

between the single crystal and the powder catalyst.

If we consider that the illumination condition was almost the same between the experiments using the single crystal and the powder, the reaction rate seems to be entirely controlled by the illumination condition. The photosensitized oxidation process as the partial process of the photocatalytic reaction is controlled by the number of photons striking the catalyst surface.<sup>26</sup> Then, in order to achieve a comparable rate of photocatalytic reaction between the single crystal and the powder catalysts as was observed, the rate of oxygen reduction as the other partial process must be roughly the same between the two kinds of catalysts.

The open circuit potential of the electrode with 50 monolayers of Pt in the dark was almost the same as the onset potential of the oxygen reduction which was ca. -0.3 V vs. SCE and was positive of the flat-band potential (see Figure 6). By illuminating the electrode, therefore, a photovoltage must arise, resulting in weakening of the band bending. Then, electron transfer from the conduction band to the electrolyte via surface states occurs easily. In this respect, the reduction process is also affected by illumination. Since only the powders onto which photons struck are effective for photocatalytic reaction, the reaction rate will be entirely controlled by the illumination condition if the catalyst loading is more than enough to absorb all the incident photons.

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## Surface Reactions of Oxygen Ions. 4. Oxidation of Alkenes by O<sub>3</sub><sup>-</sup> on MgO

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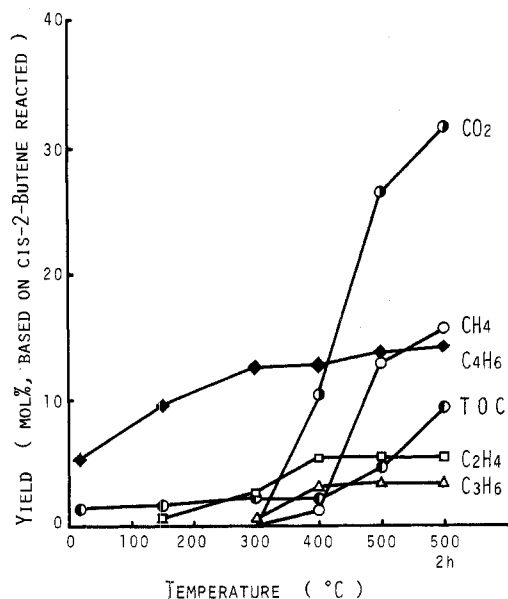
Surface reactions between simple alkenes and O<sub>3</sub><sup>-</sup> ions on MgO were observed at 25 °C. Following the reaction of ethylene or propylene with O<sub>3</sub><sup>-</sup>, CO<sub>2</sub> and CH<sub>4</sub> were detected as major products upon heating the sample. The reaction of *cis*-2-butene with O<sub>3</sub><sup>-</sup> resulted in the formation of butadiene and oxygen-containing organic compounds, as well as CO<sub>2</sub> and CH<sub>4</sub>. Thermal desorption patterns and infrared spectra of surface complexes suggest that carboxylate ions are intermediates in the formation of CO<sub>2</sub> and CH<sub>4</sub> and peroxy radicals are intermediates in the formation of oxygen-containing organic molecules.

Determining the role of oxygen ions remains a fundamental problem in heterogeneous oxidation catalysis. Stoichiometric reactions of O<sup>-</sup> ions on MgO with simple alkanes and alkenes have been reported,<sup>1,2</sup> and the study has been extended to include the catalytic role of O<sup>-</sup> in the oxidative dehydrogenation of ethane over supported molybdenum oxide.<sup>3</sup> Moreover, reactions between O<sub>3</sub><sup>-</sup> ions on MgO with simple alkanes have been described in a recent publication from this laboratory.<sup>4</sup>

In general, experimental evidence suggests that both O<sup>-</sup> and O<sub>3</sub><sup>-</sup> ions on MgO react with hydrocarbons by hydro-

gen-atom abstraction.<sup>1,2,4</sup> The resulting alkyl or alkenyl radicals then react with surface oxide ions, forming stable intermediates which may be decomposed at elevated temperatures. In this note reactions between O<sub>3</sub><sup>-</sup> on MgO and simple alkenes are described.

The preparation of the MgO samples, as well as the purification of the gases, was the same as previously reported.<sup>4</sup> The ozonide ion, O<sub>3</sub><sup>-</sup>, was formed by irradiation (254 nm) of the MgO sample in the presence of 10–50 torr of N<sub>2</sub>O for 10–60 min at 25 °C. The formation and reaction of O<sub>3</sub><sup>-</sup> was followed by EPR spectroscopy. Stable



**Figure 1.** Yield of products as a function of the thermal desorption program following the reaction of *cis*-2-butene with  $O_3^-$  at 25 °C. The curve indicated by TOC represents the total amount of oxygenated organic compounds.

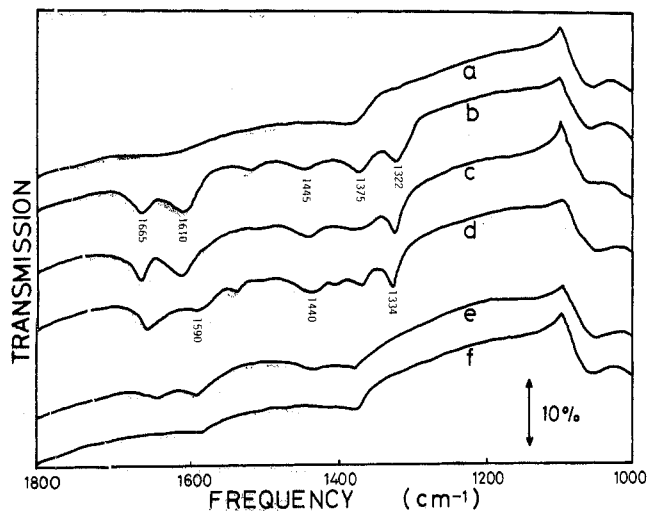
surface intermediates were detected by infrared spectroscopy. Reactions and analyses were carried out with the same apparatus and procedure as described earlier.<sup>1,4</sup>

After recording the EPR spectrum of  $O_3^-$  on MgO at -196 °C, 900 nmol of alkene (0.3 torr) diluted in helium was introduced to the sample at 25 °C. In all cases the  $O_3^-$  ions reacted with the alkene with a half-life of ca. 5 min. The amounts of  $O_3^-$  and alkene reacted (ca. 300 nmol) were essentially equivalent. During the course of the reaction the dominant spectrum of the  $O_3^-$  ion ( $g_1 = 2.017$ ,  $g_2 = 2.010$ , and  $g_3 = 2.0017$ ) disappeared, and a less reactive form of  $O_3^-$ , having  $g_1 = 2.016$ , became apparent. After 10 min at 25 °C this spectrum essentially disappeared, and only the spectra of  $O_2^-$  and an unreactive form of  $O^-$ , which were present as impurity components in the original  $O_3^-$  spectrum, were observed.

No gas-phase products were observed following the reaction of ethylene or propylene with  $O_3^-$  at 25 °C; however, when the samples were heated to 500 °C for 3 h, significant amounts of  $CO_2$ ,  $CH_4$ , and a small amount of  $C_2H_4$  were detected. Based upon the mole percent of ethylene reacted, the amount of  $CO_2$ ,  $CH_4$ , and  $C_2H_4$  was 39, 11, and 2%, respectively. Similar results were obtained with propylene, only the yield of  $CO_2$  was 82%. The amount of gas-phase hydrocarbons and carbon dioxide was small at temperatures less than 400 °C. For both reactants trace quantities of *n*-butane, *n*-butenes, and butadiene were formed at elevated temperatures.

By contrast the reaction of *cis*-2-butene with  $O_3^-$  resulted in the formation of butadiene, even at 25 °C, as shown in Figure 1. The final yield of butadiene was 14%. Ethylene and propylene were also observed at moderate temperatures, and in the 300–500 °C range  $CO_2$ ,  $CH_4$ , acetaldehyde, acrolein, and acetone were detected. Apart from  $CO_2$  the predominant oxygen-containing product was acetaldehyde.

An infrared study was carried out on self-supported MgO wafers in order to determine the nature of surface intermediates. The background spectrum of MgO is described in Figure 2, curve a. After the reaction between  $O_3^-$  and  $C_2H_4$  at 25 °C, absorption bands (curve b) appeared at 1322, 1375, 1445, 1515, 1610, and 1665  $cm^{-1}$ . Thermal treatment at 150 °C (curve c) resulted in a decrease in intensity for several of the bands; thermal

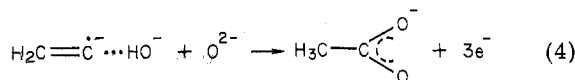
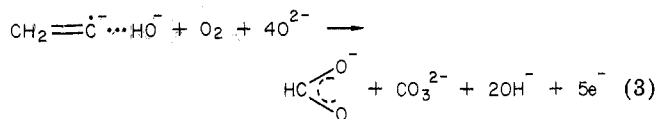


**Figure 2.** Infrared spectra following the reaction of ethylene with  $O_3^-$ : (a) MgO background; (b) after the reaction at 25 °C; (c) after thermal treatment under vacuum at 150 °C; (d) 300 °C; (e) 400 °C; (f) 500 °C.

treatment at 300 °C (curve d) caused the appearance of bands at 1590  $cm^{-1}$  and a shift in the frequency of the band at 1322  $cm^{-1}$  to 1334  $cm^{-1}$ . The band at 1445  $cm^{-1}$  also shifted to 1440  $cm^{-1}$ . Progressive heating of the sample to 500 °C caused most of the remaining bands to decrease to background intensity.

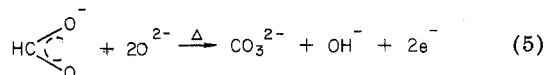
The reaction between ethylene and MgO without  $O_3^-$  was examined separately. No significant absorption bands were observed after 200 torr of ethylene had been added and the gas phase was evacuated for 1 h at 25 °C.

By analogy with the reactions between  $O_3^-$  and simple alkanes,<sup>4</sup> we propose that the reaction with alkenes is initiated by hydrogen-atom abstraction. In the case of ethylene the resulting radical may then react according to the following scheme:



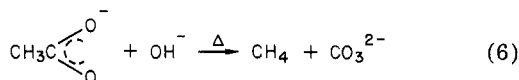
The  $H_2C=\dot{C}\cdots HO^-$  complex previously has been shown to result from the reaction between  $O^-$  and  $C_2H_4$ .<sup>5</sup> In the present experiments we have independently demonstrated that this complex reacts with molecular oxygen (eq 3) to form a diamagnetic species at temperatures where reaction 1 occurs; thus  $CH_2=\dot{C}\cdots HO^-$  was not observed as an intermediate.

Evidence for the formate ions is found in the infrared bands at 1610 and 1375  $cm^{-1}$ .<sup>6</sup> In addition, bands at 1665 and 1322  $cm^{-1}$  have been assigned to carbonate ions on MgO.<sup>4</sup> Thus, the decrease in the 1610- $cm^{-1}$  band upon heating the sample to 300 °C is consistent with reaction 5. The weak band at 1590  $cm^{-1}$ , which is believed to have



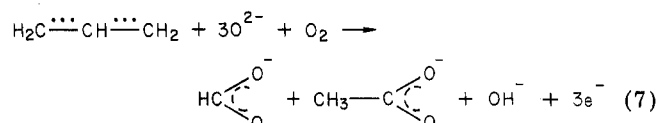
been present as a shoulder on the band at 1610  $cm^{-1}$ , along with the band at 1440  $cm^{-1}$ , is attributed to acetate ions. We have shown that these ions on MgO decompose to form

CH<sub>4</sub> and CO<sub>3</sub><sup>2-</sup> ions according to reaction 6.<sup>4</sup>



A major difference between the reaction of C<sub>2</sub>H<sub>4</sub> with O<sup>-</sup> or O<sub>3</sub><sup>-</sup> is the relatively small amount of CH<sub>4</sub> detected in the latter case. This difference may be understood by considering that reaction 3 occurs when O<sub>2</sub> is present, whereas with O<sup>-</sup> reaction 4 resulted in acetate ions as the dominant surface intermediate.

The similar product distribution which was observed following the reaction of propylene with O<sub>3</sub><sup>-</sup> suggests a related reaction mechanism. The allyl radical formed by hydrogen-atom abstraction may react by reaction 7. One



cannot, however, rule out the formation of peroxy radicals which would result in the formation of CO<sub>2</sub> and H<sub>2</sub>O.<sup>4</sup>

In the reactions of 1-butene with O<sup>-</sup>, butadiene was the principal hydrocarbon product,<sup>2</sup> and in this respect 1-butene acted more like an alkane than like ethylene or propylene, whereas *n*-butane gave a low yield of butene when reacted with O<sub>3</sub><sup>-</sup>.<sup>4</sup> It was somewhat surprising, therefore, when significant amounts of butadiene were

observed in the present experiments following the reaction of *cis*-2-butene and O<sub>3</sub><sup>-</sup>. Apparently in this case alkoxide ions are formed as a major intermediate since these result in the production of butadiene. The oxygen-containing products are attributed to peroxy radical intermediates of the type CH<sub>3</sub>-CH=CH-CH<sub>2</sub>OO<sup>-</sup>.

These results demonstrate that reactions between alkenes and O<sub>3</sub><sup>-</sup> on MgO generally lead to nonselective oxidation. One would hope to gain insight into the possible role of this ion in epoxidation catalysis, but rapid surface reactions, for example, between ethylene oxide and MgO, make it difficult to obtain such information.<sup>2</sup> Moreover, there is no evidence for the formation of thermally stable ozonide ions on more acidic metal oxide surfaces.

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## A 1,2 Hydrogen Shift and Other Thermally Induced Free Radical Reactions in X-Irradiated Methyl $\alpha$ -D-Glucopyranoside Single Crystals. An ESR-ENDOR Study

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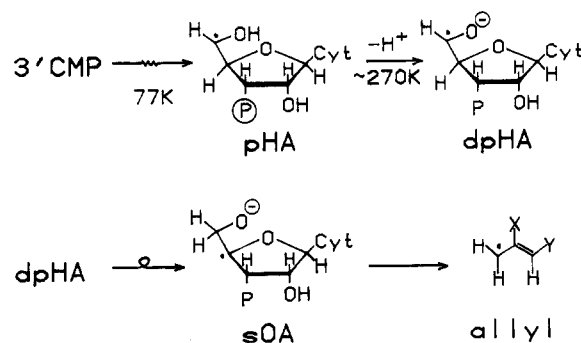
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Upon warming single crystals of methyl  $\alpha$ -D-glucopyranoside X-irradiated at 77 K, three free radical reactions have been observed. At  $\sim$ 190 K the deprotonated primary hydroxyalkyl radical, centered at C6, converts by a 1,2 hydrogen shift to a C5-centered secondary oxyalkyl radical. Further warming to  $\sim$ 230 K causes a conversion of the C5 secondary oxyalkyl radical to a primary hydroxyalkyl radical, centered at C2, opening the pyranose ring. It is postulated that the C2 radical, at  $\sim$ 320 K, abstracts a hydrogen from C5, re-forming the C5 secondary oxyalkyl radical. Thus a chain reaction is propagated through the crystal until terminated in yet another free radical product. This latter free radical has been characterized by ENDOR but its structure is uncertain.

### Introduction

Formation of a primary hydroxyalkyl (pHA) radical is a common event in crystalline carbohydrates containing a primary alcohol group. On warming to higher temperatures, the pHA radical reacts to form other more stable free radicals. The structure of these secondary radicals varies in different crystals. For example, in 5-chlorodeoxyuridine the pHA radical decay, under slow warming conditions, yields a radical due to hydrogen addition at the base.<sup>1</sup> In contrast, decay of the pHA radical in 3'-cytidylic acid (3'-CMP) leads to an allylic radical.<sup>2</sup>

Formation of the allylic radical in 3'-CMP involves a number of free radical intermediates. The first three steps, proposed in an earlier study, are as follows:<sup>2</sup>



The identification of the pHA radical is certain; however,