The Isomerization of Ethylene Oxide to Acetaldehyde

A Thesis Presented

by

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Abstract

A system consisting of an argon resonance lamp, photolysis cell, gas sampling valve and gas chromatograph has been assembled to complement the studies of ion-molecule reactions performed with ion cyclotron resonance techniques. Preparations are under way to study the proposed isomerization via an ionic mechanism of ethylene oxide to acetaldehyde by irradiating ethylene oxide and isolation and identifying the products on a 10' column of 25% β,β'-oxydipropionitrile on Chromosorb P.

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I. Introduction

Despite their importance in atmospheric reactions and high temperature processes the chemistry of gaseous ion-molecule reactions has been largely neglected for many years. Only recently with the advent of ion cyclotron resonance spectroscopy has a systematic investigation of ion-molecule reactions been possible. However, the technique has the disadvantage that it is highly dependent on the mass/charge (m/e) ratio. Although high resolution mass spectrometry can resolve two nearly m/e equivalent compounds of different empirical formulas (e.g., CO_2H^+ and $C_2H_5O^+$)[1] and ion cyclotron resonance techniques can be used in some cases to distinguish isomeric ions with different functional groups of different reactivity (e.g., the keto-enol ions of acetone)[1], no method exists currently to conveniently and in general isolate and identify isomeric products of ion-molecule reactions.

To overcome this disadvantage and thereby complement ion cyclotron resonance techniques a system consisting of a gas chromatograph, photolysis cell and ultraviolet light source has been assembled. Eventually this system will be improved by replacing the gas chromatograph with a single gas chromatograph-mass spectrometer instrument, thereby enabling positive identification of the isolated products associated with ion-molecule reactions to be made.

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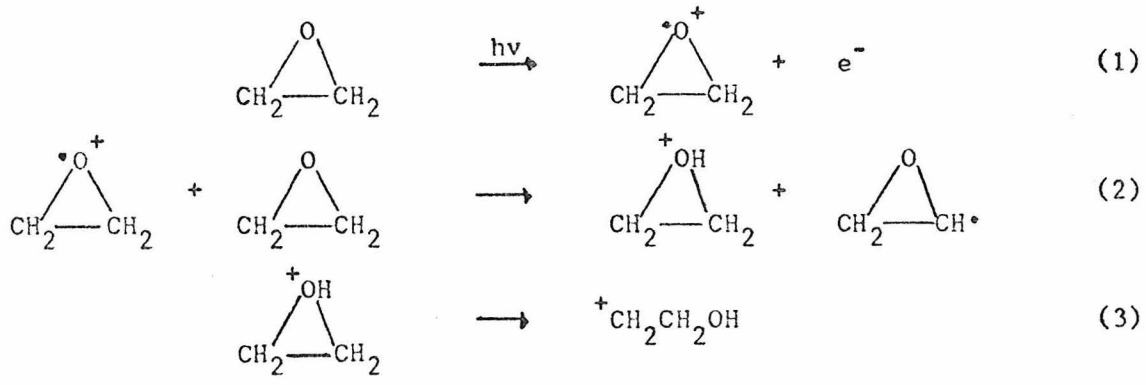
[1] J.L.Beauchamp and R.C.Dunbar, J. Amer. Chem. Soc., 92, 1477 (1970).

This system will initially be used to investigate the proposed rearrangement of protonated ethylene oxide to protonated acetaldehyde, the possibility of which is likely on the basis of recent ion cyclotron resonance studies of $C_2H_5O^+$ isomeric ions[1].

II. The Chemical Problem

Ion-molecule reactions of ethylene oxide and acetaldehyde have been recently studies using ion cyclotron resonance techniques.[1] The proton affinity and hence the heat of formation of protonated ethylene oxide was determined; a comparison of protonated ethylene oxide with protonated acetaldehyde shows that the latter is approximately 27 kcal/mole more stable. A mixture of protonated ethylene oxide and 2-propanol reacts to yield the same product distribution as is obtained from a mixture of protonated acetaldehyde and 2-propanol (polar species other than 2-alkanols result primarily in only proton transfer products and hence are less informative). Hence, because it is less stable than but reacts identically as protonated acetaldehyde, protonated ethylene oxide possibly rearranges during or after generation to protonated acetaldehyde.[2]

It was proposed to investigate this reaction further by photolyzing ethylene oxide and analyzing the products by gas chromatography. A proposed mechanism for this reaction follows:



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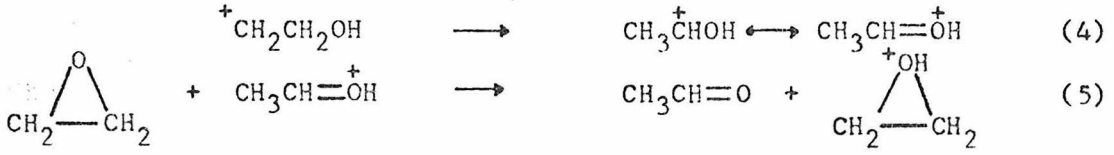
[2] The preceding paragraph was condensed from reference 1.



(4)

(5)

Ethylene oxide's ionization potential is 10.6 eV[3], and hence the reaction is initiated by irradiating ethylene oxide with light from the vacumn ultraviolet.

The radical produced in the second step might initiate a competitive reaction sequence. Studies by Gomer and Noyes[4] indicate that the C_2H_3O radical, obtained from irradiating mercury dimethyl to yield CH_3 radicals which, in turn, abstracted a hydrogen from ethylene oxide, is relatively stable. The C_2H_3O radical dissociates into carbon monoxide and a CH_3 radical, thus propagating the sequence. Propanal is found as a reaction product in addition to methane, ethane and carbon monoxide.

A second source of competition for the ion propagation is the direct photochemical decomposition of ethylene oxide by light between 1600 Å and 2000 Å. Gomer and Noyes report hydrogen, methane, ethane and carbon monoxide as the major products, with small amounts of formaldehyde and acetaldehyde, when ethylene oxide was irradiated by light from a H_2 discharge source. Radiation of this wavelength will be present in the argon lamp if water outgassing is not eliminated.

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3 Ionization Potentials, Appearance Potentials and Heats of Formation of Gaseous Positive Ions, NSRDS-NBS 26, page 123.

4 R.Gomer and W.A.Noyes, Jr., J. Amer. Chem. Soc., 72, 101 (1950).

Competition from radical reactions was not present in the studies performed with the ion cyclotron resonance spectrometer. There ethylene oxide was protonated from RH^+, where RH^+ was produced from electron impact induced fragmentation or previous ion-molecule reactions. If radical reactions are competitive they can be quenched by the addition of nitric oxide.

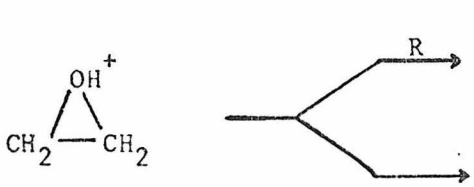
If an asymmetric epoxide is used, such as propylene oxide, it will be interesting to observe in step three whether the epoxide opens up to yield a primary carbonium ion and hence a ketone or a secondary carbonium ion and hence an aldehyde. It seems likely that if steps three and four are distinct an aldehyde will result, as the ring opening will be irreversible and favor formation of a secondary carbonium ion. On the other hand if steps three and four are concerted the ketone would be favored, reflecting its greater thermodynamic stability. In either case the epoxide would lose whatever optical activity it possessed: 1) if there are two distinct steps free rotation would racemize the sample; 2) if it is concerted there are two equivalent ways of effecting a $\left[\sigma^2_s + \sigma^2_a\right]$ change, and hence once again optical activity would be lost.

A chain mechanism has been postulated for the isomerization of ethylene oxide, and step five represents this mechanism's propagation step. The length of the chain propagation step can be determined by comparing the primary quantum yield for ionization with the product quantum yield.

This propagation step can be interrupted by addition of an appropriate ionic inhibitor R (e.g., NH_3),

$$R + CH_3CH{=}\overset{+}{O}H \longrightarrow RH^+ + CH_3CH{=}O \qquad (6)$$

Furthermore, information on the lifetime of the protonated ethylene oxide can be obtained by varing the amount of R added:



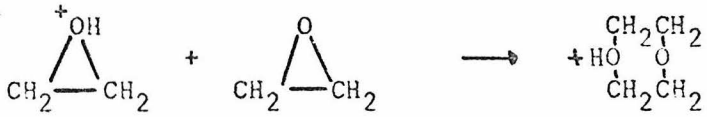
$$+ RH^+ \qquad (7a)$$

$$+ CH_2CH_2OH \qquad (7b)$$

Thus, if R has a higher proton affinity than ethylene oxide the ratio of the product quantum yield to the primary quantum yield will decrease as the concentration of R increases relative to ethylene oxide. The limit of this ratio will be at most 1.0 and may be less, depending on the relative importance of reaction (7a).

Alternative ionic reactions that might prove competitive are clustering reactions (8), which would prohibit chain propagation by proton transfer,[1] and S_N2 displacements (9), which are the gas phase analog of an acid catalyzed reaction of ethylene oxide in a non-polar solvent where ethylene oxide is the best nucleophile available[5]:

$$CH_3CH{=}\overset{+}{O}H + CH_3CH{=}O \longrightarrow CH_3CH{=}\overset{+}{O}HO{=}CHCH_3 \qquad (8)$$



(9)

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5 J.D.Roberts and M.C.Caserio, Basic Principles of Organic Chemistry (W.A.Benjamin, Inc., 1964), pages 410-416.

III. Experimental

A line source of radiation is obtained from an argon lamp using a microwave discharge. Energy to excite the first electronic transition of argon is provided by a Raytheon Microwave Power Generator operating at 85+ watts and 2400-2500 MHz. The two resulting resonance lines of argon at 1048 Å and 1067 Å (11.8 and 11.6 eV, respectively) provide in turn sufficient energy to ionize ethylene oxide.

The 1048 Å line is the more intense (the raie ultime) and the ratio of its intensity relative to 1067 Å line can be increased within limits by increasing the pressure. It might also be possible to achieve a further increase in intensity by using a mixture of 10% argon and 90% helium at a total pressure of one torr.[6]

Prolonged bakeout under vacumn, a titanium getter and a liquid nitrogen sleeve will be used to minimize water outgassing.

LiF windows approximately 1 mm thick and transmitting approximately 30% at 1048 Å and room temperature will be used.[7]

The photolysis cell is 22cm long and 5 cm in diameter. Two 10 cm copper plates inside the cell permit measurement of the ion current, and hence the intensity of the lamp,

$$I_o \phi = \frac{i/e}{(1 - I/I_o)} \qquad (10)$$

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6 J.A.R.Samson, Techniques of Vacumn Ultraviolet Spectroscopy, (John Wiley & Sons, Inc., 1967).

7 Private communication from J.M.Weigel.

can be calculated (I_o is the incident intensity, I the intensity at the opposite end of the cell, ϕ the primary quantum yield of ionization (approximately equal to 1.0), i the ionization current and e the electronic charge).[6]

I/I_o (which will be nearly zero) can be measured using a photomultiplier and a glass slide that has been coated with 1 mg/cm^2 of sodium salicylate. Sodium salicylate has a maximum intensity of fluorescence at 4200 A and hence the other end of the photolysis cell need not have LiF windows. If outgassing is significant it can be corrected for by removing the argon lines with CaF_2 or sapphire windows and then subtracting from the original measurement the response of the photomultiplier to the impurity. This method assumes a constant response of sodium salicylate over the wavelengths involved, which is approximately correct. A thermopile could be used to check both this assumption and equation (10) (ϕ need not be 1.0 if dissociation of ethylene oxide into excited atoms or radicals, such as observed by Gomer and Noyes, is significant). There are no suitable chemical actinometers for light at 1050 Å, although hydrogen bromide is reported useful in the range 2500-1800 Å and nitrous oxide in the range 1470-1849 Å.[8]

An eight-port gas sampling valve was installed in a Varian Aerograph 90-P gas chromatograph (see Figure I). To minimize any undesired catalytic effects stainless steel was used for all con-

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8 J.G.Calvert and J.N.Pitts, Jr., Photochemistry (John Wiley & Sons, Inc., New York, 1966).

nections except the two connections to the gas chromatograph itself (where copper was used). An already existing glass vacumn line was used to complete the connection of the photolysis cell to the gas sampling valve. To minimize the pumping time, 3/16" O.D. tubing was used for the sample loop, and ¼" O.D. tubing was used to connect the glass vacumn line to the valve. Teflon ferrules were used in connecting the thin glass-to-metal seals to the stainless steel tubing from the valve (see Figure 2).

None of the gas chromatographic liquid phases listed in the literature[9] for separating ethylene oxide and acetaldehyde were readily available. Thus, nearly all of the readily accessible liquid phases were tested in order to determine if a suitable substitute for a literature-recommended column could be found. Propylene oxide and propanal, which are liquid and hence more convenient to work with, were used to test the efficiency of the various liquid phases. The results are summarized in Table I, where the optimum performance of each column is given. 25% β,β'-oxydipropionitrile on Chromosorb P was found to a suitable coulum material, and a 10', ¼" O.D. column was consequently prepared and installed.

The ethylene oxide was obtained from Matheson Co. and a preliminary gas chromatogram failed to show any impurities.

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9 Gas Chromatography Abstracts

IV. Results

Preliminary examinations indicate that ethylene oxide and acetaldehyde are completely separated with retention times of 9.8 min. and 11.1 min., respectively, at a flow rate of 54 ml/min. and a column temperature of 65°C. The retention times can be increased to 30.5 min. and 35.5 min., respectively, at a flow rate of 51 ml/min and a column temperature of 20° C. The separation is better, which is advantageous for detecting minute amounts of acetaldehyde, but there is a corresponding loss of peak sharpness. This can be compensated somewhat by increasing the flow rate.

Sensitivity is greatly improved by immersing the sample loop in liquid nitrogen and thereby concentrating the sample. Preliminary examinations indicate that at least one part in eighty of acetaldehyde in ethylene oxide can be determined if the sample is condensed (see Figures 3 and 4).

One torr of ethylene oxide was irradiated for 50 min. by light from the argon resonance lamp. There was significant coloring of the LiF windows, indicating a drop in transmission. Approximately one part in 500 of the analyzed sample was acetaldehyde. Assuming 10^{11} quanta/sec, this yield corresponds to a chain length of 100. However, no ion current was detected.

V. Conclusion

A gas sampling system has been assembled which will be useful in checking gas purities. By coupling this system to a photolysis cell and an ultraviolet lamp a means of studying ion-molecule reactions is obtained which complements studies performed with ion cyclotron resonance techniques.

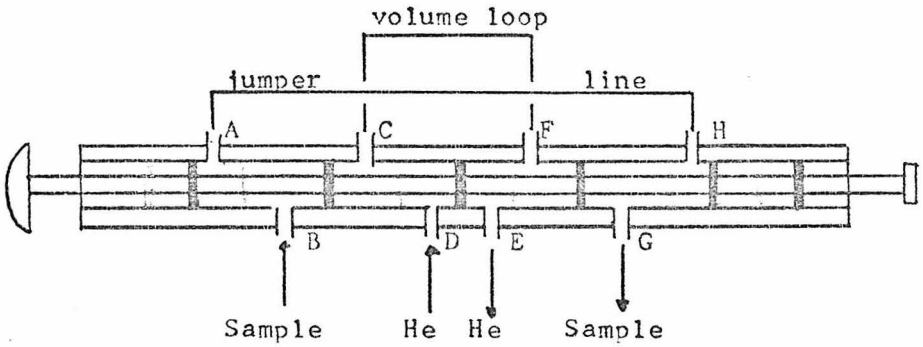
With regards to the specifically proposed isomerization of ethylene oxide it is intended that further sensitivity measurements will be made to determine the minimum amount of acetaldehyde in ethylene oxide that can be detected. Further photolysis runs will be performed with the intention of increasing the isomerization of ethylene oxide to acetaldehyde. Ideally this isomerization will be about 1% to avoid complications due to the photolysis of acetaldehyde itself.

VI. Acknowledgment

I would like to thank Drs. David Holtz and Jesse L. Beauchamp for suggesting the problem and their helpful suggestions along the way. I would like to also thank the men in the chemistry shops who were so tolerant of my mechanical ignorance.

Figure I

Eight-Port Gas Sampling Valve

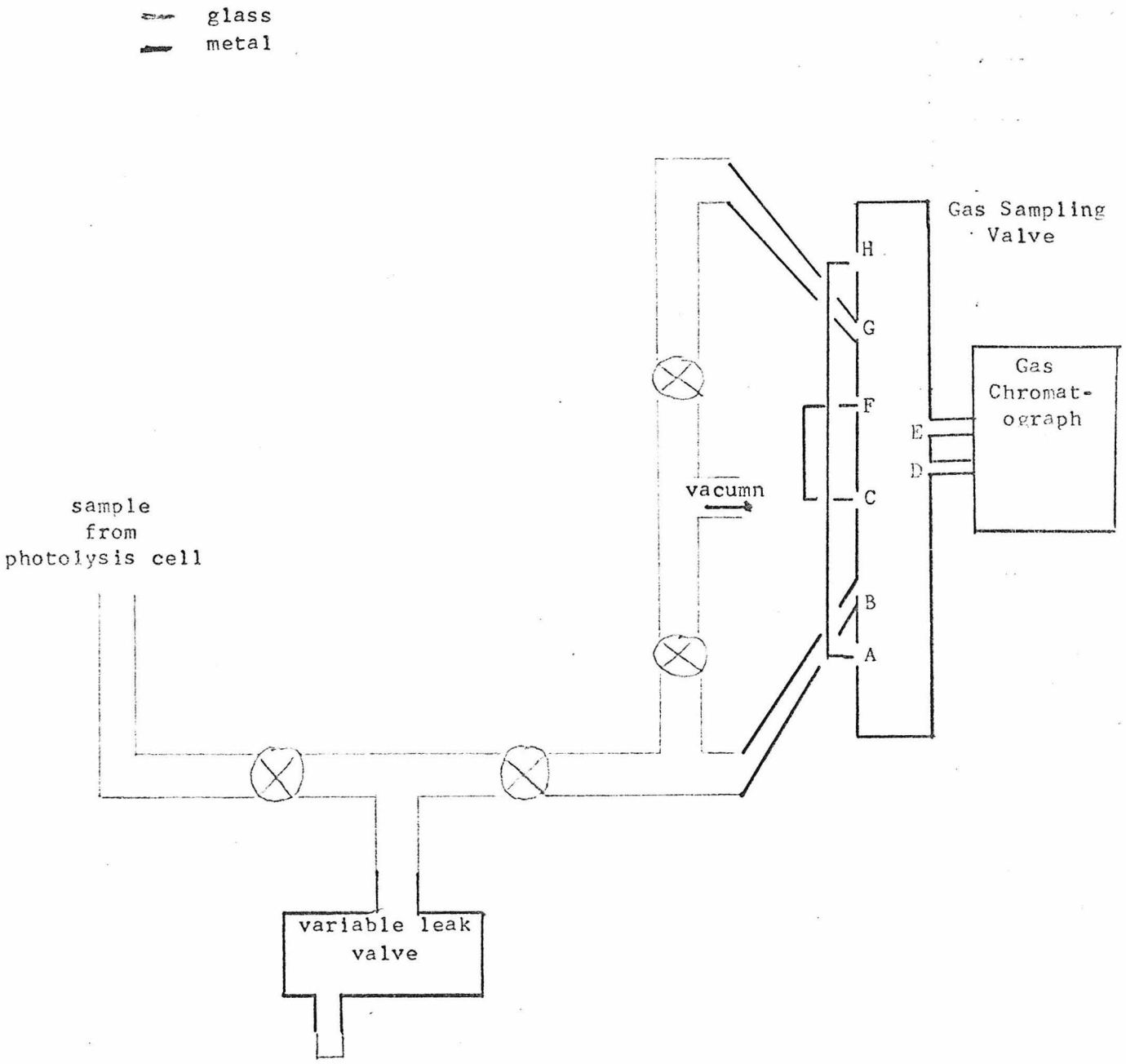


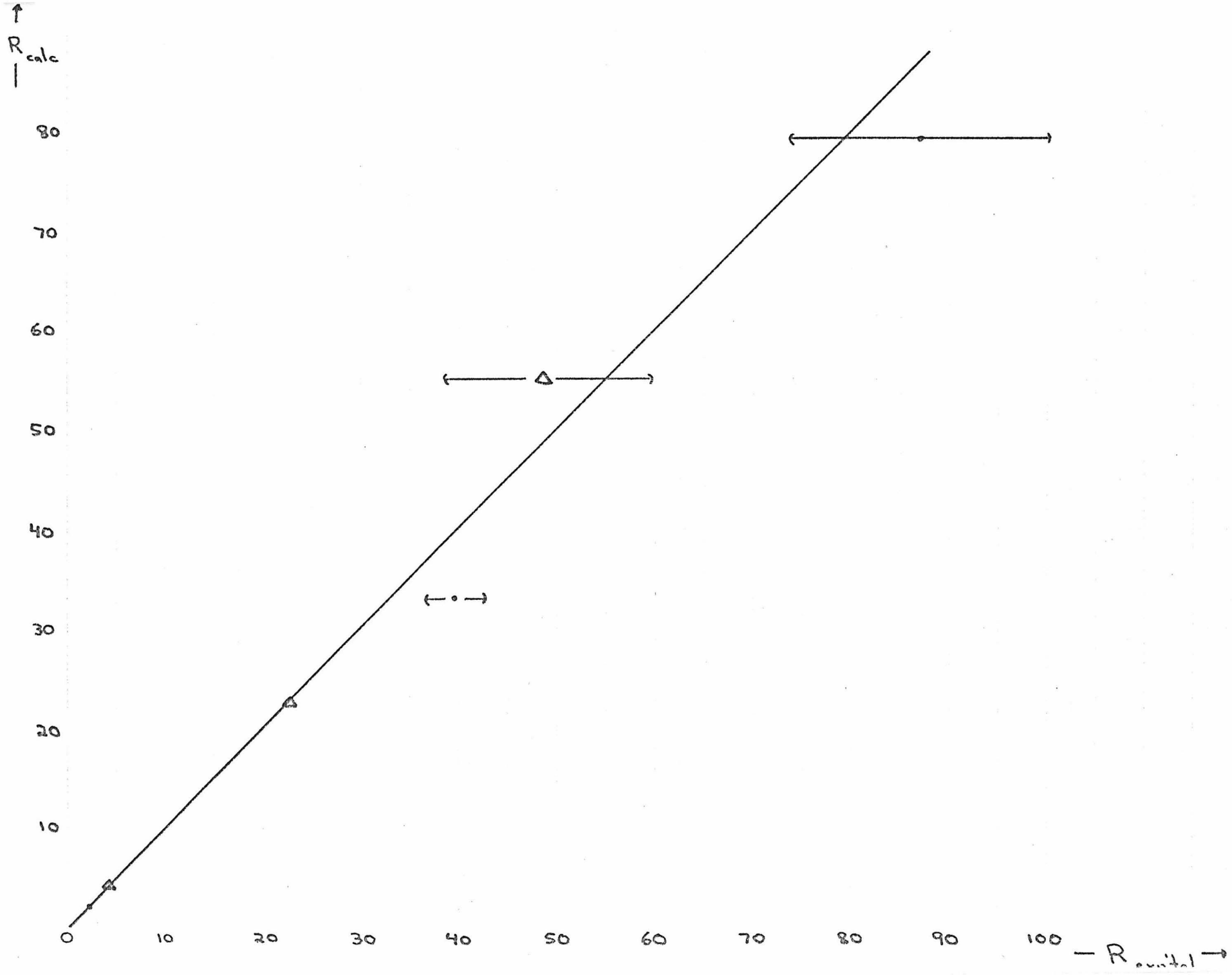
Pick-up Position

Inject Position

Figure 2

Schematic Diagram of Apparatus




R calc
80
70
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100
R control

Figure 4

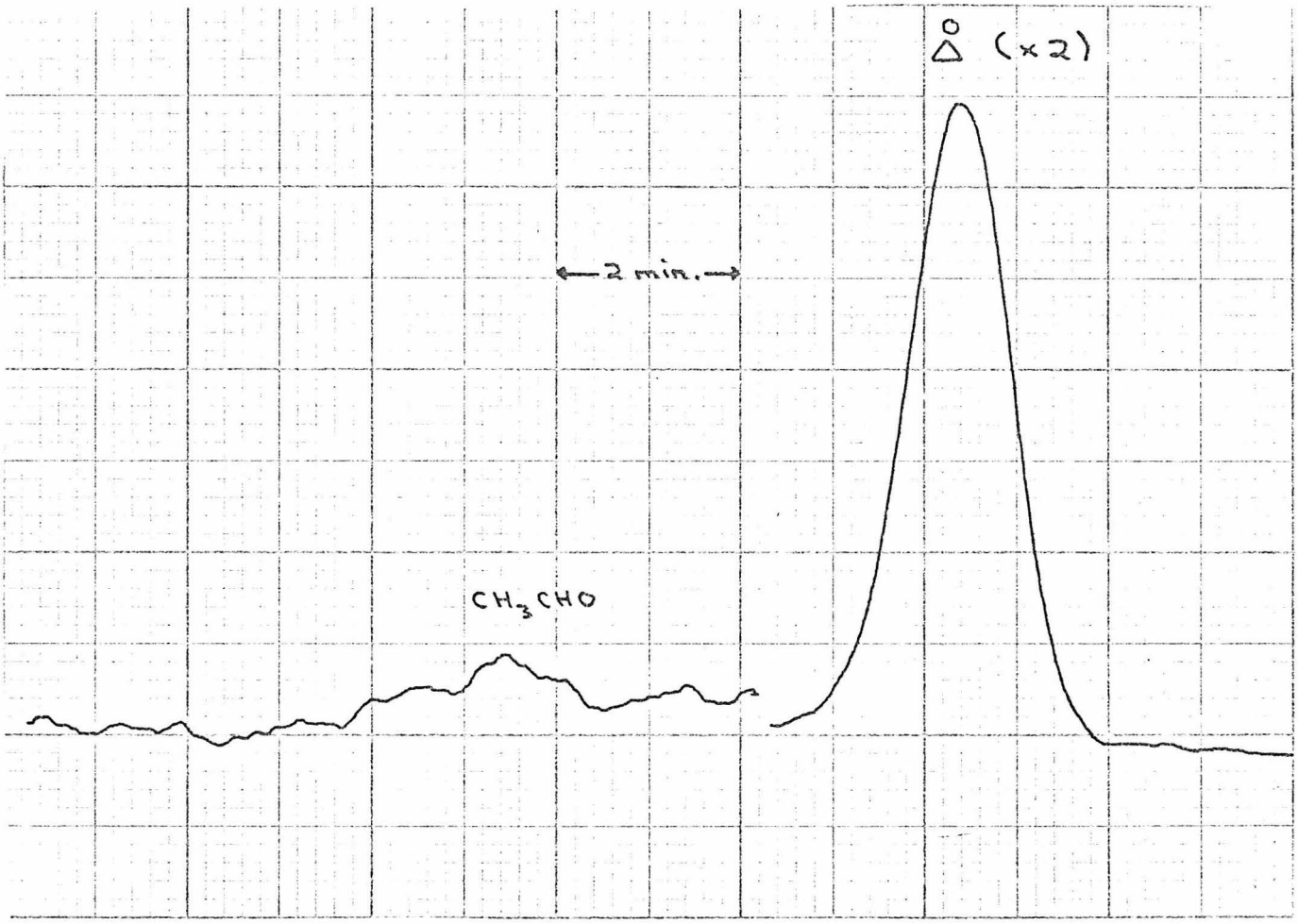

Table I

Column Material	Column Temp. (°C)	He Flow (ml/min.)	Retention Time (min.) CH_2 CH CH_3	Retention Time (min.) CH_3CH_2CHO	Remarks
5% Carbowax on Chromosorb G, 5'	10	60	1.3	2.0	incomplete
20% Carbowax on Firebrick, 9'	95	40	3.7	5.0	nearly complete, but 6 min. tailing
5% SE-30, 5'	-20	60	6	6	very broad, no separation
10% UCON on Chromosorb G, 5'	27	30	7.7	9.0	incomplete, broad
4% Apiezon-L on Chromosorb P, 9'	9	46	3.3	3.3	none
35% Apiezon-L on Chromosorb P, 5'	23	43	4.9	4.9	none, tailing
20% TCEP on Chromosorb P, 10'	125	32	5.2	4.0	complete, but ethylene oxide isomerizes to acetaldehyde on column
5% DEGS, 10'	23	14	8.5	11.6	nearly complete, tailing
25% , -oxydipropionitrile on Chromosorb P, 10'	85	32	10.6	15.0	complete, acetone also completely separated

Figure Captions

Figure I: With the valve in the pick-up position the carrier gas comes in Port D and out Port E. The sample meanwhile comes in Port B, out Port C, through the volume loop, in Port F, and out Port G. With the valve in the inject position the carrier gas which comes in Port D goes out Port C, through the volume loop, in Port F, and out Port E. The sample stream, if allowed to flow, will come in Port B, out Port A, through the jumper line, in Port H and out Port G.

Figure 3: The ratio of ethylene oxide to acetaldehyde, determined from pressure measurements (R_{calc}) is plotted vs. the the ratio determined from the peak height of the gas chromatogram. ($R_{exp'tal}$). No correction was made for any possible difference between the thermal conductivity of ethylene oxide and acetaldehyde. Recorder noise becomes important at low concentrations of acetaldehyde; hence the larger errors as R increases.

Figure 4: Representative chromatogram, R = 22. The sensitivity was doubled for acetaldehyde relative to ethylene oxide.