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# NOTES

## Anionic Intermediates in Surface Processes Leading to $O_2^-$ Formation on Magnesium Oxide

The formation of $O_2^-$ at oxide surfaces is well authenticated by ESR studies (*1*, *2*). The simplest mechanism which can be invoked is a direct electron transfer from the oxide to an adsorbed oxygen molecule. However, there is an alternative pathway to $O_2^-$ formation on basic oxides which involves the production of $O_2^-$ through the agency of presorbed species. The aim of this Note is to examine the existing evidence for $O_2^-$ formation on MgO, to present some new results in which ESR and uv reflectance spectra have been jointly studied, and to advance a general mechanism for the formation of $O_2^-$ via electron transfer from presorbed species.

ESR studies have shown that $O_2^-$ ions will not form directly when oxygen is contacted with MgO [although they will form if the MgO has first been artificially activated by irradiation (*3*, *4*)]. However, Iizuka and Tanabe (*5*, *6*) made the intriguing discovery that $O_2^-$ ions can be readily produced on normal MgO if pyridine is first presorbed. It is now known that pyridine similarly sensitizes $O_2^-$ formation on CaO and SrO (*6–9*). The presorption of pyridine generates an ESR signal per se, and this has been assigned to the dipyridyl anion radical (*5*, *6*, *9*): in the case of SrO, Coluccia *et al.* have demonstrated by spin counting that $O_2^-$ ions are formed directly at the expense of the dipyridyl radical anions (*9*). Recently it has been shown that presorption of hydrogen, ethylene, and CO is also effective in sensitizing MgO towards $O_2^-$ formation (*10*, *11*). The effect of hydrogen probably accounts for a previous report that $O_2^-$ can be formed on MgO without prior irradiation (*12*).

It has been suggested by Che *et al.* (*8*) in connection with the pyridine work that the original source of the $O_2^-$ electron in the MgO is a surface $O^{2-}$ ion in low coordination; the uv spectra of finely divided MgO (*13*) provide evidence for the surface states of such ions. With regard to hydrogen sensitization, Cordischi *et al.* (*11*) consider the active center in the MgO to be a pair of adjacent surface $O^-$ ions, on to which homolytic dissociation of $H_2$ occurs. No proposals have been made as yet for the cases of sensitization by CO or ethylene.

In our studies we have confirmed this previous work on sensitization by presorption and have extended the subject by examining the effect on $O_2$ adsorption of presorbing propene, but-1-ene, and acetylene. These molecules have the merit that they give relatively simple uv spectra in the chemisorbed state on MgO, so one can study the system both by ESR and by diffuse reflectance. This has enabled a closer insight to be gained of the mechanism of $O_2^-$ formation.

In contrast to pyridine, no ESR signal is developed when well-outgassed MgO is contacted at room temperature with propene or but-1-ene. Subsequent exposure to $O_2$, however, immediately produces a strong ESR spectrum characteristic of $O_2^-$ (Fig. 1). The result with acetylene is identical in respect of $O_2^-$ formation: the only distinction with the olefin case is that prolonged contact of acetylene with the virgin outgassed MgO does produce in this case a slowly growing symmetric ESR signal near $g = g_e$.

As regards uv spectra, it is appropriate to mention acetylene first, since the result has already been published (*13*). On dosing acetylene to outgassed MgO, the uv reflectance measurements show conclusively that an initial rapid chemisorption

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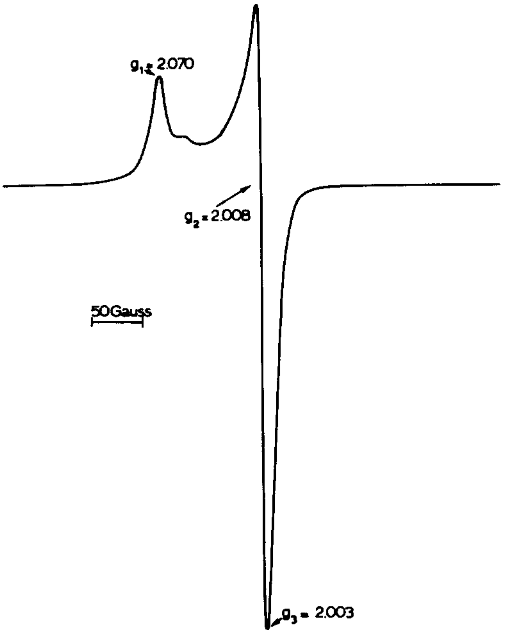

FIG. 1. ESR spectrum of $O_2^-$ on MgO which had been outgassed at 800°C, contacted with propene at 20°C and then with oxygen. Spectrum recorded at X-band frequency and room temperature using a Varian E-3 spectrometer.

takes place, followed by a slow process generating broad uv absorption. The spectrum was interpreted (*13*) as heterolytic dissociation of the C–H bond, leading to surface acetylide and hydroxyls. The slow process is polymerization of acetylene residues. Heterolytic dissociative chemisorption of acetylene on MgO has recently been confirmed by ir spectroscopy (*14*). The uv diffuse reflectance spectra of propene and but-1-ene chemisorbed on MgO have not previously been reported, and these are now shown in Fig. 2. The experimental setup was the same as that described earlier (*13, 15*). The solid curve is the fluorescence-quenched background spectrum of MgO; the bands at 46,000 $cm^{-1}$ and the shoulder at 36,000 $cm^{-1}$ are due to surface states, as discussed elsewhere (*15*). Both propene and but-1-ene are seen to give two bands at 26,000 and 34,000 $cm^{-1}$, respectively, along with some erosion of the surface spectrum of the oxide. This establishes that, notwithstanding the absence of an ESR spectrum (see above), the gases are certainly *chemisorbed* (and not merely physically adsorbed): the parent olefins do not absorb in this region of the spectrum. A discussion of the results in Fig. 2 will be given elsewhere (*16*). For the present the main point to be emphasized is that we consider the bands at 26,000 and 34,000 $cm^{-1}$ to be due to n − π* transitions in adsorbed allyl anions (methyl-allyl in the case of but-1-ene), formed as a result of heterolytic dissociation of C–H bonds at the basic MgO surface:

$$RCH_2{-}CH{=}CH_2 \rightarrow [RCH{\cdots}CH{\cdots}CH_2]^- + H^+$$

Allyl anions, allyl radicals, and allyl cations can be expected to have n − π absorptions at similar energies; the (unadsorbed) allyl cation absorbs at 36,600 $cm^{-1}$ (*17*). Assignment of the bands as allyl anions is entirely in accord with the fact that alkaline earth oxides catalyze olefin isomerization by an allyl carbanion mechanism (*18*).

The common feature in the adsorption of acetylene, propene, and butene is therefore the formation of carbanions and protons,

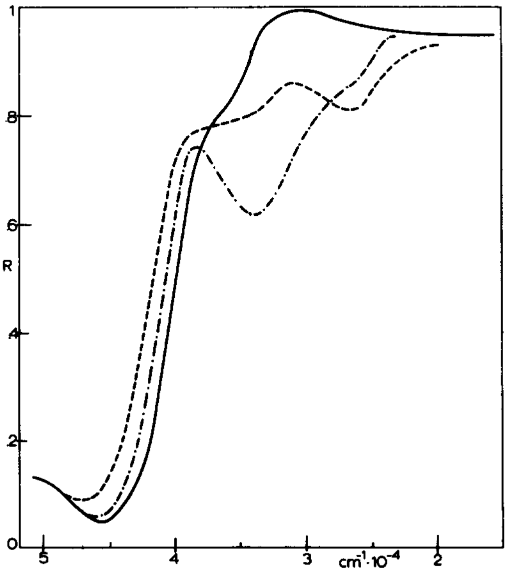

FIG. 2. uv reflectance spectrum of 800°C outgassed MgO before and after contact with propene or butene at 20°C. ———, MgO reference spectrum (15); -·-·-·-·, MgO plus propene at 10 Torr pressure; --------, MgO plus butene at 10 Torr pressure.

the latter forming surface hydroxyls with the coordinatively unsaturated (cus) surface $O^{2-}$ ions:

$$XH \rightarrow X^- + H^+ \quad (1)$$

$$O^{2-}_{cus} + H^+ \rightarrow OH_s^- \quad (2)$$

We consider that the carbanion $X^-$ will be unstable toward molecular oxygen. This is a well-known feature of carbanions in homogeneous solution chemisty (e.g., Grignard reagent chemistry), where the accepted reaction scheme (*19*) is the formation of the radical $X^{\cdot}$ and production of X–O–O–X, followed in most cases by further oxidation. We propose an analogous sequence for the carbanions adsorbed on the surface of MgO. The first step will be:

$$X^- + O_2 \rightarrow X^{\cdot} + O_2^- \quad (3)$$

In contrast to the solution chemistry case, the superoxide ion $O_2^-$ will be stabilized by the basic oxide surface. The hydrocarbon radical, on the other hand, is unstable and will react with molecular oxygen in a second step:

$$2X^{\cdot} + O_2 \rightarrow X\text{–}O\text{–}O\text{–}X \quad (4)$$

and so to further oxidation.

The above mechanism accounts for the formation of $O_2^-$ *without the need for electron transfer from the solid or from a preexisting radical.* The source of the electron on the superoxide ion is the heterolytic reaction accompanying chemisorption of the molecule XH on the basic surface. This is the reaction which sensitizes formation of $O_2^-$.

If the molecule XH has a large enough electron affinity, say comparable to that of $O_2$, it is likely that it will itself engage in an electron transfer reaction with the carbanion $X^-$:

$$X^- + XH \rightarrow X^{\cdot} + XH^- \quad (5)$$

followed by

$$2X^{\cdot} \rightarrow X\text{–}X \quad (6)$$

Note that, in addition to the dimerization product, there is the formation of the anion radical $XH^-$. This anion radical is formed, as with $O_2^-$, *without any electron transfer from the solid.* The dimer X–X can also react with $X^-$:

$$X^- + X\text{–}X \rightarrow X^{\cdot} + X\text{–}X^- \quad (7)$$

followed again by Reaction (6). The dimer can also react with $XH^-$:

$$XH^- + X\text{–}X \rightarrow XH + X\text{–}X^- \quad (8)$$

$X\text{–}X^-$ will be another anion radical, and in principle capable of reacting with $O_2$ [as in Reaction (3)] to produce $O_2^-$.

These reaction schemes are general and afford an understanding of surface processes on MgO without invoking electron donor properties in the oxide. We are inclined to think that the electron donor properties of MgO (and other alkaline earth oxides) may have been overemphasized in the past. Certainly the schemes we have outlined satisfactorily explain the features of adsorption and oxidation of many molecules. An oxide does not necessarily have to be directly involved in an electron transfer step to produce adsorbed ion radicals detected by ESR.

Pyridine is an example of a molecule with a high electron affinity which can accordingly give the dimerization (and probably trimerization, etc.) reactions generalized as Reactions (*5*)–(*7*) above. An ESR signal is therefore produced when MgO is exposed to pyridine. Propene and but-1-ene, on the other hand, are molecules which do not undergo these successive reactions at room temperature on MgO. Thus no anion radical species $XH^-$ or $X\text{–}X^-$ are formed upon chemisorption and no ESR signal results, as we have found. In the case of acetylene, the slowness with which the ESR spectrum develops strongly suggests that electrons are transferred from acetylide anions only to adsorbed polymeric species [which take time to form, as the uv spectra (*13*) show] rather than to monomer acetylene by Reaction (5). The absence of hyperfine structure in the ESR spectrum from acetylene is in agreement with this.

Returning to $O_2^-$ production, we now remark on the effect of presorbing $H_2$, $C_2H_4$, and CO. All these molecules sensitize $O_2^-$ formation on MgO. The effect of hydrogen can be interpreted as the trivial case of Reaction (1), where X = H, and $O_2^-$ is formed by electron transfer from an adsorbed hydride ion $H^-$. However, in this case (and in the CO case mentioned below), Reaction (4) is probably inadequate to describe the fate of $X^•$ radicals. Considering the basic nature of MgO, $H^•$ can be expected to undergo the reaction

$$H^• + O_2(g) + O^{2-}_{cus} \rightarrow OH_S^- + O_2^- \quad (9)$$

The ethylene case can be seen as a heterolytic chemisorption yielding the vinyl anion, followed by Reaction (3). It may be recalled that isotopic exchange of deuterium with ethylene will occur over alkaline earth oxides, and the reaction has been explained by a mechanism involving heterolytic adsorption of ethylene (*20*). The low electron affinity of $C_2H_4$ (cf. propene) satisfactorily explains why Indovina and Cordischi (*10*) did not observe an ESR signal until $O_2$ was admitted.

The CO case deserves special comment. Spectroscopic work (*21, 22*) has established that CO forms carbanion dimers and polymers $[(CO)_n{}^{x-}]$ when chemisorbed on MgO. The $(CO)_n{}^{x-}$ species with $n > 4$ are conjugated and are reactive to oxygen (*13, 22*); we regard them as the source of the electrons for formation of $O_2^-$ by electron transfer. The mechanism for formation (*21*) of $(CO)_n{}^{x-}$ is:

$$x\, O^{2-}_{cus} + \left(n + \frac{x}{2}\right) CO \rightarrow (CO)_n{}^{x-} + \frac{x}{2} CO_3{}^{2-} \quad (10)$$

Reaction (10) is then the analog of the reaction

$$O^{2-}_{cus} + 2XH \rightarrow XH^- + \tfrac{1}{2}X\text{–}X + OH_s^- \quad (11)$$

obtained by combining Reactions (1), (2), (5), and (6). The CO and XH reactions are therefore similar in that the molecules undergo mutual oxidation and reduction, accompanied by dimerization (polymerization) and radical formation. One may say that whereas in Reaction (11) MgO is behaving as a Brønsted base, in Reaction (10) it is behaving rather as a Lewis base. Indeed, the analog of Reaction (5), with XH replaced by CO, could account for the slow development of the ESR signal known to occur when CO is contacted with MgO (*23–25*).

It follows that there is a general theme here, namely, that the role of MgO in all these examples of $O_2^-$ formation and self-reaction of XH and CO is to act as a base. The electron donor property of MgO, while having merit as a description for some purposes, should be regarded as subordinate to this more general tenet.

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