The Journal of the American Chemical Society

VOL. 50 APRIL, 1928 No. 4

[Contribution from the Physical Chemistry Laboratory of Princeton University]

I. THE EFFECT OF RADIATION ON THE DECOMPOSITION OF OZONE AND NITROUS OXIDE

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Received August 18, 1927 Published April 5, 1928

The radiation hypothesis has been subjected to many proposed theoretical modifications. Experimentally there has been little direct substantiation of either the simple hypothesis or the more complex substitutes. The failure of absorption bands to correspond with the activating frequency, as calculated from the critical increment, has been noted.[2] Most significant have been the observations of H. A. Taylor[3] and Daniels[4] that the decomposition of nitrogen pentoxide is unaltered by infra-red radiation. This has been extended by the latter to include the oxidation of alcohol vapor and the decomposition of hydrogen chloride. Regardless of the particular mechanism of molecular activation by radiation, there should be a disturbance in the reaction rate when the available energy from the possible activating frequencies or frequency is increased. The present work provides two more examples of chemical gas reactions which are unaffected by infra-red radiation.

Experimental Part

Gaseous nitrous oxide and ozone were both exposed to the infra-red radiation emitted by a carbon arc. The latter consumed 20 amperes and was located 10 cm. from the reaction vessels. A 200cc. transparent quartz tube and a similar glass tube with sealed on polished fluorite window, served as reaction vessels. Thermal conduction from the arc was avoided by means of air currents and filters. Except from the side exposed to the arc, the vessels were surrounded by an electric furnace or ice-bath and kept at constant temperature.

It is obvious that the radiation density of any possibly activating

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[1] National Research Fellow.

[2] Langmuir, This Journal, **42**, 2190 (1920), and others.

[3] H. A. Taylor, *ibid.*, **48**, 577 (1926).

[4] Daniels, *ibid.*, **48**, 607 (1926).

frequencies in the infra-red must be materially increased in order that there may be any material alteration in the reaction rate. The actual radiation density at different frequencies from a carbon arc (at 3800° K.) is calculable from Planck's radiation law. However, only a part of the emitted radiation actually falls on the reaction vessel. Of this part a portion is reflected and a portion adsorbed, the amount depending on the frequency. The actual radiation received by the gas in the vessel is only a small part of the emitted energy. The foregoing considerations lead to the following conclusions for these particular experiments: namely, (1) that for wave lengths longer than 2.5μ there is no appreciable increase in their radiation density within the reaction vessel, as a result of exposure to the arc, the reaction vessel being at 883° K.; (2) that for wave lengths longer than 9.6μ there is likewise no appreciable radiation density increase resulting from the arc's emission, the reaction vessel being at a temperature of 273° K. The possible effectiveness of the infra-red radiation, therefore, is experimentally limited to these spectral regions; that is, in the case of nitrous oxide decomposition to 2.5μ and in the case of the ozone decomposition to 9.6μ.

The decomposition of the nitrous oxide was followed by means of a mercury manometer connected to the apparatus with a capillary tube and the increase in pressure during the reaction measured. The reaction was repeated several times at the same initial pressure. With complete illumination, with total darkness and with alternate illumination and darkness there was *no alteration in the reaction rate.* The temperature was maintained at 883° K. by means of an electric furnace. At lower temperatures, with the fluorite window vessel, no effect was noticeable. While the velocity constant at half-time decomposition is in agreement with the value found by Hinshelwood and Burk,[5] the total variation of the constant is over twofold greater than that observed by them. The values are as follows.

TABLE I

DECOMPOSITION OF NITROUS OXIDE

Total press., mm. of Hg	Partial press., N_2O	Time, minutes	$K \times 10^6$, seconds
227	227	0	..
237	207	200	7.1
250	181	400	9.3
262.5	156	600	11.1
272.5	126	800	12
287.5	106	1000	15.3
300	81	1200	20
312.5	56	1400	28.4
320	41	1600	37.2

The values are the same whether the nitrous oxide be illuminated or the reaction carried out in the dark. The nitrous oxide was obtained from

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[5] Hinshelwood and Burk, *Proc. Roy. Soc.* (*London*), **106A**, 284 (1924).

cylinders but was distilled and dried before using. The departure from the homogeneous bimolecular reaction rate was attributed (by Hinshelwood) to the effect of by-products in reaction. The time of half decomposition at different initial pressures indicates, nevertheless, a bimolecular reaction.

Similar experiments were carried out with ozone. The ozone was prepared by means of a discharge in oxygen at 0.1 mm. pressure, the discharge tube being immersed in liquid air. When several cubic centimeters of the liquid ozone had collected, the oxygen was pumped off and the ozone allowed to distil into the previously evacuated reaction system.

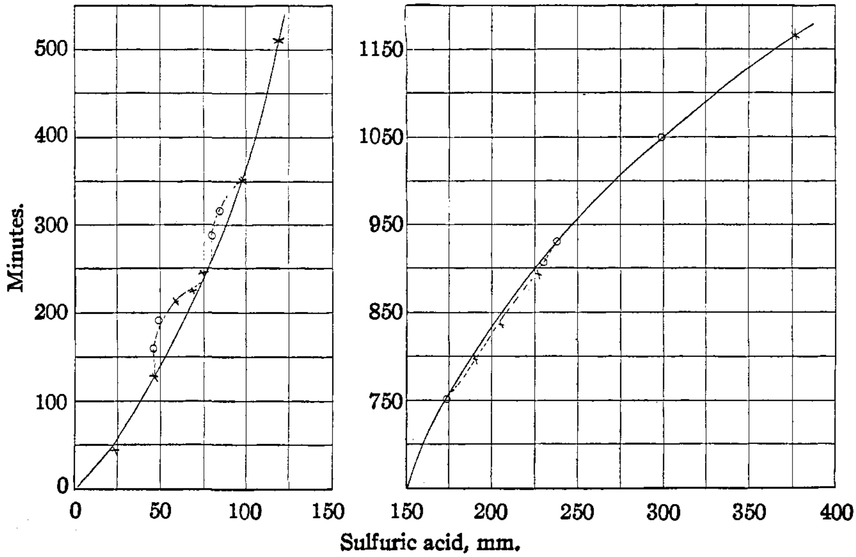

Fig. 1.—Ozone decomposition.

The product varied from 60 to 75% pure ozone after distillation. The reaction vessel was immersed in an ice-bath. The surface exposed to the arc lamp was unprotected, however, except by means of an air stream. The reaction vessel was connected to a sulfuric acid manometer by capillary tubing and the reaction was followed from the increase in pressure. A certain amount of segregation of different portions of the infra-red spectrum was possible by the use of quartz, biotite and iodine in carbon disulfide filters. The visible and ultraviolet were eliminated in each experiment. There was no appreciable alteration in the decomposition rate on alternate illumination and darkening. A typical curve is presented in Fig. 1. The light reaction is represented by × and the dark by O. The curve is divided into two parts, the first being from 0 to 550 minutes and the second from 650 to 1200 minutes. An appreciable expansion is noticeable on illumination. An equivalent contraction, however, takes place when the light is cut off. Due to the erratic behavior of ozone decompositions, the alternate dark and light reactions were necessarily tried within the same experiment. An inter-experiment comparison as in the case of nitrous oxide decomposition is not practical.

Summary

A simple, homogeneous, high temperature reaction, the decomposition of nitrous oxide, has been investigated from the point of view of the radiation hypothesis and found unresponsive to an increase in the radiation density of frequencies corresponding to the infra-red.

A heterogeneous low temperature reaction, the decomposition of ozone, has similarly been found to be uninfluenced by infra-red radiation.

In view of the somewhat similar experiments with nitrogen pentoxide, hydrogen chloride and alcohol,[3,4] together with the failure of predicted activating frequencies to correspond with absorption bands,[2,3] molecular activation through the absorption of single or multiple frequencies seems improbable.

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II. THE LOW PRESSURE DECOMPOSITION OF NITRIC AND NITROUS OXIDES

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RECEIVED AUGUST 18, 1927 PUBLISHED APRIL 5, 1928

In a previous publication[2] the various radiation and collision theories of molecular activation were mentioned, together with some experimental data. Of the most significance to the present publication, which deals with collisions in chemical gas reactions, however, is the original theory of Lindemann.[3] This has been amplified by Hinshelwood[4] and others.[5] Lindemann has accounted for the existence of unimolecular reactions by the assumption that dissociation does not take place instantly on collision but only after a time which, on the average, is greater than that necessary to reëstablish Maxwellian distribution. Otherwise the rate of dissociation would depend on the rate by which this distribution was reëstablished or upon the collision frequency. At high pressures, the concentration of active molecules is therefore maintained constant and the

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[1] National Research Fellow.

[2] Hibben, *Proc. Am. Acad. Sci.*, August, 1927.

[3] Lindemann, *Trans. Faraday Soc.*, **17**, 598 (1922).

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

[5] (a) Fowler and Rideal, *ibid.*, **113A**, 570 (1926); (b) Rice and Ramsperger, THIS JOURNAL, **49**, 1617 (1927); (c) Lewis and Smith, *ibid.*, **47**, 1514 (1925). Tolman, Yost and Dickinson, *Proc. Nat. Acad. Sci.*, **13**, 188 (1927).