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Hydrogenation of Nitrobenzene over Palladium–Silver Catalysts

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The rates of hydrogenation of nitrobenzene in *n*-butanol have been measured over catalysts of the palladium–silver alloy system. Variation of the experimental activation energy from low (about 5 kcal mole^{-1}) values on palladium rich alloys, to much higher values on silver-rich alloys (about 25 kcal mole^{-1}) is consistent with the electronic band theory of catalysis, and the view that the promotion of electrons from within the conduction band of the solid to its Fermi surface under the influence of the adsorbate is rate determining.

The catalytic behavior of the transition metal–noble metal alloy systems Pd–Au (*1*, *2*), Pd–Ag (*3*, *4*, *5*) and Cu–Ni (*6*) have provided much of the evidence supporting the electronic band theory of catalysis (*7*). These investigations have been confined, however, largely to reactions at the vapor metal interface, and consequently to reactions involving relatively simple molecular species and proceeding by simple mechanisms. Evidence for the band theory provided by studies of reactions at metal–liquid interfaces is less substantial. Although the presence of electron d-band vacancies are clearly essential for low activation energy catalytic hydrogenation even in the liquid phase (*8*, *9*), the detailed dependence of a catalyst's activity and its band structure are uncertain (*10*). The importance of surface geometry (*11*) and lattice defect structure (*12*) cannot be disregarded in the comparison of alloys for which changes in the height of the Fermi surface are small.

The present work was initiated in an attempt to clarify the role of the electronic factor in liquid phase heterogeneous catalysis, particularly the suggestion (*4*) that promotion of electrons from adsorbent bonding levels within the conduction band to the Fermi surface is rate determining.

EXPERIMENTAL

Catalyst Preparation and Characterization

Pure metal and alloy catalysts were prepared by co-precipitation of the oxides, from aqueous solutions containing appropriate ratios of Ag^+ and Pd^{++} ions. The oxides were reduced with alkaline hydrazine sulphate, washed free of reducing agent, vacuum dried, and after further reduction with hydrogen at about 5 Torr, vacuum annealed at 400°C for about 2 hr (*5*). The annealed powders were examined by X-ray powder photography using Cu K_α radiation, and their lattice parameters determined. The sharpness of diffraction lines was indicative of satisfactory homogenization and the absence of phase separation. Alloy compositions were determined from their lattice parameters (*4*).

The large grain size of the catalysts precluded the use of gas adsorption methods for the measurement of specific surface areas. Estimates of surface areas were derived from particle size distributions obtained using optical microscopy.

Hydrogenation rate studies were carried out in a conical reaction vessel, attached to a constant pressure gas burette containing dibutyl phthalate. Provision was made to allow flushing of the system with hydrogen or nitrogen, and for filling the system with hydrogen or with mixtures of the two gases at known partial pressures. The total pressure in the system was maintained at 1 atm. The contents of the reaction vessel, whose walls were indented to promoted turbulence, were agitated with a magnetic stirrer. Reaction temperatures between 0 and 80°C were maintained by a thermostated liquid bath.

Simple rate studies were carried out by placing about 50 ml of a solution of nitrobenzene in *n*-butanol in the reaction vessel, flushing out the system with hydrogen, and after the system had reached equilibrium, breaking the small bulb containing the catalyst sealed under nitrogen. The bulb was attached to a glass rod which passed through a leak-free gland in the lid of the reaction vessel.

A similar procedure was used to investigate the reaction rate order in hydrogen, by filling the system with mixtures of hydrogen and nitrogen of known partial pressure.

The effect of hydrogen poisoning on hydrogenation rates was studied in the same apparatus; placing the catalyst, with 50 ml of *n*-butanol in the reaction vessel where it was exposed to hydrogen gas for periods up to 60 hr. Reaction was initiated over the catalyst containing hydrogen by breaking the bulb which contained pure nitrobenzene.

RESULTS AND DISCUSSION

Measurements of the dependence of reaction rate on the weight of catalyst revealed a constant specific rate over the range of conditions used in this work, indicating that absorption of hydrogen at the gas–liquid interface, and its diffusion to the surface of the catalyst were not rate determining.

The dependence of reaction rate on nitrobenzene concentration in the solvent, *n*-butanol, is shown in Fig. 1 for pure palladium and for an alloy containing 1.2% of the metal. These results show a progressive decrease in the rate with increasing solute concentration above about 0.15 mole fraction, and are consistent with results reported by Bond (*13*). Comparative studies of hydrogenation over the whole alloy composition range were, therefore, determined for solutions containing 0.12 mole fraction of nitrobenzene in *n*-butanol, at which concentration rates are relatively insensitive to errors in nitrobenzene concentration.

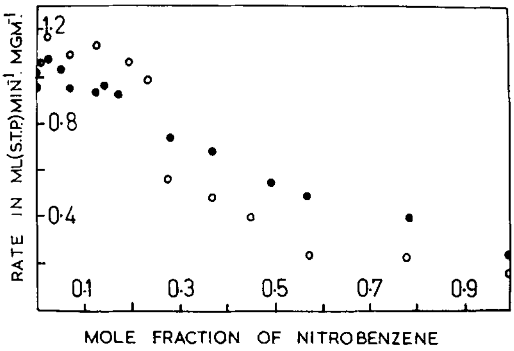

FIG. 1. Dependence of hydrogenation rate on concentration. ●, Pd at 30.0°C; ○, 1.2 At. % Pd at 73.1°C (rate × 50).

The rates of hydrogenation over palladium-rich alloys were fast, and constant for an initial period of about 10 min before decreasing; whereas silver-rich alloys were found to be less active, requiring higher temperatures to achieve measurable rates. Pure silver was inactive at even the highest temperature used (80°C). Silver-rich alloys also displayed induction periods of up to 5 min before reaching full rate. Measurements of the initial rate of hydrogenation over pure palladium exposed to hydrogen for various times (Fig. 2) indicate that hydrogen poisoning does not significantly affect the rate in the first 10 min, and the maximum rates were taken as characteristic of the Pd–Ag alloy system rather than the Pd–Ag–H system.

Experimental activation energies and pre-exponential frequency factors were obtained by fitting experimental data to the Arrhenius equation using a linear least-squares method, and probable errors in the activation energy determined statistically (*14*). Table 1 contains the experimental activation energies, pre-exponential

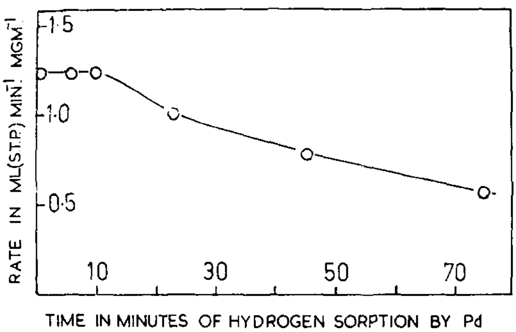

FIG. 2. Effect of hydrogen sorption on hydrogenation by palladium catalyst.

frequency factors (B_m molecules cm^{-2} sec^{-1}) and specific surface areas of the alloy catalysts used in nitrobenzene hydrogenation. Values of B_m greater than the surface collision frequency of hydrogen gas at 1 atm ($\sim 10^{25}$ molecules cm^{-2} sec^{-1}) which are found for the high activation energy catalysts are not uncommon in heterogeneous systems (*7*) and may have their origins in large positive entropies of activation.

There are no data available for the solubility of hydrogen in the nitrobenzene–*n*-butanol reactant solution; the heat of solution of the gas in nitrobenzene, ethanol, and isobutanol is estimated (*15*) to be about 1 kcal mole^{-1}. Measured experimental activation energies, which contain a contribution from the heat of solution of hydrogen must accordingly be reduced by this amount over the whole alloy range. In addition the reduction of hydrogen partial pressure over the reactant solution by the vapor of the solution introduces a further correction dependent upon the heat of evaporation of *n*-butanol. This amounts, for measurements made in nitrobenzene and *n*-butanol mixtures, to the addition of only 0.1 kcal mole^{-1} for alloys studied over the lowest temperature range (palladium-rich alloys), but the addition of about 2.5 kcal mole^{-1} to experimental activation energies derived from measurements at the highest temperatures (on silver-rich alloys). Contributions from the heat of evaporation of nitrobenzene are negligible for all alloys.

The experimental activation energy increases with increasing silver content of the alloy, and increases rapidly for catalysts containing more than about 50 At. % silver. The difference in activation energy between the extremes of the composition range (about 20 kcal mole^{-1}) is appreciably

TABLE 1

ACTIVATION ENERGIES, FREQUENCY FACTORS, AND SURFACE AREAS OF CATALYSTS USED FOR NITROBENZENE HYDROGENATION

At. %	Activation energy (kcal mole^{-1})	Surface area (10^3m^{2}g^{-1})	Frequency factor (molecules cm^{-2} sec^{-1})
100	3.53 ± 0.15	5.8	2.5×10^{20}
100[a]	4.10 ± 0.26	—	—
100[b]	12.2 ± 0.12	—	—
88.8	4.22 ± 0.06	14.0	2.9×10^{20}
62	4.63 ± 0.09	3.6	3.3×10^{21}
57.8	8.33 ± 0.01	7.4	6.4×10^{23}
57.8[a]	2.81 ± 0.14	—	—
49.8	5.61 ± 0.72	7.4	5.0×10^{21}
49.8	8.43 ± 0.11	—	—
40.1	15.49 ± 0.45	3.1	2.5×10^{28}
23.7	19.5 ± 1.2	21.9	3.3×10^{30}
16	17.8 ± 2.2	3.7	2.3×10^{30}
13.6	24.2 ± 1.6	3.1	7.7×10^{32}
1.2	24.8 ± 2.0	4.2	1.12×10^{34}

[a] In pure nitrobenzene.

[b] Exposed to hydrogen for 60 hr.

larger than the range found for the parahydrogen conversion on palladium–silver alloys (about 13.5 kcal mole^{-1}) and the difference in Fermi energies of palladium and silver, so the suggestion (*4*) that the rate-determining step in the parahydrogen reaction involves electron promotion to the Fermi surface would not seem applicable to hydrogenation of nitrobenzene. However, there is evidence (*16*) that nitrobenzene hydrogenation proceeds through the relatively stable intermediates nitrosobenzene, *N*-phenylhydroxylamine and possibly azobenzene and azoxybenzene. The appearance of an induction period for the reaction over silver-rich catalysts suggests that the rate-determining step in hydrogenation is preceded by a step or steps of comparable rate, but which does not involve the consumption of hydrogen. Over palladium-rich alloys, there is no evidence of a delay in the achievement of maximum rate, suggesting that the relative importance of the steps has changed. The measured rate orders with respect to hydrogen (Fig. 3) for palladium and 62% palladium alloy are 1.28 ± 0.01 and 1.23 ± 0.01, respectively, which again suggests that at least two reaction steps proceed with similar rates and that their relative importance depends upon the alloy composition. A linear correlation between the experimental activation energy and $\log_{10}B_m$ (See Table 1) is also characteristic (*17*) of a reaction whose mechanism consists of two or more steps, of comparable rate, but with different activation energies.

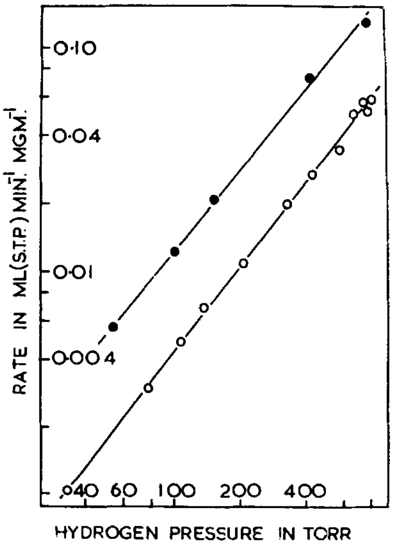

FIG. 3. Dependence of hydrogenation rate of nitrobenzene in *n*-butanol upon hydrogen pressure. ●, on 62 At. % Pd, ○, on Pd (rate × 10^{-1}).

CONCLUSIONS

Nitrobenzene, nitrosobenzene and *N*-phenylhydroxylamine are similar in structure, and it is expected that the hydrogenation transition state complexes derived from them will be similar also. The energy of formation of the activated complexes and hence their rates of formation will be very close. Subtle differences in the stabilization of transition states on different alloys are likely to decide the relative importance of these steps in the hydrogenation of nitrobenzene.

A simple electron promotion mechanism would require a close parallel between the height of the Fermi surface of the alloy and the activation energy of the catalytic process. A shift in rate-dominating step, as a result of the slight changes in lattice parameters or redistribution of the density of states within the conduction band of the alloy, could distort the parallelism if the levels from which electrons must be promoted to allow bonding of the activated complexes are different in the two steps. Thus the behavior of Pd–Ag alloys towards the hydrogenation of nitrobenzene found in this study is consistent with the electronic band theory of catalysis and an electron promotion mechanism.

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