CHEMISTRY LETTERS, pp. 799-802, 1980.

OXIDATION OF ALKANES AND ALKENES BY N_2O OVER UV IRRADIATED MgO

Chebock YUN, Masakazu ANPO, Yasuo MIŻOKOSHI, and Yutaka KUBOKAWA*
Department of Applied Chemistry, University of Osaka Prefecture, Sakai,
Osaka 591

The reactions occurring under UV irradiation of a mixture of N_2O and alkanes or alkenes over MgO have been investigated. From the distribution of the products it is concluded that the oxygen species responsible for the reactions are O^- ions. In disagreement with the results of the reactions of O^- ions reported by Lunsford et al.[2], in the case of alkanes most of the alkene formation proceeds at room temperature and in the reactions of 2-C_4H_8 the dehydrogenation is not the major reaction.

Photocatalytic oxidation of hydrocarbons on oxides using oxygen as the oxidant has been investigated by a number of workers.[1] Different characteristics of the oxidation are expected when N_2O is used as the oxidant. In such studies it seems important to obtain information on what kind of oxygen species participates in the oxidation. For this purpose MgO appears to be an appropriate material, since Lunsford et al.[2] have made extensive studies on the reactions of oxygen anion radicals with hydrocarbons over MgO. Accordingly, we have investigated the reactions occurring on UV irradiation of a mixture of N_2O and alkanes or alkenes over MgO.

MgO (from Mitsuwa co., surface area, 18 m^2g^{-1}) was used. It was subjected to oxygen treatment at 720 K followed by evacuation at 770 K for 4 hr. A mixture of N_2O and hydrocarbons was irradiated at 293 K using a high pressure mercury lamp. The temperature of MgO was raised from room temperature to 673 K. The reaction products desorbed were analyzed by gas chromatography. The nitrogen formed was determined by a Pirani gauge.

Fig. 1 shows the change in the desorption products formed from the reaction of C_3H_8 with increasing desorption temperature. The product distributions obtained with other alkanes are shown in Table 1.

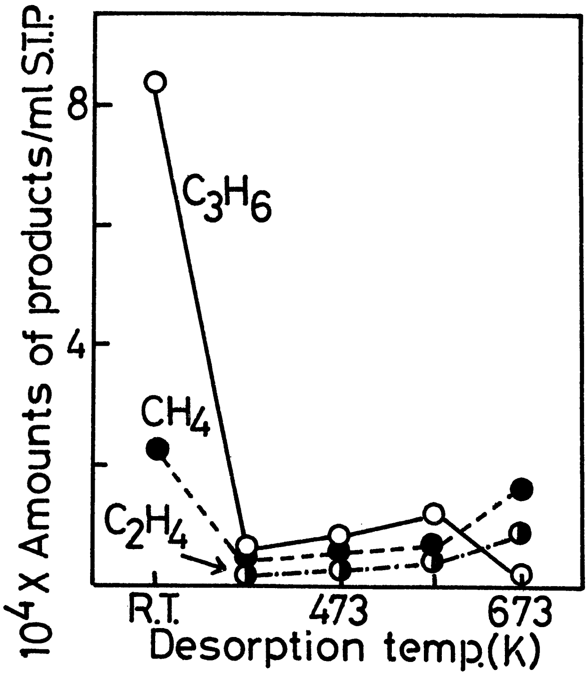

Fig. 1. Photoformed products from a mixture of C_3H_8 and N_2O. C_3H_8, 7.5 X 10^{-2} ml at S.T.P. ; N_2O, 3.0 Torr (1 Torr = 133.3 Pa) ; Irradiation, 180 min. The amount of N_2 formed is 9.8 X 10^{-3} ml at S.T.P.

As to the possible oxygen species responsible for the reactions under UV irradiation of N_2O, the following ones may be mentioned ; O^-, O_2^-, O_3^-, and O atoms. According to the work of Lunsford et al.[2], the oxygen species on MgO consists of mainly O_3^- ions after UV irradiation of N_2O at 77 K. Although the mechanism of O_3^- formation is unclear at present, it appears that the first reaction step is trapping of electrons by N_2O, i.e.,

$$N_2O + e^- \longrightarrow N_2 + O^- \qquad (1)$$

and then O_2^- as well as O_3^- ions are formed by the subsequent reaction steps. Considering[2,3] that O^- ions are much more reactive than O_3^- and O_2^- ions, O^- ions

Table 1. Photoproducts from a mixture of N_2O and alkanes

Reactants (X10^{-2}ml at S.T.P.)	Products (X10^{-5}ml at S.T.P.)	
Desorption temp.	room temp.	up to 673 K
CH_4 (9.5)	C_2H_6 (15), C_2H_4 (1)	CH_4, C_3H_6, C_2H_4
C_2H_6 (10)	C_2H_4 (58), n-C_4H_{10}(21), CH_4 (7), C_3H_8 (5)	C_2H_4, CH_4, C_4H_8, C_3H_6
n-C_4H_{10} (7.6)	t-2-C_4H_8 (116), c-2-C_4H_8 (67), 1-C_4H_8 (20), C_2H_6 (16), CH_4 (13)	C_4H_8, CH_4, C_3H_6, C_2H_4
iso-C_4H_{10} (8.6)	iso-C_4H_8 (245), C_2H_6 (28), CH_4 (18), C_3H_6 (16)	iso-C_4H_8, CH_4, C_3H_6, C_2H_4
n-C_5H_{12} (7.1)	t-2-C_5H_{10} (64), c-2-C_5H_{10} (36), 1-C_5H_{10} (8), C_3H_8 (19), n-C_4H_{10} (11), C_3H_6 (12), CH_4 (10), C_2H_6 (9)	C_5H_{10}, CH_4, C_4H_8, C_2H_4, C_3H_6

will play a significant role in the reactions taking place under UV irradiation of N_2O. In fact, the product distributions(Fig. 1, Table 1) are quite different from those with the reactions of O_3^- ions with alkanes.[2] In the case of O_3^- ions, the alkene yield decreases in the order $C_2H_6 > C_3H_8 > C_4H_{10}$, in disagreement with the results (Fig. 1, Table 1) where the reverse order is observed. Furthermore, little formation of CO_2 was observed in this work, in contrast with a marked formation of CO_2 in the reaction of O_3^-. In addition, the rate of N_2 formation was found to increase linearly with increasing amounts of alkene formed. Such a behavior is explicable in terms of the concept that the alkene formation proceeds via O^- ions formed by reaction (1). The contribution of O_2^- ions to the reactions may be neglected, since its reactivity is less than that of O_3^- ions. No formation of oxygen-containing compound appears to exclude the possibility that neutral oxygen atoms participate in the reactions. Although the product distributions are similar to those with the reactions of O^- ions reported by Lunsford et al.[2], the features of alkene formation are quite different from each other. As seen in Fig. 1, about 90 % of the total amount of C_3H_6 is formed at room temperature. Another maximal rate of the C_3H_6 formation is observed with higher temperature region. This suggests that two different mechanisms are involved in the alkene formation. In the higher temperature region, the same mechanism as that proposed by Lunsford et al.[2] appears to be operating ; i.e., alkenes are formed from the thermal decomposition of alkoxides. They have proposed that the alkene formation at room temperature proceeds via carbonium ions formation ; $C_3H_8 + O^- \longrightarrow C_3H_7\cdot + OH^-$ (2), $C_3H_7\cdot \longrightarrow C_3H_7^+$ (3), $C_3H_7^+ \longrightarrow H^+ + C_3H_6$ (4). Although this mechanism cannot be excluded in the present work, it should be noted that in the reaction of CH_4 a marked formation of C_2H_6 takes place. With C_2H_6, the C_4H_{10} formation is also observed. Such a formation suggests that during the reaction an appreciable amount of alkyl radicals is present on the surface. The alkyl radicals are not immediately converted to carbonium ions. Accordingly, the dehydrogenation of alkyl radicals by O^- ions appears to offer a reaction pathway to alkene formation. On the basis of this mechanism it is concluded that about 40 % of the amount of O^- ions formed is consumed for the formation of C_3H_6. As to the fact that the formation of alkenes occurrs efficiently even at room temperature, the following explanation may be offered . It appears that under the conditions of the work of Lunsford et al.[2] O^- ions are stabilized on special sites. In the present work such a stabilization will be unexpected. Furthermore, the concentration of O^- ions participating in the reactions will be higher than that expected with their work.

Similar experiments were carried out with 2-C_4H_8 (Fig. 2). In contrast to the case of alkane, only one type of the mechanism is operating in the whole temperature range. Although the reaction products are similar to those of the reactions of O^- ions with alkenes reported by Lunsford et al.[2], it is to be noted that the fraction of CH_4 in the products is extremely higher and the formation of 1,3-C_4H_6 is much less than those with the reactions of O^- ions. As seen in Fig. 2, most part of the products is undesorbed, remaining on the surface, thus making it very difficult to clarify the reaction mechanism. It may be allowed to conclude, however, that the dehydrogenation reaction is not the major reaction pathway. There seems some possibility that a reaction other than hydrogen abstraction of O^- ions, e.g., addition to alkenes, which might result in formation of polymers, takes place under UV irradiation. Further work is necessary to obtain definite conclusions.

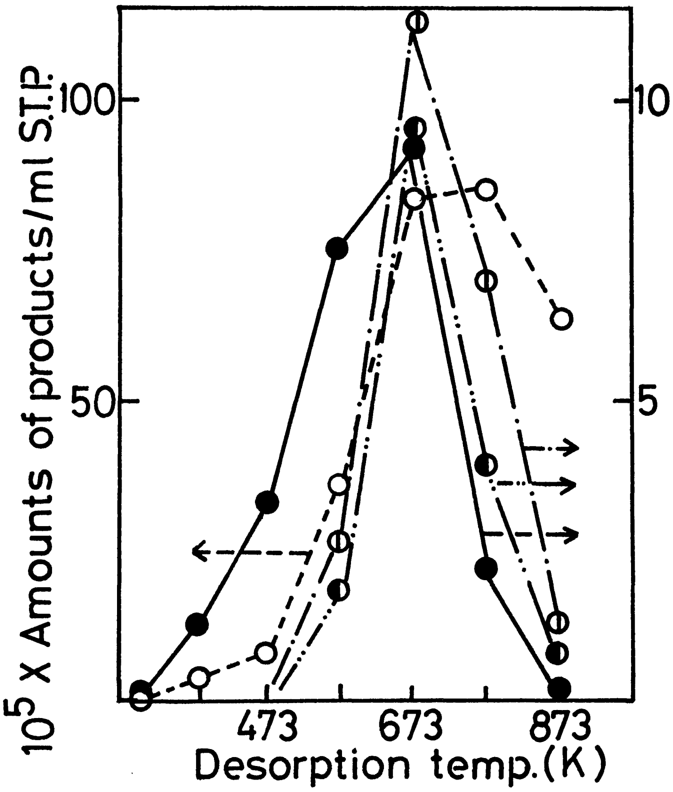

Fig.2 Photoformed products from a mixture of 2-C_4H_8 and N_2O. 2-C_4H_8, 7.0 10^{-2} ml S.T.P. ; N_2O, 3.0 Torr ; Irradiation, 180 min. The amount of N_2 formed is 1.38 10^{-2} ml S.T.P. ○ , CH_4 ; ⦶ , C_2H_4 ; ◐ , C_3H_6 ; ● , 1,3-C_4H_6

References

1. M. Djeghri, M. Formanti, F. Juillet, and S. J. Teichner, Discuss. Faraday Soc., 58, 185 (1974) ; R. I. Bickley, G. Munuera, and F. S. Stone, J. Catal., 31, 398 (1973) ; R. I. Bickley, and R. K. M. Jayanty, Discuss. Faraday Soc. 58, 194 (1974).
2. K. Aika, and J. H. Lunsford, J. Phys. Chem., 81, 1393 (1977) ; 82, 1794 (1978) ; Y. Takita, and J. H. Lunsford, J. Phys. Chem., 83, 683 (1979).
3. C. Naccache, and M. Che, 5th Inter. Congr. Catalysis, 101, 1389 (1972)

(Received May 9, 1980)