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THE DECOMPOSITION OF NITROGEN PENTOXIDE BY LIGHT*

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The decomposition of nitrogen pentoxide by light has been investigated by Daniels and Johnston[1] with the view of testing the Lewis and Perrin radiation hypothesis of chemical reactions. According to this theory, the frequency of the light (ν) which should decompose this substance is given by $\nu = E/Nh$, where N is the number of molecules per gram molecule, h is Planck's radiation constant, and E is the critical energy increment for the decomposition of the pentoxide.

From the thermal decomposition of nitrogen pentoxide in the dark, Daniels and Johnston[2] found the critical energy increment to be 24,700 calories per mole. Thus, light of wave length 1.16μ should decompose nitrogen pentoxide. They found, however, that *pure* nitrogen pentoxide is not decomposed by light having a wave length in the region of 1.16μ, nor is it decomposed by light of any wave length between 1.16 and 0.400μ; but when mixed with nitrogen dioxide, the pentoxide is decomposed on exposure to blue light having a wave length between 0.460 and 0.400μ.

Hasselberg[3] found that nitrogen dioxide has practically complete absorption in this spectral region. Daniels and Johnston also found that by screening the reaction tube with nitrogen dioxide, the photo-decomposition was completely stopped.

They further found that the rate of photo-decomposition of the nitrogen pentoxide depended on the initial pressure of the nitrogen dioxide, but the nitrogen dioxide was not found to be a catalyst for this reaction in the dark. This has been confirmed by the recent experiments of White and Tolman.[4]

In view of these facts, it is impossible to assume that the reaction is a direct effect of light of the region 1.16 to 0.400μ, on the nitrogen pentoxide. It is necessary that the photo-decomposition depend in some intimate way on the absorption of light by the dioxide. In the present article, the authors desire to point out that all of the experimental facts are accounted for, if the energy absorbed by the nitrogen dioxide molecules from the light is transferred to the nitrogen pentoxide molecules by means of collisions of the *second type*.

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[1] Daniels and Johnston, THIS JOURNAL, **43**, 72 (1921).

[2] Daniels and Johnston, *ibid.*, **43**, 53 (1921).

[3] Hasselberg, *Mem. Acad. St. Petersburg*, **7**, 286 (1878).

[4] White and Tolman, THIS JOURNAL, **47**, 1240 (1925).

In general, when two particles collide, there will be an interchange between the kinetic and potential energies of the system. A collision is elastic if there is no resultant change in the total kinetic energy of the particles, due to the collision.

If the collision is such that some of the kinetic energy is converted into molecular or atomic potential energy, the collision is an inelastic one of the first type. The result of such a collision is an activation of the molecule or atom.

A collision of the *second type* is one in which some of this internal energy of activation is transferred from one particle to another. Such collisions may be studied by means of the changes brought about in the receiving particle by the energy transferred. A collision of the second type may result in such effects as dissociation, decomposition, ionization or other forms of activation. It may even reverse the process of a collision of the first type by converting the energy of activation into kinetic energy of the particles.

Collisions of the second type between electrons and atoms were first suggested by Klein and Rosseland[5] from their studies of the statistical equilibrium between atoms, electrons and radiation. Their ideas were extended by Franck,[6] to include atomic and molecular collisions. He also pointed out important chemical and physical consequences of such collisions.

Collisions of the second type giving rise to dissociation have been studied by Cario and Franck.[7] In these experiments hydrogen was exposed to the light of a mercury-vapor arc and no dissociation was found because the pure hydrogen was unable to absorb this light. However, when the hydrogen was mixed with a little mercury vapor and then exposed to light from the arc, the hydrogen was dissociated. In this case, the mercury became activated by absorption of light energy and by a collision of the second type transferred sufficient energy to the hydrogen to cause its dissociation. A number of other investigators[8] have studied collisions of this type.

The transfer of the energy from the activated nitrogen dioxide to the nitrogen pentoxide presents the same phenomena as the transfer from the activated mercury to the hydrogen. The pentoxide is unable to absorb light of the critical wave length 1.16μ. Also, it cannot absorb light of any shorter wave length in the region studied, but the dioxide absorbs light in the region 0.400 to 0.460μ, which activates it. The energy is then transferred to the pentoxide by collision and the decomposition of this molecule results.

[5] Klein and Rosseland, *Z. Physik*, **4**, 46 (1921).

[6] Franck, *ibid.*, **9**, 259 (1922).

[7] Cario and Franck, *ibid.*, **11**, 161 (1922).

[8] Cario and Franck, *ibid.*, **17**, 202 (1923). Dickinson, *Proc. Nat. Acad. Sci.*, **10**, 409 (1924).

The amount of energy which is resident in the activated nitrogen dioxide is about two and a half times that necessary to activate the nitrogen pentoxide molecule for decomposition. The way in which this energy is used up is at present unknown. Observations on the number of molecules of nitrogen pentoxide decomposed per quantum of light absorbed by the nitrogen dioxide should give some indications as to the process. A chain reaction may exist in which the energy of activation is converted into heat of reaction through successive activation and decomposition brought about by collisions of the second type. It should be possible to cause this reaction by light of much longer wave length by using other molecules in place of nitrogen dioxide which have absorption in the longer wave-length region of the spectrum.

Warburg and Leithauser[9] have found a number of absorption bands in the infra-red for nitrogen pentoxide. These are located at wave lengths greater than 2.82μ. It is not to be expected that light of these frequencies will cause appreciable decomposition as the quanta are smaller than the critical energy increment for the reaction. The only way that decomposition of nitrogen pentoxide could be brought about by light of these wave lengths would be by cumulative or simultaneous absorption of more than one quantum of light. Probability considerations indicate that this would be a rare event.[10]

Summary

The photo-decomposition of nitrogen pentoxide is brought about by collisions of the second type with activated nitrogen dioxide molecules. The dioxide molecules are able to absorb light in the blue (0.460μ) and transfer this energy by direct collision (without intervention of radiation) to the pentoxide, causing its decomposition; on the other hand, the pentoxide is not able to absorb light corresponding to its critical energy increment or any light of shorter wave length up to 0.400μ. Thus, it does not undergo photo-decomposition, unless the energy is made available for it by nitrogen dioxide.

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

[10] Tolman, THIS JOURNAL, **47**, 1524 (1925).