

Formation of Peroxo Radicals on Tin Dioxide

As previously reported, it is possible to show the formation of peroxo radicals on slightly reduced titanium dioxide and zinc oxide with the ESR method (1). From new experiments it is concluded that similar phenomena occur on tin dioxide. When

oxygen is added to tin dioxide, pretreated during 4 hr at 500°C and under a vacuum of 10^{-3} torr, the ESR spectrum shown in Fig. 1 can be observed. This spectrum is very similar to that obtained with titanium dioxide except for a difference in its temperature dependency. Whereas the TiO_2 signals are strongly dependent on tempera-

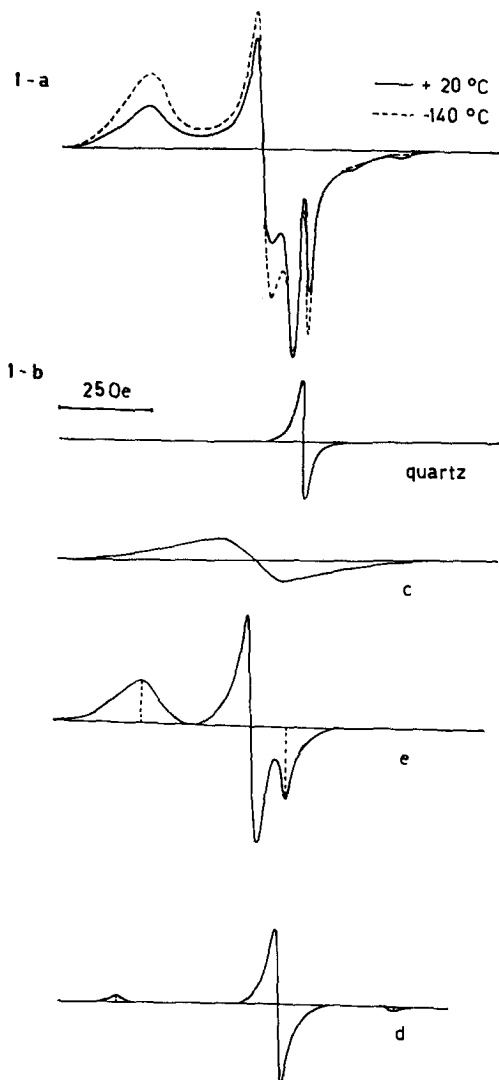


FIG. 1. (a) ESR spectrum as observed on SnO_2 after contacted with O_2 ; O_2 pressure, 3 torr. (b) Separate ESR signals.

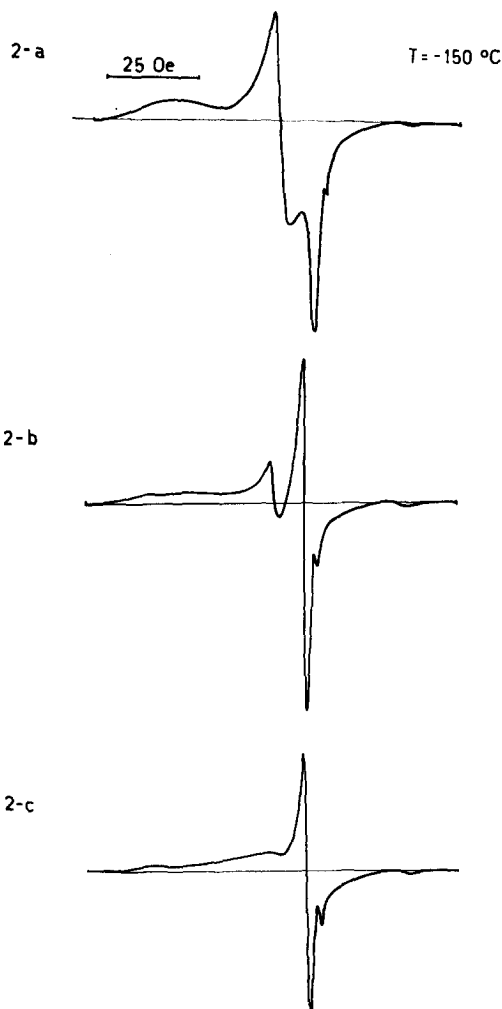


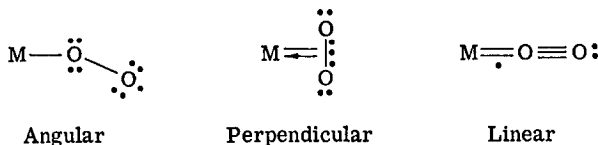
FIG. 2. ESR spectra as observed on SnO_2 after contacted with a mixture of oxygen and 1-butene: a, immediately after addition; b, after 3 hr; c, after 100 hr.

ture, the spectrum obtained from SnO_2 is almost the same at room temperature and at -160°C .

In spite of this difference we would like to interpret these spectra on similar lines.

Three different signals occur simultaneously in the ESR spectrum: Signal c, a broad almost symmetric signal with $g = 2.010$; Signal d, a narrow three g value signal with $g_1 = 2.033$, $g_2 = 2.005$, $g_3 =$

the perpendicular and linear arrangement can only occur with metal ions with empty or partly filled d orbitals. Accordingly Zn^{2+} with the electron configuration $[\text{Ar}] 3d^{10}$ does not show these bonding structures. However, as Sn^{4+} with the electron configuration $[\text{Kr}] 4d^{10}$ did show the signals ascribed to these arrangements, we have to conclude, to outer shell bonding ($5d$ orbitals) in this case.



1.986; Signal e, a narrow three g value signal with $g_1 = 2.029$, $g_2 = 2.010$, $g_3 = 2.004$.

When a mixture of 1-butene and oxygen is added, the three oxygen signals can be observed again. However, Signal e decreases slowly and finally disappears, while Signal d remains nearly unaltered (Fig. 2). This is an additional proof for the correctness of the interpretation of the spectrum.

Each of the signals, c, d, and e, is supposed to correspond with a special form of adsorbed molecular oxygen. Signal c corresponds with the linear, Signal d with the perpendicular, and Signal e with the angular arrangement. As explained in ref. (1)

It is further interesting that butene addition removed the signal assigned to a species that is similar to a radical in the classical sense, i.e., with a single electron in an atomic orbital.

REFERENCE

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A Relationship between Infrared Frequencies of Adsorbed Carbon Monoxide and Metal Electron Population

As part of a wider investigation a study has been made of the perturbation of vibrational frequency of the carbon monoxide molecule following adsorption as "linear carbonyl" on face-centered cubic transition metals. A rather uniform increase in frequency with increase in electronic specific heat constant γ_{el} of the bulk metal was noted. That the two properties are genuinely

interdependent is suggested by expressing observed frequencies as the valence-electron content $E(\text{CO})$ of the adsorbed carbon monoxide species using the formula of Gardner and Petrucci (1). $E(\text{CO})$ is clearly integral for gaseous forms of carbon monoxide but may be nonintegral for adsorbed species. Figure 1 shows that a reasonably linear relationship (not previously re-