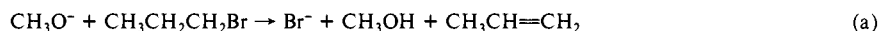


A Gas-Phase E2 Reaction: Methoxide Ion and Bromopropane<sup>†</sup>Mark E. Jones<sup>†</sup> and G. Barney Ellison\**Contribution from the Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309-0215. Received May 25, 1988*

**Abstract:** We describe a procedure for studying gas-phase ion-molecule chemistry in which the reaction pathway is elucidated by direct detection of the neutral products. Our experiment uses a flowing afterglow device configured with a novel cold finger trap coupled to a GC/MS. Material collected by the trap is separated by capillary gas chromatography and the individual components identified by their retention times and electron impact mass spectra. We have used this device to study the reaction of methoxide ion with 1-bromopropane.

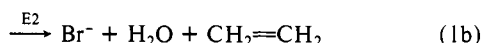
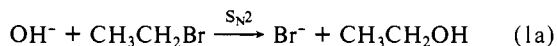


We find that the reaction produces only products resulting from elimination a; there is no evidence for the species resulting from displacement b. The E2 product, propylene, is detected while the S<sub>N</sub>2 product, 1-methoxypropane, is not. Our *gas-phase* results contrast sharply with *solution* studies, which show an overwhelming preference for the displacement channel b.

## I. Introduction

When ionic reactions occur in solution the solvent molecules play an important, often dominant, role. Investigating the reactions of ions in the gas phase enables probing of the intrinsic reactivities of the ions unperturbed by solvent molecules and counterions. Studies of ionic organic reaction mechanisms in the gas phase are generally more direct and less complicated than similar studies in solution, but there are limitations. One is usually constrained to monitoring only the charged species participating in the reaction and only the charged reaction products are detected. As the complexity of ion-molecule systems increase, mere identification of the charged species becomes inadequate to describe the chemical reaction.

For a fundamental reaction like ethyl bromide reacting with hydroxide ion, it is not known whether the neutral product is that expected from a nucleophilic displacement (ethanol) or from a bimolecular elimination (ethylene).



Conventional methods only observe the charged leaving group which is the same for both channels. Traditional methods only measure the rate of conversion of OH<sup>-</sup> to Br<sup>-</sup>. From this measurement, the overall rate of the reaction can be calculated without knowing which reaction, 1a or 1b, takes place.

Gas-phase ion-molecule rate constants are of less use for mechanistic studies than might be anticipated. In the gas phase, ions and neutrals are attracted to one another by ion-dipole or ion-induced dipole forces of up to about 20 kcal mol<sup>-1</sup> at typical reaction distances.<sup>1</sup> Many reactions that might be slow in solution occur rapidly and without apparent activation energy in the gas phase. Without knowledge of the neutral products of such reactions, the reaction mechanism cannot be known.

At this point, it is pertinent to recall the solution chemistry of alkyl halides. The reactions of a huge number of alkyl bromides with a considerable number of nucleophiles have been scrutinized in a variety of solvents. As reaction 1 points out, alkyl halides can undergo substitution or elimination. The factors controlling the ratio of S<sub>N</sub>2 versus E2 products have been exhaustively studied.<sup>2-4</sup>

**Table I.** Variation of Elimination versus Substitution with Alkyl Bromide Structure<sup>a</sup>

$$\text{R}-\text{Br} + \text{CH}_3\text{CH}_2\text{O}^-\text{Na}^+ \xrightarrow[55^\circ\text{C}]{\text{anhydrous EtOH}} \text{ether} + \text{olefin} + \text{Na}^+\text{Br}^-$$

alkyl bromide	% olefin
CH <sub>3</sub> CH <sub>2</sub> Br	0.9
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> Br	8.9
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Br	9.8
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Br	8.9
(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> Br	59.6

<sup>a</sup>Source: Dhar, M. L.; Hughes, E. D.; Ingold, C. K.; Masterman, S. *J. Chem. Soc.* **1948**, 48, 2055.

Reactions of primary alkyl halides with strong bases largely lead to displacement in solution. Studies of the reactions of alkyl bromides with sodium ethoxide<sup>5</sup> can appropriately be compared to gas-phase results. In solution, displacement accounts for approximately 90% of the observed products in the reactions of alkoxide ions with primary bromides, as summarized in Table I. Only branched alkyl bromides are observed to prefer E2 over S<sub>N</sub>2; all of the primary bromides favor S<sub>N</sub>2. On the basis of the solution results, the gas-phase reaction of OH<sup>-</sup> with CH<sub>3</sub>CH<sub>2</sub>Br would be expected to yield predominantly CH<sub>3</sub>CH<sub>2</sub>OH and Br<sup>-</sup> (eq 1a).

Several groups have devised means of identifying neutral products resulting from ion reactions. In pioneering work,<sup>6</sup> the products of positive ion-molecule reactions were identified by photoionization mass spectrometry. Initial studies<sup>7,8</sup> of negative ion reaction products were conducted in an ICR configured to allow for a static gas sample. The products of anion-molecule reactions were identified by electron impact (EI) ionization of the background gas. The neutral products were identified on the basis of their distinctive positive ions. Several nucleophilic displacement reactions of the form X<sup>-</sup> + RY → RX + Y<sup>-</sup> were studied. Morton's laboratory<sup>9,10,11</sup> has developed an electron

(1) Bierbaum, V. M.; DePuy, C. H. *J. Am. Chem. Soc.* **1981**, 103, 5034.

(2) Gould, E. S. *Mechanism and Structure in Organic Chemistry*; Holt-Dryden: New York, 1959; pp 485-489.

(3) March, J. *Advanced Organic Chemistry*; Wiley: New York, 1985; pp 874-880.

(4) Saunders, W. H., Jr.; Cockerill, A. F. *Mechanisms of Elimination Reactions*; Wiley: New York, 1973.

(5) Dhar, M. L.; Hughes, E. D.; Ingold, C. K.; Masterman, S. *J. Chem. Soc.* **1948**, 48, 2055.

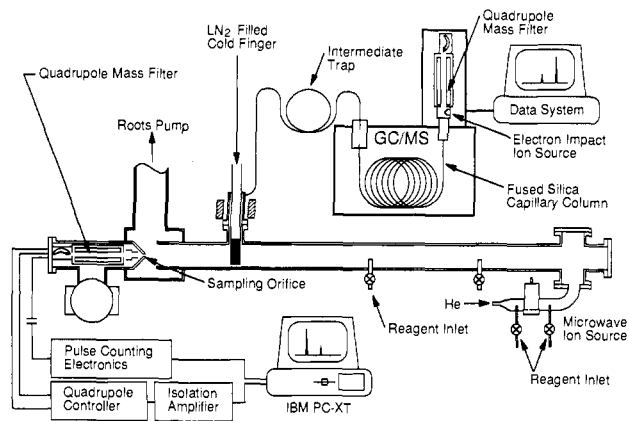
(6) Lesclaux, R.; Searles, S.; Sieck, L. W.; Ausloos, P. *J. Phys. Chem.* **1970**, 74, 3336. Lesclaux, R.; Searles, S.; Sieck, L. W.; Ausloos, P. *J. Phys. Chem.* **1971**, 75, 3411.

(7) Lieder, C. A.; Brauman, J. I. *J. Am. Chem. Soc.* **1974**, 96, 4028.

(8) Lieder, C. A.; Brauman, J. I. *Int. J. Mass Spectrom. Ion Phys.* **1975**, 16, 307.

<sup>†</sup>This paper is dedicated to an extraordinary pedagogue, Professor Edward Bobko, Scovill Professor of Chemistry, on the occasion of his retirement from Trinity College.

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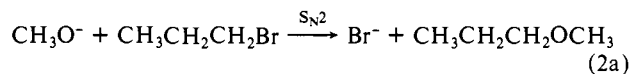


**Figure 1.** Schematic representation of the flowing afterglow apparatus used to collect the neutral products of gas-phase ion-molecule reactions. Shown are the cold finger trap and its connections to both the flowing afterglow and the gas chromatograph/mass spectrometer (GC/MS) used to separate and identify the reaction products.

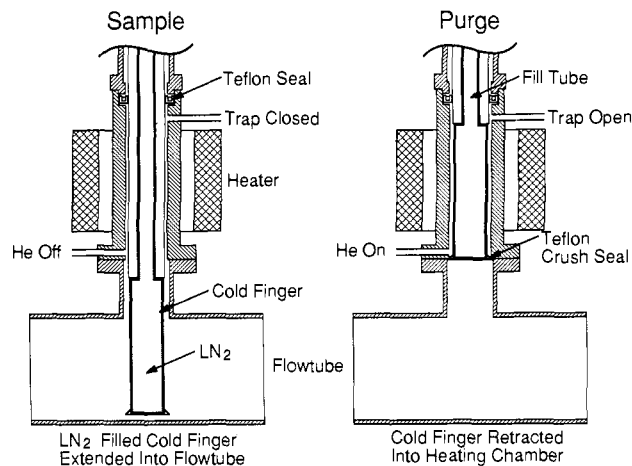
bombardment flow reactor to study the neutrals generated by cation-molecule chemistry. Infrared chemiluminescence and LIF have been used to detect reaction products.<sup>12</sup> Molecules that have been detected are HF, HCl, HO, HCN, and CNH. Our group has used a flow afterglow configured with cryogenic trapping columns to investigate two negative ion systems.<sup>13,14</sup>

We have improved on our earlier work by developing a technique for neutrals collection and detection based on a flowing afterglow configured with a novel cold finger trap and a gas chromatograph/mass spectrometer (GC/MS) for product separation and identification. A schematic view of the apparatus is shown in Figure 1, and the operation of the cold finger trap is depicted in Figure 2. Ion-molecule reactions are carried out in the flowing afterglow and a fraction of the neutrals present in the plasma are collected on the surface of the liquid nitrogen cooled cold finger. Collected material is thermally desorbed and transferred to the chromatographic column for analysis. Compounds are identified by their retention times and electron impact mass spectra.

This technique has limitations and attempts to elucidate the reaction mechanism in reaction 1 were inconclusive. Alkyl bromides always contain traces of alcohols and these tiny quantities of alcohols present generally exceed the amount that would be formed by ion-molecule chemistry. Alcohols formed by reaction would represent a small change in the observed ROH signal and would be impossible to identify. Consequently we shifted our attentions to a related system and investigated the fast<sup>15</sup> reaction of 1-bromopropane (*n*-propyl bromide) and methoxide ion, reaction 2. Our goal was to deduce whether the reaction proceeds by



bimolecular nucleophilic substitution ( $\text{S}_{\text{N}}2$ ), bimolecular elimination (E2), or a mixture of the two. Both reaction channels are



**Figure 2.** Schematic representation of how the cold finger trap functions. Samples are collected by moving the liquid nitrogen ( $\text{LN}_2$ ) filled cold finger into the flowtube. Molecules present in the flowing afterglow plasma adhere to the cold surface. After an appropriate time, the cold finger is moved into its heating chamber and the collected material is purged from the heating chamber by a flow of helium. Shown are the positions of the Teflon seals.

quite exothermic:  $\Delta H^\circ_{298}(2a) = -54 \text{ kcal mol}^{-1}$  and  $\Delta H^\circ_{298}(2b) = -40 \text{ kcal mol}^{-1}$ . (See Appendix A.)

We have concentrated on using the GC/MS to detect the reaction products  $\text{CH}_3\text{CH}=\text{CH}_2$  and  $\text{CH}_3\text{CH}_2\text{CH}_2\text{OCH}_3$ . Propylene was unambiguously identified by retention time on a fused silica capillary column and correct electron impact mass spectrum. The ether characteristic of the  $\text{S}_{\text{N}}2$  channel was never observed as the product of the reaction. Since propylene is the only product detected, we conclude that E2 is the predominant reaction pathway (eq 2b). Notice that this result is quite different than the solution findings (Table I) which suggest that roughly 90% of the products should be  $\text{CH}_3\text{CH}_2\text{CH}_2\text{OCH}_3$ , the  $\text{S}_{\text{N}}2$  product.

## II. Experimental Section

**A. Flowing Afterglow.** These experiments were performed with use of a flowing afterglow<sup>16</sup> device that was built to facilitate the collection of neutral reaction products. Our flowing afterglow has not been previously described in the literature.<sup>17</sup> In the standard flowing afterglow,<sup>18</sup> a neutral plasma is created in a fast flow of purified helium. The device consists of an ion source, a stainless steel flowtube, and a quadrupole mass spectrometer for monitoring the ions present in the plasma. The flowing afterglow used for these experiments is similar in many ways to devices built by other experimentors.<sup>19</sup> An overview of the flowing afterglow configured for the collection of neutral products is shown in Figure 1.

The reaction vessel is a 127 cm  $\times$  7.20 cm i.d. stainless steel tube in which ions are generated and allowed to react in a buffer of purified helium. The tube is constructed in a building-block style and consists of six 16.5-cm interchangeable sections. This allows the various components to be connected in any desired configuration. The sections are sealed together with O-ring flanges with fluorocarbon elastomer<sup>20</sup> O-rings.

The flowtube is outfitted with two ion sources: an electron impact ion source and a microwave ion source. The electron impact source uses a tungsten filament to create 100 V electrons at emission currents up to 50 mA. The microwave ion source consists of a 1-in. (2.54 cm) Pyrex discharge tube through which flows the entire flow of helium buffer. The discharge tube is surrounded by a scaled up version of an Evenson cavity.<sup>21,22</sup> A microwave generator operating at 2450 MHz is used to supply

(9) Burns, F. B.; Morton, T. H. *J. Am. Chem. Soc.* **1976**, *98*, 7308.  
 (10) Marinelli, W. J.; Morton, T. H. *J. Am. Chem. Soc.* **1978**, *100*, 3536.  
 (11) Redman, E. W.; Morton, T. H. *J. Am. Chem. Soc.* **1986**, *108*, 5701.  
 (12) Bierbaum, V. M.; Ellison, G. B.; Leone, S. R. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1984; Vol. 3, pp 1-56.  
 (13) Smith, M. A.; Barkley, R. M.; Ellison, G. B. *J. Am. Chem. Soc.* **1980**, *102*, 6851.  
 (14) Jones, M. E.; Kass, S. R.; Filley, J.; Barkley, R. M.; Ellison, G. B. *J. Am. Chem. Soc.* **1985**, *107*, 109.  
 (15) The rate constant for this reaction has been measured to be  $2.1 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  by Amy S. Mullin, Veronica M. Bierbaum, and C. H. DePuy, private communication. This represents a rate equal to 99% of the calculated (ADO) collision rate.

(16) Ferguson, E. E.; Fehsenfeld, F. C.; Schmeltekopf, A. L. *Adv. At. Mol. Phys.* **1969**, *5*, 1.

(17) This device has been mentioned in: (a) Jones, M. E.; Ellison, G. B. *Rev. Sci. Instrum.* **1986**, *57*, 1432. (b) Jones, M. E.; Barlow, S. E.; Ellison, G. B.; Ferguson, E. E. *Chem. Phys. Lett.* **1986**, *130*, 218.

(18) Bierbaum, V. M.; DePuy, C. H.; Shapiro, R. H.; Stewart, J. H. *J. Am. Chem. Soc.* **1976**, *98*, 4229.

(19) Zwier, V. M.; Bierbaum, V. M.; Ellison, G. B.; Leone, S. R. *J. Chem. Phys.* **1980**, *72*, 5426.

(20) Fluorocarbon elastomer frequently is referred to as Viton (E. I. duPont deNemours Co., Wilmington, DE) or Fluorel (3M, St. Paul, MN).

power to the cavity.<sup>23</sup> The microwave ion source is preferred for the neutrals collection experiment since it affords higher ion densities than are possible with the electron impact source. The discharge tube has ports upstream and downstream of the cavity for the introduction of ion precursors.

In a typical experiment, helium (99.995%) buffer gas is pumped through the flowtube at pressures of 0.5 Torr and flow velocities of 80 m s<sup>-1</sup>. The fluid dynamics and diffusion characteristics of such a system are well defined.<sup>16</sup> The flow of helium is controlled by a mass flow controller<sup>24</sup> after it is purified by passage through one or two liquid nitrogen cooled traps filled with molecular sieves.<sup>25</sup> The flowtube has several reagent inlets through which neutral reactants may be added to react with the ions present in the plasma. The amount of reagent added, as well as the total pressure in the flowtube, is monitored with a capacitance manometer.<sup>26</sup>

Reactions are monitored by observing the ions present in the plasma. At the end of the flowtube most of the reaction mixture is exhausted through a Roots blower (679 L s<sup>-1</sup>) backed by a mechanical pump.<sup>27</sup> A fraction of the plasma is sampled through a 0.25-mm orifice in a 0.254-mm molybdenum disc. This orifice acts much like an effusive beam source into the mass spectrometer region. The molybdenum disc is isolated from ground on a Kel-F insulator.<sup>28</sup> A few volts attractive potential is applied to the disc to sample the ions with maximum efficiency. A three-element cylindrical lens is used to focus the sampled ions into the throat of a quadrupole mass filter. The quadrupole chamber is pumped with a 200 L s<sup>-1</sup> turbomolecular pump.<sup>29</sup> Pressure in the chamber is held below 10<sup>-5</sup> Torr.<sup>30</sup>

The mass spectrometer consists of a quadrupole mass filter, ion detector, pulse counting electronics, and a computer to control the system and to collect data. The mass filter originally was part of a UTI 100C Residual Gas Analyzer<sup>31</sup> and has been modified for use in the flowing afterglow. The most severe of the required modifications was the addition of the ability to float the UTI with respect to laboratory ground. This is necessary since the ions in a flowing afterglow are born at ground potential and must be accelerated for mass analysis. To enable detection of negative ions, the standard UTI CuBe discrete dynode electron multiplier was replaced with a floated anode continuous dynode electron multiplier (CDEM).<sup>32</sup> The high voltage supply provided in the UTI 100C could not be used for negative ion detection and was replaced by a laboratory high voltage supply.<sup>33</sup> The analog detection used by UTI was abandoned in favor of pulse counting. Signals from the CDEM are capacitively coupled into an amplifier,<sup>34</sup> through a discriminator,<sup>35</sup> and detected with a ratemeter.<sup>36</sup> All the fast electronics are powered by a single NiM supply.<sup>37</sup> The experiment is under the control of an IBM PC-XT computer using commercially supplied interface boards.<sup>38</sup> The computer supplies an analog signal to control the UTI. The control voltage is sent through an isolation amplifier to enable the computer to remain at laboratory ground and control the UTI which is floated with respect to ground. The 0–300 amu range of the UTI is controlled with full 12 bit resolution. Signal is obtained in analog form from the rate

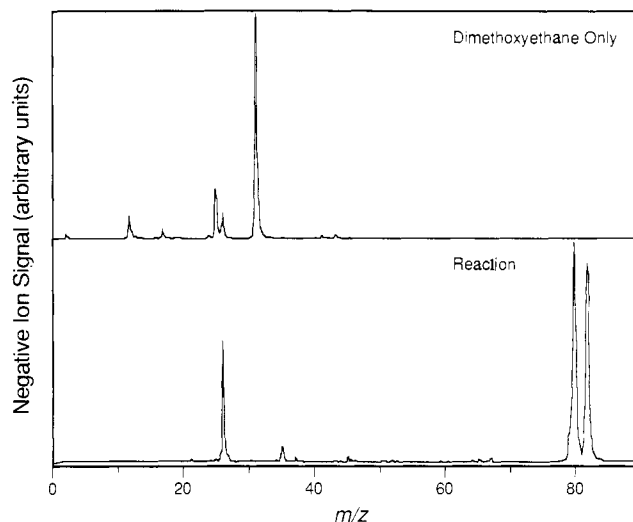


Figure 3. Shown are mass spectra of negative ions observed by the flowing afterglow mass spectrometer. The top trace, labeled Dimethoxyethane Only, is observed when 1,2-dimethoxyethane is added below the microwave discharge ion source. When 1-bromopropane is added subsequently, the bottom trace, labeled Reaction, results. This corresponds to the reaction of CH<sub>3</sub>O<sup>-</sup> (*m/z* 31) with 1-bromopropane to produce Br<sup>-</sup> (*m/z* 79, 81). The vertical scales on the plots are not identical.

meter at full 10 bit resolution. Both positive and negative ions may be sampled, analyzed, and detected by appropriate choice of the polarities of the applied voltages in the mass spectrometer, on the sampling orifice and the CDEM.

Methoxide ion is formed by the action of a microwave discharge ion source on 1,2-dimethoxyethane (99+%). Maximum methoxide signals are obtained with the microwave power as low as possible (about 6 Watts). Use of 1,2-dimethoxyethane as an ion precursor offers two clear advantages over formation of methoxide by other means.<sup>18</sup> Since the ion is formed by direct action of the microwave discharge, no other reagents are added to complicate the neutrals detection. The amount of 1,2-dimethoxyethane used is less than can be measured by our pressure sensor (<10<sup>-4</sup> Torr).<sup>39</sup> This means that very little of the compound will be present to complicate the detection of the neutral products. In the reaction of 1-bromopropane (99+%) with methoxide ion, reaction 2, approximately 1 mTorr of alkyl bromide is added. The negative ions detected by the flowing afterglow mass spectrometer are shown in Figure 3. The top trace shows the ions produced by the action of the microwave ion source on 1,2-dimethoxyethane. The largest signal is methoxide ion, CH<sub>3</sub>O<sup>-</sup>. Clearly visible are signals from C<sub>2</sub>H<sup>-</sup> (*m/z* 25) and CN<sup>-</sup> (*m/z* 26). Upon addition of 1-bromopropane, Br<sup>-</sup> (*m/z* 79, 81) ion appears as shown in the bottom trace. Also prominent in the lower trace is CN<sup>-</sup> which is attenuated only slightly by addition of bromopropane. The amount of 1-bromopropane added is determined by observation of the CH<sub>3</sub>O<sup>-</sup> signal measured by the flowing afterglow mass spectrometer. Bromopropane was added until the methoxide ion signal was reduced by a factor of 10. Attenuation of the ion signal by only an order of magnitude produces effectively the same neutral product density as completely eliminating the ion signal while introducing as little of 1-bromopropane as possible. Addition of minimal amounts of reagents greatly reduces the risk of clogging the capillary column used in analysis.

**B. Collection Technology.** Earlier work used tubes loosely filled with glass wool which was coated with an inert polymer.<sup>13,14</sup> Use of the trapping columns required that sample runs be in excess of 1 h to trap a detectable amount of neutral product. Our experience indicated that keeping the flowtube plasma stable for this period of time is very difficult. The trapping columns also had to be opened to atmosphere while making connections to the GC. This introduced atmospheric contaminants which were later detected. To shorten the trapping time and eliminate contamination we developed a new cold finger trap.

The cold finger trap consists of a movable, liquid nitrogen filled stainless steel cylinder which protrudes into the flowtube as shown in Figure 2. The flowtube plasma comes into contact with the cold surface and neutral molecules are physisorbed on the surface. After some period of time, the cold finger is translated into a heating chamber and the

(21) Fehsenfeld, F. C.; Evenson, K. M.; Broida, H. P. *Rev. Sci. Instrum.* **1965**, *36*, 294.

(22) Design of the cavity was suggested by Dr. T. M. Miller, Department of Physics, University of Oklahoma, Norman, OK 73019. Our cavity is described in: Jones, M. E.; Ellison, G. B. *Rev. Sci. Instrum.* **1986**, *57*, 1432.

(23) Ophos Instruments, Inc. (Rockville, MD), Model MPG-4.

(24) Tylan (Carson, CA) FC261 Mass Flow Controller.

(25) Union Carbide (Danbury, CT) type 5A MG size 16×40 molecular sieves are used.

(26) MKS (Andover, MA) Baratron Model 220B, 1 Torr.

(27) The pumping system used consists of a Leybold-Heraeus (Enfield, CT) WA-2000 blower backed by an S-400 mechanical pump.

(28) Kel-F is a fluorocarbon plastic and is a registered trademark of 3M.

(29) Balzers (Hudson, NH) Pfeiffer TPU-200.

(30) Pressure in the quadrupole chamber is measured by a Granville-Phillips (Boulder, CO) Model 260 Ionization Gauge Controller.

(31) UTI is a trademark of Ion Technology International (Sunnyvale, CA).

(32) The CDEM was purchased from Detector Technologies (Brookfield, MA) and was mounted in the alumina side plates of an old UTI multiplier. This enabled continued use of UTI's mounting brackets.

(33) John Fluke Manufacturing Co. (Everett, WA), Model 410B.

(34) Phillips Scientific (Suffern, NY) Model 771 Quad Variable Gain Bipolar 300 MHz Amplifier.

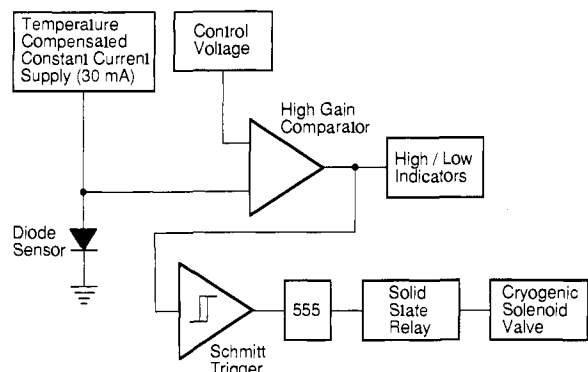
(35) Phillips Scientific (Suffern, NY) Model 730 Five Channel Tri-Mode 100-MHz Discriminator used exclusively in leading edge discriminator mode.

(36) Tennelec (Oak Ridge, TN) TC527 Log/Lin 100 MHz Ratemeter.

(37) Canberra Industries (Meriden, CT) Model 2100 NiM bin and power supply.

(38) Boards used are Data Translation (Marlborough, MA) Model DT-2808 Analog and Digital I/O System and DT-2815 D/A System.

(39) Directly coupling the MS from the GC/MS to the flowtube and using it like a residual gas analyzer showed that the action of the microwave discharge destroyed between 1% and 10% of the 1,2-dimethoxyethane added.



**Figure 4.** Block diagram of liquid nitrogen controller. The sensor is a 1N914 diode. Discrete transistors form the constant current supply and a potentiometer controlled voltage regulator provides the control voltage. The comparator and Schmitt trigger use LM741 op-amps. The 555 is configured as a monostable multivibrator. Not shown are circuits that indicate failure conditions (open circuit or short circuit sensor) and a manual override.

material frozen on its surface is vaporized and carried out of the chamber by a stream of helium for analysis.

The cold finger is a stainless steel cylinder of radius 1.19 cm and length 8.89 cm. It is attached to a 55.9 cm  $\times$  1.27 cm o.d. fill tube. The fill tube is surrounded by a 1 in. (2.54 cm) o.d. vacuum jacket that also acts as the support for the cold finger. A piston is welded to the vacuum jacket and forms an integral part of the pneumatic drive mechanism used to translate the cylinder between the flowtube and its heating chamber. The heating chamber has an i.d. of 2.58 cm and is heated by an electrical heating unit.<sup>40</sup> At the top of the heating chamber, vacuum seal is made by using a spring loaded Teflon seal.<sup>41</sup> The bottom of the heating chamber is sealed when the cold finger is in the heating chamber by a Teflon crush seal<sup>42</sup> attached to the bottom of the cold finger. The force of the pneumatic drive mechanism is used to make the crush seal. When the cold finger is retracted, the seals form a chamber isolated from atmosphere and the flowtube as shown in Figure 2. An evacuated chamber sits atop the heating chamber to ensure that no atmospheric contaminants can reach the cold finger. This chamber is evacuated continually by a rough pump and seals are made with use of fluorocarbon elastomer<sup>20</sup> O-rings and U-cups. The heating chamber has a gas inlet on the bottom and an outlet on top. Through these connections, the trapped material is transferred to the GC/MS.

Liquid nitrogen is added to the cold finger through a 35.6 cm  $\times$  0.64 cm tube in the fill tube of the cold finger. The 0.64-cm tube is equipped with a flow arrester that diverts gaseous nitrogen away from the surface of the liquid nitrogen in the cold finger reservoir. Liquid nitrogen is allowed to flow out of the bottom of the arrester into the reservoir. Helium, used as a buffer gas in the flowing afterglow, conducts heat exceedingly well. The rate at which it transfers heat to the cold finger causes rapid boil off of liquid nitrogen. Rapid boil off and the small volume of liquid nitrogen contained in the cold finger combine to require frequent fillings during sample collection. The level of liquid nitrogen in the cold finger is maintained by using a temperature controller.

The temperature controller was designed specifically for use with the cold finger<sup>43</sup> since no commercially available cryogenic controllers could be used. The sensor used is a commonly available rectifier diode,<sup>44</sup> a 1N914.<sup>45</sup> The temperature controller makes use of the temperature dependence of a silicon P-N junction to serve as a sensor. Figure 4 is

(40) Two Lindberg (Watertown, WI) Model 50211 semicylindrical heating elements are used.

(41) Bal Seal Engineering Co., Inc. (Santa Ana, CA) 316-HBCC-321-SP23.

(42) Virgin PTFE is machined with a 45° chamfer to mate with the bottom of the heating chamber.

(43) The controller built is an inexpensive solution to the problems of controlling liquid nitrogen. It will work in most applications except where strong magnetic fields are present.

(44) The original temperature controller designed for this purpose used a standard 1/4 W carbon resistor as the sensor. Resistors proved unsatisfactory due to their tendency to disintegrate when they were cycled from liquid nitrogen temperature to room temperature. Small pieces of the resistor would fall out, changing the resistance and requiring recalibration of the control voltage setting. The diode sensor requires virtually no readjustments.

(45) Any common diode will work. Small signal diodes are preferable since their small size makes them more responsive to changes in temperature. The 1N914 is a General Electric product.

a block diagram showing the major components of the controller. The voltage drop at constant current across a forward biased diode increases with decreasing temperature.<sup>46</sup> Our temperature controller consists of a temperature compensated, constant current source which provides current through the diode sensor to ground. The voltage drop across the diode is compared to the voltage set by the operator by an op-amp comparator. The output of the comparator is sent through a Schmitt trigger to a monostable multivibrator.<sup>47</sup> The monostable output actuates a solid state relay which controls a cryogenic solenoid valve. The monostable is used to keep the liquid nitrogen flowing for a short time after the sensor detects that the cold finger is full to lengthen the time between filling cycles. The performance of the controller is enhanced by having the current sufficient to cause slight heating of the sensor diode. Since the liquid nitrogen is more efficient at cooling the diode, the temperature at the diode is lower when it is immersed. When the level of liquid nitrogen has dropped sufficiently to remove the diode from the liquid, a rapid temperature rise occurs. Self-heating the diode is advantageous since the temperature difference between the liquid nitrogen and the vapor above the liquid is very small.

The operation of the cold finger trap during each stage of the sampling cycle is illustrated in Figure 5. During the trapping cycle, the cold finger is filled with liquid nitrogen and lowered into the flowtube for sufficient time to collect a sample. A sample time of 10 min was used throughout this work. Once a sample is collected, the cold finger is retracted into the heating chamber using the pneumatic drive mechanism. The heating chamber is kept at 150 °C using an electric heater controlled by a thermocouple temperature controller,<sup>48</sup> using a thermocouple mounted in the wall of the heating chamber. The heating chamber is pressurized with ultra-pure helium<sup>49</sup> once the cold finger is retracted. A fitting which seals the heating chamber during the collection is removed and the collected material is carried out of the heating chamber (purged) for analysis. This is illustrated in Figure 2.

The total volume entrapped when the cold finger is in the heating chamber is 7.34 cm<sup>3</sup>. The maximum flow rate through the capillary chromatographic column is 1 mL min<sup>-1</sup>. The time required for efficient transfer of material from the heating chamber directly onto the capillary column with such a low flow rate is prohibitively long.<sup>50</sup> Therefore, the transfer of trapped material to the GC is done in two steps which takes less time than a single transfer at a uniform, slow flow rate. With use of a flow rate of 14 mL min<sup>-1</sup>, the material trapped by the cold finger is transferred to an intermediate trap as shown on Figure 5. Transferring to the intermediate trap can be done with a relatively fast flow rate in a comparatively short time. Once the collected material is trapped in the small volume of the intermediate trap, the transfer to the GC column can be completed in a reasonable time. The intermediate trap is made of 107 cm of 1.19 mm i.d. thin wall stainless steel tubing, roughly 45 cm of which is immersed in liquid nitrogen. A 61-cm section of the tubing is coiled with a 6.35-cm radius and partially immersed<sup>51</sup> to form the trap. The time required for the first transfer is 6 min.<sup>52</sup> Once the material is collected in the intermediate trap, the liquid nitrogen is removed and

(46) The voltage drop is described by the following expression:

$$V = \frac{\eta T}{11600} \ln \left( \frac{I}{KT^m} \right) + V_{GO}$$

where  $K$  is a constant equal to  $1.6 \times 10^{-2}$  in appropriate units. For a Si diode,  $\eta = 2$  V/deg K,  $m = 1.5$ , and  $V_{GO} = 1.21$  V. This expression is readily derived from equations found in: Millman, Jacob; Halkias, Christos C. *Integrated Electronics: Analog and Digital Circuits and Systems*; McGraw-Hill, New York, 1972; pp 59-63, 752-753.

(47) The comparator and Schmitt trigger are made using LM 741 operational amplifiers (op-amps). The monostable multivibrator is a 555. These are generic integrated circuits available from many vendors.

(48) An Omega Engineering (Stamford, CT) type 6100 controller is used.

(49) The helium used is split from the GC/MS supply.

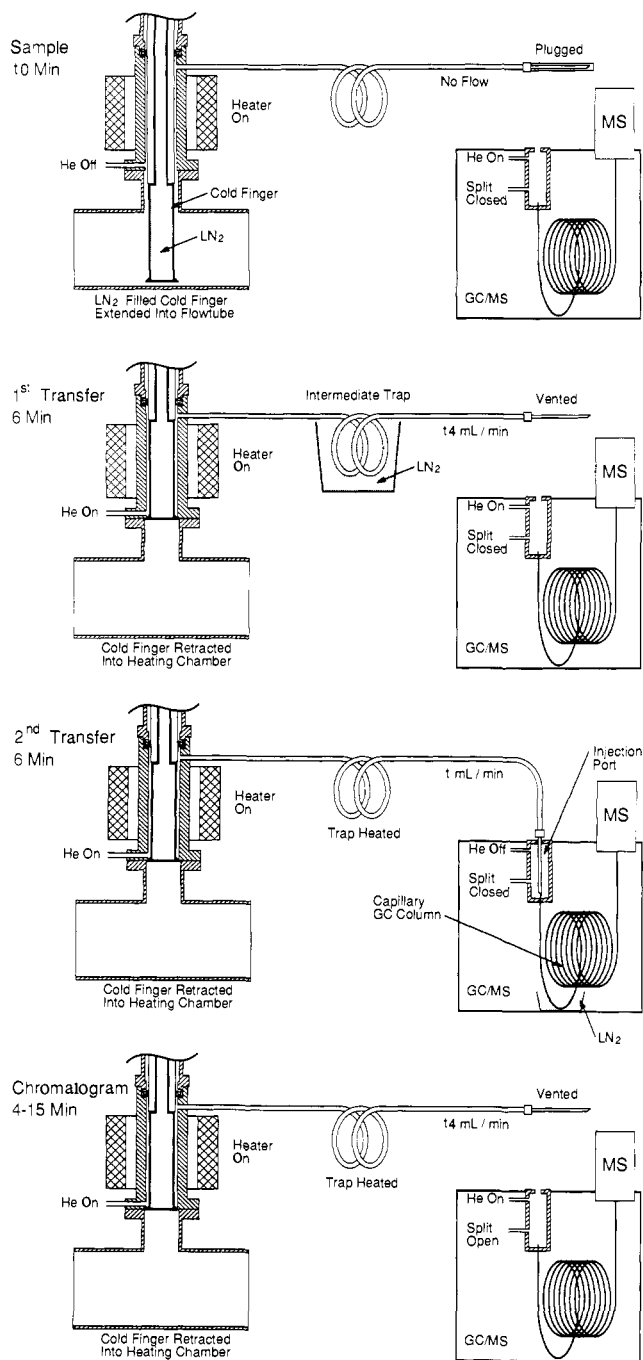
(50) The concentration,  $C$ , of material in the heating chamber will vary as:

$$C(t) = C(t=0) \exp(-\nu t / V)$$

where  $V$  = volume of the heating chamber and  $\nu$  = flow rate of the helium carrier gas (mL min<sup>-1</sup>).

(51) (a) O'Hara, D.; Vo, T.; Vedder, J. F. *NASA Tech Briefs* 1987, 11, 52. (b) O'Hara, D.; Vo, T.; Vedder, J. F. *NASA Technical Support Package ARC-11671*.

(52) The efficiency of the transfer depends on the diameter of the trap, the flow rate of helium, and the diffusion coefficient for the material being trapped. A calculation of the trapping efficiency was completed (see Appendix B) in order to find appropriate flow rates of helium for >95% trapping efficiency. The calculated efficiency was tested by transferring samples and checking the efficiency with the GC/MS.



**Figure 5.** Position of the cold finger and other important components during the various stages of the trapping cycle. During "Sample" the LN<sub>2</sub> filled cold finger is in the flowtube and the intermediate trap is plugged. During the "1st Transfer" the cold finger is retracted into the heating chamber. The chamber is pressurized with helium which carries collected material into the intermediate trap. Position of the cold finger and other important components during the various stages of the trapping cycle. During the "2nd Transfer" the intermediate trap is heated and the material collected is directed onto the capillary GC column. A small section of the column is immersed in LN<sub>2</sub> to cryofocus the material at the beginning of the column. The LN<sub>2</sub> is removed and the chromatogram is begun. During "Chromatogram" the intermediate trap is heated while helium flow continues to purge any remaining sample prior to the next sample.

the trap is resistively heated by passing a high current through the walls of the trap. During the heating of the intermediate trap, the flow out of the trap is directed into the injection port of a GC/MS as shown in Figure 5.

**C. Neutrals Separation and Identification.** A Hewlett-Packard 5993B GC/MS was used to separate and identify the collected neutrals. The injection port used was a standard HP 18740B Capillary Column Control used in splitless mode with a straight, unpacked Pyrex liner. The GC/MS

was modified for our use and the modifications have been reported elsewhere.<sup>14</sup> Helium carrier gas (99.999%) with a linear flow velocity of 34 cm s<sup>-1</sup> was used. The column used was a 30 m, 0.25 mm i.d. 1.0 μm film thickness DB-5<sup>53</sup> fused silica wall-coated open tubular (capillary) column. The only flow into the chromatographic column is from the intermediate trap. Chromatography requires that a plug of the mixture to be analyzed be introduced to the column for analysis. The introduction of the sample in plug occurs at a retention time of zero. Our sample is bled onto the column over a period of 6 min and must be focused into a plug to facilitate separation by GC. During transfer from the intermediate trap, a section of the capillary chromatographic column is immersed in liquid nitrogen and the normal supply of helium to the port is interrupted. Immersion of a short section (about 10 cm) of the column in liquid nitrogen serves to cryofocus<sup>54</sup> (cold trap) the sample on the head of the column. At a retention time of zero, the liquid nitrogen is removed and the chromatogram is begun.

Authentic samples of propylene and 1-methoxypropane<sup>55</sup> were used to find an adequate temperature program for GC analysis. The temperature program decided upon was to hold at -50 °C for 3 min followed by a 10 °C min<sup>-1</sup> ramp. Under these conditions, propylene elutes at 3.0 (±0.2) min and 1-methoxypropane elutes at 11.2 (±0.1) min. The added neutral reactants, 1,2-dimethoxyethane and 1-bromopropane, both elute well after the possible neutral products. At the end of each chromatographic run, the column temperature was raised to 200 °C for 10 min to allow all material remaining on the column to elute. This protocol was used for all of the GC runs completed.

A description of the mass spectrometer used in the GC/MS and the method used for tuning it have been fully described elsewhere.<sup>14</sup> The mass spectrometer is equipped with only an EI source.<sup>56</sup> For all of the chromatographic runs used in this work, the instrument was operated in full scanning mode.<sup>57</sup> The MS was scanned over the range 13–100 amu at 145 amu s<sup>-1</sup>. Positive identification of neutral products required that the retention times and mass spectra match those of the authentic samples.

Operation of the cold finger during a typical sampling sequence is shown in Figure 5. Illustrated are the four stages of a typical analysis. The position of the cold finger, condition of the intermediate trap, and flow through the injection port are all indicated. All afterglow samples were collected for 10 min. Transfer to the intermediate trap took 6 min and transfer to the GC column took 6 min. At the end of the transfer to the GC column, the connection between the intermediate trap and the injection port was severed and normal, split flow through the injection port was resumed. Once the switch from split to splitless port flow was complete, a delay of 1 min was added to ensure that all material in the port was either vented or deposited on the column. After this delay, the chromatogram was started. Using the previously described temperature program, the chromatograms take up to 15 min each. After each run, the columns must be heated to remove any material left on the column. The minimum time required between the start of 2 consecutive sampling runs is about 1 h. The flowing afterglow can be kept relatively stable for a period of 4–8 h. Stability is monitored by observing the signals of ions produced by the microwave discharge. After some period of time, there is a marked reduction in the anion signals observed. This usually correlates with an increase in the amount of contaminants present in the helium stream. We attribute this to saturation of the traps used to purify the helium. All data were collected while the afterglow was stable. In spite of our persistent efforts to stabilize the afterglow, we find that deviations in chromatographic peak area during the neutrals collection of a factor of 100 are not uncommon. All attempts to make the experiment stable from one day to the next failed. Consequently, only data taken on a single day are compared to make conclusions.

**D. Signal Estimate.** It is instructive to estimate the number of neutral product molecules present in the flowtube and to estimate the efficiency of our trapping technique. Ion density can be estimated to be of order 10<sup>8</sup> cm<sup>-3</sup> in the reaction region;<sup>19</sup> these will be converted to neutral products by chemical reaction.

To estimate the amount of material trapped on the surface of the cold finger, the wall collision rate derived from the kinetic theory of gases<sup>58</sup>

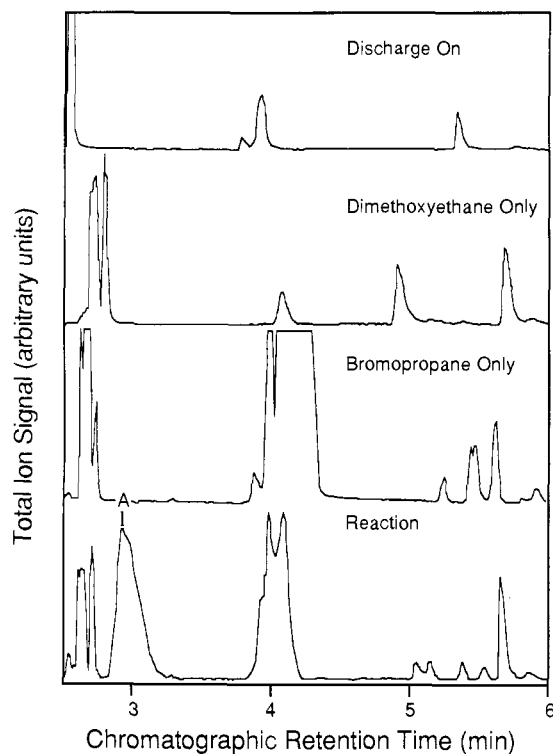
(53) DB-5 is a cross-linked 1% vinyl, 5% phenyl, methyl polysiloxane; a nonpolar stationary phase. The column was manufactured by J&W Scientific (Rancho Cordova, CA).

(54) Pankow, J. F. *J. High Resolut. Chromatogr. Chromatogr. Commun.* **1983**, *6*, 292.

(55) Synthesis of 1-methoxypropane was accomplished with phase-transfer-catalyzed etherification of alcohols. The synthesis used is included as Appendix C.

(56) Ionization is accomplished with a 220 μA emission current of 70 eV electrons from a rhenium filament.

(57) Software used in Hewlett-Packard's *Acquire* routine from their SIDS, Rev. F package.



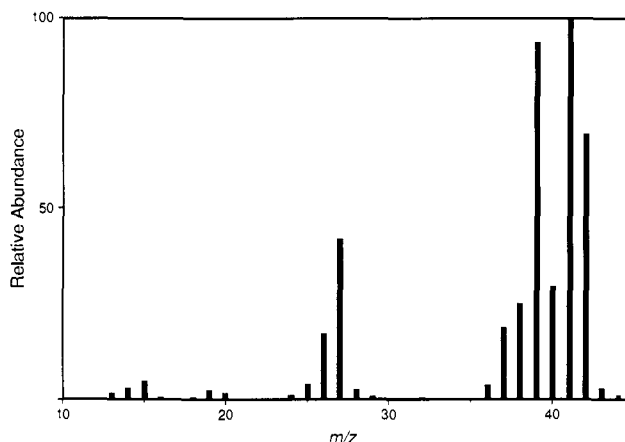
**Figure 6.** Chromatograms resulting from analysis of samples collected from the flowing afterglow. The traces shown are obtained in full scanning mode and are total ion chromatograms. All plots use the same vertical scale. The top trace, labeled Discharge On, shows a sample taken with 0.5 Torr of helium in the flowtube and the discharge ion source on. Without varying the ion source conditions, 1,2-dimethoxyethane is added and the trace labeled Dimethoxyethane Only results. Addition of 1-bromopropane with the ion source on produces the trace labeled Bromopropane Only. Simultaneous addition of both reagents produces the bottom trace labeled Reaction. The peak labeled A in the bottom trace is propylene.

may be used. Assume a density of  $10^8 \text{ cm}^{-3}$  of a molecule of molecular weight 100 at 300 K. The wall collision rate is approximately  $6 \times 10^{11} \text{ cm}^{-2} \text{ s}^{-1}$ . The dimensions of the cold finger create  $66.5 \text{ cm}^2$  of surface area. This means that the surface of the cold finger is struck by neutral products at a rate of  $3.98 \times 10^{13}$  collisions  $\text{s}^{-1}$ . Assuming unity sticking probability,  $3.97 \text{ nmol min}^{-1}$  will be collected. In a typical 10-min sample, up to 40 nmol of neutral product will be collected. It should be noted that this trapping rate exceeds the rate of the glass wool traps in our earlier work by over 3 orders of magnitude.

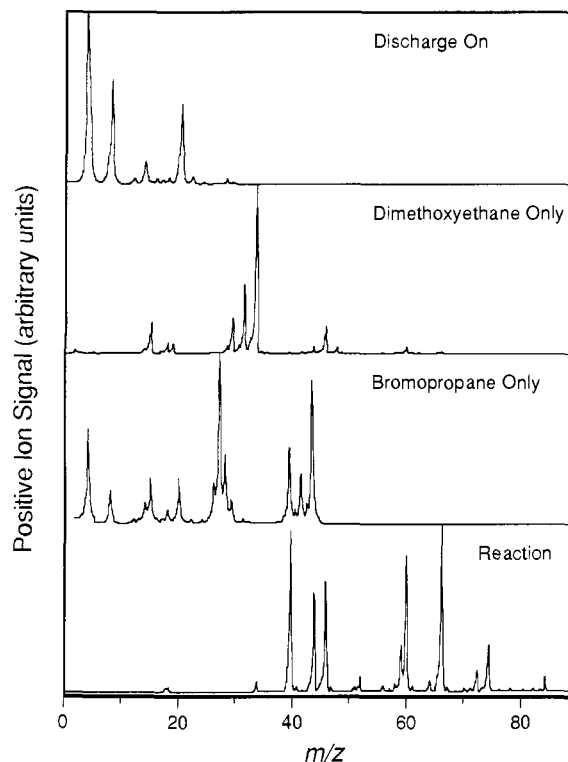
### III. Results

A single data set consists of 6 sample runs, all taken on the same day, which are compared to draw conclusions. They are (a) helium only, ion source off; (b) helium only, ion source on; (c) only 1,2-dimethoxyethane added, ion source on; (d) only 1-bromopropane added, ion source on; (e) 1,2-dimethoxyethane and 1-bromopropane added, ion source off; and (f) 1,2-dimethoxyethane and 1-bromopropane added, ion source on. Sample runs under condition f permit the reaction of methoxide ion with 1-bromopropane. Propylene was observed only in the type f samples. The signal of propylene exhibited large day-to-day deviations, but consistently was present only in the runs where both  $\text{CH}_3\text{O}^-$  and  $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$  were present. Some of the results from a typical day are shown in Figure 6. Propylene is only observed when 1-bromopropane is added to a plasma containing  $\text{CH}_3\text{O}^-$ , as seen in the trace labeled Reaction. The peak labeled A matches the retention time and mass spectrum (see Figure 7) of propylene. 1-Methoxypropane was not observed in any of the samples.

There is no doubt that a chemical reaction is producing propylene in the afterglow. Can we be certain that it is produced



**Figure 7.** The electron impact mass spectrum of the peak labeled A in Figure 6.



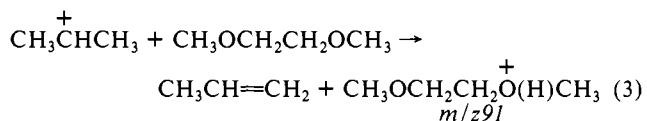
**Figure 8.** Shown are mass spectra of positive ions observed by the flowing afterglow mass spectrometer. The top trace, labeled Discharge On, shows a spectrum obtained with 0.5 Torr of helium in the flowtube and the discharge ion source on. Without varying the ion source conditions, 1,2-dimethoxyethane is added and the trace labeled Dimethoxyethane Only results. Addition of 1-bromopropane with the ion source on produces the trace labeled Bromopropane Only. Simultaneous addition of both reagents produces the bottom trace labeled Reaction.

by the ion chemistry shown in reaction 2? In the afterglow plasma, many reactive species are present and many different reactions take place. The neutrals collection experiment has shown that many products of unknown origin are produced. Present in the afterglow neutral plasma are negative ions, positive ions, and radical species all of which are reactive. Neutralization of anions and cations by collisions with the walls of the flowtube produces unknown products. The cold finger trap collects many of the products of these side reactions. As well, the cold finger traps reactive species in a frozen matrix on its surface making reactions on the surface of the cold finger a possibility. In this work, there are in excess of 10 peaks which differ in type e and f collection runs. Our experimental philosophy has been to focus on the plausible products of the reaction of interest and to ignore other observed products.

(58)  $Z_w = p/(2\pi mkT)^{1/2}$ . This formula used can be found in most Physical Chemistry texts. As an example see: Atkins, P. W. *Physical Chemistry*; W. H. Freeman Co., San Francisco, 1982; p 873.

There are several mechanisms that could produce propylene with reactive positive ions being the greatest concern. The positive ions present in the afterglow plasma are shown in Figure 8. The flowing afterglow plasma is neutral and the positive ion density was measured to be equal to the negative ion density. Measurement of the ion density was accomplished by configuring the quadrupole mass filter for radio frequency only operation. This allows ions of all masses to pass through the mass filter. In this mode, the quadrupole can be biased to pass either all negative or all positive ions entering the mass filter. The currents produced by ions striking a metal plate at the exit of the mass filter were identical for both positive and negative ions. Use of a magnetic field at the entrance to the mass filter had no effect on the signal observed when the filter was biased to pass negative ions. This indicates that the free electron density in the plasma is low. The  $\text{CH}_3\text{O}^-$  signal exceeded the signals of all positive ions present in the plasma. The lower number densities of the positive ions, when compared with methoxide ion, effectively preclude them as a source of the observed product.

Action of the microwave discharge on 1,2-dimethoxyethane is insufficient to destroy all of the very reactive species present;  $\text{He}^+$ ,  $\text{He}_2^+$ , and  $\text{C}^+$  are all still observable, though severely diminished, after the addition of the small amount of 1,2-dimethoxyethane. These ions are further attenuated when 1-bromopropane is added and an ion of  $m/z$  43 is formed. The identity of this species is most assuredly the propyl cation,  $\text{C}_3\text{H}_7^+$ . Neutralization of this ion might well proceed to produce propylene<sup>10</sup> by reaction with a species having a proton affinity greater than propylene. In particular, we must consider the following:



No signals at  $m/z$  91 are observed and reaction 3 can be dismissed as a source of the observed propylene. Protonated bromopropane is not observed, indicating that it too does not deprotonate propyl cation. Since neither of the added neutral reagents are observed to deprotonate the propyl cation under our experimental conditions we conclude that gas phase positive ion chemistry is not producing the observed propylene.

Neutralization of the propyl cation by collisions with the walls could possibly form propylene. We do not believe this is the case from evidence gathered by adding only 1-bromopropane to the flowtube with the ion source on. This produces large ion signals of the  $m/z$  43 cation, yet neutrals collection under these conditions shows only a large propane signal with no evidence of propylene.

Clearly evident in the bottom trace of Figure 8 are cations formed in association reactions. Reactions within these ill-defined clusters could be producing propylene. We made attempts to suppress cluster formation by addition of  $\text{N}_2$  and  $\text{CH}_4$  while making methoxide ion with only limited success. The addition of these reagents altered the association products formed but did not alter the neutral products formed. No completely satisfactory method was developed to cope with the reactive positive ions present. It is our contention that the positive ions are not producing the propylene observed since it is only observed when the negative ion chemistry indicates reaction 2 is occurring.

Of the radical channels that may produce propylene, we are more or less blind; we can make no direct observation of the radicals present in the flowtube. Propyl radicals produced by dissociative attachment of thermal electrons by 1-bromopropane, as illustrated in reaction 4, are a possibility. We have confirmed



the dissociative attachment channel for formation of  $\text{Br}^-$  in the absence of 1,2-dimethoxyethane by addition of an electron scavenger ( $\text{SF}_6$ ). Since no propylene is observed in the samples taken with the ion source on and only 1-bromopropane flowing, we must conclude that propyl radicals do not react to produce propylene. We also believe that reaction 4 is suppressed when 1,2-dimethoxyethane is added to the plasma.

oxyethane is added to the plasma.

In earlier work, an ion shutter was used to stop the reactant ions prior to addition of the neutral reactant<sup>13</sup> in order to prove that ion chemistry was creating the observed products. Our experience has indicated that this is not a worthwhile test. At high flowtube ion densities, the shutter only destroys between 1 and 2 orders of magnitude of reactant ion signal. The variation in our neutrals data exceeds the attenuation of the ion signal making the experiment inconclusive. The shutter has also been shown to produce other neutral products, presumably by causing nonthermal collisions. The ion shutter was not used for any of the experiments reported here. Technical constraints also prevented us from depositing 1-bromopropane on the cold finger and subsequently exposing the cold finger to methoxide ion. This experiment was attempted to prove that ion-molecule chemistry in the matrix was not contributing the observed product. Results from this experiment would have been welcomed, yet we do not feel the results are demanded.

Our detection of propylene only when reaction 2 is occurring indicates that it is the product of the reaction. Before concluding that the sole neutral product of reaction 2 is propylene, we had to confirm that we can detect the other possible product, 1-methoxypropane, using our apparatus. To confirm that we have sensitivity for the  $\text{S}_{\text{N}}2$  product, we studied the reaction<sup>59</sup> of methyl bromide (99.5%) with propoxide ion (reaction 5). Propoxide ion was formed by the action of the discharge on 1-propanol (AR grade). 1-Methoxypropane was unambiguously identified by its retention time and mass spectrum as a reaction product.



With this experiment, we have demonstrated that we have sensitivity for both possible reaction products at levels consistent with our signal estimate. Detection of propylene in the absence of 1-methoxypropane confirms that reaction 2 proceeds by elimination. The amount of propylene observed is consistent with our signal estimate. Experiments have indicated that we have slightly higher sensitivity for 1-methoxypropane than for propylene. Exact calibration is impossible, but we believe that our result indicates that more than 99% of the reactants follow the E2 pathway.

#### IV. Discussion

Our result indicates that extremely exothermic gas-phase reactions can show astounding selectivity. To help interpret our result, it is useful to examine other reported cases where E2 is shown to predominate over  $\text{S}_{\text{N}}2$ . Review of cases where inter- and intramolecular selectivity is displayed is also useful in placing our result in context.

Nucleophilic displacement ( $\text{S}_{\text{N}}2$ ) reactions have been studied extensively in the gas phase.<sup>60</sup> They often compete with other processes, such as base-induced elimination (E2)<sup>1,61,62</sup> and proton transfer.<sup>63</sup> In traditional methods only the ion products can be observed and the charged leaving group is identical in many  $\text{S}_{\text{N}}2$  and E2 processes as illustrated in reaction 1. As a result, qualitative observation of the charged species does not indicate which reaction is occurring. There are four methods that have been used to probe competition between  $\text{S}_{\text{N}}2$  and E2. These are (1) direct detection of the neutral product, (2) detection of an ion cluster indicative of E2, (3) systematic study of reaction rate constants, and (4) observation of kinetic isotope effects.

Brauman and co-workers have reported<sup>8</sup> observation of an  $\text{S}_{\text{N}}2$  product resulting from the reaction of  $\text{F}^-$  and  $\text{CH}_3\text{CH}_2\text{Cl}$ . Neutral products of reactions carried out in an ICR cell were identified by characteristic EI mass spectral peaks. This was accomplished by reionizing the gas present in the reaction cell after reaction

(59) The heat of reaction 3 is calculated to be  $-49 \text{ kcal mol}^{-1}$ .

(60) (a) Bowie, J. H. *Acc. Chem. Res.* **1980**, *13*, 76. (b) DePuy, C. H.; Bierbaum, V. M. *Acc. Chem. Res.* **1981**, *14*, 146. (c) Comita, P. B.; Brauman, J. I. *Science* **1985**, *227*, 863. (d) Riveros, J. M. *Adv. Phys. Org. Chem.* **1985**, *21*, 197.

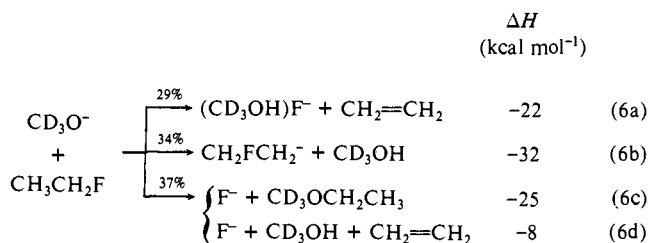
(61) Ridge, D. P.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1974**, *96*, 3595.

(62) de Koning, L. J.; Nibbering, N. M. M. *J. Am. Chem. Soc.* **1987**, *109*, 1715.

(63) Sullivan, S. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1976**, *98*, 1160.

and ingeniously using the ICR reaction cell as a positive ion mass spectrometer. In some cases, the unique positive ion peaks of the neutral products were unobscured by the large excess of reactant gas and could be observed. The reaction of  $F^-$  and  $CH_3CH_2Cl$  produced  $CH_3CH_2F$  (the  $S_N2$  product) which was identified by the presence of characteristic positive ions in the reaction mixture. Detection of the E2 product, ethylene, was impossible because the mass spectrum of ethylene contains no unique ions; all ions formed are also present in the mass spectra of the neutral reactants. In contrast, our results indicate that E2 predominates for the reaction of  $CH_3O^-$  with  $CH_3CH_2CH_2Br$ .

Beauchamp and co-workers studied gas-phase eliminations by detection ion cluster products resulting from reactions of ethyl fluorides.<sup>61</sup> In the case of  $F^-$  reacting with  $CH_3CH_2F$ , the cluster  $(FHF)^-$  ion is observed as a reaction product. This product can only be produced by an E2 process and is clear evidence that the reaction proceeds by elimination. In the reaction of  $CH_3O^-$  with  $CH_3CH_2F$ , determination of the reaction channel is not so straightforward. The three reaction products observed are shown below.



Clearly, proton transfer (reaction 6b) and elimination (reaction 6a) can compete with substitution. It cannot be known from observation of only this reaction whether (6c), (6d), or both take place. Note that reaction 6d and reaction 6a are both E2 channels; in (6d), products are clustered and in (6a) they are not. The difference in exothermicity is just the bond strength of the cluster. Observation of multiply substituted ethyl fluorides indicates that as the reaction energy drops below the bond strength of the cluster, the reaction follows only paths analogous to (6a) and (6b). This is taken as evidence that reaction 6d is the channel producing the observed  $F^-$  and that nucleophilic displacement does not occur. An ab initio treatment<sup>64</sup> based on this work reveals a preference for E2 as well. Reactions of  $CH_3O^-$  with  $CH_3CH_2Cl$  and  $CH_3CH_2Br$  do not form clusters and no information of the reaction channel can be gained by observation of only the ion products.

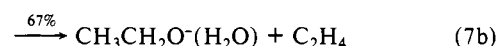
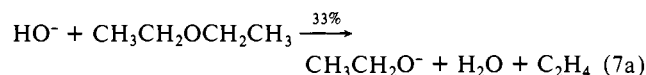
Some researchers conclude that observation of clusters can be viewed to indicate a preference for a *syn* elimination while lack of clustering indicates an *anti* elimination.<sup>61,62</sup> These conclusions are difficult to rationalize for the ethyl halides since it would propose a mechanism for ethyl fluoride which differs from that for ethyl chloride and ethyl bromide. Cluster ion formation is always thermodynamically favorable and the lack of clustering exhibited by alkyl chlorides, bromides, and iodides is unsettling.

The work just cited<sup>61</sup> also exposes a reaction that exhibits incredible selectivity in choosing a reaction channel. If one accepts the authors' interpretation of the  $CD_3O^-$  with  $CH_3CH_2F$  result, 66% of the total observed reactions proceed via elimination. The remaining 34% proceeds by proton transfer, which is the most exothermic reaction channel (-32 kcal mol<sup>-1</sup>). As the authors point out, it is surprising that E2 can compete with proton transfer since the frequency factor for proton transfer should be much higher and since both reaction channels are exothermic. The fact remains that E2 does not compete, which illustrates the tendency of gas-phase reactions to exhibit selectivity even when reaction energies are high.

Another tactic used to observe the preference for E2 over  $S_N2$  is to study the reactions of substrates that are blocked with respect to elimination. Choosing reagents with  $\beta$ -hydrogens and close analogues without  $\beta$ -hydrogens is one of the most direct approaches to this problem. Reactions of a variety of bases with fluoro-

methanes show a generally slow rate of reaction for substitution.<sup>65</sup> Sullivan and Beauchamp studied reactions of a variety of bases with fluoroethanes<sup>63</sup> and observed substantially faster reaction rates suggestive of a change in reaction mechanism. From kinetic data and observations of some cluster ions they conclude that fluoroethanes react predominantly via E2.

Dimethyl ether and methyl *tert*-butyl ether are almost completely unreactive in the gas phase to even the strongest base, while diethyl ether reacts rapidly with either amide or hydroxide ion.<sup>1</sup> This is considered evidence that E2 reactions occur readily in the gas phase even in molecules for which  $S_N2$  processes are extremely slow. Further evidence for the E2 mechanism is the appearance of a hydrate between the water formed in the elimination and the alkoxide leaving group. Such a product cannot be formed by an  $S_N2$  process.



Other examples of gas-phase E2 processes occur in studies of cyclic ethers.<sup>66</sup> For example, ethylene oxide reacts only slowly with  $HO^-$  or  $NH_2^-$  by substitution. In contrast, propylene oxide, which contains  $\beta$ -hydrogens, reacts much more rapidly, probably by elimination. Again, this is evidence that E2 is preferential to  $S_N2$  when the channels compete.

For reactions of strong bases ( $NH_2^-$ ,  $OH^-$ ,  $CH_3O^-$ ) with alkyl halides,  $S_N2$  and E2 are always extremely exothermic (>20 kcal mol<sup>-1</sup>) and occur on almost every collision. Systematic studies<sup>63,67</sup> using a number of reactant ions and neutrals have been used to gain insight into competition between possible reaction channels. These studies are difficult since evidence for barriers on the reaction surface is observed only for weak bases and extending the results to strong bases is questionable. It has been observed that there are intrinsic barriers to nucleophilic displacements.<sup>68</sup> Theoretical treatments of this phenomenon have had some success in predicting the barrier heights for displacement reactions.<sup>69</sup> For a particular substrate, reducing the basicity of the nucleophile can cause an abrupt reduction in reaction rate. The rapid change in rate occurs as the calculated barrier height for  $S_N2$  begins to approach the available energy. A change in reaction mechanism is one interpretation of the observed reduction in reaction rate. On plausible explanation for the abrupt change in reaction rate observed in the systematic studies is simply that E2 becomes energetically prohibitive as the base strength decreases. The slow reaction observed for very weak bases may be due to the  $S_N2$  channel that can be observed in the absence of competition.

Systematic studies of reaction kinetics can be interpreted in a number of ways. Observations of intermolecular kinetic isotope effects are a far more definitive way to detect the mechanism of a reaction. Reactions involving ethers have been shown to exhibit kinetic isotope effects indicative of an E2 mechanism. In experiments using strong bases ( $NH_2^-$ ,  $OH^-$ ) with deuterated and undeuterated diethyl ether extremely large kinetic isotope effects are observed.<sup>70</sup> Observation of an isotope effect in the reactions of alkyl chlorides, bromides, and iodides is difficult. These alkyl halides react at essentially the collision rate with most strong and moderate bases. Under such conditions, observation of an isotope effect is impossible; the reaction is already as fast as it can be. Only when the base is weak and the reaction is slower can isotope effects be observed. Such isotope effects, characteristic of an E2 mechanism, have been observed in the reactions of ethyl iodides.<sup>71</sup>

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This serves as further evidence of the intrinsic preference for E2 over  $S_N2$ .

The apparent preference for E2 over  $S_N2$  may well be interpreted in at least two ways. Calculations on one system have shown<sup>70</sup> that the barrier for E2 lies below that for  $S_N2$ . While this result cannot be generalized to other systems with absolute certainty, it may be indicative of a common trend. Clearly, one plausible explanation for the observed preference for E2 is that the activation barrier is always lower. A more subtle possibility is that the amount of available phase space at the transition state is larger for E2 than for  $S_N2$ . The  $S_N2$  reaction requires backside attack on a carbon center along a narrow trajectory. This means that little phase space is available at the transition state. The E2 process involves attack on one of multiple  $\beta$ -hydrogens and multiple trajectories should allow the reaction to occur. Multiple trajectories mean that more phase space is available at the transition state. There is also the possibility that both factors contribute to favor the E2 channel.

The results of this study together with other findings in the literature suggest that in gas-phase reactions where E2 and  $S_N2$  channels compete, E2 is favored. Direct observations of only an E2 neutral product in the reaction of  $\text{CH}_3\text{O}^-$  with  $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$  is clear evidence of this trend. Our gas-phase results are in stark contrast to solution findings (see Table I) that indicate a preference for  $S_N2$ .

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## Appendix A

**Calculation of Heats of Reaction.** This appendix collects the thermochemical data used to calculate the heat of reactions reported.

molecule	$\Delta H^\circ_{298}$ (kcal mol <sup>-1</sup> )	ref
$\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$	-20.79	a
$\text{CH}_3\text{CH}_2\text{CH}_2\text{OCH}_3$	-56.93	a
$\text{CH}_3\text{CH}=\text{CH}_2$	4.78	a
$\text{CH}_3\text{OH}$	-48.16	a
$\text{CH}_3\text{Br}$	-8.485	a
$\text{CH}_3\text{O}^-$	-33.3	b
$\text{Br}^-$	-50.6	c
$\text{CH}_3\text{CH}_2\text{CH}_2\text{O}^-$	-50.9	b

<sup>a</sup>Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*, 2nd ed.; Chapman and Hall: New York, 1986.

<sup>b</sup>Bartmess, J. E.; Scott, J. A.; McIver, R. T., Jr. *J. Am. Chem. Soc.* **1979**, *101*, 6047. <sup>c</sup>Hotop, H.; Lineberger, W. C. *J. Phys. Chem., Ref. Data* **1985**, *14*, 731.

## Appendix B

**Calculation of Trapping Efficiency.** In order to estimate trapping efficiency, an expression describing wall losses in a cylindrical tube was developed. This was done in an approximate way by reducing the problem to two dimensions.

Begin by assuming that a mixture of A and B with uniform concentration is flowing into a cylindrical tube. Assume that a B molecule sticks to the wall on every collision. Assume that the only movement of molecules perpendicular to the flow is diffusion controlled and that diffusion of the molecules with the flow can be neglected. Removal of the diffusion in the direction of the flow

(71) Bierbaum, V. M.; DePuy, Charles, H., unpublished results received in a private communication.

greatly reduces the complexity of the problem by reducing it to two dimensions. The variables remaining are the concentration ( $C$ ), the distance away from the center of the tube ( $r$ ), and time ( $t$ ).  $D$  is the diffusion coefficient and can be estimated from the kinetic theory of gases.<sup>72</sup> The differential equation describing the motion is

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial r^2} + \frac{1}{r} \frac{\partial C}{\partial r} \quad (\text{B1})$$

A solution to this differential equation, as published by Rideal and Tadayon,<sup>73</sup> is

$$C(r,t) = C_0 \int_0^\infty du J_1(r_0 u) J_0(r u) e^{-D u^2 t} \quad (\text{B2})$$

$J_0(z)$  and  $J_1(z)$  are the usual Bessel functions of order zero and one, respectively, and  $r_0$  is the radius of the tube. When  $r = r_0$  the molecule is lost by collision with the wall. Thus, the amount remaining in the tube is found by integration from  $0 \rightarrow r_0$ . Solving for the amount remaining by integration over  $r$  yields

$$\begin{aligned} C(t) &= C_0 \int_0^\infty du J_1(r_0 u) e^{-D u^2 t} \int_0^{r_0} r dr J_0(r u) \\ &= 2C_0 \int_0^\infty du \frac{J_1^2(r_0 u)}{u} e^{-D u^2 t} \end{aligned} \quad (\text{B3})$$

Expression B3 can be solved numerically to yield the amount of B remaining in the flow at some time  $t$ . This treatment assumes plug flow through the tube where time and length ( $L$ ) of the tube can be equated by the following expressions:

$$\text{time in trap} = \text{volume of trap} / \text{flow rate} \quad (\text{B4})$$

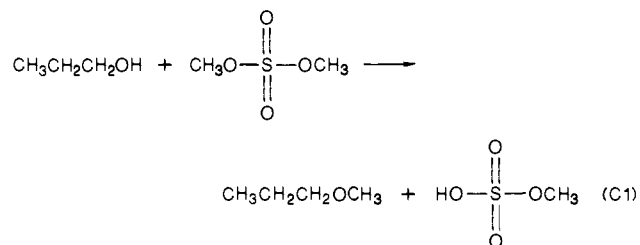
$$\text{volume of trap} = \pi L r_0^2 \quad (\text{B5})$$

$$L / \text{flow rate} = \text{time} / \pi r_0^2 \quad (\text{B6})$$

This treatment compared favorably with the approximate solution of Gormley and Kennedy.<sup>74</sup> When used with a reasonable integration routine and Bessel function, our solution is quite tractable.

## Appendix C

**Synthesis of 1-Methoxypropane (Methyl *n*-Propyl Ether).** Production of 1-methoxypropane (methyl *n*-propyl ether) was accomplished by phase-transfer-catalyzed alkylation of *n*-propyl alcohol with dimethyl sulfate.<sup>75</sup> No synthesis of this particular ether could be found in the literature. The two-phase method was chosen over the classic Williamson ether synthesis on the basis of its experimental simplicity. The overall reaction is



The phase-transfer-catalyzed method of etherification of alcohols involves dissolving the alcohol in an inert organic solvent immiscible with water. Once the reaction has occurred, the ether produced will partition itself in the organic phase. Under normal

(72) Descriptions of the calculation of diffusion coefficients can be found in: (a) Hirschfelder, J. O.; Curtiss, C. F.; Bird, R. B. *Molecular Theory of Gases and Liquids*; J. Wiley and Sons: New York, 1954; pp 539-583. (b) Bird, R. B.; Stewart, W. E.; Lightfoot, E. N. *Transport Phenomena*; J. Wiley and Sons: New York, 1960; pp 496-511.

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circumstances, it is desirable to have the organic phase somewhat volatile to facilitate the separation of the ether produced. The methyl propyl ether is very volatile (bp < 40 °C) and a high boiling solvent seemed preferable. Propyl alcohol is very soluble in water and a polar solvent was chosen to help keep the alcohol partitioned in the organic phase. The organic solvent chosen was chlorobenzene.

0.0625 mol of propanol	6 mL
tetrabutylammonium iodide (TBAI)	0.125 g
chlorobenzene	25 mL
0.1625 mol 50% NaOH solution	9 mL
0.075 mol dimethyl sulfate	7 mL
concentrated NH <sub>4</sub> OH	1.5 mL
total volume =	49 mL

Propanol, chlorobenzene, and TBAI are mixed and allowed to equilibrate with the NaOH solution for 15-30 min. During this step, the mixture is cooled in an ice bath to absorb the heat evolved. The dimethyl sulfate is added dropwise over a period of 45-60 min. The ice bath is continued during this step. Considerable foaming and thickening of the mixture occurs. The reaction must be carefully monitored to ensure that vigorous stirring is main-

tained. The ice bath is removed and replaced with a water bath. The mixture is allowed to stir for 2 h. At this point, the reaction should be complete. Concentrated NH<sub>4</sub>OH is added and stirred for an additional 30 min to destroy any unreacted dimethyl sulfate. The mixture is washed over water and the organic phase is retained. Care must be taken to be sure that the organic phase is retained. The first washing produces an organic phase that is less dense than the basic aqueous phase. The next washing produces an aqueous phase that is less dense than the organic phase. Presence of the ether was confirmed by EI mass spectrometry using the HP 5993B GC/MS and a published EI mass spectrum.<sup>76</sup> Reaction efficiency was not investigated and the sample was not further purified. Determination of the retention time was completed with use of the ether dissolved in chlorobenzene. This synthesis was also used to make 2-methoxypropane (isopropyl methyl ether) from isopropyl alcohol.

Registry No. CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>Br, 106-94-5; CH<sub>3</sub>O<sup>-</sup>, 3315-60-4.

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## Experimental Study of the Potential Energy Surface of the Protonated Cyclohexene Oxide/Cyclohexanone System. Isomerization, Dissociation, and Ion-Molecule Reactions of the Isolated Ions in the Gas Phase

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**Abstract:** The structures and properties of gaseous protonated cyclohexene oxide and cyclohexanone are studied by employing dissociation and ion-molecule reactions occurring in a triple quadrupole mass spectrometer, a quadrupole ion trap, and a hybrid BQ tandem mass spectrometer. Upon activation by collisions with either a gas-phase target or a surface, isomerization occurs and results in identical dissociation products with similar abundances for the two ions. This is explained by the small barrier of isomerization (ca. 12 kcal/mol) estimated for the epoxide ion. The product arising from the lowest energy dissociation reaction (H<sub>2</sub>O loss) is the cyclohexenyl cation and not a methylcyclopentenyl cation as suggested earlier. In contrast to its behavior in superacid media, cyclohexenyl cation does *not* undergo facile ring contraction in the gas phase. Protonated cyclohexene oxide and protonated cyclohexanone do have distinct structures at low internal energies, as indicated by their different product distributions from gas-phase reactions with various organic reagents, including 1,3-pentadiene, dimethoxymethane, crotonaldehyde, and methyl formate. Reactivity with ethyl vinyl ether is particularly noteworthy since this reagent forms, in great abundance, a stable adduct with the epoxide ion but not with ions incorporating other oxygen-containing functionalities, e.g. protonated ketones, esters, ethers, and alcohols. The mechanism of the adduct formation reaction is discussed. The proton affinity of cyclohexene oxide was determined by energy-resolved bracketing experiments, a technique in which a proton-transfer reaction is judged as endo- or exothermic on the basis of its dependence on the reactant ion kinetic energy. The value for cyclohexene oxide was found to be 202 ± 5 kcal/mol, which yields a heat of formation for protonated cyclohexene oxide of 135 ± 5 kcal/mol. Results obtained by examination of the dissociation and ion-molecule reaction products of parent ions with differing amounts of internal energy, and determination of kinetic energy thresholds for collision-activated dissociation reactions of stable parent ions, indicate that about 10 kcal/mol is required for isomerization as well as for water loss from protonated cyclohexene oxide. The potential energy surface obtained for the protonated cyclohexene oxide/cyclohexanone system is compared with those calculated or estimated earlier for other epoxides.

Acid-catalyzed reactions involving opening of an epoxide ring are of wide interest.<sup>1-6</sup> Aside from their synthetic importance, acid-catalyzed nucleophilic addition reactions of epoxides play an important role in metabolic activation of carcinogens.<sup>1,6-9</sup> Accordingly, many experimental studies have focused on the mechanisms and energetics of reactions of protonated epoxides

in condensed phases.<sup>1-5,8</sup> Several groups have employed theoretical calculations to gain a better understanding of the parameters

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