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On the Electron Donor and Electron Acceptor Properties of the γ-Alumina Surface

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Direct spectroscopic evidence is presented that it is the radical anion, not the radical cation of perylene that is generated on the surface of a suitably prepared γ-alumina surface. The implications of this result as concerns the nature of the donor and acceptor sites on this surface are developed. A model involving cooperative interaction between the two types of redox sites, similar to that proposed by Pines for acid–base sites on this surface, is developed to explain the chemistry of aromatic hydrocarbons adsorbed on this form of alumina.

INTRODUCTION

When appropriate conditions of pretreatment are used, an alumina surface exhibits chemical properties that have been shown to derive from certain of its surface sites acting as electron acceptors while others behave as electron donors. Under favorable circumstances examples can be found in which both the acceptor and donor processes are observed to operate simultaneously.

The first observation of this redox effect and the experimental evidence demonstrating the correctness of the interpretation was given in a series of papers by Flockhart and co-workers (*1*, *2*). Their initial work was done with gibbsite, γ-alumina, and η-alumina, but later they observed the same phenomena, to a varying degree, in silica-alumina (1e) and certain zeolites (*3*).

The principal experimental observation concerning the phenomena centers on the fact that it is possible to obtain superimposed ESR spectra from both trinitrobenzene (TNB) and perylene when a catalyst sample is exposed simultaneous or consecutively to both reagents. TNB is known to be a strong electron acceptor while perylene is *assumed* to act as an electron donor. Hence the surface reaction to provide two different paramagnetic species presumably reflects the presence of both donor and acceptor sites in the surface (*4*).

Other investigators (*5*) have used the phenothiazine/tetracyanoethylene system in this type of study and in later work Flockhart *et al.* have considered the use of the iodine/iodide couple in this regard (*6a*), as well as the use of aromatic amines to study the donor sites alone (*6b*). In our laboratory we have found quinhydrone to be similarly applicable to the study of donor–acceptor surface properties.

Our interest in this general question of surface redox sites stems from recent work concerning electron transfer effects (*7*) and ion-pair formation (*8*) on a silica-alumina surface. In this work, a variety of aromatic radical cations, including that of perylene, were known to possess considerable mobility on the surface (*9*), the product distribution

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being quantitatively described in terms of a redox equilibrium (*10*).

Given this surface mobility and tendency toward chemical equilibrium among the species on a silica-alumina surface, we were led to conjecture concerning the nature of an alumina surface that would permit, according to the Flockhart–Pink interpretation, a positive radical cation to exist simultaneously, and in close proximity to, a negative radical anion without the mutual annihilation of the two species. Such annihilation reactions are well known and have been thoroughly studied (*11*).

The requirement that the species exist in close proximity to each other is a hypothesis introduced (*2*) to explain another observation concerning the ESR spectra obtained in these systems. Namely, the measured total integrated intensity of the spectrum obtained when perylene and TNB are both present on the surface is greater than the sum of the intensities obtained when each reagent alone is available to the surface. In the following we refer to this curious and interesting phenomena as the "intensity enhancement effect."

A final point that piqued our interest in the general questions involved is that, as classified by Szwarc (*12*), perylene is a powerful electron *acceptor* and much of the chemistry of perylene is understood on the basis of this fact (*12, 13*). Thus one wonders why perylene, perhaps if only in the absence of TNB, is not reduced at the donor sites (as is TNB) to give a radical *anion* product.

In the following we present the results of our study of these questions as concerns the donor/acceptor phenomena on γ-alumina. In particular we provide direct spectroscopic evidence that it is the perylene radical *anion*, not the *cation*, that is formed on the surface. The implications of this result as concerns the surface reactions are then developed.

We emphasize that, although we discount evidence concerning the nature of acceptor sites on γ-alumina based on reported observations of the perylene radical *cation* on this surface, it is our position that such acceptor sites are indeed present and involved in the *reduction* reactions observed.

Also we note that our remarks concern only γ-alumina pretreated as detailed below. Since sample preparation, in particular the dehydration temperature, has a marked effect on the radical-forming characteristics of the surface (*1*), care in extrapolating our results to cover other types of samples and treatment schemes is certainly warranted.

EXPERIMENTAL

The ESR spectra were recorded on a Varian E-12 spectrometer, usually in the first derivative mode with a field modulation frequency of 100 kHz. Second derivative spectra were obtained using the double modulation scheme (*14*), the modulation frequencies being 100 and 1 kHz. Integrated ESR intensities were obtained by the comparison method (*15*), using a ruby internal standard.

The reagent used were purified by suitable recrystallization prior to use. "Spectroscopic grade" benzene, previously equilibrated with a sample of the alumina catalyst, was used as a solvent in all the experiments reported here.

The catalyst sample used was a Catapal SB alumina, a trademark designation of the Continental Oil Company for an α-alumina (Boehmite). It was activated according to the manufacturer's directions (*16*), i.e., 3 hr in air at 900°F (482°C), to convert to the γ-alumina form. The surface area (nitrogen BET) was estimated to be ~230 m^2/g. Samples to be prepared in the absence of oxygen were identically activated except that the treatment was performed *in vacuo*.

RESULTS

If only incompletely resolved ESR spectra are available, the use of this method to distinguish between the presence of the

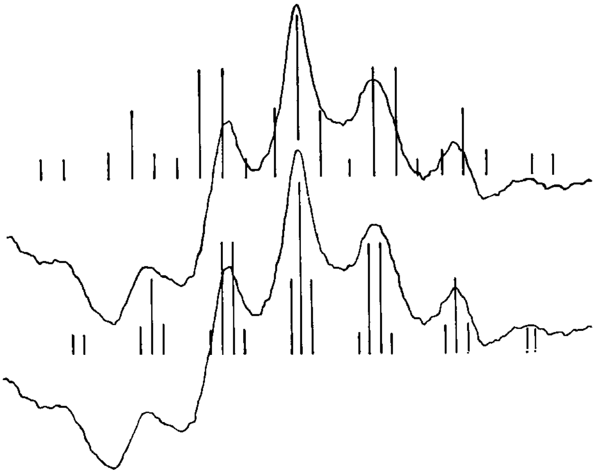

FIG. 1. Second-derivative presentation of the ESR spectrum of perylene adsorbed on alumina with "stick" spectra superimposed. The top spectrum corresponds to the radical cation system, the bottom to that of the radical anion.

radical cation versus the radical anion of perylene requires special care for the hyperfine constants of the two species are remarkably similar. Thus, in solution, the hyperfine coupling constants for the three nonequivalent protons are 4.10, 3.10, and 0.46 G for the radical cation and 3.53, 3.08, and 0.46 G for the radical anion (*17*).

This similarity in the corresponding values is readily understood in terms of the General Pairing Theorem for alternant hydrocarbons (*18*). This theorem also predicts, and experiment verifies (19), that the radical cation and anion species are expected to exhibit essentially the same electronic absorption spectra. Thus the observed color of a sample containing one of these species is not easily used to distinguish between the presence of anion and cation radicals.

In prior work with silica-alumina (*9*), it was shown that line-sharpening techniques (*20*) can be usefully applied to obtain an unequivocal identification of the paramagnetic species present. When this instrumental technique is applied in the case of the perylene–alumina system of present interest, the results (Fig. 1) clearly show that the experimental spectrum is more closely fit by the radical anion hyperfine values than those for the radical cation. The small shifts expected in the coupling constants due to surface interactions (*21*) are not of sufficient magnitude to noticeably improve the agreement between the radical cation "stick" spectrum and the experimental version.

The same perylene radical anion spectrum is obtained whether TNB is present on the surface before the perylene is added, or the TNB is added after the perylene has interacted with the surface. This is an important observation and much care was taken in the experiments that were used to establish the result.

Note that the closeness in magnitude of the two larger coupling constants in the anion species relative to the values in the radical cation readily explain the observation (*2*) that the ESR spectrum obtained exhibits poorer resolution when the perylene paramagnetic product is generated on alumina than when generated on silica-alumina (cf. Fig. 2). The difference in resolution is to be attributed to the difference in the species present.

The generation of hydrocarbon radical anions rather than cations on the alumina surface is also independently demonstrated by using 9,10-dimethylanthracene (DMA), which like perylene is known to be an electron acceptor (*12*). DMA is particularly useful in this regard for the larger difference (*22*) in the methyl proton hyperfine coupling constants in the anion and cation radicals, 3.88 versus 8.0 G, respectively (*17*), eliminates the difficulty of having to resolve small line splittings.

The theoretical spectrum is quite complex (*8*), there being 41 lines with an intensity equal to at least 20% that of the central line. Yet as seen in Fig. 3, the dominant splitting is 3.8G for the highest intensity lines, as expected if the radical anion is present. The resolved DMA spectrum is observed only if TNB is also present. In the absence of TNB, only a single narrow line is observed (Fig. 3) indicating exchange effects, a behavior quite distinct from that exhibited by perylene.

As concerns the intensity enhancement effect, our results verify those reported (*2*) to the extent that the *total* integrated intensity in the TNB-plus-perylene case is approximately 10% greater than the sum of the integrated intensities when TNB and perylene are each alone present on the surface and the surface is saturated in its capacity to generate radicals. Thus there is a large discrepancy between our value and the factor-of-two value (for TNB intensity enhancement) reported (*2*).

The difference may simply be due to difference in sample properties, e.g., ours had a 35% greater surface area, for the discrepancy seems to be too large to be attributed to errors in intensity measurements (*15*), troublesome as these may be in the presence instance where three separate double integrations are required for each determination of the enhancement factor.

Also as concerns the intensity enhancement effect, we offer three additional observations. First, we found that the magnitude of the enhancement depends critically and in a nonlinear fashion on the concentration of perylene and TNB in the supernatant liquid (*23*). Second, if perylene is replaced in the supernatant liquid with an equivalent number of moles of durene or naphathalene, one obtains approximately the same intensity enhancement in the TNB spectrum intensity. (Neither durene nor naphthalene give paramagnetic products when adsorbed on alumina.) Third, when viewed in second-derivative presentation, there is a small but readily perceptible broadening of the perylene lines and narrowing of the TNB lines as the concentration of perylene/TNB is raised in the supernatant liquid.

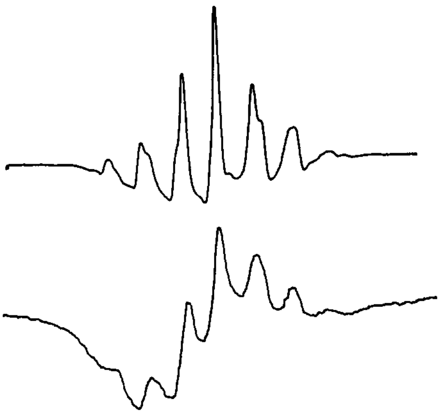

FIG. 2. Comparison of the ESR spectra (second-derivative presentation) of the perylene radical cation generated on silica-alumina (top) and that of the perylene radical anion generated on alumina (bottom).

The first two observations indicate that the intensity enhancement effect may simply arise from nonlinearities in the absorption isotherm while the third point indicates the presence of electron-transfer between perylene and TNB radical species. Of course the dependence of the radical concentration on the solution concentration necessarily implies an "equilibrium" between the various species present, both on the surface and in solution.

The electron-transfer interaction noted above is also readily demonstrated by

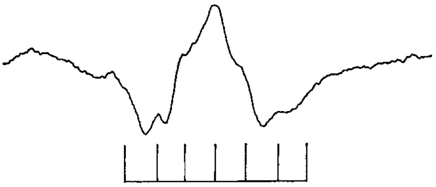

Fig. 3. Second-derivative presentation of the ESR spectrum of the DMA radical anion generated on alumina in the presence of TNB. The interval between the lines in the stick spectrum is 3.8 G.

adding a third species, in particular an electron acceptor, to the system. We have found *p*-benzoquinone (pBQ) in this regard. When added to samples containing perylene or TNB alone or to a sample containing both perylene and TNB, strong electron exchange narrowing effects are observed (cf. Fig. 4) although the total integrated intensity of a given sample is unchanged by the addition of pBQ. Interestingly the addition of the conjugate electron donor, hydroquinone, has quite a negligible effect on the intensity and hyperfine resolution of the adsorbed perylene and/or TNB species. This behavior of pBQ may be taken as additional evidence that both TNB and perylene are present as anion radicals.

As a part of our work we also confirmed the report (*2*) that oxygen must be present in the system for the perylene hyperfine spectrum to be observed. However we were unable to demonstrate that in the absence of oxygen, the presence of perylene still gives rise to an intensity enhancement of the TNB spectrum (*2*). With our samples, the effect (if real) is of the same order of magnitude as the experimental error in the intensity measurements.

DISCUSSION

The experimental results demonstrate that, whether TNB is present or not, it is the perylene radical anion rather than the radical cation that is the reaction product on the "oxygen-treated" alumina surface. Thus it remains to explain the other observations in view of the presence of a negative, rather than a positive perylene species as assumed by Flockhart and coworkers (*1*, *2*). Central to our thinking in this regard is the possible significance of the surface mobility of, chemical equilibria between, and ion-pair formation among the various species present, all taken in view of the known redox chemistry of the perylene molecule.

First note that given that both the perylene and TNB radicals are negatively charged removes one concern that initially prompted this work. Namely, there is no need to postulate special features of the alumina surface that permits positive and negative radical hydrocarbon species to exist in close proximity to each other and yet whose only manifestation of an interaction is an induced effect transmitted through the surface giving rise to an intensity enhancement effect.

From a spectrum simulation scheme (*7*) we estimate that the surface mobility of the perylene radical species on the alumina surface is comparable to that on silica-alumina and only two orders of magnitude (correlation time $\sim 10^{-9}$ sec) below that found in solution. Given this mobility, if the perylene species was a radical cation, interaction with the TNB radical anion would be

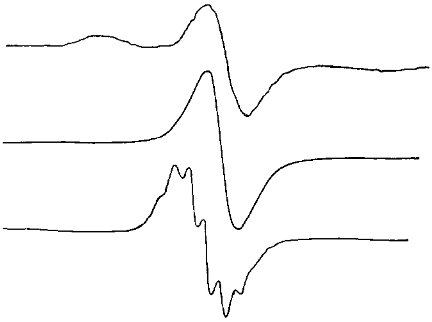

Fig. 4. First-derivative ESR spectra of TNB (bottom) and perylene (top) radical anions generated on alumina. The center spectrum is that obtained when pBQ is added to the samples corresponding to either the top or bottom spectra. The width of the exchanged-narrowed center spectrum depends on the concentration of the species present.

expected to have a pronounced effect on the ESR spectra of both species (*24*), even, if for some unknown reason, mutual annihilation (*11*) did not occur.

As concerns the chemistry of the perylene molecule, the presence of radical anions on oxygen-exposed alumina and radical cations on suitably treated silica-alumina also readily explains another observation (*2*). Namely that, using suitable techniques, perylene can be desorbed from silica-alumina in essentially a quantitative fashion and is chemically unchanged, while, in the alumina case, a wide variety of oxidized products, e.g., peroxides, quinones, etc., (*2*) are obtained rather than the perylene molecule per se.

Such a behavior on alumina is quite consistent with the well-known propensity of carbanions to react with oxygen (*13*). On the other hand, perylene radical cations as formed on silica-alumina not only require the presence of oxygen for their formation but also apparently are stable for extended periods in the presence of excess oxygen without chemical degradation (*25*).

The requirement that oxygen be available for the perylene ESR spectrum to develop was presumably one of the reasons (*2*) that it was assumed that the radical cation was present on the alumina surface also. Clearly, given that it is radical anion present, the explanation of the "oxygen effect" is to be found elsewhere.

In the absence of oxygen, the adsorbed perylene species presumably is diamagnetic (*26*). If this species was simply a neutral perylene molecule, perhaps chemisorbed, it would be difficult to understand the lack of formation of a radical *cation* upon subsequent exposure to oxygen. The other possible diamagnetic species that occur to us are a spin-paired dimer of perylene radical anions and a dinegative perylene ion. The existence of both of these species has been amply demonstrated in various solution-phase studies (*12*, *27*).

If the hypothetical dimer was known to possess an electronic absorption spectrum sufficiently different from the neutral molecule and the dinegative ion (*19*), then optical spectroscopy presumably could settle the identity of the diamagnetic species present. At present, facilities to undertake such work are not available to us. Hence in the following we simply offer, in brief fashion, comments concerning several of the questions involved.

First note that the formation of the radical anion must necessarily be an initial step prior to the formation of dimers or dinegative perylene species. The oxygen effect is then a "secondary" reaction not occurring as a part of the radical ion formation. Thus in our proposal, the initial reduction reaction of perylene exactly parallels that of TNB, certainly an attractive feature.

Yet ion-pair effects are known to depend critically on solvent acidity, molecular conformation, etc. (*27*), and such would readily explain the subsequent difference in behavior of perylene relative to that of TNB. The latter "stops" at the radical anion stage because it forms a particularly strong ion-pair with a nucleophilic surface site as evidenced by an anisotropic hyperfine interaction with a *single* nitrogen (of the three available); such stabilizes the radical anion form (*28*). With perylene, such particular interactions are not possible, the electron distribution being rather uniform over the ring systems (*29*).

The "oxygen effect" is then readily explained by subsequent reaction of the dimer or dinegative ion by the general mechanism (*13*), well-established in solution-phase studies, giving the ubiquitous superoxide ion (O_2^-). Thus for the dinegative ion, a *simple oxidation* reaction occurs (P = perylene): $P^{=} + O_2 = P^{\dot{-}} + O_2^-$.

Actually to our thinking, the presence of a spin-paired dimer is more difficult to understand for such would require isolation at a pair of essentially adjacent nucleophilic surface sites. It seems too much to expect that these sites occur in pairs in sufficient numbers to accommodate *all* of the adsorbed perylene. Also, although spin-paired diamagnetic ion-pairs are known (*30*), a more common situation involves paramagnetic dimers (*31*), such species also being observed in hydrocarbon systems adsorbed on silica (*32*) and certain zeolites (*33*).

But actually the difference between dimers and dinegative ions may be simply a matter of chemical equilibrium. Thus we usually consider the negative ion formed by a two step reduction. (N = nucleophilic surface site):

$$\mathrm{P} + \mathrm{N} = \mathrm{P}^{\cdot-} + \mathrm{N}^{+}$$

$$\mathrm{P}^{\cdot-} + \mathrm{N} = \mathrm{P}^{=} + \mathrm{N}^{+}$$

But the evidence (*27*) is that in ion-pair systems, the disproportionation reaction reaction is the important step (*34*):

$$2\,\mathrm{P}^{\cdot-} = \mathrm{P} + \mathrm{P}^{=}$$

the driving force being a large entropy increase rather than the lowering of the energy of the system (*12*, *27*).

And this brings us to our final observation concerning the questions involved. On a surface that provides *both* donor *and* acceptor sites, an addition mechanism to drive the disproportionation reaction, and not available in solution, must also be considered (E = electrophilic surface site):

$$\mathrm{P}^{\cdot-} + \mathrm{E} = \mathrm{P} + \mathrm{E}^{-}$$

$$\mathrm{P}^{\cdot-} + \mathrm{E}^{-} = \mathrm{P}^{=} + \mathrm{E}$$

The sum of these two reactions is the disproportionation reaction; this is our point. One now has a *cooperative* interaction between the donor sites to form the radical anion and the acceptor sites, *in effect*, to reduce further the anion to the dinegative ion (*35*).

It is clear that for this mechanism to be effective, the hydrocarbon species must possess considerable surface mobility while the donor and acceptor sites must be sensibly "fixed" in the surface. If the latter were also mobile they would necessarily be expected to be involved in a separate, internal, and independent redox equilibrium (*36*) and only the net difference, i.e., donor or acceptor, would be observed. Such is the situation in solution.

As concerns the "clustering" (*8*), ion-pair, and dimerization effects on the surface, we note that such a phenomena have been the subject of independent studies involving hydrocarbons (*37*) and even oxygen (*38*) adsorbed on alumina.

In considering the postulated cooperative effects between donor and acceptor sites, one is immediately struck by the similarity here proposed for redox effects with that proposed by Pines and Manassen (*39*) for cooperative acid–base effects on alumina as exhibited in certain dehydration reactions. It seems that a general mathematical formalism including both redox and acid–base effects can be constructed (*10*).

The perylene–TNB system seems inappropriate for an experimental test of the ideas involved since only reduction processes are indirectly observable while acid–base effects are difficult to discern. Thus we have undertaken a study of the question using quinhydrone as the "model" system. The results of the study are to be submitted separately.

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