On the Competition of Homogeneous and Heterogeneous Chain Terminations in Heterogeneous Photooxidation Catalysis by Zinc Oxide

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(Received June 12, 1964)

It has previously[1] been shown that the photoexcited adsorption or desorption of oxygen takes place on zinc oxide when lights of 3650—4350 Å are irradiated. In connection with this finding, the photooxidation of isopropyl alcohol has been investigated on zinc oxide in the presence of oxygen, the products being identified as acetone and hydrogen peroxide exclusively.[2] The same photooxidation was investigated also by Kriascose and Markham[3] on zinc oxide in pure isopropyl alcohol and aqueous suspensions. The ratio

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[1] Y. Fujita and T. Kwan, This Bulletin, 31, 803 (1958).

[2] I. Komuro, Y. Fujita and T. Kwan, ibid., 32, 884 (1959).

[3] J. Kriascose and M. C. Markham, *J. Catalysis*, 1, 498 (1962).

of the oxygen uptake to the hydrogen peroxide formed was always greater than unity, especially when zinc oxide was suspended in pure liquid, suggesting that hydrogen peroxide is decomposing or participating in the oxidation of alcohol to a certain extent.

Despite the simple reaction, however, little is yet known about the photooxidation mechanism, probably because of the complex nature of the reactions occurring in the heterogeneous phase. In this paper we shall show some significant aspects of the photooxidation kinetics and then discuss them with respect to the competition of homogeneous and heterogeneous chain terminations.

Experimental and Results

The photooxidation of isopropyl alcohol by zinc oxide in the presence of oxygen has been characterized by a certain induction period.[2] This can be eliminated, however, by stirring the zinc oxide - alcohol mixture in an oxygen atmosphere prior to photoirradiation. The initial steady-state rate for the consumption of oxygen was thus obtained within twenty minutes at the most. The apparatus and procedure for the measurements of the photooxidation catalysis were almost the same as those described previously.[2,4] The reaction was carried out at a constant oxygen pressure above 30 cmHg, where the rate of oxygen consumption was found to be independent of the oxygen pressure. The volume of oxygen consumed was determined by a conventional gas burette kept in a thermostat. Typical rate data, expressed by the volume of oxygen consumed upon irradiation, are shown in Fig. 1.

It was found in this way that the rate of oxygen uptake increases with the increase in the amount of zinc oxide added, suggesting that the light quanta absorbed increases with an increase in the concentration of photocatalysts. A further increase in the amount of zinc oxide, however, caused the rate of oxygen uptake to decrease gradually, hence giving rise to a maximum in the plot of the rate against the amount of zinc oxide present. Such a curve obtained at the reaction temperature of 60°C is illustrated in Fig. 2.

The quantum yield for the oxygen uptake is calculated in Table I at various amounts of zinc oxide.

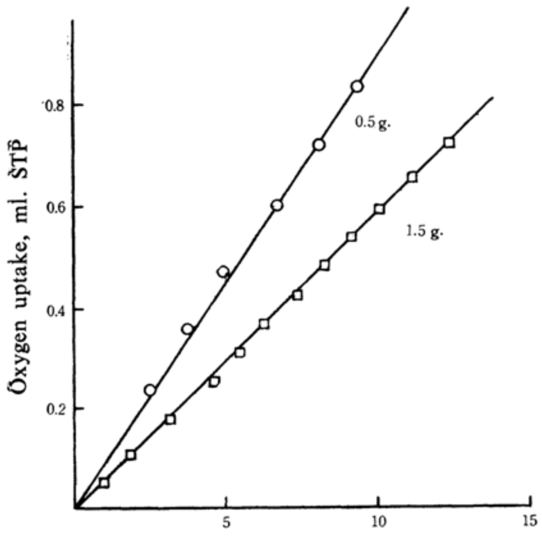

Fig. 1. Initial photooxidation rate of isopropyl alcohol on zinc oxide.
Isopropyl alcohol: 50 ml.
Partial pressure of oxygen: ca. 45 cmHg. Reaction temperature: 60°C.
Intensity of entering light I_0: $4.3^6 \times 10^{17}$ quanta/l. sec.

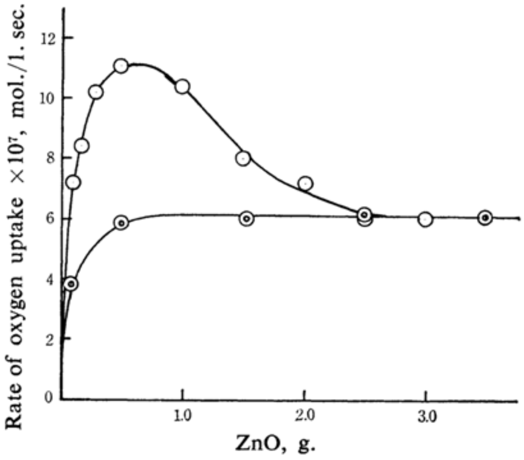

Fig. 2. The relationship between the rate of oxygen uptake and the amount of zinc oxide present.
Isopropyl alcohol: 50 ml.
I_0: $4.3^6 \times 10^{17}$ quanta/l. sec.
Reaction temperature; 40 and 60°C.
○ 60°C ◎ 40°C

TABLE I. QUANTUM YIELD FOR THE OXYGEN UPTAKE.

Intensity of entering light I_0 (determined by uranyl oxalate actinometry): $4.3^6 \times 10^{17}$ quanta/l. sec.
Reaction temp.: 60°C
Isopropyl alcohol: 50 ml.

ZnO g.	0.1	0.2	0.5	1.0	2.0	3.0
Φ	1.0	1.1	1.5	1.4	1.0	0.8

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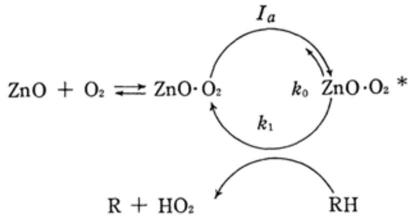
[4] M. Kamiya, Y. Fujita and T. Kwan, *Shokubai (Catalyst)*, **6**, 15 (1964).

Discussion

It is generally accepted that the liquid phase oxidation of alcohol at high temperature is of a chain character. It has already been shown[4] that the anthraquinone-sensitized oxidation of isopropyl alcohol proceeds with a chain mechanism above 50°C. The quantum yield given in Table I, probably showing the lower limit due to the light scattering on the suspensions and also to the light penetration through the liquid phase at lower concentrations of zinc oxide, may be indicative of the chain reaction participating to some extent.

The following mechanism is, therefore, assumed to be the principal process for the photooxidation of isopropyl alcohol on zinc oxide. The primary process may be schematically represented by:



where I_a is the intensity of light absorbed or the rate of the excitation of oxygen on zinc oxide, k_0 and k_1 are rate constants of the respective steps, and RH denotes the isopropyl alcohol molecule. No description will be made at the moment regarding the adsorbed state of oxygen and the mechanism of photoexcitation; detailed investigations will soon be reported in association with adsorption, conductivity and ESR measurements of zinc oxide and adsorbed oxygen.[5] The steady state rate of the primary process may readily be derived as:

$$R_i=\frac{k_1 I_a(\mathrm{RH})}{k_0+k_1(\mathrm{RH})} \tag{1}$$

The secondary process may be thermal, and the following steps are expected to participate at least:

$$\mathrm{R}+\mathrm{O_2}\xrightarrow{k_2}\mathrm{RO_2}$$

$$\mathrm{RO_2}\xrightarrow{k_3}\begin{matrix}\mathrm{CH_3}\\\mathrm{CH_3}\end{matrix}\!\!>\!\mathrm{CO}+\mathrm{HO_2}$$

$$\mathrm{RH}+\mathrm{HO_2}\xrightarrow{k_4}\mathrm{R}+\mathrm{H_2O_2}$$

$$\mathrm{HO_2}+\mathrm{HO_2}\xrightarrow{k_5}\mathrm{H_2O_2}+\mathrm{O_2}$$

$$\mathrm{HO_2}+\mathrm{HO_2}\xrightarrow[\mathrm{M}]{k_5'}\mathrm{H_2O_2}+\mathrm{O_2}$$

where the last step indicates the heterogeneous chain termination effected on the third body, M, or on the surface of zinc oxide competing with the homogeneous bimolecular chain termination given just above.

The steady state treatment of the overall reaction yields the expression:

$$-\frac{\mathrm{d}(\mathrm{O_2})}{\mathrm{d}t}=R_i+\frac{k_4}{\sqrt{k_5}}\sqrt{R_i}\,(\mathrm{RH}) \tag{2}$$

for the homogeneous chain termination. The substitution of k_5' (M) for the k_5 of Eq. 2 gives, of course, the rate equation for the heterogeneous chain termination:

$$-\frac{\mathrm{d}(\mathrm{O_2})}{\mathrm{d}t}=R_i+\frac{k_4}{\sqrt{k_5'(\mathrm{M})}}\sqrt{R_i}(\mathrm{RH}) \tag{3}$$

It seems more likely that the heterogeneous chain termination on zinc oxide is monomolecular rather than a third-body collision involving M. The rate of oxygen uptake is, then, given by:

$$-\frac{\mathrm{d}(\mathrm{O_2})}{\mathrm{d}t}=R_i+\frac{k_4}{k_5''(\mathrm{M})}\,R_i(\mathrm{RH}) \tag{4}$$

The $\mathrm{RH}+\mathrm{HO_2}\rightarrow\mathrm{R}+\mathrm{H_2O_2}$ step requires a definite energy of activation, so the chain can not propagate around room temperature.[4] In other words, the second term on the right of Eq. 2 will only be significant at elevated temperatures. This may be applicable not only in the homogeneous phase but also in the heterogeneous phase provided the concentration of zinc oxide is low enough.

On the other hand, the chain will not propagate, according to Eq. 3 or 4 even at elevated temperatures in the heterogeneous phase, if sufficient amounts of M or zinc oxide are present, leaving only the first term in the rate expression. Thus, the rate of oxygen uptake may be expected to decrease with an increasing M value and finally to approach a limiting value which may be identified to R_i. The decreasing curve of Fig. 2 observed at high concentrations of zinc oxide may probably be ascribed to such a predomination of the heterogeneous chain termination.

A low temperatures, where the chain propagation is suppressed, the rate may be expected to increase monotonously with an increase in the amount of zinc oxide, finally attaining R_i without showing any maximum. The supposition was supported by experiments at the temperature of 40°C, where the chain reaction was almost negligible.[4] As is shown by the double circles of Fig. 2, the results were found to be strikingly consistent with the expectation.

Mashio,[6] who studied the benzoyl peroxide-initiated oxidation of isopropyl alcohol above 80°C, estimated the temperature coefficient of

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[5] Y. Fujita and T. Kwan, *Shokubai* (*Catalyst*), **5**, 206 (1963).

[6] F. Mashio, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **63**, 699 (1960).

$k_4/\sqrt{k_5}$ to be 9.8 kcal./mole. Hence, the temperature coefficient of the rate of oxygen uptake should assume a more or less rapid increase with a rise in the temperature from room temperature to, say, 80°C, because the reaction around room temperature is photochemical, involving radical recombinations, and so the rate should be little dependent on the temperature.

In the presence of excess zinc oxide, the rate of oxygen uptake was found actually to agree with that of the primary process. The temperature coefficient of the rate is, then, expected to be very small, even beyond the temperature where the chain propagation actively participates. On the other hand, such would not be the case when the amount of zinc oxide is sufficiently small; the temperature coefficient of the rate is expected to increase with the increasing temperature, much as in the homogeneous phase.

In Fig. 3 the plot of $\log(-\mathrm{d}(O_2)/\mathrm{d}t)$ vs. $1/T$ with 0.1 g. zinc oxide added on the one hand and that with 2.5 g. zinc oxide on the other hand are compared.

As can be seen from Fig. 3, the temperature coefficient of the oxidation rate increases distinctly from near zero to about 10 kcal./mole. at around 45°C when the amount of zinc oxide present was small, whereas it was nearly constant at a very small value on excess zinc oxide over the same temperature range.

The decreasing curve of Fig. 2, already explained as being due to the heterogeneous chain termination of HO_2, might resemble the effect of the third gases in the photochemical dissociation of the bromine or iodine molecule worked out by Rabinowitch and Wood⁷⁾ many years ago, although the increase in the third gases, in the latter reaction, serves to accelerate the homogeneous recombination of dissociated atoms and, hence, to decrease the concentration of halogen atoms.

The effect of the electronic properties of zinc oxide on the photocatalytic activity will be discussed next. It has previously been shown²⁾ that the rate of oxygen uptake continues, even when the light is interrupted, when a sample of oxidized zinc oxide is subjected to photooxidation catalysis. No such memory was perceptible on a reduced zinc oxide sample. Investigations of these phenomena led to the conclusion that the dark oxidation of isopropyl alcohol on oxidized zinc oxide is due to the hydrogen peroxide-initiated oxidation of alcohol.

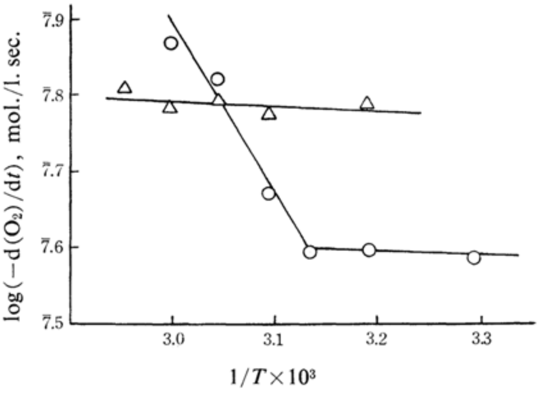

Fig. 3. The temperature coefficient of the photooxidation rate at low and high concentrations of zinc oxide.
○ ZnO 0.1 g. △ ZnO 2.5 g.

In view of the dual nature of the photoresponses for the oxygen adsorbed on reduced and oxidized zinc oxide samples on the one hand and on alumina-doped and lithia-doped zinc oxide samples on the other hand, it seemed of interest to find the difference in the activity in the photo-primary process using doped zinc oxide samples. Preliminary experiments have shown that the rate of oxygen uptake is much greater on lithia-doped zinc oxide than on an alumina-doped sample at the temperature of 60°C. The rate on the lithia-doped sample was autocatalytic, controlled even by the diffusion of oxygen into the liquid phase at the later stage of the reaction. It was considered that the thermal oxidation of isopropyl alcohol, initiated by the decomposition of hydrogen peroxide, occurs simultaneously on the surface of lithia-doped zinc oxide. At the initial stage of the photoreaction, the rate of oxygen uptake was greater on lithia-doped zinc oxide than on an alumina-doped sample; $ZnO(Li_2O) > ZnO(Al_2O_3)$.

It is interesting to note that the sequence of the activity is reversed at a lower temperature, i. e., at 30°C. The rate of oxygen uptake upon irradiation was the greatest on alumina-doped zinc oxide, as $ZnO(Al_2O_3) > ZnO > ZnO(Li_2O)$. Markham and Kuriacose did not investigate the effect of doping zinc oxide on the photocatalytic activity, but they noted that the addition of hydrogen peroxide to a zinc oxide suspension does not affect the rate of acetone formation at 25°C. If the decomposition of hydrogen peroxide to give oxygen and water is the only side reaction on zinc oxide samples around room temperature, then the activity sequence mentioned above may be quite natural, for Sedaka of this laboratory found that the decomposition of hydrogen

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7) E. Rabinowitch and W. C. Wood, *J. Chem. Phys.*, **4**, 497 (1936). See also W. A. Noyes, Jr., and P. A. Leighton, "The Photochemistry of Gases," Reinhold Publishing Co., New York (1941), p. 195.

peroxide in an aqueous solution occurs more rapidly on lithia-doped zinc oxide than an alumina-doped sample. The decomposition of hydrogen peroxide on lithia-doped zinc oxide may compensate for the consumption of oxygen to some extent.

In this connection, reference may be made to the work by Bernas and Doo-Kingue.(8) Bernas reported that the photoirradiation of an aqueous suspension of zinc oxide produces hydrogen peroxide more efficiently on reduced zinc oxide than on an oxidized sample. The efficient production of hydrogen peroxide on zinc oxide of a reduced state, according to Bernas and Dook-Kingue, might be due to its inefficient activity in the thermal decomposition of hydrogen peroxide; this is in accordance with the finding by Sedaka.

In studying the photooxidation of carbon monoxide on zinc oxide, Stone(9) found that the relative catalytic activity is the sequence: $ZnO(Li_2O) > ZnO > ZnO(Cr_2O_3)$. A similar result was found concerning oxygen exchange catalysis on zinc oxide samples.(10) The activity of doped zinc oxide samples in the decomposition of hydrogen peroxide, as well as in the oxidation of isopropyl alcohol, may be correlated with the data available in the literature.

Summary

The photooxidation catalysis of isopropyl alcohol on zinc oxide has been investigated with special reference to the chain termination mechanism. It has been proposed that homogeneous and heterogeneous chain terminations compete in this system. At a low concentration of zinc oxide, the homogeneous termination predominates, while at a high concentration the heterogeneous termination may come into play. As a result, a maximum may appear in the relation of the rate of oxygen uptake to the amount of zinc oxide present. With excess zinc oxide, chain reactions are suppressed, so no maximum may appear in the corresponding plot and the temperature coefficient should be very small. The experimental results have been found to be consistent with the expectations. The effect of doping zinc oxide on the photooxidation kinetics has been investigated and discussed, mainly on the basis of the data available on the formation and decomposition of hydrogen peroxide on doped zinc oxide samples.

It has been suggested that lithia-doped zinc oxide is more active than alumina-doped zinc oxide at higher temperatures because of the accompanying hydrogen peroxide-initiated oxidation of isopropyl alcohol on the former, while it is less active at lower temperatures because of the efficient decomposition of hydrogen peroxide, giving oxygen and water.

This work was supported in part by a grant of the Ministry of Education, to which the authors' grateful acknowledgements are made.

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(8) A. Bernas and M. Doo-Kingue, Photochemistry Symposium, March 27—29, 1963, Rochester.

(9) F. Romero-Rossi and F. S. Stone, 2nd International Congress on Catalysis, 1960, Paris.

(10) V. I. Gorgoraki, V. Yu. Levin and L. A. Kasatkina, *Kin. Kata.*, **4**, 422 (1963).