more probable than collisions with *n*-butanol molecules at the higher electron energy.

VARIATION OF THE REPELLER FIELD. By applying a small repeller field to the electron entrance plate of the ion source, (−6 V, dc), the residence time of ions inside the source can be reduced. However, the distribution of reaction products was not observed to change significantly as the repeller potential was varied over this range.

VARIATION OF SOURCE TEMPERATURE. Varying the ion source temperature over the range 100–190°C while other parameters are kept constant, resulted in little change in the ratio of relative intensities of *m/e* 93 to 39. Apparently, the competition between $(HF)F^-$ and $(M + F)^-$ production is rather insensitive to temperature. However, the relative intensities of both the *m/e* 39 and 93 ions, with respect to *m/e* 19, decrease markedly as the temperature increases.

VARIATION OF SAMPLE PRESSURE. A series of NF_3-NICI spectra of *n*-butanol were obtained at various *n*-butanol pressures ranging from 1 to 40 μm at a total pressure of 80 μm and with all other parameters held constant. Listed in Table 5 are the relative intensities of the major ions observed, and the ratios of relative intensities of two successive cluster ions. At higher *n*-butanol pressures, large clusters are observed, *m/e* 79 and 99, which result from successive HF additions. At butanol pressures above 4 μm, a peak is observed at *m/e* 167. This probably corresponds to an $M(M + F)^-$ ion, which is formed by clustering of another butanol molecule with the $(M + F)^-$ ion. The I_{59}/I_{39} ratio is seen to increase sharply as the sample pressure increases. Moreover, the ratios, I_{79}/I_{59}, I_{99}/I_{79}, and I_{113}/I_{93} also increase proportionately with pressure. This indicates that *n*-butanol plays an important role in the cluster ion formation. It is probable that *n*-butanol is the most significant source of hydrogen atoms for the reactions yielding HF molecules. With increasing *n*-butanol pressure, the yield of HF molecules therefore increases. These HF molecules then react further with F^- to produce cluster ions of various orders. The ratio, I_{167}/I_{93}, is also observed to increase gradually as the sample pressure increases. This is because at higher concentrations of sample molecules, the formation of the $(2M + F)^-$ ion is enhanced. Finally, as seen in Table 5, at sample pressures above 4μm, the cluster ion, *m/e*

59, formed by association of two HF molecules with F^- is preferred to other cluster ions.

ADDITION OF OTHER GASES TO THE NF_3 REAGENT GAS. In order to reduce the population of highly energetic electrons in the ion source, certain gases can be added to the reagent gas which act as electron scavengers. Removal of these electrons is desirable because the reaction of high energy electrons with NF_3 is considered to be the major source of F radicals. In the present study, the use of argon as a high-energy electron moderator was investigated. Argon was mixed with the NF_3 gas in different proportions, while maintaining a total ion source pressure of 80 μm. The *n*-butanol sample pressure was maintained at about 0.5 μm, while other parameters were kept constant, as before. It was observed that the ratio of relative intensities of *m/e* 39 to 93 obtained with various pressures of Ar added to the source gas mixture did not decrease, as was expected.

In both solution and gas phase reaction studies, oxygen has been employed as an inhibitor, owing to its ability to scavenge atoms or radicals, thus forming species which are incapable of participating in the chain-propagation steps. It was considered feasible, therefore, that the addition of oxygen to the NF_3-butanol gas mixture in the ion source might reduce the population of F radicals. Small quantities of oxygen gas (pressure ranging from 2 to 6 μm were therefore added to the source, in a series of experiments, in which the total pressure was maintained at 50 μm, the *n*-butanol pressure was kept constant at 2 μm, and other parameters were not varied. The ratio of the relative intensity of *m/e* 93 to that of *m/e* 39 observed in the NICI spectrum was observed to increase by a factor of six, as the pressure of oxygen increased from 0 to 6 μm. Thus, oxygen clearly appears to inhibit the formation of the fluorine radical. However, the overall ion intensities decrease as O_2 pressure increases, and in addition, the lifetime of the tungsten filament is shortened, both of which are undesirable results.

Negative Ion Chemical Ionization Mass Spectra from Reactions of F^- With Various Organic Compounds

As described in the foregoing sections, impact of electrons on gaseous NF_3 produces a large population of F^- ions, which can be used as reactant ions to generate negative chemical ionization mass spectra. Since F^- has a large gas phase proton affinity, reactions of this ion with many molecules to produce $(M - 1)^-$ products by proton transfer are expected to be common. Furthermore, F^- is a strong nucleophile, and so bimolecular nucleophilic substitution reactions with this ion are expected to be observed in some cases. The organic compounds, for which F^- NICI mass spectra were examined in this study, were selected as representative of a variety of functional group classes. The detailed experimental results obtained for each functional group class are discussed in the following sections. The experimental conditions used in obtaining these NICI spectra were selected on the basis of the results obtained in the previously described studies of the effects of pressure, temperature and other experimental parameters.

Carboxylic Acids. The F^- NICI mass spectra of formic, acetic, isobutyric and mercaptoacetic acids are shown in Table 6. It is seen from these data that the most intense ion in the spectra of all these carboxylic acids is the $(M - 1)^-$ ion. This ion is formed by the abstraction of a proton, probably from the COOH group. In mercaptoacetic acid, both the SH and the COOH groups contain active hydrogen, but more likely, abstraction occurs preferentially from the COOH group.

F^- attachment to these carboxylic acids to form $(M + F)^-$ ions was also observed, as indicated by the spectra shown in Table 6, but the relative intensities of these ions are much smaller than those of the $(M - 1)^-$ products. At higher ion source pressures, the NICI spectra of formic acid and acetic acid show clusters of these molecules

Table 5. Relative intensities of major ions and ratios of relative intensities of successive cluster ions in the NF_3-NICI spectra of *n*-butanol at various *n*-butanol pressures.[a]

$P_{n\text{-butanol}}$, μm	Relative intensity, %								I_{59}/I_{39}	I_{79}/I_{59}	I_{99}/I_{79}	I_{113}/I_{93}	I_{167}/I_{93}
	I_{19}	I_{39}	I_{59}	I_{79}	I_{93}	I_{99}	I_{113}	I_{167}					
1	8.2	19.5	7.3	1.5	2.0	—	0.7	—	0.37	0.21	—	0.35	—
4	18.3	86.1	80.0	19.8	12.7	—	5.6	1.3	0.93	0.25	—	0.44	0.1
8	16.4	28.9	100.0	28.7	4.4	11.7	7.3	—	3.46	0.29	0.41	1.66	—
12	14.8	13.8	100.0	19.3	5.0	14.3	8.0	5.0	7.25	0.19	0.74	1.6	1.0
16	9.8	9.8	100.0	21.9	4.1	15.3	10.5	5.5	10.2	0.22	0.7	2.56	1.34
40	4.2	1.1	100.0	44.6	5.1	7.4	13.0	8.2	90.0	0.45	—	2.55	1.61

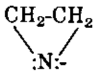
[a] The total source pressure was maintained at 80 μm.

Table 6. F^- NICI mass spectra of carboxylic acids (RCOOH).

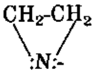
Compounds (M)	Mol. wt.	Relative intensity, %[a]				Other ions		
		m/e 19	$(M-1)^-$	$(M+F)^-$	$(2M-1)^-$	m/e	Relative intensity	Identity
Formic acid (HCOOH)	46	21.2	100	2.4	38.1	42 111	5.5 15.0	CNO^- (HF) $(2M\text{-}1)^-$
Acetic acid, CH_3COOH	60	68.7	100	8.0	9.2	42	5.9	CNO^-
Isobutyric acid, $(CH_3)_2CHCOOH$	88	94.6	100	14.1	—	57	46.3	$CH_3COCH_2^-$
Mercaptoacetic acid $HSCH_2COOH$	92	73.4	100	2.7	—	59	35.2	CH_3COO^-

[a] Ions less than 5% relative intensity are omitted except the quasi-molecular ions.

with the $(M-1)^-$ ions, that is, $(2M-1)^-$ ions. Cluster ions formed by association of product ions with HF molecules, were also observed in the formic acid NICI mass spectrum. A very weak intensity ion at m/e 42 was observed in the spectra of acetic acid and formic acid. Possibly, this ion is CNO^-, as suggested by Alpin et al. (*15*), or



as postulated by Field (*10*). The mechanism of formation of this ion is unclear, but it seems more likely that CNO^- would be formed than



because neither formic acid nor acetic acid contains an acetylenic group. Other observed ions having m/e values which do not correspond to any expected fragments for the compounds undergoing chemical ionization are quite possibly formed from impurities contained in the samples.

Carboxylic Acid Esters. The F^- NICI mass spectra of isopropyl acetate, ethyl acetate, ethyl formate, and methyl methacrylate are shown in Table 7. Both isopropyl acetate and ethyl acetate exhibit an intense m/e 59 peak in their F^- NICI spectra, while ethyl formate exhibits an intense m/e 45 peak, and methyl methacrylate is characterized by a strong m/e 85 peak. These peaks correspond to the carboxylate anions from each of these esters, $CH_3CO_2^-$, HCO_2^-, and $CH_2 = C(CH_3)CO_2^-$, respectively, which are formed by an O-alkyl cleavage, resulting from F^- attack on the alcohol alkyl group and subsequent displacement of carboxylate ions. This can be visualized as a bimolecular nucleophilic substitution reaction.

A weak $(M-1)^-$ ion is also observed in each of the esters studied here, with the exception of ethyl formate. This ion is expected to be primarily formed by abstraction of a relatively acidic hydrogen from the molecule. In isopropyl acetate and ethyl acetate, an alpha hydrogen is available for abstraction by the F^- ion, but in methyl methacrylate, an allylic hydrogen must be abstracted. No $(M-1)^-$ ion is observed in ethyl formate, since this molecule contains no active hydrogen atoms.

Since alkoxide ion, $R'O^-$, is more nucleophilic than F^- (*16*), the attack of F^- at the carbonyl-carbon center, to release the alkoxide ion, does not occur with this group of ester compounds. This is demonstrated by the NICI spectrum of ethyl acetate, since no m/e 45 peak ($C_2H_5O^-$) is observed.

Ions at m/e 26, 42, and 46, having very weak intensities, also appear in the spectra of these compounds. In addition, a low intensity ion at m/e 41 appears in the spectrum of each ester except that of ethyl formate. This ion probably corresponds to the ketene anion, $^-HC = C = O \rightleftarrows HC \equiv C\text{-}O^-$ (*15*), which is rather commonly observed from oxygen-containing compounds. The ion at m/e 61 in the spectra of ethyl acetate and isopropyl acetate is quite puzzling. It is possible that this ion is $^-CH_2COF$. Two possible mechanisms can be conceived for its formation. One mechanism would involve nucleophilic attack of F^- on the carbonyl carbon, resulting in displacement of the alkoxide ion, yielding an acyl fluoride compound (CH_3COF), followed by abstraction of an alpha hydrogen by F^-. Another possible mechanism would involve addition of an HF molecule to the ketene anion. As mentioned above, nucleophilic displacement reactions involving attachment of F^- at the carbonyl carbon apparently do not occur with esters. Therefore, the first mechanism is not probable. Other minor ions observed in the spectra shown in Table 7 are again likely due to impurities.

Table 7. F^- NICI mass spectra of carboxylic acid esters (RCOOR′)

		Relative intensity, %[a]			Other ions		
Compounds (M)	Mol. wt.	m/e19	$RCOO^{-b}$	$(M-1)^-$	m/e	Relative intensity	Identity
Ethyl acetate,	88	21.4	100 (m/e 59)	3.4	39	23.6	(HF)F
$CH_3COOC_2H_5$					61	10.2	$^-CH_2COF$
Isopropyl acetate,	102	20.6	100 (m/e 59)	3.5	39	18.4	$(HF)F^-$
$CH_3COOCH(CH_3)_2$					57	6.4	$CH_3COCH_2^-$
			CH_3COO^-		61	8.4	$^-CH_2COF$
					79	5.2	$(HF)(RCOO^-)$
Ethyl formate,	74	45.8	100 (m/e 45)		39	64.3	$(HF)F^-$
$HCOOC_2H_5$					59	23.6	CH_3COO^- or $(HF)_2F^-$
			$CHOO^-$		65	28.9	$(HF)(RCOO)^-$
Methyl methacrylate,	100	100	34.2 (m/e 85)	0.4	26	6.8	CN^-
$CH_2=C(CH_3)COOCH_3$					39	16.4	$(HF)F^-$
			$CH_2C(CH_3)COO^-$		40	26.9	$^-CH_2CN$
					45	8.3	$HCOO^-$
					59	19.6	CH_3COO^- or $(HF)_2F^-$

[a] Ions less than 5% relative intensity are omitted except the quasi-molecular ions.

[b] R = H in the ethyl formate.

Ketones and Aldehydes. The F^- NICI mass spectra of acetone, 2-hexanone, 4-heptanone, 2,5-hexadione, and cyclopentanone are shown in Table 8. It is seen that the $(M\text{-}1)^-$ ion is the predominant ion for all compounds of this type which were examined. The mechanism of formation likely involves abstraction of the active alpha hydrogen in each of these compounds. In addition, $(M + F)^-$ ions, in varying relative abundances (1.2-22%), are also observed in the spectra. These probably are formed by way of tetrahedral intermediates resulting from the attack of the F^- ion at the carbonyl carbon, this being a typical reaction of ketones and aldehydes (*17*). The molecular anion M^- is also detected in the spectra of these compounds, but in very weak intensity. This ion probably results from resonance electron capture by the molecule. An ion at m/e 26, apparently CN^-, is also observed in each of the ketone spectra.

Similar to the ketones, the F^- NICI mass spectra of aldehydes, including acetaldehyde, propionaldehyde and 2-ethylbutyraldehyde, are all characterized by an intense $(M - 1)^-$ ion, as shown in Table 9. Undoubtedly, the reaction mechanism in these cases also involves abstraction of an active alpha hydrogen from the molecule. The $(M + F)^-$ ion is also a prominent species in the spectra of this group of compounds, and again, formation of these ions probably involves a tetrahedral intermediate. Analytically insignificant ions, such as m/e 26, 39, 42, and 59, are all present in quite high concentrations.

Aliphatic Alcohols. The F^- NICI mass spectra of *n*-butanol, isobutanol, and *tert*-amyl alcohol are shown in Table 10. All of these compounds exhibit significant $(M + F)^-$ ions. In contrast to the compounds previously discussed, however, aliphatic alcohols show no $(M - 1)^-$ ion in their F^- NICI spectra. This is likely attribut-

Table 8. F^- NICI mass spectra of ketones (RCOR′).

		Relative intensity, %[a]				Other ions		
Compounds (M)	Mol. wt.	m/e 19	$(M-1)^-$	$(M+F)^-$	M^-	m/e	Relative intensity	Identity
Acetone, CH_3COCH_3	58	79.6	100	1.2	2.0	26	6.3	CN^-
2-Hexanone,	100	34.0	100	13.0	4.6	26	11.6	CN^-
$CH_3CO(CH_2)_3CH_3$						39	5.1	$(HF)F^-$
4-Heptanone,	114	26.3	90.8	11.4	5.1	26	25.5	CN^-
$CH_3CO(CH_2)_4CH_3$						39	13.4	$(HF)F^-$
2,5-Hexadione,	114	42.9	100	22.0	5.8	26	6.1	CN^-
$CH_3CO(CH_2)_2COCH_3$								
Cyclopentanone	84	71.0	100	15.4	4.1	26	30.6	CN^-
C_5H_8O						39	23.1	$HF(F^-)$

[a] Ions less than 5% relative intensity are omitted except the quasi-molecular ions.

Table 9. F^- NICI mass spectra of aldehydes (RCHO).

Compounds (M)	Mol. wt.	Relative intensity, %[a]			Other ions		
		m/e 19	$(M - 1)^-$	$(M + F)^-$	m/e	Relative intensity	Identity
Acetaldehyde, CH_3CHO	44	15.7	100	7.0	26	42.1	CN^-
					39	15.5	$(HF)F^-$
					42	6.9	CNO^-
Propionaldehyde, C_2H_5CHO	58	—	100	19.2	26	77.9	CN^-
					39	64.3	$(HF)F^-$
					42	14.7	CNO^-
					59	27.5	$(HF)_2F^-$
Ethylbutyraldehyde, $CH_3CH(C_2H_5)CH_2CHO$	100	39.3	14.1	7.7	26	53.7	CN^-
					39	23.4	$(HF)F^-$
					59	100	$(HF)_2F^-$
					79	36.8	$(HF)_3F^-$

[a] Ions less than 5% relative intensity are omitted except the quasi-molecular ions.

able to the fact that aliphatic alcohols are very weak acids, and thus it is relatively difficult to remove a proton from the –OH group.

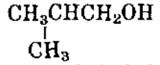
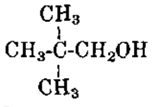
As discussed earlier, the reactions of F^- with the sample molecule are in competition with reactions of this ion with HF. It is evident from the data in Table 10, that in the case of the alcohols, formation of $F^-(HF)$ is more favorable than the formation of the $(M + F)^-$ ion. However, F^- NICI may be useful in distinguishing structural isomers of the alcohols. As can be seen by comparing the spectra of *n*-butanol and isobutanol, the relative intensities of the $(M + F)^-$ ion in the two spectra are markedly different.

Alkyl Chlorides and Halobenzenes. The F^- NICI mass spectra of carbon tetrachloride, chloroform, methylene chloride and 1-chlorobutane are shown in Table 11. All of these compounds exhibit intense m/e 35 and 37 peaks, which correspond to the two isotopes of Cl^-. Formation of these ions apparently occurs via bimolecular nucleophilic substitution reactions. The observation of prominent Cl^- product ions from these reactions supports the conclusion that the nucleophilicity of F^- is greater than that of Cl^- in the gas phase (*16*).

Since F^- is a stronger Lewis base than Cl^-, it is also possible for F^- to abstract a chloronium ion, Cl^+, from the CCl_4 molecule to form a CCl_3^- ion, although this product is formed in relatively small amounts (1.4% relative intensity at m/e 117). The characteristic chlorine isotope ratio leads to the observation of CCl_3^- ions at m/e 117, 119, and 121, in the intensity ratio, 3:3:1, which confirms the identity of this ion.

In the F^- NICI mass spectrum of chloroform ($CHCl_3$), an intense CCl_3^- ion is also observed (about 73.4% relative intensity at m/e 117). This is consistent with the expectations of the "inductive" effect in this molecule. Chloroform contains three equivalent chlorine atoms located at the

Table 10. F^- NICI mass spectra of aliphatic alcohols (ROH).

Compounds (M)	Mol. wt.	Relative intensity, %[a]		Other ions		
		m/e 19	$(M + F)^-$	m/e	Relative intensity	Identity
n-Butanol $CH_3CH_2CH_2CH_2OH$	74	82.7	58.8	39	100	$(HF)F^-$
				59	11.0	$(HF)_2F^-$
				113	6.9	$(HF)(M + F)^-$
Isobutanol,  $CH_3\underset{\underset{CH_3}{\mid}}{C}HCH_2OH$	74	100	22.1	39	61.1	$(HF)F^-$
tert-Amyl alcohol,  $CH_3\text{-}\overset{\overset{CH_3}{\mid}}{\underset{\underset{CH_3}{\mid}}{C}}\text{-}CH_2OH$	88	51.5	17.5	26	12.0	CN^-
				39	100	$(HF)F^-$
				59	20.9	$(HF)_2F^-$
				93	19.6	$(\text{butanol} + F)^-$

[a] Ions less than 5% relative intensity are omitted except the quasi-molecular ions.

Table 11. F^- NICI mass spectra of alkyl chlorides (RCl) and Halobenzene (ArO).

		Relative intensity, %[a]						Other ions		
			Cl^-		Br^-					
Compounds (M)	Mol. wt.	*m/e* 19	*m/e* 35	*m/e* 37	*m/e* 79	*m/e* 81	(M − 1)	*m/e*	Relative intensity	Identity
Carbon tetrachloride CCl_4	152	100	34.2	11.6	—	—	—	117	1.4	CCl_3^-
								119	1.3	
								121	0.6	
Chloroform, $CHCl_3$	118	41.1	100	30.9	—	—	73.4[b]	26	6.9	CN^-
							71.7[b]	55	12.2	$(HF)Cl^-$
							22.5[b]	57	3.8	
							2.8[b]	70	8.1	Cl_2^-
								72	5.2	
Methylene chloride, CH_2Cl_2	84	8.0	100	34.4	—	—	0.3	70	0.4	Cl_2^-
								105	0.5	Cl_3^-
								107	0.5	
								117	0.6	$CHCl_3^-$
								119	0.6	
								121	0.2	
1-Chlorobutane, n-C_4H_9Cl	92	13.7	100	29.4	—	—	—	55	7.2	$(HF)FCl^-$
								57	2.4	
Chlorobenzene, C_6H_5Cl	112	84.4	100	30.7	—	—	—	39	40	$(HF)F^-$
								55	24	$(HF)Cl^-$
								57	8	
2-Chlorophenol, C_6H_4ClOH	128	100	59.1	17.8	—	—	13.0	55	10.2	$HFCl^-$
Bromobenzene C_6H_5Br	156	29.2	—	—	58.9	57.9	—	39	100	$(HF)F^-$
								59	19.8	$(HF)_2F^-$
								99	10.0	$(HF)Br^-$
								101	10.0	

[a] Ions less than 5% relative intensity are omitted except the quasi-molecular ions.

[b] These are isotopic peaks.

Table 12. F^- NICI mass spectra of phenols (ArOH).

Compounds (M)	Mol. wt.	Relative intensity, %[a]				Other ions		
		m/e 19	$(M-1)^-$	$(M+F)^-$	$(2M-1)^-$	m/e	Relative intensity	Identity
2-Chlorophenol,	128	100	13.0	—	—	35	59.1	Cl^-
$C_6H_4(Cl)OH$						37	17.8	
Salicylaldehyde,	122	—	94.3	100	33.7	79	28.8	$(HF)_3F^-$
$C_6H_4(CHO)OH$						161	37.9	$(HF)(M+F)^-$

[a] Ions less than 5% relative intensity are omitted except the quasi-molecular ions.

methane carbon center, and since chlorine is an electron-withdrawing substituent, the presence of these serves to pull the electron pair, shared by the carbon and hydrogen atoms, away from the hydrogen. This enhances the probability of a proton being released from the molecule upon reaction with F^-. In methylene chloride, the formation of the observed $(M - 1)^-$ ion can be attributed to a similar mechanism. In the latter case, however, the molecule contains only two chlorine atoms, and so the inductive effect should be reduced substantially, and only a very weak $(M - 1)^-$ ion is observed (about 0.3% relative intensity).

Other weak intensity ions, such as the isotopic groups beginning with m/e 70 in the spectra of both chloroform and methylene chloride, and with m/e 105 and 117 in the spectrum of methylene chloride, are also observed. These ions are assumed to be Cl_2^-, Cl_3^-, and $CHCl_3^-$, respectively, and are probably produced in subsequent reactions of the chloride ion. However, the 1-chlorobutane spectrum shows no significant ions other than Cl^-.

Ions at m/e 55 and 57, which presumably correspond to the two isotopic ions having the structure, $(HF)Cl^-$, are observed in all of the spectra listed in Table 11, except that of carbon tetrachloride. This again suggests that the HF molecule, which is observed to cluster with ions in many of the F^- NICI spectra, is directly derived from sample molecules which contain hydrogen.

Cl^- is observed to be the most abundant ion in the F^- NICI spectra of chlorobenzene and 2-chlorophenol. Similarly, Br^- is the most abundant ion in the spectrum of bromobenzene. The Br^- ion is easily identified by the presence of the two isotopic peaks at m/e 79 and 81, which are approximately equal in intensity. Formation of the halide ions can also be visualized as occurring by a mechanism which involves the attack of a nucleophilic reagent upon the ring to form a carbanion intermediate, followed by ejection of the halide ion.

F^- NICI mass spectrometry offers no apparent advantages for either analysis or structural determinations of aliphatic or aromatic halides, since the spectra of all such compounds studied here exhibit halide ion as the only intense product.

Table 13. F^- NICI mass spectra of nitriles (RCN) and nitrobenzene.

Compounds (M)	Mol wt.	Relative intensity, %[a]						Other ions		
		m/e 19	CN^-	NO_2^-	$(M-1)^-$	$(M+F)^-$	M^-	m/e	Relative intensity	Identity
Acetonitrile,	41	54.8	11.7	—	100	3.2	—	39	12.8	$(HF)F^-$
CH_3CN								59	10.1	$(HF)_2F^-$
Propionitrile,	55	100	83.2	—	—	1.4	—	39	40.5	$(HF)F^-$
C_2H_5CN								50	5.7	C_3N^-
								59	5.0	$(HF)_2F^-$
Benzonitrile,	103	48.3	42.0	—	—	4.2	1.2	39	100	$(HF)F^-$
C_6H_5CN								50	23.9	C_3N^-
								59	30.1	$(HF)_2F^-$
								70	10.7	$(HF)C_3N^-$
								74	7.1	C_5N^-
								94	6.8	$(HF)C_5N^-$
								98	0.9	C_7N^-
Nitrobenzene,	123	17.0	—	100	—	—	1.2	39	5.3	$(HF)F^-$
$C_6H_5NO_2$								66	4.02	$(HF)NO_2^-$
								86	13.6	$(HF_2NO_2^-$
								93	14.3	$C_6H_5O^-$

[a] Ions less than 5% relative intensity are omitted except the quasi-molecular ions.

Table 14. F^- NICI mass spectra of ethers (ROR).

	Relative intensity, %[a]			Other ions		
Compounds (M)	Mol. wt.	m/e 19	RO^-	m/e	Relative intensity	Identity
Diethyl ether, $C_2H_5OC_2H_5$	74	29.2	8.6	26	100	CN^-
				39	7.5	$(HF)F^-$
				42	60.0	CNO^-
				43	21.6	$C_2H_3O^-$
				62	7.2	$(HF)CNO^-$
Isopropyl ether, $(CH_3)_2CHOCH(CH_3)_2$	102	19.2	9.9	26	100	CN^-
				39	6.1	$(HF)F^-$
				42	27.3	CNO^-
				57	6.2	$CH_2=C(CH_3)O^-$
				62	6.6	$(HF)CNO^-$

[a] Ions less than 5% relative intensity are omitted except the quasi-molecular ions.

2-Chlorophenol and Salicylaldehyde. The F^- NICI mass spectra of 2-chlorophenol and salicylaldehyde were investigated during this study. As shown in Table 12, the spectrum of 2-chlorophenol exhibits mainly Cl^- ion and a smaller intensity of $(M - 1)^-$ ion. Salicylaldehyde also shows an intense $(M - 1)^-$ ion. Since phenols are rather strong acids, it is relatively easy for the F^- reactant to abstract a proton from the hydroxyl group of these compounds, yielding stable phenoxide ions (ArO^-). Since the 2-chlorophenol molecule contains an active hydrogen atom in the hydroxyl group, it would be expected to complex readily with the F^- ion to form a $(M + F)^-$ product. However, while an abundant $(M + F)^-$ ion appears in the spectrum of salicylaldehyde, no such ion is detected in the 2-chlorophenol spectrum. This may indicate that production of the Cl^- ion is kinetically favored over the addition reaction. At fairly high source pressures, the $(M - 1)^-$ ion clusters with another molecule of salicylaldehyde to form the $(2M - 1)^-$ ion.

Nitriles. The F^- NICI mass spectra of acetonitrile, propionitrile and benzonitrile are shown in Table 13. The spectra of all nitriles studied here are dominated by a very intense CN^- ion peak (*m/e* 26).

The spectrum of acetonitrile exhibits an $(M - 1)^-$ ion as the major peak. This can be reasonably explained by the fact that the cyano group (CN) is a strongly electron-withdrawing group, which can readily activate the hydrogen atoms attached to the adjacent carbon atom (α hydrogen). The reaction of the F^- ion with this molecule in the gas phase thus results in abstraction of a proton, yielding a carbonion, which can be stabilized by electron delocalization. Since benzonitrile does not contain an α hydrogen, no significant $(M - 1)^-$ ion is observed in its spectrum. Strangely, the $(M - 1)^-$ ion is also absent in the spectrum of propionitrile, although it does contain an α hydrogen. Possibly, this is explained by the electron-donating inductive effect of the methyl group, which reduces the residual electron affinity of the α carbon atom, and thus makes removal of the attached hydrogen more difficult.

All of the nitriles investigated here exhibit weak $(M + F)^-$ ions, which are probably formed by a mechanism which involves F^- ion attack on the carbon center adjacent to the cyano group. The F^- NICI spectra of these compounds also display a series of peaks corresponding to C_nN^- ($n = 1, 3, 5,$ and 7), which appear at *m/e* 26, 50, 74, and 98. In the spectrum of acetonitrile, only the

Table 15. F^- NICI mass spectra of amines.

		Relative intensity, %[a]		Other ions		
Compounds (M)	Mol. wt.	*m/e* 19	$(M+F)^-$	*m/e*	Relative *intensity*	*Identity*
Diethylamine, $(C_2H_5)_2NH$	73	100	0.8	26	33.4	CN^-
				39	17.7	$(HF)F^-$
				42	7.5	CNO^- or $CH_2CH_2N^-$
n-Butylamine, $C_4H_9NH_2$	73	100	—	26	19.1	CN^-
				39	12.3	$(HF)F^-$
				42	8.2	CNO^- or $CH_2CH_2N^-$

[a] Ions less than 5% relative intensity are omitted except the quasi-molecular ions.

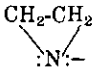
peak at *m/e* 26 is observed. The propionitrile spectrum shows both CN^- and C_3N^-, at *m/e* 26 and 50, respectively. In the spectrum of benzonitrile, all four peaks at *m/e* 26, 50, 74, and 98 are present. These ions were also observed by Alpin et al. (*15*) in their study of the negative ion mass spectra of these compounds produced by electron impact.

Nitrobenzene. The F^- NICI mass spectrum of nitrobenzene, shown in Table 13, is dominated by a very intense NO_2^- ion peak. Neither the $(M - 1)^-$ ion, nor the $(M + F)^-$ ion is observed in the spectrum of this compound. However, a very weak molecular anion, M^- is observed (1.2% relative intensity). The ion at *m/e* 93 may be characteristic of this compound, but the mechanism of formation is not clear.

Ethers. Ethers are very weak acids, and the F^- NICI mass spectra of diethyl ether and isopropyl ether, which appear in Table 14, exhibit no $(M - 1)^-$ ions. The oxygen in diethyl ether is apparently not sufficiently electronegative to activate the hydrogen on neighboring methylene groups, and so abstraction of protons from these groups by F^- does not occur. Although a number of intense peaks of no particular significance are observed in the ether spectra (*m/e* 26, 42, etc.), the only ions of interest produced from these compounds are those at *m/e* 45 (possibly $C_2H_5O^-$) and *m/e* 43 (possibly $C_3H_3O^-$). Apparently, these ions are displaced as a result of nucleophilic attack of F^- at the methylene carbon. The ion at *m/e* 43 must be formed by loss of H_2 from the $C_2H_5O^-$ ion, yielding an allyl-type structure which is resonance-stabilized (*10*). Similarly, in the spectrum of isopropyl ether, the ions at *m/e* 59 and 57, which correpond to $(CH_3)_2CHO^-$ and $CH_2 = C(CH_3)O^-$, respectively, are the dominant ions in the spectrum. No $(M + F)^-$ ions were observed in the spectrum of either ether.

Amines. The F^- NICI mass spectra of diethylamine and *n*-butylamine are shown in Table 15. Amines are basic, and so no $(M - 1)^-$ ion can be formed by abstraction of a proton from these molecules by the F^- ion. The spectra of the amines are similar to those of the ethers in that they also exhibit several very intense, but analytically insignificant ions (*m/e* 26, 42, etc.). In contrast to the ethers, however, no larger fragment ions are observed in the amine spectra. This is understandable because the amino group (NH_2) is a stronger nucleophile and does not behave as a good leaving group.

Smit and Field (*10*) suggested that a possible structure for the ion with *m/e* 42, which is observed in the spectra of the amines, is



This is the anion comprising the conjugated base of ethylenimine (aziridine). The mechanism of its formation is not yet clear. In the spectrum of diethylamine, a weak $(M + F)^-$ ion, which is probably formed by hydrogen bonding, is also observed. However, no such ion was found in the spectrum of *n*-butylamine.

Aliphatic Alkanes and Alkenes. The F^- NICI mass spectra of *n*-pentane, *n*-hexane, cyclohexane, 1-octene, and cyclohexene are shown in

Table 16. F^- NICI mass spectra of hydrocarbons.

		Relative intensity, %[a]		Other ions		
Compounds (M)	Mol. wt.	*m/e*	$(M + F)^-$	*m/e*	Relative intensity	Identity
n-Pentane $CH_3(CH_2)_3CH_3$	72	100	1.0	39	14.8	$(HF)F^-$
n-Hexane $CH_3(CH_2)_4CH_3$	86	100	1.1	39	6.4	$(HF)F^-$
Cyclohexane	84	100	1.3	39	8.9	$(HF)F^-$
1-Octene $CH_2 = CH(CH_2)_5CH_3$	112	26.2	—	26	15.5	CN^-
				39	100	$(HF)F^-$
				59	17.7	$(HF)_2F^-$
Cyclohexene	82	100	—	26	69.9	CN^-
				39	37.8	$(HF)F^-$
Benzene C_6H_6	78	100	—	39	8.5	$(HF)F^-$
Toluene $C_6H_5CH_3$	92	100	—		—	
o-Xylene, $C_6H_4(CH_3)_2$	106		49.3	39	69.7	$(HF)F^-$
				59	6.3	$(HF)_2F^-$

[a] Ions less than 5% relative intensity are omitted except the quasi-molecular ions.

Table 17. Major ions in the F^- NICI spectra of various classes of compounds.

Major product ion	Compound type
$(M-1)^-$	Carboxylic acids
	Ketones
	Aldehydes
	Phenols
$(M+F)^-$	Aliphatic alcohols
	Aliphatic alkanes
	Cycloalkanes
CN^-	Nitriles
NO_2^-	Nitrobenzene
X^-	Halogenated molecules
RO^-	Ethers
$RCOO^-$	Carboxylic acid esters
None	Amines
	Olefins
	Aromatic compounds

Table 16. All of the aliphatic alkanes investigated here exhibit weak $(M + F)^-$ ions in the spectra. The hydrogen atoms in these compounds are not sufficiently acidic to be abstracted by the F^- ion, and thus no $(M - 1)^-$ ion is observed. The F^- NICI spectra of the aliphatic alkenes (olefins) show neither $(M - 1)^-$ nor $(M + F)^-$ product ions in their spectra.

Aromatic Hydrocarbons. The F^- NICI spectra of benzene, toluene, and *o*-xylene are also shown in Table 16. Benzene is not ionized by F^- ion, which indicates that the ring hydrogens are insufficiently acidic to be removed by the F^- ion. The hydrogens in the side chains of the aromatic hydrocarbons examined here are also not sufficiently acidic to facilitate reaction, as indicated by the absence of $(M - 1)^-$ ions in the spectra of toluene and *o*-xylene. However, *o*-xylene does produce a very weak $(M + F)^-$ ion.

Conclusions

A summary of the major product ions observed in the F^- NICI mass spectra of various types of organic compounds studied in the present investigation is given in Table 17. The ability to generate intense quasi-molecular anions, such as $(M - 1)^-$, and/or $(M + F)^-$ ions, from a variety of organic compounds, as was demonstrated to be possible in the present experiments, is certainly of value for analytical applications. The product ions resulting from nucleophilic displacement reactions of F^- are, obviously, of less analytical value, owing to their lower masses. Some of the compounds, examined here, such as carboxylic acids, phenols, aldehydes and alcohols, exhibit both quasi-molecular anions, $(M - 1)^-$, as well as $(M + F)^-$ products, in their F^- NICI mass spectra, and thus two ionic products are available which indicate the molecular weight of the sample species.

F^- NICI mass spectrometry is also potentially applicable for distinguishing chemically similar compounds, such as isomers, as was demonstrated in the case of *n*-butanol and isobutanol in the present experiments. For at least some types of compounds with multiple functional groups, the F^- NICI mass spectra show peaks characteristic of both groups. For example, for 2-chlorophenol, which contains both chloro and hydroxy groups, the F^- NICI spectrum exhibits Cl^- ion, and an $(M - 1)^-$ ion.

It seems clear that F^- NICI is a useful technique which is complementary to positive ion CI and electron impact mass spectrometry. F^- NICI mass spectrometry also appears to offer several advantages over NICI mass spectrometry using other reagent ions. Among these advantages are the following: (a) some aliphatic alkanes exhibit small but measurable $(M + F)^-$ ions in their F^- NICI mass spectra, while these compounds are generally unreactive with all other NICI reagent ions for which studies have been reported thus far; (b) Since the F^- ion has only one isotope of significant natural abundance, F^- NICI mass spectrometry yields a much simpler and more easily recognizable spectral pattern than that produced by reagent ions such as Cl^-. The $(M + F)^-$ ion can be readily identified, since it differs in mass by 19 amu from other ions in the region of the molecular ion. With other typically used NICI reactant ions, product species formed by electron and/or ion attachment processes may sometimes interfere with those produced by chemical ionization. (c) In O_2^- NICI mass spectrometry, O_2^- will not react with weaker gas-phase acids such as phenol, chlorophenols and dichlorophenols. The ionization of these compounds by proton transfer reactions with the F^- ion to form $(M - 1)^-$ ions occurs readily in F^- NICI mass spectrometry. Finally, (d) F^- NICI mass spectrometry is considerably more sensitive than Cl^- NICI mass spectrometry for some organic compounds, such as aldehydes and ketones.

Investigations are currently in progress in our laboratory to determine the applicability of F^- NICI mass spectrometry for the analyses of more complex molecules, including various pesticides, drugs, and hydrocarbon mixtures.

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