JOURNAL OF CATALYSIS 61, 293–295 (1980)

Radical Anions/Cations and the γ-Alumina Surface: A Reply to Flockhart and Pink

The demonstration by Flockhart, Pink, and co-workers (*1*) that when suitably prepared, certain oxide materials can possess simultaneously both electron donor and electron acceptor sites is to be recognized as a major contribution to the understanding of the redox chemistry of these systems. In the solution phase, such a combination of donors and acceptors would possess sufficient mobility to allow them to react with each other, the product distribution then being predicted from the usual free energy considerations. When immobilized on a surface, this *direct* donor–acceptor reaction is not possible and new and interesting effects may be expected due to selective and perhaps consecutive reactions involving reagents adsorbed on the surface.

As an example of a "consecutive" reaction, consider an added reagent that reacts at a donor site to form a radical anion, said species then being free to diffuse to, and react with, an acceptor site. The *net* effect then is simply a transfer of an electron from a donor site to an acceptor site, i.e., an *indirect* reaction equivalent to the direct donor–acceptor reaction noted above for the solution phase; an ESR measurement of the radical anion concentration would give a null result.

Thus the first point we wish to make: if surface diffusion is possible in the system to be considered, a measurement of the integrated ESR intensity may not, in itself, give a valid measure of the redox surface site density.

A second point follows from the first. Some reagents used in past studies of surface redox properties, e.g., perylene, are known to be able to act as either electron donors or electron acceptors depending on the other features of the chemistry of the system (*2*). If such a reagent is added to a surface that contains both donor and acceptor sites, one should expect *both* radical cations and radical anions will be formed on the surface. Further if these species possess sufficient mobility, one must expect that they will react (annihilate) with each other and that the final product distribution will reflect the nature of the interactions and the mobilities of the species present in the system. Again, unless considerable care is exercised in analyzing the results, ESR data may lead to unfounded conclusions.

In a recent publication (*3*) we gave an approximate quantitative formulation of these ideas along with the results of an experimental test of their validity.

In the preceding letter (*4*), Flockhart and Pink outline their views on the conclusions given in a second publication (*2*) dealing specifically with the perylene–alumina system. Our reading of their comments is that, in this system at least, they discount the possible significance of the two points developed above. In particular, it seems that they hold that perylene can react *only* at acceptor sites (to form a radical cation) and having so reacted, remains sensibly bound to the site executing only a "molecular tumbling at the particular site"; possible consecutive reactions occasioned by surface diffusion are unlikely given "the size and shape of the perylenium ion."

Our analysis of the observed ESR linewidth effects using computer-simulation techniques in this and related systems (*2, 5*) leads to the opposite conclusion: the radical ion formed possesses a considerable degree

0021-9517/80/010293-03$02.00/0
Copyright © 1980 by Academic Press, Inc.
All rights of reproduction in any form reserved.

of freedom as concerns a rotational-diffusion motion and this motion is sensibly *isotropic* with respect to the surface, the size and shape of the (probably solvated) ion not withstanding. But such a motion necessarily implies that there is no preferred direction along any of the molecular axes for a specific "bonding" interaction which would constrain the ion to remain bound to the surface site. The "bonding" is isotropic, i.e., electrostatic, of the type expected in ion-pair systems. And, "contact" ion pairs excepted, such structures readily and commonly admit considerable separation of the two components by rotational diffusion (*6*).

The presence of contact ion pairs is readily recognized by the appearance of superhyperfine lines or distinctive linewidth effect in the ESR spectrum (*6*). A quite appropriate example of the situation would be that noted by Flockhart and Pink (*4*) involving the appearance of ^{27}Al lines in the perylene ion spectrum on a specially prepared surface. Here the ESR spectrum is isotropic (*7*) and hence the *entire* complex (i.e., perylene + Al) must be executing an isotropic motion with respect to the surface. Such superhyperfine effects are absent in the perylene–alumina spectrum.

As an example of a system in which, in our view, a specific interaction of a radical ion with a surface site exists and hence the effect of surface diffusion of the ion can be properly discounted, we cite the trinitrobenzene (TNB) radical anion generated on alumina as noted by Flockhart and Pink (*4*). In this case the ESR spectrum exhibits strong anisotropic effects because of the specific interaction of *one* of the nitrogens (of the three present in TNB) with the surface site and thereby prevents motional averaging of the g-tensor interaction.

In our view the evidence on the matter of surface diffusion effects in another system cited by Flockhart and Pink (*4*) is less clear. The ESR spectrum of the radical ion of certain amines generated on alumina is a single structureless line of width comparable to that expected in a system undergoing spin exchange. This exchange mechanism, which involves the rapid transfer of the electron between the radical ion and adjacent diamagnetic species (perhaps physically adsorbed molecules), is a truly powerful mechanism for diffusion of the spin across the surface. We have observed and reported on the phenomena in a number of systems (*2, 5, 8*). But in the absence of appropriate data on this particular system, we must reserve comment.

If, in the perylene–alumina system, it is held that the radical ion formed on the surface possesses considerable mobility, then in our view it is self-evident that interactions between sites and between adsorbed species must be considered in interpreting the experimental results. Note that in addition to redox reactions, a proper treatment of the problem would require the inclusion of possible acid–base reactions (*9*) at Bronsted sites among the interactions to be considered. In the perylene case, such is a complicated task and it is for this reason that we chose a different reagent in our general study (*3*) of the problem.

In principle, if the equilibrium constants of all the major interactions in the perylene–alumina system were known, the product distribution could be calculated. Such data are not available; thus we can only note that our evidence indicates that the *net* reaction of perylene on alumina is such to produce predominantly the radical anion while on silica–alumina the radical cation is the dominant product. Our views, based as they are on the notion of the establishment of equilibrium between all of the species on and "in" the surface, certainly admit that other products may be present and indeed such is the evidence from studies using, for example, optical spectroscopy. The ESR technique permits observation of only the paramagnetic products and further, the broad-line spectra obtained, relative to that obtained in low-viscosity solution-phase work, permit only the dominant paramagnetic species to be observed.

The evidence for the presence of the perylene radical anion on the alumina surface rather than the radical cation as held by Flockhart and Pink (*4*) consists of three independent parts. The discussion given in Ref. (*2*) should be consulted for details. Also described therein is the spin exchange effects observed when both perylene and TNB are present on the surface and "competition for the (surface) sites" (*4*).

One final point deserves mention. It is most likely a poor approximation to assume implicitly as above that all of the surface sites have the same redox strength. If the strength distribution is sufficiently broad, then two different reagents chosen to measure the site density may give widely different results if the reagents themselves differ greatly in their tendency toward oxidation/reduction. Such a situation clearly complicates the calculation of a product distribution. This general problem has been previously noted in work on the silica–alumina system (*9*). Thus we agree with Flockhart and Pink (*4*) that our results for the donor site density on alumina may be too low and we noted such in our published report (*2*).

REFERENCES

1. Flockhart, B. D., Mollan, P. A. F., and Pink, R. C., *J. Chem. Soc. Faraday Trans. 1* **71**, 1192 (1975), and reference cited therein.
2. Muha, G. M., *J. Catal.* **58**, 470 (1979).
3. Muha, G. M., *J. Catal.* **58**, 478 (1979).
4. Flockhart, B. D., and Pink, R. C., *J. Catal.* **61**, 291 (1980).
5. Muha, G. M., *J. Chem. Phys.* **67**, 4840 (1977); *J. Phys. Chem.* **82**, 1843 (1978).
6. Sommerdijk, J. L., and de Boer, E., *in* "Ions and Ion Pairs in Organic Reactions" (M. Szware, Ed.), Chap. 8. Wiley, New York, 1974.
7. Garrett, B. R. T., Leith, I. R., and Rooney, J. J., *Chem. Commun.*, 222 (1969).
8. Muha, G. M., *J. Phys. Chem.* **71**, 640 (1967); **74**, 787 (1970).
9. Muha, G. M., *J. Phys. Chem.* **74**, 2939 (1970).

G. M. MUHA

Department of Chemistry
Rutgers University
New Brunswick, New Jersey 08903

Received August 27, 1979