

ation of naphthalene with benzoyl chloride and traces of catalysts at reflux temperatures reportedly favors the formation of **1** predominantly.<sup>20-22</sup>

The mechanistic and synthetic implications of the results reported in this communication, which represent the most significant evidence to date of the incursion of reversibility in Friedel-Crafts acylations, is under active investigation.

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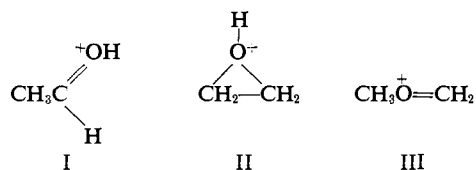
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### Nucleophilic Attack on Protonated Oxiranes in the Gas Phase. Identification of the $C_2H_5O^+$ Isomeric Ion Corresponding to Protonated Ethylene Oxide

Sir:

In recent years the  $C_2H_5O^+$  structural isomers corresponding to protonated acetaldehyde (I), protonated ethylene oxide (II), and the methoxymethyl cation (III)



have been the subject of extensive investigations directed primarily at developing methods for identifying isomeric ions.<sup>1-9</sup> These investigations have utilized labeling experiments in conjunction with studies of metastable ion characteristics,<sup>1,2,6-8</sup> collision induced decompositions at high energies,<sup>2,6</sup> thermochemical studies,<sup>3,5,9</sup> and a number of studies in which ion-molecule reactions involving  $C_2H_5O^+$  isomers as reactants, intermediates, or products have been reported.<sup>3-5</sup> While the possibility of distinguishing I and II from III on the basis of metastable ion characteristics and specific ion-molecule reactions has been clearly demonstrated, it has not proven possible to provide definitive evidence for the existence of a unique ion corresponding to structure II. The only possible exception are some subtle differences in proton transfer reactions involving I and II as reported by Blair and Harrison.<sup>3</sup> Failure to identify II has been attributed to the possible rearrangement of this isomer to the sig-

(1) B. G. Keyes and A. G. Harrison, *Org. Mass. Spectrom.*, submitted for publication.

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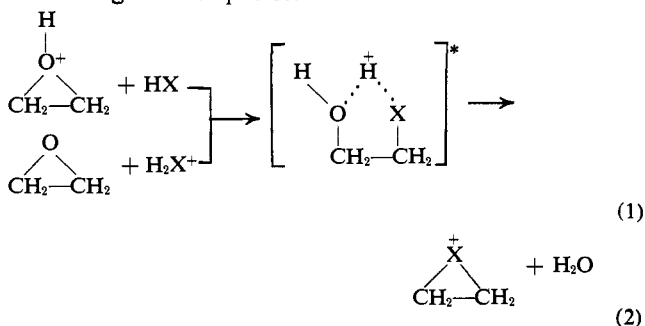
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nificantly more stable protonated acetaldehyde isomer I.<sup>10-14</sup> We wish to report a straightforward method, based on the identification of specific ion-molecule reactions using the techniques of ion cyclotron resonance (icr) spectroscopy,<sup>15</sup> for distinguishing the  $C_2H_5O^+$  structural isomer II from I and III. The reactions observed have implications for further studies of the gas-phase reactions of various nucleophiles with protonated oxiranes and related strained ring compounds and bear an interesting relationship to recently reported studies of neighboring group effects in the ionization of  $\beta$ -substituted alcohols.<sup>16</sup>

The gas-phase ion chemistry of ethylene oxide has been reported by several investigators.<sup>3-5</sup> The parent ion reacts to form the protonated parent and, in a higher order process, an ion corresponding to  $m/e$  57 ( $C_2H_5O^+$ ).<sup>3</sup> The gas-phase ion chemistry of phosphine has been extensively investigated using icr techniques<sup>17</sup> and high-pressure mass spectrometry.<sup>18</sup> At thermal energies the parent ion reacts to generate only the protonated parent ion.<sup>17,18</sup> The variation of ion abundance with time observed in a trapped ion icr<sup>11</sup> study of a mixture of phosphine and ethylene oxide is shown in Figure 1. In addition to the ions expected, at long times a prominent condensation product is observed at  $m/e$  61, corresponding to  $C_2H_6P^+$ .<sup>19</sup> Double resonance experiments identify reactions 1 and 2 with  $HX = PH_3$  as leading to this species.<sup>20</sup>



(10) Recent trapped ion experiments<sup>11</sup> in our laboratory give the proton affinity of ethylene oxide as being 1.0 kcal/mol greater than acetaldehyde.<sup>12</sup> Using  $\Delta H_f(\text{CH}_3\text{CHOH}^+) = 143$  kcal/mol<sup>13</sup> gives 169 kcal/mol as the heat of formation of protonated ethylene oxide. The methoxy methyl cation is of intermediate stability,  $\Delta H_f(\text{CH}_3\text{OCH}_2^+) = 158$  kcal/mol.<sup>14</sup>

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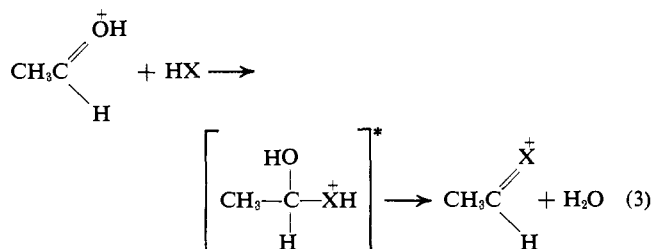
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(19) The ion at  $m/e$  48 is formed in the reaction  $C_2H_4O^+ + \text{PH}_3 \rightarrow \text{CH}_2\text{PH}_3^+ + \text{CH}_2\text{O}$ . Since this ion is formed at the expense of  $m/e$  57 ( $C_2H_5O^+$ ) normally observed in ethylene oxide alone, it is probable that the reactant is the energetically modified  $C_2H_4O^+$  ion discussed by Blair and Harrison, who report observations of a similar reaction in a mixture of acetone and ethylene oxide.

(20) With continuous ejection of  $m/e$  35 ( $\text{PH}_4^+$ ) during the reaction sequence,  $m/e$  61 still forms to a substantial extent. Reaction 1 is thus an important source of  $m/e$  61.

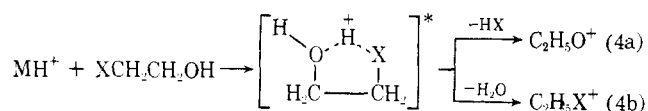
Reactions 1 and 2 are not specific for  $\text{PH}_3$  in that they occur as well with other hydrides. For example, in a mixture of ethylene oxide and hydrogen sulfide, reactions 1 and 2 ( $\text{HX} = \text{H}_2\text{S}$ ) are observed to produce an ion at  $m/e$  61 corresponding to  $\text{C}_2\text{H}_5\text{S}^+$ . In contrast to the behavior observed with ethylene oxide, in mixtures of acetaldehyde with  $\text{PH}_3$  and  $\text{H}_2\text{S}$ , reactions corresponding to the generalized process 3 are not



observed. In mixtures of 1,2-dimethoxyethane with  $\text{PH}_3$  and  $\text{H}_2\text{S}$ , the  $\text{C}_2\text{H}_5\text{O}^+$  isomer III does not lead to a condensation product at  $m/e$  61. Clearly reaction 1 serves to identify the protonated oxirane structure II, distinguishing it from I and III.<sup>21</sup>

In comparing reactions 1 and 3, the replacement of oxygen by phosphorus or sulfur in the three-membered rings is likely to be favored on energetic grounds, there being considerably less strain energy with the second-row atom.<sup>22</sup> In contrast, replacement of oxygen with phosphorus or sulfur in reaction 3 is unfavorable since  $\pi$  bonding to carbon is ineffective in the product ion.<sup>23</sup> In fact it is highly probable that reaction 3 proceeds favorably in the reverse direction in accordance with recently proposed rules for nucleophilic attack on substituted carbonium ions.<sup>24</sup>

Our observations bear an interesting relationship to the recent study of gas-phase ion chemistry of  $\beta$ -substituted alcohols reported by Caserio and coworkers.<sup>16</sup> They identified the preferred product in reaction 4 for



various proton donors  $\text{MH}^+$  to involve loss of  $\text{HX}$  for  $\text{X} = \text{F}$  and  $\text{Cl}$  and loss of  $\text{H}_2\text{O}$  for  $\text{X} = \text{Br}$ ,  $\text{OR}$ ,  $\text{SR}$ ,  $\text{SH}$ , and  $\text{NH}_2$ . Their suggestion that product stability is a major factor determining the mode of dissociation is corroborated by our experiments, in which similar intermediates are postulated, the mode of formation being *via* the reverse of reaction 4a.

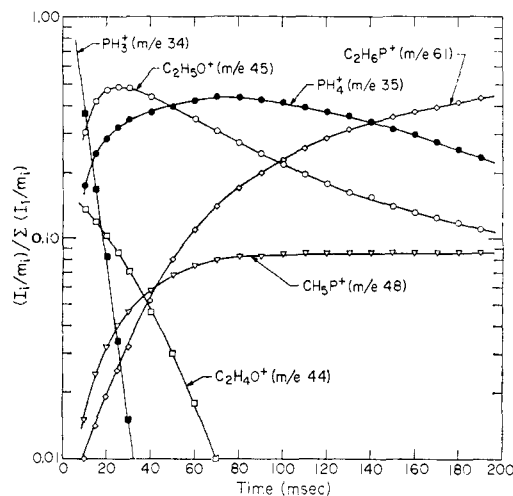
In addition to providing ion structural information and being of mechanistic interest, studies such as those reported above have interesting implications relating to the stability of strained cyclic ions. We are currently investigating the occurrence and preferred direction of reactions involving nucleophilic attack on strained cyclic ions containing oxygen, nitrogen, sulfur, phosphorus, and halogen heteroatoms.

(21) The reactant ion in process 1 may not be the initially formed  $\text{C}_2\text{H}_5\text{O}^+$  since this species may undergo further collisions with  $\text{C}_2\text{H}_4\text{O}$  prior to reactions with  $\text{PH}_3$ .

(22) Thermochemical estimates in ref 15 indicate that reaction 1 is  $\sim 32$  kcal/mol exothermic for  $\text{HX} = \text{H}_2\text{S}$ .

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**Figure 1.** Variation of ion abundance with time for a mixture of ethylene oxide ( $3.3 \times 10^{-6}$  Torr) and phosphine ( $3.7 \times 10^{-6}$  Torr) at an electron energy of 12 eV. Ionic species less than 5% of the total ionization are not shown.

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(25) Earle C. Anthony Predoctoral Fellow, 1973-1974.

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### The Nature of Electron Delocalization in a Heteropoly "Blue" Anion. Evidence for Valence Trapping at Low Temperatures

Sir:

A number of heteropoly oxo complexes of molybdenum(VI) and tungsten(VI) are reducible to a series of mixed valence (V, VI) complexes known as heteropoly blues.<sup>1</sup> In most cases the several reducible metal atoms in a heteropoly complex are structurally equivalent, and as a result there is some uncertainty as how best to describe the electronic structures of the reduced substances. We report here the electron spin resonance (esr) spectrum of a heteropoly anion at temperatures between 6 and 300°K. The spectra reveal a valence oscillation that can be described as an intramolecular electron hopping process, and we can show that the electron becomes trapped on a single metal atom at very low temperatures. Although such a thermal electron delocalization has been postulated for other mixed valence systems,<sup>2</sup> the present results constitute the first demonstration of temperature-dependent valence trapping in a polynuclear complex. The temperature be-

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