

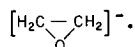
## EPR Study of O<sup>-</sup> Anion Radicals and Their Reaction with Ethylene on WO<sub>3</sub>/SiO<sub>2</sub> Catalyst

V. A. SHVETS, V. B. SAPOZHNIKOV, N. D. CHUVYLKIN,  
AND V. B. KAZANSKY

*N. D. Zelinsky Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow, USSR*

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An EPR spectrum with  $g_{11} = 2.012$ ,  $g_{\perp} = 2.026$ , and  $A_{11}^* = 14.5$  G, observed after N<sub>2</sub>O adsorption on a supported tungsten/silica-gel catalyst, has been assigned to O<sup>-</sup> anion radicals stabilized in the first coordination sphere of the W<sup>6+</sup> ions. The interaction of C<sub>2</sub>H<sub>4</sub> with these O<sup>-</sup> species at 77 K is shown to lead to the formation of C<sub>2</sub>H<sub>4</sub>O<sup>-</sup> radicals which have an EPR spectrum with five hyperfine components ( $A = 25.4$  G) and  $g = 2.003$ . The character of the spectrum and the quantum chemical calculations by the INDO method show that the structure of this radical resembles that of the anion radicals of ethylene oxide



A dissociation of the C<sub>2</sub>H<sub>4</sub>O<sup>-</sup> radicals resulting in the formation of the adsorbed radicals H<sub>2</sub>C=ĊH occurs at 90 K. Their spectrum coincides with that of C<sub>2</sub>H<sub>3</sub> radicals adsorbed on the surface of molybdenum/silica-gel catalyst.

### INTRODUCTION

The formation and reactivity of adsorbed O<sup>-</sup> anion radicals have been studied for only two catalysts containing transition metal ions, namely, V<sub>2</sub>O<sub>5</sub>/SiO<sub>2</sub> (1-3) and MoO<sub>3</sub>/SiO<sub>2</sub> (3-6). The O<sup>-</sup> anion radicals are shown to be very reactive species and in some cases they can react with molecules giving rise to adsorbed intermediate radicals as has been observed for O<sup>-</sup> interacting with ethylene on MoO<sub>3</sub>/SiO<sub>2</sub> (6). The study of the nature of such intermediate radicals is of importance in understanding the mechanism of catalytic oxidation reactions.

In this work we have investigated the formation of O<sup>-</sup> on a supported tungsten-silica-gel catalyst. An interaction of O<sup>-</sup> with ethylene has been also examined.

### EXPERIMENTAL

The supported tungsten/silica-gel samples (4 wt% W) were prepared by impregnation of silica gel ( $S = 300$  m<sup>2</sup> g<sup>-1</sup>) with an aqueous solution of (NH<sub>4</sub>)<sub>2</sub>W<sub>5</sub>O<sub>16</sub>. The samples were dried at 70-80°C and heated in air at 500°C for several hours. They were then treated in 200 Torr of oxygen for 1 h at 500°C, reduced in 300 Torr of hydrogen for 30 min, and evacuated for 1 h at the same temperature.

The adsorption of N<sub>2</sub>O (300 Torr) was carried out at room temperature for 5 min and then the samples were evacuated (10<sup>-5</sup> Torr) for 15 min at the same temperature.

EPR spectra were recorded at liquid nitrogen temperature in the X band.

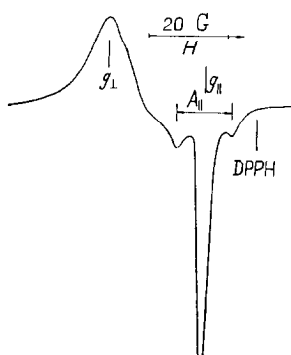


FIG. 1. EPR spectrum of the  $O^-$  anion radical.

### RESULTS AND DISCUSSION

When the samples are reduced their color changes from white to dark blue but no EPR spectra are observed either at liquid nitrogen or at room temperature.  $N_2O$  adsorption at room temperature on such reduced samples gives rise to an EPR spectrum with the parameters:  $g_{11} = 2.012 \pm 0.001$ ,  $g_{\perp} = 2.026 \pm 0.001$ ,  $A_{11}^W = 14.5 \pm 0.5$  G (Fig. 1). The superhyperfine structure is observed due to  $^{183}W$ ,  $I = 0.5$ , the natural abundance being 14%. The shape and parameters of the EPR spectrum are in good agreement with those for the  $O^-$  anion radicals adsorbed on  $MoO_3/SiO_2$  and  $MgO$  and analogously obtained by adsorption of  $N_2O$  (3, 7) as the species in question. These reasons allow us to assign this spectrum to the  $O^-$  anion radicals stabilized in the first coordination sphere of  $W^{6+}$  ions as a result of oxidation of  $W^{5+}$  and, perhaps, lower valance states of tungsten.

It is interesting to note that the  $g_{11}$  value for  $O^-$  adsorbed on  $WO_3/SiO_2$  is considerably larger than the  $g_e$  factor of a free electron. This cannot be explained theoretically on the basis of a purely ionic model for the  $O^-$  anion radicals (8), and, as has been pointed out earlier (9), the partially covalent nature of the bonding of  $O^-$  with the cation has to be taken into account. Support for this conclusion is that the difference between  $g_{11}$  and  $g_e$  for  $O^-$  stabilized on  $Mg^{2+}$ ,  $Mo^{6+}$ , and  $W^{6+}$  ions

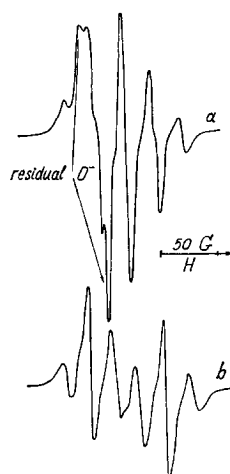


FIG. 2. EPR spectra of (a)  $C_2H_4O^-$  and (b)  $C_2H_3$ .

increases successively with the growth of the spin-orbital coupling constant of the cations, as follows from comparison of their  $g_{11}$  values: 2.0013, 2.006, and 2.012, respectively.

The  $O^-$  anion radicals adsorbed on  $WO_3/SiO_2$  are stable *in vacuo* at room temperature but they react with various molecules both at room temperature and at low temperatures. Adsorption of ethylene at 77 K results in a strong decrease of the EPR spectrum of the  $O^-$  anion radicals and the simultaneous appearance of a new spectrum with  $g = 2.003 \pm 0.001$ . The spectrum consists of five lines with intensity ratio of 1:4:6:4:1 and hyperfine splitting of  $25.4 \pm 0.5$  G (Fig. 2a). When the temperature increases this signal decreases and a second, new signal appears. This spectrum, which can be obtained in pure form at 90 K (Fig. 2b), is a doublet

TABLE I

Isotropic Hyperfine Coupling Constants ( $a$ ) and Charges ( $Q$ ) for the H, C, and O Atoms of the Radical  $C_2H_4O^-$

Structure	$a^H$ (G)	$a^C$ (G)	$a^O$ (G)	$Q^H$	$Q^C$	$Q^O$
I	70.8	186.7	-0.3	-0.20	0.10	-0.40
II	54.9	182.3	-0.5	-0.18	0.03	-0.34
III	-3.0	15.1	-49.7	-0.09	0.02	-0.68

of triplets with a doublet splitting of  $64 \pm 1$  G, a triplet splitting of  $21.5 \pm 0.5$  G, and a  $g$  factor of  $2.004 \pm 0.001$ . The latter signal disappeared at temperatures higher than 150 K without the appearance of any new signals.

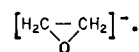
The number of hyperfine components and the ratio of their intensities for the spectrum after the adsorption of ethylene at 77 K provide evidence that the unpaired electron of the radical in question interacts with four equivalent hydrogen atoms. Therefore it is reasonable to assign this radical to a  $\pi$ -type complex of the ethylene molecule with the O<sup>-</sup> anion radical located under the C<sub>2</sub>H<sub>4</sub> plane. To support this conclusion we carried out the quantum chemical calculations by the INDO method (10, 11). Three structures of the  $\pi$  complex were considered: (I) wherein the bond length,  $r_{CC}$ , corresponds to the double C=C bond (1.34 Å) and the interatomic distance  $r_{CO}$  is characteristic of the single C-O bond; (II) wherein  $r_{CC} = 1.52$  Å is typical for the single C-C bond and  $r_{CO}$  is the same as for structure I; (III) wherein  $r_{CC}$  is the same as for I and  $r_{CO}$  is elongated by 15%.

The results of the INDO calculations are summarized in Table I and indicate that the isotropic hyperfine coupling constants are almost independent of the C-C bond length but rather sensitive to the  $r_{CO}$  distance. The quantitative reproduction of the experimental hyperfine coupling constants can be fitted with less than 15% elongation of  $r_{CO}$ .

The spectrum observed after heating the samples to 90 K is identical to the spectrum of H<sub>2</sub>C=ĊH radicals formed on the surface of MoO<sub>3</sub>/SiO<sub>2</sub> catalysts (6, 12) as a result of dissociation of H<sub>2</sub>C-CH<sub>2</sub>O<sup>-</sup> radicals obtained by the interaction of O<sup>-</sup> with ethylene: C<sub>2</sub>H<sub>4</sub>O<sup>-</sup> → OH<sup>-</sup><sub>surf</sub> + C<sub>2</sub>H<sub>3</sub>.

Thus, the dissociation of the primary

radicals formed by the addition of O<sup>-</sup> anion radicals to ethylene molecules leads to the same C<sub>2</sub>H<sub>3</sub> radicals on the surface of both MoO<sub>3</sub>/SiO<sub>2</sub> and WO<sub>3</sub>/SiO<sub>2</sub>. However, the geometrical structures of the primary radicals C<sub>2</sub>H<sub>4</sub>O<sup>-</sup> are different. On the surface of the molybdenum-containing catalyst these species resemble H<sub>2</sub>Ċ-CH<sub>3</sub> radicals (6, 12), whereas on the surface of the tungsten-containing catalyst they may be considered as the anion radicals of ethylene oxide



The capability of O<sup>-</sup> to form the structurally different complexes with C<sub>2</sub>H<sub>4</sub> is, apparently, caused by the difference in the covalent character of the bonding between the O<sup>-</sup> anion radical and the cation of the adsorption center.

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