EPR Studies of Charge-Transfer Adsorption on Group VIII Metal Oxides

The "self-activation" of platinum oxide by organic compounds has already been reported (*1*). The advantages of the technique have been evaluated for exchange reactions between organic substrates and isotopic water (*2–5*). A charge-transfer theory (π-complex adsorption) has been proposed to account for the observed reactivities in these exchange reactions (*2, 6*) with prereduced platinum catalysts.

We now wish to report EPR evidence for charge-transfer complex formation in the adsorption of aromatic molecules on platinum oxide ($PtO_2 \cdot 2H_2O$). The observed paramagnetic resonance is attributed to a low-lying, thermally populated, triplet state of the complex (*7*) for which the term *diradicaloid* has been suggested (*8*). EPR spectra have previously been observed with catalysts other than platinum oxide (*9*) but these were attributed to radical-ion formation.

EPR spectra are observed when platinum oxide is mixed with a wide variety of organic solids and liquids; however, no paramagnetism has been detected under similar conditions with other Group VIII transition metal oxides ($RuO_2 \cdot H_2O$, RuO_2, Rh_2O_3, $IrO_2 \cdot 2H_2O$) with the possible exception of PdO. As an example of the facility with which spectra may be obtained, a signal in excess of 10^{17} spins occurs when platinum oxide (20 mg) is dispersed in an equal volume of powdered anthracene, merely by shaking for 1 min at room temperature.

The crystalline compounds in Group I (Table 1) readily yield broad unresolved spectra ($g = 2.0$) at room temperature under the above conditions, whereas Group II give detectable signals only on heating. If the EPR tubes are evacuated to 5×10^{-3} mm, signal intensity is reversibly increased and is accompanied by narrowing of the spectrum; thus oxygen at the surface appears to contribute to broadening. To date, no fine line structure has been observed over a wide range of conditions (tempera-

TABLE 1
EPR Spectra from Organic PtO_2 Interactions

Group	Compound	Temperature necessary for signal in solid mixtures (°C)	Energy of highest occupied MO[a] (M_m)	Relative signal intensity in solution (spins/mg PtO_2)
I	Diphenylamine	25	—	—
	Phenylene diamine	25	—	—
	Triphenylamine	25	—	—
	Pyrene	25	0.445	1×10^{17}
	Anthracene	25	0.414	3×10^{16}
	Chrysene	25	0.520	2.9×10^{16}
	Phenanthrene	25	0.605	1.7×10^{16}
	Naphthacene	25	—	1.2×10^{16}
II	Biphenyl	50[c]	0.704	5×10^{15}
	Naphthalene	50[c]	0.618	5×10^{15}
	o-Terphenyl	50[c]	—	—

[a] Reference *15*.

[b] Signal observed 72 hr after benzene added to an equivolume solid mixture organic/PtO_2.

[c] Signal observed within approximately 30 min at this temperature.

ture —196°C to 200°C, microwave power 5 mw–0.5 mw, dilution with inert solids or with solvents).

Signal intensity is also a function of the organic particle size and of the platinum oxide–organic compound ratio. Results indicate that at high oxide/reagent ratios, the relative surface contact areas as a function of particle size are important. At low oxide ratios, the substrate acts as a diluent. With Group I compounds, the intense resonance obtained almost instantaneously after mixing is not an equilibrium value but increases with time, substantially approaching equilibrium within several hours. This time dependence may involve diffusion of the solid organic component to various adsorption sites. This conclusion is consistent with the sudden increase, up to sixfold, in signal intensity when solvent is added. However, the solvent may also assist charge transfer, or the increase may merely reflect oxygen or water displacement from the surface.

A marked increase in spin concentration which occurs at elevated temperatures (threefold for anthracene at 200°C) suggests the formation of new active catalytic sites. An explanation for this phenomenon may be found in semiconductor treatments of adsorption (*10*); however, the importance of the state of hydration of the oxide should not be neglected.

The effect of solvent on the EPR spectra is interesting since the immediate increase in signal intensity when benzene is added to an equal volume of premixed PtO_2–solid organic is followed by (i) an initial rapid drop in intensity of about 50% over a period of minutes and (ii) a slow decline which occurs over several days, although a substantially constant level is reached within a few hours.

The relative signal intensity for a series of polycyclic aromatics in benzene solution is shown in Table 1. The reported values were obtained after 72 hr; however, the observed trends in signal intensity were maintained at all stages of the organic catalyst interaction. Preliminary data indicate the absence of a simple correlation between the energy of the highest occupied molecular orbital and relative signal intensity. This result suggests that charge-transfer adsorption on platinum oxide may be governed by additional factors other than the ionization potential of the organic and electron affinity of the catalyst. The exceptionally intense signal obtained with pyrene, the most symmetrical molecule studied, indicates that orbital symmetry may be of importance.

TABLE 2

EPR SPECTRA FOR LIQUID ORGANIC/PtO_2 INTERACTIONS

Compound	Temperature necessary for signal (°C)	Relative signal intensity[a]	Time at temperature for signal to appear (hrs)
Isopropyl benzene	70	1	1
cis-Stilbene	100	1.4	2
Mesitylene	70	2.8	1
t-Butyl benzene	70	3.6	1
m-Xylene	70	4.6	1
Tetralin	70	15.0	1
Ethyl benzene	70	21.4	1

[a] Estimated 2 hr after commencement of heating. However, it should be noted that relative intensities vary with time.

By contrast with the crystalline compounds (Table 1), the liquids (Table 2) yield much lower over-all spin intensities. With isopropyl benzene, radical species were detected in the solution of the compound even after removal from contact with PtO_2. The paramagnetic species formed from this series may be peroxides or quinones (*11, 12*) since these compounds generally have a relatively strong affinity for oxygen (*13*). EPR spectra were also obtained with PtO_2 and the following liquids: toluene, *o*-xylene, *p*-xylene, *sec*-butyl benzene, anisole, bromo-, chloro-, and iodobenzenes at temperatures of 70–120°C. Benzene requires 6 hr in an evacuated tube at 120°C before paramagnetism is observed whereas cyclohexane and cyclohexene give no signals after 4 hr at 120°C. By comparison, it is also of interest to recall that in adsorption studies with silica and alumina, no EPR signals were obtained with benzene.

In conclusion, it is important to note some general significant consistencies between aspects of the present EPR work and catalytic self-activation. For example, differences, up to tenfold, in EPR signal intensity are observed in mixtures of anthracene and PtO_2 when four different commercial oxides are used, whereas reproducibility is satisfactory with different batches of PtO_2 from the same supplier. An analogous catalytic effect is observed in self-activation (*14*) and it is noteworthy that the most efficient commercial PtO_2 in self-activation is also the oxide which gives the most intense EPR signals with anthracene. Further, the only other transition metal oxide to give an EPR signal under the present conditions is PdO, a small signal only being detected after 7 days at 120°C. In self-activation with benzene, PdO was the only other oxide to catalyze an exchange reaction between benzene and D_2O, even though the extent of deuteration was again remarkably small by comparison with PtO_2 (*14*). It is also noteworthy that only aromatic compounds have given EPR spectra in the present work and it is recalled that these aromatic compounds self-activate and exchange more efficiently than aliphatics (*1*). Finally, the decrease in EPR signal on prolonged heating at 120°C is consistent with the observed onset of reduction (i.e., "self-activation") of the oxide.

A full discussion of the present EPR work including other catalysts and possible correlations with catalytic reactions will be published in detail elsewhere.

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