pressure and a balance and technique for the weighing of very hygroscopic substances have been described.

MINNEAPOLIS, MINNESOTA

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A FURTHER TEST OF THE RADIATION HYPOTHESIS

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Introduction

Since its statement by Perrin[2] the Radiation Hypothesis has been subjected to many experimental tests, with results that have been uniformly opposed to it. Its present position has been summarized by Daniels.[3] This recent rapid decline of the Radiation Hypothesis has been accompanied by the production of an improved theory of activation by collision. Christiansen suggested that the number of internal degrees of freedom of the molecule must be taken into account, and this suggestion was adopted by Hinshelwood[4] and by Fowler and Rideal,[5] who worked out a simple theory of what the former has called "quasi-unimolecular" reactions, that is, reactions which are unimolecular at high enough pressures, but whose rate begins to fall off at lower pressures. Several such reactions are known, as well as some whose rates have not been shown to decrease.

The theory of Hinshelwood was extended by Rice and Ramsperger,[6] and a second theory developed which was in better agreement with the facts; this differed from the former one only in assigning different specific reaction rates to activated molecules of different energy content. A somewhat similar theory, in equally good agreement with experiment, was worked out by the author.[7] Both Rice[8] and the author[9] have since given quantum theories of the effect, also, but without changing much the numerical results obtained. The position of these theories with respect to the experimental facts is that they can account quantitatively for the way in which the rate falls off with decreasing pressure in the decompositions of propionaldehyde, ethyl ether, methyl ether and azo-

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[1] National Research Fellow in Chemistry.

[2] Perrin, *Ann. Physik,* **11,** 5 (1919).

[3] Daniels, *Chem. Rev.,* **5,** 39 (1928).

[4] Hinshelwood, *Proc. Roy. Soc.,* **113A,** 230 (1926).

[5] Fowler and Rideal, *ibid.,* **113A,** 570 (1926).

[6] Rice and Ramsperger, THIS JOURNAL, **49,** 1617 (1927); **50,** 617 (1928).

[7] Kassel, *J. Phys. Chem.,* **32,** 225 (1927).

[8] Rice, *Proc. Nat. Acad. Sci.,* **14,** 113, 118 (1928).

[9] Kassel, *J. Phys. Chem.,* **32,** 1065 (1928).

methane; they can also account for the fact that it has not fallen off noticeably at the lowest pressures studied with acetone, pinene and azo-*iso*propane; they can account for the decomposition of nitrogen pentoxide around atmospheric pressure without difficulty, a thing which the older theories were unable to do, and indeed down to about three mm. pressure; but Hibben[10] finds that the rate is maintained down to much lower pressures, 0.03 mm. at least. It is hard for the theories mentioned to account for more than 50% maintenance of the rate at this pressure, using kinetic theory diameters, such as are found satisfactory for the other substances. It would be possible to account for the results down to 0.03 mm. by using a "diameter for collisional deactivation" of 10^{-6} cm. The case for such large diameters has been stated by Bernard Lewis,[11] but the author, at least, is as yet reluctant to use them.

Thus, of all the unimolecular reactions known, nitrogen pentoxide is the only one whose rate causes any difficulty. It is possible to account for the variation of rate with pressure in all the other reactions quantitatively; more important for this comparison, there is a considerable margin of safety, so that if the rates were greater than they are, or were maintained to lower pressures, they could still be accounted for. In nitrogen pentoxide, on the other hand, if the method of activation is collisional, there seem to be a hundred times as many activations and deactivations as the theory allows. In searching for a way out of this difficulty, it occurred to the author that radiation, which has been shown to be without effect at higher pressures,[12] might still be the mechanism responsible for maintaining the rate at low pressures. The general reason why this would be so is that collisional activations and deactivations are of course bimolecular, while radiational ones are unimolecular; the latter would thus gain in importance as the pressure decreased. The results with azomethane and the other quasi-unimolecular reactions show that in these cases at least radiation has not become of importance in time to prevent the falling off in rate, and it is a little hard to see how enough radiation can be absorbed to be of much use, but it nevertheless seemed worth while to investigate the action of infra-red radiation on nitrogen pentoxide at low pressures.

Experimental Part

The most difficult problem in work of this character is to obtain a good source of light. Nernst glowers have been used, but, although they may be operated at a very high temperature, the actual area of the emitting surface is small; for this reason it seemed best to use some other source. The one adopted was a rod of a substance whose trade name is "Glowbar" and which is used as the heating element in some of the small

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[10] Hibben, *Proc. Nat. Acad. Sci.*, **13**, 626 (1927); THIS JOURNAL, **50**, 940 (1928).

[11] Bernard Lewis, *Science*, **66**, 331 (1927).

[12] Daniels, THIS JOURNAL, **48**, 607 (1926); Taylor, *ibid.*, **48**, 577 (1926).

domestic electric heaters now in common use. This is a black substance of unknown composition, with a rather fine granular structure; it has a moderately high electric resistance, and may be conveniently heated by the passage of a current through it. A piece 20 cm. long and 9 mm. in diameter was ground down to about 6 mm. diameter in the central 4 cm. It was shielded along most of its length by a hollow fire-clay cylinder, to reduce heat losses; this had a rectangular opening, 1.5 × 3.6 cm., cut in it to serve as a source of light. The ends were mounted in heavy brass electrodes cooled by a blast of air and a potential of 220 volts was applied. The entire central portion, both the rod and the surrounding cylinder, attained an intense white heat, while the constricted portion of the rod reached a temperature evidently considerably greater.

It seemed almost impossible to place a reaction vessel within a few cm. of a source such as this and prevent it from heating up, and accordingly the light was focused some distance away by a simple optical system. A concave mirror of 30.5 cm. radius of curvature and 20.3 cm. diameter was placed at a distance of 60 cm. from the source; the reflected light was intercepted by a small plane mirror placed about 17 cm. from the large mirror and making an angle of 45° with the path of the light; this second mirror reflected the light down, and it came to a focus upon the window of the reaction vessel. Both mirrors, of course, were silvered on their outer surfaces. The energy flux through the window was determined by absorbing the radiation in a 2% solution of cupric chloride, which absorbs everything beyond 0.6μ. As the mean of a number of determinations made in this way, there was obtained the value 6.2×10^7 ergs/sec. It was estimated that the temperature of the rod was 2200°K. and that of the protecting cylinder 1800°. Using those figures, and those given for the dimensions of the apparatus, it is possible to calculate the energy flux which would be expected; it is found to be 6.6×10^7 ergs/sec.; if the lower temperature is taken as 1700°, the expected flux comes out 6.0×10^7 ergs/sec. This shows that the temperatures assumed are approximately correct. If the enclosure was all at a uniform temperature of 1900°, it would produce a flux of 5.5×10^7 ergs/sec., and at 2000° one of 6.7×10^7 ergs/sec. In all of these calculations the losses on reflection at the mirrors and transmission by the window have been neglected. The necessary corrections could be made, but they would not change the conclusions in any way.

The reaction vessel used was a 250-cc. bulb; the neck was cut off near the bulb and ground very carefully; a window of rock salt, which has very good transmission in the infra-red region, was attached by sealing wax, care being taken to get the wax only on the outer edge, so that the contact with the reacting gas would be very poor; no visible change took place in the sealing wax, nor was there any other reason to suspect that an appreciable amount of reaction was occurring at the window. The bulb was placed in a jar, which was filled with water or ice and water to a point just below the window, during all of the runs. The pressure readings were obtained by a bifilar quartz fiber gage and were at all times accurately reproducible.

The nitrogen pentoxide was prepared by letting nitrogen dioxide vapor diffuse into a stream of ozonized oxygen and passing the resulting gases through a trap cooled to about −50°. It usually required about ten minutes to collect sufficient nitrogen pentoxide for a run. The supply of nitrogen dioxide would then be sealed off and the ozone continued for a few minutes longer; then it, too, would be sealed off. The nitrogen pentoxide was next cooled with liquid air and connected through a stopcock to a two-stage mercury vapor pump, a second liquid-air trap preventing diffusion of any mercury vapors into the apparatus. After the pumping had been continued for some time, and a vacuum of 10^{-5} mm. or better obtained, the jar around the reaction vessel was filled with ice and water, the liquid air surrounding the nitrogen pentoxide replaced by a mush of frozen ethyl acetate (−83.6°) and the pumping continued; after some time, usually about one-half hour, the liquid air was replaced, and the apparatus sealed off from the pumps; at this stage it consisted merely of the reaction bulb, the fiber gage, and the trap containing solid nitrogen pentoxide. The residual pressure was then read on the fiber gage, after which the liquid air was replaced by the ethyl acetate mush, and the decomposition allowed to proceed thermally for a definite period; the liquid air was then replaced and after equilibrium had been reached the pressure was again read; the increase represented oxygen liberated by the decomposition; the source of infra-red light was then turned on, the ethyl acetate replaced and the reaction allowed to proceed for the same period as before, after which liquid air was replaced and the pressure read. Runs were made alternately with and without the light in this fashion.

There was no heating of the bulb when the light was on and except for the presence of the radiation all conditions were unaltered. Hence it is only necessary to compare the pressure increases during the period with illumination with those without to see whether radiation has had an effect. In some of the later runs solid chloroform (−63.5°) was used as a refrigerant and the reaction vessel was kept at 25° instead of at 0°. This gave pressure increases which were considerably larger and easily measurable, so that the same relative increase in rate could have been more easily detected than before. On the other hand, it made conditions less favorable, so that a smaller relative increase was to be expected.

The usual period of each run was thirty minutes, though some were shorter. With ethyl acetate as a refrigerant and the reaction vessel at 0° no pressure increase was ever noted except on one occasion, which was afterward found to be due to a leak which developed at the window. With chloroform and the reaction vessel at 25°, the pressure increases found with illumination were no greater than those without. A typical set of results under the latter conditions is: initial pressure, 0.00035 mm.; increase, dark, 0.00141; increase, light, 0.00147; increase, dark, 0.00153; increase, light, 0.00140. The third figure is not accurate, the probable error being of the order of the fluctuations in the values given. Similar results were found on several occasions. There was no evidence that infra-red radiation influences the rate of reaction of nitrogen pentoxide under the experimental conditions used, although a 10% increase in rate could have been definitely detected.

The vapor pressure equation of Daniels and Johnston[13] gives a pressure of 0.00068 mm. at −83.6° and one of 0.0245 mm. at −63.5°.

A simple calculation shows that the reaction rate constant found in the experiment quoted is about the same as that at higher pressures. This is not to be regarded as a measurement of the thermal rate at low pressures, however, since the experimental conditions did not permit absolute rate measurements. Thus it was impossible to bake out the reaction vessel; the possibility of slight reaction with the sealing wax is not excluded; adsorption on the walls may have affected the pressure measurements. Due to the comparative method used, it is not believed that any of these objections affect the conclusions as to the inactivity of radiation.

Discussion

It having been found that under the experimental conditions used no additional reaction was produced, it becomes important to decide for what spectral region the test is significant. This may be done by comparing the amount of radiation present in the reaction bulb normally with the amount introduced at various wave lengths. The calculation has been made for the rod at 2200°K. and the protecting cylinder at 1700°K., and also for the entire area at 1900°K. This may be very

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[13] Daniels and Johnston, This Journal, **42**, 1131 (1920).

easily done from a knowledge of the geometry of the apparatus, assuming that the source of light behaves as a black body. The volume of the reaction system was taken as 300 cc. and the average length of path of the light through the nitrogen pentoxide as 12 cm. Absorption by the nitrogen pentoxide was neglected. It was found that at 5μ the average intensity in the reaction system was increased about 7 times when the vessel was at 0° and 3 times when it was at 25°. Nearly the same result was obtained whether the calculation was made for the rod at 2200°K. and the cylinder at 1700° or for both at 1900°. It is possible that the use of the black body law is not justified, but in that case the actual temperature of the source must have been greater, and the amount of radiation in the far infra-red would scarcely be much less than that calculated. For wave lengths shorter than 5μ the relative increase is much greater, while for only slightly longer wave lengths the increase is too small to be significant. Therefore this test applied only to wave lengths of 5μ and less. Since in the experiments at 25° a 10% increase in rate would have been observed, and was not, and since the intensity of all wave lengths less than 5μ was increased at least 3 times, one is tempted to say that not more than 3% of the thermal reaction at this temperature can depend upon radiation of this spectral region. Closer analysis, however, shows that this statement is unjustified, and it is necessary to be content with the milder conclusion that not more than 3% of the total thermal reaction can be caused exclusively by radiation of wave lengths less than 5μ.

Now there is no difficulty about the production of any except the more highly activated molecules. Collisions are quite capable of accounting for the maintenance of the Maxwell-Boltzmann quota of all the unactivated molecules and even of the activated molecules of low energy content; these, however, do not contribute very much to the total reaction. Thus if radiation is to be of any help, it must produce the final activation, that is, it must keep up the quota of highly activated molecules. If radiation of the wave lengths tested was able to do this effectively, a considerable increase in the reaction rate would have been obtained. The experiments do not show that this radiation is unable to produce highly activated molecules, but they do seem to show that in the actual thermal reaction it is not the important agency in their production. There remains the possibility that radiation of longer wave lengths is of importance. A quantum even at 10μ corresponds to about 3000 calories per mole, which is far from negligible; the addition of that much energy to a molecule just barely activated, which has very little chance to react, will convert it into one which will probably decompose before its next collision. Still longer waves may be of some use, but it is hard to believe that they can be the really important factor in the reaction. It would seem that the final hope of the Radiation Hypothesis rests in the region from 5 to 10μ. Even here it is difficult to understand how sufficient radiation can be absorbed to maintain the rate. Some calculations which have been made by Dr. Ure, in this Laboratory, seem to show that radiation is doomed to fall short by a factor of about 100; these calculations have taken into account the internal degrees of freedom of the molecule and are about as favorable to radiation as seems at all reasonable.

Thus the decomposition of nitrogen pentoxide at low pressures remains mysterious. There are a hundred times too few collisions to account for the rate; there does not seem to be any help from radiation of wave lengths less than 5μ, and it is hard to see how radiation of any wave length can account for more than a very few per cent. of the reaction. There are apparently three possible explanations of the difficulty. One is that the low pressure experiments have been incorrectly interpreted, due perhaps to adsorption; there is evidently some feeling in various quarters that this is the proper solution, but the burden of proof surely rests upon those who wish to adopt this view. Another is to assert that the long wave length radiation is responsible, even though it is impossible to give a theoretical explanation of how it can be. It seems very hard to test this view, a suitable source being non-existent. A third escape is in the acceptance of diameters for collisional deactivation of about 10^{-6} cm. It has been said that the use of a large diameter for deactivations does not mean that an equally large one is required for other collisions, in particular for activations. Let us examine this statement closely. A large diameter for deactivations means that the high-energy molecule has a very great desire to get rid of its extra energy. The result of this large diameter is that the number of deactivations is increased; to maintain the Maxwell-Boltzmann quota of high energy molecules an increased number of activations is required, and these may be obtained either by a large diameter for activations also, or by an abnormal tendency to produce activation whenever it is energetically possible, that is, by having nearly all of the energy of both molecules flow into one of them oftener than the distribution laws for harmonic oscillators would require. The existence of equilibria maintained in this last way is denied by the Principle of Microscopic Reversibility. According to this principle, if the mechanism of deactivation is the transfer of energy across distances large compared to molecular dimensions, the mechanism of activation must be of the same nature.[14] The author has been among those guilty of talking about diameters for collisional deactivation, with the implication that they might be much larger than other diameters. But if we are going to use large diameters for internal energy transfers, it would be better to use them consistently. It would of course be possible that the diameter for

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[14] See also Tolman, Yost and Dickinson, *Proc. Nat. Acad. Sci.*, **13**, 188 (1927).

such transfers might be a function of the amount of energy involved; but in the application of the author's theory to azomethane the chief difficulty was to get sufficient spread between the theoretical curves at different temperatures; the same trouble was experienced by Rice and Ramsperger; if the diameter for internal energy transfers increased very much with the amount of energy involved in this case, it would become impossible to fit the experimental data. If, as therefore seems not unlikely, the diameter for internal energy transfer is approximately independent of the energy, and if it is really much larger than kinetic theory diameters, the heat conductivity of nitrogen pentoxide should be abnormally large. There do not seem to be any data on this.

As a matter of fact, it seems rather strange to speak either of collisions or of diameters in connection with energy transfer at such a distance, for the phenomenon, if it occurs, is more nearly "coupling" of the type suggested by Polanyi,[15] with the difference that the result of the energy transfer is only activation, not immediate dissociation.

In this connection it may be pointed out that the chief objection to these "large diameters" is not an *a priori* one, since they are not inherently unreasonable (at least, not until they are somewhat greater than 10^{-6} cm.) but is based on a reluctance to use diameters for nitrogen pentoxide at least 15–20 times greater than for any of the other substances which decompose unimolecularly, but there is apparently some feature about nitrogen pentoxide which is unique, so that some abnormality in the explanation of its rate can scarcely be avoided.

Since the submission of this paper, Rice, Urey and Washburne[16] have found that a molecular ray of nitrogen pentoxide is not decomposed by black body radiation. Loomis and Smith[17] have reported experiments which seem to show that under some circumstances adsorption may vitiate low pressure reaction rate measurements on nitrogen pentoxide. Sprenger[18] has found the very curious result that at low pressures the decomposition of nitrogen pentoxide does not go to completion, even at 100°; and Rice, Urey and Washburne[16] mention that preliminary experiments in their Laboratory show a falling off in rate even at several millimeters' pressure. Thus five separate researches on the thermal reaction at low pressures have led to five widely different conclusions.

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[15] Polanyi, *Z. Physik*, **3**, 31 (1926).

[16] Rice, Urey and Washburne, THIS JOURNAL, **50**, 2402 (1928).

[17] Loomis and Smith, *ibid.*, **50**, 1864 (1928).

[18] Sprenger, *Z. physik. Chem.*, **136**, 49 (1928).

ment, in particular Professor R. C. Tolman and Dr. M. E. Nordberg. The very excellent rock salt windows used were kindly furnished by Mr. Rene Engel of the Geology Department of this Institute.

Summary

1. It has been suggested that the maintenance of rate in the decomposition of nitrogen pentoxide may be due to assistance from radiation, which becomes important only at low pressures.

2. It has been found experimentally, however, that radiation of wave length less than 5μ is not able to increase the reaction rate even at low pressures.

3. It is concluded that the important region, if there is any, will probably lie between 5 and 10μ, but that it is hard to see how enough radiation can be absorbed to maintain the rate. An experiment which might detect this activity, if it exists, has been suggested.

4. The other possible escapes from the nitrogen pentoxide dilemma have been considered. No definite conclusion has been reached.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

STUDIES OF COPPER CATALYSTS PREPARED FROM PRECIPITATED HYDROXIDE. I.

ACTIVITY AS A FUNCTION OF THE TEMPERATURE OF PRECIPITATION

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In the course of a study of the high pressure synthesis of methanol undertaken by this Laboratory some three years ago, it was observed that certain catalysts prepared from precipitated hydrates showed variations in activity which might be attributed to differences in the temperatures at which the hydrates had been precipitated from the corresponding nitrate solutions. To obtain more quantitative information concerning this temperature effect, a series of experiments was made with copper catalysts under carefully controlled conditions in order to eliminate in so far as possible the effect of variables other than the temperature of precipitation. The copper hydroxide was precipitated with ammonium hydroxide from aqueous solution of one of the standard makes of high purity (C. P.) copper nitrate. Since any occluded ammonium hydroxide or nitrate was easily volatilized in subsequent operations, the resulting catalysts might be expected to be of identical chemical composition.