CCXI.—*Photochemical Equilibrium in Nitrogen Peroxide. Part IV. The Relation between Fluorescence and Photochemical Action.*

By Ronald G. W. Norrish.

The comparison between the homogeneous photochemical and thermal decompositions of nitrogen peroxide (Part III, preceding paper) led to certain conclusions concerning the nature of the

photochemical activation of the peroxide molecule, on the basis of which a fluorescence showing definite relationship to photochemical activity was indicated. The expected effects have been observed, and are herein shown to conform closely to the requirements of the theory by which they were predicted.

Experimental.

After some unsuccessful attempts by various means, the fluorescence was finally observed by a simple method used by R. W. Wood for iodine vapour ("Physical Optics," Macmillan, 1923, p. 581); this consisted in sharply focusing a strong beam of monochromatic radiation through the gas in a darkened room. Pure dry nitrogen peroxide at a pressure of about 20 mm. was enclosed in a bulb of about 600 c.c. capacity, with a stem which could be cooled in liquid air to control the pressure of the enclosed gas. As a light source, a small mercury vapour lamp was employed, combined with the colour filters described in Part II of this series (this vol., p. 1161). The room was completely darkened and the lamp thoroughly shaded by a suitable box with a hole of 6 cm. diameter for emitting the light. The hole was covered by the colour filter, and the beam of light focused to a sharp pencil by a strongly convergent lens.

When the blue line from the mercury lamp was used, interposition of the bulb of nitrogen peroxide caused a bright streak of orange luminescence, which sharply defined the path of the exciting light beam. With violet light the fluorescence stimulated was slightly weaker and more greenish. With ultra-violet light of 365 $\mu\mu$ no fluorescence was observed at first, but subsequently a very faint orange glow was found which lay at the limit of visibility (see below).

When the nitrogen peroxide was frozen by placing the stem of the bulb in liquid air, the fluorescence disappeared, and it reappeared before the colour of the nitrogen peroxide vapour when the solid was allowed to become warmer, and soon increased to an approximately constant intensity; while the pressure of the gas further increased up to the total pressure of 20 mm. it showed no sign of abating.

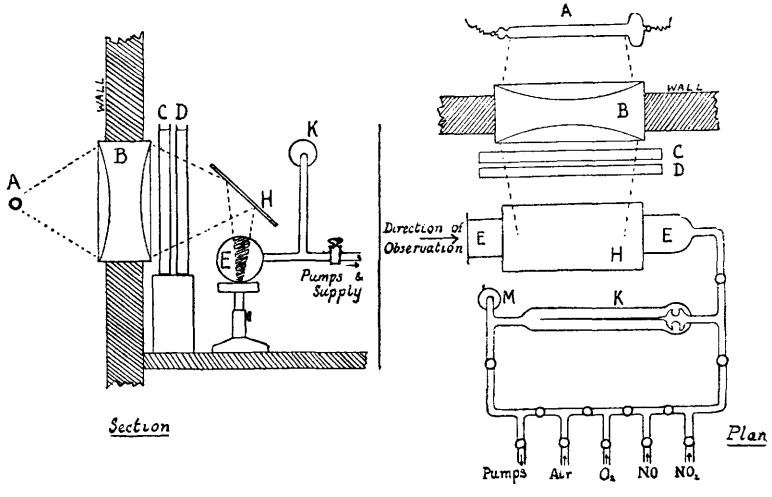
When the bulb was heated to 200—300° the fluorescence was strongly diminished, probably owing to the thermal decomposition of the nitrogen peroxide into nitric oxide and oxygen, since, as was found later, small quantities of oxygen exert a strongly inhibitory action on the glow.

In order to obtain the fluorescence more strongly developed, the apparatus shown in Fig. 1 was devised. The mercury-vapour

lamp A was of the horizontal tubular type, and was situated outside the dark room, the light being focused through a hole in the wall by means of a large condenser B of 11 in. aperture, which was completely covered by cells C and D containing the appropriate colour filters.

The fluorescence chamber, a horizontal tube E, 6 cm. by 30 cm., had a plane glass window cemented to one end, and was connected at the other end through drying tubes to a Hyvac pump, a Bourdon pressure gauge K communicating with a vertical mercury manometer M, and to the nitrogen peroxide and other gas supplies. The light beam after entering the dark room was reflected vertically downward to a focus along the axis of the tube by means of a

FIG. 1.



plane mirror H. In this way a column of gas about 20 cm. long could be illuminated intensely by monochromatic light. The fluorescence was best seen on looking along the axis of the tube through the window at the end.

With this apparatus the fluorescence was intense enough for visual examination in a constant-deviation spectroscope, and photographs of its spectrum on neocyanin plates hypersensitised with ammonia were finally obtained after exposures of about 80 hours with a slit width of $\frac{1}{2}$ mm.

Visually the spectra stimulated both by blue and by violet light appeared almost continuous, but betrayed a faint structure which was too confused for accurate measurement on account of the wide slit necessary to obtain sufficient intensity for observation. They extended in both cases from about 665 $\mu\mu$ to about 500 $\mu\mu$,

but there was evidence of a very faint emission of still shorter wave-length between 480 μμ and 450 μμ. On account of the impracticability of accurate visual observation, further measurement was carried out photographically.

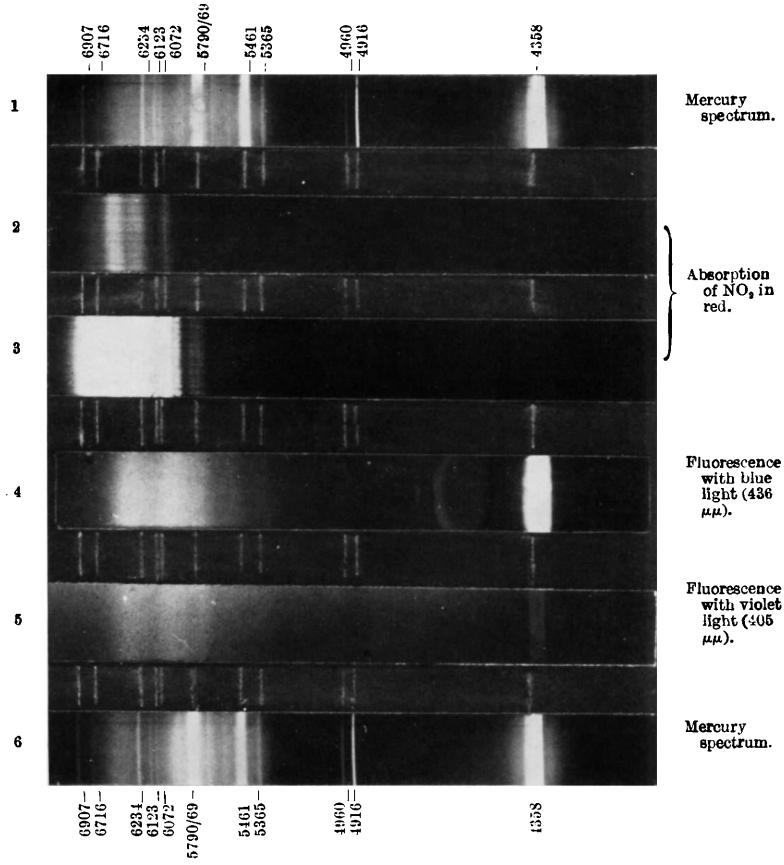
The optimum pressure for observation was about 5—10 mm. of nitrogen peroxide, but the fluorescence was visible at about 1 mm. pressure before the colour of the gas became apparent. Beyond about 20 mm. the fluorescent streak gradually receded towards the point of entry of the exciting light, owing to the more rapid absorption of the beam, and simultaneously there was a decrease in its intensity due to partial reabsorption by the gas. It still remained apparent, however, up to 90—100 mm.

The addition of oxygen at a pressure of 20 mm. of mercury almost completely extinguished the fluorescence : this effect recalls the similar action of oxygen in other cases of fluorescence, particularly that of iodine (Wood, *loc. cit.*), and if we assume that every collision between excited nitrogen peroxide molecules and oxygen molecules is effective in quenching the fluorescence, it follows from the above result that the duration of the excited state is 5×10^{-8} sec., a value of the same order as that found for other substances such as the halogens (see, *e.g.*, Franck and Jordon, " Anregung von Quantum Sprüngen durch Stösse," Springer, 1926).

This effect of oxygen rendered difficult the production of durable intensities with violet light suitable for photographing, since oxygen is set free in the photochemical decomposition. For the same reason it was also impossible to use Wood's " light furnace," the heat of which would have produced a considerable thermal dissociation of the peroxide. The difficulty was partly overcome by adding nitric oxide at about 1 cm. pressure, which is less effective than oxygen in diminishing the fluorescence and reduces the partial pressure of oxygen by throwing back the photochemical equilibrium. Nevertheless, although an instantaneous bright intensity of fluorescence could be obtained in pure peroxide with violet light, the equilibrium intensity even with the above precautions was so weak as to necessitate long exposures of 100 hours or more, and even then the resulting photographs were faint compared with those obtained by blue light with shorter exposures.

The photographs reveal unmistakable structure in the spectra. The main emission is seen to be confined to two broad bands lying in the red-orange and in the yellow-green parts of the spectrum, between wave-lengths 655—625 and 605—560 μμ. The latter band particularly shows developed a finer structure of narrower bands, the greatest intensity being on its long wave-length side. Beyond these two strong fluorescence regions towards the blue, other bands,

FIG. 2.



Fluorescence and absorption in red of NO_2.

Owing to difficulties of reproduction the full detail of the fluorescence spectra is not apparent in the figure. A careful measurement of the original negatives has, however, revealed absolute identity of wave-length and structure of the blue and violet fluorescence spectra.

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spaced fairly regularly, are faintly discerned. A careful examination of the " blue " and " violet " fluorescence spectra has shown them to be identical in structure, and to extend between the same limits, though there is a very important difference in the distribution of intensity. Thus in the case of the " blue " fluorescence the maximum intensity occurs in the red band, imparting a general orange-red tint to the luminescence. On the other hand, in the case of the " violet " fluorescence, the intensity of the red band is so much diminished that it is practically invisible to visual spectroscopic observation, and the greenish-yellow band, being apparently unaffected, determines the predominating colour.

Photographs of the absorption spectrum of nitrogen peroxide in the red and yellow were made with the same setting of the spectrograph, for comparison with the fluorescence spectra, in order to see if the structure of the latter was that of the impressed absorption spectrum. From a comparison of these spectra shown in Fig. 2, it will be seen that, although similarities exist, the structure of the fluorescence spectrum is, in part at least, independent of the structure of the absorption spectrum.

The fluorescence was found to be unpolarised. This observation is in agreement with the comparatively long life of 5×10^{-8} sec. found for the excited molecule, and in this respect, and also in the comparatively great width of its emission bands, the fluorescence differs from the scattered radiation of the Raman effect. These facts, and the persistence of the fluorescence at high pressures, are indeed all in favour of the conclusion that in the pure gas the NO_2 molecule, excited by the absorption of blue or violet light, may suffer many molecular encounters before it re-emits its energy. This will have the effect of partly obliterating the fine structure, and would account for the rather wide diffuse bands observed.

Fluorescence and Photochemical Activity.

From a knowledge of the magnitudes of the quanta of the exciting and fluorescent radiation, we can calculate the quantity of energy degraded to heat as vibration and rotation within the molecule. In accordance with the principles developed in Part III (*loc. cit.*), this localised heat energy is available for chemical reaction if it equals or exceeds in magnitude the quantity, $26{,}000/N$ cals., required for the endothermic change, N being the Avogadro number. Thus, if the excited peroxide molecule makes a favourable collision with a second non-excited molecule, such that this quantity of energy at least is degraded to heat, we may expect reaction to occur. In such a case, fluorescence will be absent, since the excited molecule is destroyed by the reaction, and the excess energy must

remain located in the reaction products and appear as heat in the system. On the other hand, if less than $26{,}000/N$ cals. of energy are available for the two colliding molecules, the collision will be unfruitful of reaction, and fluorescence may follow.

Now the limit of fluorescence caused both by blue and violet light lies at *ca.* 655 μμ. With blue light (436 μμ) the maximum energy which remains in the molecule is therefore $(65{,}700-43{,}500)/N = 22{,}200/N$ cals., a quantity insufficient for reaction and far outside the range of probable supplementary thermal activation. There is thus no observable photochemical effect in blue light, and a strong fluorescence. With violet light (406 μμ) the maximum energy which can remain in the molecule is $70{,}100-43{,}500/N = 26{,}600/N$ cals. In this case the molecule is thus capable of reaction : other molecules retaining a slightly less favourable amount of thermal energy will also be on the brink of decomposition, and susceptible of reaction upon only a very slight supplementary activation by the colliding molecule.

If we assume the value of 5×10^{-8} sec. determined above for the life of the excited peroxide molecule, we may calculate that at 10 mm. pressure it will make some 4 or 5 collisions during its period of excitation, and at higher pressures proportionately more. Small amounts of auxiliary activation up to $900/N$ cals. or so will generally be available on the course of 4 collisions. This quantity is sufficient to cover the whole of the supplementary activation required by any molecule excited by violet light to the condition of emitting the red fluorescence, so that there is a strong probability that such molecules at pressures exceeding 10 mm. will react before fluorescence can occur. In this way we can explain the relative weakness of the red-orange fluorescence band between 655 and 625 μμ produced by violet light.

We thus see that with violet light, photochemical activity is restricted to molecules excited to the condition of red fluorescence, since those capable of emitting the yellow-green fluorescence (605—560 μμ) would require much greater auxiliary activation than is available from thermal sources. This is in harmony with the limited photochemical activity already found for violet light (Part II, *loc. cit.*), and there is thus indicated spectrally a slight thermal activation for the photochemical reaction with violet light, involving a small temperature coefficient, as has already been concluded on other grounds (Part III, *loc. cit.*).

Fluorescence with Ultra-violet Light.—It follows from the ideas developed above that fluorescence and photochemical activity are respectively conditioned by the stimulation of the electronic and of the vibration–rotation degrees of freedom of the molecule. It is clear, therefore, that fluorescence is not necessarily alternative to

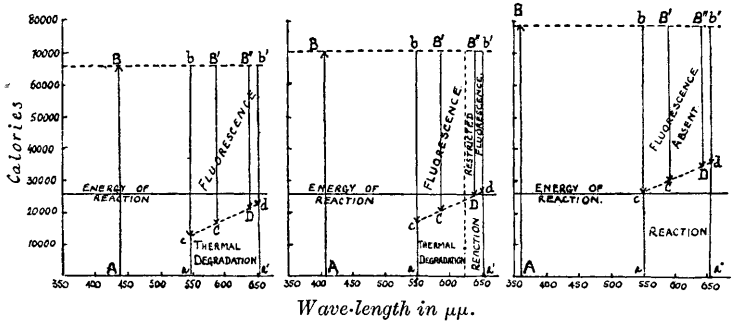
chemical reaction, although by virtue of the fact that at pressures over 1 mm. the excited and chemically active molecule makes more than one collision in its lifetime, it usually happens that reaction occurs before de-excitation by fluorescence can take place. We may conceive, however, that at pressures between 1 and 10 mm. a certain small residue of excited molecules will escape collision during their lifetime, and these will fluoresce before reaction occurs. Such molecules will retain their thermal energy of vibration and rotation after fluorescence, and will still be in a position to react chemically when a collision is later effected. Now, with ultra-violet light of wave-length 365 $\mu\mu$, the quantum efficiency of the photochemical reaction is very closely 2; consequently, every excited molecule reacts upon subsequent collision, and therefore, except for the small residue of molecules mentioned above, which escape reaction during their period of excitation, the possibility of fluorescence is absent. This conclusion is in accord with the fact that originally no fluorescence was observed with ultra-violet light. In view of the above consideration, however, it was thought that a slight residual fluorescence should still be detectable, and it was therefore determined to seek the effect. The bulb method described in the earlier part of this paper was used, the pressure of the nitrogen peroxide being about 10 mm. The source of light was again the mercury-vapour lamp, used in conjunction with a Wratten 18a ultra-violet filter, and special precautions were taken for excluding all stray light from the apparatus. By this means a glow of a yellow tint was obtained in the nitrogen peroxide which was so faint as to be almost at the limit of visibility, although the beam of exciting light was in this case stronger than those employed to stimulate the " blue " and the " violet " fluorescence. The effect was if anything strongest at a pressure somewhat less than the maximum pressure of 10 mm. which could be obtained in the bulb, and although this could not be observed quantitatively it was confirmed by independent observers.

This experiment, which was suggested by the above conclusions respecting the independence of the states of excitation and photochemical activation, thus gives confirmatory evidence of their essential correctness. The almost complete absence of fluorescence with ultra-violet light of wave-length 365 $\mu\mu$ shows that the excited molecules practically all react before they can emit their energy as fluorescence, and is in agreement with the fact that this light exhibits practically the maximum quantum efficiency of 2. The very faint residual fluorescence which is at a maximum at some pressure between 1 and 10 mm., at which the nitrogen peroxide is still known to decompose with the same quantum efficiency, is evidence that even after fluorescence the molecule is still chemically

active by virtue of the vibrational–rotational energy retained in the system. The yellowish tint of the fluorescence is also in accord with the view that molecules excited by ultra-violet light tend to give out the same fluorescence spectrum as those excited by blue and violet.

The relationships discussed above are illustrated quantitatively in Figs. 3*a*, 3*b*, and 3*c*. These diagrams are in no sense to be regarded as complete, and are meant to illustrate the principle involved rather than any exact formulation of the energy levels of the molecule. (Any attempt at the latter must, of course, await the elucidation of the complicated absorption spectrum of nitrogen peroxide.) The ordinates represent the quantum magnitudes of the exciting and the fluorescent radiation, and the associated

FIG. 3*a*. FIG. 3*b*. FIG. 3*c*.



thermal degradation involving vibrational levels within the molecule expressed in terms of $Nh\nu$ and measured in calories. Along the abscissæ are plotted corresponding wave-lengths. The energy of the exciting radiation is represented by AB, and the energies of the two fluorescence maxima by $B'C$ and $B''D$. The whole fluorescence region, or potential fluorescence region, is represented by the area $bb'cd$, which should be variously shaded to represent the variation in intensity of the fluorescence spectrum. Below this, the area $aa'cd$ represents the energy degraded thermally which is associated with the various vibrational and rotational degress of freedom in the molecule. Of these, two suggested vibrational levels are indicated at C and D corresponding to the fluorescence maxima at 640 and 590 μμ whose energy difference (3800 cals.) corresponds with that of the absorption maxima of nitrogen peroxide at 3·38 and 6·11 μ (3760 cals.) found by E. Warburg and Leithauser (*Sitzungsber. K. Akad. Wiss. Berlin*, 1908, 148). It will be seen that the same electron transition is assumed in each of the three diagrams, associated with different vibrational levels for the blue, violet, and ultra-violet excitation. Although this is definitely indicated for

blue and violet light by the identity of their fluorescence spectra, it is admittedly an assumption for the case of the ultra-violet, but it is perhaps not ill-founded in view of the successful prediction of the residual fluorescence in the latter case, particularly as this fluorescence has essentially the same tint as in the other cases.

Thus, to summarise, excitation with the blue light (Fig. 3*a*) is associated with insufficient thermal degradation for chemical reaction, and de-excitation occurs exclusively by fluorescence. With violet light (Fig. 3*b*) the thermal degradation for some molecules surpasses, and for some others approaches closely, the quantity required for the endothermic decomposition, and for the latter the slight supplementary activation required is in general available during their life. With these, therefore, reaction occurs and fluorescence is prevented; with others whose thermal degradation is outside the range of probable supplementary activation, chemical reaction cannot occur. Fluorescence is therefore restricted in the red and unaffected in the yellow regions.

With ultra-violet light (Fig. 3*c*) thermal degradation is in all cases sufficient to supply the necessary energy for reaction without supplementary activation, and, except for a very slight residual effect corresponding to those excited molecules which escape collision during their lifetime, fluorescence is impossible, since the excited molecule reacts on its first collision.

The Energy of Thermal Activation.

In the thermal decomposition of nitrogen peroxide we distinguish the quantity 32,000 cals. as the energy of activation of the homogeneous bimolecular reaction. This quantity, which is calculable both from the temperature coefficient and from the speed of reaction, is for bimolecular reaction apparently mainly drawn from the energy of the translational degrees of freedom, when two molecules of peroxide make a sufficiently violent collision. Since, however, we have seen that reaction follows when the vibrational-rotational degrees of freedom of one of the colliding molecules hold the energy of decomposition, 26,000 cals., it would appear that a collision involving 32,000 cals.—the energy of activation—is just sufficient to stimulate vibration within the molecule to the extent of 26,000 cals. required for reaction.

If these views are generalised for homogeneous bimolecular reactions, they suggest that the energy of activation represents the minimum collisional energy required to activate the vibrations of one of the participating molecules up to an energy content equal to the energy of reaction of some primary endothermic change. In certain cases, *e.g.*, that of the decomposition of nitrogen peroxide, this primary change will represent the ultimate extent of the

reaction; but in other instances, *e.g.*, in the decomposition of chlorine monoxide, its product may be unstable, and the primary change will then be followed by others which mask the energy relationships of the primary reaction and may even involve a net exothermic effect.

The relationship now disclosed between fluorescence and photochemical activity was predicted by a comparison of the kinetics of the homogeneous thermal and photochemical decompositions of nitrogen peroxide (Part III, *loc. cit.*), and the experimental confirmation of these predictions may be taken as establishing the identity of the immediate effects of thermal and photochemical activation. In addition, the present work suggests that the molecule of nitrogen peroxide is active for decomposition when it holds within its vibrational–rotational degrees of freedom the energy required for endothermic change.

It is then seen that from chemical considerations we are led to deduce both (1) the limited availability of absorbed light energy, and (2) the general recognition of associated levels of thermal and electronic vibration within the molecule, which may be severally stimulated by the absorption of a single light quantum—a conclusion in full accord with the modern developments of molecular spectroscopy.

Summary.

The fluorescence predicted for nitrogen peroxide by the theoretical considerations developed in Part III (preceding paper) has been detected and photographed. Blue light (436 μμ) produces an orange luminescence, and violet light (405 μμ) a greenish-yellow luminescence. The spectra show identical structures, involving in the main two wide maxima at *ca.* 640 and 590 μμ, respectively, but with violet light the relative intensity of the former maximum is much less than with blue light. Under similar conditions there is an extremely faint fluorescence with ultra-violet light of 365 μμ. The fluorescence appears at a pressure of about 1 mm. and is still apparent at pressures as high as 100 mm.; it is rapidly quenched by oxygen at 20 mm., a result which leads to an estimate of 5×10^{-8} sec. as the life of the excited molecule.

The energy relationships confirm the theoretical conclusions of Part III of this work, and a general scheme connecting fluorescence with photochemical activity in nitrogen peroxide is suggested. The bearing of this result on the nature of the thermal heat of activation is further discussed.

The author is indebted to the Government Grant Committee of the Royal Society for a grant which has covered the main cost of this work, to Professor T. M. Lowry, F.R.S., for sympathetic aid

in granting facilities for carrying it out, and to his friends, Mr. C. P. Snow and Dr. A. M. Taylor, for valuable criticisms and suggestions.

DEPARTMENT OF PHYSICAL CHEMISTRY,
CAMBRIDGE UNIVERSITY. [*Received, April 25th,* 1929.]