

NOTE

ESR Evidence for the Activation of Oxygen on Platinum Black

Preliminary experiments for the reaction between diphenylpicrylhydrazine (DPPH₂) and O₂ in the presence of platinum black have been reported (1). The procedure is a convenient method for the preparation of the radical diphenylpicrylhydrazyl (DPPH) for ESR studies. The technique may also be utilized for the measurement of active surface areas for certain catalysts such as Adam's black.

In a further mechanistic investigation of this reaction, we have now obtained kinetic data which unequivocally prove that O₂ is activated on platinum black surfaces. In a typical reaction, a bulk amount of platinum black was prepared by the addition of sodium borohydride to a suspension of PtO₂·*n*H₂O (*n* = 4.5, white) in water (2). Since flocculation of particles was observed, the reaction was carried out in a mortar, the oxide being ground after each lot of sodium borohydride had reacted. The reduced oxide was dried in an evacuated dessicator over silica gel, then the batch was divided into two parts, one of which was heated to 120°C for one and a half hours before use. Samples of each of these two pre-reduced platinum oxides (0.027 g) in H tubes were then reacted with outgassed (5×10^{-4} torr) benzene solutions 10 ml of DPPH₂ (2.882×10^{-3} moles l⁻¹). The rate of reaction was followed by determining the concentration of DPPH produced using a Varian V4500 X-band ESR spectrometer with 100 kc modulation. All concentration determinations were performed under vacuum. Solvent evaporation was compensated for by the necessary addition of benzene.

The results for the two batches of catalyst (Fig. 1) show that both curves tend towards a stationary state of 6.9×10^{-5} moles l⁻¹

of DPPH. Curve A which depicts the behavior of the platinum heated to 120°C reached its stationary state after 40 minutes while curve B (nonheated batch) required 180 minutes to attain this stationary state. This difference in rates for the two batches is attributed to the presence of water, especially since in degassing the H tube system, the arm containing the platinum was immersed in dry-ice acetone, thus reducing water elimination. Evidence to support the suggestion concerning the effect of water comes from detailed studies of an analogous ESR reaction involving the scavenging of oxygen from the surface of a number of inorganic oxides (3), MnO₂ being particularly active. For the reaction between DPPH₂ and MnO₂ an increasing delay in the attainment of the stationary state has been observed with increasing water content.

The attainment of a stationary state in the platinum systems indicates that all of the available O₂ in the system has been utilized in the reaction. If the tube is now broken and O₂ bubbled through the solution, the intensity of the ESR signal is increased greatly. After 20 minutes steady bubbling, the intensity is 5-8 times the stationary state concentrations. Oxygen alone is not capable of abstracting H atoms from DPPH₂. The present reaction appears to be zero order with a rate constant of 2.02×10^{-5} moles l⁻¹ min⁻¹ (linear part of Fig. 1, O₂ effect). If the stationary state given above for DPPH (Fig. 1) is taken as the basis for calculation, then a surface area of ~1.1 m²/g is obtained for the active surface area of the platinum. This is significantly lower than the value obtained by CO adsorption (1) or from the BET-

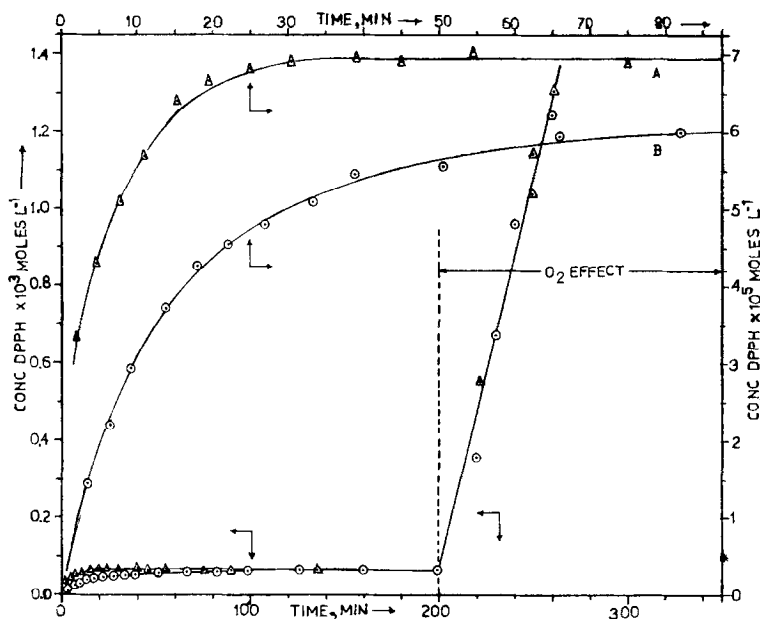


FIG. 1. Kinetic curves for reaction between DPPH_2 and oxygen on platinum black. Conc. DPPH vs. time. Curve A refers to batch heated at 120°C for $1\frac{1}{2}$ hrs prior to use. Curve B represents the result for the non-heated batch.

method and thus accentuates the fact that the method yields active surface areas.

The results prove unequivocally that oxygen is activated on platinum surfaces which have been prepared by reduction of the oxide. A similar result has been obtained with a platinum black coating on a platinum electrode obtained by electrolysis of H_2PtCl_4 (3). The data are also of mechanistic significance in explaining why deuterium exchange reactions between aromatic compounds and heavy water do not proceed efficiently at room temperature on prerduced platinum if the surface is poisoned by oxygen (4).

When this oxygen is scavenged (by hydrogen at room temperature, or by the organic compound itself at temperatures above 80°C) exchange proceeds readily. Thus, the catalytic sites necessary for the exchange reaction are associated with the oxygen chemisorption sites and the present ESR procedure yields realistic active surface areas for pre-reduced platinum in these reactions.

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