

THE THERMAL AND PHOTOCHEMICAL DECOMPOSITION OF AZO COMPOUNDS AND THE PROBLEM OF REACTION RATES

BY HERMAN C. RAMSPERGER¹

CHEMICAL LABORATORIES OF THE UNIVERSITY OF CALIFORNIA AND OF STANFORD UNIVERSITY

Communicated November 14, 1927

The discovery that the decomposition of azomethane² (CH_3NNCH_3) is homogeneous and unimolecular suggested the probability that all of the azo compounds will decompose in like manner. This type of compound decomposes at lower temperatures than aldehydes, ketones and ethers, some of which decompose unimolecularly,^{3,4,5,6} but at such high temperatures that the first products formed are not the most stable ones. Consequently, the rate constants of both azomethane and azoisopropane are more accurate. They have also been determined to much lower pressures. The data on these two reactions now give an opportunity to test various theories of reaction velocity.

Azomethane² was found to decompose almost entirely by the equation $\text{CH}_3\text{NNCH}_3 = \text{C}_2\text{H}_6 + \text{N}_2$. At high pressures the unimolecular rate constant was independent of the initial pressure of the gas. From the change of rate with temperature the heat of activation was found to be 51,200 cal. per mol. At 4 cm. initial pressure the rate constant was appreciably lower and it became steadily lower as the initial pressure was decreased until at 0.025 cm. the rate had dropped to 22% of the high-pressure value when the temperature was 290°C. and to 10% for 330°C.⁷ Experiments just completed with azoisopropane show that *the rate constant does not become lower even at a pressure of 0.025 cm.*

Azoisopropane is a light yellow liquid boiling at 88.5°C. and was prepared by the method of Lochte, Noyes and Bailey.⁸ Rate constants were determined at temperatures from 250°C. to 290°C. and initial pressures from 0.025 cm. to 4.60 cm. The method used was similar to that used with azomethane at low pressures,⁷ except that it was necessary to surround the McLeod gage with an air bath at a temperature high enough to prevent condensation of the gas in the capillary of the gage. An increase of five-fold in the surface by means of small pyrex tubing made no difference in the rate even at the lowest pressures. The heat of activation is found to be 40,900 cal. per mol. ≈ 500 cal. The rate constant is given by the equation $K = 5.6 \times 10^{13} \times e^{-\frac{40900}{RT}}$. It has recently been shown by Hibben⁹ that the rate constant of the decomposition of nitrogen pentoxide is constant to very low pressures.

We have now at least these two unimolecular reactions which show no

reduction in the rate at the lowest pressures for which accurate results are possible. In addition we have a number of reactions^{3,4,5,6,7} which are strictly first order only at high pressures, and at least two which have not been studied at low pressures.^{10,11} These may be taken as strong evidence in favor of a collision theory of activation since the argument of Perrin which necessitated a radiation theory of chemical reaction if the rate was independent of pressure even at infinitely low pressures is no longer valid. Furthermore, the radiation theory has been disproved by Lewis and Mayer¹² at least in the case of the racemization of pinene. Earlier attempts to provide activated molecules by collisions at a rate sufficient to explain the experimentally observed rates failed because they disregarded the internal energy as a source of activation energy. This was first pointed out by Lewis and Smith¹³ and was extended by Hinshelwood and Lindemann¹⁴ and by Christiansen.¹⁵ Later, Rice and the author¹⁶ developed a more complete equation for the same theory (theory 1) which showed the way in which the rate would fall off with decreasing pressure. This theory required only that the total energy of the molecule should equal or exceed a minimum energy and that the chance that an activated molecule should react was independent of the amount of energy in excess of this minimum. A second theory (theory 2) required that a certain minimum of energy should be located in one degree of freedom of the molecule to cause its reaction. The energy within the molecule could be redistributed among the various degrees of freedom between collisions. In this theory the chance of reaction depends upon the excess of energy in the entire molecule beyond the minimum required in a particular degree of freedom.

In a second theoretical paper Rice and the author¹⁷ have applied these theories to the decomposition of azomethane. Using theory 2 and assigning 25 degrees of freedom we were able to show that the theoretical curve of $\log K/K_\infty$ against $\log p$ coincided with the experimental curve very well. Here K is the rate constant (which becomes lower as the pressure is lowered), K_∞ is the rate constant at high pressures and p is the pressure. It should be noted that theory 1 could not fit the data at all over the 3000 fold pressure range. Furthermore, theory 2 requires that $\log K/K_\infty$ decrease more rapidly with decreasing pressure at the higher temperature which is experimentally the case, while theory 1 has practically no such temperature coefficient. The theory of Fowler and Rideal¹⁸ was used by Bernard Lewis¹⁹ to explain the decomposition of azomethane before the data on azomethane at low pressures was published. This theory has not been developed so far as to show the manner in which the rate will change at low pressures. It requires fewer degrees of freedom but has the disadvantages pointed out by Tolman, Yost and Dickinson.²⁰

Two new experimental results will now be considered in relation to

theory 2. First, the decomposition of azoisopropane can only be explained by allowing at least 50 degrees of freedom. A similar number of degrees of freedom is required on theory 1. The large size of the molecule, however, does not make this impossible. Twenty-five degrees of freedom were required for azomethane¹⁷ and this was not inconsistent with the specific heats of molecules of similar size and structure. Azomethane has ten atoms and ten chemical bonds while azoisopropane has twenty-two atoms and twenty-two chemical bonds.

Second, the photochemical decomposition of azomethane was carried out by the author, with the result *that approximately two molecules were decomposed by each quantum of light absorbed over a wide range of pressures.* The quantitative absorption curve for azomethane gas was determined from 4060 to 2370 Å by the method of Ramsperger and Porter.²¹ There was an absorption maximum at 3390 Å with increasing absorption again toward the far ultra-violet. No evidence of a band spectrum was obtained. Nearly monochromatic light was obtained by use of a filter of phenosaphranine solution in a cell containing cobalt glass windows. The three lines, 3650, 3654, and 3663 Å and a small amount of deep red and ultra-red was practically the only light transmitted by this filter. The total energy falling on the reaction cell was determined by means of a thermopile and the fraction of light absorbed was calculated from the absorption coefficient. The rate of decomposition was followed by pressure measurements. Four experiments were made at pressures from 0.1207 cm. to 25.74 cm. The temperature coefficient was found to be very nearly zero.

The nature of the photochemically activated molecule may not be similar to molecules activated thermally with the same total amount of energy and it is not certain that the mechanism of the two types of reactions is the same. We may, however, determine whether the result of this photochemical experiment is the result expected if the mechanism of the two types of reactions is alike. The equations of theory 2 permit us to calculate the ratio of activated molecules of given energy which react to those which are deactivated. This ratio is b_e/aN where b_e and a are given by equations (18) and (3) of reference 16 and N is the number of molecules per cc. If we take for the energy ϵ that of the quantum (77,800 cal. per mol.) plus the energy of an average molecule (roughly 5000 cal. per mol.), $\epsilon_0 = 50,600$, $n = 25$, $T = 563$, $K = 1.38 \times 10^{-4}$, $s = 6 \times 10^{-8}$ and N corresponding to a pressure of 25 cm. we find for this ratio 47/1 and the ratio is, of course, much greater at low pressures. That is, reaction is practically certain at pressures of 25 cm. or less. If we assume deactivation at collision (which was assumed in the derivation of theory 2) this result requires that a molecule of this energy must react in less than 2×10^{-10} sec. which is the time between collisions at 25 cm. pressure. But this would also be required by the constant photochemical efficiency

over the large pressure range of these experiments. Since there was not a long reaction chain in the photochemical decomposition it seems likely that the thermal reaction which is due largely to molecules of considerable less energy is not a chain reaction. The quantum efficiency of the dissociation of HI was found by Bernard Lewis²² to be unchanged at 0.1 mm. and here, too, the molecule must dissociate before collision at high pressures.

It is to be noted that any of these first order reactions will become second order on either theory at sufficiently low pressures but that these pressures are, in the case of very large molecules, lower than can be attained. It was noted by Hinshelwood that all bimolecular reactions were those of simple diatomic or triatomic molecules while all unimolecular reactions were of more complex molecules. Analogously, azoisopropane is strictly unimolecular while the simpler azomethane deviates considerably at low pressures. We may expect that the compound CH_3NNH (methyl diimide) would only be unimolecular at very high pressures and bimolecular at the lowest possible pressures. An attempt will be made to prepare this unknown compound. The compound N_3H will also be tried but will probably be found to decompose bimolecularly if the decomposition is homogeneous.

Finally it is the opinion of the writer that not sufficient is known about the transfer of energy between molecules at collision or between internal degrees of freedom to account very accurately for all homogeneous reactions. The fundamental assumptions of all of the collision theories differ on these questions. What little evidence we have indicates some very specific effects as, for example, the experiments of Stuart²³ which show that the quenching of the resonance fluorescence of mercury differs very widely for different gases being greatest for H_2 and least for He. The experiments of Hinshelwood show that of a number of inert gases only hydrogen can maintain the high pressure rate constant of a "quasi" unimolecular reaction at low pressures. Nevertheless, it seems probable that the more complicated the molecule the more likely it is that the assumptions of statistical mechanics and of statistical equilibrium at collision will be fulfilled, and that the fewer quantum states of simpler molecules may introduce special restrictions of energy transfer. In agreement with this view it was found with azomethane that at low pressures the first order rate constant was reasonably constant from one time interval to the next in any given experiment, indicating that the products of the reaction had about the same influence in maintaining the rate as their equivalent of azomethane would. The products from a simple molecule decomposing bimolecularly do not contribute toward activation else the reaction would not be second order throughout its course.

The complete results of the photochemical decomposition of azomethane and of the decomposition of azoisopropane will be published elsewhere.

- ¹ NATIONAL RESEARCH FELLOW IN CHEMISTRY.
- ² Ramsperger, *J. Am. Chem. Soc.*, **49**, 912, 1927.
- ³ Hinshelwood and Hutchison, *Proc. Roy. Soc.*, **111A**, 245, 1926.
- ⁴ Hinshelwood and Thompson, *Ibid.*, **113A**, 221, 1926.
- ⁵ Hinshelwood, *Ibid.*, **114A**, 84, 1927.
- ⁶ Hinshelwood and Askey, *Ibid.*, **115A**, 215, 1927.
- ⁷ Ramsperger, *J. Am. Chem. Soc.*, **49**, 1495, 1927.
- ⁸ Lochte, Noyes and Bailey, *J. Am. Chem. Soc.*, **44**, 2556, 1922.
- ⁹ Hibben, *Proc. Nat. Acad. Sci.*, **13**, 626, 1927.
- ¹⁰ Smith, *J. Am. Chem. Soc.*, **47**, 1862, 1925.
- ¹¹ Smith, *Ibid.*, **49**, 43, 1927.
- ¹² Lewis and Mayer, *Proc. Nat. Acad. Sci.*, **13**, 623, 1927.
- ¹³ Lewis and Smith, *J. Am. Chem. Soc.*, **47**, 1508, 1925.
- ¹⁴ Hinshelwood, *Proc. Roy. Soc.*, **113A**, 230, 1926.
- ¹⁵ Christiansen, *Proc. Camb. Phil. Soc.*, **23**, 438, 1926.
- ¹⁶ Rice and Ramsperger, *J. Am. Chem. Soc.*, **49**, 1617, 1927.
- ¹⁷ Rice and Ramsperger, forthcoming.
- ¹⁸ Fowler and Rideal, *Proc. Roy. Soc.*, **113A**, 571, 1927.
- ¹⁹ Lewis, *Proc. Nat. Acad. Sci.*, **13**, 546, 1927.
- ²⁰ Tolman, Vost and Dickinson, *Proc. Nat. Acad. Sci.*, **13**, 188, 1927.
- ²¹ Ramsperger and Porter, *J. Am. Chem. Soc.*, **48**, 1267, 1926.
- ²² Lewis, *Proc. Nat. Acad. Sci.*, **13**, 720, 1927.
- ²³ Stuart, *Zeit. Physik*, **32**, 262, 1925.