Measurements of Active Site Concentrations at Rhodium, Osmium, Iridium, and Platinum Surfaces by 1,1-Diphenyl-2-picrylhydrazine Oxidation in the Liquid Phase, and by Carbon Monoxide Chemisorption from the Gas Phase

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Oxygen atoms chemisorbed at the surfaces of pre-reduced rhodium, iridium, and platinum powders react with diphenylpicrylhydrazine in benzene solution at 25°C to yield water and the stable free radical diphenylpicrylhydrazyl. The number of reactive oxygen atoms chemisorbed, and hence the number of active surface sites present per gram of powder have been calculated from concordant determinations of the free radical concentration by (i) esr spectrometry and (ii) optical spectroscopy. This method cannot be applied satisfactorily to osmium powders.

Samples of the same powders, in the reduced state, have been examined in a high-vacuum system at 22°C, and the concentrations of sites active for carbon monoxide chemisorption have been determined.

Active site concentrations determined by these widely different methods were in satisfactory agreement for rhodium and platinum, and in fair agreement for iridium.

In 1967, Garnett et al. (1) reported (i) that diphenylpicrylhydrazine in benzene solution at room temperature reacts with oxygen atoms chemisorbed at a platinum surface, the products being water and the stable free radical diphenylpicrylhydrazyl, and (ii) that a determination of the free radical concentration by esr spectrometry provides a means of determining the "active surface area" of the platinum. Bulk oxides of ruthenium, iridium, and platinum also undergo this reaction slowly.

The present work has had three objectives. First, we have demonstrated that the experimentally simpler method of optical spectroscopy is sufficiently sensitive for the estimation of liberated diphenylpicrylhydrazyl. As part of the calibration procedure, we have shown that radical concentrations determined by optical spectroscopy agree with those obtained from esr spectrometry. Secondly, besides studying platinum, we have attempted to extend the use of this reaction to the determination of active site concentrations at the surface of other noble group VIII metals. Thirdly, we have compared the active site concentrations so determined with a more conventional type of surface area measurement, namely carbon monoxide chemisorption. This method suffers from the well-known disadvantage that carbon monoxide may chemisorb in linear or bridged forms (2), and further, that little is known about carbon monoxide chemisorption on osmium (3) or iridium (4). However, the available alternatives were less attractive; hydrogen chemisorption would have been complicated by occlusion, especially at the iridium surface, oxygen chemisorption might have been accompanied by some bulk oxidation at the osmium surface, and physical adsorption measurements by the BET method would

have been suspect since the surface area represented by the active sites under examination might not have been equivalent to the total surface area of the sample. Thus carbon monoxide chemisorption was, in our view, best suited for the comparison that we wished to make.

EXPERIMENTAL METHODS

Materials. Rhodium, osmium, iridium, and platinum powders were prepared by reduction of the metal chlorides in a hydrogen stream at 200°C for about 75 hr.

Diphenylpicrylhydrazyl and diphenylpicrylhydrazine were obtained from Koch Light Ltd., and were used without further treatment. According to the manufacturer, the 13.5% impurity in the former was diphenylpicrylhydrazine.

Analar or Spectrosol benzene was dried over sodium, distilled, and purged of oxygen by a benzene-saturated nitrogen stream. Solutions of diphenylpicrylhydrazine in benzene were normally in the range 0.0006 to 0.0120 M.

Apparatus and method. Portions (5 to 20 ml) of diphenylpicrylhydrazine solution were placed in tubes, metal powder was added, and the tubes were sealed with stoppers. Solutions were normally shaken mechanically at 20°C; this shaking accelerated the rate but did not affect the final extent of reaction. The optical density of the solution increased with time until a steady value was obtained. This took up to 4 hr in the cases of osmium and platinum and 12 to 15 hr in the cases of iridium and rhodium. These observations were not affected by the presence of air above, or dissolved in, the solutions since the results obtained when the mixtures were made up with oxygen-free solvent in a nitrogen atmosphere were identical to those obtained when the mixtures were made up in air. In this respect, our observations for platinum disagree with those of Garnett et al. (1) who reported that the system became catalytic if oxygen was freely available.

Optical densities of solutions were measured using a Hilger and Watts Uvispec or a Unicam SP600. All readings were taken at a wavelength of 524 nm. 1-cm cells were

used. Molar extinction coefficients from linear Beer's law plots were 257 ± 4 for diphenylpicrylhydrazine over the range 10^{-4} to $3 \times 10^{-3} M$ (four determinations), and $10\,300 \pm 300$ for diphenylpicrylhydrazyl over the range 10^{-5} to $1.3 \times 10^{-4} M$ (four determinations). Esr spectra were obtained using a Hilger and Watts microspin spectrometer.

A standard grease-free high-vacuum apparatus was used to obtain the chemisorption isotherms. Each powder (ca. 0.1 g) was evacuated at room temperature, treated at 200°C with 100 mm of deuterium (purified by diffusion through palladium) for 3 hr, and then pumped for 16 hr at this temperature. Carbon monoxide chemisorption at 22°C was then investigated. Pressures of carbon monoxide were measured using a McLeod gauge (Os, Ir, Rh) or a thermal conductivity gauge (Pt).

RESULTS AND DISCUSSION

Determinations of the strength of diphenylpicrylhydrazyl solutions. Esr spectra of a range of diphenylpicrylhydrazyl solutions of known strength were recorded. Peak-to-peak heights were used as a measure of spin concentration. Figure 1a
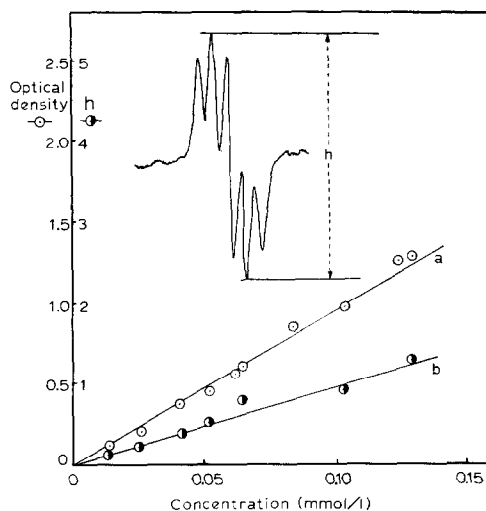

FIG. 1. The linear dependence of (a) optical density at 524 nm; and (b) spin concentration, measured as the peak-to-peak height h from esr spectra, upon the concentration by weight of diphenylpicrylhydrazyl in benzene solution.

shows a linear relationship between spin concentration, measured in this way, and the known concentration of diphenylpicryl-hydrazyl. Calibration of the peak-to-peak measurement was carried out by double integration of several esr spectra using (i) planimetry, and (ii) a computer programme (5). A typical result was one in which the double integration by each method gave a value for the spin concentration of $7(\pm2)$ $\times 10^{16}$ spins per cm length in the cavity (calibrated against a standard sample of pitch) and this compared with an expected value of 6.4×10^{16}.

Figure 1b shows a typical Beer's Law plot obtained using diphenylpicrylhydrazyl solutions. The linear relationships shown in Figures 1a and 1b, taken together, show that measurements of optical absorption at 524 nm provide a quantitative measure of the concentration of free radicals in the solution.

Measurements of active site concentrations. Reaction mixtures were made up as described above. The concentration, c, of the free radicals formed was determined using Eq. (1) where α is the optical density,

$$c = (\alpha_{\text{sample}} - \alpha_{\text{blank}})/(\epsilon_2 - \epsilon_1), \quad (1)$$

and ϵ_1 and ϵ_2 are the molar extinction coefficients of diphenylpicrylhydrazine and diphenylpicrylhydrazyl, respectively. The number of active sites present at the surface of 1 g of catalyst, n_s, was then obtained

using the relation (2) where V is the volume of the solution, g is the weight of the powder in grams, and N is Avogadro's number.

$$n_s = cNV/100g \quad (2)$$

The results are shown in the Table 1. One series of experiments was carried out soon after the preparation of the powders, and a second series was carried out 12 months later. Results were fairly reproducible except for the platinum powders used in the second series (for which no explanation is available).

Active site concentrations for the same powders were determined by carbon mon-
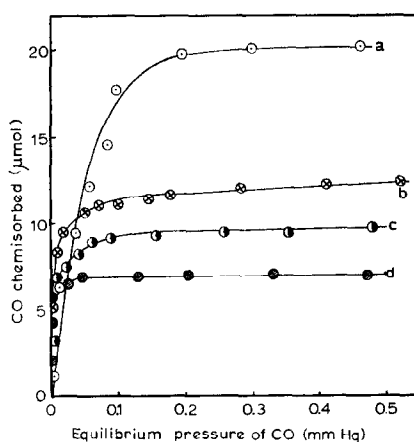

FIG. 2. Isotherms for the chemisorption of carbon monoxide at 22°C on metal powders: a, 0.144g Ir; b, 0.151g Os; c, 0.211g Pt; d 0.078g Rh.

TABLE 1

CONCENTRATIONS OF ACTIVE SITES OBTAINED BY DIPHENYLPICRYLHYDRAZINE OXIDATION (A) AND BY THE CHEMISORPTION OF GASEOUS CARBON MONOXIDE (B)

| Metal | Method A | | | Method B | |
| | No. of determinations | Active site concentration (10^{19} sites/g) | | No. of determinations | Active site concentration[b] (10^{19} sites/g) |
		Range	Mean		
Rh	5	1.7–1.9	1.8	2	1.1, 1.2
	5[a]	1.1–2.2	1.6		
Os	4	0.008–0.0012	0.01	2	0.9, 0.9
Ir	4	5.6–6.6	6.1	3	0.9, 1.2, 1.7
	4[a]	3.0–3.7	3.6		
Pt	4	0.7–1.0	0.8	2	0.5, 0.6
	4[a]	0.3–2.1	1.3		

[a] Results obtained after exposure of powder to air for 12 months.
[b] Calculated assuming a bridged form for adsorbed CO.

oxide chemisorption at 22°C. Typical isotherms are shown in Fig. 2; for each metal, well-defined saturation limits were obtained from which active site concentrations were calculated. Results are shown in Table 1; each value quoted is correct to within $\pm 0.1 \times 10^{19}$ sites/g. (Values have been calculated on the assumption that carbon monoxide is chemisorbed in the bridged form, and thus occupies *two* surface sites. An assumption of chemisorption in the linear form would give active sites concentrations equal to one half of the values quoted in Table 1.) The values quoted for iridium differ from each other probably because this metal, which had the highest surface area as originally prepared, may have sintered during the reduction that preceded carbon monoxide chemisorption.

Method B (see Table 1) shows unequivocally that the osmium powder exhibited a "normal" value for the active site concentration. Hence, we conclude, from the low value given by Method A, that oxygen chemisorbed at the osmium surface does not react quantitatively with diphenylpicrylhydrazine under the conditions used.

Clearly, for rhodium and platinum, the active site concentrations calculated from diphenylpicrylhydrazine oxidation are in good agreement with those obtained from carbon monoxide chemisorption. Consequently, it is likely that the surface metal atoms that constitute sites for oxygen chemisorption and reaction with the hydrazine are also those that function as sites for carbon monoxide chemisorption. The situations concerning iridium and aged platinum are less clear; in these cases there appears to be a considerable number of metal atoms which constitute sites for the chemisorption of oxygen, but not for carbon monoxide.

In this account, we have referred to active site concentrations and not to active surface areas, because the calculation of the latter requires a knowledge (that we do not possess) of what constitutes a site. However, if reasonable assumptions are made about the nature of the site for the chemisorption of carbon monoxide in the bridged form, and assuming also that full surface coverage is achieved, the results in Table 1 give active surface areas for the powders in the range 4 to 12 m^2/g. The values are of the magnitude expected.

CONCLUSIONS

The reaction at room temperature between diphenylpicrylhydrazine and chemisorbed oxygen may be used to determine, in a simple manner, active surface site concentrations for rhodium, iridium, and platinum powders. The method is not suitable for osmium. A fair correlation exists between active site concentrations determined by this method and by measurements of carbon monoxide chemisorption.

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