Development of an Automatic Recording Apparatus for Gasometric Analyses at Constant Pressure

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Abstract

Rate studies on the evolution of carbon dioxide from diortho-substituted benzoic acids in hot, strong sulfuric acid have in the past been carried out with a manually operated apparatus. To improve the quality of the data obtained, an automatically operated recording apparatus was designed and built which would produce a continuous record of the carbon dioxide evolved as a function of time at constant pressure. The automatic gasometric apparatus was calibrated and applied in a preliminary fashion to kinetic studies of the decarboxylation reaction. Computer plots show that the reaction follows first order kinetics wtih individual points having good precision.

The kinetics of the acid-catalyzed decarboxylation of diortho-substituted benzoic acids has been under investigation for a number of years. In sulfuric acid concentrations of 70-90% and in the temperature range of 60°-100°C, mesitoic acid yields mesitylene and carbon dioxide (1), and duroic acid goes to durene and carbon dioxide (2), both reactions proceeding smoothly to completion. These reactions were run in a closed system under conditions of constant pressure and temperature, with the increase of volume due to the evolved carbon dioxide counteracted by manually draining liquid from a buret sealed into the system. The volume of liquid removed was measured as a function of time, yielding rate data which could be analyzed in the study of the reaction mechanism. The chief difficulties with the manual gasometric technique have been (a) variations in operator technique making reproducible data hard to obtain, and (b) unavoidable slight variations in internal pressure which affect the solubility of carbon dioxide in the sulfuric acid reaction medium. A gasometric apparatus has therefore been designed which permits collection of data automatically and with smaller variations in internal pressure.

Recently a constant volume variable pressure gasometric apparatus was designed by Timberlake and Martin (3) which permitted automatic data collection. The basic idea of this apparatus seemed suitable for use in the study of the decarboxylation reaction, but the variation in carbon dioxide solubility in sulfuric acid solutions with small changes in pressure required changing to a constant pressure, variable volume system. We have, therefore, made the appropriate changes in design and constructed a gasometric apparatus which produces a continuous record of volume increase as a function of time with pressure held constant.

The kinetic apparatus was set up as shown in Figure 1 with the reaction vessel immersed in a thermostatted oil bath and fitted with a gas condenser leading to an insulated gas manifold. Attached to the manifold are a U-tube barostat open on one end to the atmosphere and a collection buret containing mercury which is connected to a motor

driven syringe. In operation, evolution of carbon dioxide caused the mercury in the open end of the barostat to make contact with an electrode, activating the motor driven syringe which then removed a volume of mercury from the collection buret equal to the volume of gas evolved. Increasing the system volume caused the electrical contact in the barostat to be broken, stopping the motor driven syringe. The worm drive moving the syringe plunger was attached directly to a 10-turn helical potentiometer. By means of a variable voltage divider network (3) a signal was produced which was recorded on a 1 mV chart recorder. As constructed, the apparatus was capable of measuring gas volumes up to 7 ml.
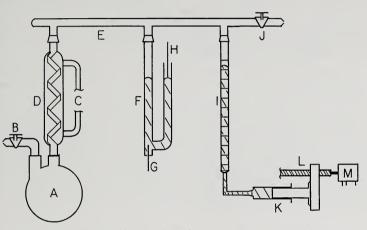

FIGURE 1. Schematic diagram of the gasometric apparatus. A, 250 ml, 2-necked reaction flask immersed in an oil bath; B & J stopcocks, C, water bath circulating coolant to gas condensor D; E, gas manifold insulated with glass wool and aluminum foil; F, barostat with mercury; G, platinum electrode; H, stainless steel electrode; I, gas collection buret containing mercury; K, motor-driven syringe; L, worm drive; M. 10-turn helipot.

Difficulties were experienced with the barostat at the mercury surface where contact was made and broken. Not until a stainless steel hypodermic needle was used as the electrode would the mercury surface remain smooth and liquid. The needle was positioned as close to the surface as possible to keep pressure variations at an absolute minimum.

The system was checked for accuracy and the output was calibrated by adding measured volumes of concentrated sulfuric acid to the closed system through the second neck of the reaction vessel. The temperature of the reaction vessel and of the circulating water which cooled the gas condenser were close to the usual reaction conditions. The measured additions of sulfuric acid equalled the volumes of mercury removed from the collection buret and produced on the recorder a linear response with less than ±1% error.

A typical run began with adjustment of the constant temperature baths; the oil bath was set at 80.0 ±0.1°C and the water bath which was the source of the water circulated to the gas condenser was set at 25.0 ±0.1°C. Into the reaction vessel was placed 100 ml of 86.3%

sulfuric acid from a volumetric buret. This was stirred at a constant rate by means of a Teflon-covered stirring bar and a magnetic stirrer placed under the oil bath. Vigorous stirring is necessary to achieve good results. Then sulfuric acid-dried carbon dioxide was bubbled through the sulfuric acid reaction medium and the whole system was flushed with carbon dioxide for 10 min. The acid in the reaction vessel absorbed more than the equilibrium amount of carbon dioxide and after the gas tube had been removed and the system closed, outgassing would occur, sometimes up to 36 hours. This was allowed to proceed until the recorder showed no further evolution of carbon dioxide for at least 30 min, at which time it was assumed that the carbon dioxide and sulfuric acid mixture had reached equilibrium. The manifold stopcock was then opened, the collection buret was refilled with mercury, and the recorder was zeroed making the apparatus ready for the addition of the acid to be decarboxylated.

In test runs, mesitoic acid (sample size ~40 mg) was weighed in a platinum boat and stored under vacuum until it was transferred, boat and acid sample, to the reaction vessel through the side neck. The removable stopcock was then quickly replaced, the stopcock closed and gas evolution was recorded automatically. Recorder response was read at 1-min intervals and by means of a computer program was converted to moles of carbon dioxide evolved at STP and then to concentrations of mesitoic acid as a function of time. Figure 2 shows a least squares computer plot indicating good pseudo first order kinetics up to 86% completion of reaction.
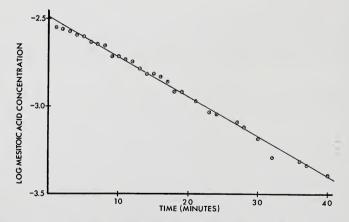

FIGURE 2. *Typical computer plot showing pseudo first order kinetics in the decarboxylation of mesitoic acid. In this run, 48.1 mg of mesitoic acid was dissolved in 100 ml of 86.3% sulfuric acid. Reaction conditions: pressure—739.0 mm Hg, oil bath temperature—79.9°C, water bath temperature—25.1°C. Pseudo first order rate constant was 0.88 x 10^{-3} sec^{-1} with a standard deviation of ± 0.02 x 10^{-3} sec^{-1}. The reaction had proceeded 86% of the way to completion after 40 min.*

Nine independent determinations of the rate constant for the decarboxylation of mesitoic acid gave an average value of $k = 1.2 \times 10^{-3}$

sec^{-1} with a standard deviation of $\pm 0.3 \times 10^{-3}$ sec^{-1}. Earlier, Schubert (1) had reported a value for the pseudo first order rate constant for this decarboxylation reaction of 4.85×10^{-3} sec^{-1}. Work in our laboratory (G. R. Bakker and L. E. Overman, unpublished data) had yielded a k = 3.0×10^{-4} sec^{-1} at a reaction temperature of 60°C. Because reaction conditions in these studies were not identical with what we used, and the handling of data was also different, we cannot yet judge if the automatic gasometric apparatus we have devised is without systematic error. Fit of data points to the line over the extent of reaction as we have followed it indicate, however, that random errors are minimal.

Acknowledgements

Literature Cited

1. SCHUBERT, W. M. 1949. The aromatic elimination reaction. I. The mechanism of the decarboxylation of mesitoic acid. J. Amer. Chem. Soc. 71:2639-2644.

2. SNOW, J. T., and G. R. BAKKER. 1970. A kinetic study of the decarboxylation of duroic acid in sulfuric acid solutions. Proc. Indiana Acad. Sci. 79:122.

3. TIMBERLAKE, J. W., and J. C. MARTIN. 1973. Reaction rate analysis by gas evolution: a constant volume variable pressure kinetic apparatus. Rev. Sci. Instru. 44:151-153.