and invariably accompanied by complex redistributions of electrons in the molecule.

These observations are entirely in accord with the following premise: *if there are a number of possible arrangements of the atoms in a molecule which have the same number of electrons per atom and which satisfy equally well the tendencies of the more electronegative elements to complete their octets of electrons, that form will be the most stable which gives a minimum of repulsion between the atomic kernels.*[7]

BERKELEY, CALIFORNIA

THE MECHANISM OF HOMOGENEOUS GAS REACTIONS. II. THE ABSORPTION SPECTRUM OF NITROGEN PENTOXIDE AND ITS METHOD OF DECOMPOSITION

BY H. C. UREY, L. H. DAWSEY AND F. O. RICE

RECEIVED MARCH 8, 1929 PUBLISHED NOVEMBER 8, 1929

The thermal and photochemical dissociation of nitrogen pentoxide has been the subject of a number of important investigations during the past few years. Daniels and Johnston[1] showed that the thermal dissociation followed a unimolecular law and that the temperature coefficient of the velocity constant gave a mean value for the energy of activation calculated from the Arrhenius equation of 24.7 kg. cal. The average deviation of this quantity is 0.42 kg. cal. They illuminated their nitrogen pentoxide with infra-red radiation of approximately $\lambda = 1.16\mu$, corresponding to the energy values of the heat of activation, but found that there was no increased reaction due to illumination. Later investigations[2] have provided ample confirmation that neither this nor any other wave length in the infra-red causes appreciable decomposition of nitrogen pentoxide. Daniels and Johnston illuminated nitrogen pentoxide and a mixture of nitrogen pentoxide and nitrogen peroxide contained in a glass vessel by direct sunlight and found that nitrogen pentoxide decomposes only in presence of nitrogen peroxide. They isolated the region from 4000 to 4600 Å. (blue light) by filters and found that these were active wave lengths. By interposing a filter of nitrogen peroxide they showed that decomposition did not take place. Fazel and Karrer[3] proposed that the effect was due to the absorption of light by the nitrogen peroxide molecule, which then transferred its energy by a collision of the second kind to the nitrogen pentoxide molecules.

---

[7] These observations are also in accord with the conclusion of Pauling and Hendricks (ref. 1) regarding the stability of certain inorganic isomers.

[1] Daniels and Johnston, THIS JOURNAL, **43**, 53, 72 (1921).

[2] Daniels, *ibid.*, **48**, 607 (1926); Taylor, *ibid.*, **48**, 577 (1926); Mayer, *ibid.*, **49**, 3033 (1927).

[3] Fazel and Karrer, *ibid.*, **48**, 2837 (1926).

The effect of light on nitrogen peroxide has been studied by Norrish,[4] who concluded that there is an equilibrium established according to the equations

$$NO_2 + h\nu \longrightarrow NO_2'$$
$$NO_2' + NO_2 \longrightarrow 2NO + O_2$$
$$2NO + O_2 \longrightarrow 2NO_2$$

He then assumed that the photochemical decomposition of nitrogen pentoxide was a secondary dark reaction represented by the equation

$$NO + N_2O_5 \xrightarrow{\text{Dark}} 3NO_2$$

Dickinson and Baxter[5] confirmed Norrish's view that gaseous NO_2 is decomposed by light into NO and O_2; they determined the quantum yield of the reaction at sufficiently low pressures that the rate of recombination of NO and O_2 was negligibly slow. The quantum yields secured were 0.0046 at 4350 Å., 0.36 at 4050 Å. and 0.77 at 3660 Å.

Busse and Daniels[6] then showed that nitric oxide and nitrogen pentoxide react very rapidly to give nitrogen peroxide according to the last equation; they also showed that the addition of inert gases to the nitrogen pentoxide–nitrogen peroxide mixture does not inhibit the photochemical decomposition. This indicates that the mechanism of Fazel and Karrer is not the correct one, because quenching of the excited nitrogen peroxide molecules should recur under these conditions. It appears that the mechanism is the photochemical production of nitric oxide molecules, which then react with the nitrogen pentoxide molecules to form nitrogen peroxide.

Recently Harris[7] has studied the absorption spectra of nitrogen peroxide and nitrogen tetroxide. The absorption spectrum of NO_2 molecules consists of a large number of bands, many with fine structure, from 6000 to 2250 Å.; the absorption due to N_2O_4 in the gaseous phase is continuous. Two bands, one with a maximum at 3500 Å. and another with a maximum further in the ultraviolet, merge at high pressures of N_2O_4 into one continuous band which extends from 4000 Å. into the far ultraviolet.

The Absorption Spectrum of Nitrogen Pentoxide.—Since the ultraviolet absorption spectrum of nitrogen pentoxide has not been studied previously, we have investigated it and present the results in this paper. We have photographed the ultraviolet absorption spectrum and found it to be continuous, with no evidence of a banded structure. The absorption begins at about 3050 Å. and extends into the Schumann region. Nitrogen pentoxide was distilled through a long absorption cell at low pressures. Any gases produced by photochemical decomposition were removed by a

---

[4] Norrish, *J. Chem. Soc.*, **130**, 761 (1927).

[5] Dickinson and Baxter, This Journal, **50**, 774 (1928).

[6] Busse and Daniels, *ibid.*, **49**, 1257 (1927).

[7] Harris, *Proc. Nat. Acad. Sci.*, **14**, 690 (1928).

vacuum pump and liquid-air traps. Weak bands due to nitrogen peroxide were always present on our plates when the experiments were carried out in this way. These weak bands disappeared when the nitrogen pentoxide was treated with ozone before taking the absorption spectrum, but the continuous spectrum was unchanged. Light of wave length longer than 3000 or 3050 Å. is always transmitted.

The Energy of Dissociation of Nitrogen Pentoxide.—If we assume that the Franck theory for the dissociation of diatomic molecules by light can be applied to these more complicated molecules, it leads to the conclusion that the molecule is disrupted into two or more fragments by the absorption of light. The heats of dissociation of nitrogen pentoxide into nitrogen dioxide and oxygen or nitrogen dioxide, nitric oxide and oxygen are

$$N_2O_5 = 2NO_2 + \frac{1}{2}O_2 - 16.0 \text{ kg. cal.}$$

$$N_2O_5 = NO_2 + NO + O_2 - 27.7 \text{ kg. cal.}^{8}$$

Taking the heat of dissociation of oxygen[9] as 160,000 cal., we obtain for the heat of dissociation of nitrogen pentoxide into two molecules of dioxide and an atom of oxygen the value

$$N_2O_5 = 2NO_2 + O - 96 \text{ kg. cal.}$$

Nitrogen pentoxide commences to absorb at 3050 Å., which is equivalent to 93.2 kg. cal.; this agrees very closely with the last equation and indicates that the primary photochemical reaction may be dissociated into an oxygen atom and two nitrogen dioxide molecules. It is, of course, possible that the primary photochemical reaction is any reaction which has an energy change less than 93.2 kg. cal., corresponding to the long wave length limit of the continuous spectrum of nitrogen pentoxide; several diatomic molecules are known whose energy of dissociation is considerably less than that corresponding to the wave length at which they begin to absorb.

The Mechanism of the Thermal Dissociation of Nitrogen Pentoxide.—The energy of activation for the thermal decomposition is well established as 24.7 kg. cal. and accordingly[10] this is equal to the difference between the mean energy of the molecules which react and the mean energy of all the molecules. This is very close to the amount of energy necessary to dissociate N_2O_5 into NO_2, NO and O_2, leaving these molecules with only a small amount of energy. Using the I.C.T. values for the energies of formation we find that

$$N_2O_5 = NO_2 + NO + O_2;\ \Delta E = 29.0 \text{ kg. cal.}$$

---

[8] "International Critical Tables," Vol. 5, p. 178.

[9] Birge and Sponer, *Phys. Rev.* (N. S.), **28**, 259 (1926). Birge, *Phys. Rev.*, **34**, 1062 (1929) has recently revised the value for the heat of dissociation of oxygen. His suggested value will change the calculated energy change of the reaction $N_2O_5 = 2NO_2 + O$ to $- \sim 85$ kg. cal. This does not disagree with our conclusions.

[10] See Tolman, THIS JOURNAL, **47**, 2657 (1925).

This is the energy at constant volume required to produce NO_2, NO and O_2 molecules having the mean translational, rotational and vibrational energy at 18° from an N_2O_5 molecule also having the mean energy at this temperature. If an excited N_2O_5 molecule decomposes during the time of free flight, its translational energy must appear as translational energy of the dissociated molecules in order that the linear momentum may be conserved. Therefore the NO_2, NO and O_2 molecule produced in this way must have this much translational energy, namely, about 0.6 kg. cal., but may have no more translational energy and no rotational or vibrational energy. Using the heat capacity data for these gases from the I.C.T., assuming that the heat capacity of NO_2 is the same as that of CO_2 and also assuming that the heat capacity, C_v, is constant to absolute zero, the total energy of vibration, rotation and translation of these molecules is found to be about 4.8 kg. cal. Subtracting from 29.0 and adding the 0.6 kg. cal. of translational energy, we find that the energy required to decompose the average N_2O_5 molecule at 18° to NO_2, NO and O_2 having no vibrational or rotational energy and the 0.6 kg. cal. of translational energy is 24.8 kg. cal. This agrees very closely with the energy of activation, namely, 24.7 kg. cal., and since either may be in error by considerable amounts, this calculation shows that, so far as energy relationships are concerned, the N_2O_5 molecule may undergo a primary unimolecular dissociation into these three products.

It seems possible that the dissociation of nitrogen pentoxide is analogous to radioactive decomposition as discussed recently by Gurney and Condon.[11] Applying their ideas to the dissociation of nitrogen pentoxide we can say that it is possible that sufficient energy may be localized in the right degree of freedom to cause dissociation of the molecule and yet the molecule will exist in a quantized steady state for a finite length of time and then spontaneously dissociate, the time of dissociation being determined by pure probability.

Another possible mechanism would be the dissociation from a steady state in which the energy is not localized in the particular degree of freedom involved in the dissociation. This case would be similar to the dissociation of the excited hydrogen molecule into two normal atoms as proposed by Blackett and Franck[12] to account for the continuous hydrogen spectrum. The hydrogen molecule in the $2^3\Sigma$ state spontaneously dissociates[13] into two normal atoms and the energy of excitation of the hydrogen molecule appears as kinetic energy of translation of the hydrogen atoms. This is essentially the theory proposed by Rice and Ramsperger and by Kassel.[14]

The present authors do not believe that any evidence presented as yet

[11] Gurney and Condon, *Nature*, **122**, 439 (1928).

[12] Blackett and Franck, *Z. Physik*, **34**, 389 (1925).

[13] See Winans and Stueckelberg, *Proc. Nat. Acad. Sci.*, **14**, 867 (1928).

[14] Rice and Ramsperger, THIS JOURNAL, **49**, 1617 (1927); **50**, 617 (1928); Kassel, *J. Phys. Chem.*, **32**, 225 (1928).

will permit us definitely to decide between these two mechanisms; there is also the possibility that there are other mechanisms which will give a unimolecular rate.

Summary

1. The absorption spectrum of nitrogen pentoxide has been measured and shows continuous absorption commencing at 3050 Å. and extending to the far ultraviolet.

2. The long wave length limit of this continuous spectrum corresponds very closely to the energy change in the reaction $N_2O_5 = 2NO_2 + O$ and indicates that this may be the primary photochemical reaction.

3. The mechanism of the thermal decomposition has been discussed and two possible mechanisms have been pointed out which are analogous to the radioactive decomposition of nuclei and the spontaneous dissociation of the excited hydrogen molecule.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE HEAT CAPACITY OF NITRIC OXIDE FROM 14°K. TO THE BOILING POINT AND THE HEAT OF VAPORIZATION. VAPOR PRESSURES OF SOLID AND LIQUID PHASES. THE ENTROPY FROM SPECTROSCOPIC DATA

BY H. L. JOHNSTON AND W. F. GIAUQUE

RECEIVED MARCH 11, 1929 PUBLISHED NOVEMBER 8, 1929

In a recent paper[1] the entropy of oxygen has been discussed. This was particularly interesting due to the effect of two spinning electrons. In this paper nitric oxide will be considered.

Jenkins, Barton and Mulliken[2] have measured the fine structure of the β-bands of nitric oxide and have given a very satisfactory interpretation of them. It is evident from their work that the nitric oxide gas molecules exist in a double electronic level under ordinary conditions. This arises from one-half unit of electronic spin which may couple with or against the one unit of electronic angular momentum which is directed along the figure axis of the molecule. The energies and probabilities associated with the rotation of the molecule as a whole are much influenced by the nature of the electronic coupling and are correspondingly different for the two cases referred to above.

The unbalanced angular momentum responsible for the strong paramagnetism of the nitric oxide molecule has a considerable effect on the entropy to be considered in the latter part of this paper. The theoretical treatment of the magnetic susceptibility of the nitric oxide molecule has

---

[1] Giauque and Johnston, THIS JOURNAL, **51**, 2300 (1929).

[2] Jenkins, Barton and Mulliken, *Phys. Rev.*, **30**, 150 (1927).