CCX.—*Photochemical Equilibrium in Nitrogen Peroxide. Part III. A Comparison of the Thermal, Photochemical, and Electrical Decompositions, and a General Theory of the Change.*

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A COMPARISON of the corresponding thermal and photochemical reactions in a given system has at times yielded results of importance to the theory of chemical reactivity; of this the study of the hydrogen–bromine reaction by Bodenstein and his co-workers (*Z. physikal. Chem.*, 1923, **107**, 1; 1924, **114**, 208), the demonstration of the atom-chain mechanism in the hydrogen–chlorine reaction by Pólányi (*Trans. Faraday Soc.*, 1928, **24**, 607), and the study of autoxidation in liquid systems by Bäckström (*Trans. Faraday Soc.*, 1928, **24**, 601) are outstanding examples. In the present paper, an attempt is made to extend this method of attack to the case of the homogeneous decomposition of nitrogen peroxide, since sufficient relevant data now exist for a complete study. This reaction differs from those mentioned above in that primary molecular dissociation into atoms plays no part, nor is any kind of chain mechanism involved; it occurs both under thermal and photochemical conditions as the result of a collision between two molecules without any complicating side or secondary changes. Thus we shall deal with a type of gas reaction not hitherto treated in this way, and the results to be expected are likely to be of no less importance than those accruing in the examples cited above.

It will be convenient briefly to recapitulate the facts. The thermal change $2NO_2 \rightleftharpoons 2NO + O_2$ was studied by Bodenstein, Boës, Lindner, and Ramstetter (*Z. physikal. Chem.*, 1922, **100**, 68), who found that the decomposition occurs as a homogeneous bimolecular reaction, taking place with measurable velocity over the temperature range 300—400°, with a temperature coefficient of 1·5. The present author (*Nature*, 1928, **122**, 923) re-examined their data and showed that this reaction is in accord with the theory of kinetic activation (Hinshelwood, "Kinetics of Chemical Change," 1927), affording an additional illustration of the mechanism of gaseous bimolecular change. According to this view, which on account of its simplicity and satisfactory confirmation we shall adopt throughout this work, two molecules (*e.g.*, of NO_2) react on collision when their joint kinetic energy exceeds a certain limiting quantity E, termed the heat of activation. The theory can be tested by calculating E by two independent methods—from the velocity coefficient and from the temperature coefficient—and in the present instance is confirmed by the agreement of the two values, *viz.*, $E = 32{,}000$ and 33,200, respectively, for $[2NO_2]$ at 627° Abs. It is, then, possible to say that the thermal decomposition of nitrogen peroxide occurs as a homogeneous bimolecular reaction strictly in accord with modern kinetic views of chemical reactivity.

The thermal data for the reaction were further studied by Bodenstein and Lindner (*loc. cit.*), who, from accurate measurements of the effect of temperature on the equilibrium constant, calculated that the decomposition of 2 mols. of NO_2 occurs with the absorption of 26,000 cals. at constant volume. The decomposition is thus endothermic, and the result of Bodenstein and Lindner is in full agreement with those of Berthelot and Thomsen for the reverse reaction, which, after correction for the heat of association of NO_2, give values of 25,900—26,200 cals. for the direct oxidation of 2NO to $2NO_2$.

The corresponding photochemical change

$$2NO_2 \underset{\text{Dark}}{\overset{\text{Light}}{\rightleftarrows}} 2NO + O_2$$

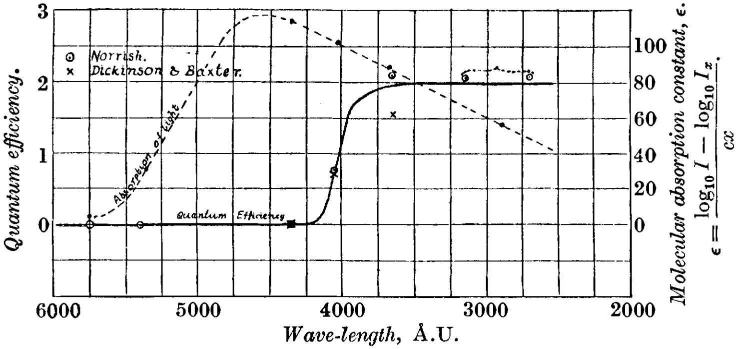
was first observed and studied by the present author (J., 1927, 761). The forward light reaction was found to occur as a homogeneous change involving collision between a photoactive and an inactive molecule of peroxide, the absence of any primary photochemical dissociation into atoms being indicated by (1) the fine structure shown by the nitrogen peroxide absorption spectrum, deep into the ultra-violet (Harris, *Proc. Nat. Acad. Sci.*, 1928, **14**, 690),

(2) the impossibility of liberating atomic oxygen in an endothermic reaction by the comparatively low energy of visible radiation, and (3) possibly by the failure to detect water formation when the photodecomposition is effected in the presence of hydrogen. The non-existence of a chain mechanism is demonstrated by the fact that the quantum efficiency of the reaction rises to a limiting constant value of 2 with decreasing wave-length, as shown in Table III of Part II (Norrish, this vol., p. 1167). We shall therefore adopt the mechanism

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

as being the only one fully consistent with all the facts of the reaction.

Fig. 1.



One of the most important facts relative to the photochemical reaction is the demonstration by Dickinson and Baxter (*J. Amer. Chem. Soc.*, 1928, **50**, 774) of a sharp photochemical threshold in the middle of the region of strongest absorption, 436—405 μμ, an observation fully confirmed in Part II of this series (*loc. cit.*). In Fig. 1 of this paper are plotted the combined results of the quantum-efficiency measurements of Dickinson and Baxter and of Norrish, together with an approximate curve showing the mean light absorption by nitrogen peroxide. From the curve we may take the wave-length 350 μμ as the first at which the quantum efficiency reaches its theoretical maximum of 2 : this means that every quantum exceeding a limiting magnitude given by $Nh\nu =$ 80,000 cals., which is absorbed, generates an active molecule NO_2', which unfailingly reacts on subsequent collision with an inactive molecule of NO_2. Quanta of smaller magnitude, *e.g.*, those corresponding to $\lambda = 405$ μμ, given by $Nh\nu = 70{,}000$ cals., are not completely efficient, and the quantum efficiency of 0·7 indicates that only a fraction 0·7/2 = 0·35 of the impacts between active and inactive molecules results in reaction. Quanta of still smaller magnitude corresponding to $\lambda = 436$ $\mu\mu$, given by $Nh\nu = 64{,}000$ cals., are rarely if ever capable of activating molecules sufficiently for reaction, so that virtually all collisions between active and inactive molecules in this case must involve the dissipation of the energy by some process not leading to chemical reaction.

To account for these results, we shall assume that, by analogy with thermal reactions, the probability of reaction between a photoactive and an inactive molecule in cases where the quantum efficiency is less than the maximum, is conditioned by the joint energy of impact of the two molecules; this, for a given degree of photochemical activation, must exceed a certain limiting amount. We shall term this quantity the kinetic increment, and note that it represents the amount by which the photochemical activation must be augmented from kinetic sources to occasion chemical reaction on impact. On this view the absorption of light of wavelength shorter than 350 $\mu\mu$ generates photoactive molecules which are capable of reacting on collision with the average NO_2 molecule and thus require no kinetic increment. Since every collision in such cases is effective, the temperature coefficient of the photochemical reaction in light of shorter wave-length than 350 $\mu\mu$ should be very nearly unity. For light of wave-length longer than 350 $\mu\mu$, the temperature coefficient may be calculated on the basis of the theory of kinetic activation in the following way: the ratio of fruitful impacts to total impacts between photoactive and inactive molecules will be in the ratio of the observed quantum efficiency γ to the maximum possible quantum efficiency, 2. This again is given in terms of the kinetic increment E by $e^{-E/RT}$. Hence

$$\frac{\text{Fruitful impacts}}{\text{Total impacts}} = \frac{\gamma}{2} = e^{-E/RT}.$$

From the values of E so obtained we may calculate the temperature coefficients of the photochemical reactions for various wave-lengths by the usual Arrhenius equation. Thus, corresponding to the magnitudes $\gamma = 0{\cdot}7$ and $\gamma = 0{\cdot}005$, we calculate temperature coefficients of $1{\cdot}035$ and $1{\cdot}3$, respectively, the values increasing steadily as the quantum efficiency diminishes. From these results, it is probable that considerable photochemical decomposition should be detectable in blue light at high temperatures. (Such an investigation is understood now to be in progress elsewhere.)

We now come to the important contrast between the thermal and the photochemical reaction. On the one hand, we note that the heat of activation of the former is 32,500 cals. per $2NO_2$, and that two molecules of peroxide unfailingly react when they collide with *thermal* energy exceeding this amount. On the other hand, for the photochemical reaction a minimum excitation to the extent of some 80,000 cals. is required in order that reaction may inevitably follow on the next collision, whilst excitation to the extent of 64,000 cals. (436 $\mu\mu$)—although this is double the energy required by the thermal reaction—is totally ineffective in causing decomposition. The inevitable conclusion is that a photoactive molecule of nitrogen peroxide may hold more than double the energy required for its disruption in the thermal reaction without reacting, and that, in spite of this, a small additional kinetic activation to the extent of a few thousand calories or so is sufficient to precipitate chemical change.

It is clear that only part of the absorbed light energy becomes available for purposes of chemical activation; we shall assume, therefore, that in order that the latter may occur, there must be a definite transference of energy from the light quantum to the molecular degrees of freedom of rotation and vibration. This view is based on the concept which Franck has so successfully applied to explain the mechanism of the photochemical dissociation of the halogens and other substances (*Trans. Faraday Soc.*, 1925—26, **21**, 536), and the present case may perhaps be regarded as the first extension of Franck's idea to embrace the process of photochemical activation as distinct from dissociation. In this sense, photoactivation and thermal activation must be considered akin, and though differently caused, they must give rise to the same effect—a stimulation of the molecular rather than the electronic degrees of freedom of the molecule.

This principle of the limited availability of absorbed light energy must therefore involve the partition of the absorbed energy between several degrees of freedom—electronic, vibrational, and rotational—and in this respect the chemical evidence adduced above is in full accord with the recent results of the study of molecular absorption spectra showing fine structure. The work of V. Henri, of Franck, and of Mulliken has shown that when light is absorbed by a molecule, quantised molecular vibrational and rotational changes are associated with each electron level, which may involve the direct transference of an appreciable part of the energy of the light quantum to vibration. This activation of the vibrational degree of freedom as a result of light absorption may also take place by a secondary process involving collisions of the second kind between excited and non-excited molecules—a process with which, as will appear shortly, we cannot in the present instance be concerned.

It would therefore seem to be necessary to distinguish carefully between two distinct molecular conditions of excitation and activation. In the former, the molecule may hold far more energy than is required for its decomposition without reacting, as in the case of molecular iodine (Oldenberg, *Z. Physik*, 1923, **18**, 1) and hydrogen (Franck, *Trans. Faraday Soc.*, 1925—1926, **21**, 536) and in the present instance, whilst *activation* occurs only when the vibrational and rotational energy is raised to the critical level required for reaction. A mechanical analogue may be found in the flywheel of an engine, which, like the electron, may hold more energy than is required to disintegrate the structure, but only becomes dangerous when it induces throughout the body of the machine sympathetic vibrations which the framework is not strong enough to withstand.

Activation by this process will only give rise to photochemical change if the activated molecules contain all or very nearly all the thermal energy required for the bimolecular reaction, since the inactive partner of the collision will, in general, be an average molecule and contribute nothing to the energy pool for reaction purposes. Thus, in cases where the activation following excitation is even only 2000 cals. short of that required for the bimolecular reaction, the subsequent collision will probably be deactivating rather than fruitful of reaction, since the necessary kinetic increment of 2000 cals. will only be forthcoming in exceptional cases. Thus, in such a case, according to the method of calculation adopted above, the quantum efficiency for the decomposition of nitrogen peroxide will have fallen to

$$\gamma = 2e^{-2000/600} = 0{\cdot}075.$$

It is believed that this principle of the distinction between activation and excitation is one which can be usefully applied throughout the whole of photochemistry, and that no molecule can be said to be in a truly chemically active state until sufficient energy has been introduced into its " thermal " degrees of freedom.

If the above arguments be accepted as sound, we may propound the question : What becomes of such absorbed light energy as, in the present case of nitrogen peroxide, does not lead to decomposition ? In blue light there is no chemical effect ; yet molecular absorption occurs to the extent given by $Nh\nu = 64{,}000$ cals., a quantity which, if degraded to heat through the medium of a collision of the second kind, would provide practically double the energy required for thermal activation, and therefore inevitable decomposition.

The inference is obvious : no such complete degradation of the absorbed energy to heat can be admitted, and we are thrown back on the only alternative, that of re-radiation. Such fluorescence should occur as a result of the de-excitation of the electronic degree of freedom, and the energy of the fluorescent radiation should show a deficiency equal to that part of the absorbed energy which has passed to the thermal degrees of freedom as pictured above. Now the life of an excited molecule is of the order 10^{-8} sec., and at 0·1 atm. pressure the time between collisions of nitrogen peroxide molecules is of the order 10^{-9}. It therefore follows that the excited molecule must make several collisions without parting with its energy as heat, and *a priori*, that the fluorescence should occur independent of pressure within wide limits.

From a further consideration of the facts, it follows that in violet light which shows incomplete photochemical efficiency, the minimum of 26,000 cals. of energy, which must be introduced into the vibrational degree of freedom to supply the endothermic heat of decomposition, is very nearly reached; only a further small kinetic increment of 600 cals. (as calculated above from the quantum efficiency) is required. Excited molecules which obtain this energy increment on collision will therefore react photochemically without fluorescence, since the peroxide molecule is destroyed in the process; but those molecules unable to make a favourable collision will lose their electronic energy as fluorescence, the wave-length of which will correspond to 69,000—25,000 = 44,000 cals., *i.e.*, 620 $\mu\mu$. There will thus be a restricted fluorescence in violet light.

In the case of the reaction in ultra-violet light, where the photochemical efficiency is complete, there are no ineffective collisions. Hence the energy introduced into the thermal degrees of freedom must exceed that required for reaction, and no kinetic increment is required. It follows that no fluorescence should be observable, since the excited molecule is decomposed and the surplus energy must therefore be carried away by the products as heat.

The fluorescence predicted above has now been observed and is described in Part IV (following paper), but it may be mentioned here that a light emission by nitrogen peroxide in the region suggested above (620 $\mu\mu$) has already been noted by Zenneck and Strasser (*Physikal. Z.*, 1911, **12**, 1202) in the discharge tube. Thus, when the gas is led at low pressure through a long tube in which it is subjected to the effect of an alternating discharge, a sequence of four coloured zones occurs along the tube from the point of entry in the order orange-yellow, green, violet, red. The explanation of this effect was first given by Zenneck and Strasser, and later fully confirmed by Kneser (*Ann. Physik*, 1926, **79**, 591), who proved that in the first zone decomposition of the peroxide to nitric oxide and oxygen occurred, whilst the succeeding zones represent later stages in the decomposition to nitrogen. This decomposition of nitrogen peroxide must occur through the agency of electron collisions, which, since light emission is stimulated, must first involve the generation of excited peroxide molecules. When we remember the identity of excitation produced by electron collisions of the first kind and by light absorption, the parallelism between the photochemical and electrical decomposition of nitrogen peroxide seems complete. We may therefore regard the luminescence as being produced by such excited molecules as do *not* decompose on collision, whereas other molecules, more strongly activated in the chemical sense, are decomposed on collision without the possibility of luminescence. The luminescence observed by Zenneck and Strasser extends over a considerable spectrum range from the orange to the yellow as an apparently continuous emission; the absence of fine structure is perhaps not difficult to understand in view of the complexity of the nitrogen peroxide absorption spectrum and the wide range of energy in the exciting electrons. Its wave-length limits correspond roughly with those of the fluorescence of the gas to be described in the sequel, and extend on either side of the luminescence indicated by the photochemical theory above.

Summary.

A comparison has been made of the data relating to the homogeneous thermal and photochemical decompositions of nitrogen peroxide. It is indicated that far more energy is required to decompose the molecule photochemically than thermally. On the basis of these considerations a general distinction based on Franck's views is drawn between spectral excitation and photochemical activation, a principle of limited availability of absorbed light energy being involved. This hypothesis leads to certain conclusions and predictions connecting fluorescence with photochemical activity in nitrogen peroxide. The decomposition of nitrogen peroxide in the discharge tube is considered and is shown to be accompanied by a luminosity in the predicted region.

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