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The Kinetics of the Thermal Decomposition of Methyl Ethyl Ether

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The kinetics of the decomposition of methyl ethyl ether have been reinvestigated. The results obtained differ considerably from those of Glass and Hinshelwood. The

heat of activation is found to be $54,500 \pm 1500$ calories. This value brings the activation energy of methyl ethyl ether into line with those of the other ethers.

INTRODUCTION

HINSHELWOOD and his coworkers have investigated a series of unimolecular ether decompositions.¹ These furnish the most complete existing set of kinetic investigations involving chemically related substances. The comparison of the rates and temperature coefficients of these reactions is therefore of considerable interest.² If we consider the series dimethyl ether, methyl ethyl ether, diethyl ether, we have energies of activation of 58,500, 47,000, and 53,000 calories, respectively. Kassel suggests that the low value for methyl ethyl ether is due to the asymmetry of the molecule as compared with the symmetrical ethers.

In the course of another investigation³ a few runs were made with methyl ethyl ether. These indicated that the temperature scale in the investigation of Glass and Hinshelwood was considerably in error, and that much higher temperatures were necessary for the attainment of a given rate of reaction. This conclusion is substantiated by the fact that in the investigation of Clusius⁴ the rates given for the decomposition of methyl ethyl ether catalyzed by iodine are *slower* than those given by Glass and Hinshelwood for the uncatalyzed reaction.

It was therefore considered to be worth while repeating the work of Glass and Hinshelwood. The present investigation has been confined to a

determination of the temperature coefficient of the reaction, inasmuch as a thorough investigation of the mechanism is being made elsewhere.⁵

EXPERIMENTAL PROCEDURE

The reaction velocities were measured in the usual way by observing the rate of pressure change in a system at constant volume. The reaction vessel was of fused silica. The apparatus was identical with one which has been used in a number of previous investigations.⁶ The required temperatures were obtained by the use of a bath of molten lead of about 6 liters capacity, which has been previously described.⁷ Temperatures were measured with a chromel-alumel thermocouple in conjunction with a Cambridge thermocouple potentiometer. The temperature could be maintained constant to within 0.1°C .

Eastman's C.P. methyl ethyl ether was used. It was dried over sodium and fractionally distilled, the middle third being retained (B. P. $8-10^\circ\text{C}$).*

EXPERIMENTAL RESULTS

As in the investigation of Glass and Hinshelwood, the reaction rates have been inferred from a comparison of the times for a given fractional pressure increase. As the reaction is by no means an ideal unimolecular one, it is desirable to use

¹ Hinshelwood, *Proc. Roy. Soc. A* **114**, 84 (1927); Hinshelwood and Askey, *ibid.* **A115**, 215 (1927); Glass and Hinshelwood, *J. Chem. Soc.* **1929**, 1804.

² See Kassel, *Kinetics of Homogeneous Gas Reactions*, New York, 1932.

³ Steacie, *J. Phys. Chem.* **36**, 1562 (1932).

⁴ Clusius, *J. Chem. Soc.* **1930**, 2607.

⁵ W. Ure, private communication.

⁶ Steacie, *Can. J. Research* **6**, 265 (1932); *J. Phys. Chem.* **36**, 1562 (1932).

⁷ Steacie, *J. Chem. Phys.* **1**, 313 (1933).

* The Eastman Kodak Co. have kindly informed me of the method of preparation. The ether was prepared from sulphuric acid and a mixture of methyl and ethyl alcohols. It was therefore entirely free from iodides.

rates as near the start of the reaction as possible, and hence the times for a 25 percent increase in pressure have been used. In the absence of a detailed knowledge of the mechanism of the reaction, the amount of reaction to which this corresponds is unknown. It should, however, give a reasonably accurate criterion of the relative rates of reaction under different conditions of temperature and pressure.

The experimental observations are given in Table I.

TABLE I.

Temperature (°C)	Initial pressure (cm)	T_{25} (sec.)	Temperature (°C)	Initial pressure (cm)	T_{25} (sec.)
460	72.17	2508	500	19.20	536
460	56.76	2760	500	14.18	617
460	37.58	3222	500	11.49	738
460	25.45	3804	500	7.80	876
480	72.06	882	520	74.33	153.6
480	57.44	942	520	44.83	165.0
480	50.34	1020	520	33.84	189.0
480	31.89	1290	520	24.26	214.2
480	22.84	1464	520	17.06	240.0
480	20.06	1530	520	12.16	283.2
480	14.46	1800	520	9.32	317.4
480	11.66	1812	540	59.90	72.0
480	8.48	2124	540	35.57	86.4
500	72.13	328	540	23.00	101.4
500	56.88	341	540	14.13	118.8
500	35.91	438	540	9.22	136.8
500	26.05	490	560	65.00	25.8

The high pressure rates of reaction have been obtained by plotting T_{25} against the reciprocal of the initial pressure, so as to obtain lines of slight curvature, and extrapolating to infinite pressure. The curve for 520°C is shown in Fig. 1.

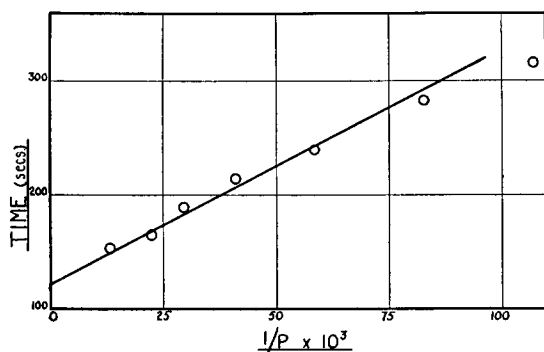


FIG. 1. Extrapolation of rates of reaction to infinite pressure.

The heat of activation has been calculated in the usual way by plotting $\log T_{25}$ against $1/T$, and measuring the slope of the line. For the sake of comparison, the values of $\log T_{25}$ for an initial pressure of 65 cm have been used, as well as those for infinite pressure. The data are given

TABLE II.

Temperature (°C)	460	480	500	520	540	560
$T_{25}(P_0 = 65 \text{ cm})$	2616	930	336	156.0	71.4	25.8
$T_{25}(P_0 = \infty)$	1836	648	252	120.0	55.2	—

in Table II, and are plotted in Fig. 2. The values of the heat of activation thus obtained are:

from $P_0 = 65 \text{ cm}$ 55,200 cal./gram mol.
from $P_0 = \infty$ 53,800 cal./gram mol.

The mean value is thus 54,500 cal., with a probable error of about 1500 calories.

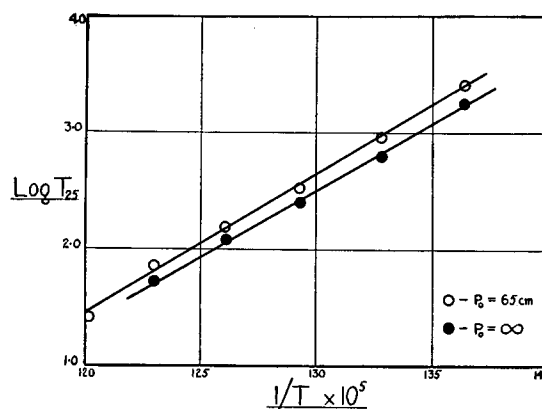


FIG. 2. The temperature coefficient of the reaction.

This is considerably higher than the value previously reported by Glass and Hinshelwood. This result gives a more regular gradation of activation energy with chemical composition for the various series of ethers which may be chosen. Thus for the series dimethyl, methyl ethyl, methyl propyl ether instead of 58,000, 47,000, 49,000 cal., we have 58,000, 54,500, 49,000. And for the series dimethyl, methyl ethyl, diethyl ether we now have 58,000, 54,500, 53,000 cal.

The main result, therefore, is to bring the heat of activation of methyl ethyl ether into line with those of the other ethers.