out at the dropping Hg electrode. $E_{1/2}$ for the first wave is -1.69 V.

(14) This assumes that the electron-releasing effect of the *tert*-butyl and methyl groups is comparable.

(15) Estimates range[1c] from 40 to 84. The low numbers are clearly wrong, and the most probable value is in the 60–70 region.

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Flowing Afterglow Studies of the Reactions of Hydroxide, Amide, and Methoxide Ions with Ethylene Oxide and Propylene Oxide

Veronica M. Bierbaum, C. H. DePuy,* R. H. Shapiro,* and John H. Stewart

Contribution from the Chemistry Department, University of Colorado,
Boulder, Colorado 80309. *Received September 22, 1975*

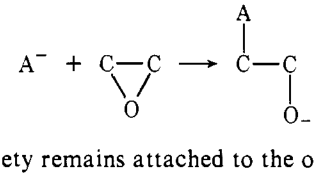
Abstract: Rates and mechanisms of the gas-phase reactions of OH^-, NH_2^-, and CH_3O^- with ethylene oxide and propylene oxide were studied at 300 K using the flowing afterglow technique. Helium buffer gas pressures of 0.2–1.0 Torr were employed. The reactions of OH^- and NH_2^- with ethylene oxide may be characterized as addition followed by elimination of molecular hydrogen across the newly formed carbon–oxygen or carbon–nitrogen bond. Methoxide ion adds to ethylene oxide followed by third body stabilization without hydrogen loss. All three anions react with propylene oxide exclusively by proton abstraction presumably with simultaneous opening of the three-membered ring. Rate constants for these reactions were measured and compared with the prediction of the average dipole orientation theory. For either neutral reactant, reaction probabilities decreased in the order $OH^- > NH_2^- > CH_3O^-$.

The study of organic ion–molecule reactions in the gas phase has been stimulated by a desire to discover more detail about the intrinsic properties of reactions uncomplicated by the very significant effects of solvation.[1] Unsolvated ions generated in the gas phase at low pressures often react differently from the same ions in solution, where coordinating solvent molecules cause extensive charge delocalization. These effects are most evident in the different ordering of acidities and basicities between solution and gas phase chemistry. Less is known about the effect of solvation on reaction mechanisms.

In studying differences between gas-phase and condensed-phase ion–molecule reactions, chemists have, in recent times, relied heavily on the powerful techniques of ion cyclotron resonance spectrometry,[2] high-pressure mass spectrometry,[3] and the flowing afterglow.[4] These techniques have added a new dimension to the understanding of the kinetics and energetics of chemical reactions. Although each technique offers its own unique advantages, several valuable assets of the flowing afterglow method can be enumerated: both the ionic and the neutral species involved in the reaction process possess thermal, i.e., Maxwell–Boltzmann, energy distributions; an unparalleled variety of ionic and neutral reactants may be prepared; the necessity of accurate time resolution for these gas phase reactions is eliminated by the equivalence of time and distance; the technique is rather easily extended to include energy variability; and finally, in a flowing gas, vapor–surface interactions can be allowed to reach a steady state so that adsorption–desorption problems do not exist.

Nucleophilic substitution reactions have been studied extensively in solution and therefore represent a fertile area for comparison with gas-phase chemistry. In 1970, Bohme and Young[5] published the first flowing afterglow study of nucleophilic substitution reactions; they reported rates and mechanisms for the reactions of oxide anion radical, hydroxide anion, and various alkoxide ions with methyl chloride. Recently, Brauman[6] has shown that such nucleophilic substitution reactions occur extensively with Walden inversion much like SN2 processes in solution chemistry. However, a rather serious constraint in the study of nucleophilic substitution and other gas-phase ion–molecule reactions is that only the ionic reactants and products are usually detected. Since much of the mechanistic and stereochemical information resides in the organic product of the reaction, it is desirable to have the organic fragment retain the charge. However, with the exception of simple proton abstraction reactions to form carbanions, this is often not the situation. For example, in the aforementioned nucleophilic substitution reactions of several anions with methyl chloride, the only ionic product is chloride ion.[5,7]

If an analogy can be drawn with solution chemistry, the epoxides appear to be a promising class of organic substrates for gas-phase ion–molecule reaction studies. In solution, epoxides react with nucleophiles by substitution to form organic ions, the alkoxide ions, as products. In this reaction (eq 1), the



(1)

displaced moiety remains attached to the organic substrate. Two elimination processes are also observed in solution (eq 2 and 3). The opening of the three-membered epoxide ring relieves strain and contributes to the exothermicity of these reactions.

This paper reports the first gas-phase study of the reactions of two epoxides, ethylene oxide and propylene oxide, with a series of anionic nucleophiles, OH^-, NH_2^-, and CH_3O^-. The

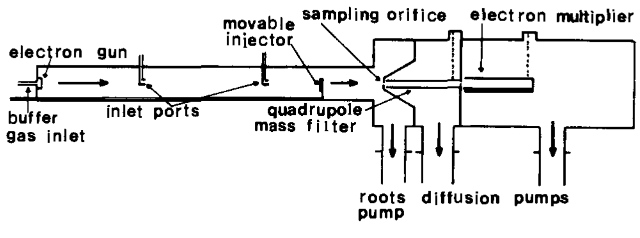
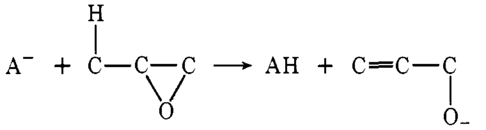


Figure 1. Diagram of the flowing afterglow system.



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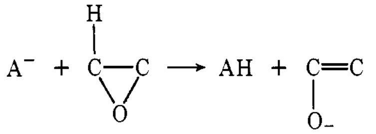


(3)

flowing afterglow technique was employed. Products of the reactions are determined and possible mechanisms are discussed. Bimolecular rate constants are measured and compared with theoretical collision rate constants. The striking differences between reaction channels for an ion with ethylene oxide and with propylene oxide are noted.

Experimental Section

The flowing afterglow system employed in the experiments described in this paper was adapted from systems developed by Ferguson, Fehsenfeld, Schmeltekopf, and co-workers at the National Oceanic and Atmospheric Administration (NOAA) laboratories in Boulder, Colo.[8] The apparatus is diagrammed in Figure 1. A large flow of helium buffer gas is purified by passage through a liquid nitrogen cooled trap filled with Davison 4A molecular sieves. This buffer gas then flows through a calibrated triflat flowmeter and enters the upstream end of a 100 × 7.6 cm i.d. stainless steel reaction tube where ionization is effected by an electron gun. The first 35 cm of the reaction tube constitutes a region for ion production and thermalization, as well as for full development of a laminar velocity profile and attenuation of higher diffusion modes; the remaining 65 cm constitutes a region for reaction of these ions with neutral molecules, which may be added to the system through the movable injector or through other inlets. At the end of the reaction region most of the reaction mixture is exhausted from the flow tube through a Roots blower backed by a Kinney mechanical pump. A fraction of the plasma is sampled through a 0.25-mm orifice in a molybdenum nose cone, and the ions are separated by a quadrupole mass filter and detected with a Bendix electron multiplier. The quadrupole was designed and built at the NOAA laboratories. By appropriate choice of the sign of the applied voltages in the detection system either positive or negative ions may be sampled, analyzed, and detected. The residual pressure behind the sampling orifice is maintained at 10^{-6} Torr by two oil diffusion pumps.

The electron gun consists of a thorium oxide coated iridium filament maintained at −100 V relative to a grounded accelerating grid, and is operated in a constant emission current mode. Reactant ions are produced by adding small flows of other gases to the helium stream either before the electron gun or at a port downstream of this ionizer. Amide ion is produced by a dissociative electron attachment process when ammonia is allowed to flow past the ionizer. For the experiments involving hydroxide ion, oxygen and methane or oxygen and ammonia are added before the ionizer. Dissociative ionization or dissociative electron attachment of oxygen (forming O^-) followed by rapid hydrogen atom abstraction from methane or ammonia produces hydroxide ion.[9] In the presence of ammonia, hydroxide forms cluster ions, principally $OH^-(NH_3)$ and $OH^-(NH_3)_2$ under our experimental conditions. Since this decreases the concentration of the hydroxide ion and complicates the total ion spectrum, hydroxide was preferentially generated from oxygen and methane. Deuteroxide ion, OD^-, is formed from oxygen and deuterated ammonia. Methoxide ion, CH_3O^-, is formed either by rapid proton abstraction from methanol added to a plasma containing hydroxide ions,[10] or less efficiently, by direct electron impact on O-methylhydroxylamine, H_2NOCH_3.

The neutral reactant, ethylene oxide or propylene oxide, is introduced into the reaction region through a perforated copper loop designed to provide uniform addition.[11] The position of this inlet may be varied from 15 to 65 cm from the end of the reaction zone, providing a variable ion–neutral reaction time for kinetic determinations. Alternatively, the inlet may be placed in a fixed position and the neutral reactant concentration may be varied by changing its flow rate into the system. Both techniques provide identical results, within experimental error; however, moving the inlet position is more convenient for it eliminates the need for careful variation of the flow of the neutral reactant. This is especially difficult to do with high-boiling liquids, which were used in other experiments. The neutral reactant flow was measured by monitoring the increase of pressure in a calibrated volume as a function of time using a Viatran pressure transducer connected to a strip chart recorder.

Gas purities were: helium (99.995%), oxygen (99.6%), methane (99.0%), ammonia (99.99%), and ethylene oxide (99.7%). Propylene oxide was obtained from Eastman Kodak (bp 34–35 °C) and was distilled before use. Methanol was reagent grade. Deuterated ammonia was prepared from D_2O (minimum isotopic purity 99.7%) and magnesium nitride (99.5%). *O*-Methylhydroxylamine was prepared by basic hydrolysis of the hydrochloride salt.

Several extremely stable anions, such as F^- (*m/e* 19), Cl^- (*m/e* 35 and 37), and NO_2^- (*m/e* 46) regularly appeared as minor impurities in the ion spectrum and did not vary with injector position. Since these ions were completely unreactive toward ethylene oxide or propylene oxide, they did not complicate the kinetic data and were convenient as a check of the mass scale calibration. Their ion intensities were monitored but are not included in the figures reported in this paper. Except for these three ions, all ions which were ≥1% of the total ion signal are reported.

Both the helium buffer gas pressure in the flow tube and its flow rate can be varied. In the experiments reported here pressures of 0.2–1.0 Torr were used as measured by a Baratron capacitance manometer. The range of helium flows was from 100 to 250 atm cm^3/s and the neutral reactant flows ranged from 0.003 to 0.6 atm cm^3/s. All measurements were performed at room temperature.

Data Analysis

When the movable injector is employed for kinetic measurements, data are analyzed as follows.

The rate of reaction of an anion A^- with a neutral N can be described by

$$d[A^-]/dt = -k[A^-][N] \tag{4}$$

where k is the bimolecular reaction rate constant. Since [N] ≫ $[A^-]$ (typically [N] ~ 10^{12} cm^{-3} and $[A^-]$ ~ 10^8 cm^{-3}), pseudo-first-order kinetics apply and eq 4 becomes

$$d(\ln[A^-]) = -k[N]\,dt \tag{5}$$

The term dt can be equated with $dz/\alpha\bar{v}$, where z is the length of the reaction region, $\bar{v}$ is the average buffer gas velocity, and $\alpha = 1.59$[12] converts the average flow velocity to the average transport velocity of the ions. Equation 5 now becomes

$$d(\ln[A^-]) = \frac{-k[N]\,dz}{1.59\bar{v}} \tag{6}$$

or upon rearrangement,

$$k = \frac{-d(\log[A^-])}{dz}\,\frac{(2.303)(1.59)\bar{v}}{[N]} \tag{7}$$

The average buffer gas velocity may be expressed as

$$\bar{v}\left(\frac{cm}{s}\right) = \frac{F_{He}\left(\frac{atm\ cm^3}{s}\right) \times 760\left(\frac{Torr}{atm}\right)}{P_{He}\,(Torr) \times area\,(cm^2)} \tag{8}$$

where F_{He} and P_{He} are the flow and pressure of helium buffer gas, respectively, and area represents the cross sectional area

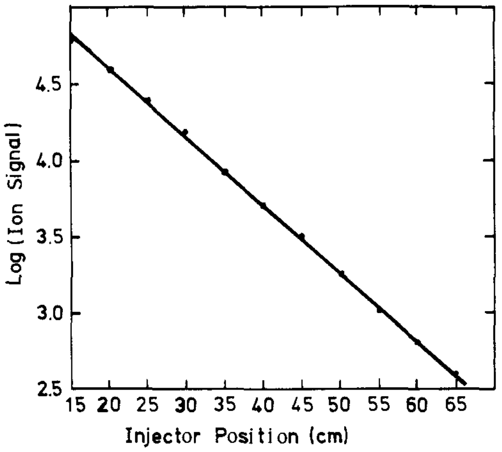


Figure 2. Decay of OD^- upon increased reaction time with ethylene oxide. The slope is $-0.0442\ cm^{-1}$.

of the flow tube (45.36 cm^2). The neutral reactant concentration can be expressed by

$$[N]\left(\frac{\text{particles}}{\text{cm}^3}\right) = \frac{P_{He}(\text{Torr}) \times F_N\left(\frac{\text{atm cm}^3}{\text{s}}\right) \times 3.26 \times 10^{16}\left(\frac{\text{particles}}{\text{cm}^3\ \text{Torr}}\right)}{F_{He}\left(\frac{\text{atm cm}^3}{\text{s}}\right)} \quad (9)$$

where F_N is the neutral reactant flow. Using eq 8 and 9, eq 7 becomes

$$k\left(\frac{\text{cm}^3}{\text{particle s}}\right) = \frac{-d(\log[A^-])}{dz\ (\text{cm})} \times \frac{F_{He}^2\left(\frac{\text{atm cm}^3}{\text{s}}\right)^2 \times 1.88 \times 10^{-15}\left(\frac{\text{cm Torr}^2}{\text{particle atm}}\right)}{P_{He}^2\ (\text{Torr})^2 \times F_N\left(\frac{\text{atm cm}^3}{\text{s}}\right)} \quad (10)$$

Since the pressure and flow of helium and the flow of neutral reactant are easily measured, all that is necessary to obtain a rate constant is to monitor the change in the reactant ion intensity as a function of injector position z. Ion intensities as monitored by the mass spectrometer are of arbitrary units directly proportional to the true ion concentration. The distance of the movable injector from the sampling orifice of the detection system defines the reaction region and is measured in centimeters. A typical set of data for the reaction of OD^- with ethylene oxide is shown in Figure 2. For this particular experiment the helium flow was 210 atm cm^3/s, the ethylene oxide flow was 0.0954 atm cm^3/s, and the helium pressure was 0.410 Torr. Substituting these values and the slope from Figure 2 into eq 10 yields

$$k = \left(\frac{0.0442}{\text{cm}}\right) \times \frac{\left(210\,\frac{\text{atm cm}^3}{\text{s}}\right)^2 \times 1.88 \times 10^{-15}\left(\frac{\text{cm Torr}^2}{\text{particle atm}}\right)}{(0.410\ \text{Torr})^2 \times \left(0.0954\,\frac{\text{atm cm}^3}{\text{s}}\right)} \quad (11)$$

$= 2.29 \times 10^{-10}\ cm^3/(\text{particle s})$. Multiplication by 6.02×10^{20} particle l./(mol cm^3) converts this rate constant to units of l./(mol s).

Since this paper reports the first flowing afterglow studies from our laboratory, two known reaction rates were examined to assess the accuracy of our quantitative measurements. For the reaction of $He^+ + N_2$, an average of six experiments yielded a rate constant of $1.2 \times 10^{-9}\ cm^3/s$ (standard deviation of 11%), in exact agreement with the value of Dunkin et al.[13] For the proton abstraction reaction of $OH^- + CH_3CHCH_2$, an average of seven experiments yielded $k = 2.5 \times 10^{-10}\ cm^3/s$ (standard deviation of 13%), in good agreement with the results of Bohme et al. (2.7×10^{-10}).[4] Rate constants are estimated to be accurate to ±25%.

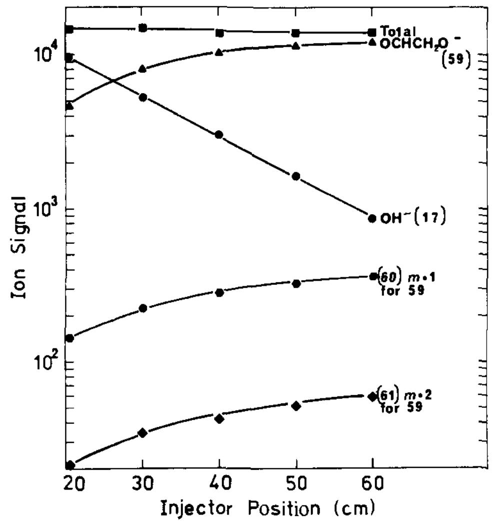
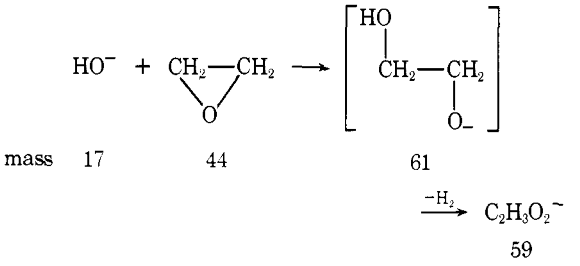


Figure 3. Complete reactive ion spectrum for the reaction of OH^- + ethylene oxide.

Results and Discussion

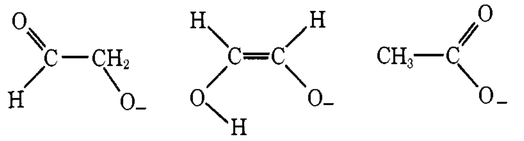
The total ion spectrum for the reaction of hydroxide ion with ethylene oxide is presented in Figure 3. The intensities of the various ionic species are plotted along the logarithmic ordinate, and the reaction distance, the distance between the movable neutral reactant inlet and the sampling orifice, is plotted along the abscissa. The total ion intensity in Figure 3 is nearly independent of reaction time. This implies that mass discrimination is not an important factor and that all reactive ions are accounted for. In addition, associative electron detachment (i.e., $A^- + N \rightarrow AN + e^-$) is apparently not a contributing mechanism and indeed simple thermochemical calculations predict it to be endothermic. The linear semilogarithmic decay of OH^- is indicative of pseudo-first-order kinetics as described by eq 7. Ions with mass to charge ratios (m/e) of 59, 60, and 61 increase as the reaction proceeds and appear as the only ionic products. The reaction of hydroxide with ethylene oxide may be written as shown in eq 12. For an ion of m/e 59 with empirical formula $C_2H_3O_2^-$, the ratio of the ions 59/60/61 due to naturally occurring isotopes is expected to be 1/0.023/0.0042.[14] The observed ratio of 1/0.029/0.0044 is in good agreement with the theoretical value, indicating that m/e 60 and 61 are the M + 1 and M + 2 peaks, respectively, of the m/e 59 product ion. Note the extreme simplicity of the reaction; only a single organic product ion is produced in amounts ≥1% of the total ion spectrum, despite the fact that a number of other exothermic reaction channels may be envisaged. In our experience, gas-phase organic anion-molecule reactions



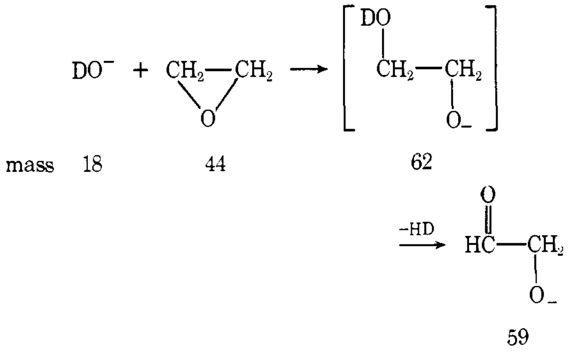
(12)

have proven to be highly selective, usually forming only one or two organic products.

Three possible structures for the m/e 59 product are shown below. The first of these could arise by loss of H_2 from the C-O bond, and the second by loss of H_2 from the C-C bond. There is no obvious way that acetate ion could be formed in this reaction except by a major atomic reorganization, but its great stability made it necessary to consider it as a possibility.

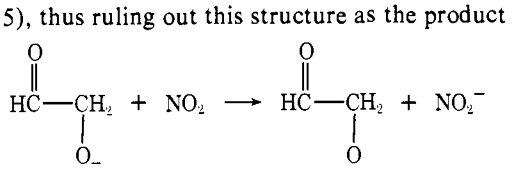


To distinguish between the first two possibilities the reaction of ethylene oxide with deuterioxide (eq 13) was examined. As for the hydroxide-ethylene oxide reaction, excellent kinetic data were obtained. The major product ion is m/e 59, with m/e 60 and 61 occurring only with isotopic abundances expected for M + 1 and M + 2 peaks of $C_2H_3O_2^-$. Therefore, within the limits of our detection sensitivity, HD is exclusively eliminated, indicating loss across the C-O bond.

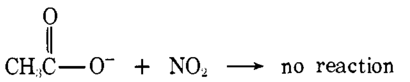


(13)

To rule out acetate ion as a possible structure, its reactivity was compared with the reactivity of the m/e 59 ion from the ethylene oxide reaction. The electron affinity of the acetoxyl radical is 3.4 eV,[15] compared to ~1.5-2.0 eV[16] for a typical alkoxyl radical. Nitrogen dioxide, NO_2, has an electron affinity between these two values (2.4 eV).[17,18] Therefore, if the m/e 59 product has the structure of an alkoxide ion, it could electron transfer to NO_2 (eq 14), whereas if it has the acetate structure it could not. In fact, when NO_2 is added to a plasma containing only the ionic product of eq 12, the sole ion formed is m/e 46, corresponding to NO_2^-.[19] However, acetate ion, produced by proton abstraction from acetic acid, does not react with NO_2 (eq 15), thus ruling out this structure as the product for the hydroxide-ethylene oxide reaction.



$$\mathrm{HC(=O)CH_2O^-} + \mathrm{NO_2} \longrightarrow \mathrm{HC(=O)CH_2O} + \mathrm{NO_2^-} \qquad (14)$$



$$\mathrm{CH_3C(=O)O^-} + \mathrm{NO_2} \longrightarrow \text{no reaction} \qquad (15)$$

Figure 4 presents the total ion spectrum for the reaction of amide ion with ethylene oxide. The occurrence of OH^- (from proton abstraction by NH_2^- from traces of water vapor) and of the ammonia cluster ions, $OH^-(NH_3)$, $OH^-(NH_3)_2$, and $NH_2^-(NH_3)$, adds considerable complexity to the spectrum. Note that the hydroxide ion reacts more rapidly than amide, which in turn reacts more rapidly than the cluster ions. The decreased reactivity of clustered ions is a common phenomenon.[5]

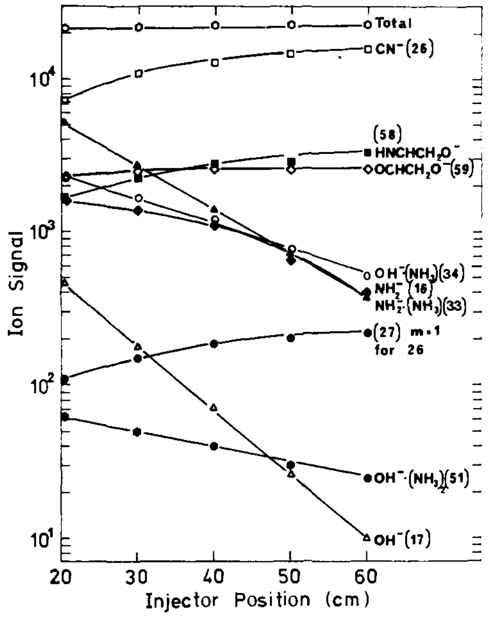
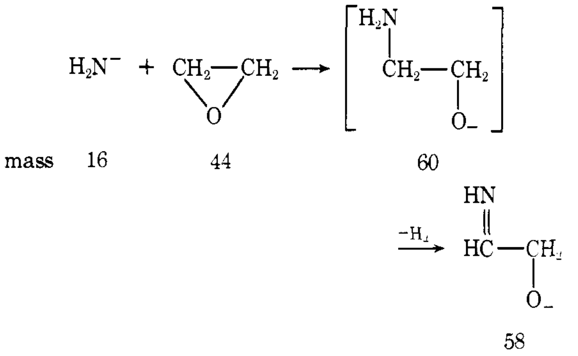


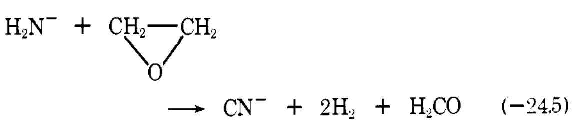
Figure 4. Complete reactive ion spectrum for the reaction of NH_2^- + ethylene oxide.

Since the m/e 59 ion arises from the reaction of hydroxide with ethylene oxide (and probably of the hydroxide clusters with ethylene oxide), the ions of m/e 26, 27, and 58 appear to be the ionic products of the reaction of amide with ethylene oxide. The formation of the m/e 58 product may be written by analogy with that for the hydroxide ion (eq 16).



(16)

The observed 26/27 ion ratio of 1/0.014 suggests that the m/e 26 ion is CN^- (expected isotopic ratio of 1/0.015)[14] rather than $C_2H_2^-$ (expected isotopic ratio of 1/0.022).[14] Cyanide formation may occur by three thermodynamically allowed reactions, which yield different neutral products (eq 17-19; ΔH values (kcal/mol) given in parentheses). Although analysis of the neutral products would be necessary to distinguish among these possibilities, the first reaction appears most favorable, since it involves the least bond reorganization. One possible mechanism for this reaction is shown in eq 20. The



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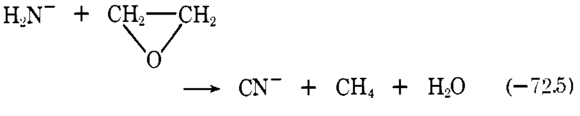

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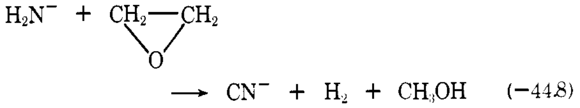

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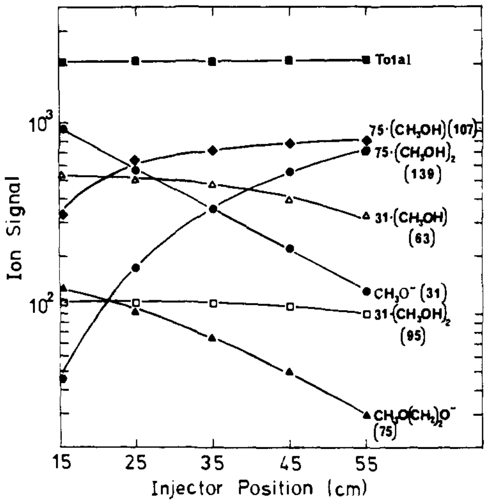
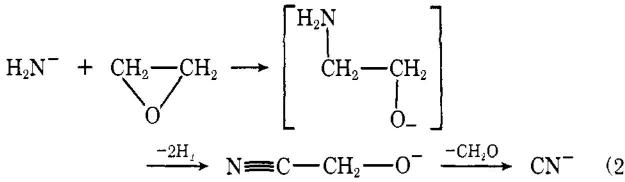


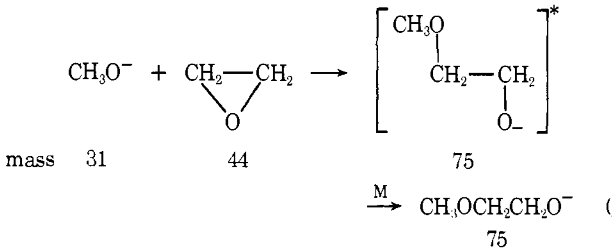
Figure 5. Complete reactive ion spectrum for the reaction of CH_3O^- + ethylene oxide.


(20)

formation of formaldehyde as a neutral product has been postulated for several ion-neutral reactions studied in this laboratory.

Small peaks at *m/e* 60 and 61 corresponding to isotopic abundances of *m/e* 58 and 59 were evident, but were omitted from Figure 4 for clarity.

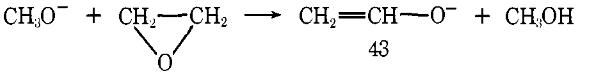
The reaction of ethylene oxide with CH_3O^- (which contains no hydrogen attached to the heteroatom) was examined, since the hydrogen atom in the previously studied nucleophiles was attached to the heteroatom and was involved in loss of H_2. The results are summarized in Figure 5, and show clearly that simple addition, not followed by loss of H_2, occurs. Instead the excess energy of the initially formed adduct must be removed by collision with a third body, M, as shown in eq 21.


(21)

In the experiment of Figure 5, the methoxide ion was produced by proton abstraction from methanol, and so an excess of methanol is present in the reaction mixture. As a consequence, the cluster ions $CH_3O^-(CH_3OH)$ and $CH_3O^-(CH_3OH)_2$ are present, and again the decreasing reactivity with increasing cluster size is evident. Besides the addition product (*m/e* 75), its cluster ions with one methanol (*m/e* 107) and two methanols (*m/e* 139) appear as products. Any product of *m/e* 73 (corresponding to loss of H_2 from *m/e* 75) amounts to less than 1% of the total ion current.

Since the cluster ions of the product are presumably formed sequentially from the initially formed *m/e* 75 ion, this ion and the *m/e* 107 ion have both formation and loss terms. The *m/e* 75 ion decreases as a function of reaction distance in the example of Figure 5 because under these experimental conditions its rate of loss to *m/e* 107 exceeds its rate of formation from *m/e* 31.

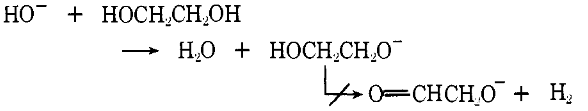
The *m/e* 75 ions formed from methoxide ion and ethylene oxide could conceivably have arisen in another way, namely elimination to an ion of *m/e* 43 and subsequent clustering with methanol (eq 22 and 23). The absence of an ion of *m/e* 43 in


(22)

$$CH_2{=}CH{-}O^- + CH_3OH \xrightarrow{M} m/e\ 75 \qquad (23)$$

our spectrum argued against this possible pathway, but the rate of reaction 23 may be sufficiently large under our experimental conditions to reduce the *m/e* 43 ion intensity below our detection sensitivity. To test the mechanism represented in eq 22 and 23, a new source of methoxide ion was sought. Addition of O-methylhydroxylamine (CH_3ONH_2) to the helium stream before the ionizer gives reasonable intensities of methoxide ion in the absence of methanol. Upon addition of ethylene oxide the *m/e* 75 ion appears with no evidence of peaks at *m/e* 43, 107, or 139. This effectively rules out an elimination-clustering mechanism for the process and further substantiates eq 21 as the correct mechanism for the reaction.

The loss of H_2 from the reaction of ethylene oxide with OH^- and NH_2^- is an interesting reaction, and must be due to an excess of energy in the initial adduct. On the basis of simple bond energies, loss of H_2 from an alcohol to form an aldehyde is endothermic by approximately 15 kcal.[20] As expected, ethylene glycol anion, formed in our flowing afterglow system by proton abstraction from ethylene glycol (eq 24), does not lose hydrogen.


$$HO^- + HOCH_2CH_2OH \longrightarrow H_2O + HOCH_2CH_2O^- \not\longrightarrow O{=}CHCH_2O^- + H_2 \qquad (24)$$

There are two sources of excess energy in the initial adduct formed in the anion-ethylene oxide reaction. First, 28 kcal[20] of strain energy is released in the opening of the three-membered epoxide ring. Secondly, there is collisional energy resulting from the attractive ion-induced dipole and ion-permanent dipole potentials of the reactant species. Some of the excess energy of the adduct is dissipated by elimination of molecular hydrogen and the relative kinetic energy of the separating ion and neutral particle, plus vibrational and rotational excitation of the products.

Obviously there is insufficient energy in the system to cause loss of one hydrogen atom at a time; the loss of H_2 must be a concerted reaction. We can envision two different pathways leading to products, one a stepwise addition followed rapidly by loss of H_2 (eq 12), the other a reaction in which hydrogen is lost simultaneously with addition, as shown schematically in eq 25. The lack of a solution phase analogy certainly argues against such a concerted reaction. Perhaps a lack of deuterium isotope effect (OD^- and OH^- react at the same rate within experimental error) might also be cited against it, although isotope effects on gas phase ion-molecule reactions are fre-

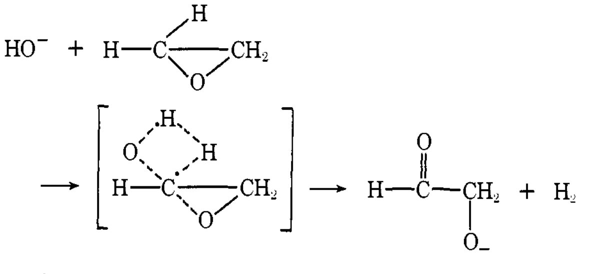
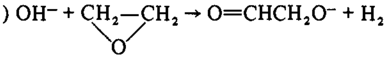
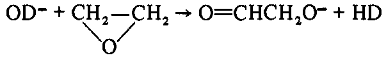
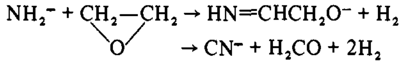
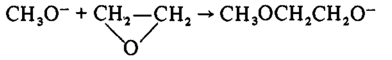
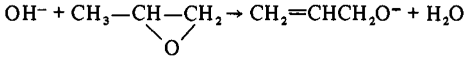
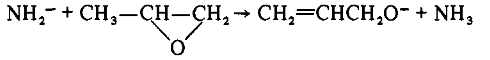
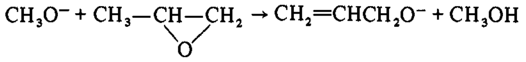
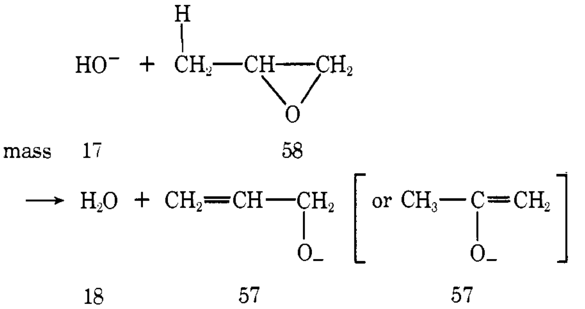

(25)

Table I. Summary of Experimental and Theoretical Rate Constants

Reaction	k_{exptl}, cm³/s	k_{ADO}, cm³/s	Reaction probability
(12)  $OH^- + \underset{O}{CH_2{-}CH_2} \rightarrow O{=}CHCH_2O^- + H_2$	2.5×10^{-10}	2.53×10^{-9}	0.10
(13)  $OD^- + \underset{O}{CH_2{-}CH_2} \rightarrow O{=}CHCH_2O^- + HD$	2.5×10^{-10}	2.48×10^{-9}	0.10
(16)  $NH_2^- + \underset{O}{CH_2{-}CH_2} \rightarrow HN{=}CHCH_2O^- + H_2$	1.5×10^{-10}	2.59×10^{-9}	0.058
(17) $\rightarrow CN^- + H_2CO + 2H_2$			
(21)  $CH_3O^- + \underset{O}{CH_2{-}CH_2} \rightarrow CH_3OCH_2CH_2O^-$	6.9×10^{-11}	2.08×10^{-9}	0.033
(26)  $OH^- + CH_3{-}\underset{O}{CH{-}CH_2} \rightarrow CH_2{=}CHCH_2O^- + H_2O$	1.9×10^{-9}	2.69×10^{-9}	0.71
(27)  $NH_2^- + CH_3{-}\underset{O}{CH{-}CH_2} \rightarrow CH_2{=}CHCH_2O^- + NH_3$	1.2×10^{-9}	2.75×10^{-9}	0.44
(28)  $CH_3O^- + CH_3{-}\underset{O}{CH{-}CH_2} \rightarrow CH_2{=}CHCH_2O^- + CH_3OH$	6.5×10^{-10}	2.17×10^{-9}	0.30

quently small.[21,22] On the other hand if an adduct of *m/e* 61 is a true intermediate it might have proved possible to transfer its excess energy to the buffer gas before loss of H_2. Neither increasing the helium pressure nor adding neutral nonreactive gases which are efficient in collisionally deactivating molecules increased the intensity of the *m/e* 61 ion signal. This rapid H_2 loss is surprising because a concerted $_\sigma 2_s + {}_\sigma 2_s$ reaction is forbidden on orbital symmetry grounds.[23] Possibly there is sufficient vibrational energy present to make a $_\sigma 2_a + {}_\sigma 2_s$ reaction pathway accessible. More subtle experiments to distinguish between a single step and a stepwise reaction are planned.

In contrast to ethylene oxide, propylene oxide reacts with OH^-, NH_2^-, and CH_3O^- in the gas phase exclusively by loss of a proton to form $C_3H_5O^-$. In the reactions of methoxide, the ions $C_3H_5O^-(CH_3OH)_n$ where n = 1, 2, and 3, also appear when methanol is present, but not in its absence. This indicates that these cluster ions are formed by termolecular association of $C_3H_5O^-$ with methanol rather than by addition of methoxide to propylene oxide. We believe the proton abstraction reaction to be a concerted E2 reaction in the gas phase, as shown in eq 26. Deuterium labeling studies on this system are



(26)

planned, in order to rule out the possibility of loss of a ring proton to give an enolate ion, but since we saw no proton abstraction from ethylene oxide it seems unlikely that loss of one of the epoxide hydrogens could be occurring. From previous studies of the relative acidity of molecules in the gas phase we also conclude that the elimination is unlikely to be stepwise, i.e., $E1_{CB}$, since these bases are not strong enough to abstract a proton from the methyl group without help from ring opening in the transition state.

The bimolecular rate constants for the reactions of OH^-, OD^-, NH_2^-, and CH_3O^- with ethylene oxide and of OH^-, NH_2^-, and CH_3O^- with propylene oxide were measured and are summarized in Table I. These rate constants were found to be independent of pressure, confirming that second-order processes were being observed. Bimolecular kinetics are expected for reactions 12, 13, 16, 17, 26, 27, and 28 in which the exothermicity of the reaction is converted into relative kinetic energy of the ion and neutral products. However, in the association reaction 21, in which no neutral product is formed, collision with a third body is required to remove the excess energy and the process must be termolecular.

The termolecular process may be considered in terms of an energy transfer mechanism where the ion combines with a neutral to form an energy rich complex, AN^{-*}. This complex can either dissociate back to reactants or be collisionally stabilized by a third body, M:

$$A^- + N \underset{k_d}{\overset{k_c}{\rightleftarrows}} AN^{-*} \qquad \begin{matrix}\text{combination}\\ \text{dissociation}\end{matrix} \tag{29}$$

$$AN^{-*} + M \xrightarrow{k_s} AN^- + M \qquad \text{stabilization} \tag{30}$$

Assuming that the concentration of AN^{-*} is in steady state, the rate of loss of A^- is given by

$$R = \frac{k_c k_s [A^-][N][M]}{k_d + k_s[M]} \tag{31}$$

Under low-pressure conditions, i.e., $k_d \gg k_s[M]$, the kinetics are termolecular with

$$k_{\mathrm{exptl}}{}^{\mathrm{III}} = k_c k_s / k_d \tag{32}$$

Under high-pressure conditions, i.e., $k_d \ll k_s[M]$, the rate is given by

$$R = k_c[A^-][N] \tag{33}$$

Every AN^{-*} complex formed is collisionally stabilized and the kinetics are second-order (or "saturated termolecular") with $k_{\mathrm{exptl}}{}^{\mathrm{II}} = k_c$. The existence of saturated termolecular kinetics explains the apparent bimolecular rate constant for methoxide with ethylene oxide.

The rate constants for combination of an ion with a neutral, k_c, span several orders of magnitude. For example, for the reaction $O_2^+ + O_2 \rightarrow O_4^+$, $k_c = 5.5 \times 10^{-12}$ cm³/s[24], while for the reaction $Li^+ + CHF_2CH_3 \rightarrow Li^+(CHF_2CH_3)$, $k_c = 1.0 \times 10^{-9}$ cm³/s.[25] In general, increasing bond energy or vibrational complexity of the associated complex increases the value of k_c and decreases the pressure at which saturation occurs. In view of the extensive study by Spears and Ferguson,[25] saturated termolecular kinetics at pressures of 0.25 Torr and with $k_c = 6.9 \times 10^{-11}$ cm^3/s is reasonable for the reaction of methoxide ion with ethylene oxide.

The magnitude of bimolecular ion–molecule reaction rate constants can be discussed in terms of a theoretical collision rate constant predicted by the average dipole orientation (ADO) theory[26]

$$k_{\mathrm{ADO}} = 2\pi e \left(\frac{\alpha}{\mu}\right)^{1/2} + c2e\mu_{\mathrm{D}}\left(\frac{2\pi}{\mu kT}\right)^{1/2} \qquad (34)$$

where e is the absolute value of the charge on the ion, μ is the reduced mass of the reactants, α is the polarizability and μ_{D} is the permanent dipole moment of the neutral molecule, k is the Boltzmann constant, T is the absolute temperature, and c is a parameter which will be described below. The term $2\pi e(\alpha/\mu)^{1/2}$ is the Langevin rate constant[27] arising from a point charge–induced dipole potential. The expression $2e\mu_{\mathrm{D}}(2\pi/\mu kT)^{1/2}$ is the contribution arising from a point charge–permanent dipole interaction,[28] assuming alignment of the permanent dipole in the lowest energy orientation. The factor c is a parameter between 0 and 1 which allows for the thermal rotational energy of the molecule and measures the effectiveness of the charge locking in on the dipole. Su and Bowers[26] have presented a table of c values as a function of $\mu_{\mathrm{D}}/\sqrt{\alpha}$ for a range of common dipole moments and polarizabilities. A recent modification of the ADO theory by Bass et al.[29] yields very similar c values.

Theoretical collision rate constants have been calculated using eq 34 and the following values: for ethylene oxide, $\mu_{\mathrm{D}} = 1.89$ D,[30] $\alpha = 5.2$ Å^3 [31] and $c = 0.204$;[26] for propylene oxide, $\mu_{\mathrm{D}} = 2.01$ D,[30] $\alpha = 7.0$ Å^3 and $c = 0.192$.[26] The polarizability of propylene oxide was estimated from that for ethylene oxide by noting the increase in polarizability in going from ethane (4.5 Å^3) to propane (6.3 Å^3).[32] The average dipole orientation rate constants are summarized in Table I along with the calculated reaction probabilities, $k_{\mathrm{exptl}}/k_{\mathrm{ADO}}$.

The rate constants and reaction probabilities for reaction of OH^- and OD^- with ethylene oxide are identical within experimental error; this is consistent with the small or nonexistent isotope effects observed by other workers for exothermic gas phase ion-molecule reactions.[21,22]

Both the experimental rate constants and the reaction probabilities decrease on proceeding from OH^- to NH_2^- to CH_3O^- for either neutral reactant. This trend does not follow the order of exothermicities of the reactions nor the basicities of the reactant ions ($NH_2^- > OH^- > CH_3O^-$), but does correlate with the increasing charge delocalization and increasing steric hindrance of the ions. In contrast to these results, Bohme and co-workers[5,7] have found that, within experimental error, these three ions react with methyl chloride with identical reaction probabilities.

The reaction probability of a given ion with propylene oxide is about an order of magnitude larger than for its reaction with ethylene oxide. These large rate constants are typical of exothermic proton transfer reactions with little or no activation energy barrier. More than 95% of all exothermic proton transfer reactions observed to date proceed with rate constants exceeding 10^{-10} cm^3/s at thermal energies.[33]

Conclusion

Epoxides serve as extremely useful neutral reactants for studies of both addition and elimination reactions in the gas phase. The loss of hydrogen from the initial adduct of ethylene oxide and hydroxide or amide ion is an unexpected but intriguing reaction, and may furnish information about the importance of orbital symmetry rules in excited vibrational states of molecules. These studies of gas phase reactions will continue to elucidate the role of solvation on the intrinsic nature of ion–molecule mechanisms.

Acknowledgment. We wish to express our sincere thanks to Drs. E. E. Ferguson, A. L. Schmeltekopf, and C. J. Howard of the NOAA Laboratories for their invaluable assistance in the construction of the system, and for their many helpful discussions and suggestions. We gratefully acknowledge support of NSF Grant No. GP-33877.

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