Photocatalytic and Thermal Catalytic Decomposition of Nitrous Oxide on Zinc Oxide

By KEN-ICHI TANAKA and GEORGE BLYHOLDER*
(*Department of Chemistry, University of Arkansas, Fayetteville, Arkansas* 72701)

Summary The thermal catalytic decomposition of N_2O on ZnO in the range 370—430° is first order in N_2O pressure and independent of O_2 pressure while the photocatalytic reaction at the same temperatures obeys an expression of the type rate $= kP(N_2O)/k' + k''P(N_2O) + k'''[P(O)_2)]^{\frac{1}{2}}$.

THE catalytic decomposition of nitrous oxide was adopted as a test reaction to investigate the catalytic action of an oxide surface. Since Dell, Stone, and Tiley[1] pointed out a relation between the catalytic activities of oxides and their electronic properties, the importance of electron-transfer process in the catalytic decomposition of nitrous oxide has been emphasized.[2] The aim of this work is to study the kinetics of the steady-state photocatalytic decomposition of nitrous oxide on zinc oxide and to show the roles of electrons and holes in photocatalysis and in thermal catalysis. The most remarkable results in the present experiments are that the thermal catalytic and photocatalytic reactions occur simultaneously on zinc oxide under illumination and that these two reactions obey completely different kinetics. The results obtained cast doubt on the electronic expressions widely adopted for the thermal catalytic decomposition of nitrous oxide on oxides.

The photocatalytic and thermal catalytic decomposition of nitrous oxide were carried out on zinc oxide (Kadox-25) in a closed circulation system over the temperature range 371—431°. The reactor with its 63 mm diameter Pyrex window was mounted in a furnace and illuminated from the bottom. The catalyst, 2·38 g of ZnO, was activated by repeated oxidation and evacuation at 410°. The catalyst was pre-treated with nitrous oxide under the reaction conditions, followed by a few minutes' evacuation, before each series of experiments. The product mixtures, oxygen and nitrogen, were analysed in an on-line gas chromatograph using molecular sieve 5A column.

It was established that the thermal catalytic decomposition of nitrous oxide on zinc oxide is described by the equation, $r = kP(N_2O)$. The kinetics of the photocatalytic decomposition, however, are markedly different from those of the thermal catalytic reaction.

Typical results for the reaction rate under illumination are shown in Figure 1. The straight lines in the Figure show the expected thermal catalytic reaction rate. This Figure reveals that the reaction under illumination consists of photocatalytic reaction and a thermal catalytic reaction. The photocatalytic reaction may be obtained by subtracting the thermal catalytic reaction rate from the overall reaction rate. Plots of the reciprocal of the photocatalytic reaction rate against the reciprocal of $P(N_2O)$ at various temperatures (418, 400, 391, 387, 378, and 371°) at a constant O_2 pressure give straight lines, indicating that the dependence of the rate on $P(N_2O)$, as given in the rate expression above, is obeyed. Oxygen has no effect on the thermal catalytic decomposition of nitrous oxide on zinc oxide. However, the reaction under illumination is markedly retarded by oxygen. Figure 2 shows the oxygen effect on the photocatalytic reaction rate obtained by subtracting the thermal catalytic reaction rate from the overall reaction rate. When the reciprocal of the photocatalytic reaction rate at constant $P(N_2O)$ is plotted against $[P(O_2)]^{\frac{1}{2}}$ at various temperatures, straight lines are obtained again in accordance with the rate expression given above.

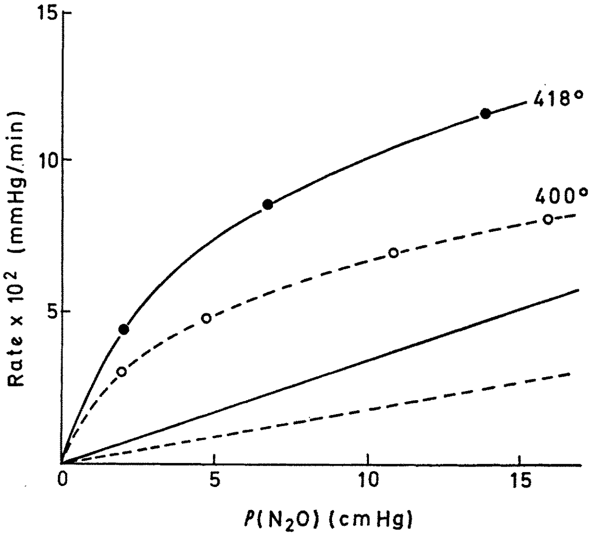

FIGURE 1. *Nitrous oxide pressure-dependence of the reaction rate under illumination. Straight lines show the thermal catalytic reaction.*

The electronic structure of the catalyst is generally described in terms of the band model. Electrons in the valence band are excited into the conduction band by illumination. Most of the holes probably stay at the surface, but the electrons are repelled from the surface by the potential barrier at the surface. It has been demonstrated by Morrison *et al.*[3] that electron injection and/or hole injection from surface species to the solid rarely occur in the electron-transfer processes of zinc oxide surfaces. Assuming that this behaviour occurs during the photocatalytic decomposition of nitrous oxide, the rate of electron capture by electron scavengers (V_2 for N_2O and V_2' for O_2, which is assumed to dissociate into atoms on the surface to form 2 O^- ions) and the rate of recombination of captured electrons with holes (V_3 and V_3') are given by

$$V_2 = k_2P(N_2O)\ (e)_S \qquad V_3 = k_3(N_2O^-)(h)_S$$
$$V_2' = k_2'[P(O_2)]^{\frac{1}{2}}\ (e)_S \qquad V_3' = k_3'\ (O^-)\ (h)_S$$

At a steady state, $V_2 = V_3$, $V_2' = V_3'$ and $(h) = (O^-) + (N_2O^-)$, where $(e)_S$ and $(h)_S$ are the concentration of electrons and holes at the surface. These correlate with the concentration of electrons (e) and holes (h) as follows:

$$(e)_S = (e) \exp - qV/\boldsymbol{RT},\ (h)_S \approx (h)$$

where q is the electron charge and V is the potential barrier at the surface. Then, the electron concentration at the surface is given by the equation

$$(e)_S = \frac{(h)_S}{\exp qV/\boldsymbol{RT} + \dfrac{k_2P(N_2O)}{k_3\ (h)_S} + \dfrac{k_2'[P(O_2)]^{\frac{1}{2}}}{k_3'\ (h)_S}}$$

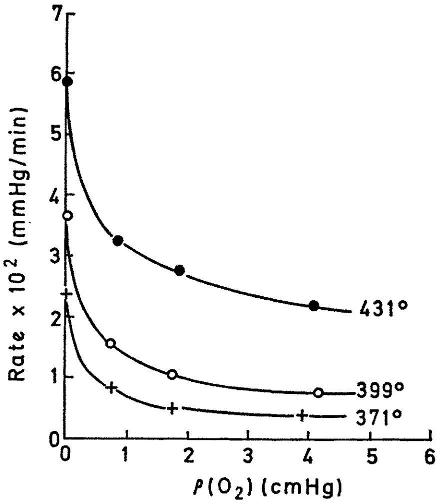

FIGURE 2. *Effect of oxygen pressure on the photocatalytic reaction rate at various temperatures.* $P(N_2O) = 4{\cdot}6$ cmHg.

Assuming that the photocatalytic decomposition of nitrous oxide passes through the intermediate, N_2O^-, which at a steady state is given by the following equation

$$[N_2O^-] = (e)_S\,\frac{k_2P(N_2O)}{k_3\ (h)_S}$$

The reaction rate is given by

$$r = k(N_2O^-) = k(e)_S\,\frac{k_2P(N_2O)}{k_3\ (h)_S}$$

Upon substitution of the expression for $(e)_S$ this yields an expression of the form given in the summary, which fits the data quite well.

Because the good electron-scavengers, N_2O and O_2, inhibit the photocatalytic decomposition, it may reasonably be suggested that the photocatalytic reaction proceeds *via* an electron-transfer process to form an ionic species, here N_2O^-, at the surface. However, it is clear that on zinc oxide the thermal catalytic decomposition does not pass through the same intermediate as that in the photocatalytic decomposition. This suggests that the thermal catalytic reaction may not include electron transfer in its reaction process as has so often been suggested previously.

This investigation was supported in part by a United States PHS Research Grant from the National Air Pollution Control Administration.

(*Received, June* 15*th*, 1970; *Com.* 921.)

---

[1] R. M. Dell, F. S. Stone, and P. F. Tiley, *Trans. Faraday Soc.*, 1953, **49**, 201.
[2] F. S. Stone, *Adv. Catalysis*, 1962, **13**, 1.
[3] S. R. Morrison and T. Freund, *J. Chem. Phys.*, 1967, **47**, 1543.