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Reaction of Alkenes with O^- on MoO_3/SiO_2 Catalyst

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Reaction of C_2H_4 with O^- on MoO_3/SiO_2 leads to the formation of the $-OC_2H_4^{\cdot}$ radical and no abstraction of hydrogen has been observed. This radical is very stable in the absence of excess ethylene and the ESR spectrum is strongly temperature dependent. Using C_2H_4 labelled with carbon-13 we obtained the coupling constants $a_H{}^{\alpha} = 22.5$ G, $a_H{}^{\beta} = 27.75$ G, $a_C{}^{\alpha} = 39$ G, $a_C{}^{\beta} = 13.1$ G. The presence of different coupling constants for the two carbon atoms confirms the σ_β structure for the $-OC_2H_4$ radical. The reaction of C_3H_6 and C_4H_8 with O^- leads to the formation of methyl radicals and $-OC_2H_4^{\cdot}$ radicals and possible mechanisms are discussed.

INTRODUCTION

During recent years the formation of paramagnetic oxygen species on the surface of oxides has been extensively studied (*1*) because of the importance of catalytic oxidation reactions. Ethylene is known to react very easily with adsorbed O^- to give paramagnetic species. On MgO this reaction was studied by Naccache and Che (*2*) and more recently, by Ben Taarit *et al.* (*3*), who, using both C_2D_4 and C_2H_4 enriched with ^{13}C, suggested that $CH_2{=}\dot{C}^- \cdots {}^-OH$ was formed on the surface, probably via an intermediate radical $CH_2{=}\dot{C}H$ which was not detected. Under different experimental conditions Aika and Lunsford (*4*) showed that the former radical was stable up to 253 K. However, the reaction of C_2H_4 with O^- at low temperatures on molybdenum supported on silica (*5*) leads to the formation of $-OC_2H_4^{\cdot}$ which decomposes at higher temperatures to give the $CH_2{=}CH^{\cdot}$ radical. The present work was undertaken to obtain more information on the structure of these radicals using labelled compounds and also to compare the reaction of ethylene with that of propene and butene.

EXPERIMENTAL

MoO_3/SiO_2 catalyst was prepared following an experimental procedure similar to that described by Vorotyntsev *et al.* (*6*). Silica (Degussa, 380 m^2/g) was impregnated using a suitable volume of ammonium molybdate solution ($(NH_4)_6$ Mo_7O_{24}, $4H_2O$ Analar from Hopkin and Williams) to obtain 2% of molybdenum by weight. After slow evaporation with constant stirring of the water excess the impregnated powder was dried at 373 K and heated in air at 873 K (2 h/g) to decompose the ammonium molybdate.

Then 0.10 to 0.15 g of MoO_3/SiO_2 were treated in silica ampoules with a dome-break seal according to the following procedure:

(a) evacuation at 773 K;

(b) heating at 773 K in 2×10^4 Pa (150 Torr) of O_2 (1 h) and evacuation (1 h) at the same temperature;

(c) reduction at 773 K in 4×10^4 Pa (300 Torr) of H_2 and evacuation at a pressure of less than 1.3×10^{-2} Pa (10^{-4} Torr).

The samples were then sealed off under vacuum and connected by the dome-break-seal side to a vacuum line. O^- was formed by decomposition of N_2O at 373 K (1.3×10^4 Pa) for 1 h and after evacuation this was followed by reaction with the appropriate alkene at low pressure (10 to 100 Pa at 373

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and 298 K). All the gases (O_2, H_2, N_2O from B.O.C.) and alkenes (C_2H_4, C_2D_4, C_2H_4 (1,2-^{13}C), C_3H_6, C_4H_8 supplied by Prochem B.O.C.) were spectroscopically pure and used without further purification. The ESR spectra were recorded using a Varian V-4502 spectrometer with a 100-kHz modulation and a dual cavity. Measurements were carried out in the range 77 to 300 K and g values were determined by comparison with g values of DPPH or Varian "Strong Pitch."

RESULTS

The asymmetrical lines present in the ESR spectrum of the sample after reduction under H_2 at 773 K are characteristic of Mo(V) in two different coordinations (*6*). After reaction with N_2O at 373 K Mo(V) partially disappeared while a new line with principal g values of 2.055 and 2.020 developed. This ESR spectrum is known to arise from O^- in the coordination sphere of Mo(VI) (Fig. 1a) (*6, 7*).

1. Reaction with Ethylene

During the adsorption of ethylene at low pressure (100 Pa) the ESR signal of O^- faded away and a new isotropic signal centered at $g = 2.0023$ developed at room temperature (Fig. 1b). The hyperfine structure is consistent with two pairs of equivalent protons with $a_H = 22.5$ and 27.75 G. In the presence of excess ethylene that spectrum disappeared and no new paramagnetic species was observed. This signal is stable for several days when the sample is prepared at 373 K (10 Pa of C_2H_4) provided that excess ethylene is evacuated. The ESR spectrum is strongly temperature dependent. When the temperature is lowered the lines broaden and the larger coupling constant increases slightly (32.5 G at 100 K).

At low temperature the ESR signal was found to be identical to the signal described by Sapozhnikov *et al.* (*5*) and assigned to $-OC_2H_4^{\cdot}$ in a σ_β conformation but, contrary to the earlier results, in this work the radical was stable in a wide temperature range in the absence of ethylene in the gas phase and much better resolution was obtained at the highest temperature. The reaction of O^- with C_2D_4 gives a nine-line spectrum consistent with coupling constants of 3.5 and 4.12 G for the two pairs of deuterium nuclei; these hyperfine splitting constants are in good agreement with the proton work.

Reaction of O^- with C_2H_4 enriched with ^{13}C is more interesting because not only should it confirm the nature of the radical but the value of the hyperfine splittings for ^{13}C should give additional structural information. The intensity of the spectrum obtained after reaction of O^- with C_2H_4 enriched with ^{13}C is smaller than expected (Fig. 2) and a broadening of the lines is

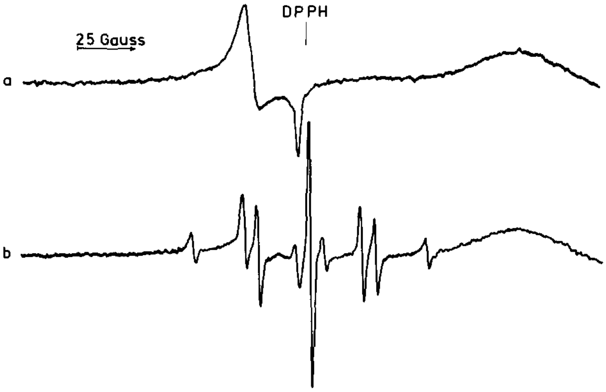


FIG. 1. (a) ESR spectrum recorded at 298 K for O^- on the surface of reduced Mo/SiO_2 catalyst; (b) ESR spectrum recorded at 298 K after reaction of O^- with C_2H_4 at 373 K.

evident in the low-field part of the spectrum. The stick spectrum drawn with coupling constants of 13.1 and 39 G for ^{13}C is in good agreement with experimental data. This accounts for those molecules which contain two ^{13}C atoms (83.9% of total ethylene); however, some lines, two of them labelled with a star, do not belong to this system. The distance between these two lines (13 ± 0.5 G) shows that they are due to a species containing only one ^{13}C atom with a_C = 13.1 G (7.7% of total ethylene). The linewidth, 2.3 times smaller than that of the main species, accounts for the higher apparent intensity. So the line broadening observed in the spectrum of the major species with two ^{13}C atoms is due to the other carbon atom (a_C = 39 G). Because of that line broadening the second species with one ^{13}C atom (a_C = 39 G) is not apparent in the overall spectrum.

2. *Reaction with Propene and 1-Butene*

Reaction of O^- with C_3H_6 (10 Pa) at 373 K gave a spectrum (recorded at 298 K) which is interpreted as due to the superimposition of two organic radicals (Fig. 3a), firstly methyl radicals with a_H = 22.5 G and secondly radicals with a spectrum similar to the one observed after reaction of O^- with C_2H_4. The latter developed more strongly after standing at room temperature particularly in the lower part of the sample (Fig. 3b). It is important to realize that the appearance of the signal in the lower part of the sample occurs after evacuation of the excess propene. The same type of reaction occurs with 1-butene though the intensity of the lines is smaller than that observed after reaction with C_3H_6.

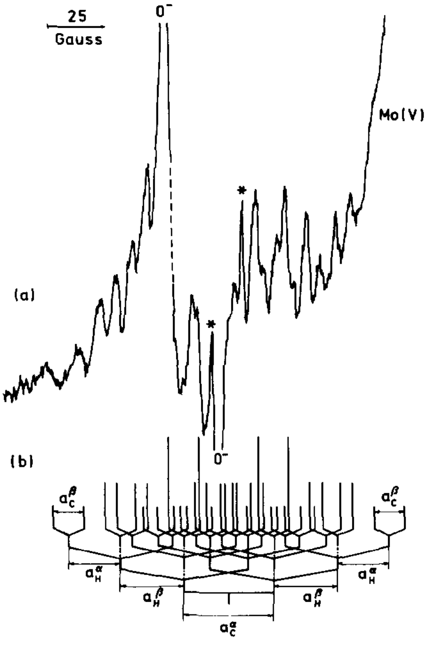
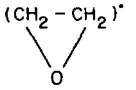


FIG. 2. ESR spectrum of the radical obtained after reaction of O^- on Mo/SiO_2 with $^{13}C_2H_4$ at 373 K on Mo/SiO_2. (a) Spectrum recorded at 298 K; (b) stick spectrum.

DISCUSSION

Reaction with C_2H_4

Reaction of O^- ions with ethylene appears to go either by addition or by abstraction reactions, depending on the system. The addition reaction can give either $(OCH_2{-}CH_2)^{\cdot}$ called "linear species" or



$$\underset{\mathrm{O}}{(\mathrm{CH_2-CH_2})^{\cdot}}$$

called "bridged species." From the shape of the room temperature ESR spectrum and

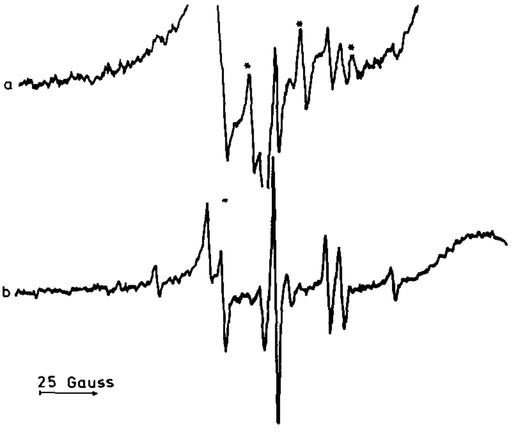


FIG. 3. ESR spectrum recorded at 298 K for the radicals obtained after reaction of O^- on Mo/SiO_2 with C_3H_6 at 373 K. (a) Initial spectrum; (b) after standing at room temperature.

according to Sapozhnikov *et al.* (*5*, *8*) it seems that the species observed is the linear one:

$$\begin{array}{ll} -\underset{\beta}{OCH_2}-\underset{\alpha}{CH_2}^{\cdot} & a_H{}^{\alpha} = 22.5\ G \\ & a_H{}^{\alpha} = 27.75\ G \end{array}$$

For ethyl radicals adsorbed on silica gel at 77 K Shiga and Lund (*9*) reported values of 20 and 29.9 G for the perpendicular and parallel components of the hyperfine splittings for α protons (a_{iso} = 23.3 G). For β protons the corresponding values were 26 and 27.9 G. So the widening of the lines observed in our case when the temperature is lowered comes from the anisotropic character of hyperfine splitting for the α proton. At higher temperature rotation averages out this anisotropy.

The behaviour of the coupling constant for the β hydrogen against temperature is the same as that observed by Ben Taarit *et al.* (*3b*) for the linear species obtained after reaction of ethylene oxide with the $F_s{}^+$ center on MgO. It is characteristic of the in-plane structure with a relatively low barrier of rotation about the C–C bond. Reasons for this interpretation have been given by Kirino (*10*). At room temperature there is some rotation around the C–C bond and the values we found are very close to the corresponding values calculated by Sapozhnikov *et al.* for the σ_β species (*8*).

The carbon-13 data show that the two carbon atoms are not equivalent, confirming that we are not dealing with a bridged structure. Hyperfine splittings observed agree very well with theoretical calculations (*8*) for a σ_β structure ($a_C{}^{\alpha}$ = 42.8 G, $a_C{}^{\beta}$ = 11.9 G). The line broadening is due to the anisotropic character of the hyperfine interaction with the α carbon and that anisotropy is not completely removed by rotation about the C–C bond even at room temperature.

All these observations confirm the existence of the linear $-OC_2H_4^{\cdot}$ species at the surface of Mo/SiO_2 after reaction of C_2H_4 with O^-. Since the same type of species is observed on MgO after reaction of ethylene oxide with $F_s{}^+$ centers (*3b*) it seems that the bridged species is not likely to be stable on catalytic surfaces.

The reason for the enhanced thermal stability we have observed for the σ_β radical is not clear but it does suggest that in the proper circumstances some concentration of such species could exist under conditions of catalytic interest.

Reaction with C_3H_6 and C_4H_8

The spectrum recorded in the early stage of the reaction is not characteristic of a simple addition or abstraction by O^- to C_3H_6 or C_4H_8. The presence of some ethylene as an impurity in propene could give $-OCH_2-CH_2^{\cdot}$ in the early stage of the reaction but this is most unlikely because of the very low pressure used for added gases (10 Pa).

The methyl radical might be formed through cracking of the propene molecule:

$$CH_3{-}CH{=}CH_2 \rightarrow CH_2{=}CH^{\cdot} + CH_3^{\cdot}.$$

The vinyl radicals would not be detected because of their high reactivity.

As no radicals were observed in the absence of O^- we assume that the species is involved in the cracking process. The appearance of $-OCH_2-CH_2^{\cdot}$ upon standing implies the slow formation of C_2H_4 which could react with any O^- left unreacted on the catalyst. The metathesis reaction is known to occur on Mo/SiO_2 at high temperature (*11*) and although we are working in the range 298–373 K it is possible that a fairly small amount of ethylene is formed through this type of reaction. The same explanation would hold for 1-butene in which the double bond is in a good position to give ethylene by metathesis.

Recent results obtained by Aika and Lunsford (*4*) showed that methane, ethylene, propene, and butene can be desorbed from the surface of MgO after reaction of O^- with alkenes. The initial reaction step is the abstraction of a hydrogen atom by O^-. On prereduced Mo/SiO_2 we have never observed hydrogen abstraction by O^- under our experimental conditions so we could not use such a mechanism to explain the formation of C_2H_4. This indicates that O^- behaves differently on MgO and Mo/SiO_2 and this difference in reactivity presumably reflects the difference in the bonding of the O^- to the surface which is known from the observed hyperfine interaction with the surface cations.

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