

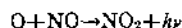
Role of Nitric Oxide in the Thermal Decomposition of Nitrous Oxide*

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The rates of decomposition of N_2O and of formation of NO were measured simultaneously in a static system. NO yields at the beginning of reaction are as high as 50 to 60%, but NO quickly inhibits its own further formation. From initial NO yields, information about the reaction of oxygen atoms with N_2O and about wall recombination was obtained. Limiting NO pressures for complete N_2O decomposition were interpreted in terms of the reaction $NO+O+M \rightarrow NO_2+M$, and its rate constant was calculated. The effect of increased surface area and of added gases was studied. The halogens were found to be efficient inhibitors of NO formation.

The chemiluminescence of reacting N_2O was observed and its dependence on temperature, pressure, and added gases studied. All evidence points to the reaction



as its origin. Inhibition of NO formation and of chemiluminescence is shown to be closely related.

INTRODUCTION

AS an example of a unimolecular reaction, the thermal decomposition of nitrous oxide has been the subject of many investigations.¹ It would seem that the processes of collisional activation, deactivation, and decomposition of a linear, triatomic molecule should now be generally understood, but such is not the case. During the past three years, several further attempts at correlating old data and new theories have been made,²⁻⁴ but their success has not been spectacular. This is due in part to the unreliability of much of the old experimental data, and to oversimplification of the reaction mechanism. It is the latter reason which formed our point of departure.

Briner⁵ first presented quantitative data for the formation of NO as a by-product of the N_2O decomposition. He found yields of NO up to 23% of the N_2O decomposed, but his data, obtained in a flow system, can not be interpreted to give reliable rate information. Musgrave and Hinshelwood⁶ studied NO formation in static systems and found that much NO was made during the early stages of the reaction, that it was not destroyed later, but seemed to inhibit its own further formation. At 722°C, 400 mm Hg of N_2O , at 5.5% decomposition, gave 13% ($NO+\frac{1}{2}N_2$) and 87% ($N_2+\frac{1}{2}O_2$), whereas at 96% decomposition, 2.7% ($NO+\frac{1}{2}N_2$) and 97.3% ($N_2+\frac{1}{2}O_2$) were formed. The origin of the NO was thought to be the reaction



* Presented in part at the Symposium on the Chemistry of the Oxides of Nitrogen, sponsored by the Office of Ordnance Research, Chicago, Illinois, September, 1953.

¹ For a recent review see H. S. Johnston, *J. Chem. Phys.* **19**, 663 (1951).

² H. S. Johnston, *J. Chem. Phys.* **20**, 1103 (1952).

³ L. S. Kassel, *J. Chem. Phys.* **21**, 1093 (1953).

⁴ H. S. Johnston and J. R. White, *J. Chem. Phys.* **22**, 1969 (1954).

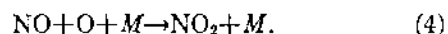
⁵ Briner, Meiner, and Rothen, *J. Chem. Phys.* **23**, 609 (1926).

⁶ F. F. Musgrave and C. N. Hinshelwood, *Proc. Roy. Soc. (London)* **A135**, 23 (1932).

after the initial step



and the inhibitory effect of NO for its own further formation could be explained by



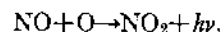
Pease⁷ later proposed a chain scheme which required the initial step to be



This is energetically prohibitive and was rigorously ruled out as a result of recent N^{15} tracer experiments by Friedman and Bigeleisen.⁸

It was the aim of this investigation to help clarify the mechanism of the N_2O decomposition and obtain rate constants for the various reaction steps, particularly those involving NO or atomic oxygen. Experimentally, this was done by accurate measurement of NO formed and N_2O decomposed as a function of time, initial temperature, and pressure, the presence of added gases, and the nature and amount of surface area.

The importance of reaction (4) led to the search for chemiluminescence resulting from excited NO_2 as observed by Gaydon⁹ in flames with added NO or in the air afterglow. Such a luminescence was indeed observed at any temperature at which N_2O decomposed at a fairly rapid rate, e.g., at 630°C and 1 atm. Later, we become aware of Whittingham's¹⁰ brief account of the luminescent decomposition of nitrous oxide and its interpretation by



Whittingham's observation that the glow could be obtained only at 850°C or above can not be accepted as our results will show.

⁷ R. N. Pease, *J. Chem. Phys.* **7**, 749 (1939).

⁸ L. Friedman and J. Bigeleisen, *J. Am. Chem. Soc.* **75**, 2215 (1953).

⁹ A. G. Gaydon, *Proc. Roy. Soc. (London)*, **A183**, 111 (1944).

¹⁰ G. Whittingham, *Nature* **159**, 232 (1947).

In a simple photomultiplier-recorder setup, we studied this N_2O reaction glow in a static system as function of time, pressure, temperature, and presence of added gases.

EXPERIMENTAL

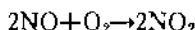
Rates of N_2O Decomposition and NO Formation

A conventional high-vacuum system was used, consisting of forepump, Hg diffusion pump, traps, mixing vessels, Hg manometers, McLeod gauge, and calibrated oil manometer. 500-cc spherical quartz vessels served as reaction flasks in a homemade furnace using helical chromel resistance elements.

Temperature measurements were taken with several Pt-10% Rh thermocouples placed at the outside of the reaction vessels and where possible, in a thermocouple well extending to the center of the flask.

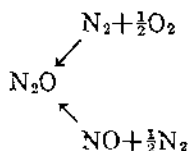
The rate of decomposition of N_2O was followed by its pressure increase using Hg or oil manometers and making correction for the cold space.

The rate of formation of NO was obtained more laboriously by allowing the reaction to proceed for the desired time, expanding the gas mixture into an evacuated optical absorption cell and analyzing by spectrophotometric methods. Most of the details are described elsewhere.¹¹ Since much of this work dealt with the initial rate of formation of NO, it was necessary to analyze 0.1 to 0.3 mm Hg of NO with some accuracy. This was achieved by adapting a Beckman long path cell (50 cm) for gas analysis use. Careful calibration showed that at the low pressures of NO_2 used (0 to 2 mm Hg), Beer's law was well obeyed at 4000 Å, since the N_2O_4 pressure was negligible. In actual analyses, O_2 was added to the gas sample to a pressure of 1 atmosphere and readings taken on a Beckman spectrophotometer, Model DU. The low rate of the reaction



at small NO concentrations made it necessary to wait 15 minutes to 2 hours for final readings to become constant.

Using the same cell with excess NO added to the gas sample made it possible to analyse small amounts of oxygen¹¹ (0.1 to 0.3 mm Hg) quite accurately and afforded an independent check of the method. Both ways of N_2O decomposition



give rise to a pressure increase of 50%, and p_{N_2O} decomposed = $p_{NO} + 2p_{O_2}$. The % N_2O decomposed was measured by its pressure increase on the oil manometer, and p_{NO} and p_{O_2} by the above optical method.

¹¹ F. Kaufman and J. R. Kelso, J. Chem. Phys. 23, 1702 (1955).

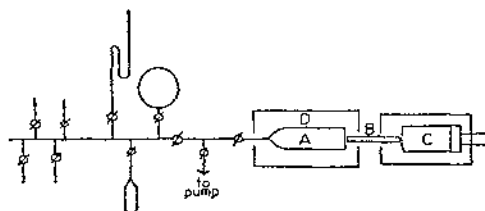


Fig. 1. Apparatus for luminescence experiments. A. Reaction vessel. B. Porcelain tube. C. Photomultiplier. D. Furnace.

At 653°C, $p_{N_2O} = 100$ mm, $t = 30$ sec:

p_{N_2O} decomposed = 0.36 mm Hg; $p_{NO} = 0.21$ mm;
 $p_{O_2} = 0.075, 0.085$ mm; $p_{NO} + 2p_{O_2} = 0.36$ to 0.38 mm.

At 758°C, $p_{N_2O} = 20$ mm, $t = 30$ sec:

p_{N_2O} decomposed = 0.64 mm; $p_{NO} = 0.32$ mm;
 $p_{O_2} = 0.155, 0.165$ mm; $p_{NO} + 2p_{O_2} = 0.63$ to 0.65 mm.

This agreement is excessively good, since, for such small amounts of NO or O_2 , the analyses are accurate to only about ± 5 to 10%.

LUMINESCENCE EXPERIMENTS

Figure 1 shows the apparatus. Cylindrical quartz vessels with plane windows were used. A small, concentric porcelain tube led to a photomultiplier tube, type 5819, which was energized by a conventional high voltage supply and operated at 700 to 1100 volts. Its output across a resistance of 5 to 20 000 Ω and capacitance of 0.1 to 10 microfarads was recorded by a Leeds and Northrup Speedomax Recorder (Azar) with variable range and suppression (1 to 20 millivolt range, 0 to 50 millivolt suppression). In some experiments, the signal was recorded photographically on a Tektronix Oscilloscope Model 513.

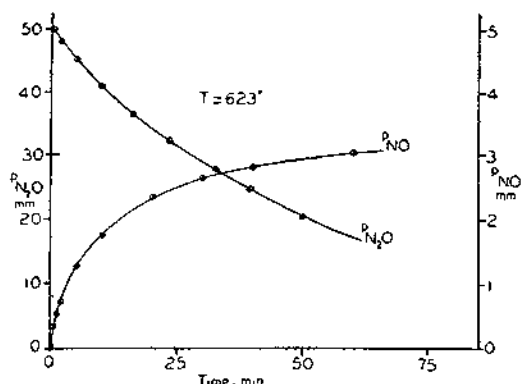
EXPERIMENTAL RESULTS

I. Rate of NO Formation

A. Initial Rates

A typical graph of N_2O disappearance and NO formation is shown in Fig. 2. The NO vs time curve shows the strong self-inhibition effect, i.e., its half-time of formation is about 8 minutes, whereas $t_{1/2}$ for the N_2O decomposition is 39 minutes. It was soon apparent, moreover, that the initial rate of formation of NO was considerably greater than earlier papers had indicated. A great effort was therefore made to determine accurately the fraction of N_2O which gives rise to NO at the start of the reaction.

The data in Table I represent several hundred experiments of durations 20 seconds to several minutes, under conditions of nearly linear rate of NO formation. Three observations can be made:

FIG. 2. Decomposition of N_2O and formation of NO as time.

1. Initially, up to 60% and probably more of the reacting N_2O produces NO.

2. At constant temperature, this fraction, $[dp_{NO}/dp_{N_2O}]_{t=0}$, increases with increasing pressure.

3. At constant initial N_2O pressure, the fraction increases slightly with increasing temperature.

The role of the surface was studied by filling the quartz flask with vycor chips and again measuring the initial rates of N_2O decomposition and of NO formation. From a determination of the average volume and size of these chips, it was found that the total surface area had been increased about 40-fold. It was apparent that the rate of formation of NO in the packed vessel was greatly reduced while the N_2O rate was only slightly increased. The possibility of surface decomposition of the NO formed could be ruled out when it was observed that much larger concentrations of NO than those produced would persist unreacted in the packed vessel for longer times under identical conditions.

Table II shows the results of several runs in the packed flask. The observed fraction, $[dp_{NO}/dp_{N_2O}]$,

TABLE I. Initial rates of N_2O decomposition and NO formation.*

T, °K	p_{N_2O} mm	$-dp_{N_2O}/dt$ mm/min	$+dp_{NO}/dt$ mm/min	$-dp_{NO}/dp_{N_2O}$
876	700	2.05	1.19	0.58
	380	0.83	0.48	0.58
	200	0.30	0.165	0.55
927	100	0.71	0.41	0.58
	50	0.25	0.130	0.52
	20	0.058	0.023	0.40
973	50	1.07	0.61	0.57
	20	0.26	0.117	0.45
	10	0.093	0.032	0.34
1031	30	2.54	1.41	0.56
	20	1.27	0.63	0.50
	10	0.44	0.177	0.40

* Papers by F. J. Lindars and C. N. Hinshelwood, Proc. Roy. Soc. (London) A231, 162, 178 (1955) reporting the measurement of NO formation have appeared since this was submitted for publication. Their lower initial rates of production of NO do not contradict our values, since they missed the initial NO rate because of its rapid formation and strong self-inhibition. This is why our p_{N_2O} or our temperatures are much lower than theirs.

is the ratio of NO formed in the packed vessel divided by N_2O reacted in the unpacked vessel, since the interpretation given below does not take into account the surface decomposition of N_2O which may proceed to $N_2 + \frac{1}{2}O_2$ by cleavage of N_2O and recombination of oxygen atoms.

B. Limiting Amounts of NO

In another series of experiments, amounts of NO were measured at long times of reaction, i.e., after decomposition of all the N_2O . The limiting pressures of NO, $p_{\infty}NO$, for varying initial p_{N_2O} , at two temperatures, are shown in Table III. $p_{\infty}NO$ increases with increasing p_{N_2O} and with increasing temperature. Its dependence on p_{N_2O} is less than linear and somewhat greater than square root. This is discussed further below.

C. Added Gases

Table IV shows the effect of O_2 , N_2 , He, and A on the initial NO and N_2O rates. The increase of the N_2O rate resulting from the added gases is in the order $He > O_2, N_2 > A$, in agreement with the data of Volmer

TABLE II. Initial rates of N_2O decomposition and NO formation in a packed vessel.

T, °K	p_{N_2O}	$-dp_{N_2O}/dt$ packed	dp_{NO}/dt packed	$-dp_{N_2O}/dt$ empty	$-dp_{NO}/dp_{N_2O}$ obs	$-dp_{NO}/dp_{N_2O}$ calc
927	50	0.53	0.015	0.25	0.06	0.056
	380	6.5	0.8	4.7	0.17	0.27
973	100	4.1	0.18	2.9	0.06	0.14
	20	1.4	0.07	1.27	0.055	0.042
1031	100	14.2	1.7	14.00	0.12	0.17

and Froehlich.¹² The initial NO yield, $-dp_{NO}/dp_{N_2O}$, is lowered in the same order in which the N_2O rate is increased.

The effect of inert added gases on the limiting pressure of NO is shown in Table V. The order of decreasing $p_{\infty}NO$ here is $A > He > N_2 > O_2$.

A few experiments with water vapor showed it to be much more efficient than any of the above gases in reducing $p_{\infty}NO$. At 980°K, 20 mm of water vapor lowered the limiting NO pressure for 380 mm of N_2O about 17%. The addition of several other compounds was also investigated where a more direct interference with the normal course of reaction might be expected. Among those were SO_2 , NH_3 , Cl_2 , and I_2 . The possible inhibition of NO formation by SO_2 could not be studied because of interference with the analytical method, but some photochemical results are given in the following.

Ammonia had a fairly strong inhibitory effect, 20 mm of NH_3 decreasing the limiting NO pressure of 380 mm of N_2O by about 40% at 980°K. This decrease is

¹² M. Volmer and H. Froehlich, Z. physik. Chem. B19, 85, 89 (1932).

actually the sum of two effects. Initially, NH_3 reacts quite rapidly and inhibits NO formation strongly. Within a short time, all the ammonia has reacted, and from then on, the decomposition takes its normal course except for the water vapor formed in the early stages. This description is supported by three experimental results:

1. The reduction of NO yield is larger near the start of reaction; runs of 10% decomposition showed a 50% decrease in NO when 20 mm of NH_3 were added initially.

2. Infrared analysis showed that all NH_3 had disappeared before 10% of the N_2O had decomposed.

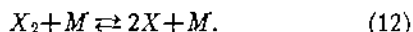
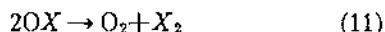
3. Photochemical experiments showed an induction period before the onset of the N_2O glow when NH_3 was added.

The most efficient inhibitors for NO formation were found to be the halogens. Atomic halogen is known to decompose N_2O catalytically in a bimolecular reaction. This catalytic reaction was recently re-examined in this laboratory¹³ and the experimental results were

TABLE III. Limiting pressures of NO.

$T = 973^\circ\text{K}$			$T = 1031^\circ\text{K}$		
$p_{\text{N}_2\text{O}}$ mm	p_{NO} mm	$k_4 \times 10^{-15}$ $\text{cc}^2 \text{ mole}^{-2} \text{ sec}^{-1}$	$p_{\text{N}_2\text{O}}$ mm	p_{NO} mm	$k_4 \times 10^{-15}$ $\text{cc}^2 \text{ mole}^{-2} \text{ sec}^{-1}$
51	3.37	7.6	10.5	1.55	5.9
98.5	4.84	7.7	20.	2.71	5.4
201	7.44	7.0	20.5	2.84	5.0
201.5	7.47	7.0	49.5	4.95	5.3
407	11.17	6.5	99.5	7.89	4.6
			204.	11.43	4.8
		av 7.2			av 5.2

found to be compatible with the scheme



Several experiments were performed at 973°K with 50 mm of N_2O containing from 1×10^{-4} to 1×10^{-2} mm of $\text{C}_2\text{H}_5\text{I}$. At this temperature, the small amount of ethyl iodide is decomposed within a small fraction of a second, and the resulting iodine is 98 to 100% dissociated into atoms. It was surprising to find that such trace amounts of I atoms would strongly inhibit the formation of NO. The pressure of atomic I necessary to decrease the initial NO yield to one-half its normal value turned out to be 3×10^{-3} mm Hg. At this concentration, the iodine catalyzed decomposition of N_2O accounted only for 10% of the total N_2O rate. Any explanation of this effect must satisfy the following conditions:

¹³ Kaufman, Gerri, and Pascale, J. Chem. Phys. 24, 32 (1956).

TABLE IV. Added gas effect of He, A, N_2 , and O_2 on initial rates.

$T = 937^\circ\text{K}, p_{\text{N}_2\text{O}} = 50 \text{ mm}$				
$\text{X} =$	p_{X}, mm	$-dp_{\text{N}_2\text{O}}/dt$ mm/min	dp_{NO}/dt mm/min	$-dp_{\text{N}_2\text{O}}/dp_{\text{N}_2\text{O}}$
...	0.	1.07	0.61	0.57
He	200.	1.72	0.41	0.24
A	200.	1.09	0.51	0.47
N_2	200.	1.21	0.43	0.36
O_2	25.	1.07	0.54	0.50
	50.	1.09	0.54	0.49
	100.	1.14	0.54	0.48
	200.	1.22	0.45	0.37

1. There is virtually no I_2 present, all iodine being in atomic form.

2. As there is only a slight increase in N_2O decomposition rate, the primary cleavage of N_2O is little affected by trace addition of iodine. If this were not the case, one would have to postulate an inhibition of normal N_2O breakdown, and a catalytic reaction of equal speed, of N_2O with traces of iodine. Such an explanation is unlikely. Moreover, the catalytic reaction would not extrapolate properly to the known rate with larger concentrations of iodine.

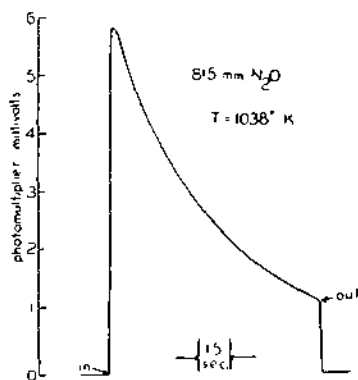
II. N_2O Chemiluminescence

A. N_2O Alone

Visual observation of the reaction tube shows a weak, greenish yellow glow as soon as N_2O is admitted. The glow is visible at temperatures of 650°C and somewhat below when the pressure is 1 atmosphere. It decreases more or less slowly with time and disappears immediately upon pumping out the reaction vessel. At higher temperatures, the glow becomes more intense and shorter in duration, and around 900°C , 1 atmosphere, a bright flash occurs indicating a thermal explosion of N_2O . Viewed through a small Spencer spectroscope, the glow or the flash appeared as a continuous spectrum extending from about 4500 to 6500 Å. Photographic exposures of series of low temperature runs, and of repeated flashes gave the same result.

TABLE V. Limiting NO pressures for added He, A, N_2 , and O_2 .

$T = 973^\circ\text{K}, p_{\text{N}_2\text{O}} = 50 \text{ mm Hg}$		
$\text{X} =$	p_{X}, mm	p_{NO}, mm
...	0	3.37
He	50	2.76
	200	2.12
A	50	2.81
	200	2.17
N_2	50	2.86
	200	2.00
O_2	25	2.67
	50	2.33
	100	2.05
	200	1.43

FIG. 3. N_2O glow vs time.

Several experiments were carried out by observing the magnitudes of the glow signal and the furnace background radiation with various Wratten filters inserted between the reaction tube and the photomultiplier. With filters of transmission maximum near 4500 Å, the glow to background ratio was 7 to 8 times greater than the same ratio in the absence of the filter; for transmission maximum at 5300 Å, it was twice as great; and for filters passing radiation of 6800 Å or higher, there was no glow signal, though furnace radiation still gave a small reading. The glow is here compared with the gray body radiation from a furnace at about 850°C which increases rapidly with increasing wavelength in the visible. At 6700 to 7000 Å the luminescence apparently has fallen to zero. Nothing can be said about the spectral region beyond 7000 Å since the photomultiplier is insensitive there.

A typical glow vs time plot is shown in Fig. 3. The intensity rapidly reaches a peak and then decreases slowly as the N_2O is decomposed. No other molecule except NO_2 can be responsible for the glow in this temperature range with only N_2O present initially. Many other investigators have observed a similar luminescence under a variety of circumstances.¹⁴

From the shape of the glow-time curve it is clear that this is a chemiluminescence and not thermal radiation of hot NO_2 . The radiation is strongest at the beginning of the reaction when there is little NO present and decays in time, approaching a small, constant signal after long reaction time. This small, residual signal must be due to thermal radiation of NO_2 viewed against the background of the cooler end of the reaction vessel. The N_2O glow was equally visible when viewed against the side of the reaction tube, at the temperature of reaction.

The initial glow intensity was repeatedly determined

as a function of pressure and temperature. The maximum intensity L_0 increases with increasing N_2O pressure, at constant temperature. Empirically, $L_0 = k p^\alpha$ with α ranging from 0.65 to 0.85.

Measurements of the half-life, $t_{1/2}$, of the glow at constant temperature and at initial N_2O pressures from 100 to 800 mm Hg gave the surprising result that $t_{1/2}$ varied inversely as the 0.7 to 0.9 power of $[\text{N}_2\text{O}]_0$, though L_0 varied directly as a similar power of $[\text{N}_2\text{O}]_0$.

The temperature dependence of the glow was also measured repeatedly. The most reliable value for $d \log L_0 / d(1/T)$ at constant $[\text{N}_2\text{O}]_0$ was obtained over the temperature range 695 to 750°C and $E \equiv 2.303 R d \log L_0 / d(1/T)$ turned out to be 60 kcal. Initial N_2O pressures were about 1 atmosphere, and this value of E is reasonably close to the experimental activation energy for the N_2O decomposition. Two other determinations gave 64 and 68 kcal for E , but they were made over temperature ranges up to 840 and 860°C, respectively. At these temperatures, the reaction is very fast, and some adiabatic heating of the reacting gas could be expected.

A very rough calculation was made of the quantum yield of the reaction, the ratio of quanta emitted per molecule of N_2O decomposed. This was done by measuring the peak glow signal L_0 and the furnace background signal simultaneously. The reaction vessel was wrapped with asbestos impregnated with Fe_2O_3 to provide high radiation emissivity and the photomultiplier and porcelain tube B positioned to look at the hot wall of the reaction vessel. At the known temperature of the reaction vessel (1039°K), the theoretical radiation intensity (Wien's Law) was corrected for the photomultiplier (S-9) response curve and for the geometry of the system. Similar corrections were applied to the glow whose wavelength distribution was assumed to be constant between 4200 and 6400 Å. With the many assumptions made in this calculation, particularly those regarding the geometry of the system, the resulting value of about 10^{-5} for the quantum yield calculated for an average wavelength of 5500 Å is reliable only to one or two orders of magnitude but probably represents an upper limit.

B. Added Gases

Experiments were carried out with various amounts of added He, N_2 , and O_2 at 770°C. Helium does not decrease the glow when present in up to fourfold excess to N_2O . Added N_2 decreases the glow. The dilution of N_2O with an equal pressure of N_2 lowers the signal 25%. The corresponding, greater lowering with O_2 is 40%.

Interesting information was obtained from luminescence experiments at low temperatures (950 to 1050°K) and low N_2O pressures (50 to 200 mm) with addition of a little NO (1 to 6%). In the absence of added NO , the onset of the glow is quite slow under those condi-

¹⁴ A. G. Gaydon, *Spectroscopy and Combustion Theory* (Chapman and Hall, London, 1948), p. 101; Y. Tanaka and M. Shimazu, *J. Sci. Research Inst. (Tokyo)* 43, 241 (1949); V. Kondratjew, *Physik Z. Sowjetunion* 11, 320 (1937); G. Whittingham, *Nature* 159, 232 (1947); C. G. James and T. M. Sugden, *Nature* 175, 252 (1955); A. L. Shneerson and E. N. Eremin, *Zhur. Fiz. Khim.* 26, 1493 (1952); *Chem. Abstracts* 47, 6250 (1953).

tions. Curve A in Fig. 4 shows the photomultiplier output at 1030°K due to 50 mm of N_2O . The rise time is about 2 minutes. (The response time of the whole system was measured by introducing some Br_2 in N_2 to the hot furnace and noting the time for the signal to become constant. The time was about 0.5 second). Curve B shows the effect of adding 3 mm of NO to 50 mm of N_2O . The glow now rises sharply again.

SO_2 was found to decrease the glow considerably, 13 mm SO_2 reducing the glow due to 600 mm of N_2O at 1045°K by 40%.

NH_3 inhibits the glow strongly and also brings about an induction period. This was discussed above. At 1045°K, 30 to 70 mm NH_3 in 200 to 450 mm N_2O gave delays of 35 to 20 seconds before any luminescence was measurable. From then on, the signal increased to a peak and decayed in a normal manner, except that the peak was only about one-quarter of that in the absence of NH_3 . This reduction is due to the decrease in N_2O pressure as a result of the rapid NH_3 - N_2O reaction, and to the quenching effect of the large amount of H_2O formed.

The halogens were found to be the most efficient inhibitors of the glow. Cl_2 , Br_2 , I_2 , C_2H_5Cl , C_2H_5Br , $t-C_4H_9Cl$, and CCl_4 were tried and all were effective. With most of these compounds, gas mixtures containing decreasing amounts of additive were made with N_2O and tested for their luminescence signal. As long as the concentration of additive was much too high, a bright flash occurred, particularly at the higher temperatures. This was the result of thermal explosions due to the catalytic decomposition of N_2O by halogen. Upon further decrease of the concentration of additive, explosions no longer occurred, and the glow was also absent. Further dilutions with N_2O brought back increasing peak luminescence signals, and in the limit, without additive, the normal N_2O signal was obtained. From series of such runs with partial pressures of additives decreasing by factors of 1.3 to 1.6, that pressure of additive, p_i , was determined which would decrease the glow to one-half its normal value.

Table VI lists the observed values of p_i for C_2H_5Cl , C_2H_5Br , and C_2H_5I . Also included are the equilibrium partial pressures of atomic halogen p_X calculated under the assumption of rapid release of all the halogen from the halide, and establishment of the $X_2 \rightleftharpoons 2X$

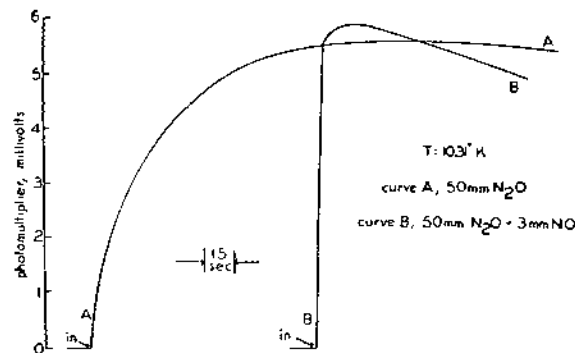


FIG. 4. N_2O glow at low pressure with and without added NO.

equilibrium. The accuracy of these determinations was low because of absorption of the added gas on the walls of tubing and mixing vessel, and in stopcock grease.

Since small amounts of added hydrocarbons were found to produce no inhibition, and since molecular halogens gave results similar to the halides, the effect of the ethyl group could be neglected.

Whether the inhibition is the result of atomic or molecular halogen cannot be deduced with certainty. In the case of ethyl iodide, it is surely due to atomic iodine, since I_2 is almost completely dissociated in this temperature range. By analogy with iodine, and in line with the catalytic N_2O -halogen reaction,¹³ it may be assumed that the atomic species are responsible for the observed inhibition in the cases of bromine and chlorine compounds, too. Both p_i and p_X increase with increasing temperature.

The relative efficiency of the halogens at constant temperature appears to be $I > Cl > Br$ or $Cl > I > Br$, but the large experimental error may be responsible for the scrambled order. The clear order $C_2H_5I > C_2H_5Br > C_2H_5Cl$ seems to reflect only the ease of dissociation of the halogen molecules.

The magnitude of p_i for ethyl iodide can be compared with the pressure of ethyl iodide which decreases the initial rate of formation of NO by 50%. The latter value, given above, is 3×10^{-3} mm at 973°K with 50 mm of N_2O . Interpolating p_i at 973°K from Table VI, we obtain approximately 1×10^{-3} mm for 800 mm N_2O and estimate 1×10^{-4} mm for 50 mm N_2O . The value of p_i comparable with that for NO inhibition under equal conditions is therefore one to two orders of magnitude smaller.

DISCUSSION

I. Rate of NO Formation

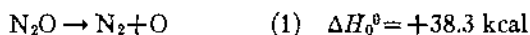
N_2O Alone

In an effort to explain most of the above results by one mechanism, we propose that the following steps

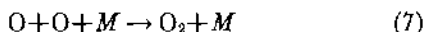
TABLE VI. Partial pressures of organic halides p_i and of atomic halogen p_X that reduce N_2O glow by 50%.

T, °K	C_2H_5Cl		$p(N_2O) = 800$ mm C_2H_5Br		C_2H_5I	
	p_i	p_X	p_i	p_X	p_i	p_X
924	0.06	6×10^{-4}	3×10^{-3}	2×10^{-3}	4×10^{-4}	4×10^{-4}
1019	0.4	6×10^{-3}	0.03	0.02	2×10^{-3}	2×10^{-3}
1111	0.5	0.02	0.1	0.07	0.05	0.05

are of importance.

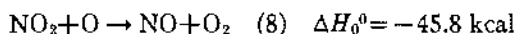


Step (1) here represents the unimolecular set of activation, deactivation, and decomposition reactions. Homogeneous recombination of atomic oxygen



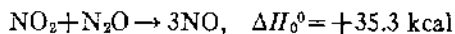
is not included because of the low probability of such triple collisions. Calculations will show, however, that it may be of marginal importance. It is clear that any NO formed in (3) will not be destroyed, but merely deplete oxygen atoms by (4) and (6) and be regenerated.

The alternate choice of



as a path for the regeneration of NO and recombination of atomic oxygen would lead to a contradiction. At the beginning of N_2O decomposition, 60% or more of NO is formed (Table I). This means that for almost every N_2O molecule decomposing, another one is destroyed by reaction with O. The NO yield decreases rapidly during the course of reaction, presumably by NO removing O more efficiently than N_2O and thereby inhibiting its own further formation. But if this occurred via (4) and (8), it is clear that each decomposing N_2O molecule would no longer lead to the destruction of another N_2O . The N_2O vs time curve should therefore show unusual curvature near time zero, the rate decreasing by almost a factor of 2 within a fairly short time.

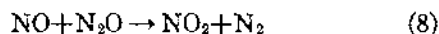
Since such behavior is never observed, it is necessary that NO_2 disappear in a manner which will destroy another N_2O , i.e., by reaction (6). It is also necessary to exclude the alternate path



since it would amount to continued NO production from N_2O , but this seems reasonable in view of its unfavorable ΔH .

The introduction of (5), the first-order approximation for diffusion to the wall is supported by recent experiments on O recombination.¹⁵ It is, moreover, strongly suggested by the results (Table I) that the initial NO yield increases with increasing N_2O pressure, since this requires a mode of O atom disappearance which is of lower than first order in N_2O .

The reaction



is presumed to be responsible for the catalytic decomposition of N_2O by NO and its rate is well known.¹⁶ In the absence of added NO, the error due to neglect of (8) is 10 to 15% in the later stages of decomposition, and much less at the beginning of reaction.

The early stages of N_2O decomposition can be represented by steps (1), (2), (3), and (5). Applying the steady state approximation to O atoms, one obtains

$$[\text{O}] = \frac{R_1}{(k_2 + k_3)[\text{N}_2\text{O}] + k_5} \quad (a)$$

where R_1 represents the rate of (1). The initial NO yield $-d[\text{NO}]/d[\text{N}_2\text{O}]|_0$ is independent of R_1 and turns out to be

$$\left. \frac{-d[\text{NO}]}{d[\text{N}_2\text{O}]} \right|_0 = \frac{1}{1 + (k_2/k_3) + (k_5/2k_3[\text{N}_2\text{O}])} \quad (b)$$

The experimental data of Table I were fitted to this expression. At each temperature, $u \equiv k_2/k_3$ and $v \equiv k_5/k_3$ were determined by drawing one line in the u - v plane corresponding to (b) for each initial N_2O pressure. This gave three intersecting lines for each T which, in order to define unique u and v values, had to intersect in one point. Such was the case at the three higher temperatures with good accuracy, and at 876°K with fair accuracy. Table VII lists the resulting values for u and v . The temperature coefficient of k_5 was now assumed to be that of a diffusion coefficient and k_5 expressed as $cT^{1.8}$.¹⁷ With these assumptions, the activation energy E_3 of k_3 was obtained from the slope of the plot of $\log v T^{-1.8}$ vs $1/T$ and $E_3 = 15.5 \pm 1$ kcal. The activation energy E_2 of k_2 was then determined from E_3 and the plot of $\log u$ vs $1/T$. u is constant at the three higher temperatures but somewhat higher at 876°K where its value is least reliable. From this, we estimate $E_2 = 14.5 \pm 2$ kcal.

In order to get semiquantitative values for k_2 , k_3 , and k_5 , we make use of Marsden and Linnett's¹⁸ estimate for the accommodation coefficient of atomic O on glass. Extrapolating to our temperature range around 700°C, we use a value of 10^{-3} for capture on quartz, and, equating the total number of collisions with the wall Z ,

$$Z = \frac{p \cdot \text{area}}{(2\pi MRT)^{1/2}}$$

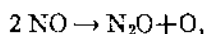
with $1000 k_5[\text{O}]$, we obtain, at 973°K, $k_5 = 17 \text{ sec}^{-1}$, $k_2 = 1.7 \times 10^7 \text{ cc mole}^{-1} \text{ sec}^{-1}$, and $k_3 = 3.5 \times 10^7 \text{ cc mole}^{-1} \text{ sec}^{-1}$. Therefore, $k_2 = 3 \times 10^{10} e^{-14.5/RT}$, $k_3 = 1 \times 10^{11} e^{-15.5/RT} \text{ cc mole}^{-1} \text{ sec}^{-1}$. It is interesting to note

¹⁵ D. G. H. Marsden and L. W. Linnett, *Fifth Symposium on Combustion* (Reinhold Publishing Corporation, New York, 1955), p. 685.

¹⁶ F. Kaufman and J. R. Kelso, *J. Chem. Phys.* 23, 602 (1955).

¹⁷ J. R. Partington, *Advanced Treatise on Physical Chemistry* (Longmans Green and Company, London, 1949), Vol. I, p. 903.

that k_2 and k_3 have pre-exponential factors 10^3 to 10^4 times smaller than the calculated collision frequency. This explains why the reverse of (3),



is probably not the slow step in the decomposition of NO at 1100 to 1300°C,¹¹ though its activation energy, $E=36+15.5=51.5$ kcal, is considerably lower than the observed value of 63.8 kcal.

The steady-state pressure of atomic oxygen at the start of reaction can now be calculated if it is assumed that R_1 is one-half the observed rate of disappearance of N_2O . It turns out to be 1.5×10^{-4} mm Hg. At this value, estimating the termolecular collision frequency $\text{O} + \text{O} + \text{N}_2\text{O}$ to be 10^{16} cc² mole⁻² sec⁻¹, homogeneous recombination would account for only 0.02% of oxygen atom reactions. But a choice of 10^{-4} for the accommodation coefficient of atomic oxygen would increase this fraction to 2%.

Further evidence for the correctness of our interpretation comes from the results with the packed flask (Table II). The calculated fraction, $-d\text{p}_{\text{NO}}/d\text{p}_{\text{N}_2\text{O}}$ was obtained from expression (b) using the value of u from the experiments with the empty flask, but replacing v by $40v$, i.e., considering the surface capture of oxygen atoms to be proportional to the surface area. Though the agreement is only fair in some cases, the striking reduction of the NO yield from about 50% in the empty flask to 5 to 6% in the packed flask at low $\text{p}_{\text{N}_2\text{O}}$ is well represented. The strong dependence of NO yield on $\text{p}_{\text{N}_2\text{O}}$ (greater relative importance of surface removal of O) is also predicted.

Turning now to a representation of the entire course of decomposition, we utilize steps (1) through (7). As a further assumption, the steady-state treatment is applied to NO_2 . At the high temperatures of reaction, this should not introduce a large error. The steady-state concentration of oxygen atoms is now given by

$$[\text{O}] = \frac{R_1}{(k_2 + k_3)[\text{N}_2\text{O}] + k_5 + k_4[\text{NO}][\text{M}]} \quad (\text{c})$$

The fractional yield of NO at any time, $-d[\text{NO}]/d[\text{N}_2\text{O}]$, becomes

$$\frac{d[\text{NO}]}{d[\text{N}_2\text{O}]} = \frac{1}{1 + (k_2/k_3) + (k_6/2k_3[\text{N}_2\text{O}]) + k_4/k_3[\text{NO}][\text{M}]/[\text{N}_2\text{O}]} \quad (\text{d})$$

$[\text{M}]$ can be approximated by $[\text{N}_2\text{O}]_0$. This is exactly true at time zero, but should continue to hold fairly well throughout, since for every mole of N_2O which has decomposed, $1\frac{1}{2}$ moles of diatomic molecules of lower third body efficiency are produced.

TABLE VII. Ratios of rate constants.

	T, °K			
	876	927	973	1031
$u = k_2/k_3$	0.67	0.515	0.47	0.47
$v = k_6/k_3$ mole cc ⁻¹ × 10 ⁷	9.2	7.1	4.8	3.4

The differential equation (d) was made homogeneous by a simple change of variables, and was integrated exactly. The boundary conditions $[\text{N}_2\text{O}] = [\text{N}_2\text{O}]_0$, $[\text{NO}] = 0$; $[\text{N}_2\text{O}] = 0$, $[\text{NO}] = [\text{NO}]_\infty$ were applied and the experimental sets of values, $[\text{N}_2\text{O}]_0$ and $[\text{NO}]_\infty$, of Table III were substituted. With the introduction of k_2 , k_3 , and k_5 from the preceding section, an equation in one unknown, k_4 , was obtained for each experimental pair, $\text{p}_{\text{N}_2\text{O}}$ and p_{NO} . This equation was solved numerically by a method of iteration and the resulting k_4 is listed in the third and sixth columns of Table III.¹⁸

Though both columns show a trend of decreasing k_4 for increasing $[\text{N}_2\text{O}]_0$, it is reassuring to find a spread of only $\pm 8\%$ and $\pm 10\%$ in k_4 when $[\text{N}_2\text{O}]_0$ changes 8- and 20-fold, and $[\text{NO}]_\infty$ changes 3- and 7-fold at the two temperatures. The magnitude of k_4 of about 6×10^{15} cc² mole⁻² sec⁻¹ is well in line with that of other termolecular recombination rate constants. The absence of a positive (and possibly the presence of a negative) temperature coefficient is in agreement with the accepted picture of such processes as having no activation energy.

It should be noted that the bimolecular recombination



cannot be used in place of (4). Its rate "constant," $k_{4'}$, would vary linearly with $[\text{N}_2\text{O}]_0$.

Added Gases

The considerable decrease of $-(d\text{p}_{\text{NO}}/d\text{p}_{\text{N}_2\text{O}})|_0$ with the addition of inert gas (Table IV) can not be explained by the above mechanism. The peculiar effectiveness of helium in speeding the rate of decomposition of N_2O is paralleled by its similar efficiency in equilibrating vibrational and other degrees of freedom in recent relaxation experiments.¹⁹ It may help to reconsider homogeneous O atom recombination, (7), but such an explanation leaves much unexplained. The great relative efficiency of He as third body in (7) would be in contrast to its normal behavior in halogen recombination²⁰; and the presumed large rate increase of (7) necessary to explain the pronounced drop in NO yield would require that N_2O itself be a very ineffective third body in reaction (7). A full understanding of

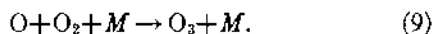
¹⁸ These computations were set up and carried out by Dr. W. C. Taylor and Mr. L. Kilian whose help is gratefully acknowledged.

¹⁹ Walker, Rossing, and Legvold, Natl. Advisory Comm. Aeronaut. Tech. Note No. 3210, 24 (1954).

²⁰ Christie, Norrish, and Porter, Proc. Roy. Soc. (London) A216, 152 (1953).

these results will probably require a comparable understanding of the effect of added gases on R_1 , and such is not yet in sight.

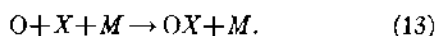
The effect of inert gas addition on the limiting NO pressure (Table V) is more understandable. The more normal sequence $O_2 > N_2 > He > A$ expresses the efficiency of the added gases as third bodies in reaction (4). If the lower initial NO rates (Table IV) are taken into account, the order becomes $O_2 > N_2 > A > He$. Helium which gives the lowest initial yield of NO is least effective in (4) and produces the second largest $p_{\infty}NO$. Though oxygen is considerably more efficient than He, A, or N_2 in (4), it may be surprising that it isn't much more so by the reaction



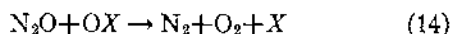
The fact that the addition of 100 mm of O_2 lowers $p_{\infty}NO$ by only 40% shows that O_2 is about two orders of magnitude less efficient than NO in removing atomic oxygen at 1000°K. This is due to the high rate of ozone decomposition by the reverse of (9), i.e., its great instability at high temperatures. Thus, if the equilibrium $O + O_2 \rightleftharpoons O_3$ becomes established, the calculated ratio p_{O_3}/p_O at 1000°K and $p_{O_2} = 100$ mm is 1/150.

As expected, the experiments with water vapor showed it to be more efficient in reaction (4) than any of the above.

Of the reactive, added gases, i.e., those which interfere chemically with some of the intermediate steps, the halogens are most effective in inhibiting NO. Since a direct interference with the initial decomposition of N_2O is ruled out, this effectiveness must be due to



The rate of N_2O decomposition being unchanged (except for some concurrent catalytic reaction amounting to ~10%) it is again necessary to postulate reaction of OX with N_2O



in an argument similar to that given above against step (8).

Application of the rate constants calculated from the experiments with pure N_2O shows that at 973°K, $p_0N_2O = 50$ mm, the NO pressure necessary to cut in half its own initial rate of formation is 0.6 mm Hg. Since 0.003 mm of atomic iodine produce an equal decrease, I must be 200 times more effective than NO in removing O atoms, or $k_{13} = 200k_4$. At most a factor of 2 to 3 of this can be due to the larger diameter of I, and in view of the normal, termolecular value calculated for k_4 , k_{13} is surprisingly high. This great efficiency of iodine for removing oxygen atoms may have a bearing on the strong inhibition by iodine compounds, of the H_2-O_2 and $CO-O_2$ reactions and explosions.

Added bromine or chlorine compounds exert a

similar inhibition of NO, but at higher pressures of added gas. This undoubtedly results from the higher dissociation energies of Br_2 and Cl_2 and correspondingly lower pressures of atomic halogen.

II. Chemiluminescence

If the glow comes from electronically excited NO_2 made in binary collisions of NO and O, its intensity, $L = k'[O][NO]$. Substituting for [O],

$$L = \frac{k'R_1[NO]}{(k_2 + k_3)[N_2O] + k_6 + k[NO][M]}. \quad (e)$$

At sufficiently high temperatures and N_2O pressures, the buildup of NO is very rapid, the last term in the denominator of (e) is larger than the first two, and (e) is approximated by

$$L = k'R_1/k_4[M]. \quad (f)$$

This explains the nature of the glow vs time curves; L is proportional to R_1 , the cleavage rate of N_2O , and decreases as $[N_2O]$ is decreasing. Near time zero, the peak intensity, L_0 , can be expressed as a function of $[N_2O]$ by substituting $[M] = [N_2O]_0$ and setting $R_1 = k''[N_2O]^\beta$ with $\beta = 1.5$ to 1.6. The latter approximation considers R_1 the rate determining step in the decomposition of N_2O (in magnitude somewhat greater than one-half the observed rate of disappearance of N_2O). The above empirical range for β was found to be correct in all our experiments. Therefore,

$$L_0 = \frac{k'k''}{k_4} [N_2O]_0^{\beta-1},$$

so that the peak glow intensity at constant T , in the absence of added gases, should be proportional to the 0.5 to 0.6 power of $[N_2O]$. The difference between this predicted and the somewhat higher observed range of exponents (0.65 to 0.85) may be due to neglecting the first two terms in the denominator of (e).

The experimental observation that the half-life of the observee glow was inversely proportional to the 0.7 to 0.9 power of $[N_2O]_0$ can be explained in the following manner. In the course of one experiment, $[M]$ remains approximately constant so that

$$L(t) \cong k[N_2O]^\beta.$$

Setting $-d[N_2O]/dt = k^*[N_2O]^\beta$, it is easily seen that $t_{1/2}$ of the glow should vary inversely as the $\beta-1$ power of $[N_2O]_0$. Again the observed range is a little higher, but this can be explained further. The cold space in all chemiluminescence experiments was large. The observed pressure increase during the course of a run was less than half of theoretical. Though this will not affect L_0 , it will affect the rate of change of $[N_2O]$ and of the glow during the latter stages, since N_2O will disappear from the reaction vessel not only by

reaction, but also by being swept into the cold space by the attending pressure increase. Such additional loss of reactant will appear as a higher effective order of reaction and as a higher inverse power in the t_1 vs $[N_2O]_0$ relation.

The approximate quantum yield of 10^{-5} for the ratio of quanta emitted per molecules of N_2O decomposed leads to an interesting comparison. Neuberger and Duncan²¹ recently reported the lifetime of NO_2 excited by radiation of wavelengths 3900 to 4600 Å to be 44 μ sec. If every decomposing N_2O molecule gave rise to an excited NO_2^* which could be deactivated by collision or could radiate, the observed quantum yield would be equal to the ratio of collision to radiation half-life. That ratio, at the conditions of our experiments, and using Neuberger's value, does turn out to be about 10^{-5} . This would seem to indicate that the above assumption is approximately correct; that NO_2^* is a major intermediate; and that reaction (4) is really a succession of two steps, binary activation, (4'), and collisional deactivation. However, it is more likely that the identification of NO_2^* present in fluorescence and in the $NO+O$ continuum is not permissible. In that case, one might expect the recombination forming NO_2^* to have a normal half-life of 10^{-7} to 10^{-8} sec, and radiative recombinations would then account for only a small fraction (about 10^{-3}) of the normal termolecular reaction (4).

²¹ D. Neuberger and A. B. F. Duncan, J. Chem. Phys. 22, 1693 (1954).

In agreement with their effect on the rate of formation of NO , added inert gases decrease the glow in the order $O_2 > N_2 > A > He$ with O_2 giving the greatest reduction. This can be thought to represent relative quenching efficiency for NO_2^* , similar to third body efficiency in (4) as discussed above for the decrease of $p_{\infty}NO$.

The experiments describing the slow onset of the glow at low N_2O pressures and its much faster rise with addition of some NO (Fig. 4) is also well explained by the above expressions. At low rates of decomposition, the first two terms in the denominator of (e) cannot be neglected and L will reach its maximum value slowly.

Using the calculated values for k_2 to 5 and the experimental values for $[NO]$ as function of time, we calculate a rise time of about 2 minutes under the experimental conditions, in good agreement with the observed value.

The strong inhibition of the glow by atomic halogen is in line with the decrease of NO formed. The fact that p_X is between 10 to 100 times smaller than the corresponding pressure of halogen which lowers the initial rate of formation of NO by one-half is also easily explained. p_X , the concentration of halogen which reduces the glow by one-half, determines the product $[NO][O]$, and since atomic halogen decreases the steady-state oxygen concentration and thereby also the rate of formation of NO , the product $[NO][O]$ is lowered more than $[NO]$ alone by a given amount of halogen. Thus, the glow is more sensitive to addition of inhibitor than is the rate of formation of NO .

Electronic and Vibrational States of Anthracene*†

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The polarized absorption and fluorescence spectra of anthracene have been measured in dilute solid solution in single crystals of naphthalene and phenanthrene at 20°K. The lowest singlet-singlet transition is proven to be polarized along the short molecular axis, and hence ${}^1B_{2u} \rightarrow {}^1A_g ({}^1L_a \rightarrow {}^1A_g)$, in agreement with theoretical predictions. Vibrational frequencies are compared in the ground state and in the first excited state. The polarization of the fluorescence of anthracene in phenanthrene has also been studied as a function of temperature. The fluorescence is partially polarized at 300°K, but is depolarized at 20°K.

I. INTRODUCTION

THE electronic spectrum of anthracene has recently received considerable study from both an experimental and theoretical viewpoint. The intense short

wavelength absorption has been photographed in the crystalline state by Craig and Hobbins.¹ The weaker long wavelength absorption spectrum of single crystals of anthracene has been photographed at 20°K by Obreimov and Prikhodjko,² and the fluorescence of crystalline anthracene has been photographed at 20°K

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¹ D. P. Craig and P. C. Hobbins, J. Chem. Soc. 1955, 539.

² I. W. Obreimov and A. F. Prikhodjko, Physik. Z. Sowjetunion 9, 48 (1936).