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Heterogeneous Photocatalysis II. The Mechanism of the Carbon Monoxide Oxidation at Dark and Illuminated Zinc Oxide Surfaces

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On the basis of kinetic and electrical measurements it can be shown that in the steady state of the catalyst the rate of oxidation of CO on zinc oxide catalysts in the temperature range between 100° and 250°C is not noticeably changed by illumination with light of 365 mμ. An increase of the rate of reaction under illumination is detectable only with catalysts pretreated with oxygen. In this case a large temperature coefficient of the conductivity and of the rate of CO_2 formation on dark zinc oxide surfaces was observed. Before a steady state is established the rate of reaction was significant under these conditions but disappeared when the steady state of the catalyst was reached. Therefore, in the steady state the mechanism of the dark- and the photoreaction is approximately the same. In the steady state the rate of CO_2 formation is proportional to the concentration of free electrons of the catalyst and to the O_2 pressure, but is independent of the CO pressure. Preliminary experiments indicate the reaction rate is independent of the CO_2 pressure. A mechanism is tentatively proposed which is consistent with both electrical conductivity and catalytic rate measurements.

INTRODUCTION

In order to elucidate the electronic exchange processes between the reacting gases and semiconducting catalysts during the reaction, many investigations in the last ten years have aimed to prove the dependence of reactions on the electronic structure of the semiconducting catalysts. Especially, one tries to find quantitative relations between the reaction rate and the concentration of free electrons or holes, or both, in the catalysts (*1*). In nonphotoconducting solids a change of the concentration of free electrons or holes is only possible by gas treatment at high temperatures or by doping with foreign ions of different valences. For reasons of electroneutrality, however, the increase of the concentration of the electronic species is connected with a decrease of the lattice-defect concentration, or vice versa. The resultant increase of the lattice-defect concentration is often undesirable because of the reactions between the defects and one of the reactants. Therefore, the photoconducting solids open a new possibility for studying the influence of the electronic structure of catalysts on the reaction rate for, due to illumination, both free electrons and holes are offered to the reactants simultaneously without any significant change of the lattice-defect concentration. Such investigations will provide new aspects to the field of heterogeneous catalysis.

In addition to earlier papers on this subject, partly quoted by Markham and Laidler (*2*), stimulating investigations on the influence of illuminated zinc oxide surfaces on the reaction rate of hydrogen peroxide formation in aqueous suspensions of zinc oxide have been carried out by several investigators (*2*, *3*, *4*). Further research has

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been done on the oxidation of alcohols (*5*) and on the conversion of isopropyl alcohol to acetone on illuminated zinc oxide as a catalyst (*6*). A review of radiation effects on the reactivity of solid surfaces has been given by Cropper (*7*). Furthermore, the carbon monoxide oxidation at illuminated surfaces of zinc oxide, which is the subject of this paper, has also been recently studied (*8, 9*).

In the preceding paper we showed that a mechanism involving an appreciable chemisorption of carbon monoxide both at dark and illuminated zinc oxide surfaces accompanied by transfer of electrons to the catalyst can be excluded. The experimental results between 25° and 250°C can be satisfactorily explained only if one assumes a reaction of carbon monoxide with chemisorbed oxygen molecules:[*]

$$\mathrm{CO(gas)} + \mathrm{O_2^-(ads)} + e' \rightarrow \mathrm{CO_2^-(ads)} + \mathrm{O^-(ads)} \qquad (1)$$

with the subsequent reaction:

$$\mathrm{CO(gas)} + \mathrm{O^-(ads)} \rightarrow \mathrm{CO_2^-(ads)} \qquad (2)$$

Considering these two reaction steps we have to investigate whether the rate of carbon monoxide oxidation at dark and illuminated zinc oxide surfaces is dependent on the CO and/or O_2 pressure under various experimental conditions.

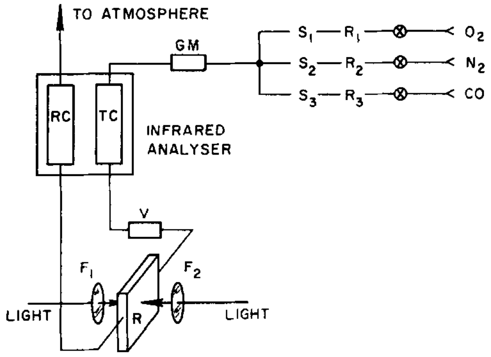

FIG. 1. Block scheme of the flow apparatus. RC and TC are the reference and the measuring chambers of the infrared analyzer, GM the gas mixing vessel, V the preheater, R the reaction chamber, F_1 and F_2 the lenses for illumination; R_1, R_2, and R_3 denote the equipment for gas purification and S_1, S_2, and S_3 are the flow meters.

Rate measurements of the oxidation of carbon monoxide at dark surfaces of zinc oxides doped with Li_2O and Ga_2O_3 have been carried out by Schwab and Block (*10*). Recently, the rate of oxidation of CO at illuminated zinc oxide surfaces was studied by Stone (*8*) and by Schwab and co-workers (*9*). Both groups report an increase of the oxidation rate by illumination. The result of Stone is surprising in that he found an increase of the rate at 400°C while we could not find any photoconductivity above 250°C.

EXPERIMENTAL APPARATUS AND PROCEDURE

Figure 1 shows a schematic representation of the flow apparatus for the kinetic measurements. CO, O_2, CO_2, and N_2, as carrier gas, were purified and then supplied to a gas-mixing vessel via flow meters. In most of our experiments CO_2 was not added to the initial gas mixture. Then the gas mixture passed the reference chamber of an infrared analyzer of high sensitivity (URAS-1 of Hartmann & Braun)[†] operating in the spectral range between 2 and 15 μ. The sensitivity of this continuous flow analyzer is between 0 and 0.01 vol %. For the calibration of the analyzer a standard gas mixture was employed. With a flow rate of the gas mixture of 1 liter/hr, 1 vol % CO_2 equals 1.1×10^{-6} moles CO_2/sec. After passing the reference chamber the gas mixture flowed through a preheater and through the reaction chamber constructed from a Duran type-50 glass. Finally, the gas mixture containing the reaction product (CO_2) passed through the measuring chamber of the infrared analyzer.

Figure 2 represents the reaction chamber, consisting of a rectangular Duran glass vessel ($12 \times 10 \times 0.5$ cm) which contained the catalyst in small pellets mixed with glass spheres in order to increase the amount of the illuminated sur-

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[*] See previous paper (Part I) for the definition of symbols (preceding paper, p. 156).

[†] The authors are indebted to the Hartmann & Braun AG, Frankfurt/Main for the temporary use of the infrared analyzer URAS-1.

face. Simultaneously, two probes for electrical conductivity measurements were assembled in the reaction chamber. These zinc oxide probes had been pretreated in the same way as the zinc oxide pellets. The apparatus and the procedure for the conductivity measurements were the same as those in the preceding paper. For the control of temperature variations two thermocouples were inserted, at the entrance and exit points of the gas. During the light reaction both sides of the reaction chamber were illuminated. Preparation and pretreatment of the catalyst were the same as in the preceding paper.

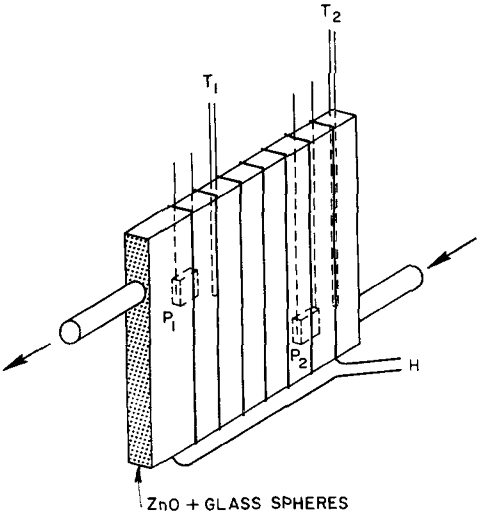

Fig. 2. Rectangular Duran glass chamber containing the catalyst in small pellets mixed with glass spheres. P_1 and P_2 are probes of the same material as the catalyst to verify the conductivity; T_1 and T_2, thermocouples, and H, the heating wire.

The Catalysis of the Oxidation of Carbon Monoxide

The Dark Reaction

As discussed in the preceding paper the dark-conductivity of zinc oxide between 20° and 250°C depends significantly on the pretreatment of the oxide and on the pressure of oxygen, or other gases, during the measurements. Due to the increase of the concentration of charge carriers by illumination the temperature gradient of the photoconductivity is considerably smaller than the gradient of the dark-conductivity, which is governed by a low concentration of charge carriers at 20°C, as was shown in Fig. 6 of the preceding paper, with a zinc oxide doped with 0.04 mole % Li_2O. Furthermore, a close interrelation exists between the temperature coefficients of the dark-conductivity and of the rate of the dark reaction. It is well known that the temperature coefficient of the dark-conductivity of zinc oxide doped with Li_2O is larger than that of pure zinc oxide and, furthermore, that the temperature coefficient of the latter is larger than that of zinc oxide doped with Ga_2O_3, or of zinc oxide annealed in high vacuum (*11*). The same applies to the temperature coefficients of the rate of the dark CO_2 formation represented in Fig. 3. A parallel behavior has also been found for the temperature coefficient of the conductivity and of the oxidation rate of carbon monoxide on pure

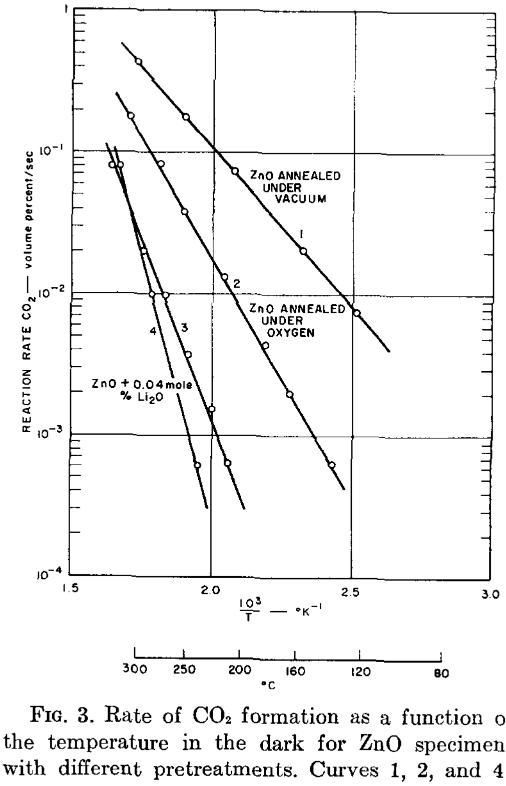

Fig. 3. Rate of CO_2 formation as a function of the temperature in the dark for ZnO specimens with different pretreatments. Curves 1, 2, and 4: $p_{O_2} = 675$ Torr, $p_{CO} = 85$ Torr; Curve 3: $p_{O_2} = 85$ Torr, $p_{CO} = 675$ Torr.

and doped nickel oxide (*10*) (the larger the conductivity at low temperatures, the smaller the temperature coefficient both of the conductivity and of the reaction rate.)

As can be seen in Fig. 4, the gas pressure dependence of the oxidation rate at 240°C is changed by doping of zinc oxide. On an undoped zinc oxide catalyst the rate of oxidation of carbon monoxide is dependent on the oxygen pressure and independent of the carbon monoxide pressure; the rate of oxidation on zinc oxide doped with 0.1 mole % Li_2O, however, is dependent only on the CO pressure. Furthermore, the reaction rate on an undoped catalyst is larger by approximately 1.5 orders of magnitude than that on a zinc oxide doped with Li_2O.

Consistent with the fact that the influence of light on the increase of the conductivity becomes smaller with increasing dark-conductivity and, therefore, smaller with decreasing temperature coefficients of the dark-conductivity of zinc oxide, we do not observe a noticeable increase of the rate of oxidation on zinc oxide samples which have a small temperature coefficient of the dark-conductivity (i.e., high concentration of free electrons). Therefore, in the investigation of the influence of the illumination on the reaction rate only zinc oxide samples with a low concentration of free electrons and, therefore, high temperature coefficient of the dark-conductivity and of the dark reaction, show an effect upon illumination.

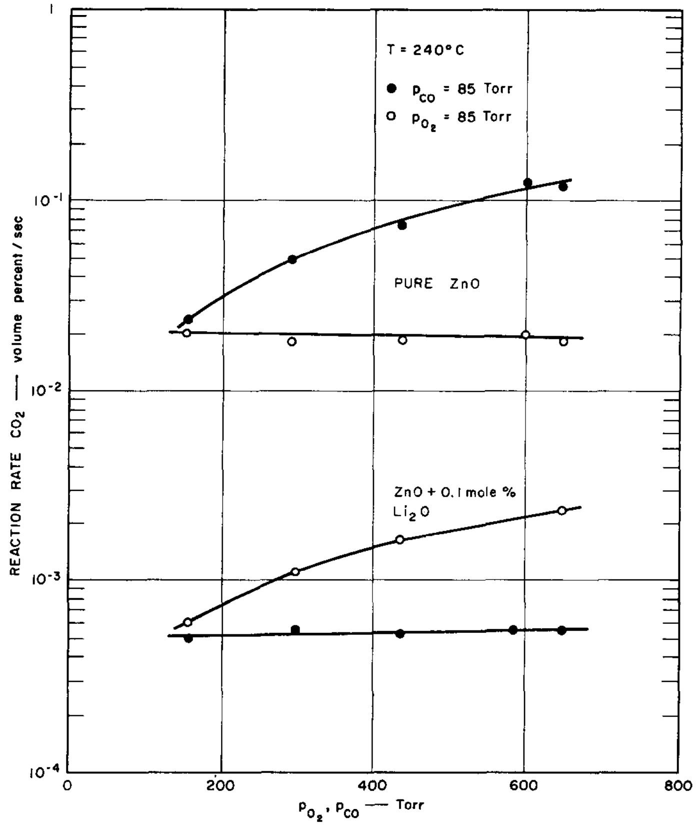

FIG. 4. Rate of CO_2 formation as a function of O_2 and CO pressures at 240°C in the dark. For ZnO + 0.1 mole % Li_2O the rate is only CO pressure dependent. For ZnO (pure) the rate is only O_2 pressure dependent.

The Influence of Illumination on the Rate of CO_2 Formation

As mentioned above, the rectangular reaction chamber was illuminated on both sides with light of 365 mμ of constant intensity (proven by thermopile). With increasing temperature beginning at room temperature, the rate of oxidation of carbon monoxide in a gas mixture of 675 Torr oxygen and 85 Torr carbon monoxide was measured in the dark and under illumination. Experimental points in Fig. 5, beginning with point (1) on curve 1, were taken after reaction periods of 30 min at one temperature. After determining point (1), the corresponding point was determined for curve 1* at the same temperature under illumination. In the subsequent dark period the temperature was rapidly increased and the reaction rate determined at the new constant temperature, etc. As shown in Fig. 5, the influence of the light on the rate of oxidation is large at low temperatures, especially with oxygen-enriched ZnO catalysts, and becomes smaller with increasing temperature. At about 250°C light influence no longer could be detected under our experimental conditions, which fact agrees well with the conductivity measurements of the preceding paper where no photoconductivity of zinc oxide was detected above 250°C. The curve pairs 2–2*, 3–3*, and 4–4* represent the experimental results under the same experimental conditions, thus proving the reproducibility of the reaction rates. Before the start of every reaction rate curve the temperature was lowered to room temperature in an oxygen stream. The temperature coefficient of the dark reaction decreased with increasing number of the rate curves (increasing reaction time) and the accelerating effect of the light on the oxidation rate decreased simultaneously (compare curves 4 and 4* at 160°C). While the rate of oxidation both at dark and under illumination changed continuously below 200°C until the steady state was established, the reaction rate above 200°C was approximately reproducible at all times.

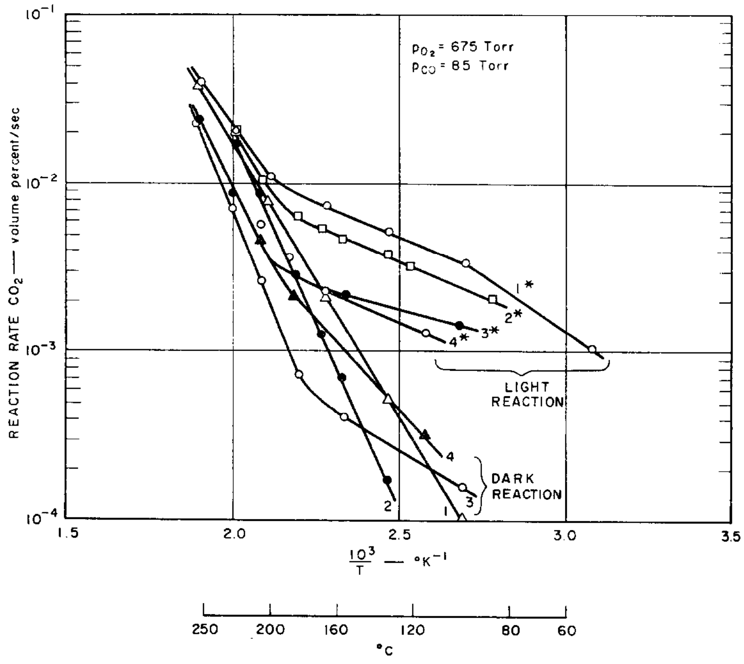

FIG. 5. Rate of CO_2 formation as a function of the temperature at constant O_2 and CO pressures; curves 1–4 dark curves, 1*–4* light reactions; light and dark periods were alternated.

The relation between the light influence and the gas pressure dependence on the rate of oxidation is remarkable. An increase of the rate by illumination, represented in Fig. 6, was observed only when the dark reaction was dependent on the pressure of carbon monoxide. In such cases, however, the dependence of the rate of oxidation under illumination on the CO pressure was smaller. At 150°C, and at a constant oxygen pressure of 85 Torr, the rate of the oxidation under illumination had the same value as the rate of the dark reaction at $p_{CO} = 675$ Torr. The experimental points of the curves were obtained in the same way as those from Fig. 5 by alternating measurements of the dark and the light reaction at 150°C. The curve pair 2–2* represents the repetition of the curve pair 1–1* starting with the lowest CO pressure.† Also in this case the decrease of the light effect on the reaction rate can be recognized. After a second repetition of the rate measurements (curve pair 3–3* in Fig. 6) a noticeable CO pressure dependence is no longer detectable and the influence of the light on the rate is small. Furthermore, the initial reaction rate corresponding to point (1) in Fig. 6 has changed from 10^{-3} to 3.5×10^{-3} vol %/sec. This behavior becomes especially evident in Fig. 7, where the ratio $\dot{n}^*_{CO_2}/\dot{n}_{CO_2}$ is plotted versus the pressure of carbon monoxide. After a second repetition of the rate measurements (curve pair 3–3* in Fig. 6) a noticeable CO pressure dependence is no longer detectable and the rate-increasing influence of the light is only small. Interesting results were obtained under the same experimental conditions by repetition of these measurements at 185°C (curve 4–4* in Fig. 6). Here, the rate of oxidation on dark zinc oxide surfaces showed a slight decrease with increasing pressure of carbon monoxide and the illumination even carried a small but noticeable inhibition.

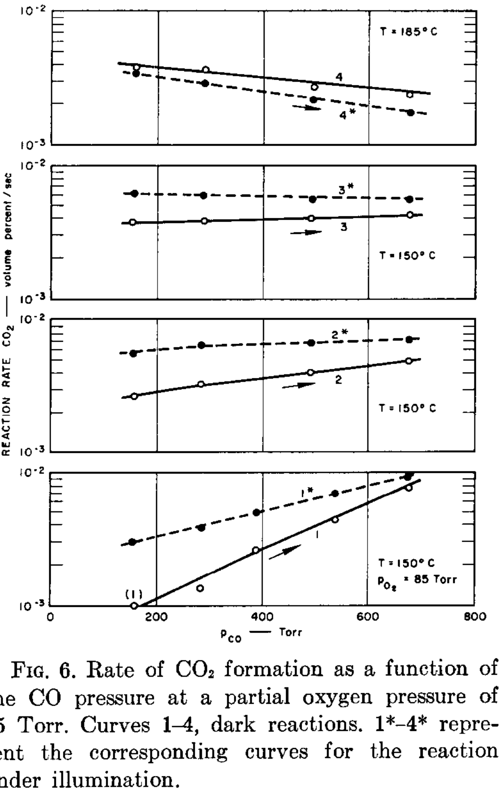

FIG. 6. Rate of CO_2 formation as a function of the CO pressure at a partial oxygen pressure of 85 Torr. Curves 1–4, dark reactions. 1*–4* represent the corresponding curves for the reaction under illumination.

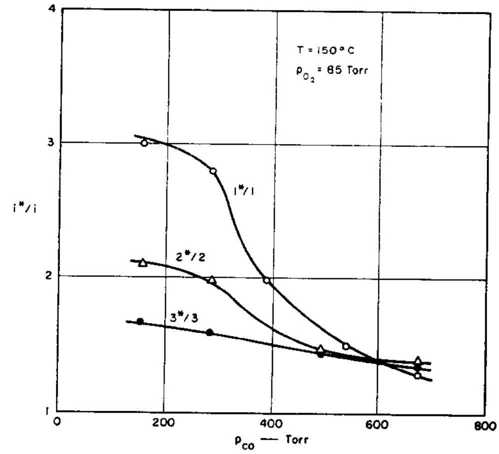

FIG. 7. Ratio of the CO_2 formation rates under light and in the dark as a function of the CO pressure at a constant oxygen pressure of 85 Torr. The values are taken from Fig. 6 and show the decrease of the ratio at a specific CO pressure with increasing numbers of measuring series. Light and dark periods were alternated.

Figure 8 represents the dependence of the oxidation rate in the dark and under illumination on the pressure of oxygen at constant pressure of carbon monoxide (85 Torr) between 158° and 250°C. The curve pairs 4–4* and 5–5* illustrate the independence of the oxidation rate on the oxygen pressure and simultaneously the in-

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† Before the measurements represented by curves 2–2*, 3–3*, and 4–4*, the CO pressure was lowered to the initial value and held constant for 2 to 3 hr until no change in the rate of the CO_2 formation with time could be detected.

crease of the rate due to illumination. These two curve pairs are consistent with the curve pairs 1–1* and 2–2* in Fig. 6 where a CO pressure dependence of the rate was found. Under these conditions, the rate of the photoreaction indicated no dependence on the oxygen pressure. At longer reaction times under illumination, however, the dark reaction became dependent on the oxygen pressure and the influence of the light on the rate disappeared. Finally, a rate-decreasing effect of the light was detectable (curves 1–1* in Fig. 8). No difference of the oxygen pressure dependence between the reactions both in the dark and under illumination could be detected. Similar results have been obtained at 210° and 250°C (curve pairs 2–2* and 3–3* in Fig. 8). Again preceding each measurement, such as shown by curve pairs 4–4* and 5–5*, the oxygen pressure was lowered to the initial pressure and a constant, time-independent rate established.

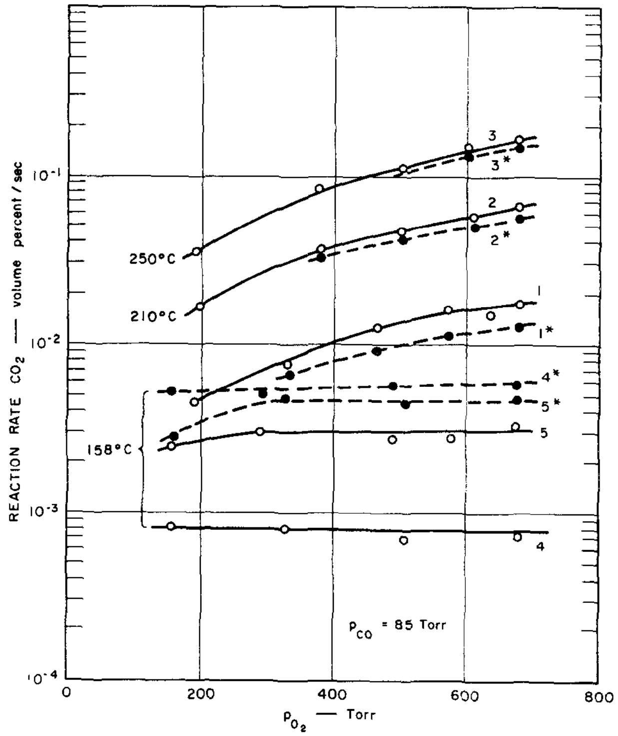

FIG. 8. Rate of CO_2 formation as a function of the oxygen pressure at a constant CO pressure of 85 Torr and at different temperatures. Curves 1–5: dark reactions; curves 1*–5*: under illumination; light and dark periods were alternated.

DISCUSSION OF THE EXPERIMENTAL RESULTS

As known from the literature, the oxidation rate of carbon monoxide at high temperatures on zinc oxide surfaces depends on the oxygen pressure and is independent of the carbon monoxide pressure. At these high temperatures the steady state of the reaction is at all times established and, here, the chemisorption of oxygen is obviously the rate-controlling step. This rate law could be found in the temperature region between 100° and 250°C only if the reacting system has reached the steady state. Otherwise, at low temperatures on oxygen-enriched zinc oxide surfaces the reaction rate can also become CO-pressure dependent and approximately independent of the oxygen pressure. But this is not the steady state, as we were able to demonstrate (see Figs. 6 and 8). This CO pressure dependence of the oxidation rate rules only so long as the excess of chemisorbed oxygen is large enough. At longer reaction times connected with further decrease of the amount of chemisorbed oxygen the CO pressure dependence becomes smaller and, finally disappears, while simultaneously the oxygen pressure dependence appears and becomes the single rate-controlling factor.

An increase of the oxidation rate caused by illumination was detectable only in the region of the CO pressure dependence of the dark reaction. On the basis of our experiments we may conclude that the action of light itself diminishes its ability to increase the rate of CO_2 formation due to an acceleration of the desorption of oxygen according to the following over-all equation

$$O_2^-(\text{ads}) \xrightarrow{h\nu} O_2(\text{gas}) + e' \qquad (3)$$

We recognize that the illumination hastens the establishment of the steady state. Therefore, in the steady state the rate of oxidation in the dark and under illumination is approximately the same.

Under conditions where a photochemisorption of oxygen on zinc oxide is observable then even in the case of an oxygen pressure dependence of the dark reaction an increase of the rate of oxidation by illumination should be detected so long as the steady state is not reached.

Therefore, we propose the following mechanism for the dark reaction

$$O_2(\text{gas}) \rightleftarrows O_2^x(\text{ads}) \qquad (4)$$

$$O_2^x(\text{ads}) + e' \rightleftarrows O_2^-(\text{ads}) \qquad (5)$$

$$CO(\text{gas}) \rightleftarrows CO^x(\text{ads}) \qquad (6)$$

$$CO^x(\text{ads}) + O_2^-(\text{ads}) + e' \rightarrow CO_2^-(\text{ads}) + O^-(\text{ads}) \qquad (7)$$

$$CO^x(\text{ads}) + O^-(\text{ads}) \rightarrow CO_2^-(\text{ads}) \qquad (8)$$

$$CO_2^-(\text{ads}) \rightarrow CO_2(\text{gas}) + e' \qquad (9)$$

Since the rate of oxidation of CO has the same value and the same dependence on the partial pressure of the gases at both dark and illuminated zinc oxide surfaces, the same mechanism with the additional light reaction governs in this case.

$$O_2^-(\text{ads}) + |e|^{\bullet} \sim e' \rightarrow O_2^x(\text{ads}) + e' \qquad (10)$$

But this light reaction has no influence in the steady state. Therefore, in the steady state we obtain in the first approximation the following rate law

$$dn_{CO_2}/dt = kc_- p_{O_2} \qquad (11)$$

which is in agreement with our experimental results.

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