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Infrared Studies of the Oxidation of 2-Methyloxirane and Propionaldehyde Adsorbed on ZnO

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The oxidation of 2-methyloxirane and propionaldehyde on ZnO has been studied by infrared spectroscopy. It was found that 2-methyloxirane was adsorbed on ZnO to form alkoxide species by scission of the α bond (O–CH) of the epoxy ring. With time of adsorption, this alkoxide was dehydrogenated to form the enolate complex (CH_3–CH⋯CH⋯O). The enolate complex was oxidized to formate and acetate ions at about 400°K in the presence of oxygen. In the case of oxidation by nitrous oxide, only propionate ions were formed. In the case of propionaldehyde, the adsorption occurred on zinc oxide by coordination of the carbonyl group. Upon oxidation by oxygen or nitrous oxide, scission of the C–C bond of adsorbed species took place to a much smaller extent compared to 2-methyloxirane, the majority of the carboxylate species formed being propionate ions.

INTRODUCTION

In previous papers (*1*, *2*), we investigated the oxidation of olefins, 2-propanol, and acetone adsorbed on metal oxides, such as ZnO, MgO, and NiO, by ir techniques. It was found that, before formation of CO_2 and water, those compounds were oxidized to surface carboxylates as well as to OH groups *via* precursors containing oxygen. Furthermore, in the case of oxidation by nitrous oxide, no C–C bond cleavage occurred during formation of the carboxylates. For example, in the case of propene oxidation by nitrous oxide, only propionate ions were formed, while both acetate and formate ions were formed in propene oxidation by oxygen. Such behavior was attributed to a difference between the reactivities of adsorbed oxygen species in both cases. From the standpoint of elucidation of the oxidation mechanism as well as the reactivity of adsorbed oxygen species, it seems interesting to extend such ir studies to the oxidation of 2-methyloxirane and propionaldehyde, which are partial oxidation products of olefin.

Therefore, this paper deals with the ir study of the oxidation of 2-methyloxirane and propionaldehyde adsorbed on ZnO by oxygen or nitrous oxide.

EXPERIMENTAL METHODS

Materials. The zinc oxide, Kadox 25 (New Jersey Zinc Co.), was the same as that used in the previous work (*2*). 2-Methyloxirane and propionaldehyde (Tokyo Chemical Industries Co.) were dried under vacuum over a degassed molecular sieve. Nitrous oxide (99.9%) was obtained from the Takachiho Shoji Co. and was used without further purification. Oxygen was obtained from a cylinder and was purified by being passed through a molecular sieve immersed in liquid nitrogen.

Infrared studies. The zinc oxide sample

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(0.5–0.7 g) was pressed into a disk 2.0 cm in diameter. The disk was held in a quartz disk holder and was suspended by a platinum wire in a cell for infrared studies. The cell was a quartz tube 2.5 cm in diameter and 40 cm in length. The NaCl windows were sealed to the cell with Apiezon wax W. The cell had an optical path length of 3.0 cm. The disk could be moved vertically between the lower window section and the upper furnace section by winding up the platinum wire from which the disk was suspended. The furnace section of the cell could be heated by nichrome windings. The temperature of the disk was measured by a calibrated thermocouple fixed to the furnace section of the cell.

The apparatus consisted of a conventional closed circulation system, about 600 cm^3 in volume, equipped with a circulating glass pump, a trap, a mercury manometer, a Pirani gauge, infrared cells, and a gas-dosing volume in the circulation loop.

The zinc oxide disk was subjected to outgassing treatments similar to those used previously (*2*). After 0.25–0.4 cm^3/g of 2-methyloxirane or propionaldehyde was introduced into the cell containing the zinc oxide disk, the weakly adsorbed reactant was removed by immersing the trap in liquid nitrogen. After that, oxygen or nitrous oxide of ca. 2.7 kPa was circulated over the catalyst, the temperature of which was raised in stages. Infrared spectra were recorded at room temperature before and after each treatment of the sample, such as heating or admission of oxygen or nitrous oxide, by using a Hitachi EPI-G2 grating infrared spectrometer with a spectral slitwidth of 2.8 cm^{-1} at 1000 cm^{-1}. During the spectral measurements, the trap attached to the circulation system was cooled in liquid nitrogen. A matched-path length cell containing a similar zinc oxide disk was placed in the reference beam of the spectrometer in order to offset the background of the outgassed zinc oxide. The reference cell was filled with helium of 2.7 kPa.

Oxygen uptake studies. Zinc oxide was pressed into disks as in the infrared studies and, then, was broken up. A 10-g sample was used. The circulation system with a volume of about 300 cm^3 was similar to that used for infrared studies, except for a Töpler pump as well as a McLeod gauge. After a known amount of the reactant was adsorbed at 298°K, oxygen or nitrous oxide of ca. 2.7 kPa was admitted to the reaction vessel and was circulated over the catalyst at 298°K for 1 hr. The reaction products were condensed in the liquid nitrogen trap attached to the circulation system. The amount of oxygen uptake or the amount consumed by the reactions was determined manometrically. After the experiment at 298°K, the temperature of the catalyst was raised in stages, at each of which similar experiments were carried out. In the case of nitrous oxide, the trap was cooled at 153°K instead of 77°K. The amount of oxygen atoms incorporated into the catalyst was calculated from the number of nitrogen molecules formed.

The reaction products were analyzed by gas chromatography with the use of a 6-m Porapak Q column for N_2, O_2, and CO at 195°K, a 2-m Porapak Q column for N_2O and CO_2 at 273°K, and a 3-m PEG 400 column for other products at 323°K.

RESULTS AND DISCUSSION

Adsorption of 2-Methyloxirane

Adsorption of 2-methyloxirane on ZnO caused a decrease in the background transmission. This suggests that electrons are transferred from adsorbed 2-methyloxirane to zinc oxide, since it is well known that a decrease in transmission is always associated with an increase in the number of electrons in ZnO (*3*). Such a decrease in the transmission of the disk resulted in reduced accuracy of the measurements of the spectra. Therefore, in order to minimize

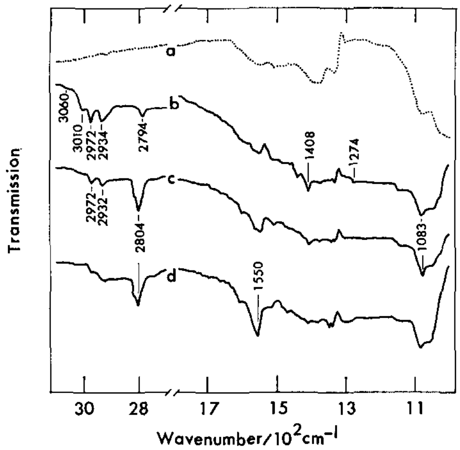


FIG. 1. Infrared spectra of 2-methyloxirane adsorbed on ZnO. (a) Background (743 mg); (b) after 4 min of adsorption at 298°K; (c) followed by 1.5 hr of adsorption at 298°K; (d) 14.5 hr of adsorption. Amount adsorbed was 0.3 cm^3 g^{-1}.

the decrease in background transmission on adsorption, small amounts were usually adsorbed. Figure 1 shows the change with time in the spectra of chemisorbed 2-methyloxirane. The spectrum obtained immediately after the adsorption of 2-methyloxirane on zinc oxide was similar to that obtained with its adsorption on Aerosil. A summary of the observed bands and their assignments is shown in Table 1. The bands at 3060, 3010, and 1274 cm^{-1}, which are attributable to the epoxy structure (*4*), appear clearly, although the intensity of these bands is much weaker compared to that of the other bands, such as those at 2972, 2934, and 1408 cm^{-1} observed with Aerosil as well as with zinc oxide.

The bands at 3060, 3010, 2972, 2934, 1408, and 1274 cm^{-1}, which had appeared instantaneously upon adsorption of 2-methyloxirane, gradually reduced in intensity with time of adsorption, while the bands at 2794, 1550, and 1083 cm^{-1} were intensified (Fig. 1c). In addition, it is apparent that, after 14.5 hr, the band at 1550 cm^{-1} was intensified, while the bands at 2804 and 1083 cm^{-1} were slightly reduced in intensity. This suggests that 2-methyloxirane adsorbed without dissociation changes to other species having no epoxy structure. In addition, the species associated with the band at 1550 cm^{-1} is different from the species which shows the absorption at 2804 and 1083 cm^{-1}, the latter being the precursor of the former. The band at 1083 cm^{-1} coincides in position with that for the C–O stretching vibrations. For oxides such as Al_2O_3, ZnO, and MgO, the ν(C–O) bands of propoxide and isopropoxide appeared at 1060–1080 (*5–7*) and 1130–1170 cm^{-1} (*1*, *7–9*), respectively, indicating that the position of the ν(C–O) band is higher in frequency for the secondary than for the primary alkoxide. Thus, it is concluded that the bands at 2804 and 1083 cm^{-1} are attributed to the alkoxide species formed by scission of the α bond (O–CH) of the epoxy ring in 2-methyloxirane.

Regarding the 1550-cm^{-1} band, it is well known that the bands due to ν(C=C) or ν(C=O) range from 1500 to 1700 cm^{-1}. In addition, the position of the band at 1550 cm^{-1} is similar to that of the band due to C⋯C⋯O vibration of the enolate complex formed from adsorbed acetone and described previously (*10*). Accordingly, the band at 1550 cm^{-1} may be tentatively assigned to the complex (III) formed by dehydrogenation of the alkoxide species

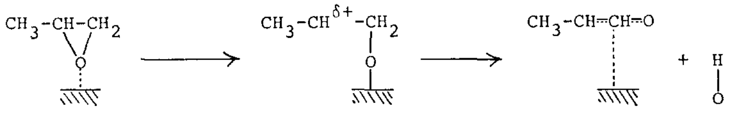
TABLE 1

Wavenumbers ($\tilde{\nu}$/cm^{-1}) of the Infrared Bands of 2-Methyloxirane Adsorbed on ZnO

On ZnO	On SiO_2	2-Methyloxirane[a]	Vibrational mode
3060	3066	3055	ν (CH_2 in ring)
3010	3014	3002	ν (CH in ring)
2972	2980	2971	ν (CH_3)
2934	2938	2932	ν (CH_3)
1408	1410	1411	
1274	1269	1267	ν (ring)

[a] Reference (*4*).

(II), as shown in the following scheme (*11*):



(I) (II) (III)

The bands at 2804, 2932, and 2972 cm^{-1} (Fig. 1c) seem to be due to the CH groups (*13*) of the intermediate (II). The intensity of the band at 2804 cm^{-1} is much higher than those of the 2972- and 2932-cm^{-1} bands. Such behavior is markedly different from what would be expected from the primary or secondary saturated alkoxides on metal oxides (*5–9*), supporting an unsaturated character of the intermediate (II).

Reaction of Oxygen with Adsorbed 2-Methyloxirane

Oxygen of 2.7 kPa was admitted to the ZnO disk with preadsorbed 2-methyloxirane at room temperature, the temperature of the disk being raised in stages. By this oxygen treatment, the transmission of the disk was enhanced. The resulting spectra are shown in Fig. 2. The band at 1552 cm^{-1} increased in intensity, and new

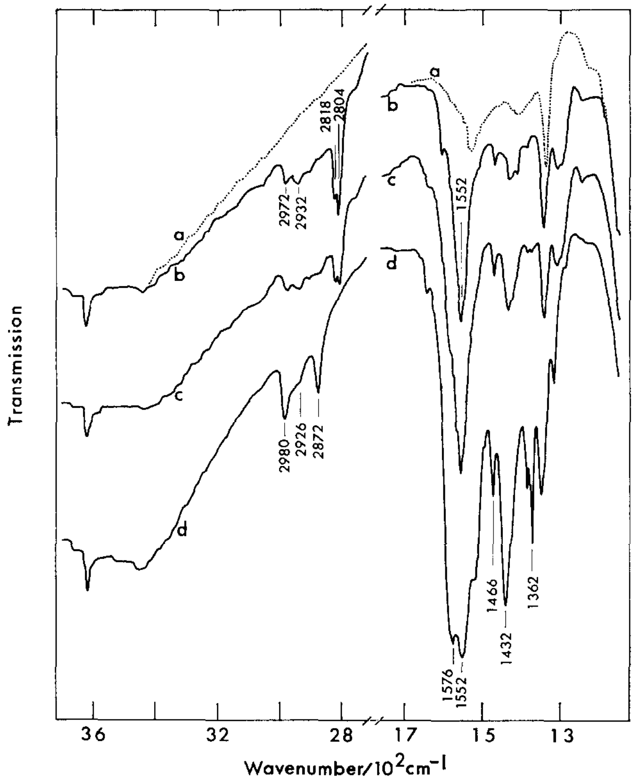


FIG. 2. Interaction of oxygen with 2-methyloxirane adsorbed on ZnO. (a) Background (750 mg); (b) after 10 hr of adsorption, followed by 5 min at 298°K in oxygen (2.7 kPa); (c) followed by 1 hr at 323°K in oxygen; (d) 1 hr at 423°K in oxygen. Amount adsorbed was 0.4 cm^3 g^{-1}. A reference disk was not used.

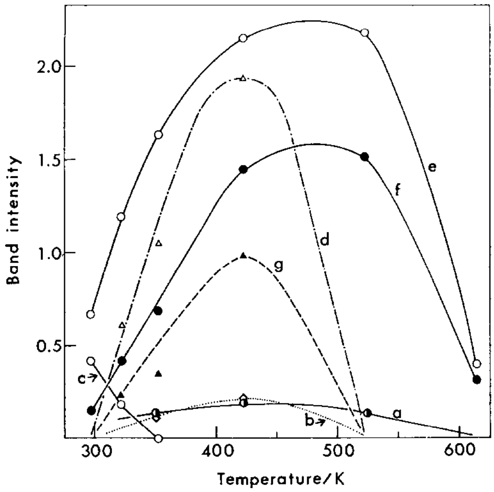


FIG. 3. Change in the band intensities with increasing temperature of ZnO. (a) 2980, (b) 2872, (c) 2804, (d) 1576, (e) 1552, (f) 1432, (g) 1362 cm^{-1}.

bands appeared at 1428 cm^{-1}. Upon raising the temperature of the ZnO disk to 323°K, the band at 2804 cm^{-1} decreased in intensity. At 353°K, new bands appeared at 2980, 2872, 1576, and 1362 cm^{-1}, while the band at 2804 cm^{-1} disappeared. Figure 3 shows the change in intensity of these bands with increasing temperature of the ZnO. Upon raising the temperature to 423°K, the new bands which had appeared at 353°K increased in intensity. At 523°K, the bands at 2872, 1576, and 1362 cm^{-1} disappeared, while the intensity of the bands at 2980, 1552, and 1432 cm^{-1} hardly changed. This behavior is essentially the same as that of the reaction of oxygen with propene adsorbed on ZnO, as described previously (*2*). Thus, the same assignment is applicable, i.e., the former and the latter groups of the bands are attributable to surface formate and acetate ions, respectively. A summary of assignments of the bands for these carboxylate species is shown in Table 2 together with the results for propene.

In a separate experiment, the reaction of oxygen with 2-methyloxirane adsorbed on ZnO was investigated by analysis of the reaction products. Oxygen of 2.7 kPa was admitted to the ZnO-containing preadsorbed 2-methyloxirane at 273°K, and its temperature was raised in stages under circulation of oxygen. The amount of oxygen uptake as well as the amounts of reaction products at each stage are shown in Fig. 4. It is seen that below 523°K, where little formation of carbon dioxide took place, an appreciable amount of oxygen uptake takes place. The observed oxygen uptake was corrected by subtracting the oxygen uptake by ZnO without adsorbed 2-methyloxirane around 523°K, 0.10 cm^3/g. Thus, it was found that the ratio of the number of oxygen atoms incorporated to the number of adsorbed 2-methyloxirane molecules, α, was 3.7, being in rough agreement with what would be expected

TABLE 2

Wavenumbers ($\tilde{\nu}/cm^{-1}$) of the Bands for the Carboxylate Species Formed from O_2 with 2-Methyloxirane Adsorbed on ZnO

2-Methyloxirane	Propene[a]	Vibrational mode[b,c]
2980	2980	ν_{as} (CH_3) (A)
2926	2920	ν_s (CH_3) (A)
1552	1548	ν_{as} (COO^-) (A)
1432	1433	ν_s (COO^-) (A)
2872	2870	ν (CH) (F)
1576	1572	ν_{as} (COO^-) (F)
1362	1365	ν_s (COO^-) (F)

[a] Reference (*2*).

[b] ν_{as}, Antisymmetric stretch; ν_s, symmetric stretch; A, acetate; F, formate ion.

[c] In regard to the CH bending vibrations of acetate and formate ions, the band at 1466 cm^{-1} may be attributed to the antisymmetric bending vibrations of CH_3 groups of the acetate ions, and the band at 1382 cm^{-1} results from the overlapping of the two bands due to the symmetric bending vibrations of CH_3 groups of the acetate ions and the bending vibrations of CH groups of the formate ions. The bands due to the CH bending vibrations are much weaker in intensity than their COO stretching vibration bands (*7*, *14*, *15*). Accordingly, quantitative examination of the change in intensity of these bands was discarded.

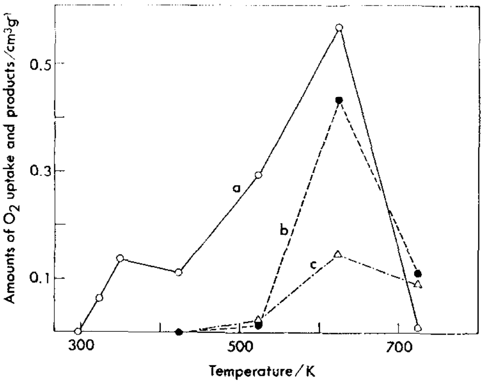


FIG. 4. Reaction of oxygen with 2-methyloxirane adsorbed on ZnO. (a) Oxygen taken up or consumed by the reactions; (b) CO_2 formed; (c) H_2O formed. Amount of 2-methyloxirane adsorbed at 298°K was 0.28 cm^3/g.

from formation of formate and acetate ions by oxidation *(16)*.

The spectral behavior above 353°K of 2-methyloxirane adsorbed on zinc oxide after increasing the temperature in the presence of oxygen is essentially the same as that of propene adsorbed on it. Below 353°K, however, both systems behave completely different from each other, particularly in the C–H stretching region (3000–2800 cm^{-1}). This suggests that propene is not oxidized via 2-methyloxirane in the oxidation on zinc oxide.

Reaction of Nitrous Oxide with Adsorbed 2-Methyloxirane

Similar experiments were carried out using nitrous oxide instead of oxygen. The spectra obtained are shown in Figs. 5 and 6. On admission of nitrous oxide of 2.0 kPa to the ZnO sample containing 2-methyloxirane at 298°K, no new bands, other than the surface alkoxy bands, were observed. The temperature of the ZnO disk was raised in the presence of nitrous oxide. At 323°K, the bands at 2804 and 1083 cm^{-1} due to the alkoxy species decreased in intensity and completely disappeared at 353°K, while the intensity of the band at 1552 cm^{-1} increased. At 423°K, the bands at 2976, 2944, 2884, 1550, 1466, and 1430 cm^{-1} increased in intensity. These bands are characteristic of the surface carboxylate

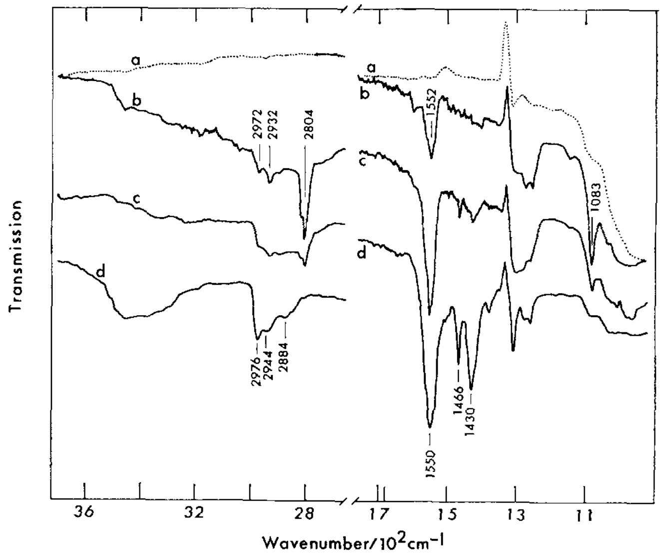


FIG. 5. Interaction of nitrous oxide with 2-methyloxirane adsorbed on ZnO. (a) Background (706 mg); (b) after 2 hr of adsorption, followed by 1 hr at 298°K in nitrous oxide (2.0 kPa); (c) followed by 2 hr at 323°K in nitrous oxide; (d) 2 hr at 423°K in nitrous oxide. Adsorbed amount was 0.35 cm^3 g^{-1}.

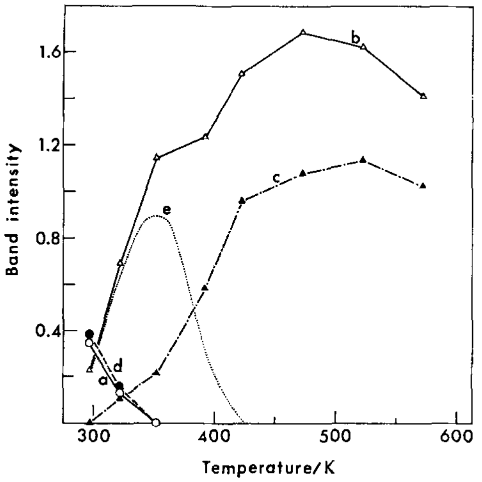


FIG. 6. Change in the band intensities with increasing temperature of ZnO. (a) 2804, (b) 1550, (c) 1430, (d) 1083, (e) 1550 cm^{-1} (precursor).

species. Obviously, no scission of the C–C bond takes place, since no bands due to formate species appeared in the COO stretching region or in the CH stretching region. As shown in Table 3, the bands described above are in good agreement with those of propionate ions, which were prepared from the oxidation of 1-propanol with oxygen. Thus, it is concluded that the bands at 2976, 2944, 2884, 1550, and 1430 cm^{-1} are due to surface propionate ions. The formation of propionate ions is in agreement with what would be expected from the α-C–O breaking of 2-methyloxirane upon adsorption.

In a separate experiment, the reaction of nitrous oxide with 2-methyloxirane adsorbed on ZnO was investigated by analysis of the reaction products in a manner similar to that used in the case of the reaction of oxygen. Above 600°K, carbon dioxide and water were formed. The amount of oxygen atoms incorporated into the adsorbed layer was determined from the number of nitrogen molecules formed. Below 353°K, no appreciable amount of nitrogen was formed. At 423°K, the ratio of the amount of oxygen atoms to the number of adsorbed 2-methyloxirane molecules was about 1.3, which coincides approximately with what would be expected from the formation of propionate ions by oxidation.

As has been described above, the enolate species (the intermediate III) should be formed before the oxidation to the carboxylate species. The position of the band at 1550 cm^{-1} due to the enolate complex coincides with that of the antisymmetric stretching vibration of the carboxylate species. Accordingly, it seems very difficult to discuss the change in concentration of the enolate complex during the oxidation reaction. In the case of oxidation by nitrous oxide, however, formation of the carboxylate species occurs at temperatures higher than those in the oxidation by oxygen. This makes it possible to determine the contribution of the enolate species to the band at 1550 cm^{-1} as follows: Above 353°K, the band at 1430 cm^{-1}, attributable to the symmetric stretching vibration of the carboxylate species, appears. In the temperature range from 423 to 573°K, the ratio of the intensity of the 1550-cm^{-1} band to that of the 1430-cm^{-1} band, R, is nearly constant, suggesting that, in this temperature range, the band at 1550 cm^{-1} arises solely from the carboxylate species. Below 423°K, the 1550-cm^{-1} band would result from the overlapping of the two

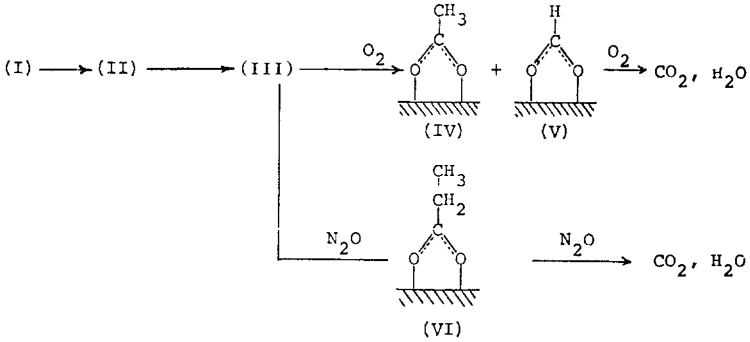
TABLE 3

Wavenumbers ($\tilde{\nu}/cm^{-1}$) of the Bands for the Propionate Species Formed from N_2O with 2-Methyloxirane Adsorbed on ZnO

2-Methyloxirane	1-Propanol	Vibrational mode[a]
2976	2976	ν_{as} (CH_3)
2944	2942	ν_{as} (CH_2)
2884	2878	ν_s (CH_3)
1550	1546	ν_{as} (COO^-)
1466	1466	δ_{as} (CH_3)
1430	1430	ν_s (COO^-)

[a] ν_{as}, Antisymmetric stretch; ν_s, symmetric stretch; δ_{as}, antisymmetric bend.

bands due to the carboxylate and enolate species. By using the constant ratio *R* described above, the contribution of the carboxylate species to the 1550-cm^{-1} band can be estimated from the intensity of the band at 1430 cm^{-1}, the remainder of the band at 1550 cm^{-1} being attributed to the enolate species. Thus, the relative change of its concentration with temperature is obtained, as shown in Fig. 6c. Oxidation by oxygen or nitrous oxide proceeds according to the following steps (*17*):



Reaction of Oxygen and Nitrous Oxide with Adsorbed Propionaldehyde

Similar experiments were carried out with propionaldehyde adsorbed on ZnO. Figure 7 shows the resulting spectra. Much less of a decrease in background transmission was observed on the adsorption compared to the case of 2-methyloxirane. The bands observed with priopionaldehyde adsorbed on Aerosil are shown in Table 4 together with the results for zinc oxide. There is no significant difference between the spectra of propionaldehyde on zinc oxide and Aerosil, except for the position of the band due to the carbonyl group. This suggests that propionaldehyde adsorbs on zinc oxide by coordination of the carbonyl group. Such a conclusion is supported by

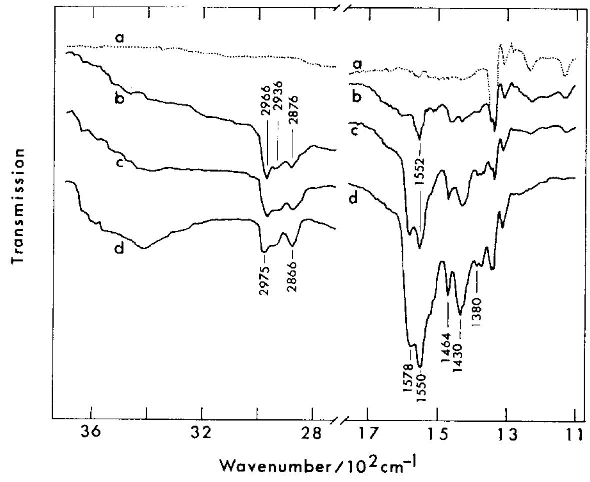


FIG. 7. Interaction of oxygen with propionaldehyde adsorbed on ZnO. (a) Background (724 mg); (b) after 1 hr of adsorption, followed by 1 hr at 298°K in oxygen (2.0 kPa); (c) followed by 1 hr at 353°K in oxygen; (d) 1 hr at 423°K. Adsorbed amount was 0.25 cm^3 g^{-1}.

TABLE 4

Wavenumbers ($\tilde{\nu}$/cm^{-1}) of the Infrared Bands of Propionaldehyde Adsorbed on ZnO

On ZnO	On SiO_2	Vapor[a]	Vibrational mode
	2992	2994	
2966	2952	2955	ν (C–H)(alkyl)
2930	2894	2915	
2876	2842	2809	ν (C–H)(–CHO)
	2742	2714	
1552	1734	1752	ν (C=O)

[a] Reference (*19*).

the fact that the band due to the aldehydic CH group shifts to a higher frequency upon adsorption, since Young and Sheppard (*20*) have pointed out that both bands due to carbonyl and aldehydic CH groups shift in such directions upon partial loss of the aldehydic character caused by adsorption. After adsorption of propionaldehyde, the temperature of the zinc oxide was increased in the presence of oxygen. At 298°K, no spectral change was observed. At 353°K, new bands appeared at 2866, 1578, and 1380 cm^{-1}. In addition, the bands at 1552, 1464, and 1430 cm^{-1} were intensified. At 423°K, the amount of incorporated oxygen was nearly equal to that of adsorbed aldehyde, but was much less compared to the case of 2-methyloxirane as described above. The bands at 2975, 1550, and 1430 cm^{-1}, as well as those of 2866, 1578, and 1380 cm^{-1}, may be attributable to carboxylate species. Comparison of Figs. 2d and 7d shows that the intensity of the bands at 2866, 1578, and 1380 cm^{-1}, which are attributable to formate ions, is much weaker for propionaldehyde than for 2-methyloxirane. This indicates that, in the former case, scission of the C–C bond of the adsorbed species occurs to a much smaller extent, compared to the latter case, i.e., the major part of the carboxylate species formed from propionaldehyde is propionate ions. As regards such a difference in the efficiency of the C–C bond scission in oxidation using oxygen, the following tentative explanation may be offered: The presence of the enolate structure (III) in adsorbed 2-methyloxirane would facilitate scission of the C–C bond. A similar example can be seen when the π-allyl species formed from olefins undergoes an efficient C–C bond scission, while little C–C bond scission is observed with adsorbed 1-propanol.

Similar infrared studies were carried out on the reaction of nitrous oxide with priopionaldehyde adsorbed in zinc oxide. No formation of formate ions was observed, i.e., no scission of the C–C bond occurred. Lack of scission of the C–C bond during oxidation is a characteristic of oxidation using nitrous oxide. Essentially the same behavior has been observed in the reactions of nitrous oxide with adsorbed olefins and 2-methyloxirane.

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11. At present, the nature of the active sites for 2-methyloxirane adsorption is unclear. Kokes and co-workers (12) have discussed in detail the nature of the active sites on zinc oxide. It seems plausible that the alkoxide species (II) may attach to the imbedded Zn ions.

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16. Since, in the case of the reaction of oxygen with propene adsorbed on ZnO, the ratio α has been found to be 4 (*2*), the α value for 2-methyloxirane is expected to be 3. The observed value of 3.7 would be explicable as follows: Formation of the formate and acetate ions is always accompanied by formation of surface OH groups. If the OH groups are removed as water, then additional oxygen uptake should be expected. In fact, trace amounts of water were formed at about 523°K (Fig. 4).
17. According to previous work (*5*, *6*, *8*, *18*), alcohols react on the surfaces of Al_2O_3 and MgO to form alkoxides or carboxylates via different mechanisms, i.e., hydrogen or methane is formed. However, in the work just cited, the reactions were carried out in the absence of oxygen.
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