

It will be observed that the catalytic activity of cobalt polysulfide under the conditions of study was even less than that of molybdenum sulfide in every comparable case except toward nitrobenzene. The rate of reduction of the nitro group by cobalt polysulfide was nearly as great as by rhenium heptasulfide.

The most noteworthy difference between the behavior of cobalt polysulfide and rhenium heptasulfide, other than the markedly lower activity of the former in most cases, can be noticed in connection with the hydrogenation of allyl phenyl sulfide. The cobalt catalyst cleaves the carbon-sulfur bond, as reported, to yield thiophenol, whereas rhenium heptasulfide does not, yielding rather *n*-propyl phenyl sulfide. Another difference is a disagreeable formation of hydrogen sulfide from the cobalt catalyst even under mild conditions, but never from the rhenium heptasulfide catalyst even under the most drastic conditions employed. The cobalt catalyst was completely dissolved by maleic acid, whereas the rhenium sulfides were unattacked even by strong, non-oxidizing, mineral acids.

A brief tabular comparison of the catalysts is presented by Table V.

TABLE V
COMPARISON OF CATALYTIC ACTIVITY OF SULFIDE CATALYSTS UNDER COMPARABLE CONDITIONS

No.	Substrate	Yield of reduction product(s), %		
		Rhenium heptasulfide	Molybdenum sulfide	Cobalt polysulfide
1	Styrene	100	8	0
2	Cyclohexene	92	22	17
3	Benzene	57		0
4	Naphthalene	0	0	..
5	Maleic acid	100	0	0
6	Nitrobenzene	100	0	100 ^a
7	Bromobenzene	100 ^b	25 ^c	..
8	<i>p</i> -Nitrobromobenzene	100	0	..
9	Diphenyl sulfide	94	40	4

^a Conditions considerably more drastic than for rhenium heptasulfide. ^b 30% benzene, 70% cyclohexane. ^c Benzene only.

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[CONTRIBUTION FROM THE JAMES FORRESTAL RESEARCH CENTER, PRINCETON UNIVERSITY]

The Oxidation of Carbon Monoxide in the Presence of Ozone¹

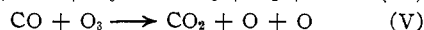
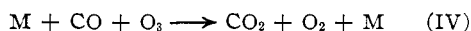
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The rate and mechanism of the oxidation of carbon monoxide in mixtures of CO, O₂, N₂ and small amounts of ozone have been studied at atmospheric pressure in the temperature range 430–565°K. The production of carbon dioxide is slight and can best be explained by the reaction (III): CO + O + M → CO₂ + M, which has no activation energy and occurs every 10⁸ three body collisions.

Introduction

A direct reaction between carbon monoxide and ozone has been considered in photochemical and combustion studies. In the former all carbon dioxide production has been attributed to reaction (III).^{2–4} Lewis and von Elbe⁵ analyzed the high pressure explosion limit of carbon monoxide-oxygen mixtures in terms of the chain breaking and branching steps



and deduced an activation energy difference $E_6^* - E_4^* = 35$ kcal.

Trautz⁶ and Kondrateev⁷ have studied the radiation emitted by heated carbon monoxide-ozone-oxygen mixtures. Both found the radiation intensity to vary approximately with the first power

(1) This research was supported in whole or in part by the United States Air Force under Contract No. AF33(038)-23976 monitored by the Office of Scientific Research.

(2) P. Harteck and U. Kopsch, *Z. physik. Chem.*, **B12**, 327 (1931).

(3) W. Groth and P. Harteck, *Z. Elektrochem.*, **44**, 621 (1938); W. Groth, *Z. physik. Chem.*, **B37**, 315 (1937).

(4) W. F. Jackson, *THIS JOURNAL*, **56**, 2631 (1934).

(5) B. Lewis and G. von Elbe, "Combustion, Flames and Explosions of Gases," Academic Press, New York, 1951, p. 78, *et seq.*

(6) M. Trautz and W. Seidel, *Ann. Physik*, **67**, 527 (1922).

(7) V. Kondrateev, S. Solnyshkova and M. Zatsiorskii, *Acta Physicochem.*, **14**, 663 (1949).

of the CO and O₃ concentrations. The latter reported that the spectrum of the radiation was identical with that of CO-O₂ flames and that reaction IV with an activation energy of 8.8 kcal. was necessary to account for the carbon dioxide production.

The unimportance of ozone in photochemical studies and its instability at moderate temperature (half life less than 5 sec. at 200°) made it questionable whether or not it could be an important intermediate at the explosion temperature. Therefore a study of the rate and mechanism of the oxidation of carbon monoxide by traces of ozone at moderate temperatures has been carried out.

Experimental

The oxidation of carbon monoxide is slower than the thermal decomposition of ozone. Both processes were studied in the temperature range 430 to 565°K. by a conventional flow method in the same apparatus.

1. Reagents.—Carbon monoxide was produced in a continuous generator⁸ from 90% formic acid and tech. acetic anhydride containing a trace of sulfuric acid as catalyst.⁹ The gas was scrubbed with 30% sodium hydroxide in a 30 inch column packed with broken unglazed porcelain, dried by calcium chloride, Drierite and magnesium perchlorate and then metered into the reaction system. Tank oxygen and prepurified nitrogen (American Oxygen Service Corp.) were used after drying with magnesium perchlorate. The

(8) E. M. Meade, *Chem. Age*, **39**, 300 (1938).

(9) G. Jacini, *Chimica e Industria*, **39**, 204 (1947).

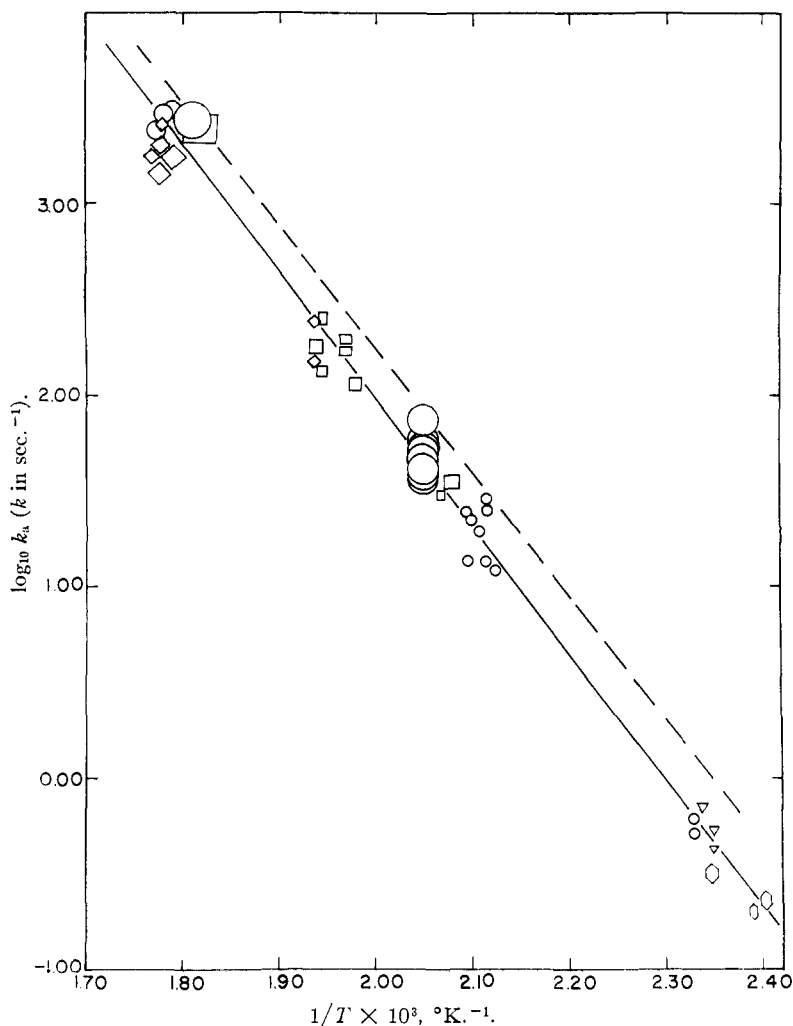


Fig. 1.—Rate constants for thermal ozone decomposition. Reactors (cc.): \diamond , 0.81; \square , 2.24; \circ , 19.25; \odot , 41.8; ∇ , 10.12 (packed). Size of symbol shows temperature uncertainty; — —, Tolman and Wolf; —, this study.

oxygen was ozonized in a silent electric discharge ozonizer (15–25 kv.) of the type described by Henne.¹⁰ Absorption and infrared spectrographic analyses of the three gases showed neither water nor carbon dioxide. Mass spectrographic analysis of the nitrogen and carbon monoxide showed less than 0.1% hydrogen, if any. No water was produced in the thermal ozone decomposition, indicating the absence of hydrogen in the oxygen.

2. **Reaction.**—The metered gas streams were mixed at room temperature, passed through fritted glass (to remove any solid particles) and then through the heated reactors. Five Pyrex reactors were used. Their volumes and surface to volume ratios were: A, 41.8 cc., 2.4 cm.⁻¹; B, 19.25 cc., 2.71 cm.⁻¹; C, 10.12 cc., 40.6 cm.⁻¹ (packed); D, 2.24 cc., 13.3 cm.⁻¹; and E, 0.81 cc., 20.0 cm.⁻¹. Reactors D and E were spirals of 5 and 3 mm. o.d. tubing, respectively, with thermocouple wells in both the inlet and outlet gas streams. Reactors A, B and C were fat cylindrical annuli. With these, either the inlet or outlet temperatures, but not both, could be measured. Reactor C was made from B by packing it with one-eighth inch Pyrex helices.

All reactors were heated by immersion in boiling organic liquids. The connecting tubing passed through about 8 cm. of heated vapor. The gas stream temperature reached that of the bath only at or below the surface of the boiling liquid. Usually the reactor temperature reached a steady value a few degrees above that of the bath (due to the heat

(10) A. L. Henne and W. L. Perilstein, *THIS JOURNAL*, **65**, 2183 (1943).

of reaction). Temperatures were measured potentiometrically with iron-constantan thermocouples.

3. **Analysis.**—The input and output gases were analyzed for ozone and carbon dioxide content. Ozone was absorbed in 2 M KI, buffered to pH 7 with phosphate, which was then acidified and titrated with 0.02 M sodium thiosulfate. Carbon dioxide was determined (in duplicate) by analysis of the 4.3 μ absorption band. The infrared spectrometer was flushed with dry nitrogen to reduce interference by atmospheric carbon dioxide. Empirically determined corrections for the change in absorption with total sample pressure were necessary. Concentrations of other components and reaction times were determined from these analyses, the flow data, reactor temperatures and total pressure (approximately atmospheric).

4. **Precision of Measurement.**—Flow rates were reproducible to 2%. Ozone analyses agreed to 3%, and carbon dioxide content to 10%. (The main source of error in the last appeared to be due to a slow, erratic carbon dioxide production during the interval (one to three hours) between sampling and analysis. This was minimized by chilling the samples to less than -20° , and blanks, based on input gas analyses, were applied to the data.)

Results

1. **Thermal Decomposition of Ozone.**—The system O_3 , O_2 , N_2 was studied at atmospheric pressure in five limited temperature ranges centering about 430, 475, 488, 515 and 560°K. Ozone mole fractions ranging from 0.0025 to 0.040 and oxygen to ozone ratios from 25 to 250 were used. The nitrogen mole fractions ranged from 0 to 0.9. The fractional decomposition of ozone varied from 0.05 to 0.85.

Rate constants calculated according to several simple empirical schemes all showed considerable scatter. The most consistent results were obtained by analysis of the data according to the scheme

$$-d[O_3]/dt = k_a[O_3]^2/[O_2] \quad (1)$$

$$k_a = \frac{1}{t} \left\{ \left(\frac{[O_{20}]}{[O_{30}]} + \frac{3}{2} \right) \left(\frac{1-x}{x} \right) - \frac{3}{2} \cdot \ln \frac{1}{x} \right\}$$

where $[O_{20}]$, $[O_{30}]$ are the input concentrations and $x = [O_3]/[O_{30}]$.¹¹ This equation was established by Tolman and Wolf¹² as applicable to their work on dilute ozone at lower temperatures.

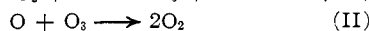
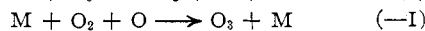
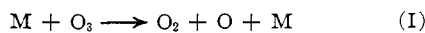
Specific rates based on equation 1 are shown in Fig. 1.¹³ They showed no dependence upon nitro-

(11) Rate constants reported herein are consistent with concentrations in moles/cc. and time in seconds. The integrated forms of the kinetic expressions were used, and, since the mole number change was small, constant volume equations were sufficient.

(12) R. C. Tolman and O. R. Wolf, *THIS JOURNAL*, **49**, 1650 (1927).

(13) The experimental conditions and specific rates for all runs on both the thermal ozone decomposition and the carbon monoxide oxidations are given in Table I, which has been deposited as Document number 4151 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting in advance \$1.25 for photoprints, or \$1.25 for 35 mm. microfilm by check or money orders payable to: Chief, Photoduplication Service, Library of Congress.

gen concentration and little, if any, variation with surface to volume ratio. A drift upward with increasing initial oxygen to ozone ratio was apparent. This is of the size and in the direction predicted by Jahn's mechanism for the thermal decomposition.¹⁴



$$-d[O_3]/dt = 2k_1k_2[M][O_3]^2/(k_{-1}[M][O_2] + k_2[O_3])$$

$$\frac{2k_1k_2}{k_{-1}} = \frac{1}{t} \left\{ \left(\frac{[O_{20}]}{[O_{30}]} + \frac{3}{2} \right) \left(\frac{1-x}{x} \right) + \left(\frac{k_2}{k_{-1}[M]} - \frac{3}{2} \right) \ln \frac{1}{x} \right\} \quad (2)$$

Unfortunately, the scatter of calculated specific rates is too great to permit estimation of the parameters in equation 2 with any accuracy.

Figure 1 leads to an activation energy for the thermal decomposition of 30.4 kcal. A reasonable accord with results of Tolman and Wolf¹² was found. Their results, extrapolated from lower temperatures, are shown for comparison.

2. Oxidation of Carbon Monoxide in the Presence of Ozone.—The system CO, O₃, O₂, N₂ was studied at atmospheric pressures in four limited temperature ranges centering about 430, 475, 515 and 560°K. Ozone mole fractions ranging from 0.004 to 0.024, CO mole fractions 0.08 to 0.8 and oxygen to ozone ratios from 23 to 60 were used. The fractional decomposition of ozone ranged from 0.25 to 0.8 with most of the work in the range 0.4 to 0.7. Carbon dioxide equivalent to as much as 65% of the ozone decomposed was produced. However, this value refers to cases where the carbon monoxide concentration was as much as forty times greater than that of ozone. Thus, for equal CO and O₃ concentrations the rate of CO₂ production is one to two orders of magnitude slower than the thermal decomposition of ozone.

Examples of the ozone decomposition and carbon dioxide production at 475°K. as a function of CO concentration are shown in Figs. 2 and 3 for several series of comparable runs. Since the CO concentration does not change appreciably due to reaction, Figure 3 indicates the dependence of CO₂ production upon CO. The same data also indicate an approximate first-order dependence upon ozone concentration. Similar results were obtained at the other temperatures.

3. Evaluation of the Carbon Monoxide Oxidation Data.—Based on the indications of reaction order and on the thermal ozone decomposition studies the data were analyzed according to the kinetic scheme

$$-d[O_3]/dt = k_a[O_3]^2/[O_2] + k_b \times f(\text{CO}) \times [O_3] \quad (3a)$$

$$d[\text{CO}_2]/dt = k_b \times f(\text{CO}) \times [O_3] \quad (3b)$$

$$B = \frac{1}{t} \times \ln \frac{x + B/A}{x(1 + B/A)} \quad (3c)$$

$$[\text{CO}_2]/[O_{30}] = B/A \times \ln \frac{1 + B/A}{x + B/A} \quad (3d)$$

where $A = k_a[O_{30}]/[O_{20}]$, $B = k_b f(\text{CO})$, $f(\text{CO})$ is an arbitrary function of the CO concentration, $[O_2]$ and $[\text{CO}]$ were assumed constant, and the other symbols have the same meanings as in equation 1.

(14) S. Jahn, *Z. anorg. Chem.*, **48**, 260 (1906).

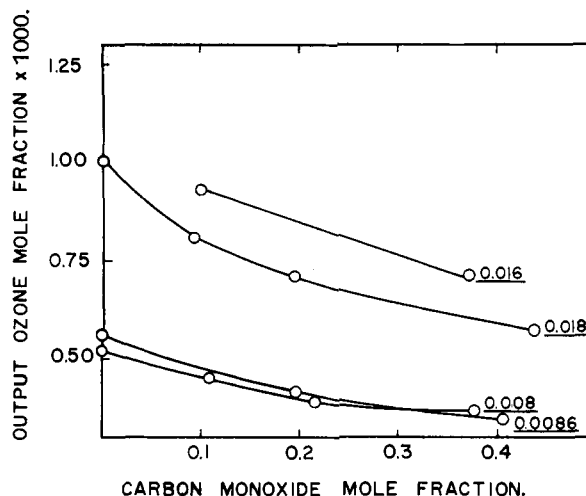


Fig. 2.—Ozone decomposition in presence of CO at 475°K.: contact time about 1–1.3 sec.; initial ozone concentration indicated for each series. Same data used in Fig. 3.

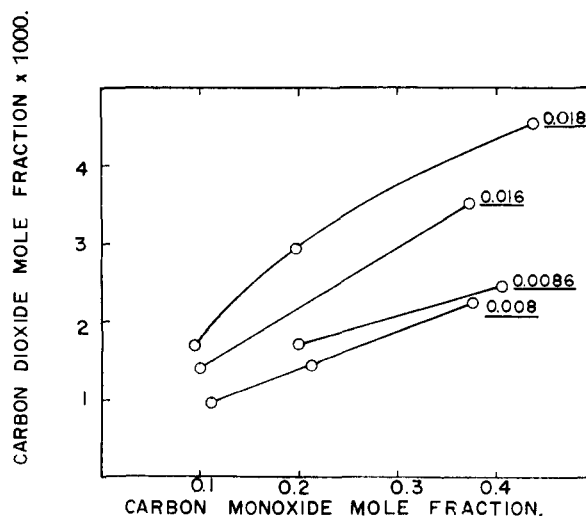


Fig. 3.

B and B/A were determined for each run. The function B was fitted to the data by trial, and a reasonable fit for any series of comparable runs was given by the form

$$B = k_b[\text{CO}]/1 + \alpha[\text{CO}] \quad (3e)$$

with $\alpha = 5.3 \times 10^4$ cc./mole at 430 and 480°, 3.7×10^4 at 515° and zero at 565°K. providing the best fit. Arbitrarily, α was set at 5.3×10^4 for processing the data at all temperatures. Except for the data at the highest temperature k_b calculated on this basis was markedly more constant than if the denominator in equation 3e were neglected. (The scatter at 565° is great enough to cast doubt on the reliability of a fit with $\alpha = 0$.)

The values of k_a , the ozone decomposition rate constant, are independent of the functional form of $f(\text{CO})$. They are in good agreement with those obtained in experiments with no CO present, except at 430° where they are consistently high. The rates k_a and k_b for each run are listed in Table I and are plotted in Fig. 4.

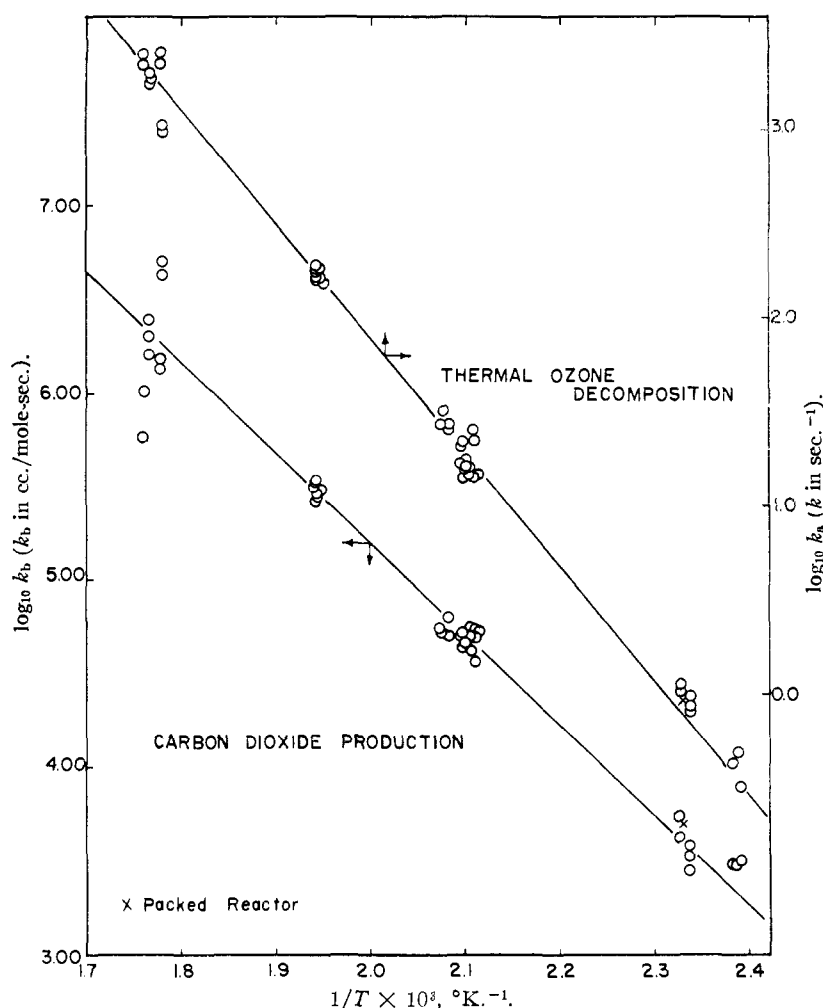


Fig. 4.—Empirical analysis of carbon monoxide oxidation data.

$$\begin{aligned}
 -d[\text{O}_3]/dt &= k_a[\text{O}_3]^2/[\text{O}_2] + k_b f[\text{CO}][\text{O}_3] \\
 d[\text{CO}_2]/dt &= k_b f[\text{CO}][\text{O}_3] \\
 f[\text{CO}] &= [\text{CO}]/1 + 5.3 \times 10^4[\text{CO}] \\
 &\text{see eq. 3a-e.}
 \end{aligned}$$

The Arrhenius plots for k_a and k_b yield the following activation energies: $E^*_a = 27.8$ kcal. (ozone decomposition), $E^*_b = 22.0$ kcal. (carbon dioxide production). The discrepancy between the above value of E^*_a , 27.8 kcal., and that determined for runs with no CO present, 30.4 kcal., is entirely due to the differing values of k_a at 430°K.

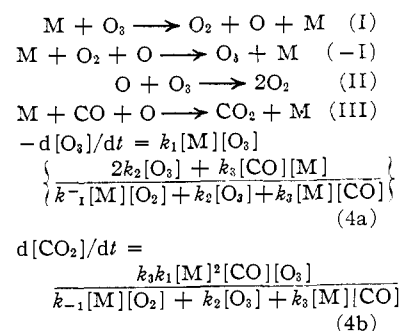
Discussion

Two major points are raised by the results of this empirical treatment of the experimental data on carbon dioxide production. First, it reproduces the thermal ozone decomposition rates determined in the absence of CO. This means that the principal mechanism for the decomposition is essentially unchanged. In terms of the Jahn mechanism (equations I, -I, and II), equation I, for which $E^* \sim 24$ kcal., remains the limiting step.

Second, the relation between the activation energies for ozone decomposition and carbon dioxide production, $E^*_a \sim 28$ kcal., $E^*_b \sim 22$ kcal., is similar to that between the over-all activation energy for ozone decomposition in an excess of oxygen, 28–30

kcal., and the endothermicity, 24.6 kcal., of the first step in the Jahn mechanism I. In other words, $E^*_a - E^*_b = 6$ kcal. is in line with Schumacher's^{15,16} estimate, 5.5 kcal., of the activation energy for reaction II.

It may be inferred from this that the carbon monoxide oxidation is dependent upon the prior occurrence of the initial step in the ozone decomposition, reaction I. This leads directly to the probability that the principal mode of oxidation is the reaction between carbon monoxide and oxygen atoms. The simplest mechanism including this fact is the following, which has been considered in most studies on the interaction of O atoms and CO.



When 4a is divided by 4b and the resultant equation integrated, an expression identical in form with 3d is obtained, where now $A = 2k_2[\text{O}_{30}]$ and $B = k_3[\text{M}][\text{CO}_0]$. Therefore, the same analysis leads to an evaluation of the ratio k_2/k_3 , which has approximately the same temperature dependence as k_a/k_b in the empirical treatment. Average values of k_2/k_3 are 0.6×10^{-3} at 418–430°K., 0.6×10^{-3} at 471–483°K., 1.5×10^{-3} at 515°K. and 1.8×10^{-3} at 561–568°K.

The internal consistency of these rate ratios is not nearly so good as that of those obtained empirically. They add no further support of the oxygen atom mechanism. In part, the scatter of individual points obscures the slight trend. In addition, the less than first-order CO dependence observed in the empirical analysis remains. This might result from either a gas phase inhibition by the products or be indicative of a surface reaction. The latter possibility was tested briefly by the use of a packed reactor (C) at the lowest temperature studied. The results were that the thermal ozone decomposition was not affected by the increased surface, and that any increase in the oxidation rate was within the experimental error. In addition, the unpacked reactors used at higher temperatures

(15) A. Glissmann and H. J. Schumacher, *Z. Physik. Chem.*, **B21**, 323 (1933).

(16) U. Beretta and H. J. Schumacher, *ibid.*, **B17**, 417 (1932).

had high surface to volume ratios and showed a more nearly first-order CO dependence than found in the lower temperature studies. While a surface reaction does not appear important, a small surface contribution with little increase in conversion is consistent with the gas phase reaction I being the limiting process. Accordingly, in a discussion of maximum gas phase rates, it appears allowable to attribute the drifts in k_2/k_3 to surface effects.

Since this analysis leads to a temperature dependence for k_2/k_3 of the order estimated for reaction II it may be concluded that III, the carbon dioxide producer, proceeds without activation energy. This is in accord with the photochemical studies of CO-O₂ mixtures mentioned earlier.

The efficiency of reaction III relative to -I is also in accord with these photochemical experiments. The observed ratio k_3/k_2 indicates a pre-exponential factor ratio A_3/A_2 between 1 and 10. The estimates of the efficiencies of reactions -I and II used by Schumacher¹⁶ to assign an activation energy of 5.5 kcal. to reaction II assume $A_{-1}/A_2 = 10^3$, since $k_{-1}[M]$ and k_2 were about equal at room temperature.¹⁵ A combination of these two ratios provides the estimate: $10^{-2} > A_3/A_{-1} > 10^{-3}$. Jackson³ estimated $A_3/A_{-1} < 7 \times 10^{-3}$.

The present work and that of Kondrateev⁷ on the radiation produced by CO-O₃ systems can be reconciled. He reported an activation energy of 8.8 kcal. for the principal oxidation reaction, but based this estimate on the assumption that reaction I has an activation energy of 28 kcal. instead of the more commonly accepted value of 24.6. Substitution of the latter value reduces his estimate to that found here. In addition, we have found that his analytical method for CO₂ (absorption in soda-lime or ascarite) leads to very high results due to a heterogeneous reaction between CO and O₃ in the absorption train. When this is taken into account, it is no longer necessary to postulate reaction IV in order to explain his results.

The mechanism of CO oxidation by oxygen atoms offers a ready explanation of the light emission reported by Trautz and Kondrateev. Since apparently it is identical with that emitted by CO-O₂

flames,⁷ Laidler's discussion of that problem would apply here.¹⁷ Unfortunately, the existence of this emission does not offer support for either the oxygen atom (III) or the direct (IV) oxidation mechanism, because energy and spin conservation considerations show that light emitters could be produced by either reaction III or IV.

The possibility that a direct reaction between carbon monoxide and ozone may occur at higher temperatures is considered unlikely, but is not definitely ruled out. This study would place a lower limit of about 22 kcal. on its activation energy. This would not vitiate the analysis made by Lewis and von Elbe of the explosion limit data, but it makes that explanation less attractive. In effect, such an activation energy means that at 1000°K. the specific rates for IV and III would just become competitive. At the same temperature, the specific rate for I would be equal to or greater than -I and the concentration of ozone would be far below that of oxygen atoms. In turn, the minor role of IV in the production of CO₂ would make the branching reaction V even less probable. It appears that the pressure dependence of the explosion limit of dry CO-O₂ should be reconsidered in terms of a set of reactions other than IV and V. Indeed, recent work by Gordon¹⁸ indicates that the mechanism of the second explosion limit of CO-O₂ mixtures involves water, and an explanation in terms of C and O compounds alone may not be necessary.

Acknowledgment.—The support of this work by the Air Research and Development Command is gratefully acknowledged. The mass spectrographic analyses of reagents were made by Dr. G. C. Bond. Prof. C. E. Bricker of the Chemistry Department of Princeton University very graciously made available the needed infrared equipment. Many fruitful discussions with Drs. M. J. Boudart and F. J. Long during the course of this work contributed to its prosecution and interpretation.

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(17) V. Griffings and K. J. Laidler, "Third Symposium on Combustion, Flame and Explosion Phenomena," p. 432.

(18) A. S. Gordon, *J. Chem. Phys.*, **20**, 340 (1952).