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On the Redox Properties of Certain Oxide Surfaces

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This study gives details of the ESR effects observed when quinhydrone and hydroquinone/*p*-benzoquinone mixtures of varying composition ratio are adsorbed on high surface-area samples of silica-alumina, γ-alumina, magnesium oxide, and zinc oxide. The purpose is to test the hypothesis that in considering the phenomena of radical formation on surfaces that posses both electron donor and electron acceptor sites, it is necessary to explicitly take into account an indirect cooperative interaction between the donor and acceptor sites in analyzing the data. The correctness of the hypothesis is demonstrated and the implications thereof as concerns the currently used method to determine redox site density on these types of oxide surfaces is briefly considered. Preliminary data are provided on the donor and acceptor site density on the four materials listed above as determined by the quinhydrone method.

INTRODUCTION

If a surface exhibits both electron donor (nucleophilic) and electron acceptor (electrophilic) sites, then in principle the properties it exhibits are not simply the totality of those intrinsic to the two types of sites acting independently, but rather additional effects and complications are to be expected due to the nucleophilic and electrophilic sites acting, in a sense, indirectly and cooperatively.

The point involved is perhaps best explained by using an example. Consider perylene (P) adsorbed on an oxide surface that possesses both electrophilic (E) and nucleophilic (N) sites. Then the oxidation reaction $P + E = P^{\dot{+}} + E^-$ gives rise to the presence of a strong *oxidizing* agent on the surface (P^+) which could then presumably react with nucleophilic sites: $P^{\dot{+}} + N = P + N^+$. The *net* effect then is the *indirect* reaction $E + N = E^- + N^+$. Clearly if as in common procedure, perylene is used to measure the surface density of electrophilic sites by measuring the integrated ESR intensity of the perylene radical ion ($P^{\dot{+}}$) generated, then the numerical value obtained would be in error to the extent that the indirect reaction between sites occurs.

For a variety of reasons we were led to conjecture that these indirect reactions are of importance in understanding the surface properties when both donor and acceptor sites are present. Hence it is the purpose of this note to develop this hypothesis in a preliminary mathematical form and also to offer an initial experimental test of its general validity when applied to the redox phenomena observed on certain oxide surfaces.

On initial viewing there seems to be two conditions necessary for this hypothesis to be valid in real circumstances. First it must be assumed that *direct* redox interactions of the form $E + N = E^- + N^+$

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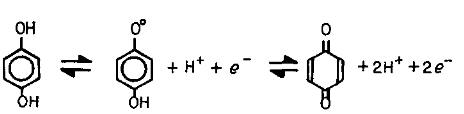
cannot occur over the temperature range of interest. Such reactions must occur, for example, when the surface is "activated" by a thermal treatment wherein the surface structure is modified. But for our purposes we simply assume that the sites are fixed in the surface in the sense that diffusion effects which would lead to these direct redox effects are slow compared to the rate of diffusion of reacting hydrocarbon species which lead to the indirect effects.

The fact that these reacting species are free to diffuse on the surface and thereby establish the equilibrium thermodynamic concentrations in the product distribution is the second (assumed) condition (*1*). That this is a reasonable condition to impose seems apparent from studies of rotational diffusion (*2*) and chemical exchange effects on silica-alumina (*3*). In this preliminary study we neglect questions concerning the effect of the distribution in the strength of the surface redox sites (*1*) as well as activity corrections to any thermodynamic equilibrium constants considered.

Our general approach is to study the quinhydrone equilibrium, long used to determine pH indirectly through redox effects (*4*), on a series of different oxide surfaces: silica-alumina, γ-alumina, magnesium oxide, and zinc oxide. The equilibrium, which is between the two components hydroquinone (H_2Q) and *p*-benzoquinone (Q), involves a paramagnetic species, a semiquinone ($HQ^{\cdot}$), as an intermediate (*5*). The last named species can be observed by the ESR method. The relation between the species H_2Q, HQ, and Q can be summarized as follows:



The use of quinones to study surface interactions is not new (*6, 7*). Indeed such reagents were used in what apparently was the first report of a surface-generated radical (*8*). However we believe that the present treatment has not been given before.

To develop the equations involved, consider a specific case: Suppose H_2Q is added to an oxide known to contain both types of surface sites. The first steps in establishing equilibrium involve the reactions:

$$H_2Q + E = HQ^{\cdot} + H^+ + E^- \quad (1)$$

$$HQ^{\cdot} + E = Q + H^+ + E^- \quad (2)$$

The Q formed in the second reaction can undergo further "side-reactions" (*9*) with the nucleophilic sites:

$$Q + H^+ + N = HQ^{\cdot} + N^+ \quad (3)$$

$$HQ^{\cdot} + H^+ + N = H_2Q + N^+ \quad (4)$$

We describe each of these equilibria by an equilibrium constant, $K_1, \ldots, K_4$, where the subscript denotes the chemical reaction as numbered above. For example, $K_1 = [HQ^{\cdot}][H^+][E^-]/[H_2Q][E]$. Note that the concentrations of the species occurring in the expressions for the K_i are those on the surface, not in the supernatant liquid.

To proceed, consider a mass balance (C) on the various quinone species present, i.e., $C = [H_2Q] + [HQ] + [Q]$. Then the fraction (α) of the total present as the semiquinone, $\alpha = [HQ^{\cdot}]/C$, is simply the relative integrated ESR intensity and:

$$\alpha^{-1} = 1 + [H_2Q]/[HQ^{\cdot}] + [Q]/[HQ^{\cdot}]$$

which, by using the definitions of the K_i's, can be written:

$$\begin{aligned}\alpha^{-1} = 1 &+ K_4[H^+][N]/[N^+] \\ &+ (K_3[H^+][N]/[N^+])^{-1} \\ &+ K_2[E]/[E^-][H^+] \\ &\quad + (K_1[E]/[E^-][H^+])^{-1} \quad (5)\end{aligned}$$

Implicit in the derivation of these equations is the assumption, mentioned above, that there is no direct interaction between the N and E sites.

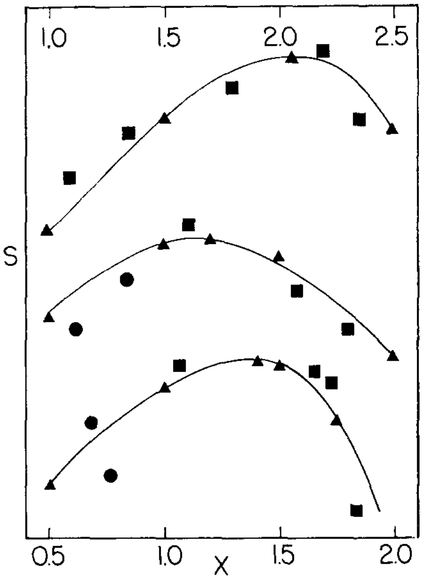


FIG. 1. Plot of S versus X for γ-alumina (top), MgO (center), and silica-alumina (bottom). For the alumina data, the scale for the abscissa and ordinate is that at the top and right side of the figure's border. The scales shown in the lower left corner are for the remaining two types of samples. Legend: Triangles, data points obtained with premixed solutions of H_2Q/Q of composition indicated; circles and squares, data points obtained by adding H_2Q and Q respectively to equilibrated samples of known S values.

Note two facts concerning this expression. First it is symmetric in the K_i's. Thus although the derivation began by considering only H_2Q to be initially present, the same result would be obtained if the reaction started with Q, or indeed with a mixture of H_2Q and Q. Thus the expression is quite general in this sense.

However, second, it is restricted in the sense that it is assumed that the intermediate is $HQ^{\cdot}$. Actually one should consider further possible *acid–base* reactions, e.g., $HQ^{\cdot} = H^+ + Q^{\overline{\cdot}}$ (radical anion formation) or $HQ^{\cdot} + H^+ = H_2Q^{\dot{+}}$ (radical cation formation). The consideration of these additional side reactions would introduce slight changes in the mathematical expression derived. In a complete analysis the effect would necessarily have to be included. As will be seen below, it appears that in certain cases, the radical cation (*10*) is the actual paramagnetic species observed.

To put the mathematical expression in a more useful form for comparison with experiment, we again make use of the definitions of the K_i's to obtain after some algebra:

$$\alpha^{-1} = 1 + 2(K_4[H_2Q]/K_3[Q])^{\frac{1}{2}} + 2(K_2[Q]/K_1[H_2Q])^{\frac{1}{2}} \quad (6)$$

If we assume the ratio $[H_2Q]/[Q]$ to be a continuous variable in the mathematical sense, then the maximum value of α occurs when

$$[H_2Q]/[Q] = (K_2K_3/K_1K_4)^{\frac{1}{2}} \quad (7)$$

a result readily obtained by differentiation. We use these relationships to determine if indeed the hypothesis concerning an equilibrium on the surface between the various species is correct and also to obtain a semi-quantitative comparison of the redox strength of the various oxide surfaces under investigation.

METHODS

The ESR spectra were recorded on a Varian E-12 spectrometer equipped with a Varian V-4531 cavity operating in the T_{102} mode. Second-derivative spectra were recorded using the double modulation method (*11*), the modulation frequencies being 100 and 1 kHz. Integrated ESR intensity data were made by the comparison method (*12*) using a ruby chip positioned within the cavity, the resulting first-derivative data being numerically integrated twice to obtain the final result.

The ZnO and MgO were obtained from commercial sources and were pretreated by hydrolyzing and extruding into pellets (*13*). The γ-alumina used was prepared from a Catapal SB commercial catalyst while the silica-alumina was the Aerocat AAA version containing 25% Al_2O_3. All four types of samples were activated by heating to 500°C for 16 hr in a stream of oxygen. The estimated surface areas (BET nitrogen) were 10, 210, 230, and 290 m^2/g for ZnO, MgO, alumina, and silica-alumina, respectively.

The organic reagents used were from commercial sources and were recrystallized prior to use (*14*). "Spectroscopic grade" benzene was used without further purification as the solvent in all work reported here.

All samples were prepared by mixing solutions of known concentrations of H_2Q, Q, or quinhydrone with catalyst samples (as prepared above) in large bore (8-mm-i.d.) quartz ESR sample tubes. The large bore tubes were used to facilitate the mixing process and thereby permit the recording of ESR spectra within 1 to 2 min after the components were joined.

For spin concentration measurements, the sample size ($\sim$0.05 g) was chosen to be small to ensure that all of the solid was within the active volume of the microwave cavity (*12*). Because of the small sample size, the limited solubility of quinhydrone and hydroquinone in benzene caused no experimental difficulties.

RESULTS

As formulated, the quantity of concern is the ratio $[H_2Q]/[Q]$ where the concentrations indicated are those established at equilibrium on the surface. Clearly as such they are not easily measured. To proceed we introduce the assumption that, at the higher concentration levels as defined below, the surface concentration is proportional to the solution concentration; i.e., we assume that over the concentration range of interest, the absorption isotherm is approximately linear.

In actual fact we have observed that the integrated ESR intensity is indeed a linear function of solution concentration in the case of MgO up to the point when exchange-narrowing of the hyperfine lines first become observable (see below). Thus there is some experimental justification for the assumption.

If we define proportionality constants δ_{H_2Q} and δ_Q relating surface to solution concentration, then Eq. (7) becomes

$$\begin{aligned} X &= ([H_2Q]/[Q])_{\text{solution}} \\ &= (\delta_Q/\delta_{H_2Q})(K_2K_3/K_1K_4)^{\frac{1}{2}} \qquad (8) \end{aligned}$$

which serves to define the independent variable X.

Further, since all of the integrated intensity measurements are made with reference to the spin concentration (C_r) of the ruby standard mounted within the cavity, we define

$$S = [HQ]/C_r = \alpha C/C_r \qquad (9)$$

as a convenient form for the dependent variable.

If the hypothesis concerning equilibrium-type interactions between the species present [i.e., Eqs. (1–4)] is correct, a plot of S versus X should show a peak at some particular value of X. As shown in Fig. 1, such is indeed the observed behavior for MgO, alumina, and silica-alumina. The value of the abscissa at each of the peak positions ($X_{\max}$) is tabulated in Table 1.

TABLE 1

Summary of Experimental Results

	$X_{\max}$	$[E]/C_r$	$[N]/C_r$	ΔH_{H_2Q}	ΔH_Q
Silica-alumina	1.4	0.31	1.39	8.3	8.8
γ-Al_2O_3	2.1	4×10^{-3}	2.04	7.5	8.0
MgO	1.1	0.81	1.21	7.5	8.5
ZnO	$\sim$1	$>2 \times 10^{-5}$	$>3 \times 10^{-3}$	—	—

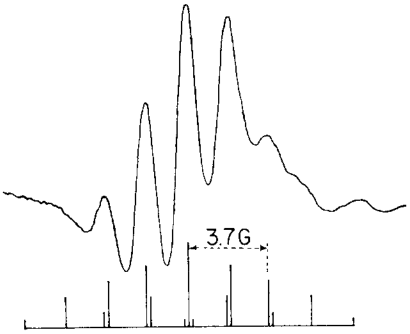


FIG. 2. Second-derivative presentation of the ESR spectrum of $p - C_6H_4(OH)_2^+$ radical ion generated by the addition of H_2Q to MgO. The stick spectrum is drawn using the values of the proton coupling constants listed in the text.

Although an approximate value for ZnO is also included in the table, the "curve" is not shown in Fig. 1 for reproducible data for low and high values of S were not obtained.

The lack of reproducibility involves an apparent change in the value of S as a function of time. With the other three types of samples, the value of S changed slowly after initial mixing but then became sensibly constant after a time interval (*15*) and remained so for periods of at least several hours. We take this time interval as that required for the system to attain chemical equilibrium, the length of the interval being a crude measure of surface diffusion effects.

With ZnO no stable period was attained in measurements continued for periods up to 4.5 hr. The matter may be related to the low surface area of the sample which limited the radical concentration and hence the sensitivity, or the cause may be a secondary chemical reaction rendering incomplete the description of the system by chemical Eqs. (1–4).

In the case of MgO, silica-alumina, and γ-alumina, that these three types of systems eventually reach an equilibrium state as specified by chemical Eqs. (1–4) seems demonstrated by the following results. After a given sample was prepared and its S value determined, an additional known amount of H_2Q or Q was added and then, after a suitable time interval (*15*), a second measurement of the S value was made. If the interaction among the species on the surface is properly described by Eqs. (1–4), the second value obtained should fall (within experimental error) on the same S vs X curve as determined from the data on the samples as initially prepared. However the second value for a given sample should be laterally displaced from the first S value by an amount determined by the change in the parameter X. Such is indeed the observed result (cf. Fig. 1).

This initial time-varying behavior of S can be made use of in another way. If it is assumed that immediately after mixing a sample of H_2Q with an oxide, that surface diffusion is rate limiting the attainment of chemical equilibrium and hence only chemical Eq. (1) need be considered, then the value of S obtained at this time is a direct measure of the concentration of surface electrophilic sites. In analogous fashion, by starting with Q alone, the initial value of S corresponds to the nucleophilic site concentration if the interpretation of the cause of the time-dependent phenomena is correct.

The data based on this reasoning are also included in Table 1. The concentrations are expressed in units per unit surface area of sample relative to the ruby spin concentration (i.e., S divided by surface area in units of m^2/g). So normalized, the data for the different types of samples can be compared directly.

In obtaining this data care was taken to ensure that the solution concentration was sufficiently high that there was a large excess of H_2Q (or Q) present over that required to saturate the surface. Under these conditions an exchanged-narrowed ESR spectrum or a superposition of two such spectra were obtained. This is an interesting phenomena which can, under certain conditions, provide useful information (*16*). The matter is not of concern for present purposes; hence we simply provide in the table for future reference the distance (units: gauss) between the inflection points in the first-derivative presentation (ΔH).

Of present concern is the analysis of the hyperfine spectra observed in the absence of exchanging-narrowing. Such a spectrum is shown in Fig. 2. The spectrum can be analyzed as arising from a pair of protons with a coupling constant of 3.7 G further split by an interaction with four equivalent protons with coupling constants of 2.2 G. The spectrum of the hydroquinone radical cation, i.e., $p - C_6H_4(OH)_2^+$, generated in sulfuric acid (*10*) has essentially the same spectrum, the corresponding coupling constants being 3.44 and 2.36 G. Hence we take such to be the species present also on the surface. For additional proof of the correctness of this assignment, we note that the same spectrum is obtained whether the starting reagent is H_2Q, Q, or quinhydrone, provided that sufficient time has elapsed to permit chemical equilibrium to be attained and the starting concentration of material is sufficiently low so that the hyperfine splittings are resolved. Under these conditions, the same spectrum (Fig. 2) is obtained whether MgO, alumina, or silica-alumina is the surface in use. To date we have been unsuccessful in attempts to obtain a resolved hyperfine spectrum on the ZnO surface.

DISCUSSION

The primary objective in undertaking this work was to test the hypothesis that a complete description of the redox behavior of these particular types of oxide surfaces necessarily involves the notion of a chemical equilibrium in which both acceptor and donor sites are involved. It appears that this hypothesis is correct in that the data presented graphically in Fig. 1 illustrate the validity of Eq. (7) at least in an approximate sense.

It is true that assumptions were made concerning the nature of the adsorption isotherm and that the identification of the paramagnetic species present as a radical cation (Fig. 2) indicates that Eqs. (1–4) must be modified to include acid–base side reactions on the redox interactions. Yet further analysis shows that inclusion of these effects, along with a correction for a distribution in the strength of the redox sites (*1*), merely serves to modify the numerical values of the K_i's and hence does not invalidate the general formalism as developed.

In summary it appears that the "indirect" interaction between donor and acceptor sites through hydrocarbon intermediaries is an important factor in understanding effects observed with the ESR method in this type of system. Thus it appears that many of the conclusions based on ESR work which neglects the effects of the interaction, require reexamination.

Throughout this paper we have used, in noncommittal fashion, the terms *electrophilic* and *nucleophilic* agents since the formalism presented is, in fact, quite general. It is a macroscopic (thermodynamic) rather than a microscopic (molecular) model in the sense described by Morrison (*17*). The difference observed in the behavior of the various oxides studied would then presumably reflect differences in the properties of the double layer at the interface (*17, 18*). In this regard it is quite satisfying that the results obtained with three of the four systems studied exhibit parallel behavior as well as the same paramagnetic intermediate. We take this to indicate the basic correctness of the model as formulated.

The physical content of Eq. (7) is readily understood on the basis of a mass-action effect. Thus large H_2Q and Q concentrations "force" chemical Eqs. (1) and (3) to the right and Eqs. (2) and (4) to the left thereby increasing the concentration of $HQ^{\cdot}$ and hence the ESR signal intensity. The optimum value of the concentration ratio ($X_{\max}$) is then expected to be *of the order of* unity if $K_1 \simeq K_3$ and $K_2 \simeq K_4$ as is experimentally observed. From a knowledge of $X_{\max}$ alone, however, clearly the values of the individual K_i's cannot be inferred.

The validity of the assumption concerning the use of the ESR intensity immediately after mixing H_2Q or Q with the sample as a measure of the surface concentration of the E and N sites, respectively, although quite reasonable, cannot be rigorously established at present. The unusually low value for the surface density of the E sites on γ-Al_2O_3 relative to that on MgO and silica-alumina (cf. Table 1) may be a real effect or may simply indicate that K_1 on this surface is quite small.

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