[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Phosgene-Sensitized Oxidation of Carbon Monoxide

BY G. K. ROLLEFSON AND C. W. MONTGOMERY

As the result of a number of investigations concerned with the inhibiting effect of oxygen on the photosynthesis of phosgene[1,2,3,4] it has been shown that at high oxygen pressures the phosgene formation becomes negligibly small, the chlorine-sensitized oxidation of carbon monoxide being predominant. In the various mechanisms proposed for this reaction[5] the formation of carbon dioxide is believed to take place through the action of oxygen on the intermediate COCl. It has previously been shown that in the case of the direct photochemical oxidation of phosgene[6] this same intermediate is produced by the action of ultraviolet light on phosgene, and evidence has been submitted that the same state obtained in such a system as is produced by the action of visible light on a mixture of chlorine, carbon monoxide and oxygen. It is therefore to be expected that the oxidation of carbon monoxide might be sensitized by phosgene in a manner entirely analogous to the chlorine-sensitized reaction. Such has been found to be the case and the reaction has been studied in the hope of arriving at a comparison with the chlorine-sensitized oxidation.

Experimental

The apparatus employed in the kinetic study was, in general, the same as that previously described for the work on the direct oxidation of phosgene.[6] The same cylindrical quartz reaction vessel was used with the same method of water cooling. The source of illumination was the full light of a 220-volt Cooper–Hewitt quartz mercury arc.

The phosgene (Kahlbaum) was distilled from a glass bomb and was purified in the manner previously described. Oxygen was prepared electrolytically, purified and dried as before.[6] Carbon monoxide was generated by heating a mixture of concentrated sulfuric and formic acids, washed in a bubbler containing strong sodium hydroxide solution, and dried in a similar bubbler containing concentrated sulfuric acid. The three gases were stored in three three-liter bulbs from which they could be admitted to the reaction vessel as needed.

The reaction was followed by means of a sulfuric acid (sp. gr. 1.84) manometer or a mercury manometer (with the mercury surface protected by 3 or 4 cm. of sulfuric acid) depending on the total pressures of the gases used. Due to the large Draper effect produced by the reaction, before readings were taken the light from the arc was cut off from the reaction vessel by means of a shutter and the pressure allowed to reach a constant value.

In several of the experiments, in order to check the stoichiometry of the reaction, pressure readings were taken both at room temperature and at

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(1) Chapman and Gee, *J. Chem. Soc.*, **99**, 1726 (1911).

(2) Bodenstein, *Sitzber. preuss. Akad. Wiss.*, **13**, 104 (1926).

(3) Schumacher, *Z. physik. Chem.*, **129**, 241 (1927).

(4) (a) Rollefson, *Trans. Faraday Soc.*, **27**, 465 (1931); (b) THIS JOURNAL, **52**, 3562 (1930); (c) **55**, 148 (1933).

(5) Lenher and Rollefson, *ibid.*, **52**, 500 (1930).

(6) Rollefson and Montgomery, *ibid.*, **55**, 142 (1933).

liquid air temperature. From these two sets of readings, the amount of sensitized oxidation according to the reaction

$$2CO + O_2 \longrightarrow 2CO_2 \qquad (1)$$

and the amount of direct oxidation of phosgene according to

$$2COCl_2 + O_2 \longrightarrow 2CO_2 + 2Cl_2 \qquad (2)$$

were calculated. This was done by means of the relations

$$\Delta P_1 = (\Delta P_R + \Delta P_A)/4;\ \Delta P_2 = -\Delta P_R + \Delta P_1$$

where ΔP_1 is the pressure change due to reaction (1), ΔP_2 is the pressure change due to reaction (2), ΔP_R the over-all pressure change at room temperature, and ΔP_A the over-all pressure change at liquid air temperature converted, by means of an empirical "freeze-out" factor, which was determined for each run, to the corresponding pressure change at room temperature. In all the runs made, the sensitized reaction went to completion according to equation (1) and was so rapid relative to reaction (2) that direct phosgene oxidation could be neglected until (1) was approximately 80% complete.

Results

In Table I are summarized the results of five experiments in which the $COCl_2$ pressure was varied from 2.45 to 20.00 cm. of sulfuric acid, the other variables being kept constant. The fourth column indicates the linearity between rate and the square root of the $COCl_2$ pressure.[7]

TABLE I

$(COCl_2)$	2.45	5.02	10.00	14.45	20.00
$(COCl_2)^{1/2}$	1.57	2.24	3.16	3.80	4.47
$d(CO_2)/dt$	1.00	1.47	1.93	2.40	2.80
$(d(CO_2)/dt)/(COCl_2)^{1/2}$	0.637	0.656	0.611	0.632	0.626

In Table II are summarized the results of a series of experiments in which the incident light intensity was varied by means of a set of calibrated screens. In the table, the intensity with no screen is taken as 100. The rate is seen to be fairly definitely a function of the square root of the incident intensity, in agreement with the previous results on the $COCl_2$ dependence. The fourth column of the table indicates the deviation from linearity, values of Δ being obtained from the best straight line through the points.

TABLE II

I_0	100.0	67.0	47.0	37.9	29.0	5.9
$I_0^{1/2}$	10.0	8.2	6.9	6.2	5.4	2.4
$d(CO_2)/dt$	0.56	0.47	0.36	0.34	0.29	0.12
Δ	+0.010	+0.020	−0.015	0.000	0.000	−0.010

Table III gives the results of a series of experiments in which the carbon monoxide pressure alone was varied. Plotting the rate against the square

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(7) In these and the following results, the pressure has been left in terms of cm. of mercury or sulfuric acid and the rate expressed in cm. of mercury or sulfuric acid per minute.

root of the carbon monoxide pressure yields a straight line indicating the dependence on the square root of the carbon monoxide pressure. In several experiments at very low carbon monoxide pressures, the rate falls away from this square root relationship. In these cases, however, the rate of oxidation of carbon monoxide is so much slower that the rate of direct oxidation of phosgene is no longer negligible in comparison. Since this direct oxidation leads to a pressure change in the opposite direction, the effect produced is to cause an anomalous lowering of the rate of the sensitized reaction.

Table III

(CO)	$(CO)^{1/2}$	$d(CO_2)/dt$
14.02	3.32	5.12
18.39	4.29	6.60
27.85	5.28	8.92
37.32	6.20	10.36
47.07	6.86	11.62
56.98	7.55	12.08
66.65	8.15	13.40
76.22	8.73	14.60
86.15	9.28	15.40

Table IV

Δ	(O_2)	$d(CO_2)/dt$
−0.40	1.47	1.15
− .50	3.24	1.62
+ .20	5.05	2.00
+ .05	6.94	2.07
+ .25	10.87	2.35
− .50	15.62	2.45
− .05	20.70	2.40
+ .10	27.40	2.50
.00	36.25	2.40

It was further necessary to investigate the dependence of the rate on the oxygen pressure, in order to afford a closer comparison with the chlorine sensitized reaction. In the latter reaction it has been shown that the rate although dependent on the oxygen pressure at low pressures, becomes independent of it as the pressure is increased. In Fig. 1 and Table IV are presented the results of a series of experiments in which the oxygen pressure was varied between 1.5 and 36 cm. ($COCl_2$, 5 cm., CO, 10 cm.). The rate obviously becomes independent of the oxygen pressure at approximately 15 cm. pressure. In order to test the oxygen dependence in the region where the curve bends down to the origin, several low pressure experiments were made, the results of four of which are shown in Table V.

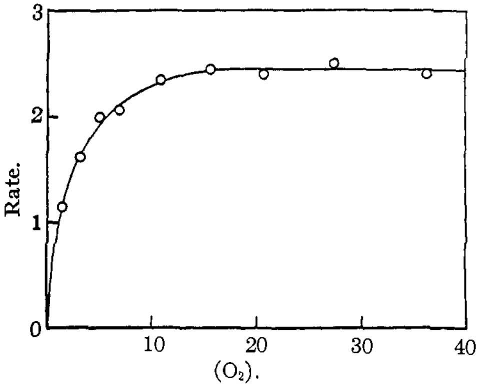

Fig. 1.

Table V

(O_2)(cm. H_2SO_4).......	1.73	3.75	6.45	9.30
$(O_2)^{1/2}$...............	1.16	1.94	2.54	3.05
$d(CO_2)/dt$............	2.56	4.28	5.72	6.80
$(d(CO_2)/dt)/(O_2)^{1/2}$....	2.21	2.20	2.25	2.23

In this low oxygen region, it is evident that the rate is a function of the square root of the oxygen pressure.

On the basis of the above experiments, the reaction appears to fall into two fairly definite pressure ranges in which the rate laws are different. For low oxygen pressures the rate may be represented by the equation

$$d(CO_2)/dt = KI_0^{1/2}(COCl_2)^{1/2}(CO)^{1/2}(O_2)^{1/2} = kI_{abs.}^{1/2}(CO)^{1/2}(O_2)^{1/2} \qquad (1)$$

(where the substitution $I_{abs.} = I_0(COCl_2)$ is justified by the low light absorption), while at higher oxygen pressures, the oxygen dependence disappears, the rate law becoming

$$d(CO_2)/dt = kI_{abs.}^{1/2}(CO) \qquad (2)$$

This change of order was confirmed by the results of two series of experiments in which the phosgene pressure and light intensity were kept constant and the carbon monoxide and oxygen pressures were kept in constant ratio but their total pressure varied. Under these conditions, the rate should be proportional to the total pressure (carbon monoxide and oxygen) in the region where equation (1) holds, but should fall off from this proportionality in the region of equation (2). The data are presented in Tables VI and VII. The correctness of the above statements is clearly evident in the small deviations from linearity (Δ) in Table VI and the increasingly large deviations in Table VII.

TABLE VI (LOW PRESSURE O_2)

$(O_2 + CO)$ (cm. H_2SO_4)	$d(CO_2)/dt$	Δ
10.10	1.9	−0.50
20.66	4.7	.00
40.78	10.0	+ .75
60.55	13.6	.00
80.35	18.1	.00

TABLE VII (HIGH PRESSURE O_2)

$(O_2 + CO)$ (cm. Hg)	$d(CO_2)/dt$	Δ
8.0	0.73	0.00
16.0	1.43	− .05
24.0	2.13	− .08
32.0	2.77	− .20
40.0	3.05	− .60

In order to obtain a clearer confirmation of this change of order and the independence of the rate on the oxygen pressure at higher pressures, as well as of the square root relation at low pressures, the data of Table IV have been treated in the following manner. In this series of experiments, the rate is a function of the oxygen pressure alone, the other variables of the system being kept constant. The rate may therefore be represented by the equations

$$d(CO_2)/dt = k(O_2)^{1/2} \qquad (1)$$

for low oxygen pressures, and

$$d(CO_2)/dt = k' \qquad (2)$$

at higher oxygen pressures. Taking the logarithms of both sides of these equations we obtain

$$\log\ d(CO_2)/dt = \log\ k + {}^1/_2 \log\ (O_2) \qquad (1')$$

and

$$\log d(CO_2)/dt = \log k' \qquad (2')$$

If, therefore, we plot the logarithm of the rate against the logarithm of the oxygen pressure, we should obtain a straight line of slope 0.5 for low oxygen pressures and a straight line parallel to the log (O_2) axis at higher pressures. This was done for the data of Table IV and the expected results obtained. In Fig. 2 d log rate/d log (O_2), *i. e.*, the slopes of the log rate *vs.* log (O_2) plot, are plotted against log (O_2). The low and high pressure (O_2) regions are clearly indicated as well as the transition range.

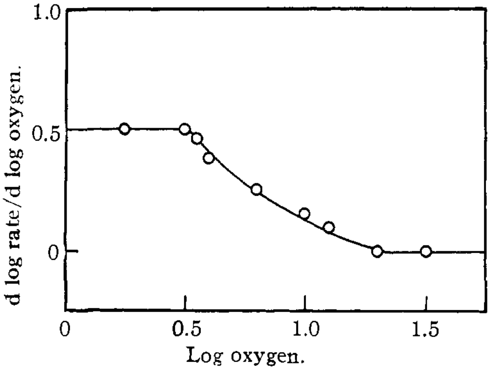

Fig. 2.

The quantum yield[8] has been found to be approximately 100 at pressures of about 40.0 mm. of $COCl_2$, CO and O_2. Schumacher[3] measured the quantum yield of the chlorine-sensitized oxidation and found it to be roughly of the order of magnitude of 1000 molecules per quantum for pressures of (CO) = (Cl_2) = $^1/_2$ atmosphere and O_2 = 1000 mm., in the region of maximum chlorine absorption. If we assume that the rate law which Schumacher found, *i. e.*

$$d(CO_2)/dt = kI_0^{0.71}\ (Cl_2)^{0.71}(CO)^{1/2} = kI_{\text{abs.}}^{0.71}\ (CO)^{1/2}$$

becomes, at lower chlorine pressures

$$d(CO_2)/dt = kI_0(Cl_2)(CO)^{1/2} = kI_{\text{abs.}}(CO)^{1/2}$$

as has been shown by Rollefson,[4b,5] we may obtain a formal expression for the quantum yield by dividing this equation by $I_{\text{abs.}}$ thus

$$\gamma = (d(CO_2)/dt)/I_{\text{abs.}} = k(CO)^{1/2}$$

At lower pressures of chlorine, the quantum yield should then be only a function of the square root of the carbon monoxide pressure. By a simple calculation we find the quantum yield of the chlorine-sensitized oxidation for a carbon monoxide pressure equal to that (4 cm. of carbon monoxide) at which the quantum yield of the phosgene sensitized oxidation was measured, to be

$$\gamma = \sqrt{40}\cdot 1000/\sqrt{380} \sim 300$$

The quantum yields of the phosgene-sensitized and chlorine-sensitized reactions are thus seen to be of approximately the same magnitude.

Discussion

From the data presented above, it is evident that at low oxygen pressures the rate of oxidation of carbon monoxide may be expressed by the equation

$$d(CO_2)/dt = kI_0^{1/2}\ (COCl_2)^{1/2}(CO)^{1/2}(O_2)^{1/2}$$

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(8) The experimental details will be published soon in connection with the determination of the quantum yields of some other reactions.

while at high oxygen pressures ($P_{O_2} > 15$ cm.) the rate becomes independent of the oxygen. As expected, the phosgene-sensitized oxidation appears to be quite similar to the chlorine-sensitized reaction. The fact that the quantum yields are of the same magnitude indicates, of course, that the chain lengths of the two reactions are the same. This gives further confirmation to the view expressed previously that there is no essential difference between the system: phosgene, carbon monoxide, and oxygen illuminated with ultraviolet light of frequency corresponding to the phosgene predissociation region, and the system: chlorine, carbon monoxide, and oxygen illuminated with visible light of frequency corresponding to the region of the chlorine absorption continuum. The similarity in the two systems is further shown by the manner in which the carbon monoxide pressure enters the rate laws of both reactions and by the fact that both reaction rates appear to involve oxygen explicitly at low oxygen pressures and become independent of it at higher pressures.[9] The only interpretation of these facts probably is that both the carbon monoxide and oxygen play identical roles in the rate mechanisms of the two reactions.

Another point of analogy between the two systems is evident in the manner in which the rate depends upon the intensity of light absorbed. A significant difference also exists, however. It has been shown[11] that, in the case of the chlorine-sensitized reaction, the rate at low chlorine pressures is proportional to the light absorbed while at higher pressures it becomes proportional to the square root of the light absorbed. In the intermediate range such exponents as Schumacher's $I_{\text{abs.}}^{0.71}$ are found. This change of function with pressure has been most plausibly explained by assuming two different methods of recombination of the chlorine atoms produced by the light. At low pressures destruction of the chlorine atoms by collision with impurities or the reaction vessel walls is greater, while at higher pressures recombination is brought about predominantly by second order collisions in the gas phase. In the case of the phosgene-sensitized oxidation no such change is found in the dependence of the rate on the light absorbed, the rate remaining proportional to the square root of the light absorbed. Reasoning by analogy, this can be interpreted by assuming the predominance throughout the range studied of some homogeneous second order chain terminating process corresponding to the disappearance of chlorine atoms in the chlorine-sensitized reaction. On the basis of the mechanism of Lenher and Rollefson this would be $COCl + Cl \longrightarrow CO + Cl_2$.

A satisfactory derivation of the rate law from any mechanism yet devised has not been obtained. The derived equations either give the wrong

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(9) The dependence of the rate of the chlorine sensitized reaction at low oxygen pressures on the oxygen has not been determined quantitatively as the phosgene formation predominates under such conditions. In that case the amount of carbon dioxide formed in a given time is determined by the law governing the division of the carbon monoxide between the two competing reactions, whereas in the system we are discussing in this paper the reaction between carbon monoxide and oxygen can be considered to be the only one occurring.

exponents for the factors involved or else do not, in the limit of high oxygen pressures, yield an expression independent of the oxygen. Likewise no satisfactory derivation has yet been made of the rate law for the chlorine-sensitized reaction. Recently Warming[10] has shown that the mechanism of Schumacher[11] is thermodynamically unsound. There can be but little question, in the light of the experimental results obtained, that practically the same mechanism will be found to fit both the chlorine-sensitized and the phosgene-sensitized reactions, with the exception of the primary process, which in the phosgene reaction must be $COCl_2 + h\nu \longrightarrow COCl + Cl$. After this initial process, it is to be expected that oxygen and carbon monoxide will take part in the same reactions in the reaction chains of both sensitized oxidations. In devising a mechanism, the principal difficulty appears to be to get a set of partial reactions the rate law of which will involve the square root of the oxygen at low oxygen pressures and will become independent of oxygen at higher pressures. It has been found possible, however, to set up the following mechanism from which the low pressure rate law may be derived.

$$COCl_2 + h\nu \longrightarrow COCl + Cl \quad (1)$$
$$CO + Cl + M \longrightarrow COCl + M \quad (2)$$
$$COCl + O_2 \longrightarrow CO_3Cl \quad (3)$$
$$CO_3Cl + CO \longrightarrow 2CO_2 + Cl \quad (4)$$
$$CO_3Cl + COCl \longrightarrow 2CO_2 + Cl_2 \quad (5)$$

This mechanism leads to the rate law

$$d(CO_2)/dt = 2I_{abs.} + kI_{abs.}^{1/2}(CO)^{1/2}(O_2)^{1/2}$$

which, considering the large value of the quantum yield, reduces to

$$d(CO_2)/dt = kI_{abs.}^{1/2}(CO)^{1/2}(O_2)^{1/2}$$

the low oxygen pressure experimental rate law. The assumption of CO_3Cl in the above mechanism presents nothing contradictory to the mechanism already given for the direct photochemical oxidation of phosgene (8), since in that mechanism process (3) as written above is kinetically identical to $COCl + O_2 \longrightarrow CO_2 + ClO$. CO_3Cl may, perhaps, be regarded as a reactive peroxide of the sort postulated by Bodenstein.[12] In the high pressure region it is conceivable that oxygen inhibits the oxidation as has been observed in other cases.[12] This might be brought about through the action of oxygen at some stage following reaction (3), resulting in a process which would terminate the chain. Except for this effect this system is in perfect agreement with the other reactions for which the intermediate COCl has been postulated and must be considered as additional evidence for the existence of that substance.

Summary

A kinetic study of the phosgene-sensitized oxidation of carbon monoxide has been made. The rate law for low pressures of oxygen has been shown

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[10] Warming, *Z. physik. Chem.*, **B18**, 156, 158 (1932).

[11] Schumacher and Stieger, *ibid.*, **B13**, 169 (1931).

[12] Bodenstein, *Sitzber. preuss. Akad. Wiss.*, 73–88 (1931).

to be: $d(CO_2)/dt = kI_0^{1/2}(COCl_2)^{1/2}(CO)^{1/2}(O_2)^{1/2}$, and for higher oxygen pressures: $d(CO_2)/dt = kI_0^{1/2}(COCl_2)^{1/2}(CO)^{1/2}$. As in the case of the chlorine-sensitized oxidation of carbon monoxide, it has not yet been possible to develop a mechanism for the reaction capable of explaining the experimental rate law over the whole range. The two reactions have been compared and have been found to be very similar in several important respects. It has been concluded, therefore, that probably very similar mechanisms will be found to apply to both chlorine- and phosgene-sensitized oxidations.

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The Reduction by Hydrogen and the Thermal Decomposition of Nitrides Made by the Reaction of Ammonia with Various Promoted and Unpromoted Iron Synthetic Ammonia Catalysts

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Phase rule investigations[1] have in the last few years shown that at least two nitrides of iron are formed by passing ammonia over iron in the temperature range 400 to 525°. At 450° and one atmosphere pressure, for example, an ammonia–hydrogen mixture containing between 30 and 70% ammonia will convert the iron into a body-centered cubic nitride whose composition is close to that of Fe_4N; ammonia percentages ranging from 70 to 100% will convert the Fe_4N into an hexagonal nitride whose composition varies with the percentage of ammonia from one approximating Fe_3N to one that closely corresponds to Fe_2N. As a part of a study being made of the mechanism by which iron catalysts are able to effect the synthesis of ammonia, the rates and nature of the decomposition and of the reduction by hydrogen of the various nitrides, prepared both from active and from inactive iron ammonia catalysts, have been determined.

Experimental

The various nitrides were prepared by passing suitable ammonia–hydrogen mixtures at about 400° over finely divided iron synthetic ammonia catalysts obtained by the reduction in hydrogen of fused Fe_3O_4. Portions of each nitride preparation were analyzed by a modified Kjeldahl method; usually samples were also taken for x-ray photographs. Table I gives the composition of the samples and in some cases the nature of their x-ray pattern. Samples for both x-ray and chemical analysis were obtained in an oxygen-free nitrogen atmosphere.

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[1] Emmett, Hendricks and Brunauer, THIS JOURNAL, **52**, 1456 (1930); Lehrer, *Z. Elektrochem.*, **36**, 383 (1930); Eisenhut and Kaupp, *ibid.*, **36**, 392 (1930); Lehrer, *ibid.*, **36**, 460 (1930); Brunauer, Jefferson, Emmett and Hendricks, THIS JOURNAL, **53**, 1778 (1931).