[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, PRINCETON UNIVERSITY]

PHOTOCHEMICAL DECOMPOSITION OF NITROSYL CHLORIDE

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The decomposition of nitrosyl chloride under action of light has been in the past an object of some study. Kiss[1] has shown that visible light produced decomposition, but that since the nitric oxide and chlorine formed recombined in the dark, the decomposition was incomplete, a stationary state being finally reached. The temperature coefficient of the photochemical reaction was determined by him to 1.0 over the temperature range 0–78°. Bowen and Sharp[2] have carried out a determination of the quantum yield which led them to believe that 0.5 molecule was decomposed per light energy quantum absorbed. The light was used from a carbon arc and the spectral regions 4380–5000 and 4480–5200 Å. were isolated by means of filters. These authors found also that the quantum yield was unaffected by the degree of decomposition, which was followed up to 10%. They failed to notice any action of "red" light and attributed this failure to a very weak absorption by nitrosyl chloride in this spectral region. The reaction mechanism offered in explanation of their results included a primary dissociation of a nitrosyl chloride molecule into nitric oxide and a chlorine atom, followed by some secondary reactions of the chlorine atom resulting in a partial recombination of nitric oxide and chlorine. Such a mechanism, while accounting formally for the deficiency of the quantum yield from the value two, is quite unsatisfactory on closer consideration because it fails to account for the independence of the quantum yield from the degree of decomposition, thus from the concentrations of nitric oxide and chlorine present, as observed by these authors.

The absorption spectrum of nitrosyl chloride has also received some attention. Magnanini[3] finds that it consists of weak bands in the region 5300–6200 Å. with a strong absorption setting in below 5300 Å. Dr. G. Cario[4] and the writer carried out some time ago[5] a preliminary investigation of the absorption spectrum of nitrosyl chloride. It was found to have a banded structure, bands being observed even below 4000 Å., although no definite information with respect to the existence of fine structure in these bands was obtained.

The behavior of nitrosyl chloride seemed thus to offer a striking simi-

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[1] Kiss, *Rec. trav. chim.*, **42**, 665 (1923).

[2] Bowen and Sharp, *J. Chem. Soc.*, **127**, 1026 (1925).

[3] Magnanini, *Z. physik. Chem.*, **4**, 427 (1889).

[4] Of Göttingen; at the time an International Research Fellow in Princeton.

[5] Unpublished.

larity to the decomposition of ammonia,[6] both substances having banded spectra and showing on illumination a deficient quantum yield unaffected by the presence of the reaction products and only very slightly (NH_3) or not at all (NOCl) affected by temperature. The deficiency of the quantum yield in both reactions, although receiving some consideration, has never been satisfactorily explained and further work in this direction seemed desirable. The nitrosyl chloride decomposition was chosen here because it has been less fully investigated and offers fewer experimental difficulties.

Experimental Details

Decomposition of nitrosyl chloride was measured manometrically. The pressure changes were followed by means of a quartz spiral manometer of the Bodenstein type, used as a zero instrument and connected to a differential manometer filled with α-bromonaphthalene. With this system pressure changes of less than 0.1 mm. of mercury could be measured. As the reaction vessel a pyrex tube 35 × 120 mm. with sealed-on polished pyrex plates was used. Nitrosyl chloride was prepared from nitrosylsulfonic acid and dry sodium chloride. It was dried over phosphorus pentoxide and purified by repeated vacuum distillations. Before an experiment the reaction vessel was evacuated by a high vacuum mercury pump, was then filled with nitrosyl chloride and finally sealed off. The details of the apparatus and of the optical system will be seen from Fig. 1. The second diaphragm separated a parallel beam of light narrow enough so that all light passing through the reaction vessel fell on the light-sensitive surface of a Moll surface thermopile placed immediately behind the vessel. Two light sources were used in the present work: a 1000-watt tungsten projection lamp and a horizontal mercury quartz lamp. The thermopile–galvanometer system was calibrated by means of a standard carbon filament lamp furnished by the Bureau of Standards. Various spectral regions were isolated by means of light filters composed of Corning colored glasses and suitable solutions. The "red" filter consisted of the "H. R. Red 100 per cent." glass and a ferro-ammonium sulfate solution. The "orange" filter was of the "Heat Resisting Yellow" glass and the same solution as the red filter. The "green" filter contained a didymium "G 55 P" glass, a "Sextant Green" glass and a solution containing ferric and nickel chlorides;

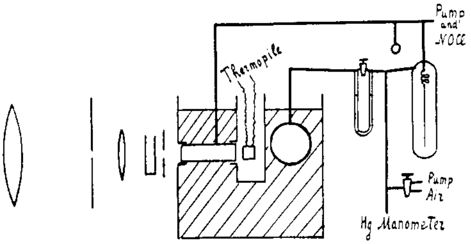

Fig. 1.

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[6] Warburg, *Sitzb. preuss. Akad. Wiss.*, 746 (1911); 216 (1912); Kuhn, *J. chim. phys.*, **23**, 521 (1926); Bonhoeffer and Farkas, *Z. physik. Chem.*, **134**, 337 (1928).

the "blue" filter a "Purple G 55" glass, a cuprammonium sulfate solution and a quinine sulfate solution. The "u. v." filter was a nickel oxide glass.

Results

To determine the average wave length transmitted through the filters and absorbed by nitrosyl chloride, the transmission curves of the filters as well as the absorption curve of nitrosyl chloride (at 620-mm. pressure) have been measured with a Koenig–Martens spectrophotometer. The light energy distribution in the spectrum of the tungsten lamp has been calculated assuming that the filament is at 2800° and that it emits as a gray body. By combining these three curves, the curves of Fig. 2 have been obtained which represent (in arbitrary units, not the same for different filters) the spectral distribution of light energy absorbed by nitrosyl chloride. These curves served to determine the average wave lengths used in calculations of the quantum yield. In conjunction with the mercury lamp the "blue" and the "green" filters are better than 99% monochromatic (4358 and 5461 Å., respectively), whereas in the light transmitted by the "orange" filter and absorbed by nitrosyl chloride about 90% belongs to the yellow lines 5769 and 5790 Å., 10% to the green line 5461 Å. and only very little to the red mercury lines. The ultraviolet filter, according to photographs taken with a quartz spectrograph, transmits an essentially monochromatic light of the 3650 Å. mercury line. With these filters

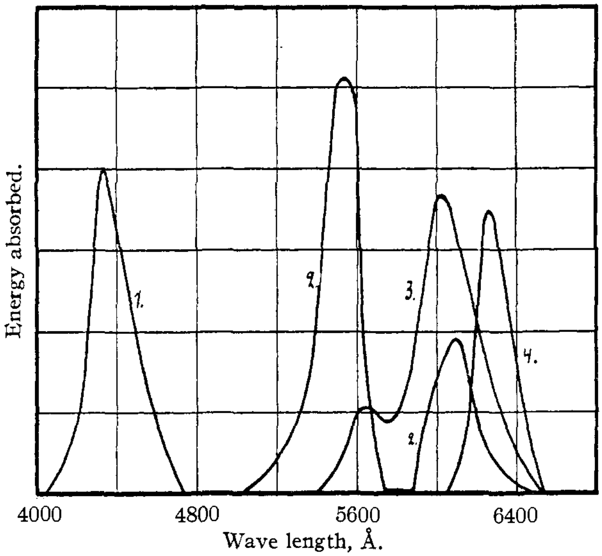

Fig. 2.—Light energy transmitted through filters and absorbed by nitrosyl chloride. 1, "Blue" filter; 2, "Green" filter; 3, "Orange" filter; 4, "Red" filter.

measurements of the quantum yield have been made and are reproduced in a summarized form in Table I. Each of the values for the decomposition rate there presented is a mean of 4 to 8 independent runs, the average deviation of the single runs from the mean amounting to about 8%. Since, in order to obtain as good a monochromasy as possible, the transmissions of the filters have been sacrificed to a considerable extent and the resulting decomposition rates were very slow, it was not possible to neglect the rate of the opposed dark reaction as Bowen and Sharp have done. Instead, the thermal reaction was measured before and after each illumination and the mean was used to correct the rate obtained on illumination. The taking of an arithmetic mean involves here an error since the thermal reaction is of the third order,[7] but the whole correction being small, this error can be neglected.

The light energy absorbed by nitrosyl chloride was determined by measuring the thermopile deflections while the vessel was alternately filled with nitrosyl chloride and emptied, the reactant being frozen out by liquid air. Considerable difficulty was experienced in the beginning since the absorption with the red filter amounted to only about 3% of the transmitted energy while the fluctuations in the lamp intensity exceeded 5% on account of the line voltage variations. This was overcome by introducing a second thermopile (a linear one of the Coblentz type) placed at some distance from the lamp and taking simultaneous readings with both thermopiles. The readings of the linear thermopile were assumed to be proportional to the lamp intensity and served to reduce the readings of the Moll thermopile to a constant lamp intensity. The values presented in Table I are the

TABLE I

QUANTUM YIELD IN THE DECOMPOSITION OF NITROSYL CHLORIDE ($T = 21.7°$)

					Rate		Energy absorbed		
Lamp	Filter	Wave length (mean), Å.	Gas	Mm.	Mm. Hg per hr.	Moles per sec. $\times 10^9$	Mm. on the scale	Cal. per sec. $\times 10^7$	Molecules, quanta
W	Red	6350	NOCl	615	1.49	5.61	7.3	1.13	2.2
W	Orange	6000	NOCl	615	6.39	24.2	36.1	5.58	2.0
W	Green	5600	NOCl	615	1.49	5.61	9.3	1.44	1.9
W	Blue	4350	NOCl	615	2.17	8.22	16.6	2.40	2.2
W	Blue	4350	NOCl	87	2.02	7.62	14.4	2.22	2.2
W	Red	6350	NOCl	87	0.258	0.973			
W	Blue	4350	NOCl N_2	87 606	1.89	7.17	14.4	2.22	2.0
W	Red	6350	NOCl N_2	87 606	0.250	0.945			
Hg	Orange	5760	NOCl	685	1.07	4.15	6.5	1.00	2.0
Hg	Green	5461	NOCl	685	0.54	2.05	3.0	0.46	2.3
Hg	Blue	4358	NOCl	685	1.14	4.30	8.2	1.26	2.2
Hg	U. v.	3650	NOCl	685	1.14	4.30	8.0	1.23	2.7

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[7] Trautz, *Z. anorg. Chem.*, **97**, 241 (1916); **110**, 248 (1920).

means of some 15 readings each, the average deviation from the mean being about 10% with the red and less with other filters. In calculations of the absorbed light energy a correction of 20% was introduced which took care of the reflection losses on the rear plate of the reaction vessel and on a quartz plate protecting the surface of the thermopile.

The absorption spectrum of nitrosyl chloride was further investigated,[8] using a Hilger E2 quartz spectrograph and a plane grating with glass optics giving a dispersion of about 3.5 Å. per mm. in the first order.

The absorption by nitrosyl chloride was found to begin above 6300 Å. and to increase gradually toward the ultraviolet. Several fairly distinct maxima of absorption, however, have been observed. They are situated at about 5990, 4690, 3300 Å. and in the extreme ultraviolet (<2500 Å.). The spectrum consists on the long wave length side of numerous fairly distinct bands which gradually fade out, the appearance of the spectrum toward the shorter wave lengths becoming more and more continuous. In the region 4000–4500 Å., only using contrast photographic plates and particularly favorable concentration of nitrosyl chloride, the existence of bands could be established. In the ultraviolet below the absorption maximum at 3300 Å. no banded structure could be detected at all.

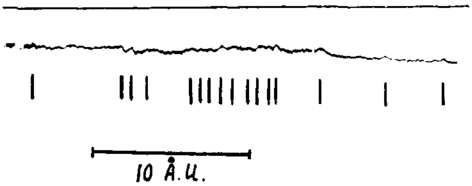

Fig. 3.

The spectrum of nitrosyl chloride thus seemed to offer the same peculiarities as the "predissociation" spectra discussed by Henri.[9] In order to ascertain this, a section of the spectrum between 4100 and 4350 Å. has been photographed in the third order of the grating, thus with a dispersion of 1.17 Å. per mm. Figure 3 is a small section of the photometer record of the plate[10] which shows that the absorption spectrum in this region has distinct line structure, although the latter is very faint. Figure 3 shows as well a reproduction of the same section of the spectrum made by hand from visual study of the plate.

Table I shows that the quantum yield observed is very near to two molecules per quantum. Indeed, if the value for the wave length 3650 Å. be excluded—we shall return to it later—the mean quantum yield is calculated to 2.1, thus a value within 5% of the theoretical 2.0. The experimental values show a slight trend to increase toward the shorter wave lengths. This is due undoubtedly to the circumstance that the correction

[8] The author is greatly indebted to Dr. Joseph C. Elgin of this Laboratory for his valuable assistance in this part of the work.

[9] V. Henri, "Structure des Molecules," Paris, 1925.

[10] A Siegbahn microphotometer of the E. I. du Pont de Nemours and Co. Experimental Station, Wilmington, Delaware, has been used for the purpose.

for reflection on the glass has been applied uniformly to all values, whereas in reality the losses by reflection and scattering increase toward the ultraviolet. The value 2.7 for the 3650 Å. wave length is the only one which deviates considerably from two. Most likely this is partially due to light of this wave length being already appreciably absorbed in the thick pyrex plates forming the ends of the reaction vessel, partially to a still further increased correction for reflection and scattering. Table I further shows that the presence with nitrosyl chloride of nitrogen in a seven-fold concentration does not in the least affect the quantum yield—neither with the blue nor with the red light.

The quantum yield obtained, 2.1, is in considerable disagreement with the value 0.48 of Bowen and Sharp. The cause of this discrepancy cannot be definitely established. The neglect to take into account the dark rate could hardly account for such a large error in Bowen and Sharp's measurements and it is more likely that either in the calibration of the thermopile by Leslie cubes some mistake was made, or that the total light energy absorbed by nitrosyl chloride was determined incorrectly.

The finding of the quantum yield of two removes the necessity of introducing into the mechanism of the reaction some secondary processes reforming nitrosyl chloride. The decision must be made between the two alternate possibilities

$$\begin{aligned} \mathrm{NOCl} + h\nu &\longrightarrow \mathrm{NO} + \mathrm{Cl} \\ \mathrm{Cl} + \mathrm{NOCl} &\longrightarrow \mathrm{NO} + \mathrm{Cl_2} \end{aligned}$$

and

$$\begin{aligned} \mathrm{NOCl} + h\nu &\longrightarrow \mathrm{NOCl}^{*} \text{ (excited)} \\ \mathrm{NOCl}^{*} + \mathrm{NOCl} &\longrightarrow 2\mathrm{NO} + \mathrm{Cl_2} \end{aligned}$$

The observed absence of influence of nitrogen on the reaction velocity could be interpreted as favoring the first possibility but two other facts decidedly support the second scheme. The first is the indication that nitrosyl chloride can be decomposed by light energy quanta smaller than its heat of dissociation. The latter is calculated from the heat of dissociation of chlorine, 56.9 cal.,[11] and the heat of formation of nitrosyl chloride, 18 cal.,[12] to be 46.4 cal., thus corresponding to a wave length of 6130 Å., whereas in experiments wave lengths up to 6400 Å. ($<$44.3 cal.) were found to be effective (see Fig. 2). More important is the evidence offered by the observations of the absorption spectrum of nitrosyl chloride. There is no doubt that this spectrum consists in the region 5500–6500 Å. of bands with line structure due to quantization of rotation. Furthermore, the plate here reproduced shows that such a structure is retained in bands of much shorter wave length. Thus, for the wave lengths employed in the present work the spectral evidence favors the formation of excited nitrosyl chloride molecules as the primary process or absorption of light energy quanta.

[11] Kuhn, *Naturwissenschaften*, **14**, 600 (1926).

[12] Trautz and Hinck, *Z. anorg. Chem.*, **97**, 127 (1916).

The excited molecule must collide with another nitrosyl chloride molecule to yield the decomposition products.

The presence of structure in the visible absorption bands of nitrosyl chloride of course does not preclude that at shorter wave lengths the phenomenon of predissociation may not show itself. The observations recorded here rather support this supposition, although indicating that the "predissociation" state of a molecule is not necessary for its chemical activation.

Summary

1. Quantum yield measurements in the nitrosyl chloride decomposition show that the quantum yield is constant and is equal to two with wave lengths from 6300 to 3650 Å.

2. Study of the absorption spectrum of nitrosyl chloride indicates that it has banded structure throughout the visible part of the spectrum.

3. It is concluded that the mechanism of nitrosyl chloride decomposition consists in formation of an excited molecule and in a subsequent decomposition on collision.

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THE SPECIFIC HEATS OF GASES AT HIGH PRESSURES. I. METHOD AND APPARATUS AT ROOM TEMPERATURE[1]

BY NORMAN W. KRASE AND B. H. MACKEY[2]

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Introduction

An obvious need for data regarding the properties of gases at high pressures has made it desirable to develop a method for measuring specific heats. This is the first of a series of papers from this Laboratory reporting methods and measurements. It is confined to a description of a continuous flow, adiabatic gas calorimeter suitable for measuring specific heats up to 1000 atmospheres at ordinary temperature.

The literature contains practically no data on this important property of gases above 200 atmospheres. Holborn and Jacob[3] have published results on air but their apparatus could not be used over the entire range of pressures. An excellent review of the existing data and methods has recently been published.[4]

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[1] Submitted in partial fulfilment of the requirements for the degree of Ph.D. in Chemistry in the Graduate School of the University of Illinois.

[2] Research Assistant in Gas Engineering. University of Illinois, Engineering Experiment Station. Work of B. H. M. published by permission of the Director.

[3] Holborn and Jacob, *Berl. Ber.*, **1**, 213 (1914).

[4] Partington and Shilling, "The Specific Heat of Gases," E. Benn, London, **1924**.