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INFRARED STUDY OF INTERMEDIATES IN PROPYNE OXIDATION ON ZnO USING [$^{18}O_2$]OXYGEN AND DINITROGEN OXIDE

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The oxidation of propyne on ZnO by $^{18}O_2$ and N_2O has been studied by IR spectroscopy. The lattice oxygen participates in the formation of diketone-like species and that adsorbed oxygen forms ketene-like species. No formate species is formed in the oxidation by N_2O.

A number of workers have studied the oxidation of alkenes on ZnO as a useful model system using IR spectroscopy, a summary of such results being provided by John.[1)] In previous work we investigated the reaction of oxygen with alkynes adsorbed on ZnO by IR techniques.[2)] On adsorption of propyne and butynes on ZnO dissociative adsorption occurs to form a propynyllic species. Diketone-like species seemed to be formed from interaction of lattice oxygen with propynyllic species. However, our understanding of the mechanism of oxidation of alkynes seems to be insufficient. Therefore, in order to clarify the intermediates in the oxidation as well as the reactive oxygen species,the oxidation of propyne by $^{18}O_2$ and dinitrogen oxide has been studied by IR spectroscopy.

The ZnO used was Kadox 25 (New Jersey Zinc Co.); its surface area was ca. 8 m^2/g. Propyne and N_2O were obtained from Takachiho Shoji Co. [$^{18}O_2$]Oxygen was obtained from British Oxygen Co. (99.1%) and used without further purification. Details of the apparatus and procedures were described previously.[2)] A similar ZnO disc was placed in the reference beam in order to offset the background of the outgassed ZnO.

After a small amount of propyne was adsorbed on a ZnO disc in the IR cell, $^{18}O_2$ of 2 kPa was admitted onto the sample, its temperature being raised under the circulation of $^{18}O_2$. The resulting spectra are shown in Fig. 1. Bands at 2920 and 1870 cm^{-1} are due to the surface propynyllic species and those at 3250 and 2122 cm^{-1} are due to the π-complex of propyne adsorbed on ZnO, as described previously.[2)] Heating at 393 K resulted in a reduction in the intensities of the latter bands and the appearance of bands around 2000 cm^{-1} and at 1550 and 1507 cm^{-1}. At 423 K the bands due to the π-complex and the propynyllic species disappeared, while the 1550- and 1507-cm^{-1} bands were intensified. In addition, bands appeared at 2870, 1563, and 1344 cm^{-1}, suggesting the formation of surface formate ions.[2,3)] At 523 K these bands were intensified with a slight change in their positions.

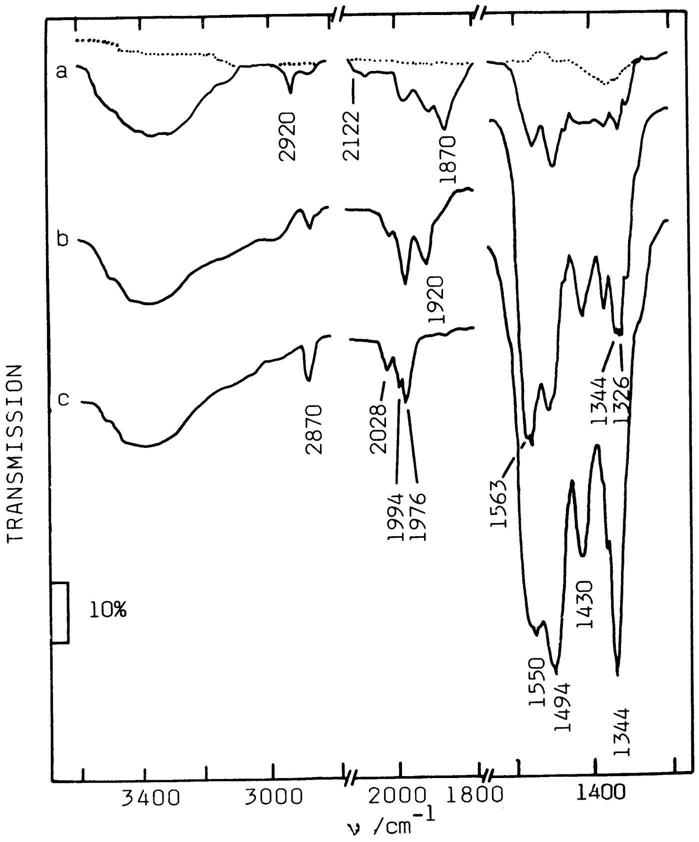


Fig. 1. Interaction of $^{18}O_2$ with propyne adsorbed on ZnO. (a) After adsorption of propyne followed by 1 h at 393 K in $^{18}O_2$ (2.1 kPa); (b) followed by 1 h at 423 K in $^{18}O_2$; (c) 1 h at 523 K in $^{18}O_2$. In Figs. 1 and 2 dotted lines show background spectra.

The ^{18}O-substitution of one or two oxygen atoms in formate ions shifts the $\nu_s(CO_2^-)$ band to lower wavenumber by 22 or 42 cm^{-1}, respectively, while the corresponding shift in the $\nu_{as}(CO_2^-)$ band is ca. 13 cm^{-1} regardless the number of substituted oxygen atoms.[4)] Therefore, in the present case the band at 1563 cm^{-1} would be attributable to the $\nu_{as}(CO_2^-)$ of the surface formate ion and those at 1344 and 1326 cm^{-1} would be due to the $\nu_s(CO_2^-)$.

In order to clarify the nature of reactive oxygen species in the oxidation of alkyne, similar experiments were carried out using N_2O instead of oxygen. The resulting spectra are shown in Fig. 2. At 423 K bands at 1982, 1950, 1922, 1550, 1500, 1440, and 1380 cm^{-1} appeared. The bands at 1550, 1506, 1434, 1342, and 1330 cm^{-1} were intensified at 523 K, while the bands around 1950 cm^{-1} disappeared. Spectral behavior of the bands around 2000 cm^{-1} is different from that in the case using $^{18}O_2$. The results, together with those for the oxidation of propyne and

[$^2H_4$]propyne using $^{18}O_2$ and normal oxygen, are summarized in Table 1.

As described above, in the case of the oxidation using $^{18}O_2$ the formate species was formed, while in the case using N_2O no formate band was observed. Such behavior suggests that adsorbed molecular oxygen causes the C-C bond-cleavage. The results are almost the same as that in the case of the oxidation of alkene and 2-propanol with N_2O.[3,5)]

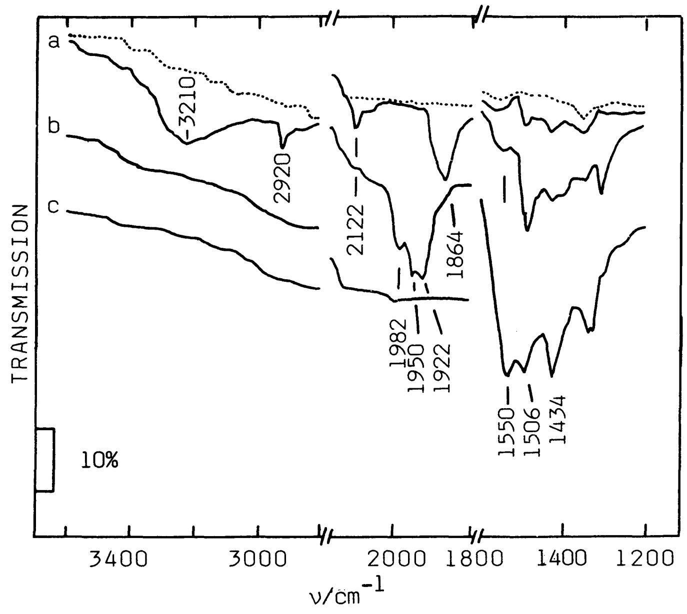


Fig. 2. Interaction of N_2O with propyne adsorbed on ZnO. (a) After adsorption of propyne at 293 K; (b) followed by 1 h at 423 K in N_2O (4.3 kPa); (c) followed by 1 h at 523 K in N_2O.

In the oxidation of propynes with normal oxygen the band around 1540 and 1434 cm^{-1} was tentatively assigned to the C=O and C=C coupled vibrations in an α-diketone-like species.[2)] However, the position of the 1540-cm^{-1} band was something unclear because of its overlapping with surface carboxylate bands (see Fig. 2 in Ref. 2). The corresponding bands appeared at almost the same positions in both cases using $^{18}O_2$ and N_2O (Table 1). This suggests that the oxygen from $^{18}O_2$ and N_2O was not incorporated in the α-diketone-like species. Although we could not obtain a spectrum in the absence of gaseous oxygen, separate experiments showed that in the reactions of propyne with $^{18}O_2$ or N_2O little or no amount of oxygen was incorporated by ZnO at the temperature range below 423 K, the exchange reaction with lattice oxygen being negligible. Presumably the lattice oxygen participates in the formation of α-diketone-like species.

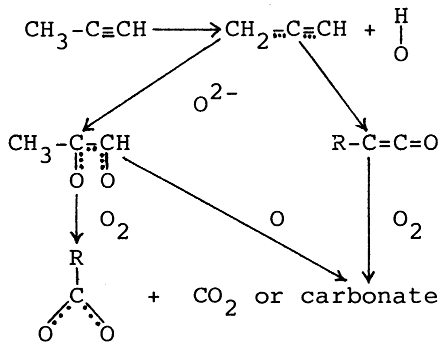
The bands around 2000 cm^{-1} in the oxidation of propyne and [$^2H_4$]propyne was attributed to a ketene-like species previously[2,6)] (Table 1). The corresponding bands in the oxidation with both $^{18}O_2$ and N_2O appeared with a slight change in their positions (Table 1). However, in the case using N_2O the bands in this region was appeared at 423 K and disappeared at 523 K, while with normal oxygen or $^{18}O_2$ the corresponding bands remained unchanged at 523 K. Such a difference of the

Table 1. Wavenumbers (ν/cm^{-1}) of the bands for the surface oxygen-containing species formed from propyne adsorbed on ZnO

This work				
Propyne/$^{18}O_2$	Propyne/N_2O	Propyne/O_2 [a]	[$^2H_4$]propyne/O_2 [a]	Vibrational mode [b]
2870		2876	2166	ν(CH or CD)(F)
1563		1572	1572	$\nu_{as}(COO^-)$(F)
1344		1364	1338	$\nu_s(COO^-)$(F)
1326				
1548 1430	1550 1434	1540 1434	1534 1426	$\nu(-\underset{O}{C}\cdots\underset{O}{C})$(A)
2028 1994 1976	1982 1950	2046 1982	2006 1982	ν(C=C=O)(K)

a) Ref. 2. b) ν_{as}, asymmetric stretch; ν_s, symmetric stretch; F, formate ion; A, diketone-like; K, ketene.

spectral behavior of the bands around 2000 cm^{-1} seems to be due to the different ketene species or the different oxygen species (O_2^- for oxygen and O^- for N_2O) which participate in the oxidation of propyne although complete explanation can not be offered. Presumably the oxidation of propyne on ZnO proceeds as follows.



Scheme 1.
(R, CH_3 or H; O^{2-}, lattice oxygen; O_2, molecular adsorbed oxygen; O, atomic adsorbed oxygen).

References

1) C. S. John, *Catalysis*, 3, 169 (1980).
2) T. Nakajima, T. Sonoda, H. Miyata, and Y. Kubokawa, *J. Chem. Soc., Faraday Trans. 1*, 78, 555 (1982).
3) K. Hata, S. Kawasaki, Y. Kubokawa, and H. Miyata, *Proc. 6th Int. Congr. Catal.*, 1976, 1102.
4) H. Junge and H. Musso, *J. Chem. Soc., B*, 1968, 369.
5) H. Miyata, K. Hata, T. Nakajima, and Y. Kubokawa, *Bull. Chem. Soc. Jpn.*, 53, 2401 (1980).
6) G. Ghiotti and F. Boccuzzi, *J. Chem. Soc., Faraday Trans. 1*, 79, 1843 (1983).

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