The Reaction of Hydrogen Atoms at Oxide Surfaces

By D. R. SMITH and A. J. TENCH*

(*Chemistry Division, Atomic Energy Research Establishment, Harwell, Berks*)

THE recombination of atoms at oxide surfaces has been studied,[1] but little attention has been paid to the possibility of observing the reactions of atoms with the surface itself. The best known example of such a reaction is the appearance of a blue colour when MoO_3 is exposed to a stream of hydrogen atoms. This colour reaction has been used to measure the rates of hydrogen-atom reactions, and a similar effect has been reported with WO_3.[2] Hydrogen-atom reactions with the matrix may play a significant role in some catalytic processes and a study of these reactions with oxides and with molecules adsorbed on oxides could give useful information on mechanisms. Recent work[3] has shown that surface paramagnetic defects can be studied at low concentrations (0·01—1% of surface sites) by e.s.r. Application of this technique to the study of the γ-irradiation of high surface area MgO in the presence of hydrogen has led to the detection of stable excess electron centres (S_H) on the surface; these defects have been well characterised.[4] We show that similar defects on the surface are also produced when MgO powder is exposed to a stream of hydrogen atoms. However, if an organic compound is first adsorbed on the surface and the powder is then exposed to hydrogen atoms, characteristic organic free radicals can be observed.

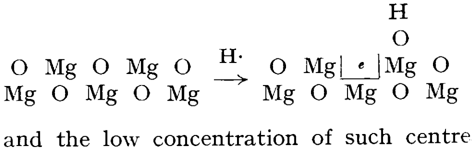
MgO was prepared as described[3] to give a material of specific surface area *ca.* 20 m.^{2}/g., and was degassed at 900°. The hydrogen atoms were produced in a 2·45 GHz microwave discharge. Optimum experimental conditions were obtained in separate measurements by monitoring the atom flow with an e.s.r. spectrometer. Photolytic effects were eliminated by the use of Pyrex tubing with a Woods horn before the reaction chamber; the experimental technique will be fully described elsewhere.[5]

When the MgO powder was exposed to the hydrogen atom stream at room temperature it turned blue within two or three seconds, and was then sealed into a side-arm for e.s.r. examination. The spectra obtained at 77°K showed a strong single anisotropic line with a minor doublet splitting of 11 G. After warming to 300°K for 24 hr. about 50% of the signal was lost; on cooling again the resolution increased and a doublet of 2 G splitting was observed. A similar run with deuterium atoms showed that these splittings arise from interaction with a nearby proton. A comparison with the results obtained on the γ-irradiated MgO/H_2 system[4] indicates that an S_H centre, *i.e.* an electron trapped at a surface anion vacancy with a nearby hydrogen nucleus, is formed. This was confirmed by the observation of a low-intensity six-line hyperfine splitting from $^{25}Mg^{2+}$ ($I = \frac{5}{2}$) ions in the lattice. The blue solid was found to react at once on exposure to oxygen and the new paramagnetic species formed was identified as O_2^{-}.[6]

The formation of these centres is unusual, since MgO is normally a stable stoicheiometric compound and cannot easily be reduced in hydrogen. It appears that the hydrogen atoms must be reacting with the oxygen ions of the lattice to release electrons which are subsequently trapped at surface oxygen ion vacancies created by reaction (1).

$$H\cdot + O^{2-} \rightarrow OH^{-} + e^{-} \qquad (1)$$

Schematically this can be written for a {100} surface as follows:



$$\begin{array}{c} \text{O Mg O Mg O} \\ \text{Mg O Mg O Mg} \end{array} \xrightarrow{H\cdot} \begin{array}{c} \text{H} \\ \text{O} \\ \text{O Mg}|\underline{\;e\;}|\text{Mg O} \\ \text{Mg O Mg O Mg} \end{array}$$

and the low concentration of such centres after

γ-irradiation of the material *in vacuo* indicates that the normal concentration of surface vacancies is certainly small, and the reaction must create new traps. These centres are known to be extremely reactive and in many situations they may be a short-lived intermediate stage. Alternatively, in some matrices, reduction of the metal ion might be favoured.

A comparison of the reactions of both the S_H centres and H atoms was made by adsorbing approximately one monolayer of degassed methyl alcohol on the surface of the MgO. In one experiment the powder was exposed to H atoms for a few seconds and then cooled to 77°K and observed at this temperature. The e.s.r. spectrum observed was a triplet with a mean splitting of $\alpha_{iso} = 16 \cdot 6$ G and an intensity ratio close to 1 : 2 : 1, indicating the interaction of two protons. The most likely reaction is the abstraction of hydrogen from the methyl groups to leave a methylene species, and this agrees with the e.s.r. data. The exact form of methyl alcohol on the MgO surface is not known, but preliminary i.r. studies[7] indicate the formation of methoxy-groups, which suggests that $(\cdot CH_2O)^-$ radicals are formed on the surface by reaction (2).

$$(MeO)^-Mg^{2+} + H\cdot \rightarrow (\cdot CH_2O)^-Mg^{2+} + H_2 \qquad (2)$$

An anisotropy of the $M_I = \pm 1$ lines is observed and can be interpreted in terms of a restricted rotational freedom of the methylene group on the surface. An identical e.s.r. triplet was formed by the addition of methanol to the S_H centre and the blue powder was decolourised immediately, presumably by reaction (3).

$$e^- + MeOH \rightarrow (\cdot CH_2O)^- + H_2 \qquad (3)$$

In this instance the radical is trapped at a surface oxygen ion vacancy and, as expected, has a greater thermal stability than radicals formed by reaction (2). Preliminary work on other alcohols indicates that the H atom and the S_H centre can react in different ways to give different products.

(*Received, June 24th*, 1968; *Com.* 826.)

---

[1] B. A. Thrush, *Progr. Reaction Kinetics*, 1965, **3**, 63.

[2] T. H. Johnson, *J. Franklin. Inst.*, 1929, **207**, 629; H. W. Melville and J. C. Robb, *Proc. Roy. Soc.*, 1949, *A***196**, 445.

[3] R. L. Nelson and A. J. Tench, *J. Chem. Phys.*, 1964, **40**, 2736; R. L. Nelson, A. J. Tench, and B. J. Harmsworth, *Trans. Faraday Soc.*, 1967, **63**, 1427.

[4] A. J. Tench and R. L. Nelson, *J. Colloid Interface Sci.*, 1968, **26**, 364.

[5] D. R. Smith and A. J. Tench, to be published.

[6] A. J. Tench and P. Holroyd, *Chem. Comm.*, 1968, 471.

[7] J. F. J. Kibblewhite and A. J. Tench, private communication.