to a second-order interaction of the chemisorbed ammonia with the adjacent oxygen ion. A similar band has been observed during adsorption of ammonia on alumina.[38]

From the ammonia-adsorption experiments we concluded that the surface of tungsten oxide-silica is heterogeneous. This can account for the broadness of the high-temperature reduction peaks and be another reason for the absence of distinct W-OH bands in our infrared spectra. Obviously, a broad spectrum of interaction strengths is to be found on all catalysts. The structures IV and V represent, therefore, only an average stoichiometry.

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Surface Reactions of Oxygen Ions. 5. Oxidation of Alkanes and Alkenes by O_2^- on MgO

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Stoichiometric reactions between superoxide ions on MgO and simple hydrocarbons were observed at 175 °C, although the O_2^- ions were much less reactive than either O^- or O_3^- ions. Several types of oxygen-containing products were formed, as well as other hydrocarbons and CO_2. The reaction of propylene with O_2^- gave no gaseous product at 175 °C; however, at elevated temperatures acetaldehyde and methanol were obtained. Following the reaction of propane with O_2^-, acetone was detected at 175 °C in addition to acetaldehyde and methanol which were observed at higher temperatures. With 1-butene as the reactant, 2-butanol was formed together with methanol, acetaldehyde, and acrolein above 300 °C. Infrared spectra of surface intermediates indicate that the reaction of O_2^- with propylene at 175 °C resulted in the simultaneous formation of formate and acetate ions which are consecutively converted to carbonate ions at elevated temperatures. It is proposed that hydrogen atom abstraction is the initial step in the reaction of O_2^- with simple hydrocarbons. The resulting radicals react with lattice oxygen ions forming carboxylate ions or with HO_2^- ions forming alkoxy or epoxide intermediates.

Introduction

The superoxide ion, O_2^-, on a variety of metal oxides has been studied by EPR techniques;[1] however, its importance in catalytic reactions has not been resolved. There exists evidence that O_2^- is the source of oxygen in epoxidation of ethylene over supported silver,[2] but this is a difficult system to explore by using EPR. On ZnO the ion does not react at room temperature with hydrogen, carbon monoxide, or ethylene and only reacts slowly with propylene.[3] Kugler and Gryder[4] proposed that π-allyl reacted with O_2^- to form 2,3-epoxypropanal (glycidaldehyde), which was an intermediate in the formation of acrolein on the surface. Reactions also have been reported between O_2^- and butene on SnO_2, TiO_2, and ZnO,[5] as well as between O_2^- and butadiene on supported MoO_3, for which the products were maleic anhydride and CO_2.[6] In addition, it has been

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TABLE I: Stoichiometric Reactions of Oxygen Ions with Hydrocarbons on MgO

ion	reactant	intermediate	major products
O^-	C_2-C_4	alkoxide ions[a]	alkenes, CO_2
	C_2, C_3 alkenes	carboxylate ions[a]	CH_4, C_2H_4, CO_2
	C_4 alkenes	alkoxide ions,[a] carboxylate ions[a]	butadiene, CH_4, CO_2
O_3^-	C_2-C_4 alkanes	alkoxide ions,[a] peroxy radicals[a]	alkenes, CH_4, CO_2
	C_2, C_3 alkenes	carboxylate ions[b]	CH_4, CO_2
	C_4 alkenes	alkoxide ions,[a] peroxy radicals[a]	butadiene, CH_4, CO_2
O_2^-	C_3 alkane	alkoxide ions[a]	alkenes, CH_4, acetone, acetaldehyde, CO_2
	C_2 alkene	carboxylate ions[b]	CH_4, CO_2
	C_3 alkene	carboxylate ions,[b] (epoxide)[a]	CH_4, acetaldehyde, methanol, CO_2
	C_4 alkenes	carboxylate ions,[b] (epoxide)[a]	CH_4, 2-butanol, CO_2, butadiene, acetaldehyde

[a] The carbon number is the same as that of the reactant. [b] The carbon number is smaller than that of the reactant because of scission reactions.

proposed that O_2^- ions play an important role in the oxidation of furan to maleic anhydride over titania or molybdena catalysts.[7]

On the surface of MgO the oxygen ions O^-, O_2^-, and O_3^- may be selectively formed. The O^- and O_2^- ions were produced by reacting N_2O and O_2, respectively, with electrons trapped at oxide ion vacancies on the surface.[8,9] Ozonide ions may be formed by several methods;[10,11] however, for investigating surface reactions with alkanes, they were produced by ultraviolet irradiation (254 nm) of MgO in the presence of N_2O.[12] In each case the selectivity to a particular type of oxygen ion was large (>95% for O^- and O_2^-; $\simeq$85% for O_3^-).

Both O^- and O_3^- ions react with hydrocarbons by hydrogen atom abstraction, and the resulting radicals form stable species with surface oxide ions.[12-15] At elevated temperatures these intermediates decompose, and products appear in the gas phase. For example, alkanes react with O^- ions to form alkoxide intermediates which decompose at ca. 300 °C, yielding the corresponding alkenes. To complete this study of oxygen ions on magnesium oxide, we have employed similar techniques to determine the stoichiometric reactions between O_2^- and alkanes and alkenes. The surface intermediates and the principal gas-phase decomposition products are summarized in Table I.

Experimental Section

The magnesium oxide samples were prepared from the hydroxide in the same manner as previously described.[8] In each reaction cycle the sample was oxidized in O_2 at 530 °C for 1 h and evacuated at the same temperature overnight in order to eliminate hydrocarbons, carbon monoxide, and water. The O_2^- ion was produced on the surface by introducing O_2 to a sample of MgO which contained trapped electrons (S centers).[9]

The EPR spectra of O_2^- ions were measured by using a Varian E-6S, X-band spectrometer with the sample at −196 °C. The g values were evaluated by using a phosphorus-doped silicon standard having a g value of 1.9987. The concentration of O_2^- ion was calculated by a double integration of the EPR spectrum. In the infrared experiments two self-supporting MgO wafers were placed parallel in a sample holder which was similar to that described elsewhere.[16] Infrared spectra were obtained at 25 °C by using a Perkin-Elmer 399 spectrophotometer with a IMSAI 8080 microcomputer system.

The hydrocarbons obtained from commercial sources were purified by vacuum distillation.[13] Hydrogen (Matheson 99.999% purity) and helium (Airco 99.999% purity) were used without further purification.

Reactants and products were analyzed by using a Carle AGC-311 gas chromatograph with both a thermal conductivity detector (TCD) and a flame ionization detector (FID). The chromatograph was connected directly to the reaction system. The column packings were Porapak Q for the separation of CO_2, CH_4, C_2H_4, C_2H_6, C_3H_6, and C_3H_8; bis(ethoxyethyl) adipate for butanes, butenes, and butadiene; Carbowax 600 for oxygen-containing hydrocarbons; and 5A molecular sieve for hydrogen, oxygen, nitrogen, and carbon monoxide.

After the formation of O_2^- ions, the gaseous oxygen was removed from the reactor; and the spectrum of O_2^- ions on MgO, loaded in the side arm of the fused quartz reactor, was recorded. The reactor was then attached to a closed recirculation system described in a previous paper.[13] About 4 μmol of hydrocarbon (1.0 torr) diluted in helium was introduced and circulated at 175 °C for 2 h unless otherwise specified. After the reaction the condensable gas-phase products were collected for 1 h in a cold trap (−196 °C) located in the circulation system. Following the isolation of the reactor from the system, the trap was warmed to 25 °C, and the gas-phase molecules were analyzed. The noncondensable gas phase remaining in the reactor was analyzed separately. After the reactor was evacuated at 25 °C for 15 min, ~50 torr of helium was introduced into the system. The reactor was heated to a prescribed temperature for 1 h while the trap was maintained at −196 °C for collecting the desorbed substances. These were analyzed in the same manner as described above.

Results

Characterization of the O_2^- Ion on MgO. Following the reaction of O_2 with S centers on the MgO surface, the O_2^- spectrum with at least four g_z components was observed.[11] These components apparently correspond to O_2^- ions adsorbed on four different sites. The existence of several kinds of O_2^- ions on MgO, indicated by the appearance of several g_z components, has already been reported by Wong and Lunsford[10] and by Cordischi et al.[17]

The thermal stability of the O_2^- species was studied in detail. Samples containing O_2^- ions were successively heated for 10 min at progressively higher temperatures under a static vacuum, until the O_2^- signal had completely disappeared. The O_2^- concentration as a function of temperature is depicted in Figure 1. The O_2^- species at all of the sites are stable up to ca. 100 °C; however, the total concentration sharply decreased between 175 and 300 °C. At the latter temperature the concentration became essentially zero.

The different thermal behavior of the g_z components confirms that several distinct forms of O_2^- ions were present on the MgO surface. The increase in the intensity of the g_z^4 component was accompanied by a decrease in the g_z^1 component, whereas the total concentration of O_2^- ions remained unchanged up to ca. 175 °C. This suggests

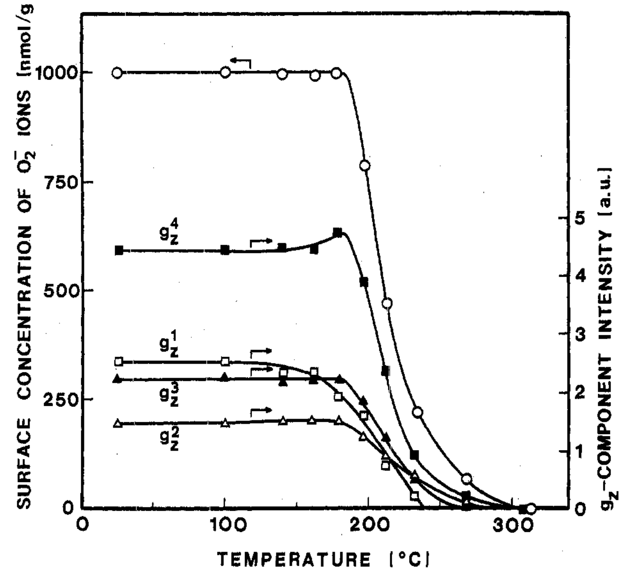


Figure 1. Thermal stability of O_2^- species on MgO surface. Intensities of g_z components are described in arbitrary units (au).

TABLE II: Reaction of Alkanes and Alkenes with O_2^- Ions[a]

hydrocarbon	concn of O_2^- ions,[b] nmol/g before reaction	after reaction	reacted	amount of HC reacted,[c] nmol/g
CH_4	1044	1025	19	25
C_2H_4	921	615	306	311
C_3H_6	1025	22	1003	979
C_3H_8	972	307	665	602
1-C_4H_8	1003	14	989	981

[a] The reaction was performed at 175 °C for 2 h.
[b] The concentration of O_2^- ions was determined by EPR.
[c] The amount of hydrocarbon reacted was measured by gas chromatography.

that the O_2^- ions with g_z^1 were converted to those with g_z^4 at higher temperature. It is noteworthy that the coexistence of water vapor caused a decrease in the total concentration of O_2^- ions around 150 °C.

Stoichiometry of the Reactions between O_2^- and Hydrocarbons. The O_2^- ions disappeared slowly at 25 °C in the presence of C_2-C_4 alkanes or alkenes. It was found that 67 and 89% of the O_2^- ions remained on the MgO surface after exposure to propylene and propane for 5 h, respectively. At higher temperatures the reaction of the O_2^- ions was accelerated; for example, most of the O_2^- ions reacted with propylene over a period of 2 h at 175 °C. In these reactions the decay of the O_2^- spectrum was observed without the formation of any other signal. In addition, the reactivities of the four types of O_2^- toward simple hydrocarbons were essentially the same. The above results are in striking contrast with the much greater reactivity of the O^- and O_3^- ions.[12-15]

The stoichiometry of the reaction of O_2^- ions with each hydrocarbon is summarized in Table II. In the table, the amount of hydrocarbon reacted represents the difference in the amount of reactant before and after the reaction. In each case the reaction temperature was 175 °C and the reaction time was 2 h. The results in Table II show that the amounts of the O_2^- ions reacted and hydrocarbon consumed are the same within experimental error. this suggests a one-to-one stoichiometry for the reaction of simple hydrocarbons and O_2^- ions.

It was further established that reactions of hydrocarbons on the surface did not proceed in the absence of O_2^- ions. When a hydrocarbon (propylene or 1-butene) was introduced onto a MgO sample without S centers, but which had been exposed to O_2, only a small amount of hydrocarbons reacted. This observation excludes the possibility that physically adsorbed or other forms of oxygen on surface defects react with hydrocarbons and supports the one-to-one stoichiometry between O_2^- and the hydrocarbon.

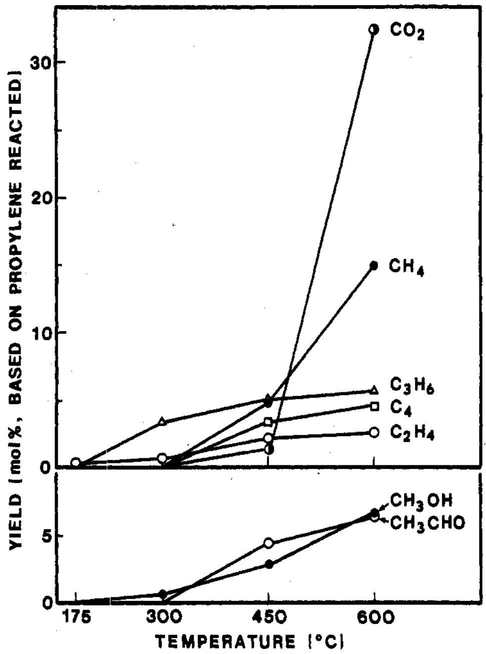


Figure 2. Yield of products as a function of the thermal desorption program following the reaction of propylene with O_2^- at 175 °C for 2 h. C_4 indicates the sum of butenes and butadiene.

Product Determination. Only a small amount of O_2^- ions and methane reacted in 2 h at 175 °C as shown in Table II. When the sample was heated, CH_4 and CO_2 were detected at 300 °C and above 450 °C, respectively. Based on the mole percent of reacted CH_4, 18% was recovered as CH_4 and 80% was recovered as CO_2. Similar results were obtained with ethylene. Approximately one-third of the O_2^- reacted, and most of the reaction product was CO_2 obtained after heating the sample to 600 °C. At 450 °C a trace amount of CH_4 was detected.

Following the reactions of O_2^- ions with propylene, propane, or 1-butene at 175 °C for 2 h, the observed products are depicted in Figures 2–4 as a function of the thermal desorption program. Several types of oxygen-containing products were observed in this study which were not reported following a similar reaction with O^- or O_3^- ions.[12-15] In particular, the reaction of propylene with O_2^- resulted in the formation of acetaldehyde and methanol as the partially oxygenated products. With propane as the reactant, acetone was detected at 175 °C in addition to acetaldehyde and methanol which were observed at higher temperatures. The reaction of 1-butene and O_2^- ion resulted in the formation of 2-butanol together with methanol, acrolein, and acetaldehyde.

At moderate temperatures of 300–450 °C, hydrocarbons having carbon number smaller or greater than the reactants were formed. In each case carbon dioxide and CH_4 were obtained upon heating the sample at 600 °C, though the amounts of these products were less than those observed following the reactions of O_2^- ions with hydrocarbons.[12,15]

Infrared Study. In order to determined stable surface intermediates in the reaction of O_2^- with hydrocarbons, we performed an infrared study on MgO wafers. It was first

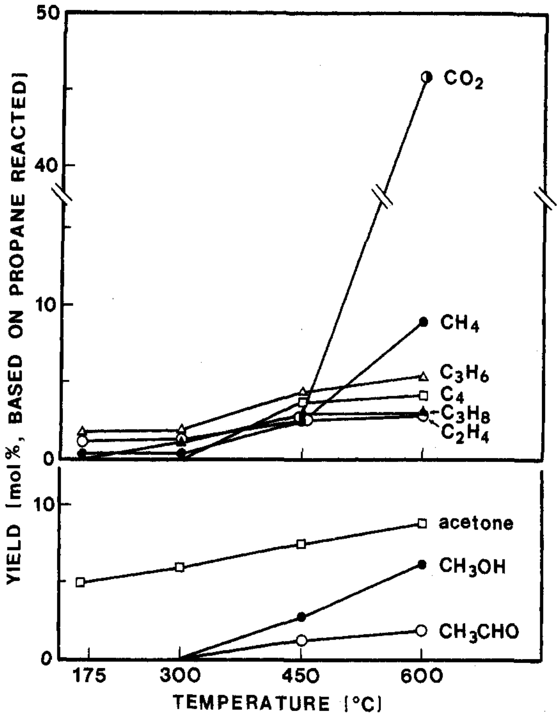


Figure 3. Yield of products as a function of the thermal desorption program following the reaction of propane with O_2^- at 175 °C for 2 h. C_4 indicates the sum of butenes and butadiene.

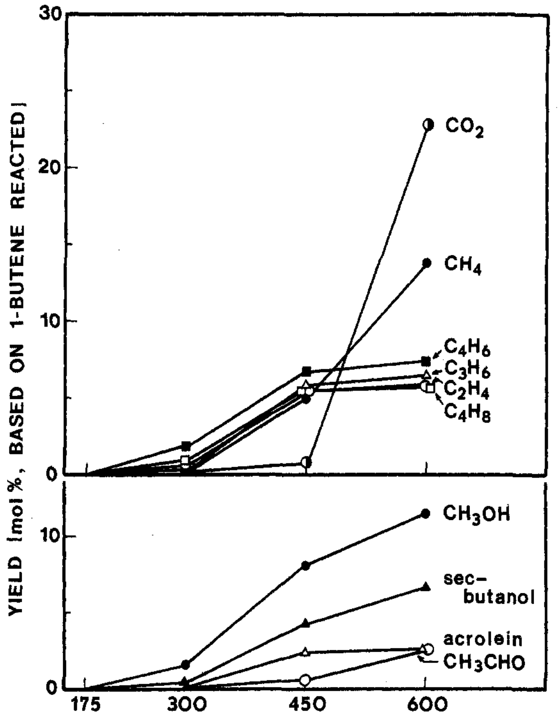


Figure 4. Yield of products as a function of the thermal desorption program following the reactions of 1-butene with O_2^- at 175 °C for 2 h.

confirmed that no absorption bands were observed upon the addition of C_3H_6 at 175 °C for 2 h to the MgO wafers without O_2^- ions and subsequent evacuation of the gas phase. It was not possible to study these samples by EPR; however, the MgO wafers took on the characteristic blue color upon UV irradiation in the presence of hydrogen at 25 °C for 5 h, and the color changed to white upon the addition of O_2 at 25 °C. This indicates the formation of O_2^- ions on MgO. Following the formation of O_2^- ions, 50 torr of C_3H_6 was introduced onto the MgO wafers at 175 °C for 2 h. After removing the gas phase at the same temperature, we obtained infrared spectra following each step in the thermal desorption program. The infrared spectra, including those obtained after background subtraction, are shown in Figure 5.

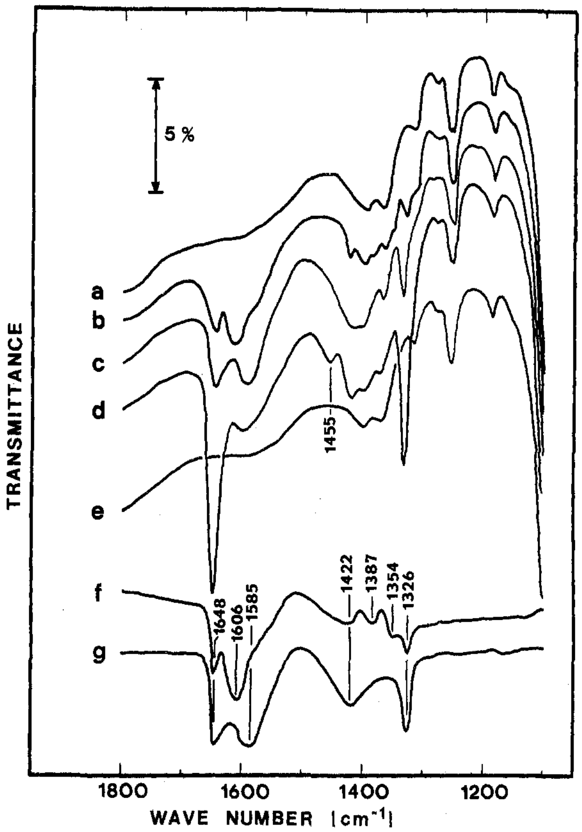


Figure 5. Infrared spectra following the reaction of propylene with O_2^-: (a) MgO background; (b) after the reaction at 175 °C; (c) after thermal treatment under vacuum at 300 °C; (d) 450 °C; (e) 550 °C; (f) difference spectrum between (b) and (a); (g) difference spectrum between (c) and (a).

Following the reaction at 175 °C, new absorption bands appeared at 1648, 1606, 1585, 1422, 1387, 1354, and 1326 cm^{-1}, as shown in Figure 5. Heating the sample to 300 °C under vacuum (curve C) resulted in a decrease in intensity for the bands at 1606, 1387, and 1354 cm^{-1}. Treatment at 450 °C (curve d) caused an increase in intensity of the bands at 1648 and 1326 cm^{-1}. When the sample was progressively heated under vacuum to 550 °C (curve e), all the bands disappeared and the spectrum was essentially the same as the background.

These spectra are attributed mainly to three species—formate ions, acetate ions, and carbonate ions. On the basis of several literature values,[18,19] the bands at 1606, 1387, and 1354 cm^{-1} are assigned as the O–C–O asymmetric and symmetric stretching modes of the formate ions which were eliminated by the thermal treatment at 300 °C. The bands at 1585 and 1422 cm^{-1} are in good agreement with literature values for the O–C–O vibrations of acetate ions.[14,18,19] The bands at 1648 and 1326 cm^{-1} are assigned to bidentate carbonate ions on MgO.[20,21] The value of 1648 cm^{-1} is different from the values of 1670 or 1665 cm^{-1} which were reported for the vibration of bidentate carbonate ions on MgO by Fukuda and Tanabe[20] or Takita and Lunsford,[12] respectively. In the latter work it is evident that the band in question shifted to lower wavenumbers (ca. 1648 cm^{-1}) upon heating the sample to 300 °C under vacuum. This variation in vibrational frequency probably resulted from the interaction of H_2O or OH^- with CO_3^{2-} ions, as indicated by Evans and Whateley.[21] The identity of an absorption band at 1455 cm^{-1}, which appeared upon the thermal treatment at 450 °C, is uncertain at the present.

Discussion

Thermal Stability of O_2^- Ions on MgO. A sharp decrease in the total concentration of O_2^- ions was observed around 200 °C, in contrast to the results of Cordischi et al.,[17] who reported that the O_2^- ions rapidly decreased in concentration above 100 °C. This difference in thermal stability may result from the difference in preparation of O_2^- ions on MgO. In the case of Cordischi et al., the O_2^- radicals were formed upon heating MgO in vacuo at 600–900 °C, addition of H_2 at 25 °C, and introduction of O_2 at 25 °C. In their work the EPR spectrum of O_2^- ions showed a doublet at the g_z components, indicating the interaction of O_2^- with a nearby proton. No hyperfine splitting due to a nearby proton was observed in the present study. Reactions leading to the formation of $HO_2\cdot$ radicals may be responsible for the removal of O_2^-.

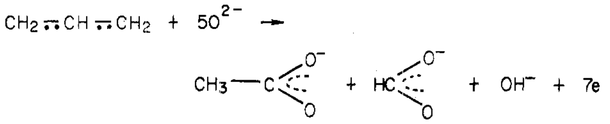
Similar differences in thermal stability have also been observed for O^- and O_3^- ions. Naccache and Che[22] have reported that O^- was more stable when MgO was irradiated with UV light for longer periods or γ-irradiated in the preparation of S centers. Likewise, O_3^- ions formed upon UV irradiation in the presence of N_2O[12] were more stable than those formed by irradiation in the presence of O_2.[11]

Mechanism for Reactions of O_2^- with Hydrocarbons. Attempts to observe initial intermediates formed by the reaction of O_2^- ions with hydrocarbons on MgO by means of EPR have not been successful, probably because of the instability of the intermediates at the high temperature required for the initial reaction. Nevertheless, from the desorption products and the infrared spectra of certain intermediates, it is possible to piece together a reasonable sequence of surface reactions.

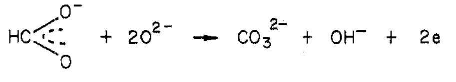
The mechanism for the reaction between O_2^- and propylene will be considered first. Based upon bond strengths and other data[23] it is generally accepted that hydrogen atom abstraction occurs at the methyl group in most oxidation reactions of C_3H_6 on metal oxides; thus we propose the formation of an allyl radical (eq 1). At the reaction

$$CH_2{=}CH{-}CH_3 + O_2^- \rightarrow CH_2{\cdots}CH{\cdots}CH_2 + HO_2^- \quad (1)$$

temperature this allyl radical would be unstable and would react immediately to acetate and formate ions which were detected in the IR study. The studies by Aika and Lunsford[14] and Takezawa et al.[24] indicate that acetate ions are not converted into formate ions. Following reaction 1, therefore, the allyl radical apparently reacts with oxide ions of the surface, forming acetate and formate ions according to eq 2. In separate experiments longer reaction times at 175 °C caused a decrease in the infrared bands of formate ions at 1606, 1387, and 1354 cm^{-1} and an increase in the carbonate bands at 1648 and 1326 cm^{-1}, indicating a consecutive slow reaction (eq 3) following reaction 2. On the basis of the amount of hydrocarbon reacted (Table II), less than 1% of the surface oxide ions are involved in reactions 2 and 3. The electrons resulting from these reactions may be trapped at oxide ion vacancies on the surface.

 (2)

$$CH_2{\cdots}CH{\cdots}CH_2 + 5O^{2-} \rightarrow CH_3{-}C(O)O^- + HC(O)O^- + OH^- + 7e \quad (2)$$

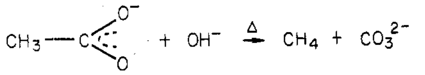
 (3)

$$HC(O)O^- + 2O^{2-} \rightarrow CO_3^{2-} + OH^- + 2e \quad (3)$$

Thermal treatment at 300 °C resulted in a conversion of all formate ions into carbonate ions. Upon heating above 450 °C acetate ions on MgO decompose to form CH_4 and CO_3^{2-} ions according to reaction 4 in a manner similar to that reported by Aika and Lunsford.[13] The carbonate

$$CO_3^{2-} \xrightarrow{\Delta} CO_2 + O^{2-} \quad (5)$$

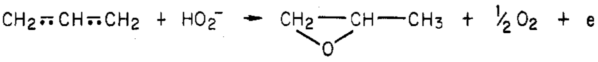
ions subsequently decompose to form CO_2.

 (4)

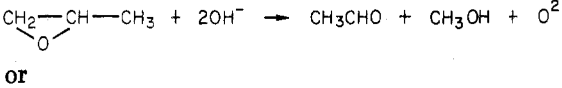
$$CH_3{-}C(O)O^- + OH^- \xrightarrow{\Delta} CH_4 + CO_3^{2-} \quad (4)$$

In support of the above mechanism it is important to note that Hata et al.[25] have observed the simultaneous formation of formate and acetate ions on ZnO as a result of the reaction of a π-allylic intermediate and molecular oxygen. These results differ, however, with the conclusion of Kugler and Gryder[4] that glycidaldehyde was formed as the surface intermediate in the oxidation of propylene over ZnO.

Significant amounts of CH_3CHO and CH_3OH were observed, as depicted in Figure 2; therefore alternate surface reactions must be proposed. The formation of oxygen-containing molecules suggests that at least one of the atoms from the superoxide ion adds to a surface intermediate, perhaps according to the following scheme:

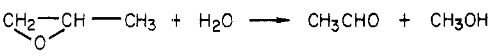
 (6)

$$CH_2{\cdots}CH{\cdots}CH_2 + HO_2^- \rightarrow \underbrace{CH_2{-}CH}_{O}{-}CH_3 + \tfrac{1}{2}O_2 + e \quad (6)$$

 (7)

$$\underbrace{CH_2{-}CH}_{O}{-}CH_3 + 2OH^- \rightarrow CH_3CHO + CH_3OH + O^{2-} \quad (7)$$

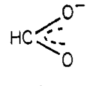
or

 (8)

$$\underbrace{CH_2{-}CH}_{O}{-}CH_3 + H_2O \rightarrow CH_3CHO + CH_3OH \quad (8)$$

In order to support this mechanism, we investigated the thermal desorption pattern of propylene oxide adsorbed on MgO in a separate experiment. Significant amounts of acetaldehyde and methanol were observed at 450 and 600 °C, indicating a decomposition of propylene oxide to those compounds. At the present it is not clear whether propylene oxide is present on the surface in the molecular form or whether an intermediate derived from propylene oxide leads to the formation of acetaldehyde and methanol.

Somewhat analogous reactions would be expected to proceed upon the reaction of C_2H_4 with O_2^- ions. The intermediate formed by the scission reaction of the carbon–carbon double bond is expected to be only thus CO_2 alone is anticipated as the reaction product. The rate for the reaction of O_2^- with C_2H_4 is smaller than that of C_3H_6, which suggests that reaction pathways may be controlled by the C–H bond energies.



$$HC(O)O^-$$

In reactions of propane and 1-butene with O_2^-, it was observed that oxygenated compounds with the same carbon number as the reactants were produced. It is reasonable that the initial step again would involve a hydrogen atom abstraction, but in this case from a secondary carbon:

$$CH_3CH_2CH_3 + O_2^- \rightarrow CH_3\dot{C}HCH_3 + HO_2^- \quad (9)$$

As depicted in Figure 3, acetone was observed even at 175 °C, which suggests the following reactions:

$$CH_3\dot{C}HCH_3 + HO_2^- \rightarrow CH_3CH(\dot{O})CH_3 + OH^- \quad (10)$$

$$CH_3CH(\dot{O})CH_3 + OH^- \rightarrow CH_3C(O)CH_3 + H_2O + e \quad (11)$$

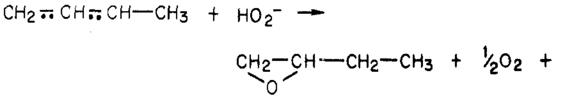
or

$$CH_3CH(\dot{O})CH_3 + O^{2-} \rightarrow CH_3C(O)CH_3 + OH^- + e \quad (12)$$

The surface isopropoxy radical was partially reacted to actone via eq 11 or 12; meanwhile most of the isopropoxy radical is believed to convert to acetate ions and formate ions leading to CO_2 and CH_4, in fair agreement with the mechanism reported in infrared studies for the reaction of oxygen with 2-propanol or acetone adsorbed on MgO.[18]

The reaction of 1-butene would then occur, in a similar manner:

$$CH_2{=}CHCH_2CH_3 + O_2^- \rightarrow CH_2{\cdots}CH{\cdots}CH{-}CH_3 + HO_2^- \quad (13)$$



$$CH_2{\cdots}CH{\cdots}CH{-}CH_3 + HO_2^- \rightarrow \underbrace{CH_2{-}CH}_{O}{-}CH_2{-}CH_3 + \tfrac{1}{2}O_2 + e \quad (14)$$

Since butene oxide or methyl vinyl ketone was not detected as a product in the programmed desorption experiment, it is likely that the intermediate formed in reaction 14 reacted with water at the elevated temperature and then desorbed as 2-butanol. The present study indicates the importance of the O_2^- ion in the formation of 2-butanol from 1-butene.

Comparison of the Reactivities of Oxygen Ions on MgO. One of the most significant observations in this series of studies was the large difference in the reactivities of the three forms of oxygen ions on MgO. Taking ethylene as an example, O^- ions react readily at −60 °C[14] and O_3^- ions react at 25 °C with a half-life of ca. 5 min;[15] whereas about two-thirds of the O_2^- ions remained unreacted after contact with C_2H_4 at 175° C for 2 h. These results, which are qualitatively the same for other simple hydrocarbons, indicate that the order of reactivity is $O^- \gg O_3^- \gg O_2^-$.

The surface intermediates proposed in this series are summarized in Table I. It is clear that the intermediates in each reaction of alkanes include alkoxide ions, regardless of the type of active oxygen species. This may be due to the stability of the corresponding alkoxide ions on the basic oxide surface.

Although carboxylate ions are believed to be the intermediate in the reactions of C_2 and C_3 alkenes, the type of carboxylate ion formed with O^- as a reactant is different from the type of carboxylate ion formed when O_2^- or O_3^- was a reactant. With O^- ions the carbon number of the carboxylate ions is the same as that of the hydrocarbon reactant, but with O_2^- or O_3^- ions carboxylate ions are formed having carbon numbers smaller than the parent hydrocarbon. This means that the molecular oxygen (O_2 or O_2^-) causes the scission of carbon–carbon double bonds following the initial step of hydrogen atom abstraction from the alkenes.

The reaction schemes of C_4 alkenes are somewhat complicated, yet it appears that they react in a manner more similar to C_2–C_4 alkanes than to C_2 or C_3 alkenes. The attack of O_2 or HO_2^- ions in the second step results in the formation of oxygenated intermediates such as peroxy radicals, without the scission of C=C bonds.

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