[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

A Study of the Photochemical Carbon Monoxide Oxidation[1]

BY WENDELL F. JACKSON

It is known that a reaction occurs in carbon monoxide–oxygen mixtures illuminated by ultraviolet light at room temperatures. Chadwick, Ramsbottom and Chapman[2] found the products of the reaction to be ozone and carbon dioxide. Moisture did not accelerate the total reaction[3] but increased the ratio carbon dioxide/ozone.

Absorption of light by oxygen of wave length longer than 1751 Å. produces excited molecules; shorter wave lengths cause dissociation into one normal and one excited atom.[4] From 1700 to 2000 Å. the quantum yield is two molecules of ozone per quantum.[5] Since the quantum yield of ozone is not decreased by the addition of nitrogen, a study of the reactivity of oxygen atoms with other gases can be made by comparing the ozone yield in oxygen–nitrogen mixtures with that in similar mixtures containing oxygen and another gas.[6] Advantage was taken of this technique in the room temperature experiments with carbon monoxide described in this paper.

The increase of the temperature coefficient with temperature found by Kistiakowsky for the photochemical oxidation of carbon monoxide[7] and the fact that carbon monoxide–oxygen mixtures can be made to explode show that chains are set up in the reacting system. The experiments of Chadwick and his co-workers show an accelerating effect of water in the photochemical reaction, and the work of Dixon[8] demonstrates that moisture favors the explosive reaction. It is not safe, however, to assume that the effect of water is the same in both cases.[9]

The purpose of the high temperature experiments recorded in the following pages is to throw more light on the mechanism of the wet and dry photochemical reactions.

Experimental Part

Preliminary experiments showed that a 30-cm. layer of carbon monoxide at 760 mm. pressure exhibits no noticeable absorption in the spectral regions 1719–1725 and 1854–1862 Å. in the temperature range 20–600°. An aluminum spark served as the light source; a quartz tube with thin windows held the carbon monoxide; and plates were exposed in a nitrogen-filled quartz spectrograph.

Room Temperature Experiments with a Flow System.—Carbon monoxide was prepared by dropping C. P. formic acid on hot concentrated sulfuric acid. The gas was passed through potassium hydroxide solution and stored over water in a glass vessel. Oxygen and nitrogen were taken directly from cylinders.

The experiments were made with the same apparatus used by Kistiakowsky[6,7] in studying the photochemical hydrogen–oxygen reaction. The light source was a condensed spark burning between aluminum electrodes. Various gas mixtures were flowed at a measured rate through a calcium chloride drying tube into a thin-walled quartz vessel whose face was 3 cm. from the light source. Pure nitrogen blown between the vessel and the spark prevented the absorption of the 1719–1725 Å. line group before it reached the reacting gases. The inlet to the quartz vessel was so connected that the gases could be admitted very close to the illuminated surface. An outlet tube led to a spiral wash bottle containing potassium iodide solution.

The experiments were conducted as follows. A certain carbon monoxide–oxygen mixture was passed through the reaction vessel until the system was completely filled with it. The spark was then run for five minutes while the flow was held constant. The gases were allowed to pass for a few minutes after illumination had ceased to make sure that all products had reached the wash bottle. The ozone formed liberated iodine from the potassium iodide. The iodine liberated was determined by titration with 0.01 *N* sodium thiosulfate from a microburet. A second wash bottle in series with the first never collected appreciable quantities of ozone. Runs were made at the rates of flow 300, 500, 700–800, 1700–1800 cc. a minute. The experiments were then repeated using nitrogen instead of carbon monoxide in the mixture. The gas mixtures used contained 6, 11, 20 and 40% of oxygen by volume. The difficulty of reproducing the light intensity prevented an accuracy greater than 10%. Representative data are plotted in Fig. 1. Since points from the runs in which the mixture contained 20% oxygen conflict with curve C, they are not included.

Preliminary absorption experiments with nitrogen and with air blown between the spark and the reaction vessel showed that a 3 cm. layer of air absorbs all the radiation below the 1850 Å. region. A few experiments so conducted that the line group 1854–1862 Å. alone reached the reaction

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(1) This paper is an abstract of part of the thesis submitted to Princeton University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

(2) Chadwick, Ramsbottom and Chapman, *Proc. Chem. Soc.*, **21**, 287 (1905).

(3) See also Coehn and Tramm, *Ber.*, **54**, 1148 (1921).

(4) Mulliken, *Phys. Rev.*, **32**, 213 (1928); Birge and Sponer, *ibid.*, **28**, 259 (1926); Herzberg, *Z. physik. Chem.*, **413**, 223 (1929).

(5) Warburg, *Sitzb. Akad. Wiss. Wien*, 216 (1912); 872 (1914); Vaughan and Noyes, THIS JOURNAL, **52**, 559 (1930).

(6) *E. g.*, hydrogen–oxygen reaction, Kistiakowsky, THIS JOURNAL, **52**, 1838 (1930).

(7) G. B. Kistiakowsky, *Proc. Nat. Acad. Sci.*, **15**, 194 (1929).

(8) H. B. Dixon, *Phil. Trans.*, **175**, 640 (1884); **184A**, 111 (1893); **200A**, 315 (1903); *Proc. Roy. Soc.* (London), **37**, 56 (1884); *J. Chem. Soc.*, **69**, 774 (1896); with Strange and Graham, *ibid.*, **69**, 759 (1896).

(9) H. N. Alyea, THIS JOURNAL, **53**, 1324 (1931).

vessel are presented in Table I. In these runs carbon monoxide–oxygen and nitrogen–oxygen mixtures were passed through the vessel at the rate of 500 cc. a minute.

TABLE I

Gas between spark and reaction vessel	Mixture in reaction vessel	Cc. of $Na_2S_2O_3$	Moles of O_3 × 10^6
N_2	N_2–O_2	6.58	35.0
Air	N_2–O_2	0.75	4.0
Air	N_2–O_2	.77	4.0
Air	CO–O_2	.65	3.4
Air	CO–O_2	.64	3.4
Air	N_2–O_2	.66	3.5
Air	N_2–O_2	.65	3.4
N_2	N_2–O_2	6.45	31.1

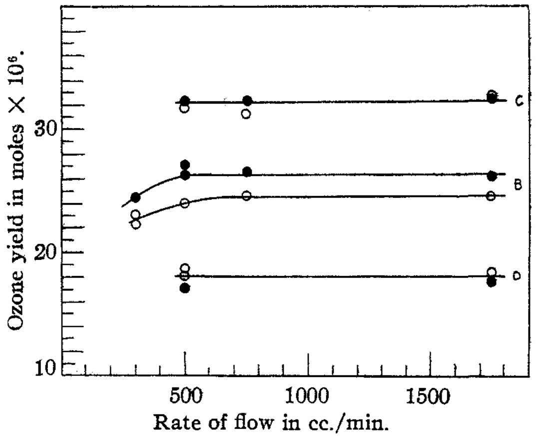

Fig. 1.—White circles represent ozone yield from CO–O_2 mixtures; black circles represent ozone yield from N_2–O_2 mixtures. Curve C refers to experiments in which the mixture contained 40% O_2; B to those with 11%; D to those with 6% by vol.

High Temperature Experiments with a Static System Apparatus.—The apparatus consisted of a furnace containing a quartz vessel which could be illuminated from the outside. The face of the vessel presented to the light was as thin as possible to allow the maximum quantity of short wave length radiation to enter. The vessel was contained in a cylindrical electric furnace turned out of block aluminum. An iron annulus of 1.5 cm. aperture fitted the well cut for the reaction vessel, protecting the latter from temperature variations. Further insulation was afforded by a quartz plate with a hole 1 cm. in diameter in the center. Two holes bored in the cylinder held a thermocouple and a platinum resistance thermometer. The latter was connected to a Leeds and Northrup temperature controller. Temperatures up to 600° could be maintained within one degree. Purified nitrogen was preheated to approximately the temperature of the reaction vessel and blown through a hole in the aluminum cylinder. It escaped through the aperture in front of the quartz vessel, serving the double purpose of preventing the spark from arcing and displacing the oxygen from the space between the light source and the reacting gases. As in the room temperature experiments, radiation of a frequency sufficient to cause dissociation of oxygen was obtained from a condensed aluminum spark. The quartz vessel was connected by a graded seal to Pyrex tubing leading to a mercury manometer and a three-way stopcock. The manometer and connections were of 2 mm. bore to minimize the volume of the system outside the furnace. The stopcock could connect the system to the pumps or with the gas inlets. Water contained in a U-tube could be introduced in definite quantities.

Preparation of Gases.—Oxygen was prepared by electrolysis of dilute potassium hydroxide with nickel electrodes and hydrogen removed with hot platinized asbestos. The oxygen, as well as the carbon monoxide, was dried by passage through concentrated sulfuric acid, calcium chloride, and phosphorus pentoxide. The gases were stored in glass over mercury.

Experiments.—The furnace temperature was brought to the value desired for a run and the system was evacuated for an hour. Carbon monoxide and oxygen were then admitted separately to the desired pressure. The system was allowed to stand until the gases were thoroughly mixed. No measurable dark reaction took place in twelve hours with any of the mixtures in the temperature range studied. Just before a run was started, nitrogen was turned on at a flow rate sufficient to blow all the air from the space between the reaction vessel and the spark. The temperature of the furnace was checked, the manometer read and the spark turned on. The pressure was read at one-minute intervals for periods of from ten to fifteen minutes. The light intensity was maintained as constant as possible by controlling the power put in the transformer and by adjusting the distance between the electrodes. These attempts, however, were not very fruitful. To counterbalance the error, runs in a given series were done at random and checks frequently made.

Eight series of experiments were made, four with dry gases, and four with varying concentrations of water vapor. With dry gases experiments were carried out with gas mixtures at 200 and 400 mm. total pressure containing various percentages of carbon monoxide at two temperatures, 500 and 550°. The results of three typical runs are plotted in Fig. 2. For these experiments the temperature was 550° and the pressure at that temperature was 200 mm.

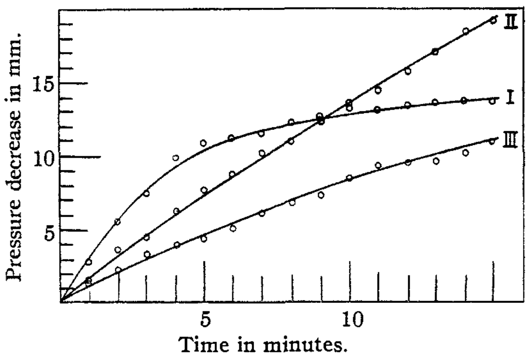

Fig. 2.

Curves I, II and III are rate curves for carbon monoxide–oxygen mixtures containing 25, 50 and 75% of carbon monoxide, respectively. Similar curves were obtained in all other experiments with dry gases. The initial rate was always high in mixtures containing 25% carbon monoxide and then decreased rapidly as curve I shows. The one-to-one mixtures gave rates practically constant for fifteen minutes while mixtures containing 75% carbon monoxide gave slow initial rates which gradually diminished with time. In Fig 3 the influence of varying carbon monoxide content on the initial rate is plotted for different temperatures and total pressures. The initial rate decreased with increasing carbon monoxide concentration over the range of concentrations studied. Starting with a one-to-one mixture of carbon monoxide and oxygen, the rate decreased approximately 30% for a three-fold increase in carbon monoxide partial pressure.

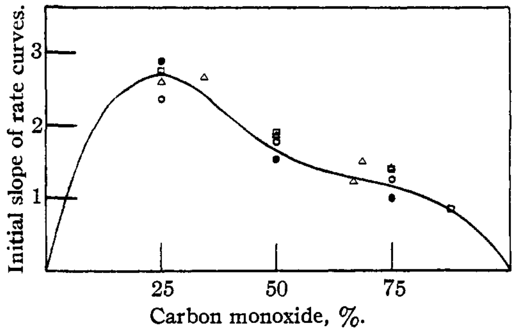

Fig. 3.—△, T = 500°, total press., 20 cm.; □, T = 500°, total press., 40 cm.; ●, T = 550°, total press., 20 cm.; ○, T = 550°, total press., 40 cm.

In the experiments with wet gases, one-to-one carbon monoxide–oxygen mixtures were used throughout, since with such mixtures the rate was approximately constant for a ten-minute period of illumination. The water vapor was admitted to the reaction system to the desired pressure and then the dry gases were let in. The runs were made exactly as the ones described. The rates are plotted against the percentage of water in the gases in Fig. 4. The curves are numbered in the order in which the experiments were made.

Discussion of Results

Room Temperature Experiments.—In all the room temperature experiments the ozone yield was constant at rates of flow greater than 700 cc. per minute. The constant ozone yield indicates that the quantity of light absorbed was constant at flow rates between 700 and 1800 cc. per minute. The low ozone yield at slow flow rates can be attributed to a smaller light absorption by oxygen, due to screening by ozone, and subsequent decomposition of the ozone.

An examination of Fig. 1 shows that the ozone yield is not appreciably different whether the oxygen is mixed with nitrogen or with carbon monoxide. Only in Series B are the yields sufficiently far apart to permit two curves. This difference is probably due to a variation in the light intensity used for the two mixtures.

The ozone yields plotted in Fig. 1 were obtained under conditions which permitted the absorption of both the 1850 Å. and the 1720 Å. line groups. Table II shows that about 10% of the ozone yield results from absorption of the longer wave length light. Consequently 90% of the yield can be attributed to the oxygen atoms produced by the higher frequency radiation.

The oxygen atoms liberated in the system by the light have four possible partners for collisions: oxygen molecules, carbon monoxide molecules, oxygen atoms and the walls of the vessel. At atmospheric pressure with the very low concentration of oxygen atoms present, the number of collisions with the walls and with other atoms is so small as to be negligible. In the experiments plotted in Curve D the oxygen atoms suffered 15 collisions with carbon monoxide molecules for every collision with an oxygen molecule. The ozone yield under such conditions was the same as in a similar nitrogen–oxygen mixture. Granting that the ozone yield might have been 10% lower in the carbon monoxide–oxygen mixture but that this difference could escape detection through experimental error, it is evident that the efficiency of the process

$$O + CO \longrightarrow CO_2 \qquad (1)$$

must be at least 150 times lower than that of the reaction

$$O + O_2 \longrightarrow O_3 \qquad (2)$$

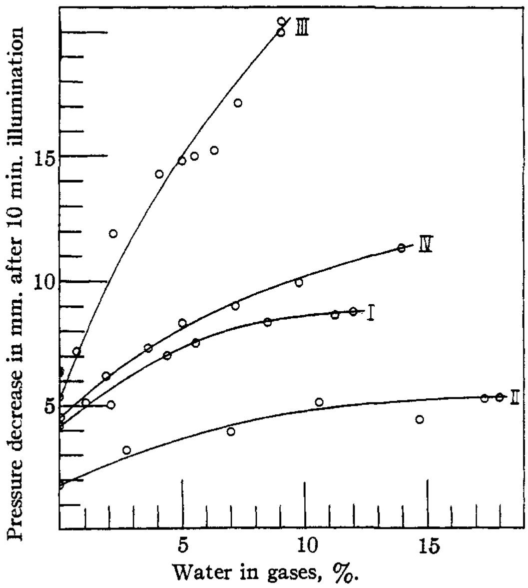

Fig. 4.—I, T = 500°, total pressure = 20 cm.; II, T = 500°, total pressure = 10 cm.; III, T = 550°, total pressure = 20 cm.; IV, T = 550°, total pressure = 10 cm.

where O represents either a normal or an excited oxygen atom. The random distribution of the points in Curves C and D indicates that the probability of (1) occurring is actually much smaller than this. The result tells nothing about the mechanics of the collision process itself, but the similarity of the reactants in the two cases points to the same mechanism for both. The activation energy of reaction (1), then, is at least 3000 cal. greater than that of reaction (2) providing the steric factors influencing the efficiency of the collisions are the same in both cases.

In a paper published since the completion of the experiments described in these pages,[10] Harteck and Kopsch[11] report a similar unwillingness of oxygen atoms to react with carbon monoxide. As a source of oxygen atoms they employed a discharge tube.

High Temperature Experiments.—According to Fig. 3 the rate of the photochemical oxidation of carbon monoxide in dry mixtures is practically independent of temperature and total pressure throughout the range studied. Curve I indicates that the carbon dioxide formed has a retarding influence on the rate which is the more pronounced the higher the ratio $[CO_2]/[CO]$. Such a curve was quite generally found in mixtures containing less carbon monoxide than oxygen.

Unlike the dry oxidation, the rate of the wet reaction depends on the total pressure and has a large temperature coefficient. The marked accelerating effect of water on the oxidation can best be explained by assuming that water takes part in a chain initiated by oxygen atoms.

By comparing Curves I with III and II with IV in Fig. 4 at a given water concentration, one can calculate a value of 23 to 30 kg. cal. for the activation energy of the total process involving water, though it is questionable whether the term "activation energy" is applicable in this case, because of the probable chain character of the reaction.

Regarding the detailed mechanism, it is certain that the initial step in both the wet and dry mixtures must be the formation of oxygen atoms, since neither carbon monoxide nor water are affected by radiation in the 1720 Å. region. The atoms so formed may be removed by collisions with themselves, with carbon monoxide or oxygen molecules, or with water molecules

$$O + CO + X \longrightarrow CO_2 + X \qquad (1)$$
$$O + O_2 + X \longrightarrow O_3 + X \qquad (2)$$
$$O + O + X \longrightarrow O_2 + X \qquad (3)$$
$$O + H_2O \longrightarrow OH + OH \qquad (4)$$

At the pressures used in the experiments the number of the three-body collisions, *ceteris paribus*, is approximately 10^{-4} that of the bimolecular collisions. With 1% of water in the gases, then, the number of collisions between oxygen atoms and water molecules is approximately 10^2 times greater than that between oxygen atoms and carbon monoxide or oxygen molecules plus a third body, and far greater than the number of oxygen atoms colliding with each other in the presence of a third body, since the concentration of atomic oxygen is small.

Although reaction (4) has been shown by Harteck and Kopsch to proceed but slowly at room temperature, it is not more than 11 kg. cal. endothermic (using 104 kg. cal. as the heat of dissociation of OH). On the other hand, half the oxygen atoms liberated by the light are in the $^1D_0$ metastable level with 45 kg. cal. excitation energy. The reaction between these excited atoms and water molecules producing hydroxyl is exothermic and may not require as high an activation energy as the process involving normal atoms.

Assuming a reasonably small activation energy, the oxygen atoms can initiate a chain consisting of the steps

$$O + H_2O \longrightarrow OH + OH \qquad (4)$$
$$OH + CO \longrightarrow CO_2 + H \qquad (5)$$
$$H + O_2 + CO \longrightarrow CO_2 + OH, \text{ etc.} \qquad (6)$$

Reactions (5) and (6) were postulated by Farkas, Haber and Harteck[12] to explain the oxidation of carbon monoxide photosensitized by ammonia. On light absorption the ammonia dissociates into NH_2 and H. Consequently the chain would start at (6) in the photosensitized reaction.

There are several processes by which the chains may be broken. Hydrogen atoms may recombine, hydroxyl radicals may react with each other, or water may be formed by collisions between hydrogen atoms and hydroxyl radicals

$$H + H + X \longrightarrow H_2 + X \qquad (7)$$
$$OH + OH \longrightarrow H_2O + O \qquad (8)$$
$$OH + H + X \longrightarrow H_2O + X \qquad (9)$$

The photochemical reaction between moist carbon monoxide and oxygen thus shows many similarities to the light initiated hydrogen–oxygen reaction. One has only to replace CO

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[10] See Kistiakowsky and Jackson, THIS JOURNAL, **52**, 3471 (1930).

[11] Harteck and Kopsch, *Z. physik. Chem.*, **12B**, 327 (1931).

[12] Farkas, Haber and Harteck, *Z. Elektrochem.*, **36**, 711 (1930); also, Bonhoeffer and Haber, *Z. physik. Chem.*, **137A**, 263 (1928).

by H_2 in the preceding reaction steps to obtain a fairly complete picture of the mechanism of the latter reaction at high temperature.

The author wishes to express his gratitude to Professor G. B. Kistiakowsky for his invaluable advice and assistance, and to Professor H. S. Taylor for his helpful criticism.

Summary

1. The photochemical oxidation of carbon monoxide has been investigated at room temperature in a flow system and at high temperature in a static system.
2. The room temperature investigation shows that oxygen atoms react with oxygen molecules to form ozone at least 150 times more rapidly than they react with carbon monoxide to form carbon dioxide.
3. The high temperature investigation indicates that the dry oxidation is practically independent of temperature and total pressure. When water is present, however, the reaction rate is no longer independent of pressure and shows a large temperature coefficient.
4. A mechanism involving hydrogen atoms and hydroxyl radicals has been suggested to explain the effect of water.

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NO_3F, An Explosive Compound

BY GEORGE HAMILTON CADY

When the reactions of fluorine with nitric acid at about 2° were studied by the method previously used for sulfuric acid[1] surprising results were obtained. In addition to a dissolved oxidizing agent the fluorine produced a large yield of a gas of great oxidizing strength. Rough calculations indicated that this substance had a volume equal to that of the fluorine from which it was prepared. The yields of gaseous and of dissolved oxidizing agents which were obtained from different concentrations of acid are shown in Fig. 1. The measurements were made by iodimetry, the strongly acid solutions being diluted enough to keep nitric acid from liberating iodine.

A careful survey of the literature failed to reveal a complete explanation for the results, but a statement, by Moissan,[2] was found that the passage of bubbles of fluorine through concentrated nitric acid produced explosions. That the acid did not need to be concentrated was suddenly discovered, during this research, when a two-liter flask, in which fluorine was reacting with cold four normal nitric acid, exploded. Afterward precautions were taken. As the work progressed it became evident that the gaseous oxidizing agent exploded only when heated or when it was being prepared. Perhaps localized heating during the reaction caused the trouble.

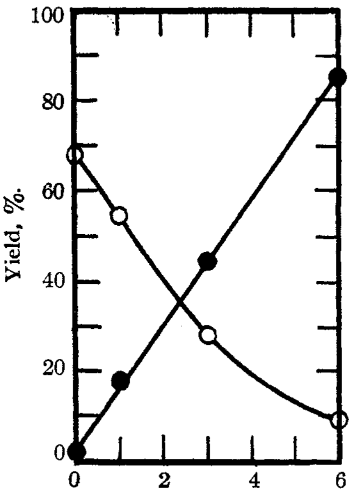

Fig. 1.—Yields of powerful oxidizing agents produced by the reaction of fluorine with an excess of cold nitric acid. ●, gaseous oxidizing agent; ○, dissolved oxidizing agent.

Preparation

The active gas was produced successfully in the reaction chamber shown in Fig. 2. A nickel tube, 1.5 cm. in diameter and 25 cm. in length, constituted the main body of the chamber, and to this were attached, by silver solder,

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[1] The procedure is described by the author in a paper which has not yet been published. A known volume of fluorine was allowed to react completely with an excess of the acid, and the gas and liquid phases were afterward separated and tested for their oxidizing strengths.

[2] H. Moissan, *Ann. chim. phys.*, [6] **24**, 224 (1891); "Le Fluor," Paris, 1900.