Gaseous Anion Chemistry. Formation and Reactions of OH⁻; Reactions of Anions with N₂O; OH⁻ Negative Chemical Ionization

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Abstract: The feasibility of using OH⁻ as reactant ion in negative chemical ionization mass spectrometry (NCI) has been demonstrated. The OH⁻ ion is formed by electron bombardment of a mixture of N_2O and either H_2 or CH_4. Dissociative electron capture by N_2O produces $O^{-}\cdot$, which abstracts a hydrogen atom from H_2 or CH_4 to form OH⁻. The spectra of OH⁻ with a variety of organic compounds have been measured and reactions have been postulated for the production of many of the observed ions. For carboxylic acids, amino acids, alcohols, ketones, and esters proton abstraction is the major reaction, and abundant $(M - 1)^-$ ions are observed. For ethers and amines, on the contrary, extensive fragmentation and no $(M - 1)^-$ ion formation is observed. For weak acids such as substituted aromatics, alkynes, and alkenes, $(M - 1)^-$ ions are formed, which appear to react with the N_2O present to form as major ions $(M - H + N_2O)^-$ and $(M - H + N_2O - H_2O)^-$. We suggest that the $(M - 1 + N_2O - H_2O)^-$ ion is a substituted pyrazole anion. No reactions are observed between OH⁻ and benzene, cycloalkanes, and alkanes. Spectra of organic compounds using N_2O as reactant gas have been determined, and the reactions are distinctly different from those using N_2O/CH_4 or N_2O/H_2 as reactant gas. Spectra of mixtures of N_2O with C_2H_6, C_3H_8, and i-C_4H_{10}, respectively, have been measured. In all cases OH⁻ is formed, but in C_3H_8/N_2O and i-C_4H_{10}/N_2O mixtures abundant ions are also found at m/e 67 and 81, respectively. We suggest that these ions are produced by the reaction of $O^{-}\cdot$ with the hydrocarbon to form $(M - 1)^-$ ions, which in turn react with N_2O to give pyrazole or methylpyrazole anions, respectively.

This report will describe the formation of OH⁻ from electron bombardment of N_2O and H-containing gases, the reactions of OH⁻ with different classes of organic compounds, and its analytical use as a reagent ion for negative chemical ionization.

Historically, negative ion mass spectrometry under low pressure conditions has been much less used than positive ion mass spectrometry. The basic reason for this is the fact that the only processes for negative ion formation with usably large ionization cross sections are resonance capture processes, and the necessity of adjusting the ionizing voltage for each substance studied constituted an obstacle which effectively precluded the practical, widespread application of the technique. For summaries of negative ion results (primarily low pressure) the reader is referred to reviews such as those of Bowie and Williams,[1] Franklin and Harland,[2] and Dillard.[3] A paper giving low pressure negative ion spectra has recently been published by Large and Knof.[4] With the development of high pressure analytical mass spectrometry (chemical ionization) this problem is markedly ameliorated. The high pressures involved result in the occurrence of many electron–molecule collisions, which in turn produces a population of electrons in the ion source with a relatively broad distribution of energies. Thus electrons will be available for capture by most substances present in the ionization chamber having capture capabilities, and the necessity for the experimenter to adjust the electron energy vanishes.

High pressure negative ion mass spectrometry (negative chemical ionization, NCI) is thus in principle no more difficult than positive chemical ionization (PCI). It is becoming clear that the promise of the principle is borne out in practice, and a beginning has been made toward the development of a body of knowledge about NCI. One of the earliest workers in the field was von Ardenne,[5] who accumulated much data but whose Duoplasmation ion source has not been widely used. Negative ion spectra can be produced by the capture by a substance of interest of the low energy electrons produced by the passage of a beam of electrons through an inert moderating gas (CH_4, i-C_4H_{10}, N_2, etc.) (a process here referred to as electron capture NCI) or by reaction with a reactant ion, which had earlier been produced by a process starting with electron capture (here called reactant ion NCI). Dougherty and co-workers have used electron capture NCI to investigate pesticides and insecticides,[6,7] and he has also used Cl⁻ as a reactant ion in reactant ion NCI.[7] Hunt and co-workers[9] have used both capture and CH_3O^- reactant ion NCI in their pulsed positive–negative chemical ionization technique. The analytical use of the superoxide anion, $O_2^{-}\cdot$, has been reported in reactant NCI[10,11] and in negative atmospheric pressure ionization.[12]

The reasons for interest in NCI are simple: from the point of view of basic chemistry NCI studies will result in additions to the rather meager body of knowledge of gaseous anion chemistry, and from an analytical point of view one wishes to determine the extent to which gaseous negative ion chemistry

will permit the mass spectrometric determination of structural features of molecules different from those found with positive ion chemistry.

We decided that it would be useful to develop a reactant NCI procedure involving the most basic reactant ion possible. Such an ion would react with the widest possible range of substances, and we hoped to find an NCI reagent with a degree of universality and applicability approximating to those of CH_5^+ and $C_2H_5^+$ from CH_4 in PCI. In order to achieve adequate sensitivities for practical analytical applications we required that the intensity of the reactant ion in the method sought have the same overwhelming intensity observed with CH_5^+ and $C_2H_5^+$ in CH_4 PCI. Our original candidates for the strongly basic reactant ion were H^-, NH_2^-, and OH^-. So far we have had no success with H^- and NH_2^-; this paper reports our findings with OH^-.

Experimental Section

Mass spectra were obtained with a Biospect mass spectrometer manufactured by Scientific Research Instruments Co., Baltimore, Md. The instrument was modified for negative ion detection using the negative ion detection system previously developed in this laboratory.[13] Compounds with sufficient volatility were introduced into the mass spectrometer by means of the gas chromatograph in order to eliminate or much reduce interferences in the spectra by impurities in the samples. A 2 mm × 1.80 mm glass column packed with 1% Dexsil on 100/110 Anachrom was used. Less volatile compounds were introduced by means of the direct insertion probe. The spectra were recorded on an Infotronics Corp. (Houston, Tex) CRS 160 mass spectrometer digital readout system. Ionization of the reaction mixture was effected either by electrons emitted from a rhenium filament or by electrons produced in a Townsend discharge.[9,11] The electron accelerating voltage was empirically adjusted to give maximum ion intensity, and it was generally about 500 V. Using a 1/1 mixture of CH_4/N_2O as the reagent gas, filament life was 40–80 h. The design of the Biospect source is such that the only location for the Townsend discharge electrodes which does not require an elaborate rebuilding of the ion source is opposite the ion exit hole, and consequently electrical noise in the experiments using the discharge modification is larger than that encountered with the filament mode. In addition, stability of operation with the filament is somewhat greater. Consequently, operation of the equipment in the filament mode is somewhat more convenient, and this mode was the preferred one in spite of the requirement of periodically replacing the filament. The source temperature was maintained at 200 °C.
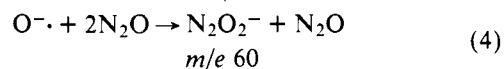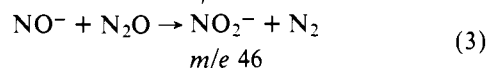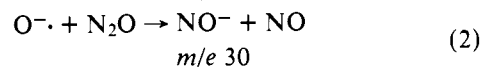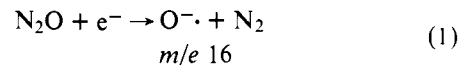
The reagent gases used were obtained from Matheson Gas Products, East Rutherford, N.J., and were of an appropriately high degree of purity: hydrogen, 99.95%; methane, 99.97%; isobutane, 99.5%; propane, 99.99%; nitrous oxide, 99.98%; and He, 99.995%. Ethane (99.99%) was obtained from Phillips Petroleum Co., Bartlesville, Okla. Most of the samples whose spectra were to be measured were obtained from Chemical Samples Co., Columbus, Ohio or Matheson Coleman and Bell, East Rutherford, N.J. As was stated above, wherever possible samples were introduced through the gas chromatograph.

Results

1. Formation of OH⁻ Ion. The hydroxyl ion (OH^-) is formed with high intensity by electron bombardment of a mixture of N_2O and H_2 or CH_4 at total pressures of 1–3 Torr, and the OH^- ions thus produced may be used as the reactant ion in negative chemical ionization. Spectra of mixtures of N_2O–He (2:1), N_2O–H_2–He (1:1:1), and N_2O–CH_4–He (1:1:1) at a total pressure of 3 Torr are given in Table I. Helium is included in the mixtures because the samples used in our chemical ionization experiments were introduced through the GC, and thus He was present in the ionization chamber in significantly large amounts in these experiments. The He probably plays no part in the ionization process except the passive but useful one of slowing the ionizing electrons. Spectra in the absence of He do not differ from those given in Table I. The ion formulas given in column 2 are deduced from the m/e values and from chemical reasonableness, but no independent

evidence confirming the correctness of these choices is available. Some variation in the relative amounts of NO_2^- (m/e 46) and $N_2O_2^-$ (m/e 60) occurs from one day to the next even under nominally identical experimental conditions. Thus factors not under our control are operating. However, this is of no importance for our studies of the formation and reactions of OH^-.

Caledonia[14] summarizes the major ionic reactions occurring in N_2O, namely

$$N_2O + e^- \rightarrow O^- \cdot + N_2 \qquad (1)$$
$$m/e\ 16$$

$$O^- \cdot + N_2O \rightarrow NO^- + NO \qquad (2)$$
$$m/e\ 30$$

$$NO^- + N_2O \rightarrow NO_2^- + N_2 \qquad (3)$$
$$m/e\ 46$$

$$O^- \cdot + 2N_2O \rightarrow N_2O_2^- + N_2O \qquad (4)$$
$$m/e\ 60$$

and our N_2O/He spectrum is understandable in terms of these reactions. The $O^- \cdot$ ion formed as the primary ionization product in (1) reacts so rapidly by (2) that it is not observable under our experimental conditions. The NO^- ion formed in (2) in turn reacts rapidly by (3) to produce NO_2^-, which is stable in N_2O and constitutes the most intense ion in the spectrum. Some NO^- does not react and is observed; some $O^- \cdot$ reacts by the three-body reaction (4) to produce $N_2O_2^-$. The m/e 32 (O_2^-) and m/e 35 ($H_2O \cdot OH^-$) ions observed in the spectrum are produced from air and water impurities in the mass spectrometer.

When H_2 is added to the N_2O/He mixture to produce a 1:1:1 N_2O/H_2/He mixture. OH^- is formed in overwhelming preponderance (rel int = 93%). A small amount of hydrated hydroxyl at m/e 35 is observed, as well as several ions with intensities less than 1%. In a 1:1:1 N_2O/CH_4/He mixture OH^- is again the preponderant ion (rel int = 72%), but in addition a significant amount of an ion with m/e 26 is observed along with ions at m/e 35, 42, and 61 with small abundances. The variations in the relative intensities of the various ions in the N_2O-M_2 and N_2O-CH_4 systems as a function of the relative proportions of N_2O and H_2 or CH_4 are shown in Figures 1 and 2. The total pressure in all mixtures is 3.0 Torr, and this includes a constant pressure of He, namely, 1.0 Torr. The figures also include a plot of the variation of total ion current (in arbitrary units) as a function of reactant proportions. We give in Figure 3 the variations in relative intensities of the ions in the N_2O/H_2/He system as a function of source temperature between source temperatures of 50 and 250 °C.

The Biospect quadrupole mass spectrometer used for these studies is not suitable for obtaining direct evidence about the reaction sequences occurring in these high pressure ionic systems, but Table I and Figures 1–3 serve as a basis for making some tentative hypotheses concerning the reactions occurring. Referring to Figure 1, the growth of OH^- as the H_2 pressure is increased constitutes convincing evidence that OH^- is formed by some kind of reaction involving H_2. All the other ions in the spectrum except m/e 35 show corresponding diminutions in intensities. Two possibilities for this behavior may be advanced: (1) The ions with decreasing intensities (NO_2^-, O_2^-, $N_2O_2^-$, etc.) may be reacting in some way with H_2 to form OH^-, or (2) the H_2 may be reacting with (intercepting) a precursor ion for the diminishing intensity species. The most obvious candidate for this precursor ion is $O^- \cdot$ formed from reaction 1.

If the first possibility above occurs, NO_2^- must be a major reactant ion producing OH^-. Using electron affinities given by Franklin and Harland[2] and heats of formation given by

Table I. Mass Spectra of N_2O Mixtures[a]

| | | Rel int[b] in | | |
| | | N_2O/He (2:1) | $N_2O/H_2/He$ (1:1:1) | $N_2O/CH_4/He$ (1:1:1) |
m/e	Ion			
17	OH^-	3	93	72
26	CN^-			18
30	NO^-	3		
32	O_2^-	13		
35	$H_2O\cdot OH^-$ [c]	2	3	4
37	$^{37}Cl^-$	1		
42	CNO^-			3
46	NO_2^-	62		
60	$N_2O_2^-$	9		
61	$CO_2\cdot OH^-$ or $N_2O\cdot OH^-$			2

[a] Total pressure in ionization chamber was 3.0 Torr. The source temperature was 200 °C. [b] Percentage of total ionization. Ions with intensities less than 1.0% were omitted. [c] Predominantly. Some $^{35}Cl^-$ also present.

Benson[15] we calculate that the production of OH^- from NO_2^- and H_2, namely

$$NO_2^- + H_2 \rightarrow OH^- + HNO \qquad (5)$$
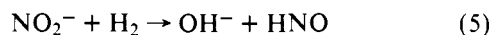
is 38 kcal/mol endothermic. Furthermore, we know of no reports in the literature of the occurrence of this reaction, and we consider its occurrence as quite improbable.

Thus we adopt the second possibility mentioned above as the more likely process involved in the formation of OH^-, and we suggest that the reaction occurring is

$$O^-\cdot + H_2 \rightarrow OH^- + H \qquad (6)$$
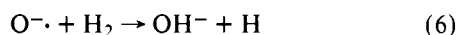
Using the electron affinities from Franklin and Harland and thermochemical values from Benson we calculate that reaction 6 is 7 kcal/mol exothermic, and thus no thermochemical objection to its occurrence exists. However, Parkes[16] has published a value of 0.33×10^{-10} cm^3/mol s for reaction 6 at room temperature, and this value corresponds to a rather slow reaction. By contrast, while we have not made quantitative measurements of rate constants because of limitations of the Biospect mass spectrometer, the quite large intensities of OH^- that we have produced in the N_2O-H_2 system do not seem to be compatible with a slow reaction. To provide some basis of comparison, we measured the total negative ionization in a system consisting of 0.75 Torr of H_2 and 1.25 Torr of N_2O and the total positive ionization in a system consisting of 2.0 Torr of CH_4. Amplifier gains and other experimental conditions were kept as constant as possible between these two measurements. The total ionization obtained in the H_2-N_2O negative ion case was 39 000 arbitrary units compared with 79 000 of the same arbitrary units in the positive CH_4 case. As is well known, the major ions in the CH_4 case are CH_5^+ and $C_2H_5^+$ formed by ion–molecule reactions with rate constants of approximately 1×10^{-9} cm^3/mol s, and since the major ion in the N_2O-H_2 case is OH^- formed by an ion–molecule reaction, we conclude tentatively that the rate constant of the reaction producing OH^- is on the order of 5×10^{-10} cm^3/mol s. As the minimum conclusion from this experiment it seems reasonable to question whether the rate constant involved in the reaction occurring in our system is as small as 0.33×10^{-10} cm^3/mol s.

Another matter to take into account in these considerations is the fact that a reaction competitive with (6) has been reported, namely

$$O^-\cdot + H_2 \rightarrow H_2O + e^- \qquad (7)$$
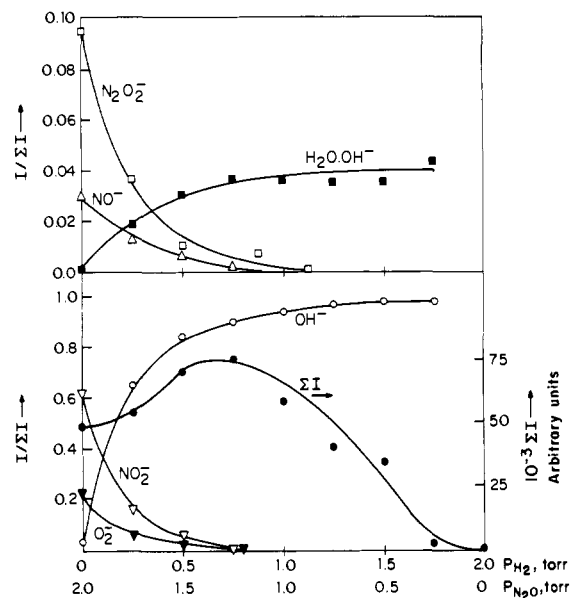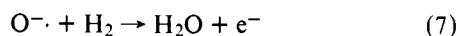
Figure 1. N_2O/H_2 pressure study. 1.0 Torr of He present. Total pressure = 3.0 Torr. Source temperature = 200 °C. The intensity of m/e 35 $(H_2O\cdot OH)^-$ in all figures is corrected for the presence of ^{35}Cl calculated from the measured ^{37}Cl intensity.
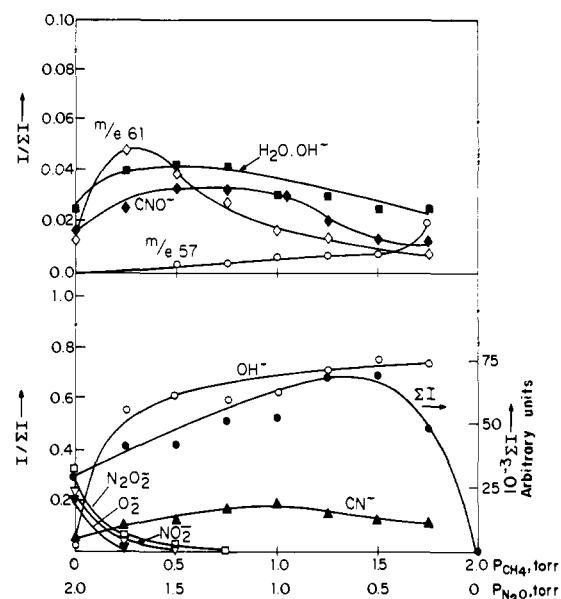
Figure 2. N_2O/CH_4 pressure study. 1.0 Torr of He present. Total pressure = 3.0 Torr. Source temperature = 200 °C.

The exothermicity of reaction 7 may be calculated to be 82 kcal/mol, and Parkes[16] indicates that the rate constant for (7) is 20 times larger than that of (6). It appears that the rate of (7) is fast enough that in flowing afterglow experiments hydrogen is oftentimes used to scavenge unwanted $O^-\cdot$ ions without production of other ions. Obviously, our results as recorded in Table I and Figures 1 and 2 are not in accordance with this kind of behavior.

We suggest that the apparent differences in behavior between the results obtained in our study and those found previously may be ascribed to the fact that our measurements are made at the relatively elevated temperature of 200 °C, whereas Parkes' experiments and flowing afterglow experiments were made at approximately room temperature. To investigate this possibility we measured the effect of temperature on the results obtained in our $N_2O/H_2/He$ system, and the results are represented in Figure 3. The most significant result of this ex-
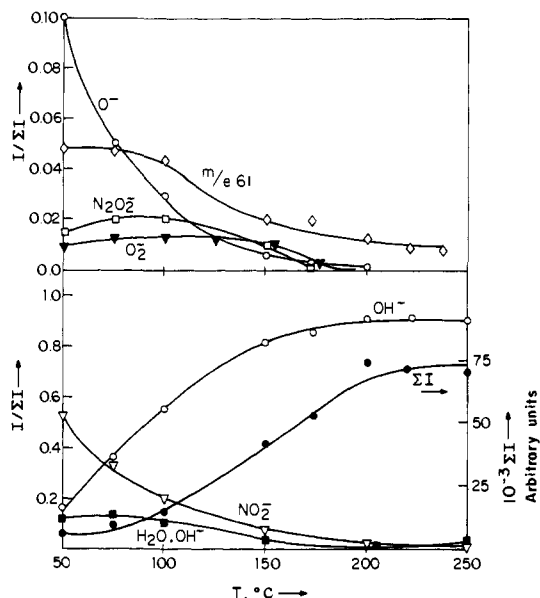
Figure 3. $N_2O/H_2/He$ temperature study. $P_{N_2O} = P_{H_2} = P_{He} = 1.0$ Torr.

periment is that the total ionization starts to decrease with decreasing temperature at about 200 °C, and at 50 °C is only 0.1 times as large as its high temperature value. The relative intensity of OH^- shows a corresponding decline. On the other hand, the intensities of NO_2^- and $O^-\cdot$ increase by a roughly comparable amount as the temperature is lowered. We suggest that these results are explained by the hypothesis that reaction 6 has an activation energy, which results in a positive temperature coefficient. This reaction is a hydrogen atom abstraction reaction, and in neutral systems an activation energy of a few kilocalories per mole for such a reaction is generally encountered. Another aspect of the postulate is that reaction 7 either has no activation energy or an activation energy that is significantly smaller than that involved in reaction 6. It will also be noticed from Figure 3 that significant amounts of $O^-\cdot$ are present in the ionization chamber at low temperature, and the amount diminishes as the temperature increases. We suggest that at low temperatures the reaction of H_2 with $O^-\cdot$ to produce OH^- (reaction 6) is slow enough that it cannot compete with the sum of reactions 2, 3, 4, and 7, and consequently the amount of OH^- produced is small. Furthermore, the data suggest that the rate of consumption of $O^-\cdot$ by (7) is greater than the rate of consumption of $O^-\cdot$ by (2), and thus the total ionization is also small. As the temperature increases the positive temperature coefficient of (6) causes the rate of (6) to exceed that of (2) and (7), and the total ionization and the concentration of OH^- rises and reaches an asymptote when effectively all the $O^-\cdot$ is converted into OH^- by (6).

We suggest that in the $N_2O/CH_4/He$ system represented in Figure 2 similar reactions occur. Parkes[15] gives a value of 1.1×10^{-10} cm^3/mol s for the reaction

$$O^-\cdot + CH_4 \rightarrow OH^- + CH_3 \qquad (8)$$
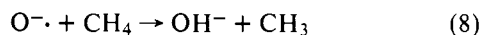
at room temperature, which confirms an earlier flowing afterglow value also obtained at room temperature.[17] In this system also we compare the total ionization with the total ionization in the positive CH_4 system, and we find that the total negative ionization in a system consisting of 1.25 Torr of CH_4 and 0.75 Torr of N_2O is 101 000 arbitrary units, to be compared with 79 000 of the same arbitrary units for the positive total ionization in a system consisting of 2.0 Torr of CH_4. This suggests that the rate constant of the reaction producing OH^- in the negative ion system is roughly comparable with those

of the reactions producing CH_5^+ and $C_2H_5^+$ in the positive system, i.e., approximately 1×10^{-9} cm^3/mol s. Thus the rate constant for reaction 8 seems to be somewhat larger than that found in the previous studies. While we have not carried out a temperature study on the methane system, it is reasonable to think that reaction 8 will have the same magnitude of activation energy and positive temperature coefficient as does reaction 6. Thus a higher reaction rate is to be expected at the higher temperature of our experiments. There is no report of an associative detachment reaction analogous to (7) occurring between $O^-\cdot$ and CH_4, and we have no information as to the extent, if any, to which this reaction occurs. We should mention at this point that total ionization obtained in these nitrous oxide systems is somewhat variable in an unpredictable way, which indicates that experimental factors not yet under our control exist. However, it is generally true that the total intensity occurring in the $N_2O/CH_4/He$ system is greater than that in the $N_2O/H_2/He$ system, and the amount of difference can be as large as the factor of 2. This can result from different amounts of initial ionization (occurrence of reaction 1 in the methane case, or it could result from the occurrence of reaction 7 in the hydrogen case with no analogous reaction in the methane case).

One observes in the $N_2O/CH_4/He$ system ions which were not observed in the $N_2O/H_2/He$ system. We wish here to comment about two of these, namely, those with m/e 26 and 42. One can see from Figure 2 that the m/e 26 ion in particular rises to a significant intensity at about equal amounts of N_2O, CH_4, and He. The only two ions with an m/e value of 26 that are at all reasonable to consider in our system are CN^- and $C_2H_2^-$. Since the identification of the ion with m/e 26 is only of peripheral interest to the main purpose of this study, no significant effort was expended in making an identification. We measured the ratio of the m/e 27 and 26 intensities as carefully as we could, and we obtained the experimental value of 0.015. The calculated ratio for CN^- is 0.0144 and that for $C_2H_2^-$ is 0.0216 using the known ^{13}C and ^{15}N natural abundances. The CN^- formula seems to be indicated. We made experiments with $N_2O/CD_4/He$ mixtures using two separate sources of CD_4 available to us, but in each case there appeared to be significant contamination of the samples with CH_4, which rendered the results of the experiments equivocal. However, to the extent that any conclusion can be drawn, the CN^- formula was supported. Thus we very tentatively assume that the ion we observed with m/e 26 is CN^-. Writing a reaction for the formation of this ion constitutes a considerable problem, and, indeed, we have been thus far unsuccessful in formulating a convincing mechanism involving the neutral entities that we have introduced into our mass spectrometer and the ions that we have determined experimentally to be present. The reaction that we have been able to think of that produces the most stable entities is

$$OH^- + N_2O + CH_4 \rightarrow CN^- + NH_3 + H_2O_2 \qquad (9)$$

and we calculate that it is 5 kcal/mol endothermic and improbable from several points of view. We find that when measurements are made on the system $N_2O/H_2/He$ immediately following measurements on the system $N_2O/CH_4/He$, the m/e 26 ion persists for a finite time after the start of the experiments with hydrogen. Furthermore, the relative intensity of the m/e 26 ion depends upon the magnitude of the ionizing current, which in turn depends upon the filament temperature. It has been suggested to us[18] that CN^- ion could be formed in our system by a reaction such as

$$C^- + N_2O \rightarrow CN^- + NO \qquad (10)$$
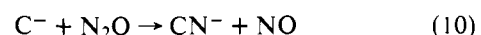
where the C^- is produced on the filament by some kind of mechanism, probably pyrolysis of CH_4, and accelerated into the ionization chamber by the potential between the filament
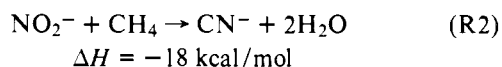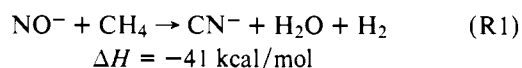
Table II. N_2O/CH_4 NCl Spectra of O, N, and S Containing Compounds[a]

Compounds	Mol wt	$(M - 1)^-$	$(M - 3)^-$	Other ions
Carboxylic acids				
Stearic acid ($C_{17}H_{35}COOH$)	284	283 (100)		
Eicosanoic acid ($C_{19}H_{39}COOH$)	312	311 (100)		
Amino acids				
Leucine $NH_2CH(i\text{-}C_4H_9)COOH$	131	130 (79)	128 (10)	72 (3)
Phenylalanine ($NH_2CH(CH_2C_6H_5)COOH$	165	164 (78)	162 (10)	72 (7)
Alcohols				
1-Pentanol ($i\text{-}C_5H_{11}OH$)	88	87 (66)	85 (34)	
3-Decanol ($3\text{-}C_{10}H_{21}OH$)	158	157 (66)	155 (34)	
2-Methyl-2-pentanol ($CH_3(CH_3)C(OH)C_3H_7$)	102	101 (97)		
3-Ethyl-3-pentanol ($C_2H_5(C_2H_5)C(OH)C_2H_5$)	116	115 (100)		
Cholesterol	386	385 (76)	383 (10)	381 (6), 367 (5), 365 (3)
Thiol				
2-Methyl-2-butanethiol ($CH_3(CH_3)C(SH)C_2H_5$)	104	103 (39)	101 (8)	33 (44), 62 (4), 109 (2)
Ketones				
3-Pentanone	86	85 (97)	83 (3)	
Cycloheptanone	110	109 (90)	107 (8)	
2.4-Pentanedione	100	99 (100)		
Esters				
Methyl acetate	74	73 (92)		59 (8)
Ethyl acetate	88	87 (60)		59 (40)
n-Propyl acetate	102	101 (42)		59 (58)
tert-Pentyl acetate	130			87 (94), 71 (6)
Methyl octanoate	158	157 (67)	155 (2)	31 (23), 143 (7)
Trimethylsilyl eicosanoate	384	383 (10)	381 (1)	311 (89)
Ethers				
Diethyl ether	74			45 (47), 43 (41)
Di-n-butyl ether	130		127 (10)	73 (52), 71 (31)
Trimethylsilyl stearyl alcohol	342			89 (100)
Amines				
tert-Pentylamine	87			42 (97), 61 (1), 82 (2)
1-Hexylamine	101	tabulated separately		
Tri-n-propylamine	143	tabulated separately		

[a] $P_{N_2O} = P_{CH_4} = 1.0$ Torr. The source temperature was 200 °C. GC introduction of sample using He carrier gas. [b] Relative intensity as percentage of total ionization attributed to sample. ^{13}C isotope ion intensities included in the tabulated intensities. Relative intensity above 1% tabulated.

and the ionization chamber. Obviously we have no real evidence that this mechanism is occurring, but we consider it to be the most likely of the possibilities that have come to our attention.

The referee of the original version of this paper expresses the opinion that some reaction of $O^-\cdot$ with N_2O will occur even in the presence of CH_4. He then suggests the following reactions as possible sources of CN^-:

$$NO^- + CH_4 \rightarrow CN^- + H_2O + H_2 \qquad (R1)$$
$$\Delta H = -41 \text{ kcal/mol}$$

$$NO_2^- + CH_4 \rightarrow CN^- + 2H_2O \qquad (R2)$$
$$\Delta H = -18 \text{ kcal/mol}$$

We are glad to present these ideas, although we do not endorse them.

2. Negative Chemical Ionization Spectra of Various Substances. The plasmas produced in the $N_2O/H_2/He$ and $N_2O/CH_4/He$ mixtures contain large amounts of OH^-, which serves as the reactant ion in negative chemical ionization. In the methane mixtures a significant amount of CN^- is also present as was discussed above, but this ion is not very reactive and does not contribute to the chemical ionization. Since the spectrum in the hydrogen system is cleaner in the sense that ions other than OH^- are present in only very small amounts, this reaction mixture is most useful for obtaining the negative

region, and thus it is not as suitable for low molecular weight chemical ionization spectra of low molecular weight compounds which might produce ions in the mass region between 30 and 65. The CH_4 reaction mixture has more ions in this additives, but, as was discussed above, the reaction ion intensity in the CH_4 mixture is oftentimes somewhat greater than that in the hydrogen mixture. In addition the operation of the ion source is more stable than with hydrogen. Thus the methane mixture is a good reactant mixture for higher molecule weight substances, and it was routinely used in this work. The OH^- chemical ionization spectra of a number of substances were investigated in this work. The substances were chosen to represent a variety of classes of compounds, and our purpose was to determine the range of compounds with which OH^- will react in the gas phase, to determine the identities (m/e values) of the ions formed, and, to whatever extent possible, to determine the identity of the reactions producing them.

We list in Table II the spectra obtained with compound types the acidities of which range from relatively strong (carboxylic acids) to relatively weak (ethers and amines). The spectra of the carboxylic acids investigated contained ions of only one type, namely, $(M - 1)^-$, which almost surely is produced by the abstraction of the -COOH proton. The amino acids, alcohols, thiol, ketones, and the carbon alcohol esters generally produced the $(M - 1)^-$ ion with large intensities. The functional groups in these different compound types are either

sufficiently acidic in themselves or sufficiently activate hydrogens in the molecules that abstraction of H^+ by the OH^- occurs readily.

In addition, a number of the compounds in these classes produced $(M - 3)^-$ ions with appreciable intensities. von Ardenne and co-workers[5] have reported the occurrence of $(M - 3)^-$ ions, as have Melton and Rudolph.[19] We assume, along with these workers, that the process producing this ion involves the abstraction of a relatively acidic hydrogen from the molecule to produce $(M - 1)^-$ ions, some of which lose H_2 to form the $(M - 3)^-$ ion. Approximately one third of the ions in the 1-pentanol spectrum are $(M - 3)^-$ ions, which can easily be rationalized by postulating that they are formed by the reaction

$$(C_3H_7CH_2CH_2O)^{*-} \rightarrow C_3H_7CH=CH-O^- + H_2$$

$$C_3H_7CH=CH-O^- \leftrightarrow C_3H_7-CH-CH=O \quad (11)$$
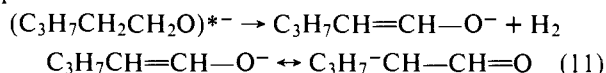
The $(M - 3)^-$ ion is an allyl type of ion and is stabilized by allylic resonance. In the case of the alcohols investigated, copious amounts of $(M - 3)^-$ ions are produced from primary and secondary alcohols, for which H_2 loss to produce allylic-type ions can occur readily; but no $(M - 3)^-$ ions are produced from the two tertiary alcohols, which cannot readily produce allylic-type ions. However, by contrast, the one thiol investigated has a tertiary structure, and it exhibits an $(M - 3)^-$ ion with relative intensity of 8%, and we offer no rationalization for the formation of this ion. Leucine and phenylalanine exhibit $(M - 3)^-$ ions with intensities of 10%, but no $(M - 3)^-$ ion is observed in stearic and eicosanoic acids. Thus the formation of the ion in leucine and phenylalanine suggests that interaction between the carbonyl and amine groups occurs. As a possible mechanism we offer reaction 12. Obviously, the mechanism
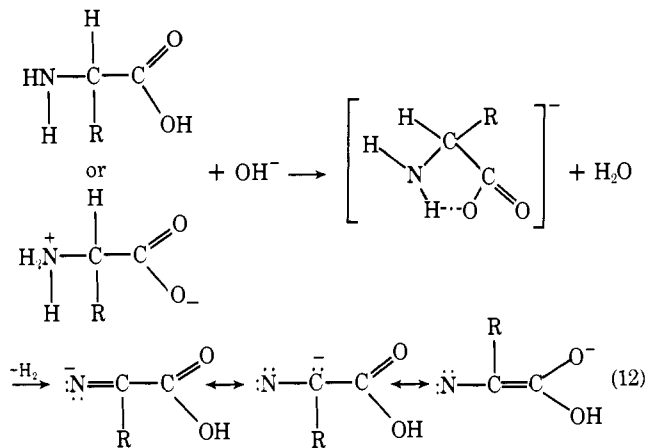
of the formation of $(M - 3)^-$ ions deserves a more detailed investigation.

In the group of compounds being discussed here (amino acids, alcohols, thiol, ketones, and carbon esters) a number of other ions are produced in the various spectra; these are listed in the rightmost column of Table II. Ions with m/e 72 are formed with small intensities in the spectra of leucine and phenylalanine, and this ion corresponds to the loss of one hydrogen atom and the α-carbon side chain. The formation of this ion can be rationalized by postulating that the cyclic intermediate in reaction 12 loses the elements of R–H to produce the ion $[HN=CH-COO]^-$, m/e 72.

Cholesterol exhibits ions at m/e 381, 367, and 365 with small intensities. The m/e 381 ion corresponds to the $(M - 5)^-$ ion, which presumably is formed by a continuation of the mechanism producing $(M - 3)^-$. The other two ions involve loss of the OH function, and their relative intensities depend significantly upon the experimental conditions used for the measurement. We are inclined to the opinion that thermal degradation processes are involved in the formation of these ions. The

thiol investigated, 2-methyl-2-butanethiol, exhibits m/e 33 as the largest peak in its spectrum. This ion is almost surely SH^- formed by a nucleophilic displacement reaction involving OH^- and the thiol molecule. Ions with m/e values of 62 and 109 appear with small intensities in the spectrum of this compound, but we have no ideas about their possible origins.

The behavior of the carbon alcohol esters studied is interesting and perhaps would not have been anticipated beforehand. In the cases of methyl acetate, ethyl acetate, and n-propyl acetate, two ions are formed in each case, namely, $(M - 1)^-$ and m/e 59. In methyl and ethyl acetate m/e 59 almost surely corresponds to the CH_3COO^-, i.e., the acetate anion. However, in n-propyl acetate it can also be n-$C_3H_7O^-$, the propoxy anion. Since CH_3COO^- is formed from the methyl and ethyl esters, we suggest that it is also formed from the propyl ester. The smooth trend in the relative amounts of $(M - 1)^-$ and m/e 59 in the series methyl, ethyl, propyl provides some support for this hypothesis. Most noteworthy in the spectra of methyl and ethyl acetate is the absence of the two ions that one would most expect to be produced by the attack of OH^- on the esters, namely, CH_3O^- (m/e 31) and $C_2H_5O^-$ (m/e 45), respectively. Thus it is clear that gas phase anionic chemistry of esters differs meaningfully from condensed phase chemistry. We have no evidence for the location of the H^+ removed from the molecules, but conventional wisdom is that the proton would be removed from methyl or methylene group α to the carbonyl. The m/e 59 is at least nominally produced by nucleophilic attack of the OH^- on the alcohol alkyl group, which results in the displacement of CH_3COO^-. We can provide no rationalization of the variation of the relative intensities of $(M - 1)^-$ and m/e 59 in the three esters.

The spectrum of $tert$-pentyl acetate bears no relationship to those of the first three esters. No $(M - 1)^-$ at all is observed, and almost all of the ionization is carried by the m/e 87 ion. We suggest that this is the $(CH_3)_2C_2H_5CO^-$ ion, and the most straightforward mechanism for its formation involves nucleophilic attack of OH^- on the carbonyl carbon, resulting in displacement of t-$C_5H_{11}O^-$. However, with this mechanism the absence $(M - 1)^-$ ions is puzzling, for there is little reason to expect that abstraction of a proton from the acetate methyl would not occur. Thus it is possible that it does occur, but that the $(M - 1)^-$ ion produced rapidly decomposes to give t-$C_5H_{11}O^- + CH_2=C=O$ (ketene). Brauman and Blair[20] find that in the gas phase the acidities of alcohols are in the order t-BuOH > i-PrOH > C_2H_5OH > CH_3OH, which implies that the energies of the corresponding alkoxy anions lie in the opposite order. The extensive formation of t-$C_5H_{11}O^-$ from $tert$-pentyl acetate may be the result of the low energy of the ion.

In methyl octanoate the intensity at $(M - 1)^-$ is comparable with the intensities at $(M - 1)^-$ in methyl, ethyl, and propyl acetates. However, in the octanoate about 30% of the ionization appears as CH_3O^- (m/e 31), presumably formed by displacement by attack of OH^- on the carbonyl. The octanoate anion (m/e 143) is formed in appreciably smaller quantities than the acetate anion in methyl, ethyl, and propyl acetates. We cannot rationalize these differences in behavior. Obviously, the gas phase anionic chemistry of esters warrants a detailed study.

The amount of fragmentation occurring in the OH^- chemical ionization of the compounds considered so far is generally relatively small ($tert$-pentyl acetate being a notable exception), and the spectra are quite simple. We do not at this time wish to make an extensive comparison of the amount and kind of fragmentation that occurs in positive and negative chemical ionization, but a few comparisons are of use. The amount of fragmentation occurring in negative chemical ionization compounds so far considered seems subjectively to us to be at least not greater than that encountered in positive

chemical ionization, and probably less. In the case of carboxylic acids the amount of fragmentation is slightly less with OH⁻ chemical ionization than with methane or isobutane positive chemical ionization,[21] although it must be noted that the amount of fragmentation in the positive ion case is quite small. In the two amino acids investigated the fragmentation in the negative ion case is meaningfully less than that in methane positive chemical ionization.[22] In alcohols the negative chemical ionization is distinctly different from positive chemical ionization in that loss of the OH group occurs readily in positive chemical ionization, especially with tertiary alcohols.[23] Similarly the SH group is very easily lost from 2-methyl-2-butanethiol in positive chemical ionization.[24] Ketones generally exhibit little fragmentation in positive chemical ionization,[25] and thus the behavior in the two modes of chemical ionization is similar. The amount of fragmentation in positive or negative chemical ionization in the esters studied is roughly the same,[26] any difference lying on the side of less fragmentation in the negative method.

We now consider the negative chemical ionization of a group of compounds for which the $(M - 1)^-$ ions are either absent or produced in only small amounts. The first of these is a trimethylsilyl ester, namely, TMS eicosanoate, the spectrum of which is given in Table II. This compound was examined because it constitutes an example of a type of derivative commonly used in mass spectrometry and GC/MS to enhance volatility. The $(M - 1)^-$ intensity is relatively small (10%), and the most intense ion is the eicosanoate ion with m/e 311 (relative intensity of 89%). The production of the acid anion in this molecule is greater than in methyl and ethyl acetates and particularly in methyl octanoate, and we suggest that the greater electropositivity of silicon compared with that of carbon enhances the amount of nucleophilic attack by hydroxyl ion on silicon to displace the acid anion. Although the silyl ester thus undergoes extensive fragmentation in OH⁻ chemical ionization, the spectrum produced is still of utility in applied mass spectrometry, for the most intense ion in the spectrum contains the information about the identity of the carboxylic acid portion of the silyl ester. Thus a carboxylic acid that was protected with the trimethylsilyl group to enhance volatility could still be identified from this type of spectrum.

Ethers and amines are very weak acids, and the OH⁻ chemical ionizations of examples of these compound types are given Table II. The oxygen in diethyl ether is not sufficiently electronegative to activate the hydrogen on neighboring methylene groups to the point where abstraction of protons from these groups by OH⁻ can occur. Thus the only ions of significant intensity produced from this compound are displacement ions resulting from nucleophilic attack at the methylene carbon, namely, an ion with m/e 45 (probably $C_2H_5O^-$) and m/e 43 (possibly $C_2H_3O^-$). We assume that the latter ion is formed from the former by loss of H_2 in a reaction analogous to that postulated to be involved in the formation of $(M - 3)^-$ ions as discussed above.

In di-n-butyl ether the ions $C_4H_9O^-$ and $C_4H_7O^-$ (m/e 73 and 71, respectively) are the dominant ions in the spectrum, but in addition 10% of the ionization occurs as the $(M - 3)^-$ ion. If it be assumed that this ion is produced by the postulated mechanism of proton abstraction followed by H_2 loss, the inference to be drawn from this result is that the hydrogens in butyl ether are slightly more acidic than those in ethyl ether. The third ether investigated is the TMS ether of stearyl alcohol, and we wished to investigate whether OH⁻ chemical ionization would be useful for compounds containing hydroxyl groups protected with a trimethylsilyl group to enhance volatility. One observes from Table II that all of the ionization in this compound occurs at m/e 89, which must correspond to the ion $(CH_3)_3SiO^-$. The exclusive formation of this ion must be taken as a manifestation of the well-recognized strength of

Si–O bonds and the relatively high acidity of RSiO–H bonds. Thus we must conclude that nucleophilic attack by OH⁻ occurs exclusively at the methylene group α to the oxygen, which results in the elimination of the observed ion. We point out that this behavior seems to be somewhat contrary to that observed in methyl octanoate and trimethylsilyl eicosanoate, for in this pair of compounds a nucleophilic attack seems to occur more extensively at silicon than at carbon. Since major factors involved in determining the behavior of organic silicon compounds are the relatively high electropositivity and d-orbital bonding capabilities (which, among other things, result in particularly strong Si–O bonds), it is conceivable that these factors would work in opposite directions in different cases producing the different kinds of behavior that we seem to observe here. In any event, the experimental result is that the spectrum of trimethylsilylated stearyl alcohol contains no information concerning the identity of the alcohol, and thus OH⁻ chemical ionization does not appear to be very useful for the analysis of TMS-derivatized alcohols.

The last compound type given in Table II is amines, and they were investigated out of curiosity concerning the acidic chemistry of materials normally considered to be quite basic. The results are not at all understandable, but they will be included here for the sake of completeness. We also mention that the amines used were not very pure, and the GC column used for their introduction was not very suitable for separating this difficult type of compound. Thus there is a higher degree of possibility that the spectra obtained contained impurity ions than is the case with other compounds investigated in this work. The spectrum of *tert*-pentylamine is very simple, and it is given in Table II. It consists essentially of one ion, namely, that with m/e 42 (97% of the amine ionization). A possible structure for this ion is

$$\begin{array}{c} CH_2\!-\!CH_2 \\ \diagdown\diagup \\ \ddot{N}\!\cdot\!^- \end{array}$$
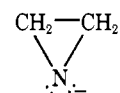
That is, it is the anion comprising the conjugate base of ethylenimine (aziridine). The formation of this ion as virtually the sole product from *tert*-pentylamine is remarkable, and it involves many rearrangements in a mechanism that we cannot even guess.

The spectra of the other two amines investigated, namely, 1-hexylamine and tri-n-propylamine are complex enough that they are given separately in Table III. We point out that ions at m/e 42 are also produced in these two compounds, copiously in the case of 1-hexylamine and in a smaller amount in tri-n-propylamine. The hexylamine exhibits a strong intensity at m/e 61, and tri-n-propylamine exhibits strong intensities at m/e 61 and 59. Strong ionization in the vicinity of the molecular weight is observed in neither compound. The formation of ions with odd m/e values in the spectra of a compound containing one nitrogen atom is unexpected. The m/e values observed cannot correspond to hydrocarbon fragments formed by loss of the nitrogen atom, and thus the only possibilities we can think of are that the ions either are radical anions from the amines or result from impurities. We do not understand the chemistry involved in the formation of the spectra, and it is quite clear that further, detailed investigation of the anionic chemistry of this type of compound is of interest.

As part of our effort to determine the range of applicability of OH⁻ chemical ionization, we undertook a set of experiments to see whether OH⁻ would react with aromatics, taken as an example of a very weakly acidic compound type. Reactions did occur, and they were novel enough and interesting enough that a relatively extensive investigation of aromatics was made. In addition the investigation was extended to another very weakly acidic compound type, namely, olefins. Interesting reactions occurred with this class of compound also. Further investiga-

Table III. N_2O/CH_4 NCl Spectra of Two Amines[a]

	Relative intensity	
m/e	$1\text{-}C_6H_{13}NH_2$ (mol wt 101)	$(n\text{-}C_3H_7)_3N$ (mol wt 143)
42	37	11
44	3	
45	3	9
49	1	
52		2
59		23
61	28	19
66	1	3
67	1	2
72		3
93		1
94	4	
96	4	3
98	7	
99	1	1
101		11
112	2	

[a] Conditions and notation same as in Table II.

tions involving several naphthenes and paraffins gave the result that no reaction occurred, and we conclude that these compound types are insufficiently acidic to react with OH^-.

Table IV presents the OH^- chemical ionization spectra of the aromatics investigated. Benzene was also investigated, but it was not ionized by OH^-. We conclude that the ring hydrogens are insufficiently acidic to be removed by OH^-, and thus the ionization occurring in the compounds listed in Table IV must involve proton removal from side chains. The compounds listed in Table IV with the simplest spectra are diphenylmethane and triphenylmethane, both of which have spectra consisting solely of the $(M - 1)^-$ ion. This is easily understandable in terms of the well-known relatively high acidity of these two compounds. The other aromatics studied exhibit more complicated spectra, and in particular ions with m/e values higher than the molecular weights of the compounds are observed. In a number of cases the m/e values observed bear fixed relations to the molecular weights; specifically, $(M + 25)^-$ and/or $(M + 43)^-$ ions are frequently observed. These ions were consistently produced in all experiments. We mention again that the compounds under investigation were introduced through the gas chromatograph, and in the case of these aromatics, separation from possible impurities would be expected to occur easily. Thus we reject as quite unlikely the possibility that the higher mass ions result from impurities. They could result from the reactions of ions produced from the additive with molecules of the additive; that is, they could result from ion–molecule reactions in the additive; but experiments showed that the relative intensities of the higher mass ions did not vary

significantly with the amount of additive introduced into the mass spectrometer. Ion–molecule reactions involving two molecules of additive should manifest themselves in relative intensities dependent upon additive pressure. The third possibility, and the one we think is most likely, is that these higher mass ions are produced by the reactions of ions formed from the additive with a component of the reactant mixture. Specifically, we believe that this component is nitrous oxide.

In the case of toluene 20% of the ionization occurs at m/e 91, which comprises the $(M - 1)^-$ ion and is almost surely the benzyl anion. Brauman and Blair[20] have previously reported the formation of benzyl anion by the gas phase reaction of OH^- with toluene. Seventy-four percent of the ionization occurs at m/e 117, which corresponds to $(M + 25)^-$. Reference to Table I shows that the $N_2O/CH_4/He$ reactant mixture contains no ion with m/e 25, and thus $(M + 25)^-$ ion cannot be explained by simple addition of a reactant ion to the toluene molecule. However, $(M + 25)^-$ ions can be produced by the addition of $(M - 1)^-$ ions to N_2O (mol wt = 44) followed by the loss of H_2O (mol wt = 18), i.e., $(M + 25)^- = (M - 1 + 44 - 18)^-$. When the experiment is carried out with toluene-d_8 the same type of spectrum is observed, but in this case the m/e values are translated to 98 for $(M - D)^-$ and 122 as the analogue of m/e 117. Thus the addition ion can be accounted for in terms of the addition of 44 mass units to the $(M - D)^-$ ion followed by the loss of 20 mass units, i.e., D_2O. In the compounds ethylbenzene, isopropylbenzene, n-butylbenzene, $tert$-butylbenzene, and 1,4-diethylbenzene ions with m/e values corresponding to $(M + 43)^-$ ions are formed, and we feel rather secure in postulating that these ions are indeed the addition ions formed by the association of $(M - 1)^-$ ions with N_2O. Decomposition of this association ion involving loss of water produces the $(M + 25)^-$ ion observed in toluene, but, as we shall see, other decompositions can also occur.

Returning to the spectrum of toluene, it is of interest to consider the reaction producing the $(M + 25)^-$ ion and to consider possible structures for it. We use as the working hypothesis the idea that the ion is formed by the nucleophilic attack of $(M - 1)^-$ ion on N_2O. The mechanisms and structures that we shall give here and in the following are speculations whose only direct tie to experiment is that the ions involved will have the observed m/e values. Thus the speculation must be looked upon as very tentative and subject to revision, but we feel that the chemistry occurring in these systems is sufficiently novel to warrant attempts at rationalization. Pauling[27] writes nitrous oxide as a resonance hybrid of the two major structures

$$^-:\ddot{N}=N^+=\ddot{O}: \longleftrightarrow :N\equiv\overset{+}{N}-\ddot{O}:^- \qquad (13)$$

Obviously nucleophilic attack can occur at the central atom, and thus we suggest reactions 14a and 14b. While the structure written for the $(M + 25)^-$ ion is perhaps not highly attractive, it is not impossible because we are dealing with a relatively high

Table IV. N_2O/CH_4 NCl Spectra of Aromatics[a]

Compounds	Mol wt	$(M - 1)^-$	$(M + 25)^-$	$(M + 43)^-$	Other ions
				Mass and rel int m/e (RI)	
Toluene	92	91 (21)	117 (79)		
Toluene-d_8	100	98 (22)	122 (78)		
Ethylbenzene	106	105 (30)	131 (5)	149 (18)	117 (27), 119 (2), 147 (13)
Isopropylbenzene	120	119 (46)		163 (44)	143 (10)
n-Butylbenzene	134	133 (36)		177 (13)	131 (46)
$tert$-Butylbenzene	134			177 (48)	149 (10), 144 (1), 143 (13), 131 (5), 93 (3), 81 (15)
1,4-Diethylbenzene	134	133 (12)		177 (17)	131 (62), 147 (2), 175 (5)
Diphenylmethane	168	167 (100)			
Triphenylmethane	244	243 (100)			

[a] Conditions and notation same as in Table II.

$$\text{(14a)}$$

$$(M + 43)^-$$

$$\longrightarrow \quad \updownarrow \quad + \ H_2O \quad (14b)$$

$$(M + 25)^-$$

energy system on the one hand, and, on the other, the energy of the ion will be somewhat reduced by the resonance as written. However, we can write another mechanism and structure, which, while more complex, is also chemically somewhat more appealing (reaction 15). The attractiveness of this mechanism is the large amount of resonance in the structure written for the $(M + 25)^-$ ion (indazole anion).

$$\xrightarrow{-H_2O} \qquad \equiv \qquad (15)$$

$$(M + 25)^-$$
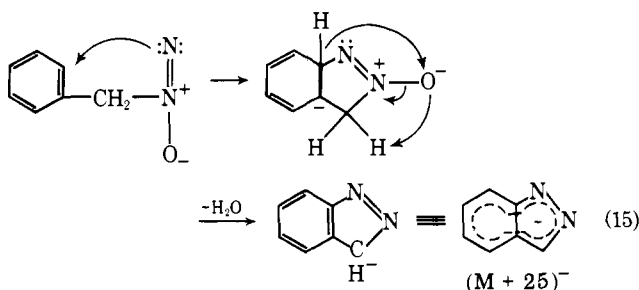
In the case of ethylbenzene, one sees the $(M - 1)^-$ ion in about the same amount as that found in toluene, but the $(M + 25)^-$ intensity is much smaller. Compensating for this is the presence in significant amounts of the $(M + 43)^-$ ion, an ion with m/e 117, which corresponds to the $(M + 25)^-$ ion in toluene, and an ion with m/e 147. We can rationalize the formation of all of these ions in terms of our hypothesis of a nucleophilic attack of the $(M - 1)^-$ ion on N_2O (reaction 16).

$$(16)$$
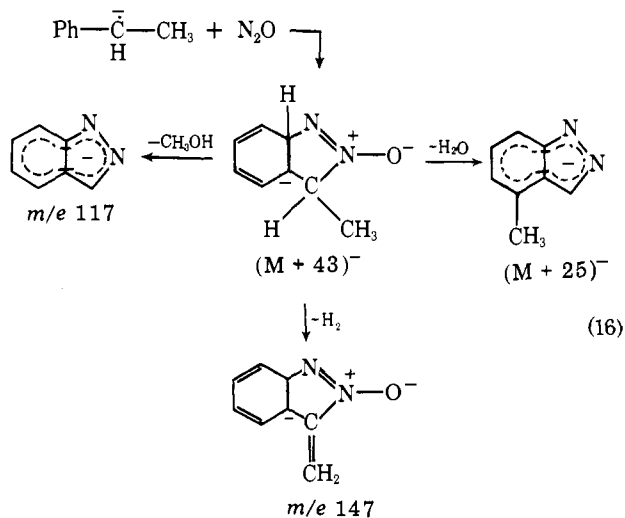
$$m/e\ 147$$

The portion of the mechanism suggested for the formation of the m/e 147 ion is an extension of the general idea, but as we have seen previously, loss of H_2 to permit a more extensive resonance apparently occurs readily in anions.

In isopropylbenzene the same ideas apply. The intensity of the $(M + 43)^-$ has increased to 44%, and the only fragmentation occurring in this ion produces the m/e 143 ion in a relatively small abundance. We suggest that a possible reaction is

$$m/e\ 143$$

$$(17)$$
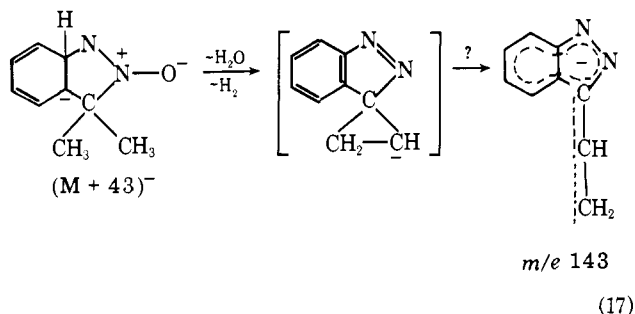
Comparing the spectra of toluene, ethylbenzene, and isopropylbenzene, we see that as the amount of methyl substitution on the benzyl carbon increases the $(M - 1)^-$ intensity increases, the $(M + 43)^-$ intensity increases, and the intensities of ions which can be formed by fragmentation of the $(M + 43)^-$ ions decrease. This behavior is consistent with the idea that the energies of benzyl anions decrease in the order $C_6H_5CH_2^- > C_6H_5CH^-CH_3 > C_6H_5C^-(CH_3)_2$. The more energetic the ion, the more extensively it reacts with N_2O providing an inverse correlation between ionic energy and the intensity of $(M - 1)^-$. The $(M + 43)^-$ ion produced by this reaction undergoes larger amounts of fragmentation for the more energetic $(M - 1)^-$ ions, which gives rise to the observed correlation between intensities of $(M + 43)^-$ and reactant ion energies and between the fragment ion intensities and reactant ion energies.

Brauman and Blair[20] found that the energies of alkoxy anions decrease as the amount of substitution on the alkyl group increases, presumably because of a stabilizing interaction of the substituents with the charge, and the same phenomenon appears to be operative in the case of substituted benzyl ion.

In the case of n-butylbenzene the most intense of the three ions in the spectrum is that with m/e 131, which corresponds to $(M - 3)^-$. A small amount of the ionization appears at $(M + 43)^-$, but one concludes that a fraction of the $(M - 1)^-$ ions initially formed by proton abstraction can stabilize themselves by loss of H_2 in a reaction that occurs more rapidly than reaction of $(M - 1)^-$ with N_2O.

The spectrum of $tert$-butylbenzene is somewhat different from those of the preceding compounds. First, we are surprised that any ionization of $tert$-butylbenzene occurs at all, for it contains no benzylic hydrogens. It exhibits no $(M - 1)^-$ ions, but the $(M + 43)^-$ intensity is quite high, which is not in accordance with the correlations observed in the other aromatics discussed. However, we can postulate a mechanism for the formation of two of the other ions observed in the spectrum in terms of fragmentation of the $(M + 43)^-$ ion. This is given in Scheme I. Obviously the cyclization postulated in this scheme is completely speculative, but one is tempted to make the postulate by the large energy stabilization produced by the resonance in the 3-phenylpyrazole and 3-methylpyrazole ions. The resonance in the pyrazole anion should be comparable with that in the cyclopentadienyl anion, which is isoelectronic.

The $tert$-butylbenzene spectrum also contains several other ions. The ion of modest intensity at m/e 149 comprises the $(M - 1 + 44 - 28)^-$ ion, which could be formed by the loss of N_2 from the $(M + 43)^-$ ion. An ion of small intensity appears at m/e 131, and this is the $(M - 3)^-$ ion, presumably formed by loss of H_2 from $(M - 1)^-$. Ions with small intensity appear with m/e 144 and 93, and we offer no speculations on their mode of formation.

Table V. N_2O/CH_4 NCl Spectra of Unsaturated Hydrocarbons[a]

Compounds	Mol wt	$(M - 1)^-$	$(M + 25)^-$	$(M + 43)^-$	Other ions
2-Decene	140		165 (68)	183 (17)	137 (15)
4-Decene	140		165 (11)	183 (59)	137 (23), 135 (5)
2-Methyl-4-octene	126		151 (47)	169 (36)	123 (13), 121 (2)
1-Octene	112		137 (76)	155 (7)	135 (5), 109 (10), 107 (2)
2-Octene	112		137 (73)	155 (6)	135 (5), 109 (12), 107 (2)
1,7-Octadiene	110	109 (9)	135 (56)	153 (11)	107 (14), 123 (10)
1,4-Octadiene	110	109 (81)	135 (8)		107 (10)
1-Octyne	110	109 (35)	135 (1)		26 (33), 82 (9), 94 (7), 107 (11), 125 (2)

[a] Conditions and notation same as in Table II.

Scheme I

$$(18)$$

m/e 81 =
3-methylpyrazole anion

m/e 143 =
3-phenylpyrazole anion
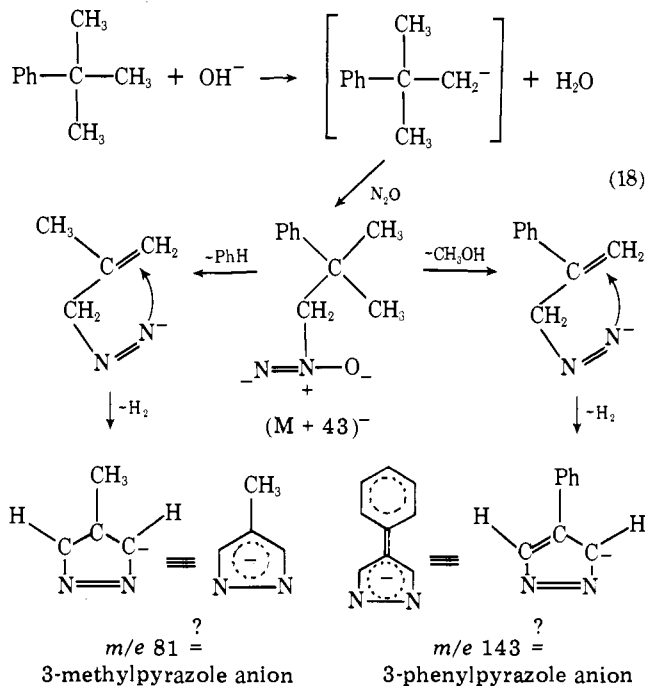
The spectrum of 1,4-diethylbenzene follows the same general pattern as the other aromatics investigated. Ions of moderate intensities appear at $(M - 1)^-$ and $(M + 43)^-$, but the most intense ion in the spectrum is that with m/e 131, which comprises $(M - 3)^-$. Since no $(M - 3)^-$ ion is produced from ethylbenzene, it seems reasonable to think that the H_2 lost comes from the second ethyl group, i.e.

$$(M - 3)^-$$
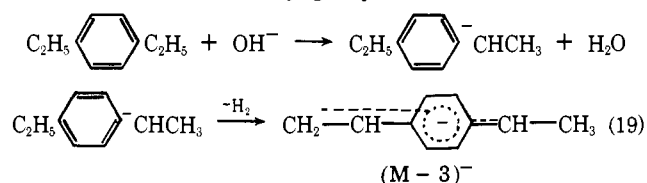
This is an interesting illustration of the previously noted tendency of gaseous carbanions to lose H_2 if a lower energy structure can be thus produced. The fact that the loss occurs at a considerable distance from the primary center of ionization is also of interest.

In principle spectra such as those listed in Table IV could be used for analytical purposes; that is to say, analyses of aromatics could be made using OH^- chemical ionization mass spectrometry, but in actuality both electron ionization and chemical ionization methods are quite adequate, and on the basis of the data given in Table IV we can envisage no significant advantage of OH^- chemical ionization.

The interesting results obtained with aromatics prompted us to investigate the ionization of olefins in our system. Bohme and Young[28] have investigated the reactions of light olefins with OH^- at room temperature in a flowing afterglow apparatus. They found that C_3 through C_4 olefins reacted to produce $(M - 1)^-$ ions at rates close to collision rate. Some of the $(M - 1)^-$ ions thus formed reacted with the O_2 which served as a reactant gas to produce various oxygenated anions. We give in Table V the spectra produced in our reaction system of five monoolefins, two diolefins, and one alkyne. As was the case with the aromatics, many ions with m/e values higher than the molecular weights of the compounds are observed, and in particular one observes $(M + 25)^-$ and $(M + 43)^-$ ions. We make the same postulate as with the aromatics; namely, these ions are produced by the reaction of $(M - 1)^-$ ions with N_2O. None of the monoolefins exhibit an $(M - 1)^-$ ion, and all of them exhibit $(M + 25)^-$ ions. In three of the monoolefins the $(M + 25)^-$ ion is the most intense in the spectrum. We suggest that an allylic proton is abstracted to form $(M - 1)^-$, which attacks N_2O to form $(M + 43)^-$, some of which can lose water and possibly cyclize to form $(M + 25)^-$. The structure we tentatively suggest for the $(M + 25)^-$ ion formed from 1-octene is

m/e 137
$(M + 25)^-$
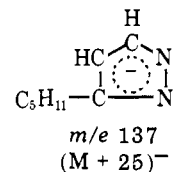
In the discussion of the spectra of aromatics we suggested that the relative intensities of $(M - 1)^-$, $(M + 25)^-$, and $(M + 43)^-$ were related to the energy of the $(M - 1)^-$ ion. If this be true, we can interpret the spectra given in Tables IV and V to mean that the $(M - 1)^-$ ions produced from monoolefins are somewhat higher in energy than those produced from the aromatics listed in Table IV (possibly excepting *tert*-butylbenzene). We might also conclude from the larger amount of $(M + 43)^-$ produced in 4-decene than in 2-decene that the $(M - 1)^-$ ion produced from 4-decene is of lower energy. The allyl anions formed from 4-decene are substituted by two alkyl groups; on the other hand, the allyl ions produced by proton abstraction from the 1-methyl group in 2-decene are only monosubstituted. The other ions produced from the monoolefins are almost completely ions produced by loss of one or more H_2 molecules from the ions we have been considering. Thus, for example, in 2-decene and 4-decene, $(M - 3)^-$ ions are formed with significant intensity, and $(M - 5)^-$ ions are formed with small intensity.

The spectra of the octadienes provide a striking manifestation of the postulated effect of the energy of the $(M - 1)^-$ ion on the extent to which it associates with N_2O. The anion produced from 1,4-octadiene will be much more extensively

Table VI. N_2O NCI Spectra of Aromatics[a]

Compound	Mol wt	$(M - H)^-$	$(M - H + O)^-$	$(M - R + O)^-$	$(M + 25)^-$	$(M + 43)^-$	Other ions
Toluene	92		107 (30)		117 (70)		
Isopropylbenz-ene	120	119 (11)	135 (53)	93 (21)[b]		163 (15)	
tert-Butylben-zene	134		149 (34)	93 (14)[c]		177 (26)	143 (14), 132 (5), 121 (3), 117 (4)
Diphenyl-methane	168	167 (30)	183 (6)	107 (14)[d]			118 (6), 119 (11), 121 (5), 147 (17), 165 (6), 181 (5)

[a] $P_{N_2O} = 2$ Torr. Other conditions are the same as in Table II. [b] $R = C_3H_7$. [c] $R = C_4H_9$. [d] $R = C_6H_5$.

conjugated and of lower energy than that formed from 1,7-octadiene, and for the 1,4 compound only 8% of the octadiene ionization appears as an ion involving N_2O. In addition, both of the octadienes show more $(M - 1)^-$ ion intensity than any of the monoolefins, which is also in accordance with one's expectations based on energy considerations.

The spectrum of 1-octyne contains ions with which we are familiar, namely, $(M - 1)^-$, $(M - 3)^-$, and $(M + 25)^-$. It also contains ions at m/e 94 and 82, the origins of which we cannot explain. Finally, 33% of the ionization of the octyne occurs as the m/e 26 ion. As we discussed previously, the N_2O/CH_4 system contains m/e 26 ions with appreciable intensity, and we think that these are CN^- ions. The intensity of m/e 26 given in Table V are ions formed in addition to these background ions, and we think they are indeed formed from the octyne additive. Goode and Jennings[29] report persuasive evidence for the existence of the $C_2H_2^-$ ion, and they postulate that the ion has the structure $CH_2=C^-$. There seems to be no evidence that $C_2H_2^-$ ion with the acetylene structure is formed. We cannot envisage a reasonable mechanism for the formation of a $C_2H_2^-$ ion with either of these structures from 1-octyne, and we think it wise to seeK further evidence about the formation of this ion by OH^- chemical ionization before speculating on its mode of formation.

We point out that none of the olefins exhibit any ions produced by fragmentation of the carbon chain. This is in marked contrast to the CH_4 positive chemical ionization of these compounds in which extensive carbon-chain fragmentation occurs.[30] For the acyclic monoolefins in particular the $(M + 1)^+$ and $(M - 1)^+$ ions comprise only a small percentage of the total ionization. It is quite possible that the smaller amount of fragmentation observed in the negative ion case will be of particular utility for the analysis of olefins.

While the main emphasis of this investigation has been on obtaining qualitative knowledge about the reactions of OH^- ion with organic compounds, a limited investigation of the quantitative sensitivity of the method was made as a matter of interest. It was pointed out earlier in the paper that the total ionization in the $N_2O/CH_4/He$ negative ion system was 101 000 arbitrary units, which is to be compared with 79 000 arbitrary units for the positive total ionization in CH_4. The intensity of OH^- in the negative ion system was approximately equal to the sum of the intensities of CH_5^+, H_3O^+, and $C_2H_5^+$ in the positive system. To provide a rough measure of the sensitivity of the negative ion system, a selected ion monitoring GC/MS technique was used. We determined the minimum detectable amount of 2,4-pentanedione using the $(M - 1)^-$ ion at m/e 99. We were able to detect 300 pg of 2,4-pentanedione injected on column with $S/N = 4$ and with the GC peak width at half-height of 10 s. In these measurements the ion detector electron multiplier was operated at the sensitivity used for obtaining spectra in the scanning mode (1900 V). We estimate that by increasing the voltage applied to the multiplier the sensitivity of the detection system could have been increased by a factor of 5 to 10 with a corresponding decrease in the minimum amount of material detectable. This sensitivity is

comparable to that which we can obtain in positive ion chemical ionization.

3. Negative Chemical Ionization Spectra Using N_2O/He. We have assumed in the preceding that the spectra observed using the $N_2O/H_2/He$ and $N_2O/CH_4/He$ systems are produced by OH^- as reactant. We feel that this assumption is reasonable given the experimental conditions, but further experiments to verify its validity are desirable. The OH^- is formed by the reaction of $O^-\cdot$ from N_2O with H_2 or CH_4, where the latter two compounds are present in amounts approximately equal to the amount of N_2O. In a typical chemical ionization experiment the additive substance is present in an amount much smaller than the amount of either N_2O or H_2/CH_4, and in the absence of complicating circumstances, only the OH^- ion is present in large enough concentrations to react with the additive to a sufficient extent to produce the observed spectra. However, a possible complicating factor might be that the rate constant for the reaction of $O^-\cdot$ with the additive is several orders of magnitude higher than the rate constant for the reaction of $O^-\cdot$ with H_2 or CH_4. There is no evidence that this is the case, and we consider it to be unlikely a priori, but an experiment to elucidate the point is still desirable. The experiment that we have undertaken is to obtain the spectra of several aromatics and several alcohols using a mixture of N_2O and He as the reactant. The spectrum produced by this mixture is shown in Table I, and consists primarily of NO_2^-, O_2^-, and $N_2O_2^-$. As we pointed out earlier, presumably all of these entities are formed from O^- as a primordial precursor which reacts too rapidly to be observed.

The spectra produced from aromatics are given in Table VI, and those from alcohols are given in Table VII. If we compare the results on aromatics in Table VI with the results produced in a N_2O-CH_4 mixture as given in Table IV, we see significant differences. In the case of toluene the spectrum with CH_4 present contains 21% of the ionization at $(M - 1)^-$, but this ion is not produced when CH_4 is not present, and in its place the $(M - H + O)^-$ ion is formed. $(M + 25)^-$ ions are formed in about the same amounts in both systems. Of most importance for our considerations here is the fact that the chemical ionization reactions occurring in the presence and absence of CH_4 are significantly different and, in particular, we conclude that the major reactant species in N_2O without methane (N_2O alone) is not producing more than at the most a few percent of the ions observed in the presence of methane. To elaborate, our sensitivity is such that an intensity of 1% or less at m/e 107 (the $M - H + O)^-$ ion) would have been observable in the N_2O-CH_4 reaction system, and none was observed. We do not know the identity of the reactant ion in the N_2O alone system, but Jennings and co-workers[31] report that $O^-\cdot$ will react with aromatics to produce $(M - H + O)^-$ ions. However, it must be kept in mind that no $O^-\cdot$ ions are observed in our spectrum of N_2O, although we think that they are initially present and react rapidly. Thus it is quite possible that they could react with additive molecules.

If we compare the spectra of isopropylbenzene and diphenylmethane in Tables IV and VI we again see major dif-

Table VII. N_2O NCl Spectra of Alcohols[a]

				Mass and rel int m/e (RI)	
Compound	Mol wt	$(M - 1)^-$	$(M - 3)^-$		Other ions
1-Pentanol	88	87 (17)	85 (83)		
3-Decanol	158		155 (16)		127 (51), 57 (34)
2-Decanol	158		155 (9)		141 (12), 43 (79)
2-Methyl-2-pentanol	102	101 (22)			85 (30), 83 (14), 57 (35)
3-Ethyl-3-pentanol	116	115 (19)	113 (1)		85 (58), 83 (10), 74 (1), 62 (10)
3-Methyl-3-hexanol	116	115 (13)			111 (4), 101 (14), 99 (10), 85 (26), 71 (32)

[a] Conditions and notations same as in Table VI.

Table VIII. Mass Spectra of $N_2O/RH/He$ Mixtures[a]

		Rel int[b] for RH =		
m/e	Ion	C_2H_6	C_3H_8	i-C_4H_{10}
17	OH^-	56	25	23
25	C_2H^-	7	5	3
26	CN^-, $C_2H_2^-$	9	8	9
32	O_2^-	1	2	3
35	$^{35}Cl^-$, $H_2O\cdot OH^-$	4	6	8
37	$^{37}Cl^-$		1	
41	$C_3H_5^-$	1	2	1
42	CNO^-	3	2	2
43		3	2	
45		2	1	1
57		1	1	3
61	$N_2O\cdot OH^-$	2	3	4
65			2	1
66		2		1
67	Pyrazole anion (?)	4	30	5
68		2	2	
81	Methyl pyrazole anion (?)	1		25

[a] Total pressure in ionization chamber = 3.0 Torr. N_2O:RH:He = 1:1:1. The source temperature was 200 °C. [b] Expressed as percent of total ionization. Ions with intensities less than 1% were omitted.

ferences in the spectra. It is quite clear that the reactant ion in the N_2O alone system is not producing any significant amount of the ions observed in the N_2O-CH_4 system. In the N_2O alone system the majority of the ionization of isopropylbenzene is carried by the $(M - H + O)^-$ and $(M - C_3H_7 + O)^-$ ions, and these ions are not observed in the N_2O-CH_4 spectrum of this compound. In the case of diphenylmethane the N_2O alone reactant produces significant quantities of unidentified other ions which are not observed when methane is present. Here, also, the conclusion to be drawn is that the reactant ions when methane is present and when it is absent are different.

The situation with *tert*-butylbenzene is not clear. The spectra produced by the two reactant systems contain ions at many common m/e values, but also ions at a few different m/e values. However, the intensities at many of the common m/e values are usually quite different. Since the evidence from the experiments with other compounds indicates quite strongly that OH^- is the active reactant in the N_2O/CH_4 system, we tentatively adopt the position that it is also the active reactant with *tert*-butylbenzene.

The N_2O alone spectra of several alcohols are given in Table VII, and the spectra of four of these alcohols were also obtained using N_2O/CH_4 (Table II). The spectra obtained using the two different reagents are markedly different, and we conclude from these experiments also that the reactant ions in the two systems are different. We think that these experiments with N_2O alone confirm our postulate that the reactant ion in the N_2O/CH_4 (or N_2O/H_2) system is OH^-.

The spectra of alcohols obtained using N_2O alone are of considerable interest in their own right. In the N_2O/CH_4

spectra of alcohols given in Table II no ions produced by C–C bond fission are to be found. However, in the N_2O spectra given in Table VII, one sees that extensive C–C fragmentation occurs in the secondary and tertiary alcohols studied. The main fragmentation reactions involve loss of the alkyl groups attached to the carbon bonded to the OH group, and the reaction occurring can be represented as

$$R_1-CH_2-\overset{\overset{\displaystyle R_2}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-R_3 + O^-\cdot(?)$$

$$\rightarrow R_1-CH=\overset{\overset{\displaystyle }{|}}{\underset{\underset{\displaystyle O^-}{|}}{C}}-R_3 + \begin{cases} R_2H + OH \\ \text{or} \\ R_2O + H_2 \end{cases} \quad (20)$$
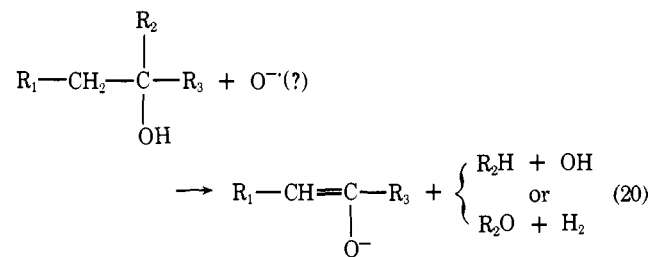
Thus in the spectrum of 3-decanol the m/e 127 ion is produced by the loss of the CH_3 group, and the m/e 57 ion is formed by the loss of the C_8H_{17} group. These fragmentations might well be useful in practical determinations of molecular structure.

4. Negative Ion Spectra of Mixtures of N_2O with C_2H_6, C_3H_8, and i-C_4H_{10}. The extensive negative ion reactions that we have observed in mixtures of N_2O with H_2 and CH_4 generate interest in the question of what reactions will occur in mixtures of N_2O with other alkanes. We have made a few preliminary experiments to provide information on the point, and the spectra obtained in mixtures of N_2O with ethane, propane, and isobutane are given in Table VIII. OH^- is the most intense ion in the ethane spectrum, and we suggest that it is formed by an H-atom abstraction reaction analogous to reaction 8, i.e.

$$N_2O + e^- \rightarrow O^-\cdot + N_2 \quad (1)$$

$$O^-\cdot + C_2H_6 \rightarrow OH^- + C_2H_5 \quad (21)$$
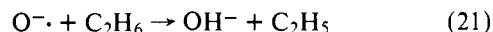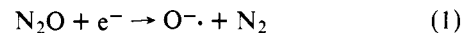
The relative intensity of the m/e 17 ion produced from ethane is slightly lower than that of the OH^- ion produced from methane, but the difference is not large enough to be of much significance.

However, in the propane and isobutane systems the OH^- ion comprises only about 25% of the total ionization, and the most intense ions in the spectra occur at m/e 67 in the C_3H_8 system and m/e 81 in the i-C_4H_{10} system. These ions are formed consistently, and we feel they are produced by ionic reactions involving the components of the reaction system. In the earlier part of this paper we suggested that ions found with m/e values higher than the molecular weights in certain aromatics and olefins are produced by the reaction of anions from the hydrocarbons with nitrous oxide. We advance as a tentative hypothesis the idea that similar kinds of reaction is occurring in the propane and isobutane systems. We suggest

$$N_2O + e^- \rightarrow O^-\cdot + N_2 \quad (1)$$

$$O^-\cdot + C_3H_8 \rightarrow CH_3CH_2CH_2^- + OH \quad (22a)$$

$$CH_3CH_2CH_2^- \rightarrow CH_2=CHCH_2^- + H_2 \quad (22b)$$

$$CH_2=CHCH_2^- + N_2O$$

$$m/e\ 67$$
pyrazole anion

The postulate of the proton abstraction in (22a) constitutes an ad hoc guess, but once one accepts the idea of the formation of the propyl anion, reactions 22b and 22c are in keeping with the reactions which we have postulated to occur with aromatics and olefins. We have seen that high-energy anions have a striking tendency to stabilize themselves by loss of H_2 if a low-energy resonating structure can be formed; hence (22b) has a number of precedents. Reaction 22c is similar to a number of reactions that have been postulated to occur in aromatics and olefins. The pyrazole anion (m/e 67) is analogous to the cyclopentadienyl anion and should be similarly stabilized by a large amount of resonance. If one accepts this hypothesis that the m/e 67 ion is formed by ion–molecule reactions involving $C_3H_7^-$ ion as a precursor, one must conclude from Table VIII that O^- reacts with propane to effect hydrogen atom abstraction (producing OH^- ion) and proton abstraction (producing $C_3H_7^-$ ion) in about equal amounts. In methane no evidence for proton abstraction is observed, and we tentatively guess that propyl anion is lower in energy than methyl anion to an extent which accounts for the formation of $C_3H_7^-$ and the nonformation of CH_3^-. However, since propane appears to react with oxygen ion both by H-atom abstraction and proton abstraction, the energies involved in the two processes must be rather similar. In reaction 22a we have represented the $C_3H_7^-$ ion as having the primary structure, but we have no direct evidence on this matter.

In the isobutane system the most intense ion in the spectrum is that with m/e 81, and we postulate that it is the 3-methylpyrazole anion formed by a set of reactions analogous to (22). In the ethane system it is stoichiometrically impossible to form the pyrazole anion, and we observe that the N_2O/C_2H_6 spectrum exhibits an intensity at m/e 67 of only 4%. This might be accounted for by the presence of a small amount of propane as an impurity in the ethane.

Our results are different from those which have been obtained by Bohme and Fehsenfeld[17] for reactions of $O^-\cdot$ with hydrocarbons using a flowing afterglow technique. They found that $O^-\cdot$ reacted with CH_4, C_2H_6, C_3H_8, and n-C_4H_{10} to produce OH^- as the major product ion in all cases. The rate constants for the reactions of $O^-\cdot$ with these hydrocarbons increased monotonically with hydrocarbon size from 1.0×10^{-10} cm^3/mol s for CH_4 to 1.2×10^{-9} cm^3/mol s for n-C_4H_{10}. Similarly, the reaction probability per collision increased from 0.08 in the methane reaction to 0.63 in the butane reaction. The source of the $O^-\cdot$ ions in these experiments was

O_2. The difference in results may be the result of the different experimental conditions, and in particular the fact that our experiments were carried out at 200 °C, whereas the flowing afterglow experiments were made at ambient temperature. Obviously, more experiments are called for to elucidate the source of the different behavior obtained in these two experiments. Equally obviously, further experiments are called for to establish the reactions occurring to produce the ions observed in the spectra given in Table VIII.

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