

In Situ Study of the Thermal Decomposition of Ethylene Oxide by InfraRed Spectrometry

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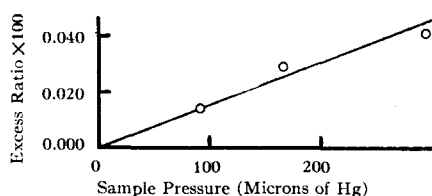


FIG. 1. Effect of sample pressure on the $m/e=45$ to $m/e=44$ ion intensity ratio for a hydrogen- CO_2 mixture.

TABLE III. Effect of addition of deuterium to 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.

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¹ 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

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THE development of a high temperature seal¹ 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strong pressure broadening could not be readily measured by infra-red and were analyzed by mass spectrometry on samples withdrawn from the reaction cell.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 emission² 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 reported³ 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.

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¹ G. L. Simard and J. Steger, Rev. Sci. Inst. **17**, 156 (1946).

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

³ 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).