

δ 4.35 (AA' of AA'XX') assigned to the C-7 methylene protons of **71a**. A triplet at δ 4.15 ($J = 6.4$ Hz) was assigned to the C-5 methylene protons of 3-ethyl-5-hydroxypentanoate lactone. Integration gave a ratio of 92:8, respectively.

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Supplementary Material Available: Preparation of **9**, **11**, a *Z-E* mixture of 2-acetoxy-1-(2'-methoxyethen-1'-yl)-3-cyclohexene, **10a**, **10b**, 6-tetrahydropyran-2-yl-1-hexanol, **26**, **52**, **53**, **54**, ethyl (*E*)-5-(*tert*-butyldimethylsiloxy)-2-pentenoate, and **64** (14 pages). Ordering information is given on any current masthead page.

Mechanism of the Ozonolysis of Ethylene in the Liquid Phase

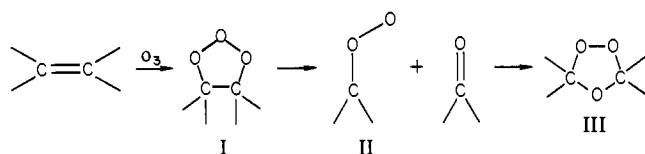
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Abstract: The ozonolysis of ethylene to ethylene ozonide was studied in a variety of solvents. The cross-ozonide yields, aldehyde-insertion yields, secondary kinetic isotope effects, and reaction stereochemistry were evaluated by using mass spectroscopy and microwave spectroscopy to follow isotopic labels. Yields of ozonide are high and can be maximized with polar solvents and low temperatures. Cross-ozonide and aldehyde-insertion yields increase with solvent polarity. They reach essentially the statistically expected limits at moderate values of solvent dielectric constants. Inverse secondary deuterium isotope ratios were observed for ethylene upon reaction with ozone and for formaldehyde incorporation in the final ozonide. Stereolabeled ethylene-1,2- d_2 yields a 1:1 mixture of *cis*- and *trans*-ozonides. These results correlate well with the Criegee mechanistic description for ozonolysis in solvents.

Introduction

The production of ozonides in solvents can be described by the three-step Criegee mechanism.¹ Recent modifications have in-



corporated stereochemistry considerations (for example, *syn* and *anti* forms for II) in order to extend the proposal to substituted alkenes where stereo effects are observed from alkene to ozonide configuration.²⁻⁴ These revisions also viewed the three reaction steps as concerted, symmetry-allowed 1,3-cycloadditions or reversions.

However, there have been results for some alkenes which do not readily incorporate into the Criegee scheme and its stereo revisions. One category of experiments involves solvent effects. For example, the amount of ozonide produced from di-*tert*-butylethylene decreases in polar solvents or when the concentration

of an added aldehyde is increased.⁵ In a study of the decomposition behavior of the primary ozonide of *trans*-3-hexene in CF_2Cl_2 and $(\text{C}_2\text{H}_5)_2\text{O}$, the amount of aldehyde produced and the stage at which it was observed varied considerably for the two solvents.⁶ Such solvent variations led Criegee to raise the question whether they can be correlated with any solvent parameters.¹ The results for di-*tert*-butylethylene have led to speculation⁵ that steps 2 and 3 in the Criegee proposal may be nonconcerted under some conditions. Nonconcerted pathways for steps 2 and 3 have also been recently proposed on the basis of a theoretical analysis.⁷

Another category of data troublesome for the revised Criegee proposals involves some stereochemistry results. For example, there are variations in the *cis/trans* yields of III as solvent and olefin concentrations are changed.^{8,9} Some of these effects have been explained by variations in the equilibration of the *syn* and *anti* zwitterion forms of II,³ although a recent theoretical analysis questions this approach.¹⁰

(1) R. Criegee, *Angew. Chem., Int. Ed. Engl.*, **14**, 745 (1975).
 (2) R. P. Lattimer, R. L. Kuczkowski, and C. W. Gillies, *J. Am. Chem. Soc.*, **96**, 348 (1974).
 (3) P. S. Bailey and T. M. Ferrell, *J. Am. Chem. Soc.*, **100**, 899 (1978).
 (4) P. S. Bailey, "Ozonation in Organic Chemistry", Vol. I, Academic Press, New York, 1978.

(5) V. Ramachandran and R. W. Murray, *J. Am. Chem. Soc.*, **100**, 2197 (1978).

(6) F. L. Greenwood and L. J. Durham, *J. Org. Chem.*, **34**, 3363 (1969); F. L. Greenwood, *ibid.*, **30**, 3108 (1965).

(7) L. B. Harding and W. A. Goddard III, *J. Am. Chem. Soc.*, **100**, 7180 (1978).

(8) F. L. Greenwood, *J. Am. Chem. Soc.*, **88**, 3146 (1966).

(9) R. W. Murray, R. D. Youssefeyeh, G. J. Williams, and P. R. Story, *Tetrahedron*, **24**, 4347 (1968).

(10) D. Cremer, *J. Am. Chem. Soc.*, **101**, 7199 (1979).

Also, stereo results for some small alkenes do not correlate with the mechanistic postulates in a straightforward fashion. For example, *cis*- and *trans*-2-butenes both yield the same ratio of final *cis*- and *trans*-ozonides. It has been suggested that when steric bulk is small, effects other than simple steric interference such as electronic or solvent effects may influence the stereochemistry.^{2,3,11} The possibility of some intramolecular, non-Criegee process complicating the stereo results seems minimal based on the definitive study with 1-hexene-*l-d* in pentane which demonstrated complete loss of stereochemistry as extent of ozonolysis and concentration were varied.¹²

Another aspect of the mechanism that has received recent attention deals with the geometric and electronic structure of intermediate II. Criegee considered this to be a chain zwitterion ($\text{H}_2\text{C}^+\text{OO}^- \leftrightarrow \text{H}_2\text{C}=\text{O}^+\text{O}^-$). However, theoretical calculations indicate that the zwitterionic state is considerably higher than the singlet diradical $\text{H}_2\text{C}\dot{\text{O}}\dot{\text{O}}$.^{7,10,13} It has been suggested that solvents could lower the zwitterionic state considerably and introduce more polarity into the ground state.⁷ Calculations have also shown that the cyclic dioxirane form is an even more stable isomer,^{7,14} and it has been detected spectroscopically in the gas phase.¹⁵ This has led to speculation that it may be the stable isomer in the gas-phase reaction.

In order to provide additional insight on these solvent, stereo, and electronic effects, four categories of experiments were undertaken involving ethylene. First, stoichiometry and product analyses were conducted for a variety of conditions. One goal here was to determine if any of the other products such as CH_3OH , CH_3CHO , and ethylene oxide, which are formed in the gas-phase reaction,¹⁶⁻¹⁸ might be produced in small amounts during the solution reaction. The initial reaction stages and early intermediates are thought to be similar in both reactions^{7,19} and detection of more products in common would help to correlate the extent of the parallel processes. Second, it was attractive to explore by the sensitive technique of microwave spectroscopy the possibility of an intramolecular stereo effect in the absence of steric bulk with $\text{CHD}=\text{CHD}$. This would extend the results of the 1-hexene-*l-d* study¹² to the simplest symmetric alkene in both polar and nonpolar solvents. Third, cross-ozonide yields and aldehyde-insertion yields were determined by using mixtures of deuterium-labeled ethylene and formaldehyde in various solvents. The goal was to evaluate the effect of the solvent cage as a function of solvent polarity. Fourth, these same isotopically labeled mixtures were examined for kinetic secondary isotope effects (KSIE). Such data provide insight into geometry changes occurring along the reaction coordinate and can yield information on whether that reaction process is likely to be concerted.

Previous mechanistic studies of ethylene in condensed phases include identification of I by matrix IR spectroscopy.^{20,21} Evidence for the second and third Criegee reaction steps was obtained from cross-ozonide and trapping experiments. Two studies using deuterated ethylenes^{22,23} were made involving identification of cross ozonides (III) while trapping experiments involving added $\text{H}_2\text{C}^{18}\text{O}$

Table I. Ethylene Ozonide and Peroxidic Oligomer Yields from $\text{C}_2\text{H}_4 + \text{O}_3$

| <i>T</i> , °C | solvent | μ , D | % ozonide ^a | % (-O-O-) ^a |
|---------------|-------------------------|-----------|------------------------|------------------------|
| -78 | isobutane | 0.13 | 53 | 4.0 |
| | CH_2Cl | 1.87 | 65 | 3.6 |
| -95 | isobutane | 0.13 | 53 ± 5 | 4.1 ± 1.2 |
| | CH_2Cl | 1.87 | 71 ± 7 | 4.1 ± 1.2 |
| -116 | isobutane | 0.13 | 61 | 4.4 |
| | CF_3Cl | 0.51 | 70 | 3.0 |
| | CF_2BrH | 1.31 | 63 | 3.3 |
| | CF_2ClH | 1.42 | 74 | 2.8 |
| | CF_3H | 1.65 | 78 | 3.8 |
| | CF_2H_2 | 1.97 | 67 | 5.1 |
| -126 | isobutane | | 77 ± 4 | 7.2 ± 1.6 |
| | neat | | 44-80 ^b | 3.0 |
| -136 | isobutane | | 79 ± 2 | 4.4 ± 0.5 |

^a Ethylene ozonide and oligomer (nonvolatile residue) yields based on input ozone. Uncertainties listed if two or more reactions were performed. ^b The slow warm-up procedure employed for neat reactions causes an unknown degree of decomposition.

or $\text{CH}_3\text{CH}^{18}\text{O}$ have yielded ozonides with the ¹⁸O label at the ether site as required by the mechanism.²⁴

Results and Discussion

Ozonolysis Products and Yields. Total analysis of reaction products is necessary to fully understand a process, but this goal was elusive in the case of ethylene. The following results were the most definitive and interesting. Only ethylene ozonide (III), H_2CO , and traces of HCOOH were detected as volatile reaction products. Efforts to detect any CH_3CHO , CH_3OH , ethylene oxide, and dioxirane were unsuccessful even for neat ozonolyses. A small amount of viscous, liquid residue (oligomer) remained after workup. Only its peroxide content could be characterized. It ranged from 3 to 7% and was rather insensitive to reaction conditions.

Table I illustrates that ethylene ozonide was the major product in yields from 50 to 80%. At warmer temperatures (-78 and -95 °C), the ozonide yields appear greater in polar than nonpolar solvents. At lower temperatures, these yields increased for the nonpolar solvent and came close to the values in polar solvents.

Other observations include the following: (1) The yields of ethylene ozonide were not dependent on the extent of reaction (i.e., amount of O_3) over the range employed in this study ($0.1 < [\text{O}_3]/[\text{C}_2\text{H}_4] < 0.6$), and they were generally insensitive to the mole fraction or concentration of ethylene dissolved in the solvent. (2) Efforts to determine the $\text{C}_2\text{H}_4/\text{O}_3$ stoichiometry were made. An average of four runs in isobutane and CH_2Cl at -95 and -116 °C resulted in a value of 0.9 ± 0.2 for this ratio.

The variations in yield data with solvent and temperature are not easily compared with results for other alkenes. Bailey recently summarized these observations,⁴ and there have been both similar and contrasting systems indicative of a complex situation.^{5,25} Moreover, for ethylene, cross-ozonide data described below indicate that most ethylene ozonide is formed in the original solvent cage ($\geq 90\%$) for a nonpolar solvent while this decreases to 10% or less for the most polar solvents. It is also likely that the yield data cover a temperature range where I is long-lived to situations where it has a much more transient lifetime.²⁶

These considerations and the absence of any systematic correlation in the peroxy content of the nonozonide residue complicate mechanistic interpretations of the yield data. There is a trend indicating some stabilizing effect in polar solvents which would readily correlate with stages in the Criegee proposal. However, it is difficult to single out whether this contribution is more important in the formation of the primary ozonide, in stabilizing a carbonyl oxide, or in formation of desired transition states. Several empirical conclusions, though, are noteworthy. First, high and

(11) S. Fliszár, J. Renard, and D. Z. Simon, *J. Am. Chem. Soc.*, **93**, 6953 (1971).

(12) R. W. Murray and G. J. Williams, *J. Org. Chem.*, **34**, 1896 (1969).

(13) P. C. Hiberty and C. Leforestier, *J. Am. Chem. Soc.*, **100**, 2012 (1978).

(14) T.-K. Ha, H. Kühne, S. Vaccani, and Hs. H. Günthard, *Chem. Phys. Lett.*, **24**, 172 (1974).

(15) R. D. Suenram and F. J. Lovas, *J. Am. Chem. Soc.*, **100**, 5117 (1978).

(16) J. T. Herron and R. E. Huie, *J. Am. Chem. Soc.*, **99**, 5430 (1977), and references therein.

(17) H. Kühne, S. Vaccani, T.-K. Ha, A. Bauder, and H. H. Günthard, *Chem. Phys. Lett.*, **38**, 449 (1976).

(18) R. Atkinson, B. J. Finlayson, and J. N. Pitts, Jr., *J. Am. Chem. Soc.*, **95**, 7592 (1973); **96**, 5356 (1974).

(19) H. E. O'Neal and C. Blumstein, *Int. J. Chem. Kinet.*, **5**, 397 (1973).

(20) L. A. Hull, I. C. Hisatsune, and J. Heicklen, *J. Am. Chem. Soc.*, **94**, 4856 (1972).

(21) B. Nelander and L. Nord, *Tetrahedron Lett.*, 2821 (1977); *J. Am. Chem. Soc.*, **101**, 3770 (1979).

(22) H. Kühne and Hs. H. Günthard, *J. Phys. Chem.*, **80**, 1238 (1976).

(23) C. W. Gillies and R. L. Kuczkowski, *J. Am. Chem. Soc.*, **94**, 6337 (1972).

(24) C. W. Gillies, R. P. Lattimer, and R. L. Kuczkowski, *J. Am. Chem. Soc.*, **96**, 1536 (1974).

(25) R. W. Murray and R. Hagan, *J. Org. Chem.*, **36**, 1098 (1971).

(26) IR matrix studies^{20,21} indicate that the primary ozonide is stable up to -80 to -100 °C where it probably decomposes.

Table II. Cis/Trans Ozonide Ratios from *cis*- and *trans*-1,2-Dideuterioethylenes in Two Solvents

| ozonide ratio | isobutane | | methyl chloride | |
|---|--|--|--|--|
| | <i>cis</i> - C ₂ H ₂ D ₂ | <i>trans</i> - C ₂ H ₂ D ₂ | <i>cis</i> - C ₂ H ₂ D ₂ | <i>trans</i> - C ₂ H ₂ D ₂ |
| <i>cis</i> (a,e)/ <i>trans</i> (a,a) | 2.03 (6) | 2.02 (6) | 2.01 (7) | 1.98 (6) |
| <i>cis</i> (a,e)/ <i>trans</i> (e,e) | 2.04 (6) | 2.00 (5) | 2.05 (6) | 2.00 (8) |
| <i>cis</i> (a,e)/[<i>trans</i> (a,a) + <i>trans</i> (e,e)] | 1.02 (4) | 1.00 (4) | 1.01 (4) | 0.99 (6) |

Table III. Ozonolysis of C₂H₄ and C₂D₄ Mixtures^a

| | isobutane (-136 °C) | | methyl chloride (-95 °C) | |
|--|------------------------|--------------------|-----------------------------|--------------------|
| | run 1 | run 2 ^c | run 3 | run 4 ^c |
| C ₂ H ₄ init | 1.48 | 1.52 | 0.743 | 0.718 |
| C ₂ D ₄ init | 1.52 | 1.53 | 0.780 | 0.751 |
| O ₃ input | 0.995 | 1.023 | 0.530 | 0.498 |
| ozonide product | 0.78 | 0.69 | 0.39 | 0.32 |
| C ₂ H ₄ final-1 ^b | 1.10 | 1.13 | 0.486 | 0.508 |
| C ₂ D ₄ final-1 | 0.932 | 0.921 | 0.520 | 0.475 |
| C ₂ H ₄ final-2 ^b | 1.11 | 1.13 | 0.488 | 0.508 |
| C ₂ D ₄ final-2 | 0.920 | 0.922 | 0.515 | 0.471 |
| oz- <i>h</i> ₄ /oz- <i>d</i> ₄ | 0.607 | 0.630 | 0.655 | 0.652 |
| oz- <i>d</i> ₂ /oz- <i>d</i> ₄ | 0.057 | 0.045 | 0.707 | 0.810 |
| <i>k</i> _{C₂H₄} / <i>k</i> _{C₂D₄} (final-1) ^b | 0.609 | 0.579 | 0.754 | 0.755 |
| <i>k</i> _{C₂H₄} / <i>k</i> _{C₂D₄} (final-2) ^b | 0.573 | 0.582 | 0.782 | 0.742 |

^a Quantities are in millimoles. ^b C₂H₄ final-1 and C₂D₄ final-1 are determined from recovered Et while C₂H₄ final-2 and C₂D₄ final-2 are determined from recovered ozonide. Last two rows use the final-1 or final-2 data to compare KSIE ratios for Et.

^c Solvent contained *o*-xylene added in a 1:1 ratio with ethylene.

comparable yields of ozonide can be obtained in polar or nonpolar solvents. This implies that ethylene is a good candidate for study of the ozonide formation process. Second, ozone consumption is not apparently accounted for by the ozonide and oligomer peroxy content alone.²⁷ Third, and relatedly, the reaction products of ethylene ozonolysis in the gas phase, namely, ethylene oxide, CH₃CHO, and CH₃OH, are absent in the observed liquid-phase reactions. In the gas-phase reaction, ethylene ozonide is absent or possibly produced in low yields while H₂CO and HCOOH are products clearly common to both gas- and liquid-phase ozonolyses. Dioxirane, which was recently observed when condensed O₃ and C₂H₄ were warmed up in a microwave absorption cell,¹⁵ was not observed in the present work. This does not necessarily preclude its presence during the solvent reaction. Dioxirane is unstable and may not survive the work-up procedure utilized in this study.

Stereochemistry. The relative amounts of the *cis*- and *trans*-*d*₂-ozonides produced from either *cis*- or *trans*-ethylene-1,2-*d*₂ were determined by microwave spectroscopy. The *cis*-*d*₂-ozonide abundance was evaluated relative to either the *trans*-*d*₂-diaxial isomer or the *trans*-*d*₂-diequatorial isomer. These results and the combined, overall *cis*/*trans* ratio are listed in Table II. The table shows that the *cis*(a,e):*trans*(a,a):*trans*(e,e) ratios are near the statistical values of 2:1:1. Stereorandomization occurs in both polar and nonpolar solvents, a result consistent with the Criegee proposal and its recent revisions,^{2,3} whether concerted or non-concerted.⁷ The data place an upper limit of 4% for any non-randomizing stereochemistry path leading to final ozonide.

C₂H₄ and C₂D₄. Approximately 50 mixtures of these two species were ozonized under various conditions of temperature, solvent, reaction extent, and ethylene concentration. The isotopic ratios in the residual ethylene and in the *d*₄, *d*₀, and *d*₂ cross ozonides were determined. These results provide information on the kinetic secondary isotope effect (KSIE) during addition of O₃ to ethylene (Criegee mechanism, step 1) and the variation of *d*₂ cross ozonide

(27) The apparent yield discrepancy is not well understood. No attempts to identify the possible products CO₂ and CO have been made. A gas chromatographic analysis for H₂CO yields has thus far been erratic and unreliable. The total oxygen content of the oligomer is also not known.

Table IV. Kinetic Secondary Isotope Effects for Ethylene Consumption in the Ozonolysis of C₂H₄/C₂D₄ Mixtures

| solvent | <i>T</i> , °C | extent ^a | <i>k</i> _{C₂H₄} / <i>k</i> _{C₂D₄} ^b | <i>k</i> _H / <i>k</i> _D ^c |
|--|---------------|---------------------|--|--|
| <i>i</i> -C ₄ H ₁₀ | -95 | 0.08 | 0.651 | 0.938 |
| <i>i</i> -C ₄ H ₁₀ | -95 | 0.15 | 0.684 | 0.945 |
| <i>i</i> -C ₄ H ₁₀ | -95 | 0.33 | 0.816 | 0.970 |
| <i>i</i> -C ₄ H ₁₀ | -95 | 0.47 | 0.870 | 0.979 |
| <i>i</i> -C ₄ H ₁₀ | -116 | 0.36 | 0.707 | 0.955 |
| <i>i</i> -C ₄ H ₁₀ | -126 | 0.51 | 0.572 | 0.933 |
| <i>i</i> -C ₄ H ₁₀ | -136 | 0.33 | 0.573 | 0.938 |
| CH ₃ Cl | -95 | 0.34 | 0.782 | 0.964 |
| CF ₃ Cl | -116 | 0.33 | 0.623 | 0.940 |
| CF ₂ BrH | -116 | 0.33 | 0.607 | 0.936 |
| CF ₂ ClH | -116 | 0.33 | 0.683 | 0.951 |
| CF ₂ H ₂ | -116 | 0.33 | 0.604 | 0.936 |
| CF ₂ H ₂ | -136 | 0.32 | 0.605 | 0.944 |
| CF ₃ H | -120 | 0.33 | 0.524 | 0.919 |
| neat | -126 | 0.02 | 0.561 | 0.931 |
| | | | | 0.945 (14) ^d |

^a Extent of reaction = (ozone in)/(ethylene in). ^b Observed ratio of rate constants. ^c Normalized ratio on per deuterium basis at 25 °C. ^d Mean value.

Table V. Fraction of Ethylene-1,1-*d*₂ Ozonide (Cross Ozonide) from Ozonolysis of C₂H₄/C₂D₄ Mixtures in Various Solvents^a

| solvent | μ , D | ϵ^b | cross fraction ^c | <i>T</i> , °C |
|---|-----------|--------------|-----------------------------|---------------|
| <i>i</i> -C ₄ H ₁₀ | 0.13 | 1.9 | 0.027 (14) | -116 |
| <i>i</i> -C ₄ H ₁₀ | | | 0.04 (2) | -136 |
| CF ₃ Cl | 0.51 | 3.0 | 0.107 (22) | -116 |
| CF ₂ BrH | 1.31 | 7.6 | 0.372 (23) | -116 |
| CF ₂ ClH | 1.42 | 10.1 | 0.384 (20) | -116 |
| CF ₃ H | 1.65 | 14.6 | 0.387 (15) | -116 |
| CF ₂ H ₂ | 1.97 | 16.1 | 0.362 (10) | -116 |
| CF ₂ H ₂ ^d | | | 0.429 (20) | -116 |
| CF ₂ H ₂ | | | 0.331 (20) | -136 |
| CF ₂ H ₂ ^d | | | 0.364 (20) | -136 |
| CH ₃ Cl | 1.87 | 17.3 | 0.300 (22) | -95 |
| neat ^{d,e} | 0.0 | | 0.08 (3) | -126 |

^a All reactions in solvents contained 0.03 mol fraction of Et and were run to 33% completion. ^b Dielectric constants.⁴¹ ^c Cross fraction = oz-*d*₂/(oz-*d*₀ + oz-*d*₄). ^d Slow warm-up procedure. ^e Run to 2% completion.

yields with conditions (Criegee mechanism, step 2 and 3).

Table III contains the data from four experiments in which ethylene and ethylene ozonide were recovered from the reaction and isotopically analyzed. A pronounced inverse deuterium isotope effect for ethylene is observed. This can be established either from the recovered ethylene or from the product ozonides.

Table IV summarizes the KSIE rate constant ratios for a wide variety of reaction conditions. The ratios are very sensitive to small errors in ethylene determinations, particularly in the limit of small ($\leq 15\%$) reaction extent, and so the data scatter show little convincing trend with any reaction parameters except possibly the expected temperature effect on the unnormalized ratios. The data are sufficient to establish an inverse KSIE involving ethylene (0.93–0.96 on a per deuterium basis).

Cross ozonide yield data are listed in Table V. The yield determined for a particular solvent is slightly variable ($\pm 10\%$) from run to run and seems to increase with slow warm-up procedures. Nevertheless, the fractional yields are clearly low for less polar solvents and rapidly level off at values of around 0.35–0.40 for the more polar solvents.

It has been widely discussed²⁸ that an inverse KSIE is generally indicative of a transition state involving a planar, trigonal carbon center undergoing a nonplanar deformation, i.e., a transformation from an sp² to an sp³ hybrid. The observed inverse ratio is therefore expected for step 1 of the Criegee proposal. It is de-

(28) For a discussion of secondary isotope effects see references in P. A. Rock, Ed., "Isotopes and Chemical Principles", American Chemical Society, Washington, DC, 1975.

Table VI. Secondary Isotope Effects for H₂CO/D₂CO Insertion during Ozonolysis of CHD=CHD^a

| | <i>i</i> -C ₄ H ₁₀ | CF ₃ Cl | CF ₂ BrH | CF ₂ H ₂ |
|---|--|--------------------|---------------------|--------------------------------|
| μ (solvent), D | 0.13 | 0.51 | 1.31 | 1.97 |
| [H ₂ CO] ₀ | 1.22 | 0.77 | 0.79 | 1.11 |
| [D ₂ CO] ₀ | 1.26 | 0.83 | 0.79 | 1.09 |
| [Et] ₀ | 1.25 | 1.11 | 1.23 | 1.56 |
| O ₃ | 0.33 | 0.47 | 0.32 | 0.67 |
| % insertion ^b | | | | |
| obsd | 24 (4) | 56 (4) | 83 (4) | 81 (4) |
| stat | 85 (2) | 76 (2) | 81 (2) | 75 (2) |
| $k_{\text{H}_2\text{CO}}/k_{\text{D}_2\text{CO}}^c$ | 0.676 (90) | 0.659 (30) | 0.634 (31) | 0.608 (21) |
| $k_{\text{H}}/k_{\text{D}}^d$ | 0.902 (35) | 0.896 (11) | 0.887 (11) | 0.877 (9) |

^a Quantities are in millimoles. $T = -116^\circ\text{C}$. ^b Observed = $100[(oz-d_1 + oz-d_3)/(oz-d_1 + oz-d_2 + oz-d_3)]$; statistical = $100 \times [(H_2CO + D_2CO)/(H_2CO + HDCO + D_2CO)]$ and includes consideration of the HDCO present in the D₂CO. ^c Observed ratio. ^d Normalized on a per deuterium basis at 25°C .

bable to infer that the KSIE supports only a concerted transition state involving both carbon centers on ethylene without a more detailed analysis using transition-state calculations. Nevertheless, the value is plausible for a concerted process, and many other [2 + 3] and [2 + 4] cycloadditions have yielded similar KSIE ratios in the range of 0.93–0.98.²⁹ The value for ethylene is also close to that determined for the ozonolysis of styrene ($k_{\text{H}}/k_{\text{D}} = 0.93$).³⁰

The cross-ozonide yields provide information on the effect of the solvent cage in terms of the Criegee process, i.e., the amounts of III formed outside the original solvent cage containing I and its subsequent cleavage pair of II and carbonyl. Doubling of the fractional yields in Table V provides a lower limit for the fraction of the reaction that produces ozonide by a random scrambling process between CH₂OO, CD₂OO, CH₂O, and CD₂O fragments. A more realistic estimate for the statistical upper limit for complete randomization must take the KSIE into consideration. A rough model containing such corrections indicates that the statistical limit for cross-ozonide fractional yields is probably in the range of 0.36–0.45, close to the observed values. This upper limit for the amount of cross fraction is estimated by the following simplified Criegee model: (1) The decomposition of the primary ozonide is the rate-limiting step. (2) The carbonyl oxide and formaldehyde so formed are unassociated. (3) Only ozonides are produced. (4) KSIE ratios in Tables IV and VI are used for Criegee steps 1 and 3. A KSIE ratio of 0.7–1.2 is taken for the decomposition of the primary ozonide.

The cross-ozonide yields for ethylene in polar solvents might be expected to approach the statistical limits by analogy with other systems. The fraction of cross ozonide formed from *cis*-4-methyl-2-pentene was 0.14 in pentane and rose to 0.42–0.44 in ethyl acetate and dichloromethane.³¹ For *cis*- and *trans*-2-pentenes, values of 0.13–0.20 were observed in pentane which increased to 0.47–0.48 in diethyl ether.³² Therefore, the fractional cross-ozonide yield for ethylene in the range of 0.35–0.40 is probably indicative of complete or nearly complete statistical scrambling. It is probably safe to conclude that the ozonide formation occurred outside the original solvent cage in excess of 90% of the time for those solvents with fractional cross-ozonide yields ≥ 0.35 . For a nonpolar solvent like isobutane less than 10% forms outside the original solvent cage.

The increased formation of cross ozonides in polar solvents has generally been interpreted as evidence for the Criegee cleavage mechanism and indicative of stabilization of the two polar species produced upon primary ozonide decomposition. It is interesting that a simplified solvent model³³ describing the activation energy

required to remove two dipolar species from a solvent cage can rationalize the leveling of cross-ozonide yields at moderate dielectric constants and can provide rough estimates of the dipole moment of the H₂COO fragment, given a plausible range for the solvent cage size. This model assumes that the ratio of cross fractions (C and C') in two solvents can be equated to an Arrhenius expression (eq 1 and 2). ΔE is the difference in activation

$$C'/C = \exp(-\Delta E/RT) \quad (1)$$

$$\Delta E = 2\mu_{\text{H}_2\text{COO}}\mu_{\text{H}_2\text{CO}}r^{-3}(1/\epsilon' - 1/\epsilon) \quad (2)$$

energies in the two solvents with dielectric constants ϵ and ϵ' . The r is the interaction distance between the two dipoles and should be comparable to the solvent cage size. With isobutane as a reference solvent, values for C'/C for the ethylene data as well as the pentene data^{31,32} range from about 2 to 10 for the more polar solvents. If r is assumed between 4 and 6 Å, the $\mu_{\text{H}_2\text{COO}}$ varies between ~ 1 and 9 D. The leveling off in cross fraction yields for moderate values of ϵ' is also reasonable from eq 2. The data are not precise enough to more narrowly estimate any parameter values for the intermediates and solvent cage. Moreover, skepticism about the model can be expressed.³⁴ Nevertheless, the general trend in cross-ozonide yields appears plausible for a solvent cage effect dominated by electrostatic interactions between solvent and the polar intermediates in step 2 of the Criegee mechanism.

H₂CO/D₂CO Insertions. It is well-known that aldehydes added to an alkene ozonolysis reaction are usually incorporated into the final ozonides. It was attractive to establish the KSIE associated with the aldehyde during this incorporation step by ozonizing small amounts of CHD=CHD in the presence of excess H₂CO/D₂CO. The KSIE ratios could then be determined by mass spectrometry from the d_1 - and d_3 -ozonides with minimal complications from the internally generated HDCO and the normal d_2 -ozonide.

The results from ozonolyses in four solvents are listed in Table VI. An inverse isotope effect is observed for the aldehyde-incorporation step with a mean value per deuterium of 0.891 (30) ($=k_{\text{H}}/k_{\text{D}}$). The data suggest a variation in the KSIE with solvent polarity but the precision is not sufficient to unambiguously establish the trend. The amounts of foreign aldehyde that are incorporated (fraction inserted) also rise with solvent polarity.

An inverse isotope effect is anticipated for the third step of the Criegee proposal (concerted cycloaddition) since the formaldehyde species undergoes a deformation from a planar sp² carbon to a sp³ carbon. The magnitude of the observed isotope effect clearly points to new bond formation at the aldehyde carbon during the transition state and seems to exclude a stepwise radical transition state ($\cdot\text{CH}_2\text{OCH}_2\text{OO}\cdot$) in which a new bond is first formed to the formaldehyde oxygen with development of a radical center at the formaldehyde carbon.³⁶ This stepwise biradical closure was recently proposed in the case of substituted ethylenes.⁷ The possibility of a stepwise closure involving development of a R₂C⁺OOCR₂O⁻ intermediate was also suggested recently,⁵ and this pathway is consistent with the ethylene data.

The amounts of foreign aldehyde which are inserted rise with solvent polarity in a manner parallel to the cross-ozonide yields from C₂H₄/C₂D₄ mixtures. The insertion fraction in the more polar solvents is close to that expected for complete randomization between H₂CO, D₂CO, and internally generated HDCO. In terms of a Criegee model, these data would imply that polar solvents

(29) (a) D. E. Van Sickle and J. Oho Rodin, *J. Am. Chem. Soc.*, **86**, 3091 (1964); (b) S. Seltzer, *ibid.*, **87**, 1534 (1965), (c) S.-H. Dai and W. R. Dolbier, Jr., *ibid.*, **94**, 3946 (1972).

(30) D. B. Denney and N. Tunkel, *Chem. Ind. (London)*, **24**, 1383 (1959).

(31) N. L. Bauld, J. A. Thompson, C. E. Hudson, and P. S. Bailey, *J. Am. Chem. Soc.*, **90**, 1822 (1968).

(32) F. L. Greenwood, *J. Am. Chem. Soc.*, **88**, 3146 (1966).

(33) E. S. Amis and J. F. Hinton, "Solvent Effects on Chemical Phenomena", Vol. 1, Academic Press, New York, 1973, pp 265–8.

(34) Some points of question would involve (a) the implied assumption that cross yields are simply proportional to the rate of solvent cage breakdown, (b) the applicability of a macroscopic ϵ to Coulombic interactions at the molecular level, (c) the neglect of averaging over all dipole orientations, and (d) the neglect of non-Coulombic interactions and more specific molecular interactions. In this regard, the solvents in this study contain neither carbonyl nor ether oxygens. Specific molecular interactions of Criegee intermediates with diethyl ether and ethyl acetate solvents have been previously suggested³¹ as well as with aromatic complexing agents.³⁵

(35) P. S. Bailey, T. M. Ferrell, A. Rustaiyan, S. Seyhan, and L. E. Unruh, *J. Am. Chem. Soc.*, **100**, 894 (1978).

(36) It has been shown that conversion of an sp² carbon to a carbon radical usually involves a small, normal KSIE or none at all.^{29a,37}

(37) J. E. Baldwin and J. A. Kopecki, *J. Am. Chem. Soc.*, **92**, 4874 (1970).

stabilize a polar $\text{H}_2\text{COO}^\ominus$ species making it susceptible to recombination with any available formaldehyde species regardless of origin.

Summary

There is continued interest in exploring the limitations of the comprehensive Criegee proposal and identifying ozonolysis data problematic for it. However, this study on the simplest alkene-ozone system generally correlates well with the Criegee postulates. The expected loss of stereochemistry was ascertained. Solvent effects on total-ozonide, cross-ozonide, and aldehyde-insertion yields have indicated increased stabilization for processes in polar solvents. Cross ozonide yield variations in polar solvents can be correlated with a solvent cage model based on electrostatic interactions. These solvent effects fit in readily with Criegee's postulate of a polar zwitterionic intermediate $\text{H}_2\text{C}^+\text{OO}^\ominus$ or a polar diradical form $\text{H}_2\text{COO}^\cdot$. Deuterium KSIE's are consistent with expectations for Criegee steps 1 and 3. They are less supportive of a stepwise process in step 3 involving an oxygen from a carbonyl adding to a diradical $\text{H}_2\text{COO}^\cdot$ intermediate. Finally, the contrast in products between the gas-phase and solution reactions also emphasizes the role of the solvent in this energetic reaction.

Experimental Section

IR spectra were obtained with a Beckman 4240 spectrometer, using a 10-cm gas cell. ^1H NMR were obtained with a Varian T-60A spectrometer. Mass spectra were obtained with an AEI MS-902 spectrometer with a cooled source to prevent ozonide decompositions. Microwave spectra were recorded with a Hewlett-Packard 8460A spectrometer. Conventional vacuum-line techniques on a calibrated manifold were employed for most manipulations of reactants and products. A Welsbach Model T-408 ozonator was employed.

Materials. CP grade ethylene and solvents were obtained from lecture bottles. These were normally dried by passage through cold traps. Deuterium-enriched samples were obtained from Merck and Co. and checked by IR spectroscopy and mass spectrometry. Ethylene- d_4 contained an overall deuterium content of 98.9%. *trans*- $\text{C}_2\text{H}_2\text{D}_2$ assayed at 98.6% *trans*- $\text{C}_2\text{H}_2\text{D}_2$, with 1.4% $\text{C}_2\text{H}_3\text{D}$ and no traces of *cis*- $\text{C}_2\text{H}_2\text{D}_2$. The *cis*- $\text{C}_2\text{H}_2\text{D}_2$ used in the stereochemistry experiments contained 77.2–80.0% *cis*- $\text{C}_2\text{H}_2\text{D}_2$, 2–5% *trans*- $\text{C}_2\text{H}_2\text{D}_2$, 14.7% $\text{C}_2\text{H}_3\text{D}$, and 3.1% C_2H_4 . The *cis*- $\text{C}_2\text{H}_2\text{D}_2$ used in the insertion experiments contained about 92% *cis*- $\text{C}_2\text{H}_2\text{D}_2$, 6% *trans*- $\text{C}_2\text{H}_2\text{D}_2$, and 2% $\text{C}_2\text{H}_3\text{D}$. The D_2CO was supplied as paraformaldehyde and contained an overall deuterium content of 98%.

Ozonolysis Procedure. The vacuum-line techniques employed previously^{2,24,38} were followed. Solubility data in the various solvents were obtained³⁸ in order to conduct runs under similar conditions of mole fraction of dissolved ethylene. Typical runs employed 20–30 mmol of solvent, 0.5–2.0 mmol of ethylene, and flow rates of 0.1 mmol of O_3 /min. When mixtures of $\text{H}_2\text{CO}/\text{D}_2\text{CO}$ were added to the solvent, the H_2CO and D_2CO were generated separately by heating paraformaldehyde and measuring their individual pressures and combined pressure before transfer to the reaction mixture. Reaction mixtures were usually condensed and vaporized several times to ensure mixing. During reaction, exit gases were bubbled through a KI trap or through three -160°C traps to recover any ethylene. All the input ozone was consumed in the reaction vessel. After reaction, a fast warm-up procedure was usually employed.²⁵ Slow warm-ups frequently resulted in sizable losses of ozonide but some data were obtained by using this procedure. The products were distilled through -78 and -196°C traps. Ozonide was found in the -78°C traps, and ethylene, solvent, and H_2CO were in the -196°C trap. The reaction vessel contained traces of a barely visible viscous residue which did not quickly distill off even with application of gentle warming with a heat gun.

Several ozonolyses of neat ethylene were carried out with about 15 mmol of material. These often exploded. The hazards were minimized by using only 0.2 mmol or less of O_3 and a slow warm-up. Apart from the greater hazards, the neat reaction seemed to parallel solvent ozonolysis in products obtained. Reactions in CF_2H_2 and CF_3Cl at temperatures below -116°C also produced violent explosions during fast product warm-up.

Nonvolatile residues left behind in the reaction cell were digested with a neutral solution of KI. After the solution was allowed to stand for 6 h, the active oxygen yield was determined with a thiosulfate standard.

Qualitative Analysis and Yields. Observation of H_2CO , HCOOH , and ozonide as the only volatile products was established by infrared, microwave, and mass spectral analyses. Only the ozonide was quantitatively determined manometrically (Table I). H_2CO was generally collected with the solvent. From total-pressure measurements it was estimated to be present in <10 –15% yield. HCOOH was present in trace amounts ($\leq 1\%$). Microwave spectroscopy was probably the most sensitive technique used to detect CH_3CHO , CH_3OH , ethylene oxide, and dioxirane. None of these species were observed, setting limits for them of less than 0.1%.

Besides the peroxidic content reported in Table I, the liquid residues left after distillation were also examined by ^1H NMR and mass spectrometry. ^1H NMR samples were prepared by vacuum distilling 2–4 mL of Silanor-D into the reaction tube. The tube was gently shaken to ensure solubilization of the residue and then opened to the atmosphere. A sample was rapidly pipetted into a 4 mm o.d. ^1H NMR tube which was capped. Under solvent, the residue was found to be stable for several days at room temperature. ^1H NMR showed a complex, strong absorption in the region δ 5–6 with smaller absorptions also around δ 7.5–9.0 and around δ 2.0. The approximate proton ratios were 60:10:30 in the three respective regions. Above m/e 40, the mass spectrum had strong signals in the region of m/e 43–47, 55–60, and 84–90 with much weaker peaks distributed throughout the spectrum, including some at m/e 100–200. These data indicated complex substances and no progress was made toward further understanding them.

Stereochemistry of HDCCOCHDO. Samples from ozonolysis of *cis*- or *trans*-ethylene-1,2- d_2 were isolated from reactions in isobutane at -126°C and CH_2Cl_2 at both -95 and -78°C .

Microwave spectroscopy was used to determine the stereoconfiguration of the ozonide. Because of the twisted ring for ethylene ozonide, the *cis*- d_2 isomer exists as two spectroscopically identical, axial, equatorial enantiomorphs. For the *trans* isomer, the equatorial, equatorial and axial, axial isomers have distinct spectra. The spectra of these forms have been reported previously.³⁹ The relative amounts of any two species were determined by comparing the intensity of a transition from each species. The procedure has been discussed previously⁴⁰ and the detailed data are summarized elsewhere.³⁸ Ten different transitions which were free of interferences were used. The ozonides were unstable in the cell and decayed with half-lives of 15–60 min, depending on conditions. However, the spectrometer allowed quick and repetitive sampling so that usable intensity-time curves could be obtained. The uncertainties in Table II reflect the statistical analysis ($\pm\sigma$) of these data. The resultant ratios obtained repetitively over several half-lives of sample decay were unchanged. This was also the case for comparisons made between the d_0 - and d_4 -ozonides discussed in the next section. Contributions from different rates of decomposition are evidently not significant.

For conversion of the raw intensity data into isomeric ratios, corrections to the intensity were made for all the usual contributions, including spin statistics, dipole moments, rotational partition functions, and line widths. The vibrational partition function ratio was assumed to be unity.

$\text{C}_2\text{H}_4/\text{C}_2\text{D}_4$ Analysis. Quantitative mixtures of these two species were ozonized. Ozonide yields were normally determined and mass analyzed. In the four runs listed in Table IV, ethylene was also recovered and mass analyzed.

The relative deuterium content in ethylene and the ozonide were obtained by mass spectrometry. The ethylene and ozonide mass spectral analyses were usually preceded by runs on standard mixtures in order to calibrate the spectrometer response. For ethylene analyses at 20 eV, the m/e peaks at 28 and 32 were used with a small correction necessary for a C_2D_2^+ fragment contributing to m/e 28. The ethylene ozonide analysis at 35 eV utilized fragments at m/e 76, 78, and 80. At these conditions only P and P-1 fragments were observed. From pure samples of the d_0 - and d_4 -ozonides as well as standard mixtures of them, the necessary spectrometer response factors and fragmentation ratios could be determined. For the d_2 -ozonide, they were estimated by linear interpolation. Mole ratios were derived from data averaged from 8 to 20 mass spectral scans. For a given sample, scale constants and mole ratios changed by less than 2% if remeasured on a different occasion. As a check on the mass spectral ozonide analysis, microwave spectroscopy was used to analyze data from four runs. It gave essentially the same results and a similar precision.³⁸

(39) R. L. Kuczkowski, C. W. Gillies, and K. L. Gallaher, *J. Mol. Spectrosc.*, **60**, 361 (1976).

(40) A. L. Larrabee and R. L. Kuczkowski, *J. Catal.*, **52**, 72 (1978).

(41) The solvent dielectric constants were estimated by using the Onsager equation.⁴² Where quantities like density or refractive index were unavailable, they were estimated from correlations with other solvents.

(42) L. Onsager, *J. Am. Chem. Soc.*, **58**, 1486 (1936); C. P. Smyth, "Dielectric Behavior and Structure", McGraw-Hill, New York, 1955, p 226.

(38) G. D. Fong, Ph.D. Dissertation, University of Michigan, 1978; *Dis. Abstr. Int. B*, **39**, 4907 (1979).

The relationship $\ln(H/H_0)/\ln(D/D_0) = k_H/k_D$ was employed to calculate KSIE ratios in Tables III and IV, where $H = C_2H_4$, $D = C_2D_4$, etc. The runs in Table III indicated that ozonide product analysis could be used to estimate ethylene consumption. This method was used to develop Table IV, since recovery of ethylene was tedious. In this procedure, a 1:1 stoichiometry between ethylene and O_3 is assumed, and the relative deuterium content of nonozonide products is assumed to be identical with that in the ozonides. The relationship $(k_H/k_D)_{298} = (k_{C_2H_4}/k_{C_2D_4})^{7/298n}$ was employed to convert to a per deuterium basis at 25 °C. The scatter in the isotope ratios in Table IV (along with data from nine other reactions) leads to the listed uncertainty in the normalized KSIE ratio of about $\pm 2\%$. The cross-ozonide fractions in Table V also resulted from the mass analysis.

H₂CO/D₂CO Insertion into CHD=CHD. The KSIE ratios in Table VI were determined with $k_{H_2CO}/k_{D_2CO} = (oz-d_1/oz-d_3)/(D_2CO/H_2CO)$. This should be a good approximation when the amounts of H₂CO and D₂CO are present in large excess or the extent of reaction is small. For the extents of reaction in Table VI, the D₂CO/H₂CO ratios decrease between 1 and 6% after ozonolysis. Hence, D₂CO/H₂CO was approximated as the median value during the reaction.

The amounts of oz-d₁ and oz-d₃ were determined by using mass spectral procedures similar to those described for the oz-d₄/oz-d₀ ratios. Fragmentation patterns for pure oz-d₄ were determined. Along with the data for oz-d₀ and oz-d₄, the necessary patterns for oz-d₁ and oz-d₃ were estimated by interpolation. This leads to expressions for the peak intensities between m/e 76 and m/e 79, corrected for ¹³C contributions in terms of the amounts of d₁-, d₂-, and d₃-ozonides. The statistical deviations in the mass spectral data and ambiguities in determining the quantities of H₂CO and D₂CO and in estimating the effect of small amounts of C₂H₃D in the ethylene lead to accuracies of about $\pm 4\%$ in the normalized KSIE ratios.

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Aromatic Substitution in the Gas Phase. A Comparative Study of the Alkylation of Benzene and Toluene with C₃H₇⁺ Ions from the Protonation of Cyclopropane and Propene

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Abstract: Gas-phase alkylation of benzene and toluene has been used as a probe to sample the isomeric population of C₃H₇⁺ ions obtained from the protonation of cyclopropane and of propene, respectively, with H₃⁺ ions in H₂ gas at pressures from 50 to 720 torr. The reagent from cyclopropane promotes extensive (over 40%) *n*-propylation, in addition to isopropylation of the arenes, in contrast to the reagent from propene that yields only traces of *n*-propylated products. The *n*-propylating reagent is identified as protonated cyclopropane, whose lifetime must exceed 10⁻⁷ s in the gaseous systems investigated. The mechanism and the selectivity of the gas-phase alkylation are discussed and compared to relevant mass spectrometric and kinetic results.

Introduction

The study of gas-phase aromatic substitution by carbenium ions generated in the dilute gas state with radiolytic techniques, or from the β decay of suitably tritiated precursors, has been reported in previous papers of this series.¹ In particular, the gas-phase reactions of methyl,²⁻⁴ ethyl,⁵ isopropyl,^{6,7} and *tert*-butyl⁸⁻¹⁰ ions with various arenes have been investigated, gathering direct information on the reactivity, selectivity, and steric requirements of free unsolvated carbenium ions.

The present paper is concerned with a comparative study of the reactivity of gaseous C₃H₇⁺ ions obtained from two different sources, namely, by protonation of cyclopropane and of propene, respectively, in their gas-phase attack of benzene and toluene.

Apart from the intrinsic interest of the reaction that extends directly to the gas phase one of the most classical routes to the preparation of Friedel-Crafts alkylating reagents, it was hoped

that contrasting the features of the two propylation processes could provide fresh evidence on the long-standing problem concerning the structure, stability, and interconversion rate of isomeric C₃H₇⁺ ions in the dilute gas state.

Experimental Section

Materials. The gases employed (Ar, H₂, D₂) were high purity products from Matheson Co., whose stated purity exceeded 99.99 mol %. *c*-C₃H₆ and C₃H₆ were obtained from the same source, with a minimum purity of 99.0 mol %; O₂ and NH₃ were locally purchased research grade gases. C₆H₆ and C₇H₈ were gas chromatographic standards from Carlo Erba Co., while their alkylated derivatives, used for identification and calibration purposes in the GLC of reaction products, were either obtained from Fluka A.G. or prepared according to established procedures.

Procedure. The gaseous samples were prepared by standard vacuum techniques and introduced into 500-mL Pyrex ampules, equipped with break-seal tips, that had been previously evacuated to 10⁻⁵ torr and carefully outgassed. The vessels were sealed off and irradiated in a 220 Gammacell (Nuclear Canada Ltd.) at 34 °C at a dose rate of ca. 0.43 Mrad h⁻¹ to total doses ranging from 2.2 to 17 Mrad, as determined by conventional Fricke dosimetry. Analysis of the products was carried out on a Sigma 1 gas chromatograph (Perkin-Elmer) equipped with a FID unit, using the following capillary columns: (i) a 300 ft \times 0.020 in. stainless-steel column coated with Apiezon L grease, operated at a flow rate of 2.0 mL/min at 100 and 130 °C; (ii) a 150 ft \times 0.010 in. stainless-steel column coated with Carbowax 20M, operated at a flow rate of 0.50 mL/min at 80 °C; and (iii) a 50 ft \times 0.02 in. stainless-steel column, coated with poly(propyleneglycol), operated at a flow rate of 2.0 mL/min at 100 °C.

The products were identified by comparison of their retention volumes with those of authentic samples on at least two different columns, and their yields were deduced from the areas of the correspondent elution

(1) For a recent review, cf. Cacace, F. In "Kinetics of Ion-molecule Reactions"; Ausloos, P., Ed.; Plenum Press: New York, 1979; p 199, and references cited therein.

(2) Cacace, F.; Giacomello, P. *J. Am. Chem. Soc.* 1977, 99, 5477.

(3) Cacace, F.; Giacomello, P. *J. Chem. Soc., Perkin Trans. 2* 1978, 652.

(4) Giacomello, P.; Schüller, M. *Radiochim. Acta* 1977, 24, 111.

(5) Cacace, F.; Cipollini, R.; Giacomello, P.; Possagno, E. *Gazz. Chim. Ital.* 1974, 104, 977.

(6) Cacace, F.; Possagno, E. *J. Am. Chem. Soc.* 1973, 95, 3397.

(7) Attinà, M.; Cacace, F.; Ciranni, G.; Giacomello, P. *J. Am. Chem. Soc.* 1977, 99, 2611.

(8) Cacace, F.; Giacomello, P. *J. Am. Chem. Soc.* 1973, 95, 5815.

(9) Giacomello, P.; Cacace, F. *J. Chem. Soc., Chem. Commun.* 1975, 379.

(10) Giacomello, P.; Cacace, F. *J. Am. Chem. Soc.* 1976, 98, 1823.