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J. J. Mitchell, R. H. Perkins, and F. F. Coleman

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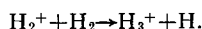
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### Secondary Processes of Ion Production in the Mass Spectrometer

J. J. MITCHELL, R. H. PERKINS AND F. F. COLEMAN\*  
Beacon Laboratories of The Texas Company, Beacon, New York  
June 1, 1948

**I**N the early days of mass spectrometer work, secondary production of ions was a common occurrence, primarily because of high gas pressures in the ionization chamber. Hogness and Lunn,<sup>1</sup> for instance, found that as the pressure of hydrogen in the ionization chamber was raised above 1 micron of mercury the ion intensity caused by  $H_2^+$  decreased and that due to  $H_3^+$  increased, both linearly with the pressure. They reasoned that the 48-volt electrons used to produce ions gave rise to metastable  $H_2^+$  ions which then took part in the reaction:



During some recent work in this laboratory, using the ratio of the  $m/e=45$  ion intensity to  $m/e=44$  ion intensity in  $CO_2$  produced by burning various samples as a measure of their  $C^{13}$  to  $C^{12}$  ratios, the secondary production of  $HCO_2^+$  was encountered at fairly low ionization chamber pressures.\*\* Sample pressures were  $150-225 \times 10^{-3}$  mm Hg on the high pressure side of the entrance leak so that the ionization chamber pressures were of the order of  $5 \times 10^{-4}$  mm Hg.

The failure of a drying agent in a  $CO_2$  purification train and a resulting high water content gave rise to spuriously high  $C^{13}$  to  $C^{12}$  ratios when the ratio of the  $m/e=45$  ion intensity to  $m/e=44$  ion intensity was used as a measure of  $C^{13}$  content. Since such an effect would interfere seriously with the accuracy of this method of determining the  $C^{13}/C^{12}$  ratio, various gases were added to pure  $CO_2$  to determine the magnitude and cause of the effect. Tables I and II show the results of adding water, hydrogen and rare gases to pure  $CO_2$  in terms of excess ratio for the Type II and Type III ionization chambers made by the Consolidated Engineering Corporation. An electron energy of 50 volts was used in the first case and 70 volts in the second. Excess ratio is the difference between the ratio of  $m/e=45$  to  $m/e=44$  for the mixture in question and that for pure  $CO_2$ . This has been used since it appears certain from the results obtained with helium mixtures that

the excess ratio is a measure of the amount of  $(HC^{12}O_2)^+$  present. Table III showing the effect of adding deuterium confirms this interpretation since no increase in  $m/e=45$  ion intensity is observed, but instead an increase in  $m/e=46$ , corresponding to  $(DC^{12}O_2)^+$ .

TABLE I. Effect of added gases on the  $m/e=45$  to  $m/e=44$  intensity ratio for  $CO_2$ . (Type II ionization chamber)

Added gas	Mole % of added gas	Excess ratio $\times 100$
$H_2O$	4.45	0.027
	5.0	0.020
	8.02	0.029
	9.0	0.012
	42.7	0.121
	62.3	0.097
$H_2$	50*	0.106
Argon	50*	-0.015
Average ratio for pure $CO_2 \times 100 = 1.178 \pm 0.011$ .		

\* Approximate.

From Tables I and II it will be seen that the effect is greater for the Type II ionization chamber than for the Type III. It is interesting to note that the results for hydrogen mixtures and for water mixtures in the Type III ionization chamber can be fitted by the relations

$$R = 0.0098M$$

and

$$R = 0.00104M,$$

where  $R$  is the excess ratio times 100 and  $M$  is mole percent of hydrogen in the first case and of water in the second, with standard errors of estimate of 0.007 and 0.006, respectively.

TABLE II. Effect of added gases on the  $m/e=45$  to  $m/e=44$  intensity ratio for  $CO_2$ . (Type III ionization chamber)

Added gas	Mole % of added gas	Excess ratio $\times 100$
$H_2$	8.99	$0.018 \pm 0.007$
	24.0	$0.023 \pm 0.007$
	49.5	$0.047 \pm 0.008$
	87.5	$0.079 \pm 0.026$
$H_2O$	7.8	0.011
	17.4	0.022
	37.0	0.030
	69.2	0.072
He	9.5	$-0.003 \pm 0.005$
	24.7	$-0.005 \pm 0.004$
	50.2	$0.003 \pm 0.003$
	50.3	$0.004 \pm 0.010$
	75.9	$0.012 \pm 0.012$
Average ratio for pure $CO_2 \times 100$ .		
During $H_2O$ measurements— $1.167 \pm 0.008$		
During $H_2$ measurements— $1.150 \pm 0.006$		
During He measurements— $1.143 \pm 0.003$		

In order to determine if the effect was similar to that reported by Hogness and Lunn for hydrogen, the  $m/e=45$  to  $m/e=44$  ratio was measured for a mixture containing 40.1 mole percent of hydrogen at three different sample pressures. As Fig. 1 shows, excess ratio, or  $HCO_2^+$  relative ion intensity, increases in direct proportion to sample pressure and hence to pressure in the ionization chamber, in complete agreement with the results on  $H_3^+$  from pure hydrogen.

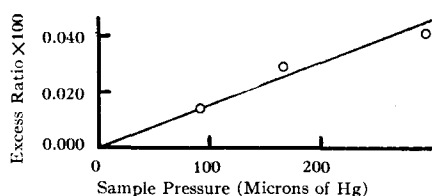


FIG. 1. Effect of sample pressure on the  $m/e=45$  to  $m/e=44$  ion intensity ratio for a hydrogen- $\text{CO}_2$  mixture.

TABLE III. Effect of addition of deuterium to  $\text{CO}_2$ .

Mole % of added gas	$(m/e=45)/(m/e=44) \times 100$	$(m/e=46)/(m/e=44) \times 100$
Type II ionization chamber.		
0	1.179	0.412
50*	1.156	0.481
Type III ionization chamber.		
0	1.155	0.407
51.3	1.153	0.429

\* Approximate.

The authors wish to thank J. E. Mapes for aiding in the measurements made on hydrogen and helium mixtures in the Type III ionization chamber.

\* Present address: U. S. Navy Electronics Laboratory, San Diego, California.

<sup>1</sup> T. R. Hogness and E. G. Lunn, Phys. Rev. **26**, 44-55 (1925).

\*\* The mass spectrometer is a Model 21-102 built by Consolidated Engineering Corporation, Pasadena, California.

## In Situ Study of the Thermal Decomposition of Ethylene Oxide by Infra-Red Spectrometry

G. L. SIMARD, J. STEGER, T. MARINER, D. J. SALLEY,  
AND V. Z. WILLIAMS\*

American Cyanamid Company, Stamford, Connecticut  
May 18, 1948

THE development of a high temperature seal<sup>1</sup> for sodium chloride plates to Pyrex made possible the construction of a cell for the direct study of homogeneous gas reactions by infra-red spectrometry. In order to evaluate this method for kinetic studies, the thermal decomposition of ethylene oxide was investigated. Firstly, decomposition products were identified from spectra recorded by wave-length scanning during reaction. Bands which persisted after complete decomposition were obviously from the spectra of final products. Bands which appeared and disappeared during reaction were from the spectra of intermediate products. The identity of the products was established in the usual manner from band positions, structures, and relative intensities. Secondly, quantitative measurements of reactant and products were made during reaction by continuous transmission recording at selected band positions. Products exhibiting strong pressure broadening could not be readily measured by infra-red and were analyzed by mass spectrometry on samples withdrawn from the reaction cell. The reaction was studied at 410°C, 440°C, and 470°C at initial ethylene oxide pressures of 200 mm and 400 mm.

Infra-red emission<sup>2</sup> was observed of sufficient intensity to be a useful adjunct to absorption spectra for the identification of products. Spectral bands were more prominent relative to background in emission than in absorption, and the techniques for emission minimized interference effects by atmospheric vapors.

The quasi-unimolecular nature of the decomposition, the activation energy, and the final products previously reported<sup>3</sup> were confirmed. Good agreement was found between the rates of decomposition of ethylene oxide determined from the spectrometer data and those from measurements of total pressures, provided the latter were based on the actual rather than on a theoretical ratio of the initial to the final reaction pressures.

Two intermediate products were identified, ketene and acetaldehyde. The formation of ketene had not been hitherto reported for this reaction. Both intermediates attained their maximum values at approximately the  $\frac{1}{4}$  reaction life. The orders of concentration were about the same, but the maximum value for acetaldehyde persisted for a longer time than that for ketene. Formaldehyde, a postulated intermediate, was not found, although its presence to the order of 1 percent of sample composition could not be excluded. The conditions of investigation were not suitable for the detection of free radicals. Their presence could only be inferred from studies with added nitric oxide and from the induced decomposition of normally stable compounds by the reaction.

In addition to the principal final products, carbon monoxide and methane, small quantities of ethane, propane, and hydrogen were formed. The percent composition of carbon monoxide, ethane, and propane based on the total quantity of products was relatively constant during reaction, but the percent of methane increased and that of hydrogen decreased.

The results and experience obtained definitely established infra-red *in situ* measurements as a rapid and effective means for obtaining kinetic data. Identification and continuous measurement of each component during reaction can be made. As in the case of any research tool, certain limitations exist and coordination with other methods may be necessary depending on the particular reaction investigated. Obviously, substances exhibiting no infra-red adsorption cannot be measured. The overlapping of spectral bands may make direct identification of components difficult, or considerably lower the accuracy of measurements for weakly absorbing materials. Substances such as light gases may exhibit pressure broadening, and their measurement will consequently be difficult. Nevertheless, considerable data can be obtained in a relatively simple manner.

A complete presentation of the data and their implication on postulated mechanisms will be made at a later date.

\* Present address: Perkin-Elmer Corporation, Glenbrook, Connecticut.

<sup>1</sup> G. L. Simard and J. Steger, Rev. Sci. Instr. **17**, 156 (1946).

<sup>2</sup> V. Z. Williams, G. L. Simard, and J. Steger, "Symposium on Molecular Structure and Spectroscopy," Ohio State University, June, 1946.

<sup>3</sup> W. Heckert and E. Mack, J. Am. Chem. Soc. **51**, 2706 (1929); C. Fletcher and G. Rollefson, J. Am. Chem. Soc. **58**, 2135 (1936); H. Thompson and M. Meissner, Trans. Faraday Soc. **32**, 1451 (1936).