

An Apparatus for Following Reactions Evolving Gas

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An apparatus for investigating the kinetics of reactions which evolve a gas is described. Manometer readings are recorded automatically, and the solution in which the reactions occur is stirred magnetically. The apparatus is used to investigate the decomposition of *o*-nitrophenylazide in dibutylphthalate solution. An *ortho*quinoid structure is proposed for the transition state in this reaction.

In 1925 Brønsted and Duus¹ developed a simple apparatus for studying the kinetics of reactions which evolve gas. Its main feature is that the reaction vessel can be shaken continuously. This prevents the reaction solution from becoming supersaturated with the gas formed by the reaction. The reaction vessel is connected to a mercury manometer by means of a glass capillary which allows motion of the reaction vessel relative to the manometer.

Equipment of this general type has been used several times since then for various investigations². Under some types of use certain weaknesses have appeared.

1. The apparatus is fairly fragile because of the glass capillary.

2. Since the manometer is not immersed in the thermostat, variations in room temperature influence its readings by changing the volume of the gas. This is particularly bad for slow reactions where the room temperature may change considerably during a run. Additional complications in this respect arise at higher temperatures.

3. The apparatus requires an observer for reading the manometer. This is especially inconvenient for measuring slow reactions.

Andersen² avoided the first two of these difficulties, but since we were primarily interested in studying fairly slow reactions we decided on a different design of the apparatus. First the shaking of the reaction vessel was abandoned in favor of a vigorous magnetic stirring. This eliminates the capillary and made the apparatus both stronger and more compact. Secondly, the manometer was changed so that it can be read electrically. As a result of this the apparatus can be immersed completely in the thermostat. Complete immersion is especially important for reactions occurring at elevated temperatures. Finally, the manometer was connected to a recording potentiometer which allows us to follow the reaction continuously for long periods.

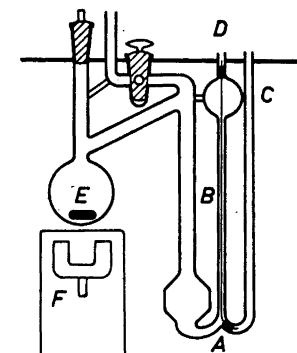


Fig. 1. B is the manometer. A and D are the two points between which the platinum resistance wire is stretched. E is the glasscovered magnet, which is moved by the motor driven magnet F.

2. Fig. 1 shows the construction of the apparatus. A platinum resistance wire is stretched from A to D through the mercury column in the manometer B. The platinum wire is straightened after it has been inserted in the glass³. At points A and D the platinum wire passes through the glass and is connected to external leads through pools of mercury. The glass bulb C is inserted to eliminate the effects of traces of air trapped in the manometer when it is filled initially. The reaction solution is stirred by the glass-covered magnet E. The magnet is moved by a motordriven magnet F which is installed under the thermostat as shown in Fig. 1. The entire apparatus is immersed in a suitable thermostat depending on the temperature required.

In order to read the closed manometer B the current from a storage battery is sent through a large constant resistance (about 300 Ω) in series with the platinum wire. The potential across the platinum wire is then a linear function of the height of the mercury in the manometer provided the diameter of the capillary is uniform, and the resistance of the wire is uniform and is much smaller than the constant resistance.

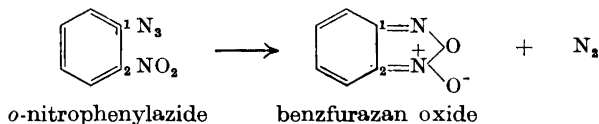
The potential across AD is recorded on a Philips recording potentiometer type PR 3210. In order to check for linearity the reading of the potentiometer was plotted against the height of the mercury read with a kathetometer for various heights of mercury. In the three pieces of apparatus of the above type we have used, the maximum deviation from linearity in the voltage across AD was found to be a few thousandths of the total change in voltage which could be observed as the height of the mercury was increased. As we have constructed it, the apparatus is capable of measuring gas over a 0—100 mm Hg range.

Since we have been interested in investigating first order reactions, we have had no reason to use this linear relationship to obtain the pressure. Instead, we have calculated the rate constant for the reaction from the recorder's curve of voltage *versus* time.

For many of the reactions we have investigated, the change in voltage with time was followed over a period of several days at thermostat temperatures close to 100°C. For such experiments the bath temperature and the voltage across the storage battery were measured continuously by the recording poten-

tiometer. This made it possible to explain most of the irregularities which were occasionally observed in the voltage-time curves and either to apply suitable corrections or reject the data.

3. In order to test the apparatus we have followed the kinetics of the reaction



which is known to be a first order reaction for which the reverse reaction can be neglected⁴. Dibutylphthalate was used as a solvent since it is stable and has negligible vapor pressure at the moderately high temperatures that were used. Preliminary experiments showed the first order rate constant to be independent of the concentration of *o*-nitrophenylazide. The following technique was employed. 10 ml of the solvent is put into the reaction vessel and stirred for an hour to reach the thermostat temperature. A small platinum bucket containing about 1 mmole of *o*-nitrophenylazide is dropped into the reaction vessel. The reaction is allowed to proceed for 10 min while the system is being evacuated with an oil pump and the reaction solution regains thermostat temperature. Under these circumstances the nitrogen dissolved in the solution may be expected to be in equilibrium with the free nitrogen when the recording of the pressure begins. If stirring is stopped during these 10 min, a supersaturated solution of nitrogen in the diphenylphthalate is generally formed. This completely distorts the voltage-time curve when stirring is resumed. If stirring is not used during a run, the pressure-time curve is more irregular than usual, and the apparent rate constant is about 10 or 15 % too low.

As is well known, it is usually not advisable to use the infinity value method when calculating first order rate constants. This seems to be true for this apparatus to an even higher degree than usual. By using the trick of estimating the asymptotic value of the voltage by the smallest value obtained during the run, the results are improved somewhat. However, repeated runs under identical conditions still tend to give rather scattered values for the rate constant, since small variations in the infinity value have a relatively large effect on the rate constant.

The rate constants obtained by the method of Guggenheim⁵, or even better by an iterative least squares method^{6,7}, are far more consistent. We have generally used the latter method in spite of the additional work it requires. Although to our knowledge there is as yet no sound theoretical basis for using a least squares method for non-linear curve fitting, the method produces remarkably consistent sets of rate constants from repeated measurements. Table I shows the results obtained for the first order rate constant for the decomposition of *o*-nitrophenylazide at various temperatures. The temperatures were read with a 1/10°C thermometer, calibrated by comparing it with a 1/10°C thermometer which had been calibrated at the Physikalisch-Technische Reichsanstalt, Charlottenburg, in 1909 and recalibrated at the Fysisk Laboratorium, Danmarks Tekniske Højskole, in 1957. The temperatures given in

Table 1.

| Temp., °C | $k \times 10^4, \text{sec}^{-1}$ |
|-----------|----------------------------------|
| 76.22 | 0.867 |
| 76.23 | 0.893 |
| 76.24 | 0.873 |
| 76.27 | 0.903 |
| 81.14 | 1.492 |
| 81.20 | 1.488 |
| 81.22 | 1.537 |
| 81.28 | 1.488 |
| 90.54 | 3.759 |
| 90.54 | 3.855 |
| 90.54 | 3.717 |
| 90.57 | 3.770 |
| 90.57 | 3.732 |
| 90.58 | 3.843 |
| 90.63 | 3.997 |
| 90.85 | 3.874 |

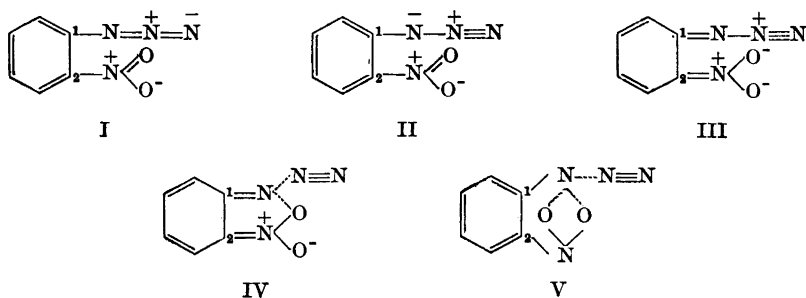
Table 1 have been corrected for exposed stem and are believed to be correct to 0.05°C. Internal consistency is somewhat better and should not be in error more than 0.02°C. It was not possible to detect variations in the temperature of the thermostat during a single run. Therefore, it is to be expected that the variations were not more than 0.02°C.

From the data given in Table 1 the activation energy of the reaction is calculated to be 25.7 cal/mole. The entropy of activation, which is derived from the equation ⁸

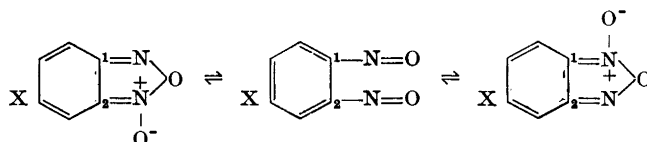
$$k = e \frac{kT}{h} e^{-E/RT} e^{\Delta S^\ddagger/R}$$

is -5.9 cal/mole deg. These values are in reasonable agreement with the results obtained by Fagley *et al.*⁴

5. The structure of *o*-nitrophenylazide is undoubtedly a resonance hybrid of classical structures I, II, and III. Wheland ⁹ gives evidence for believing that the azide group ordinarily includes contribution from structures such as I and II. It is also reasonable to expect the azide and nitro groups to interact to form a structure such as III because of the favorable charge distribution which it represents. Scale models show that this structure, which is completely planar, is not sterically hindered. We propose that the reaction proceeds through a transition state with the quinoid structure IV. Such a transition state would be expected to have a small negative entropy of activation which is in agreement with the observed one. The alternative cage-type transition state, V, on the other hand would be expected to have a fairly large negative entropy of activation. In addition, while the quinoid transition state is readily formed from the contribution of structure III to the structure of *o*-nitrophenylazide, both charge distribution and the molecule's tendency toward planarity make the formation of the cage transition state difficult.



However, without the cage model the experimental fact that 4- and 5-substituted *o*-nitrophenylazides give identical products is not easily explained. For an explanation we must assume that the following equilibrium exists:



The fact that benzofurazane oxide solutions become colored on heating and lose the color again when cooled tends to support the existence of such an equilibrium. This problem is discussed in more detail by Hammick *et al.*¹⁰

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