[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

A Photo-colorimetric Study of the Oxidation of Nitric Oxide at Low Pressures

BY J. HAROLD SMITH

Early investigation by Bodenstein[1] and coworkers has shown the reaction $2NO + O_2 \rightarrow 2NO_2$ to be termolecular and apparently homogeneous. Numerous other investigators[2–6] have studied the influence of the presence of moisture, the extent of drying, or the nature of the surface of the reaction vessel and have in some cases obtained evidence indicating that there are surface effects and that the reaction is not entirely homogeneous in character.

In a recent paper[6] Stoddart reported, in agreement with the results of Baker,[2] that no reaction occurred when very carefully dried nitric oxide was admitted to a bulb containing oxygen. On the other hand, drying did not appear to inhibit the reaction when oxygen was added to nitric oxide in a thoroughly dried tube. He explained these rather anomalous results on the basis of a surface reaction involving the postulated $(NO)_2$ complex molecule, and suggested that while the reaction takes place when a film of nitric oxide is adsorbed on the surface of the container this is not the case if a film of oxygen is first adsorbed on a thoroughly dry surface.

Further investigation of this important reaction seemed desirable. It was decided to employ a photo-colorimetric method for measuring the nitrogen dioxide concentration in order to determine the rate of the reaction over a very wide pressure range, particularly in the low pressure region. Surface effects due to adsorption or any catalytic influence of the surface should be most significant and easily detected at low pressures. Also it was of interest to determine whether or not a termolecular law is obeyed at very low pressures. Furthermore, a check on the rather unusual behavior of the reaction as observed by Baker and Stoddart was desired.

Experimental

Apparatus.—The rate of the nitric oxide–oxygen reaction was followed using a photo-electric colorimeter to determine the amount of nitrogen dioxide present at any given time after the reacting gases were mixed. A sensitive photocell[7] of the self-generating type was used in conjunction with a sensitive (15 microamp.) Weston micro-ammeter for following the current. Green light (460–600 $\mu\mu$) of constant intensity was obtained from a white incandescent source using a calcium chloride–cupric chloride filter.[8] With reaction tubes of lengths ranging from 18 to 178 cm., measurements were made with nitric oxide pressures from 50 mm. down to a few hundredths of a millimeter. The reaction tubes were immersed in a constant temperature bath adapted for measurements at 0 and 25°. The entire apparatus was of Pyrex glass, and the reaction tubes were equipped with plane optical windows.

The nitric oxide was generated by the iodide–nitrite reaction in acid solution, as described by Johnston and Giauque.[9] After being washed, it was carefully dried by passing first through calcium chloride and finally slowly over phosphorus pentoxide powder loosely packed in a tube 90 cm. in length. Tank oxygen, which was used, was dried similarly. The oxygen and nitric oxide pressures were measured with a McLeod gage of range up to 7.5 mm. An alternative procedure was to obtain the desired pressure by admitting the gas from a much smaller tube at a higher, conveniently measured, pressure.

The apparatus was outgassed by warming while evacuating with an efficient mercury vapor pump prior to making a series of determinations. While care was taken to see that the apparatus was dry, it is likely that it cannot be considered thoroughly dry since the use of stopcocks with grease was not avoided. It is quite certain, as Brown and Crist[10] have suggested, that since even at low pressures there is some reaction of nitrogen dioxide with the grease, complete removal of moisture and of traces of carbon dioxide and other gases is difficult if not impossible in such a system.

Procedure.—The experimental procedure was as follows: A measured amount of either nitric oxide or oxygen was admitted to the reaction vessel containing a known pressure of the other reactant. At the low pressures used the gases mixed very rapidly. The progress of the reaction was followed by noting at any given time the amount of brown nitrogen dioxide present, as indicated by the micro-ammeter reading. The photo-cell used for nitrogen dioxide detection was calibrated against measured amounts of pure nitrogen dioxide in the reaction vessel. With this apparatus, continuous readings were possible without disturbing the reaction in any way. Usually ten to fifteen readings were taken in a single determination. By plotting the nitrogen dioxide concentrations against the corresponding time readings smooth curves were obtained. A typical plot is shown in Fig. 1. The instantaneous rates were then found from the slope of the curves at any point. With these rate values and on the assumption of a termolec-

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(1) Bodenstein, Meinecke, Wachenheim, Ramstetter and Lindner, *Z. Elektrochem.*, **24**, 183 (1918); *Z. physik. Chem.*, **100**, 87 (1922).

(2) Baker, *J. Chem. Soc.*, **65**, 611 (1894).

(3) Briner, *J. Chim. Phys.*, **23**, 848 (1926).

(4) Hasche, THIS JOURNAL, **48**, 2253 (1926).

(5) Hasche and Patrick, *ibid.*, **47**, 1207 (1925).

(6) Stoddart, *J. Chem. Soc.*, 5 (1939).

(7) General Electric Co., Catalogue No. 88 × 565.

(8) Holmes and Daniels, THIS JOURNAL, **56**, 630 (1934).

(9) Johnston and Giauque, *ibid.*, **51**, 3194 (1929).

(10) Brown and Crist, *J. Chem. Phys.*, **9**, 840 (1941).

ular law the corresponding k values were calculated at various points along the curves on the basis of the relationship

$$k = -\frac{d(O_2)/dt}{(O_2)(NO)^2}$$

The nitric oxide and oxygen concentrations were calculated from the initial pressures, with an appropriate correction for the amounts converted to nitrogen dioxide.

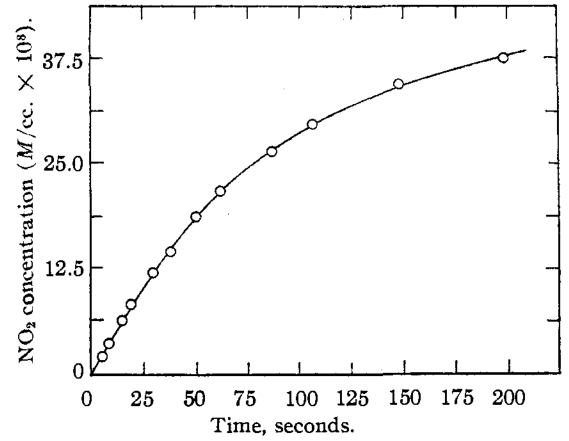

Fig. 1.—Oxidation of nitric oxide at 25°, initial concentrations: NO = 50 × 10^{-8} M/cc.; O_2 = 144 × 10^{-8} M/cc.; data obtained in a 3-liter spherical vessel.

Results and Discussion

Table I records the results of measurements taken at 25° in a carefully dried and outgassed reaction cylinder 2.5 cm. in diameter and 56.9 cm. in length. Special care was taken to see that no adsorbed nitric oxide was permitted to remain on the walls prior to the time that a known small amount of nitric oxide was added to the tube. This was done by allowing oxygen at a rather high pressure to stand for some time in the tube before starting the run. The tube was then evacuated with an efficient mercury vapor pump, after which a measured amount of nitric oxide was admitted. While there may have been a slight amount of adsorbed oxygen present as a result of this procedure its presence was not so apparent nor the error so significant as with nitric oxide under the conditions used. This is true, not only because perhaps there may have been less oxygen than nitric oxide adsorbed, but since the oxygen pressures were in general fairly high and the reaction first order with respect to the oxygen concentration while it is second order with respect to the nitric oxide concentration.

TABLE I

SPECIFIC RATE CONSTANTS AT 25°[a]

Concentrations (M/cc. × 10^9) O_2	NO	k × 10^{-9} (cc.^{2} mole^{-2} sec.$^{-1}$)
16.75	5.92	5.06
17.25	6.92	4.85
17.75	7.92	5.03
18.25	8.92	6.0

[a] Data obtained using a 250-ml. (diam. 2.5 cm.; length 56.9 cm.) cylindrical reaction tube. Special care was taken to eliminate adsorption of nitric oxide on the walls of the tube.

Data obtained using a 3-liter spherical vessel with a paraffined surface are given in Table II. While no special care was taken to ensure that no film of nitric oxide was adsorbed, the surface area was so relatively small that adsorption on the paraffined surface was probably not great nor significant except at low pressures. That there was actually some adsorption is shown by the high k value for the lowest pressure determination. All other measurements in the 3-liter sphere were at nitric oxide pressures considerably greater and no appreciable, consistent variation in the value of k is observed.

TABLE II

SPECIFIC RATE CONSTANTS AT 25°[a]

Concentrations (M/cc. × 10^9) O_2	NO	k × 10^{-9} (cc.^{2} mole^{-2} sec.$^{-1}$)
144	14.6	11.7
144	27.5	6.3
144	50	5.6
144	93	6.0
144	180	6.4
144	269	5.8
6.6	269	6.4
10.2	269	7.4
12.6	269	7.0

[a] Data obtained using a 3-liter (17.8 cm. diam.) spherical reaction vessel with a paraffined surface.

The k values shown in Tables I and II, which were obtained over a wide pressure range and under conditions where adsorption effects should be only slight if present at all, are fairly constant. Figure 2 shows these k values plotted against the corresponding nitric oxide concentrations. (This plot does not include the value obtained at the

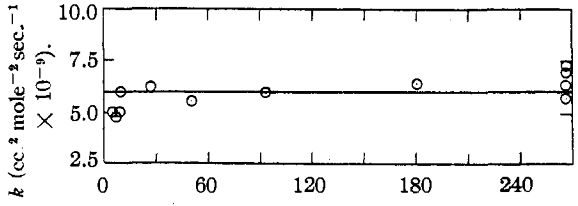

Fig. 2.—Specific rate values, $k = -(d(O_2)/dt)/(O_2)(NO)^2$, at various nitric oxide concentrations; data at 25° from Tables I and II.

lowest pressure in the 3-liter sphere, since at such a low pressure the amount of adsorbed nitric oxide apparently present even on the small surface makes a significant difference.) The constant appears to be maintained over a pressure range from 50 mm. down to less than 1 mm. with respect to the nitric oxide. The average k value from these data is 6.0×10^9 cc.$^2 M^{-2}$ sec.$^{-1}$ (at 25°), which is somewhat lower than Bodenstein's value of 7.06 (at 30°). After this research was started, Brown and Crist[10] reported data at very low pressures of 0.02 to 0.1 mm., with k(av.) $= 7.45 \pm 0.22 \times 10^9$ (25°) in good agreement with the data at much higher pressures.

The value of k varies only slightly with a considerable change of the oxygen concentration. The data of Table II show that a change from 144×10^{-8} to 6.6×10^{-8} M/cc. in the oxygen concentration alters the k value only from 5.8×10^9 to 6.4×10^9, which variation is within the range of experimental error. The reaction then appears to be established as essentially termolecular over an extremely wide pressure range for either nitric oxide or oxygen.

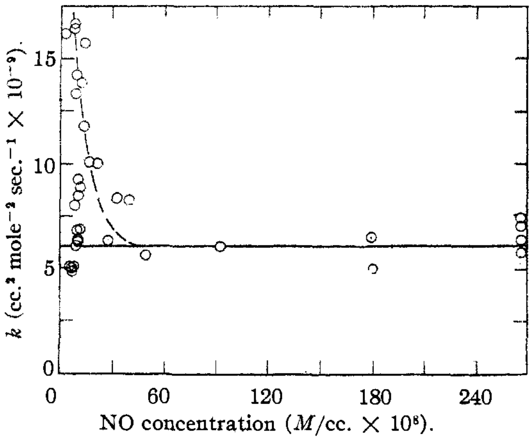

Fig. 3.—Specific rate values, $k = -(d(O_2)/dt)/(O_2)(NO)^2$, at various nitric oxide concentrations; data at 25°.

Further data were obtained in cylindrical tubes similar to the one used in obtaining the data of Table I except that no particular care was taken to ensure that nitric oxide was not adsorbed. Nitric oxide was admitted to the reaction vessel at a pressure of 15–20 mm. and removed by evacuation in order to rinse the tube. This was repeated several times. Finally more nitric oxide was added and then evacuated to the desired pressure which was measured with a McLeod gage. An alternative procedure was to rinse the tube with nitric oxide and then simply admit gas contained in a small side-tube of known volume at a relatively high measured pressure. The pressure in the large tube was then calculated from the relative dimensions of the tubes and the measured pressure.

Without special care to remove any adsorbed nitric oxide the rates observed are quite erratic. There is a sharp trend toward high k values as the nitric oxide pressure is decreased. These results are not given in tabular form because of their erratic nature, but they are shown graphically in Fig. 3 which gives the k values of all the data obtained at 25° as plotted against the corresponding nitric oxide concentrations.[11] An abrupt increase in k is apparent at low nitric oxide pressures. There appears to be no such pronounced or consistent increase in the value of k with decrease of the oxygen concentration. The data of Tables I and II (Fig. 2) obtained under conditions of little or no adsorption show no similar trend.

Additional data were obtained at 0° in a similar manner with no special attempt made to remove adsorbed nitric oxide. Results even more erratic than at 25° were found and extremely high k values obtained at the lowest pressures. The highest k value of 36.1 was found at the lowest nitric oxide concentration of 3.1×10^{-8} M/cc. (oxygen concentration at 77.8×10^{-8} M/cc.). No attempt was made to obtain data at 0° under conditions such that no adsorbed gases could have been present.

That the observed increase in k is to be attributed to adsorption is suggested by the fact that the rise is so sharp at the extremely low pressures where even a slight amount of adsorption would be of relatively high significance. It is not so apparent in the paraffined spherical vessel where the surface area is comparatively small. Furthermore, the effect is observed in the small tubes of high surface–volume ratio only when the previous history of the tube has provided opportunity for adsorption and not in the same vessel where care has been taken to remove any adsorbed nitric oxide. Extremely high k values are observed at 0°, at which temperature adsorption might be expected to be somewhat higher than at 25°. The increase

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[11] These plots are made on the assumption that with pressures in the range used change in the oxygen concentration had little or no effect on the k value. The data indicate that this approximation is reasonably justifiable.

in k therefore appears to be due perhaps not so much to a surface reaction as to the greater amount of nitric oxide present because of adsorption. There is good agreement between the results obtained with the sphere of relatively small surface–volume ratio and the data with the high surface cylinder in determinations where the possibility of adsorption was precluded. The above facts suggest that the oxidation of nitric oxide is essentially homogeneous in character, and, at reasonably high pressures at least, the rate is influenced only slightly by surface effects or a heterogeneous reaction. A similar conclusion has been reached by Briner and Sguaitamatti[12] as a result of a recent investigation.

Hasche and Patrick[5] have noted a rather sharp increase in the rate as the reaction neared completion, *i. e.*, as the concentrations became very low. This was particularly true in one run at 0° when a value for k of 39.86 was found. The increase was observed only during the latter half of the reaction. Similar behavior was found in this investigation, particularly at low pressures, except under conditions where nitric oxide adsorption was largely eliminated, in which case no increase in k was noted as the reaction proceeded toward completion. In the case of the $NO + H_2$ reaction Hinshelwood with Green[13] and Mitchell[14] have found an acceleration of the rate at low pressures.

An attempt was made to obtain data in a tube to which an appreciable amount of water vapor had been deliberately added. Several drops of water were placed in the reaction tube, and after a period of standing for several hours runs were continued. Rather anomalous results were obtained. While the reaction was found to begin at a rate only slightly slower than that in the dry tube, it appeared to stop far from completion. In some instances the amount of nitrogen dioxide actually appeared to decrease after this stop. While a clear-cut explanation for this inhibition of the reaction is not apparent, it is possible that disappearance of nitrogen dioxide due to solution in or reaction with the water may account for this apparent stoppage of the reaction. A disappearance of nitrogen dioxide more rapid than its production by the reaction could account for the observed decrease. When the tube was dried by evacuation during successive determinations, most erratic rates were observed. During this period there was evidence of considerable adsorption of nitric oxide and of pronounced surface effects. When oxygen was added to a tube which had been simply rinsed with nitric oxide and then evacuated, a very rapid reaction was observed to occur—without the addition of any nitric oxide except that which might have been present due to adsorption. The reaction was far more rapid than that with a large amount of nitric oxide in a dry tube. As runs were continued a gradual shift toward more consistent and reproducible rates was observed and finally, after a large number of evacuations, data quite comparable to those in the "dry" tubes were obtained. In some cases prolonged drying appeared to accelerate the rate somewhat.

In no case was Stoddart's observation regarding a difference due to the mode of addition of the gases to the reaction vessel confirmed. The rates observed by adding nitric oxide to oxygen appeared to be identical to those obtained when the reverse procedure was followed. It is perhaps true that the surfaces and gases used here were not as dry as were those used by Stoddart, since no such elaborate drying procedure was followed and the use of stopcocks was not avoided. It seemed likely, however, that in Stoddart's experiments, where the oxygen pressure was greater than the nitric oxide pressure at the start, a shift toward the nitric oxide bulb would start which might be expected to continue due to the contraction involved in the reaction

$$2NO + O_2 \longrightarrow 2NO_2 \rightleftarrows N_2O_4$$

A direct experimental check was made to show that this may actually have been the case. A 500-ml. round-bottom flask was connected with a similar 1000-ml. flask by a 9-cm. length of 11-mm. (o.d.) tubing. At the center of this connecting tube there was a large bore (4 mm.) stopcock. Oxygen was placed in one flask and nitric oxide in the other. With widely different initial pressures in the two flasks, a decided drift was apparent for several minutes after the stopcock was opened. Very little back diffusion was noted, and after thirty minutes only a light straw yellow color of nitrogen dioxide was apparent in the flask which initially contained gas at the higher pressure. The color in the other flask was invariably very dark. The reaction was found to occur, apparently equally well, in either

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(12) Briner and Sguaitamatti, *Helv. chim. acta*, **24**, 88–95 (1941).

(13) Hinshelwood and Green, *J. Chem. Soc.*, 730 (1926).

(14) Hinshelwood and Mitchell, *ibid.*, 378 (1936).

the nitric oxide or oxygen flask depending upon the initial pressures. However, no attempt was made to ensure complete dryness. The drift was observed toward either the nitric oxide or oxygen flask. Since the dimensions of the connecting tube in Stoddart's apparatus are not given, no estimate regarding the opportunity for diffusion from one bulb to the other can be made. It is likely that only a slight amount of nitric oxide entered the oxygen bulb in the cases where the initial oxygen pressures were greater than those of nitric oxide, and consequently one would not expect the appearance of much nitrogen dioxide in a short time.

Summary

1. A colorimetric method for accurately measuring the concentration of nitrogen dioxide is described for following the rate of oxidation of nitric oxide. This method, being specific for nitrogen dioxide, avoids some of the difficulties involved in the frequently employed manometric technique. It is particularly well adapted to high pressure measurements, where the rate is very rapid, and to low pressure determinations where minute amounts of nitrogen dioxide must be detected. At pressures of only a few tenths of a millimeter, nitrogen dioxide was easily detected and measured. Consequently it may be used conveniently over an extremely wide range. Data have been obtained over a 100-fold nitric oxide concentration range, at pressures ranging from approximately 0.5 mm. up to 50 mm. and at the two temperatures 0 and 25°.

2. Satisfactory agreement of the data with those previously reported was found at moderately high pressures and at low pressures where adsorption effects were eliminated. At very low pressures adsorption and surface effects were found to have a considerable influence on the reaction rate, as shown by a sharp increase in the rate constant at pressures in the range of only a few millimeters or less, particularly at the lower temperature. Such an increase was not found in the absence of an adsorbed film of nitric oxide. The results suggest that the oxidation of nitric oxide is essentially homogeneous in nature, but that adsorbed nitric oxide (and oxygen to a less extent) introduce complications at low pressures.

3. The influence of the presence of appreciable amounts of water vapor has been investigated.

4. Stoddart's observation that no reaction occurs when nitric oxide is added to a tube containing oxygen was not confirmed by the results of these experiments.

URBANA, ILLINOIS RECEIVED OCTOBER 7, 1942

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC COMPANY]

The System Water–*n*-Butanol–Toluene at 30°

BY RAYMOND M. FUOSS

I. Introduction

The classical method of determining liquid–liquid equilibria by observing the appearance and disappearance of turbidity is tedious, and, for work at a fixed temperature, somewhat inconvenient. The purpose of this paper is to present a rapid method of determining liquid solubilities, using the system water–*n*-butanol–toluene as an example. Briefly, the method consists in adding water, containing a trace of hydrochloric acid, in successive portions to a butanol–toluene mixture of known composition. As long as the water dissolves in the organic phase, the conductance increases; with the appearance of an aqueous phase, the conductance of the organic phase drops on further addition of water, because the aqueous phase extracts hydrogen chloride from the organic phase. The saturation point is given by the cusp in the titration curve when conductance is plotted against the amount of water added.

II. Experimental Details

The butanol and toluene were redistilled C. P. products; their densities and indices of refraction checked the values given in the "International Critical Tables." About 150 g. of toluene plus butanol was weighed into a glass-stoppered Erlenmeyer flask which was then placed in a thermostat at 30.0°. A portion of water containing several tenths per cent. of hydrochloric acid was added from a weight buret and, after temperature equilibrium had been established, the conduc-