### 4. Dehydrogenation

**2,3-Dimethylphenanthrene.**—Various hydrocarbon mixtures obtained as described above were submitted to dehydrogenation with entirely similar results. After heating 2.1 g. of a mixture of the tetra- and hexahydrides with 3 g. of selenium, added in portions, at 310° for twenty hours, the melt solidified completely on cooling. After extracting and distilling the product, one crystallization from methyl alcohol gave 1.6 g. (78%) of plates, m. p. 77–78°. On recrystallization from alcohol or petroleum ether the hydrocarbon formed fluorescent plates, m. p. 78–78.5°.

*Anal.* Calcd. for $C_{16}H_{14}$: C, 93.16; H, 6.85. Found: C, 92.86; H, 7.08.

The **picrate** formed light yellow needles from alcohol, m. p. 146–147°. The **quinone** crystallized from glacial acetic acid as glistening orange plates, m. p. 237.5–238.5° (**quinoxaline derivative,** m. p. 208–209°).

*Anal.* Calcd. for $C_{16}H_{12}O_2$: C, 81.32; H, 5.13. Found: C, 81.23; H, 5.37.

In a letter to one of us Dr. R. D. Haworth states that the original specimen of 2,3-dimethylphenanthrene picrate prepared by his method[9] melts, after two recrystallizations from alcohol, at 144–145°; the regenerated hydrocarbon melts at 79–80°, and the styphnate (Found: C, 58.47; H, 3.95) melts at 137–148° (the m. p. given as 165–167° by a typographical error should have been 145–147°). Dr. Haworth compared his hydrocarbon, picrate, quinone and quinoxaline derivative with ours and observed no depressions; the constants are all in close agreement.

A mixture of 0.5 g. of 2,3-dimethylphenanthrene, 1 cc. of concentrated nitric acid, and 2 cc. of water was heated at 180–200° for twelve hours. As the reaction was not complete, an additional 1 cc. of acid was introduced and the tube was reheated. On concentrating the clear yellow solution and adding fuming nitric acid, the oxidation product was caused to separate. The crude acid was heated at 250° and the anhydride was sublimed in vacuum and crystallized from dioxane, giving prisms containing dioxane of crystallization. After drying at 150° in vacuum to remove the solvent, the substance melted at 277–279° and gave no depression when mixed with a sample of pyromellitic anhydride purified in the same way.

## Summary

A new synthesis of phenanthrene has been developed which, in its simplest complete form, involves the following steps: (1) the preparation of γ-phenylbutyric ester, for example, by the condensation of benzene with succinic anhydride, followed by Clemmensen reduction and esterification; (2) condensation with oxalic ester; (3) cyclization to the anhydride of 3,4-dihydronaphthalene-1,2-dicarboxylic acid (the Bougault reaction, as applied by von Auwers and Möller); (4) the addition of butadiene (Diels–Alder reaction); (5) decarboxylation by fusion with alkali (a reaction which may yield a mixture of hydrophenanthrenes, but in which the carbon skeleton is not disturbed); (6) dehydrogenation.

The yields throughout are excellent, and pure products are obtainable at every step except (5). Some variation is possible in step (4), and the compounds required in (1) are already available in wide variety. Successful experiences with reactions (2), (3) and (4), using γ-arylbutyric esters of both the benzene and naphthalene series, indicate that the synthesis probably is capable of wide application.

CONVERSE MEMORIAL LABORATORY
CAMBRIDGE, MASS.
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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

# The Oxidation of Carbon Monoxide Catalyzed by Nitrogen Dioxide[1]

BY R. H. CRIST AND O. C. ROEHLING

The oxidation of carbon monoxide is recognized as being of the chain type. The rate at high temperatures is explosive and exhibits the familiar pressure limits.[1] The explosive reaction as shown by Dixon, and Weston and Garner is changed by the presence of water vapor and hydrogen. A homogeneous reaction outside of the explosive region has not been measured. However, studies of a heterogeneous reaction have been made by Bodenstein and Ohlmer in a quartz vessel at 308°, the rate being proportional to the oxygen and inversely proportional to the carbon monoxide and by Langmuir, who found similar results with platinum at 700°. McKinney[2] studied the oxidation at 80° on platinum oxide. The explosive system has been shown by Semenoff and his co-workers[1] to be very sensitive to traces of nitrogen dioxide.

The present investigation is concerned with this reaction under conditions such that the rate of the oxidation in the presence of nitrogen dioxide is measurable. Preliminary experiments show[3]

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[1] For a discussion of this reaction and the literature see Hinshelwood, "Kinetics of Chemical Change in Gaseous Systems," Oxford Univ. Press., 1933, and Semenoff, "Chemical Kinetics and Chain Reactions," The Clarendon Press, Oxford, 1935.

[2] McKinney, THIS JOURNAL, **56**, 2577 (1934).

[3] Crist and Roehling, *Science*, **80**, 338 (1934).

that the rate increases very rapidly with the nitrogen dioxide pressure and after passing a maximum decreases rapidly. Hydrogen and water were also found to increase the rate.

## Experimental Methods

**Preparation of Gases.**—The nitrogen dioxide was prepared from lead nitrate, pumped free from other oxides of nitrogen, redistilled, and stored as the solid by means of solid carbon dioxide. It was passed over phosphorus pentoxide before using.

The carbon monoxide was made by adding formic acid to concentrated sulfuric acid. The gas was passed through a solution of potassium hydroxide to remove carbon dioxide and dried by sulfuric acid and phosphorus pentoxide. When used it was passed through a liquid air trap.

Oxygen was taken from a commercial tank. The hydrogen was removed by passing it over hot copper oqide and then drying with magnesium perchlorate. The reaction was very sensitive to small traces of hydrogen so that the removal procedure had to be followed carefully.

Hydrogen was taken from a commercial cylinder and was dried before using.

**Procedure.**—The investigation was carried out at 527° in a Pyrex vessel of 260-cc. capacity. The vessel was put into the well of a sulfur boiler. The boiling point of the sulfur was controlled by maintaining a constant pressure of nitrogen over the sulfur vapor by means of a barostat arrangement.[4] The barostat consisted of a gas reservoir containing a heating element controlled by contact points on a manometer. The temperature variation on the boiler wall was less than 0.3°. The actual value of the temperature was read from a millivoltmeter giving a temperature accuracy of $\pm 2.5°$.

The measurement of the pressure of nitrogen dioxide was made by a Pirani type gage.[5] The filament consisted of a thin-walled U-shaped Pyrex capillary filled with mercury[6] with a total length of 20 cm. and a resistance of 31.2 ohms. The gage was calibrated against a McLeod gage using carbon dioxide. The pressure of a sample of nitrogen dioxide in contact with the solid at $-63.5°$ (melting chloroform) was read from the calibrated Pirani gage as 0.450 mm. while the value from the "International Critical Tables" is 0.467 mm. The error is thus 3.7%. The precision of measurement as determined from the instrument set-up was $10 \rightarrow 2.5\%$ for the pressure limits of $0.061 \rightarrow 1.53$ mm.

The nitrogen dioxide was measured in an auxiliary system and frozen into a capillary U-tube next to the reaction vessel and it was then carried into the reaction vessel by the carbon monoxide or oxygen.

The filling of the reaction vessel was first tried in the ordinary manner but certain mixtures were found to react so rapidly that it became difficult to determine the initial pressures. It was necessary, therefore, to use a special filling method for the last gas, usually the carbon monoxide. A vessel was filled to the required pressure and the gas was then forced into the reaction vessel by mercury through capillary connecting tubes. The known ratios of the volumes involved then enabled a satisfactory calculation of the initial pressures in the reaction vessel.

Experience showed that consistent results could be obtained only if a definite procedure for introducing the gases was carefully followed. The experiments with hydrogen in the reacting mixture were the most troublesome. The best results were obtained when the vessel was twice filled with hydrogen-free oxygen and evacuated. It was also found necessary to fill the system with dry oxygen before such operations as regreasing of stopcocks, for if filled with air several runs were required before consistent results could be obtained.

## Results

**Oxidation of Carbon Monoxide Catalyzed by Nitrogen Dioxide.**—This study consisted in determining the rates of the reaction with different concentrations of nitrogen dioxide, the partial pressures of carbon monoxide and oxygen being kept approximately constant at 500 and 250 mm., respectively. The temperature was 527°. The highest pressure of nitrogen dioxide was 4.85 mm., this giving a rate that was as fast as could be measured reliably. The results are given in Table I and Figs. 1 and 2.

TABLE I

THE EFFECT OF NITROGEN DIOXIDE

| No. | $p_{O_2}$ | $p_{CO}$ | $p_{NO_2}$ | $\Delta p$ (5 to 35 min.) |
|---|---|---|---|---|
| 1 | 249.2 | 501.0 | 0.061 | 15.0 |
| 2 | 253.2 | 512.0 | .133 | 36.0 |
| 3 | 250.1 | 502.6 | .171 | 46.8 |
| 4 | 253.0 | 501.4 | .171 | 48.0 |
| 5 | 246.9 | 490.2 | .171 | 50.0 |
| 6 | 249.4 | 504.6 | .204 | 55.6 |
| 7 | 250.9 | 499.4 | .221 | 47.0 |
| 8 | 242.6 | 502.8 | .265 | 56.2 |
| 9 | 249.5 | 506.8 | .265 | 49.4 |
| 10 | 246.8 | 504.8 | .315 | 62.6 |
| 11 | 248.1 | 498.4 | .315 | 39.2 |
| 12 | 250.9 | 503.6 | .320 | 43.4 |
| 13 | 252.6 | 493.8 | .375 | 42.0 |
| 14 | 253.7 | 492.8 | .398 | 44.4 |
| 15 | 243.5 | 498.6 | .585 | 22.8 |
| 16 | 249.1 | 509.8 | 1.22 | 17.4 |
| 17 | 254.3 | 507.4 | 1.72 | 21.4 |
| 18 | 253.2 | 511.6 | 2.35 | 40.6 |
| 19 | 247.8 | 504.6 | 2.42 | 33.4 |
| 20 | 248.1 | 500.6 | 4.85 | 114.6 |
| 21 | 260.8 | 530.0 | 4.85 | 123.2 |

The pressures are expressed in mm. and the rates have been determined by taking the pressure change from five to thirty-five minutes. Examination of some typical curves given in Fig. 1 for experiments at 527° with carbon monoxide and oxygen pressures approximately 500 and 250 mm., respectively, and with nitrogen dioxide at 0.061

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[4] C. C. Coffin, THIS JOURNAL, **55**, 3646 (1933).

[5] Dunoyer and Smith, "Vacuum Practice," Van Nostrand and Co., Inc., New York City, 1926.

[6] G. K. Rollefson, THIS JOURNAL, **51**, 804 (1929).

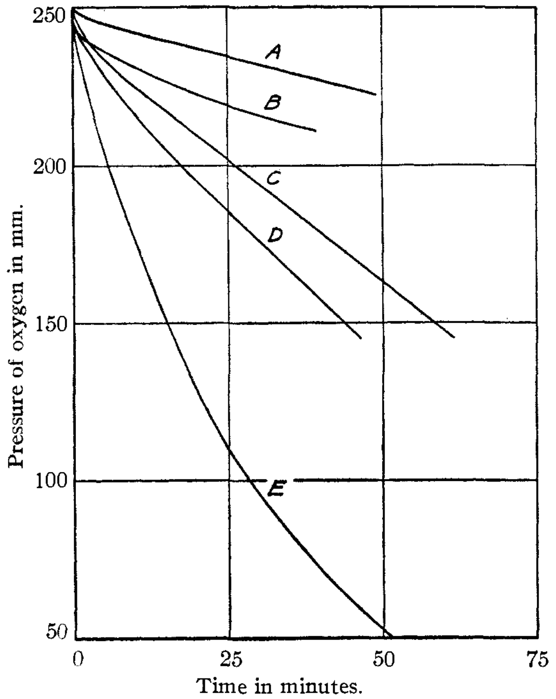

Fig. 1.—Typical runs with $CO/O_2 \sim 2$ and nitrogen dioxide as indicated: A, 0.061 mm. nitrogen dioxide; B, 0.580; C, 0.171; D, 0.315; E, 4.85.

TABLE II

THE EFFECT OF CARBON MONOXIDE

| No. | $p_{O_2}$ | $p_{CO}$ | $\Delta p$ (5 to 35 min.) |
|---|---|---|---|
| 1 | 198.2 | 102.4 | 2.4 |
| 2 | 200.7 | 215.6 | 6.8 |
| 3 | 195.2 | 307.4 | 8.4 |
| 4 | 197.7 | 504.6 | 26.6 |
| 5 | 196.4 | 404.6 | 16.4 |

TABLE III

THE EFFECT OF OXYGEN

| No. | $p_{O_2}$ | $p_{CO}$ | $\Delta p$ (5 to 35 min.) |
|---|---|---|---|
| 1 | 101.6 | 207.6 | 4.0 |
| 2 | 200.7 | 215.6 | 5.8 |
| 3 | 303.1 | 200.8 | 7.4 |
| 4 | 414.8 | 192.2 | 10.6 |
| 5 | 500.0 | 192.6 | 14.0 |

TABLE IV

THE EFFECT OF TOTAL PRESSURE; RATIO $CO/O_2 \sim 2$

| No. | $p_{O_2}$ | $p_{CO}$ | $p_{O_2} + p_{CO}$ | $\Delta p$ (5 to 35 min.) |
|---|---|---|---|---|
| 1 | 54.0 | 103.4 | 157.4 | 2.8 |
| 2 | 101.6 | 207.6 | 309.2 | 4.0 |
| 3 | 196.4 | 404.6 | 601.0 | 16.4 |
| 4 | 158.8 | 398.2 | 557.0 | 14.2 |
| 5 | 249.8 | 504.6 | 754.4 | 32.0 |
| 6 | 251.5 | 509.6 | 761.1 | 31.6 |
| 7 | 247.2 | 506.0 | 753.2 | 26.2 |

mm. shows that this should provide a satisfactory measure of the rate. Curve B of Fig. 2, where the conditions were the same as for Fig. 1, shows the very striking effect of nitrogen dioxide in the acceleration and the equally effective inhibition by the catalyst. This is similar to the catalysis by nitrogen dioxide of the hydrogen oxidation as found by Norrish.[7] In the case of carbon monoxide, however, an increasing rate is again observed with still higher concentrations of the catalyst.

The dependence of the reaction on the other components of the system was found by maintaining a constant pressure of nitrogen dioxide and varying in turn the carbon monoxide and oxygen. From these data and also from some additional runs, the effect of total pressure was obtained. The results are given in Tables II, III and IV, and in Fig. 3. The rate was estimated as before, no marked change in rate being observed in the course of the reaction during the five to thirty-five minute interval. In all cases the temperature was 527° and the pressure of nitrogen dioxide was constant at 0.585 mm.

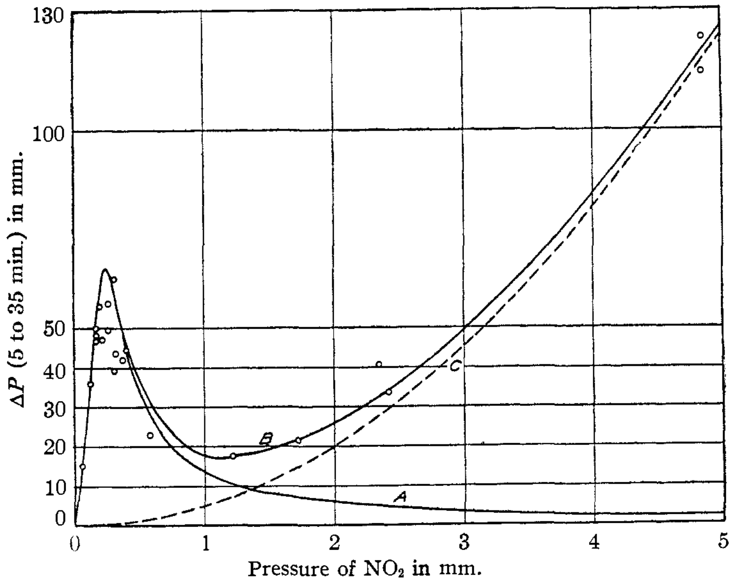

Fig. 2.—The rate of the oxidation of carbon monoxide as a function of the pressure of nitrogen dioxide; Curve B is the sum of A and C. A represents a chain process and C the trimolecular oxidation of nitric oxide.

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[7] Norrish and Griffiths, *Proc. Roy. Soc.* (*London*), **A139**, 147 (1933).

**The Effect of Hydrogen and Water on the Catalyzed Oxidation of Carbon Monoxide.**—It was found difficult to obtain a consistent set of data in this study. Some of the uncertainties may have been due to the time factors involved in introducing the gases. It was not possible to mix the gases prior to their introduction into the flask, because of the danger of explosion for which the apparatus was not designed. However, by a rigorous adherence to the definite procedure outlined in the first part it was possible to obtain fairly satisfactory data. The mixtures with more than 0.53 mm. of hydrogen had reacted completely by the time the gases were introduced, as was shown by the carbon dioxide obtained. In some cases, however, the initial rate was measurable but within a minute the manometer would drop suddenly and the reaction would be complete as evidenced by the total pressure change and by the yield of carbon dioxide. The pressures of water vapor were obtained by passing the carbon monoxide over ice at the required temperature. The results are shown in Figs. 4, 5 and 6. The carbon monoxide and oxygen pressures were approximately 500 and 250 mm. for all but Fig. 5, where the pressures were 270 and 230 mm., respectively. Figure 4 shows the relative effects of water vapor and hydrogen.

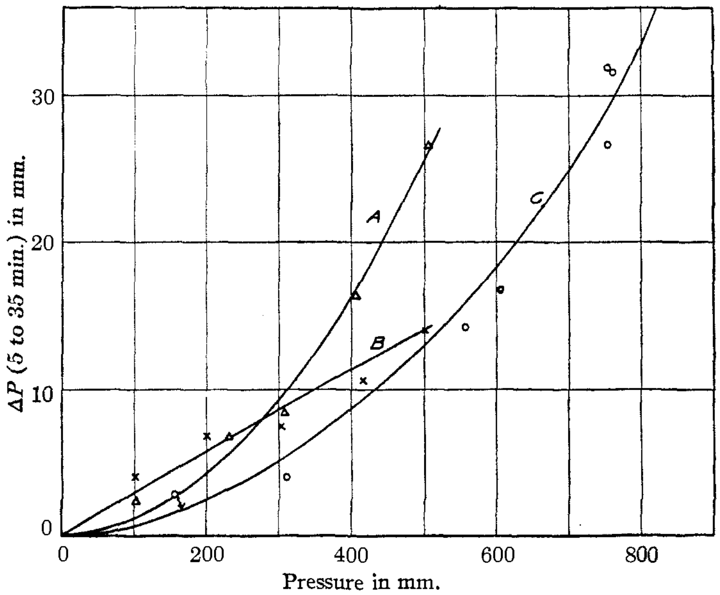

Fig. 3.—Curves A and B show the effect of carbon monoxide and oxygen, respectively. Curve C shows the rate as a function of the total pressure of carbon monoxide and oxygen. It is a composite of A and B. The pressure of nitrogen dioxide was 0.585 mm.

## Discussion of Results

**The Catalysis by Nitrogen Dioxide.**—The character of the curve, Fig. 2 for the effect of nitrogen dioxide suggests that it is a composite of two separate processes. A formal mathematical analysis on any other basis is difficult. If the analogous nitrogen dioxide catalyzed hydrogen oxidation[7] is considered one process would be that represented by Curve A in Fig. 2, which is expressed by the equation

$$y = ax/(b - cx + x^2)$$

where $x$ is the nitrogen dioxide pressure and $y$ the rate. The other process is the remainder of the experimental curve and is shown as Curve C. This has the form, $y = k_3x^2$, where $k_3$ has the value of 5.0.

The nature of the second process can be understood by an examination of Experiment 21, Table I, where the pressure of nitrogen dioxide was 4.85 mm. The rate of this reaction was sufficiently rapid so that the course of the reaction was followed conveniently to three-fourths completion. This rate was found to be first order with respect to the oxygen. The constants given in Table V are calculated for the equation

$$k_2 = \frac{2.3}{t} \log \frac{(O_2)t_0}{(O_2)t}$$

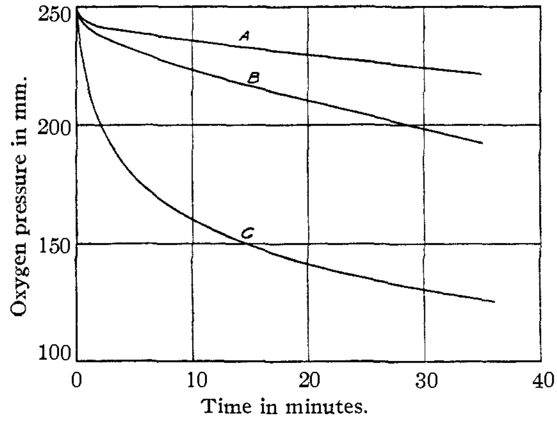

Fig. 4.—Individual runs to show the relative effect of water and hydrogen on the rate: A, no hydrogen or water; B, 0.100 mm. $H_2O$; C, 0.100 mm. $H_2$; pressure of nitrogen dioxide, 1.22 mm.; temperature, 527°.

The value for $p_{O_2}$ at $t = 0$ was obtained from the plot of log $p_{O_2}$ against time and is given in parentheses.

TABLE V

RATE OF REACTION FOR $-d(O_2)/dt = k_2(O_2)$

| $t$, min. | $p_{O_2}$ | $k_2$ |
|---|---|---|
| 0 | (248.3) | ... |
| 1 | 244.8 | 0.0143 |
| 2 | 237.0 | .0234 |
| 5 | 217.0 | .0269 |
| 10 | 186.6 | .0285 |
| 15 | 161.2 | .0288 |
| 18 | 147.6 | .0289 |
| 22 | 132.2 | .0286 |
| 35 | 93.8 | .0278 |
| 40 | 82.8 | .0274 |
| 45 | 73.8 | .0270 |
| 53 | 61.2 | .0264 |
| 63 | 51.2 | .0251 |

Let it be assumed that the nitrogen dioxide is removed rapidly by the reaction

$$NO_2 + CO \longrightarrow CO_2 + NO$$

which is followed by

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

Then, if the second reaction determines the rate, the observed velocity would be

$$-d(O_2)/dt = k_1 (NO)^2(O_2) \qquad (1)$$

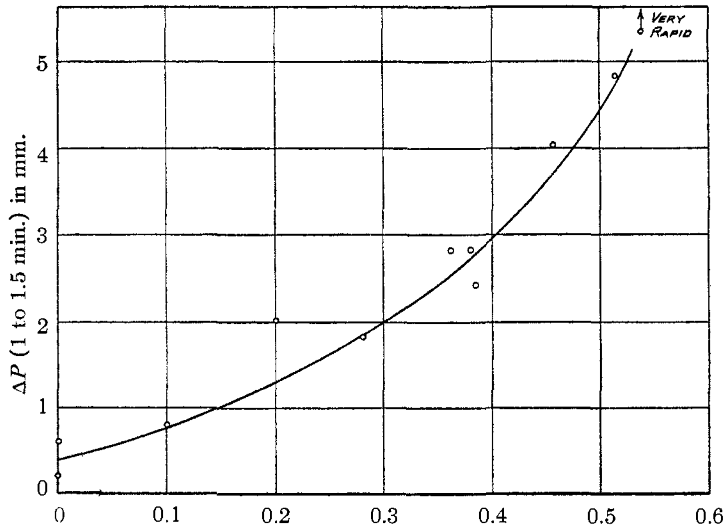

Fig. 5.—The effect of hydrogen: pressure of nitrogen dioxide, 1.22 mm.; temperature, 490°.

Since the concentration of nitric oxide is kept constant by the first of the above reactions, the rate is then

$$-d(O_2)/dt = k_2 (O_2) \qquad (2)$$

where $k_2 = k_1 (NO)^2$. This is confirmed by the data of Table V. If the nitric oxide pressure (or nitrogen dioxide pressure) is varied and the oxygen pressure is kept constant, the rate is given by

$$-d(O_2)/dt = k_3(NO_2)^2$$

These are the conditions under which the data represented by Curve B of Fig. 2 were obtained and Curve C represents the equation, Rate = $5.0[NO_2]^2$.

The average value for $k_2$ from Table V is 0.0272 min.$^{-1}$ = $4.53 \times 10^{-4}$ sec.$^{-1}$. By equations (1) and (2)

$$k_2 = k_1(NO)^2 \text{ or } k_1 = k_2/(NO)^2$$

Using (NO) = 4.85 mm. = $9.72 \times 10^{-8}$ mole cc.$^{-1}$, $k_1 = 4.79 \times 10^{10}$ cc.$^2$ mole$^{-2}$ sec.$^{-1}$. A comparison of this value with previous experimental data on the oxidation of nitric oxide cannot be made since the highest temperature used for the direct measurement of the rate was 390°. From liquid air temperatures to this temperature the rate decreases about 16 fold, and present theories concerning the rate of this reaction[8] predict an increasing rate with temperature at high temperatures. For the temperature used in this investigation a rate of 1.3 $\longrightarrow$ $9.8 \times 10^9$ cc.$^2$ mole$^{-2}$ sec.$^{-1}$ is predicted.[9] The experimental result put forward here is in line with this prediction.

It was found in this investigation that light of 3650 Å. in the first predissociation region of nitrogen dioxide had no effect on the rate. This result is rather surprising since Norrish[7] noticed a great increase in the rate of the oxidation of hydrogen catalyzed by nitrogen dioxide upon irradiation with such light. However, this negative result is in accord with the assumption that the nitrogen dioxide is removed rapidly by the carbon monoxide.

The next part of the discussion is concerned with Curve A of Fig. 2. The empirical equation for Curve A is

$$R = \frac{9.46\ (NO_2)}{0.0625 - 0.354\ (NO_2) + (NO_2)^2}$$

This equation can be derived on a formal chain theory. Thus, if ($S$) represents the number of chains in operation, then on the usual assumption of the steady state[10]

$$d(S)/dt = k_1(NO_2) + k_2(NO_2)(S) - k_3(S) - k_4(NO_2)^2(S) = 0$$

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[8] Kassel, "Kinetics of Homogeneous Gas Reactions," Chemical Catalog Co., New York City, 1932, p. 168; Gershinowitz and Eyring, THIS JOURNAL, **57**, 985 (1935).

[9] Private communication from Dr. Gershinowitz.

[10] Nitrogen dioxide is used here to conform with the empirical equation. In the interpretation of this equation to follow we have used equations involving nitric oxide. We may assume that the nitric oxide concentration is proportional to the nitrogen dioxide concentration so that the equation here would be altered by the necessary proportionality factors.

From the equation we get $(S) = k_1(\mathrm{NO_2})/[k_3 - k_2(\mathrm{NO_2}) + k_4(\mathrm{NO_2})^2]$. If the rate is proportional to the number of chains $(S)$, we have the equation of the rate as given above.

It is difficult to find an acceptable mechanism for this development. There is not sufficient information at hand to determine the nature of the initial process. The absence of a photochemical effect, which was explained previously, eliminates that as a clue to the initial step. In the case of the hydrogen–oxygen reaction catalyzed by nitrogen dioxide, the results obtained by Norrish were similar to those obtained here, showing the same kind of maximum. Also the rates were greatly enhanced by light of 3650 Å. From the known primary process on the absorption of light of wave length λ = 3650 Å. by nitrogen dioxide, namely

$$\mathrm{NO_2} + h\nu \longrightarrow \mathrm{NO} + \mathrm{O}$$

Norrish proposed a chain mechanism involving atomic oxygen in order to account for the kinetics of the light reaction. He suggested that since the thermal reaction is similar to the photo-reaction, the oxygen atoms for the thermal reaction could be provided by such reactions as

$$\mathrm{NO_2} \longrightarrow \mathrm{NO} + \mathrm{O} - 72.6 \text{ kcal.}$$
$$\mathrm{NO} + \mathrm{O_2} \longrightarrow \mathrm{NO_2} + \mathrm{O} - 44.4 \text{ kcal.}$$

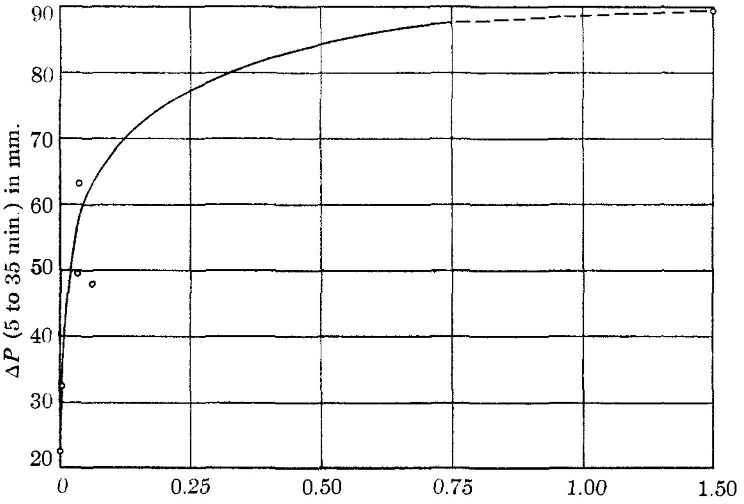

Fig. 6.—The effect of water: pressure of nitrogen dioxide, 0.585 mm.; temperature, 527°.

With these considerations in mind the following mechanism can be suggested for the oxidation of carbon monoxide.

$$\begin{array}{rcll}
\mathrm{O} + \mathrm{O_2} & \longrightarrow & \mathrm{O_3} & (1)\\
\mathrm{O_3} + \mathrm{CO} & \longrightarrow & \mathrm{CO_2'} + \mathrm{O_2'} & (2)\\
\mathrm{O'} + \mathrm{CO} & \longrightarrow & \mathrm{CO_2} + \mathrm{O} & (3)\\
\mathrm{NO} + \mathrm{O_2'} & \longrightarrow & \mathrm{NO_2} + \mathrm{O} & (4)\\
\mathrm{NO} + \mathrm{NO} + \mathrm{O} & \longrightarrow & \mathrm{NO_2} + \mathrm{NO} & (5)
\end{array}$$

The oxygen atoms could be supplied originally by nitrogen dioxide as above. Reactions (4) and (5) are set up in order to yield the equation for the Curve A of Fig. 2. Reaction (4) would require a very unusual stability to collision of the excited oxygen molecules with other molecules than the nitric oxide. Also, it would seem that any third body would serve as well as nitric oxide in (5). With regard to reactions (1) and (2), the recent work of Jackson[11] must be considered. He found that the illumination of oxygen–carbon monoxide mixtures with light of wave length λ = 1700 Å., which is capable of dissociating the oxygen molecules into atoms, produced ozone and little or no carbon dioxide at room temperature. At 500° only carbon dioxide was formed. The author does not discuss the mechanism of this formation of carbon dioxide, *i. e.*, whether it occurs directly with oxygen atoms or through the intermediate formation of ozone. The important facts of his paper in the present connection are: (1) his observation that the rate is independent of the total pressure, the ratio of the gases remaining constant; and, (2) the rate decreases if the carbon monoxide is increased, the total pressure remaining constant.

The study given in Tables II, III, IV and Fig. 3 shows the effect on the rate of the ratio of the gases and of the total pressure with constant pressure of nitrogen dioxide of 0.585 mm. The rate is directly proportional to the first power of the oxygen pressure and to the square of the carbon monoxide pressure, as is shown by Curves B and A of Fig. 3. Curve A is represented by the equation

$$R = 1.03 \times 10^{-4}(\mathrm{CO})^2$$

The effect of carbon monoxide is rather unusual, as all previous work has involved the first and negative powers of the carbon monoxide pressure. Curve C, which gives the effect of changing the total pressure with the ratio constant at 2:1, can be shown to be a composite of the separate oxygen and carbon monoxide curves.

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[11] Jackson, THIS JOURNAL, **56**, 2631 (1934).

Some further information concerning the effect of total pressure of carbon monoxide and oxygen with the ratio constant at 2:1, can be obtained from a study of individual curves. In the case of No. 15, Table I, with nitrogen dioxide = 0.585 mm., the rate dropped to 59% when the reaction had progressed 20%, while curve C of Fig. 3 would predict a drop of 64%. This agreement is to be expected as all the data of Curve C are for conditions the same as No. 15. For No. 21, the nitrogen dioxide = 4.85 mm. and at 40% completion the rate has been reduced to 71%, while if this change in rate were due to change in carbon monoxide pressure only the prediction from Curve C would be 53%. This disagreement would be expected, if our earlier interpretation of the run is correct, namely, that the rate-determining step at these pressures of nitrogen dioxide is the trimolecular oxidation of nitric oxide. If we examine the results for a very low pressure of nitrogen dioxide as given by those runs on the rising part of Curve A, the one carried farthest (40% completion) was No. 8 and it was found to be linear throughout. This result would indicate that under these conditions the rate is independent of the total pressure of the reacting gases. The work of Jackson showed that the rate was independent of the total pressure and inversely proportional to the carbon monoxide pressure. It is found here that only at very low pressures of nitrogen dioxide is the rate independent of the total pressure and further that the rate increases with carbon monoxide pressure except for very low pressures of nitrogen dioxide, where it appears to be independent. This disagreement with the work of Jackson would indicate that an atomic chain is of some doubt though it is not definitely excluded.

**The Effect of Hydrogen and Water Vapor.**—The study of the effect of hydrogen on the nitrogen dioxide catalyzed oxidation of carbon monoxide is somewhat complicated by the formation of water which undoubtedly occurs during the progress of the reaction. This effect of the loss of "catalyst" has been largely eliminated in the results given in Fig. 5 by taking the rate as the pressure change from one to one and one-half minutes. The experimental points are considerably scattered and do not justify a thorough mathematical analysis, but the rate is approximately proportional to the square of the hydrogen pressure. The curve would rise much faster if tangents to zero time could be drawn. Whether the rates above 0.53 mm. of hydrogen were very rapid or explosive could not be determined.

In order to explain the effect of hydrogen, an atomic chain mechanism can be assumed. In the work of Norrish on the oxygen-hydrogen-nitrogen dioxide system, the atomic chains are assumed to be initiated by atomic oxygen. Recently Geib and Harteck[12] have shown that when hydrogen atoms are introduced into a mixture of hydrogen, oxygen and carbon monoxide, the ratio of the water to the carbon dioxide formed increases only slightly on going from room temperature to 100°. From a consideration of their results, and assuming that there is only a slight change in the ratio of water to carbon dioxide formed on further increase of temperature, the following mechanism is reasonable

$$O + H_2 \longrightarrow OH + H + 0.8\text{ kcal.} \qquad (1)$$
$$OH + CO \longrightarrow CO_2 + H + 23.8\text{ kcal.} \qquad (2)$$
$$H + O_2 + O_2 \longrightarrow HO_2 + O_2' \qquad (3)$$
$$H + O_2 + CO \longrightarrow CO_2 + OH \qquad (4)$$
$$HO_2 + CO \longrightarrow CO_2 + OH \qquad (5)$$
$$OH + OH \longrightarrow H_2O + O \qquad (6)$$
$$OH + H_2 \longrightarrow H_2O + H + 31.1\text{ kcal.} \qquad (7)$$

(2), (6) and (7) are probably fast. (3) has a collision efficiency of about 1 and (4) has an efficiency of about 0.1 while (5) is somewhat less. In view of previous considerations, there is uncertainty about the initiation of the hydrogen chains as given in reaction (1).

The comparative effect of hydrogen and of water is given in Fig. 4; the former is seen to be very much greater. Now, if the hydrogen concentration were the most important factor in determining the rate, its complete disappearance in the formation of water would be indicated by a rate equal to that for water of the same concentration. This is indicated by the fact that the slopes of Curves B and C of Fig. 4, thirty minutes, are about the same. Final decision must be reserved until the effect of change in carbon monoxide and oxygen with water present is known. It is not possible to predict this from the earlier results, as we are now dealing with a very different mechanism. As a mechanism for the effect of water vapor, we may suggest

$$H_2O + CO \longrightarrow CO_2 + H_2$$

together with the hydrogen-oxygen-carbon monoxide mechanism previously discussed.

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[12] Geib and Harteck, *Z. physik. Chem.*, **170A**, 1 (1934).

## Summary

1. The oxidation of carbon monoxide catalyzed by nitrogen dioxide has been measured at 527°. The rate-determining reaction at low concentrations of the catalyst appears to be a chain mechanism, and at higher concentrations to be the trimolecular oxidation of nitric oxide.

2. The rate is first order with respect to oxygen at high concentrations of the catalyst and at low concentrations it is proportional to the oxygen and also to the second power of the carbon monoxide.

3. The initial rate is approximately proportional to the square of the hydrogen pressure and is infinite with the hydrogen greater than 0.53 mm.

4. The effect of water has been found.

5. The oxidation of nitric oxide at 527° has been discussed.

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[Contribution from the Department of Chemistry, New York University]

# The Solubility of Ammonium Oxalate in Water

By Arthur E. Hill and Edgar F. Distler[1]

The figures on the solubility of ammonium oxalate in water as given in "International Critical Tables,"[2] cover the range from 0 to 50°; they are based upon a small number of individual determinations[3] and lead to a curve with an estimated variation of ±3%. The present investigation was undertaken to extend the temperature range and to improve the probable accuracy.

For the experimental work, analyzed ammonium oxalate was recrystallized, giving a product which agreed upon analysis with the formula for the monohydrate. Samples were enclosed with water in glass-stoppered Pyrex vessels and rotated in thermostats; equilibrium was reached in a few hours with good stirring. The 0° temperature was obtained in an ice-bath, temperatures up to 45° in a water-filled thermostat, and higher temperatures in a glycerol-filled thermostat; the temperature variation was not greater than ±0.05° at the lower temperatures, about ±0.1° at 60 and 75° and about ±0.2° at 87 and 100°; the thermometer was compared with a standard and corrected for emergent stem. Samples for analysis were withdrawn through cotton and paper filters into pipets at the lower temperatures, and aspirated through heated tubes at the higher temperatures; the oxalate was determined by titration with 0.1 *N* potassium permanganate solution, using the method of McBride;[4] the permanganate was standardized with a sample of sodium oxalate from the Bureau of Standards.

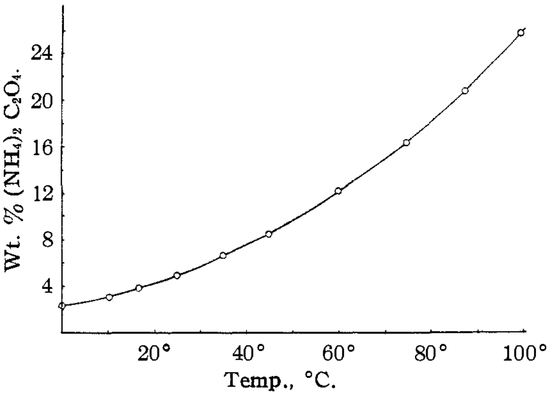

Fig. 1.

The results are shown in Fig. 1 and Table I, The curve shows no break to indicate the existence

Table I

Solubility of Ammonium Oxalate in Water

| *T*, °C. | Wt. per cent. found<br>Undersatn. | Supersatn. | Average |
|---|---|---|---|
| 0.0 | 2.264 | 2.275 | 2.269 |
| 10.3 | 3.107 | 3.107 | 3.107 |
| 16.78 | 3.897 | 3.887 | 3.892 |
| 25.0 | 4.995 | 4.976 | 4.985 |
| 34.97 | 6.627 | 6.634 | 6.630 |
| 44.75 | 8.617 | 8.621 | 8.619 |
| 60.3 | 12.28 | 12.31 | 12.30 |
| 74.8 | 16.43 | 16.44 | 16.44 |
| 87.7 | 20.82 | 20.91 | 20.86 |
| 99.8 | 25.80 | 25.79 | 25.79 |

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(1) The material of this paper is from the thesis of Edgar F. Distler, offered in partial fulfilment of the requirements for the degree of B.S. in Chemical Engineering at New York University, 1935.

(2) "International Critical Tables," New York City, 1928, Vol. IV, p. 219.

(3) Engel, *Ann. chim. phys.*, [6] **13**, 348 (1888); Foote and Andrew, *Am. Chem. J.*, **34**, 153 (1905); Woodstra, *8th Int. Cong. Chem.*, **22**, 25 (1912); Colani, *Bull. soc. chim.*, [4] **10**, 405 (1916); see also Rivett and O'Conner, *J. Chem. Soc.*, **115**, 1346 (1919).

(4) McBride, This Journal, **34**, 393 (1912).