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THE DECOMPOSITION OF NITROGEN PENTOXIDE AND INFRA-RED RADIATION

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RECEIVED JULY 1, 1925 PUBLISHED MARCH 5, 1926

The decomposition of nitrogen pentoxide has for some years aroused considerable interest as a unimolecular reaction, which unlike most of the others in that class, is not appreciably catalyzed by the walls of the containing vessel. The work of Daniels and Johnston[1] to prove this was later amplified by Daniels, Wulf and Karrer,[2] who suggested that nitrogen dioxide exerted an initial autocatalytic effect, and the sole remaining example of a true unimolecular reaction was ruled out as unsatisfactory. The theories that had been suggested for such spontaneous decompositions, and the theoretical expressions for their rates were without evidence by which they might be tested. Any failure of one of these was immediately explained as due to the catalytic effect.

The peculiarity of the autocatalytic effect of nitrogen dioxide on the reaction, there being at the same time complete absence of the typical autocatalytic acceleration which would normally be expected, led to further investigation of the decomposition. Recently White and Tolman,[3] and Hirst[4] have studied the reaction again and found no evidence for the supposed autocatalytic effect. Hunt and Daniels[5] have also repeated the decomposition using low concentrations of the pentoxide diluted with nitrogen and have shown that even at as low pressures as 0.01 mm. the reaction is still independent of the concentration and of the amount of nitrogen dioxide present.

It seems reasonably certain, therefore, that this reaction is unimolecular, and has been treated as such by G. N. Lewis and Smith[6] and by Tolman[7] in their recent general discussions on reaction rate. The possibility again arises then of the applicability of the simple radiation theory to this reaction. Daniels and Johnston in their original work obtained a value of 24,700 calories for the critical increment of the reaction, corresponding to a wave length of 1.16μ in the near infra-red. On subjecting nitrogen pentoxide however, to radiation of this wave length no decomposition was found to occur. The suggestion was immediately forthcoming[1,8] that the

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[1] Daniels and Johnston, THIS JOURNAL, **43**, 53 (1921).

[2] Daniels, Wulf and Karrer, *ibid.*, **44**, 2402 (1922).

[3] White and Tolman, *ibid.*, **47**, 1240 (1925).

[4] Hirst, *J. Chem. Soc.*, **127**, 657 (1925).

[5] Hunt and Daniels, THIS JOURNAL, **47**, 1602 (1925).

[6] Lewis and Smith, *ibid.*, **47**, 1508 (1925).

[7] Tolman, *ibid.*, **47**, 1524 (1925).

[8] Lewis, *Trans. Faraday Soc.*, **17**, 573 (1922).

thermal reaction though not occurring through one quantum at this frequency, might still occur through the absorption of three or five quanta at correspondingly lower frequencies; that is at 3.39μ or 5.81μ at which wave lengths nitrogen pentoxide had been shown by Warburg and Leithauser[9] to possess strong absorption bands. It was the purpose of this work to find whether radiation of these wave lengths does decompose nitrogen pentoxide.

Experimental Part

The nitrogen pentoxide was prepared as described by Daniels and Bright[10] from pure nitric acid and phosphorus pentoxide. The crude crystals of the nitrogen pentoxide containing some nitrogen tetroxide were partly evaporated by evacuation and resublimed giving crystals which were only slightly yellow.

Since the results of Tolman and White and of Hirst have shown that the presence even of excess of the tetroxide is without effect on the decomposition of the pentoxide it was not considered necessary to purify the product further by ozone. That the nitrogen tetroxide molecules might absorb radiation in the region studied and cause activation of the nitrogen pentoxide by collision thereby decomposing it, does not seem reasonable and is disproved by the final results.

The essential features of the apparatus were similar to that used by Hirst[4] save that the reaction chamber was as a thin transparent quartz flask sealed to the set-up with de Khotinsky cement; the surface of contact offered by the cement to the pentoxide vapors was reduced to a minimum and no change in it was visible during the course of the experiments. The pressure changes were observed by means of a Bourdon gage constructed entirely of glass. The deflections of the pointer on the gage were observed through a small microscope and balanced against a mercury manometer. Pressure changes of the order of 2 mm. of mercury were easily observable, a greater degree of accuracy being considered unnecessary.

The source of radiation employed was an automatic carbon arc, operating on 110 volts and carrying about 7 amps. The spectral range actually employed was obtained by using a thin sheet of biotite mica 0.12 mm. thick.

Coblentz[11] has shown that using a sheet of biotite 0.03 mm. thick there is but 30% transmission at 1μ rising rapidly to 80% at 2μ whence it remains constant as the wave length is increased up to 5μ followed by a decrease to practically complete absorption at 9μ. Thus we have a region of almost 80% transmission from about 2 to 5μ and 60% from 5 to 8μ, bounded on each side by regions of complete opacity. Daniels and Johnston[12] showed that blue light in the region 400 to 460μμ did decompose nitrogen pent-

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[9] Warburg and Leithauser, *Ann. Physik*, [IV] **28**, 313 (1909).

[10] Daniels and Bright, This Journal, **42**, 1131 (1920).

[11] Coblentz, "Investigations of Infra-red Spectra," Part III, *Carnegie Inst. Pub.*, **65** (1906).

[12] Ref. 1, p. 75.

oxide when nitrogen tetroxide was present, presumably by secondary collisions, rendering it necessary to use a thickness of biotite which was opaque to these wave lengths. The thickness chosen, namely, 0.12 mm., was found spectroscopically to be opaque to this region. Further, when a blue screen, transmitting only from 360$\mu\mu$ to 510$\mu\mu$ was interposed between the arc and the mica screen, the arc was rendered quite invisible, showing that the biotite completely absorbed the blue in this region.

There appear to be no data available on the ultraviolet absorption of biotite so that there was no certainty that the ultraviolet was not transmitted by the filter. Daniels and Johnston[12] used a saturated solution of *p*-nitroso-dimethylaniline as a filter for excluding the active blue region. Coblentz[13] has shown that a layer of this material in the solid state 0.035 mm., thick has absorption bands at 3.43μ and 6.86μ typical of the methyl group. In the second experiment quoted, therefore, a thin layer, less than 0.01 mm. thick was melted onto the biotite screen. The effect of this on the transmission in the infra-red is negligible, while the blue region is made further opaque and the ultraviolet now probably excluded.

Assuming the applicability of the absorption coefficients, calculated from Coblentz's data, to the thickness of the biotite used in these experiments, it was calculated that for the thickness 0.12 mm., the transmission for the desired regions namely 3.4μ and 5.8μ was from 40 to 45%. The screen was fitted to a light-tight box which completely surrounded the quartz reaction vessel. The box carried a thermometer serving as a rough indicator of the temperature of the system during exposure.

The procedure adopted in carrying out a run consisted in thoroughly evacuating the reaction chamber, admitting the pentoxide vapor from the crystals immersed in a bath at room temperature, having previously pumped off any residual gases from the crystals, and observing the pressure of the gas in the chamber. The tube of the reaction vessel which was exposed outside the box was painted black to render it opaque. The arc was struck and any change of pressure noted during the exposure.

Results and Conclusions

In the first experiment made, the pressure of the initial gases, nitrogen pentoxide with traces of the tetroxide, was 403 mm. The exposure lasted for 30 minutes with the arc 30 cm. from the reaction vessel. As soon as the light was started there was noticed a slight decrease in pressure amounting to 2 or 3 mm. followed quickly by a rise to 406 mm. The cause of this slight decrease in pressure is probably due to a change in the volume of the quartz vessel on exposure, quartz possessing a strong absorption band at 2.96μ which in itself restricts the effective region still further in favor of the desired wave lengths. The subsequent changes in pressure of the gas were small throughout the run, the final pressure being 410 mm., showing that practically no decomposition had occurred. The temperature change in the box enclosing the reaction flask during the exposure amounted to approximately 5°, that is, from 20.6° to 25.4°.

The second run was made with the biotite screen coated with *p*-nitroso-dimethylaniline. The initial pressure of the gases was 405 mm. Conditions generally were made more stringent than in the previous run, in that

[13] Ref. 11, Part I.

the light source was placed only 15 cm. from the reaction vessel and the exposure made for two hours. The same slight decrease in pressure when the arc was first struck was again observed and followed by an immediate rise to a value slightly above the original pressure. During the exposure the box temperature rose steadily throughout the two hours from an initial value of 25.3° to a final value of 30.5°. The pressure, too, rose steadily indicating some decomposition, until a value of 463 mm., was registered at the end of the two hours exposure.

Such a pressure increase may be shown by comparison with the original data of Daniels and Johnston (and the later work of Tolman and of Hirst has confirmed these) to correspond approximately to the amount of purely thermal decomposition which would have occurred had the reaction system been maintained throughout the run in the neighborhood of 25°. Allowing for the fact that the temperature in the box surrounding the reaction vessel is but a poor indicator of the actual temperature of the system, the results would show that certainly no great acceleration of reaction rate has been accomplished by the infra-red radiation.

It is interesting to calculate approximately what increase in reaction rate was to be expected on the basis of the simple radiation theory assuming black-body radiation from the carbon arc at 3800°K. as compared with that of 300°K. under the normal conditions. According to Planck the radiation density is given by $u_\nu = \frac{8\pi h\nu^3}{c^3} \cdot \frac{1}{e^{h\nu/kT} - 1}$, where u_ν is the density of black-body radiation of frequency ν at the temperature T°K., h is the Planck constant, c the velocity of light in a vacuum and k the gas constant per molecule. If we let u_1 and u_2 be the radiation densities at the higher and lower temperatures T_1 and T_2, respectively, the ratio of the two will be given by $u_1/u_2 = (e^{h\nu/kT_2} - 1)/(e^{h\nu/kT_1} - 1)$. Taking a mean wave length $\lambda = 4.5\mu$ corresponding to a frequency $\nu = 0.67 \times 10^{14}$ the ratio u_1/u_2 is found to be approximately 31,000; that is, the density of black-body radiation at 3800°K. is 31,000 times greater than that at 300°K. for a wave length of 4.5μ. On the *simple* radiation theory since the unimolecular reaction rate is directly proportional to the radiation density, the reaction during exposure should have been completed in a fraction of a second. There may be however, the question of a photochemical efficiency to be taken into account. Warburg[9] has shown that nitrogen pentoxide does absorb radiation of wave lengths 3.39μ and 5.81μ, presumably the ordinary physical absorption of radiation with degradation to longer wave lengths and re-emission, so that the most we may say from the above results is that the photochemical efficiency of radiation of this frequency is almost infinitely small.

So far then, practically the whole of the short-wave infra-red region has been shown to be inefficient photochemically, to any great extent for the decomposition of nitrogen pentoxide. The question still remains open whether some other wave length would be active. In the visible region Daniels and Johnston showed that the blue region was the only active one, and that, only when nitrogen tetroxide was present; an obvious case of photosensitization analogous to that of chlorine and bromine in several reactions. If we progress further into the infra-red the difficulty increases of differentiating between a purely localized heating effect and a true photo-effect, if in fact such a distinction is justifiable at all.

None of the experiments carried out so far using more or less monochromatic radiation could serve however, to test the suggestion of the possible efficiency of a series of frequencies, whether, as Perrin suggests by simultaneous, or, as Tolman suggests by successive, absorption by the molecule, though from the results obtained up to the present even this would not at first sight seem probable. In this connection it may be well to quote an observation made by the author a year ago. Hydrogen and ethylene are known to combine under suitable conditions, such as high temperatures, in presence of a catalyst, or by collision with excited mercury atoms.[14] A mixture therefore, of these two gases was exposed in a quartz vessel to the complete spectrum of radiation from a Nernst glower. Although the whole spectrum, limited only by the transmission of the quartz, was employed, the source being but a few centimeters away from the reaction vessel, the temperature maintained as high as 300°C. and the exposure prolonged over 48 hours, the only evidence of change was a slight decomposition of the ethylene with no prduction of ethane whatsoever. In this case at any rate it does not seem likely that even a spectrum of frequencies is going to account for reaction.

Whether a similar result as that just cited would be obtained generally, cannot be foretold with any degree of certainty. If radiation is unable to account for such reaction velocities, under any circumstances, and it has been definitely proved that collision effects cannot, the question of the reason for, and mechanism of unimolecular reactions remains unsolved. It has been suggested by Tolman "that the process of activation consists in increasing the energy of vibration of atoms within the molecules." This would correspond with the chemists' rough idea of "loosening a chemical bond" and would undoubtedly make the atoms more free to enter into new chemical combinations. May not a similar interpretation be placed upon unimolecular decomposition without the assumption of radiation? In other words in the molecule about to decompose unimolecularly the atoms are vibrating to an extent dependent on the temperature. If we raise the temperature, the probability increases that the atoms will vibrate far enough away from the rest of the molecule to lose the effect of the natural binding force and will free themselves, decomposition having

[14] Taylor and Marshall, *J. Phys. Chem.*, **29**, 1140 (1925).

then occurred.[15] The measured reaction rate on this basis would be proportional to the probability that an atom in the molecule vibrates sufficiently, to get beyond the range of molecular attraction. The temperature coefficient of the reaction velocity should then be proportional to the increase in intra-molecular vibration with temperature and the critical increment calculated from the observed rates, a measure only of the change in vibrational energy of an atom or atoms in the molecule due to change in temperature.

Summary

1. The decomposition of nitrogen pentoxide has been studied in presence of infra-red radiation between the limits 2μ and 8μ inclusive of the two absorption bands at 3.4μ and 5.8μ exhibited by the gas.

2. Although the degree of accuracy attained would not warrant a complete denial that no acceleration of the decomposition had occurred due to the infra-red radiation, it has been shown that no such marked effect as the simple radiation theory would suggest is noticeable.

3. A general discussion on the application of radiation to chemical reaction was presented with special reference to unimolecular reactions.

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A NEW METHOD FOR THE ELECTROLYTIC SEPARATION OF METALS

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RECEIVED JULY 2, 1925 PUBLISHED MARCH 5, 1926

A substitute for the auxiliary electrode used by Sand,[1] and later by others, in the separation of metals by electro-analysis is given in this paper.

A wire of the metal to be deposited is immersed in the solution from which the metal is to be deposited. This wire is connected to the cell, voltmeter, etc., in the same manner as is the auxiliary electrode used by Sand. The details of the methods used in the determinations are those given by Schoch and Brown[2] modified by the use of the wire for the auxiliary electrode. While the metal is being deposited on the cathode, the current is controlled so that the observed potential of the cathode ΔE, is —0.10

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[15] The distribution of the energy of vibration among the various molecules will presumably follow a normal Maxwellian curve and those with a high energy will be the first to decompose. How the Maxwellian distribution is to be restored does not appear any more evident than the restoration of the Maxwellian distribution among electrons between collisions, recently demonstrated by Langmuir [*Phys. Rev.*, **26**, 585 (1925)], unless it occurs by impact with quanta of radiation in some form.

[1] Sand, *J. Chem. Soc.*, **91**, 379 (1907).

[2] Schoch and Brown, *Trans. Am. Electrochem. Soc.*, **22**, 265 (1912). THIS JOURNAL, **38**, 1660 (1916).