Studies on the Decomposition of Azomethane I. Description of the Apparatus

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I. Description of the Apparatus*

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An apparatus for measuring the rates of gaseous reactions in the presence of large excesses of inert gases, using an adaptation of the Huygens manometer as the pressure measuring device, is described.

§1. Introduction

THE rate constant of a true unimolecular reaction tends to approach a constant value as the pressure is raised, but falls in value at low pressures, where the number of activating collisions is not sufficient to maintain the rate of reaction. Addition of an inert gas, which can exchange energy with the reacting molecule but which does not react chemically with it, may be expected to have the effect of increasing the rate constant by providing an additional source of activating collisions. Numerous experiments in which an inert gas has been added to a decomposing substance (usually an aldehyde or an ether) have been performed by Hinshelwood and his co-workers,[2] and they have invariably found that hydrogen apparently does have the anticipated activating effect. However, recent work has indicated that the decompositions which they have studied may be chain reactions,[3] and the interpretation of their work therefore becomes doubtful. In any event, these reactions are not as simple as they were once thought to be.[4] Others have reported similar work with nitrous oxide,[5]

nitryl chloride,[6] and fluorine oxide[7] as the decomposing substances. There is no reason to believe that these decompositions involve chains, though the nitrous oxide decompositions is probably not a simple one.[8] Thus far, however, the only work on organic substances whose reactions probably do not involve chains is that of Nelles and Kistiakowsky[9] on the effect of hydrogen, nitrogen, propane, and carbon dioxide on the isomerization of dimethyl maleate, a reaction with very peculiar characteristics, and that of Ramsperger[10] on the decomposition of azomethane in the presence of nitrogen and ethane. It is the purpose of this series of papers to extend this work on azomethane, in order to get further information on the relative activating efficiencies of different gases, and because information on the azomethane decomposition itself may be obtained by studying it over a range of experimental conditions (see §9 of the following paper).

§2. Description of the Apparatus

With pure azomethane it is possible to follow the course of the reaction at low pressures by measuring the increase in the pressure as the azomethane decomposes by means of a McLeod gauge, but the presence of an excess of inert gas precludes the effective use of this instrument. We have, therefore, made use of an adaptation of the Huygens manometer,[11] which enables one to

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[2] See, e.g., Hinshelwood, Proc. Roy. Soc. **A113**, 221 (1926); ibid. **A114**, 84 (1927); Hinshelwood and Askey, ibid. **A115**, 215 (1927); ibid. **A116**, 163 (1927); Glass and Hinshelwood, J. Chem. Soc., London 1804 (1929); Fletcher and Hinshelwood, Trans. Faraday Soc. **30**, 614 (1934).

[3] See (a) F. O. Rice and Herzfeld, J. Am. Chem. Soc. **56**, 284 (1934); (b) Sickman and Allen, ibid. **56**, 1251 (1934); Allen and Sickman, ibid. **56**, 2031 (1934); (c) Leermakers, ibid. **56**, 1537, 1866 (1934).

[4] (a) O. K. Rice and Sickman, J. Am. Chem. Soc. **56**, 1444 (1934); (b) Fletcher and Hinshelwood, Proc. Roy. Soc. **A141**, 41 (1933).

[5] Volmer and Kummerow, Zeits. f. physik. Chemie **B10**, 414 (1930); Volmer and Froehlich, ibid. **B19**, 89 (1932); Volmer and Bogdan, ibid. **B21**, 257 (1933).

[6] Schumacher and Sprenger, Zeits. f. physik. Chemie **B12**, 115 (1931).

[7] Koblitz and Schumacher, Zeits. f. physik. Chemie **B25**, 283 (1934).

[8] Hunter, Proc. Roy. Soc. **A144**, 386 (1934).

[9] Nelles and Kistiakowsky, J. Am. Chem. Soc. **54**, 2208 (1932).

[10] Ramsperger, J. Phys. Chem. **34**, 669 (1930).

[11] Ostwald-Drucker, *Physiko-Chemische Messungen*, fifth edition (Akademische Verlagsgesellschaft, Leipzig, 1931), pp. 208, 210.
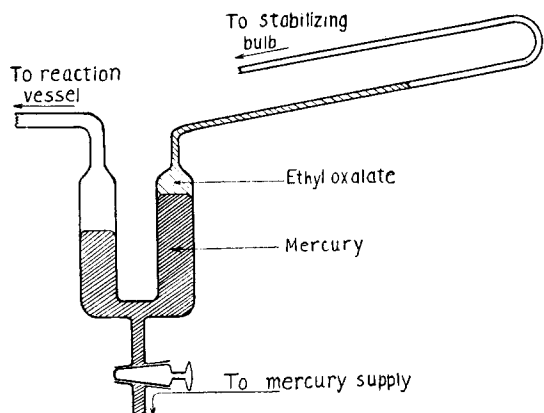
FIG. 1. Sketch of manometer.

FIG. 2. Sketch of support for manometer tube. (The size of the teeth on the rack is highly exaggerated.)

measure very small changes in a large total pressure with an accuracy independent of the total pressure.

The reaction vessel (described in previous work[4a]) was a liter Pyrex flask immersed in a salt bath whose temperature could be controlled within 0.1°. The essential features of the Huygens manometer are shown schematically in Fig. 1. The sides of the U-tube were made of Pyrex tubing of 20 mm inside diameter and the height of the U-tube was somewhat over 70 mm. The U-tube contained mercury, the amount of which could be regulated, as it communicated through the stopcock shown with a mercury supply in a leveling bulb. On the surface of the mercury on the side which communicated with the reaction vessel were placed a few drops of a saturated solution of mercury di-p-tolyl (Eastman) in dibutyl phthalate as a lubricant.[12] While it might be thought undesirable to have such a solution in contact with the gas being studied, in actual practice there was no evidence of any appreciable error caused thereby, and as the measurements depended upon the reproducibility of very small movements of the mercury surface such a lubricant was absolutely essential. Diethyl oxalate was used as the light manometer liquid because it has a low viscosity and at the same time a fairly low vapor pressure.

It was necessary to thermostat the U-tube to within a few thousandths of a degree. There was, however, a length of perhaps eight centimeters of 2-mm tubing, extending through the bottom of

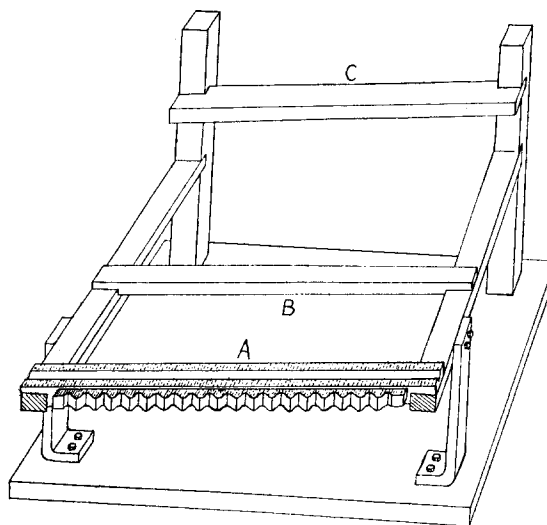[12] See Hickman, J. Opt. Soc. Am. 19, 190 (1929); J. Phys. Chem. 34, 650 (1930).

the thermostat and the table on which it rested, between the U and the stopcock, which was not thermostated. This would not be of importance except in a slow run of long duration. In order to be able in such cases to check up on errors due to this or other causes an apparatus as nearly similar as possible to the one described was made and placed directly beside it, the reaction flask being in the same salt bath, the U-tube in the same water bath, etc. This duplicate apparatus could be used as a blank. The temperature of the ethyl oxalate in the slanting tube could be controlled sufficiently well by an air thermostat. To stabilize the system in case there should be some residual gas left in the ethyl oxalate after evacuation the end of the tube was connected, as indicated in Fig. 1, to a 500-cc bulb placed in the water bath.

The position of the ethyl oxalate meniscus was observed with a microscope mounted on a small brass platform which was in turn mounted on the metal frame sketched in Fig. 2. This frame had a rolled iron base, $9'' \times 13'' \times \frac{1}{2}''$ which rested on three screws not shown in the diagram and was provided with a circular level so it could be placed so that it was exactly horizontal. The platform holding the microscope rested on slanting brass cross-pieces A and B, being held firmly against them by a spring. Its motion along these pieces was controlled by a pinion which

meshed with the rack shown at the front of A, and was guided by the groove in A. The crosspiece C was used as a support for a specially ruled glass scale and for the slanting tube containing the ethyl oxalate meniscus which was firmly clamped to the frame and so held rigidly in position. The ethyl oxalate tube from the blank apparatus was just above the other one, and the microscope was mounted so that it could be focused on either one. A flash-light bulb attached to the microscope was used to illuminate scale and meniscus. A micrometer eyepiece was available for observing slow motions of the meniscus.

In using this apparatus the greater part of the pressure in the reaction vessel was balanced by the difference in height of the mercury on the two sides of the U-tube. The initial total pressure was measured by a McLeod gauge, which was then shut off from the reaction vessel. The small changes in pressure as the reaction proceeded were measured by observing the change in height of the ethyl oxalate meniscus. It was necessary, of course, to adjust the amount of mercury in the U-tube at the beginning of the reaction so that the ethyl oxalate meniscus would be on the scale. With some practice it was found possible to make a preliminary adjustment so that only a very small amount of mercury had to be added or removed after the gas was admitted to the reaction vessel. The final adjustment could usually be made and the readings begun within less than a minute after the reaction vessel was filled. Occasionally, however, the readings made during the next minute or two were irregular, this possibly being the time necessary for the mercury to come to final temperature equilibrium with the water bath.

It is obviously not possible to use such an apparatus for a very rapid reaction, and its usefulness also seemed to be limited rather more than we expected in the direction of very slow reactions, which confined us to mixtures in which the partial pressure of azomethane was about half a millimeter or greater. The measurement of the position of the meniscus was amply accurate for much lower pressures than that, but when the rate was very slow irregular changes in the position of the meniscus would occur. We believe that this could be eliminated by mounting the whole apparatus in a much more rigid fashion. Although the table on which the water bath rested was quite sturdy and the vacuum bench was strengthened with guy wires, a certain amount of vibration was possible, and by exerting pressure on parts of the vacuum bench it was possible to

cause a motion of a millimeter or so in the position of the ethyl oxalate meniscus. The upper limit of total pressure which could be used with our apparatus was about 70 mm. The range in this direction could be increased by increasing the height of the U-tube (thus increasing the external volume, however) or by exerting a back pressure by means of an inert gas in the stabilization bulb. The limit to this method of increasing the range is set by the pressure which can be applied without driving the mercury into the horizontal part of the tube connecting the manometer to the reaction flask, and so depends on the length of the vertical part of the connecting tube.

A careful calibration of the apparatus was made by setting the ethyl oxalate meniscus at the lower end of the glass scale with the reaction flask evacuated, admitting a pressure of inert gas sufficient to move the meniscus to the other end of the scale and measuring the pressure by means of a McLeod gauge. This showed that 1 millimeter on the scale was equivalent to 0.0225 millimeter of mercury, within about two percent. The apparatus was also tested for readings on the intermediate part of the scale, taking intervals of about 30 mm (ethyl oxalate scale). These readings agreed with the over-all calibration within the accuracy attainable with the McLeod gauge (two to three percent). It is possible that the first 10 mm were off as much as five percent; however, this part of the scale was rarely used in practice. It should be noted that the calibration is made at very low pressures. At higher pressures a different part of the reaction vessel side of the U-tube is used. However, the U was so nearly uniform in diameter that any error due to this cause was negligible.

§3. ADVANTAGES OF THE APPARATUS

The apparatus described has a number of advantages in addition to the possibility it affords of measuring reaction rates in the presence of large quantities of inert gases. It is possible with it to take many readings during the first five or ten percent of decomposition, even though that occurs within three or four minutes, and thus one is able to get a very good estimate of the initial rate of the reaction. Once the apparatus is set up it is very convenient to use. It is not in general possible to follow the rate of reaction through to the end without resetting the position of the ethyl oxalate meniscus, but if one is interested in the initial rate of reaction the runs can be made very quickly and easily. Some typical runs are presented in the following paper.

ACKNOWLEDGMENT