

# Hydrogenation of Nitrocompounds with Supported Palladium Catalysts: Influence of Metal Dispersion and Nitrocompound Nature

G. CARTURAN AND G. FACCHIN

*Centro di Chimica Metallorganica del CNR, Via Marzolo, 9, Padova, Italy*

G. COCCO

*Istituto di Chimica Fisica dell'Università, D.D.2137, Venezia, Italy*

G. NAVAZIO

*Istituto di Chimica Industriale dell'Università, Via Marzolo, 9, Padova, Italy*

AND

G. GUBITOSA

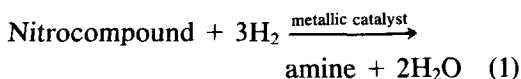
*Istituto Donegani, Via Fauser, Novara, Italy*

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Nitrobenzene, Et-NO<sub>2</sub>, and t-Bu-NO<sub>2</sub> are hydrogenated to corresponding amines using Pd catalysts in *n*-octane suspension at 90°C and at constant H<sub>2</sub> pressure. Nitrobenzene reduction to aniline has been studied with several Pd catalysts having a different degree of metal dispersion determined by X-ray methods and chemisorption analysis. Results indicate that the process is a "structure sensitive reaction"; a peculiar lowering in catalytic activity as the degree of Pd dispersion increases is observed. This fact is discussed in terms of metallic surface oxidation due to the sorbed nitrocompound. Hydrogenation kinetic patterns change with the nature of the nitrocompound. Reduction of Et-NO<sub>2</sub> and t-Bu-NO<sub>2</sub> depends on substrate concentration, while nitrobenzene hydrogenation is independent of this parameter. The relevant kinetic experiments allow the formulation of a general reaction mechanism accounting for the different kinetic patterns observed on changing the substrate. The discussion illustrates the possibility that in nitrocompound reduction with metal catalysts the rate determining step may be hydrogenation of the metallic surface oxidized by the sorbed nitrocompound.

## INTRODUCTION

The hydrogenation reaction of nitrocompounds with metallic catalysts is used industrially where, for instance, Pd supported on charcoal is a proven catalyst for the preparation of reduction products of aromatic nitrocompounds (1). Although this process has been extensively studied (2, 3), the reaction mechanism and relevant aspects have not been fully demonstrated. Indeed, the reaction



shows complex behavior: the rate and order of the reaction depend on the nature of the organic moiety, solvent, and substrate/catalyst loading ratio (4, 5). Reaction (1) may also involve possible partial hydrogenation products and/or condensation compounds, each having a peculiar thermodynamic and kinetic stability.

A further intriguing element is obviously related to the chemical interaction between the metallic surface and (i) the nitrocompound, (ii) hydrogen, and (iii) reduction products. On this topic, specific studies have been reported (6).

The kinetic complexity of reaction (1) may also be connected with the dispersion degree of the metal and structural features of the dispersed metallic phase; these parameters may control the ultimate performance of the supported catalysts. Therefore, investigation of nitrocompound hydrogenation over a significant range of metallic dispersion may be essential in disclosing some distinctive catalytic features.

Incidentally, we exploited the availability of vitreous supports with high surface area and a considerable surface -OH group content (7) in designing Ni, Pd, and Pt catalysts with a desired degree of dispersion; indeed, by appropriate coupling of the peculiar features of our supports with the Yermakov preparation method (8, 9), Ni, Pd, and Pt catalysts obtained either had very narrow metal particle size distributions or were widely ranged at higher values (10–12). With these catalysts we have already reported some results on the hydrogenation of olefins and the selective hydrogenation of alkynes and dienes (10, 13, 14).

In the present work we extend interest to nitrocompounds in the hydrogenation of organic substrates, with the aim of shedding light on the mechanism of reaction (1). Thus, Pd catalysts with different metal particle size distributions and metal loadings were used; nitrobenzene, Et-NO<sub>2</sub> and t-Bu-NO<sub>2</sub> were selected as testing substrates to study the effect of the nature of the organic moiety.

## EXPERIMENTAL

### Materials

Amines, nitrocompounds, nitrosobenzene, t-Bu-NO, (t-Bu-NO)<sub>2</sub>, and acetaldoxime were commercially available products, used after spectroscopic and gas liquid chromatography purity control. Si(OEt)<sub>4</sub> and Al(OC<sub>3</sub>H<sub>7</sub>)<sub>3</sub> were Fluka products; other chemicals were analytical grade compounds. Solvents were dried, distilled under N<sub>2</sub> before use, and degassed by freezing-pump-thaw cycle. The H<sub>2</sub> used in the

hydrogenation kinetics was purified by diffusion through a Milton Roy palladium thimble.

The vitreous supports of chemical composition SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>/Na<sub>2</sub>O = 71/18/11 were prepared according to the method described in (15) and used after heating at 240°C as a 200–240-mesh powder. The catalysts were obtained by anchoring an appropriate amount of Pd(C<sub>3</sub>H<sub>5</sub>)<sub>2</sub> to the surface -OH groups of the supports in pentane suspension. The metal dispersion was prepared by reducing the anchored Pd(II) organometallic species with H<sub>2</sub> at room temperature (7, 10, 12).

The Pd on charcoal catalysts were obtained using the conventional procedure (16).

The catalysts were kept under nitrogen in schlenk tubes.

### Instrumentation

An HP 5730A gas chromatograph equipped with a 6-ft 10% UCC 692 Chromosorb WAW DMSC column was used for glc analysis.

<sup>1</sup>H NMR spectra were recorded using a Varian FT 80. Mass spectra were obtained with a VG Micromass 16F mass spectrometer. Infrared spectra were recorded on a Perkin-Elmer 597 spectrophotometer using KBr windows.

### Kinetics

The catalysts were transferred and weighed under nitrogen into a 50-ml 2-necked flask. The desired amount of dry solvent (10 ml, *n*-octane) was added by siphon and the degassed suspension connected under H<sub>2</sub> to hydrogenation apparatus of the type described in (17, 18). After equilibration of temperature and H<sub>2</sub> pressure the substrate was injected by syringe through one arm of the flask fitted with a serum cup.

Temperature was kept constant by external circulation of a thermostat and controlled to within ±0.5°C.

Barometric pressure (760 ± 9 mm/Hg)

was maintained during the kinetic run by progressive reduction of the volume of the gas phase by using gas uptake apparatus. The progress of the reaction was followed by analyzing a sufficient number of samples withdrawn from the reacting mixture. The complexity of the factors affecting nitro-compound hydrogenation with the solution-suspended catalysts prompted us to rigorously check any relevant experimental conditions which might have distorted the kinetic data. In particular, the reacting mixture was very efficiently and thoroughly stirred to avoid possible influence of H<sub>2</sub> diffusion; the suspension was stirred with a 1.2-cm teflon coated magnetic bar at a stirring rate of 400–500 rpm, the diffusion affecting the kinetic data at a stirring rate lower than 40–50 rpm. At this rate of stirring, kinetic results became inferior to the  $\pm 4\%$  standard deviation ascertained with higher stirring rates.

#### Chemisorption and X-ray Analysis

Measurement of palladium dispersion was made by CO chemisorption at room temperature using pulsed-flow equipment. The relevant procedure has been described elsewhere (9). On the basis of infrared and chemisorption studies (20), the stoichiometric ratio Pd/CO = 1.1 was used to calculate the averaged Pd particle diameter.

Previous papers (12, 21) have detailed the experimental arrangements for the Small Angle X-ray Scattering (SAXS) and Wide Angle X-ray Scattering (WAXS) methodological approach, raw data handling, and final data treatment. Only a short definition of terms will be given here. The average weighted particle sizes, as quoted here, were calculated according to the expression

$$\bar{D} = \int_0^\infty f_s(R)dR / \int_0^\infty f_v(R)dR \quad (2)$$

where  $f_s(R)$  and  $f_v(R)$  are, respectively, the normalized mean surface and volume distribution functions;  $R$  is the size parameter.

The total metal surface areas,  $S_{sp}$  (m<sup>2</sup> g<sub>Pd</sub><sup>-1</sup>) were derived from the asymptotic behavior in the tails of the scattered intensities by means of absolute intensity measurements (12, 21, 22).

The fraction of exposed Pd,  $D_s$ , was calculated as the ratio of the number of surface atoms to the number of total atoms in the spherically averaged volume of the metal particles. The equation used was

$$D_s = \int_0^\infty \frac{R^3 - (R - 2R_0)^3}{R^3} f_v(R)dR \quad (3)$$

where  $R_0 = 2.75 \text{ \AA}$  is the atomic diameter of Pd.

## RESULTS

### Catalyst Features

Table 1 shows the degree of Pd dispersion for each catalyst in terms of metal particle diameter. The Pd surface areas  $S_{sp}$  and fraction of exposed metal  $D_s$  are also reported.

TABLE I  
Main Parameters Obtained from Catalyst Characterization<sup>a</sup>

Catalyst <sup>b</sup>	Pd wt% <sup>c</sup>	$S_{sp}$ (m <sup>2</sup> g <sub>Pd</sub> <sup>-1</sup> )	Particle Diameter <sup>d</sup> (\AA)	$D_s$ <sup>e</sup>
A <sub>1</sub>	0.69	424	13	0.95
A <sub>2</sub>	0.85	316	16	0.87
A <sub>3</sub>	1.3	250	19	0.78
B <sub>2</sub>	1.42	195	27	0.69
C <sub>1</sub>	1.75	86	54	0.43
C <sub>2</sub>	5.0	44	106	0.30
D	0.49	(164)	(31)	0.73
E	0.24	(102)	(51)	0.53
F	1.01	166	29	0.71
		(189)	(26)	

<sup>a</sup> Values in brackets refer to chemisorption measurements; other data result from SAXS analysis.

<sup>b</sup> SAXS data of Catalysts A<sub>1</sub>–A<sub>3</sub>, B<sub>2</sub>, C<sub>1</sub>, and C<sub>2</sub> were calculated from previously reported SAXS characterization (11).

<sup>c</sup> From elemental analysis.

<sup>d</sup> SAXS data refer to Eq. (2).

<sup>e</sup> From Eq. (3); chemisorption data are averaged values.

The features of catalysts constituted of Pd supported on vitreous powders which we currently prepare by the "gel route" (15, 23) can be accounted for by the observed parallelism between the -OH group content on the support surface and the degree of metal dispersion (11, 14). In particular, since the smallest metal particles are generated by the fraction of  $\text{Pd}(\text{C}_3\text{H}_5)_2$  chemically interacted with the surface hydroxides of the support (12), the content of -OH groups determines the fraction of metal particles with diameter approximately smaller than 30 Å. Thus, in agreement with the high concentration of surface -OH groups on support A (equivalent to 16.2 ml of  $\text{H}_2$  evolved per g of support titrated with LiH), the corresponding catalysts are constituted of very small Pd particles arranged in an almost monomodal particle size distribution function (11). In the case of catalysts B<sub>2</sub>, D, E, and F, where the -OH contents are, respectively, 4.9, 5.2, 3.1, and 4.6 ml of  $\text{H}_2$  evolved per g, the resulting metal dispersion is progressively

lowered. Here the largest amount of  $\text{Pd}(\text{C}_3\text{H}_5)_2$  is simply sorbed and not anchored to the support surface; in this case reduction with  $\text{H}_2$  generates metal particles larger than 30 Å.

In Table 1 some catalyst parameters come from SAXS, others from chemisorption analysis. The good agreement found in the case of catalyst F might allow us to consider the two methods as consistent with each other. On the other hand, comparison between SAXS and chemisorption analysis constitutes a topic which goes beyond the scope of this work.

### Hydrogenation Results

In all examined cases the hydrogenation of nitrobenzene displayed a very good linear trend of plots of percent conversion vs time. A typical case is shown in Fig. 1. Least squares treatment of these data obtained at constant  $\text{H}_2$  pressure allowed the calculation of standard deviations on the pseudo-zeroth-order rate constants  $k_{\text{obs}}$ . Relevant uncertainties never exceeded 4%.

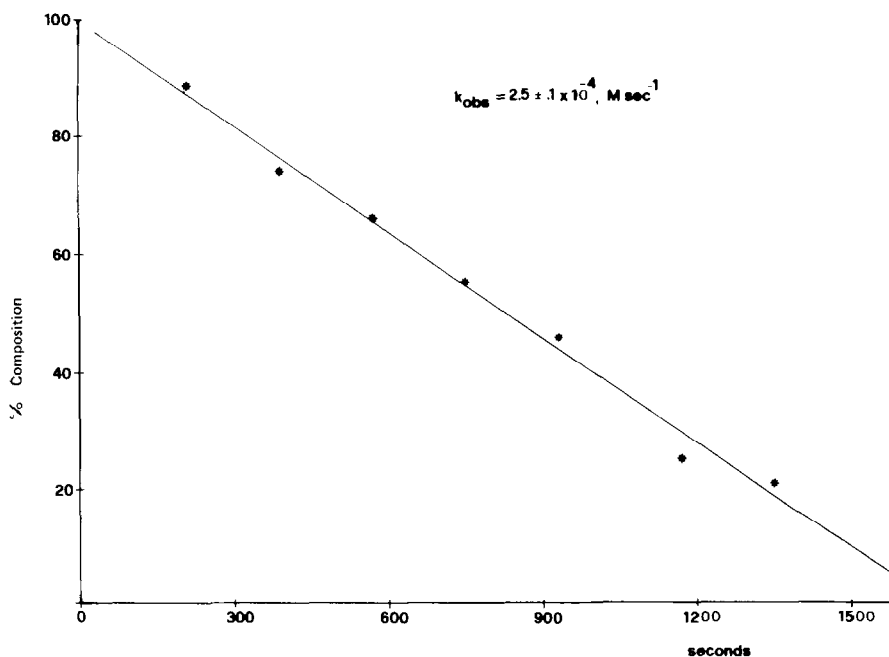


FIG. 1. Nitrobenzene hydrogenation. Catalyst E,  $t = 90^\circ\text{C}$ ;  $P_{\text{H}_2} = 520 \pm 19$  mm/Hg, 313 mg of catalyst, substrate 0.41 M.

In some cases the same run was repeated with the same catalytic system and the reproducibility of slopes based on nitrobenzene consumption displayed deviations of about 3%. This behavior was observed in the 0.2 to 0.9 *M* nitrobenzene concentration range; it may be considered a good test for the absence of poisoning.

Apart from the high stirring rate used in all catalytic experiments, kinetic behavior may be related to possible H<sub>2</sub> diffusion control; this prompted us to ascertain the linearity of the plot of  $\ln k_{\text{obs}}/T$  vs  $1/T$ . One example in the 40 to 100°C temperature range is shown in Fig. 2; the  $k_{\text{obs}}$  data refer to  $P_{\text{H}_2} = 760$  mm/Hg once the linear dependence of  $k_{\text{obs}}$  on  $P_{\text{H}_2}$  in the 0.5- to 1.0-atm interval had been ascertained. We calculated activation energy values ranging from 7.2 to 9.6 Kcal mol<sup>-1</sup>, in general agreement with the reported values for aromatic nitrocompound hydrogenations (4) in the absence of H<sub>2</sub> diffusion control.

Kinetic results are summarized in Table 2, where kinetic data are expressed per mg of Pd metal. Moreover, since the metal dispersion of the catalysts was also known,

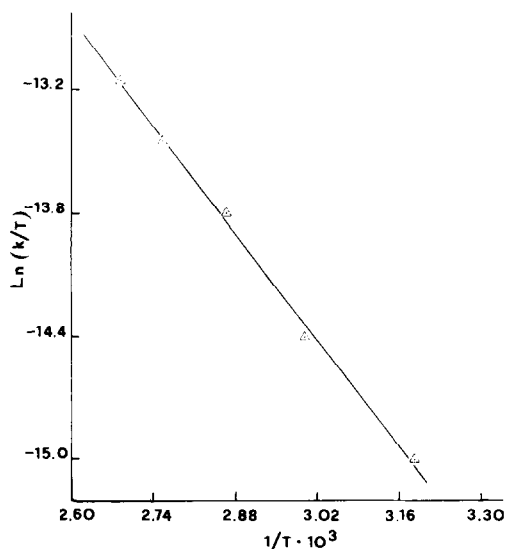


FIG. 2. Effect of temperature on nitrobenzene hydrogenation.  $k_{\text{obs}}$  data refer to  $P_{\text{H}_2} = 760$  mm/Hg, catalyst E.

TABLE 2

Hydrogenation of Nitrobenzene: Effect of Pd Metal Dispersion<sup>a</sup>

Catalyst	$10^4 \cdot k_{\text{obs}}$ ( $M \text{ sec}^{-1} \text{ m g}_{\text{Pd}}^{-1}$ )	$10^4 \cdot \text{CSA}^b$ ( $M \text{ sec}^{-1} \text{ m}_{\text{Pd}}^{-2}$ )
A <sub>1</sub>	0.76	1.8
A <sub>2</sub>	0.67	2.1
A <sub>3</sub>	0.60	2.4
B <sub>2</sub>	2.64	13.5
C <sub>1</sub>	1.73	20.1
C <sub>2</sub>	1.23	27.9
D	1.48	9.1
E	3.32	32.6
F	3.21	19.3

<sup>a</sup>  $T = 90^\circ\text{C}$ , barometric pressure  $760 \pm 9$  mm/Hg,  $P_{\text{H}_2} = 520 \pm 19$  mm/Hg.

<sup>b</sup> Calculated from  $k_{\text{obs}}/S_{\text{sp}}$  ratios.

the  $k_{\text{obs}}$  per m<sup>2</sup> of exposed metal were also calculated. These data of catalytic specific activity (CSA) expressed as  $M \text{ sec}^{-1} \text{ m}_{\text{Pd}}^{-2}$  are markedly dependent on the metal dispersion.

Et-NO<sub>2</sub> and t-Bu-NO<sub>2</sub> were hydrogenated to the corresponding amines at 90°C and barometric pressure ( $P_{\text{H}_2}$  + solvent vapor pressure) like the nitrobenzene hydrogenations. Catalysts D and E were used. The progress of the reaction was followed by nitrocompound consumption. The formation of Et-NH<sub>2</sub> from Et-NO<sub>2</sub> was also ascertained by glc analysis of the gas phase. Kinetics carried out at different substrate concentrations and with different amounts of catalyst indicated progressive deviation from the linear trend as the nitroalkane/catalyst ratio was increased. The shape of the slopes of the percent composition vs time changed so much from one case to another in the Et-NO<sub>2</sub> concentration interval 0.1–1.2 *M* that the possibility of rationalizing the system as a function of substrate concentration was prevented.

During these experiments, no side products were detected during the kinetic run. Moreover, acetaldoxime was very slowly hydrogenated to amine; this excludes the suggestion that hydrogenation of Et-NO<sub>2</sub>

involves this partial reduction product as an intermediate.

Figure 3 shows a representative result for the hydrogenation of  $t\text{-Bu-NO}_2$  to amine. The experiments were carried out at  $90^\circ\text{C}$  and therefore the amine was also present in the gas phase. The rate constant of the nitrocompound consumption can be calculated from the first-order treatment of the percent concentration data vs time. In this case too, the reproducibility of the rate constant values, obtained upon successive additions of  $t\text{-Bu-NO}_2$  to the same reaction mixture, suggested the absence of poisoning in the substrate. The  $k$  values are shown in Table 3; they depend on the initial substrate concentration  $C_0$ , according to the plot of  $k$  vs  $C_0$  of Fig. 4. This result indicates that the rate law of  $t\text{-Bu-NO}_2$  con-

sumption, within the interval of concentration used here, may be expressed as

$$-dC/dt = (A - BC_0)C. \quad (4)$$

It is noteworthy that in this case the process involves the formation and buildup of a detectable intermediate which is in turn hydrogenated to amine. Glc analysis excludes the identification of this intermediate as  $t\text{-Bu-NO}$  or as a condensation product of the type  $t\text{-Bu-N=N-t-Bu}$ ,  $t\text{-Bu-NH-NH-t-Bu}$  or  $(t\text{-Bu-NO})_2$ .  $^1\text{H NMR}$  and mass spectra of the distilled reacting solution do not give conclusive evidence for the characterization of this intermediate. Independent hydrogenation experiments of  $t\text{-Bu-NO}$  indicate that this substrate is reduced much faster than  $t\text{-Bu-NO}_2$  and the relevant kinet-

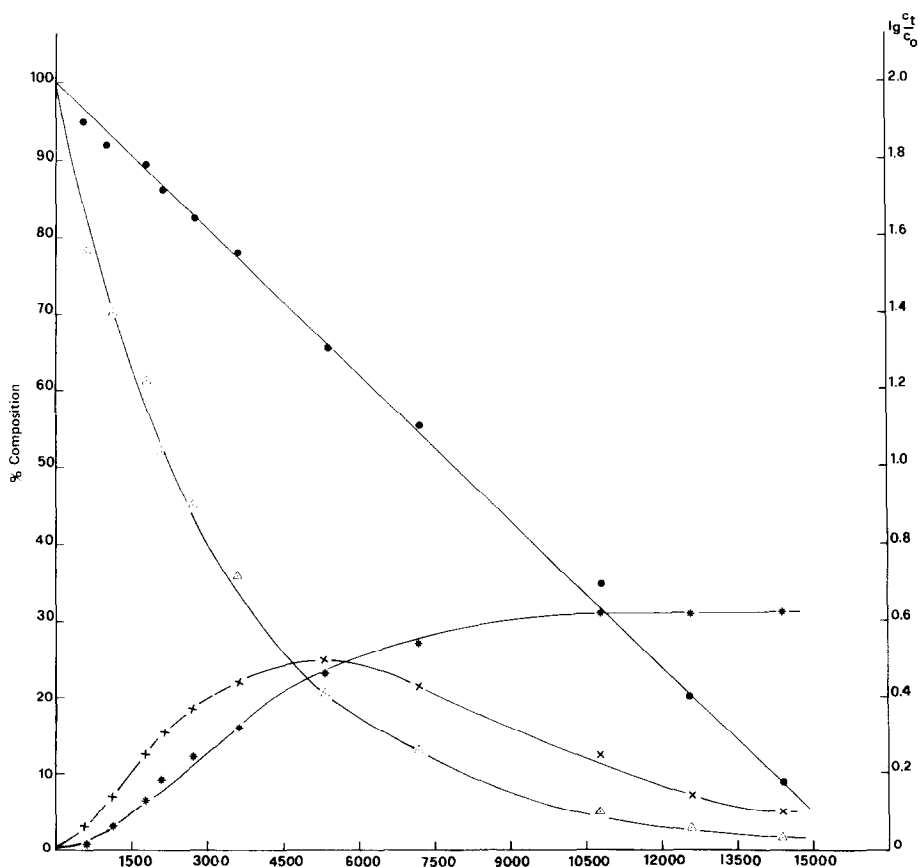


FIG. 3. Reaction profile of the  $t\text{-Bu-NO}_2$  hydrogenation:  $\Delta$   $t\text{-Bu-NO}_2$ ; x intermediate; \*  $t\text{-Bu-NH}_2$  seconds  $\bullet$  refers to the first-order treatment of  $t\text{-Bu-NO}_2$  consumption.

TABLE 3  
Kinetic Parameters for t-Bu-NO<sub>2</sub>  
Hydrogenation<sup>a</sup>

$C_0$ (M)	$10^4 \times k$ (sec <sup>-1</sup> m g <sub>Pd</sub> <sup>-1</sup> )
1.05	0.33
0.65	1.38
0.42	2.88
0.20	4.19

<sup>a</sup>  $T = 90^\circ\text{C}$ , catalyst D,  $P_{\text{H}_2} = 520 \pm 19$  mm/Hg.

ics do not show the occurrence of any intermediate.

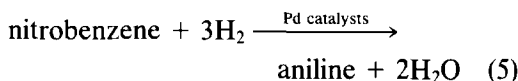
## DISCUSSION

### *Effect of Pd Dispersion on Catalytic Activity*

Nitrobenzene hydrogenation to aniline was particularly suitable for a kinetic investigation involving comparison of catalytic activity among catalysts having different kinds of dispersion of the metallic phase. However, as supports we used vitreous materials and charcoal which may interact differently with the Pd phase; the incidence of this parameter on the CSA may be significant but, unfortunately, it is difficult to evaluate because of the lack of charcoal

and vitreous powder catalysts with identical size distribution functions for the dispersed Pd. Thus, we restricted our attention to catalysts on vitreous supports excluding those of type C, for which a quite different pore diffusion may also be surmised.

Figure 5 shows the diagram of the various CSA data versus the dispersion of the corresponding catalysts. The resulting picture indicates strong dependence of CSA on metal dispersion. The experimental uncertainties in the CSA values and the approximation used for the determination of the fraction of exposed metal are clearly negligible with respect to the trend shown in Fig. 5. Thus the reaction



behaves like a structure sensitive reaction (24) with a lowering in catalytic activity as the degree of metal dispersion increases.

The kinetic behavior observed for nitrobenzene hydrogenation was identical in all cases examined and therefore leads to the formulation of a single reaction mechanism, independent of Pd dispersion. An acceptable interpretation of the independence of

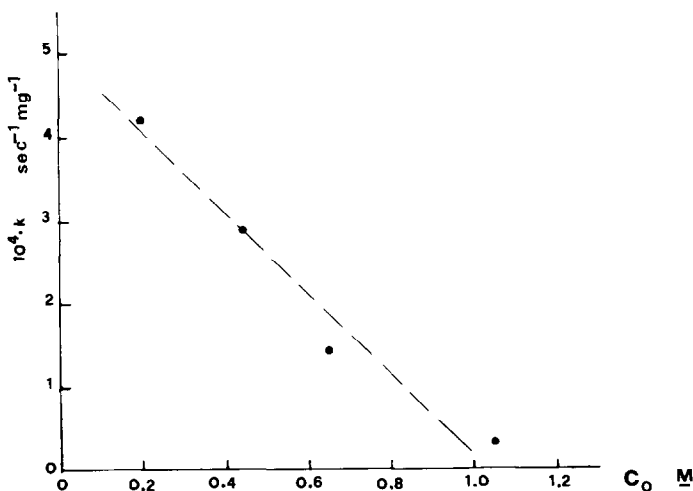


FIG. 4. Dependence of the rate of t-Bu-NO<sub>2</sub> consumption on initial substrate concentration.

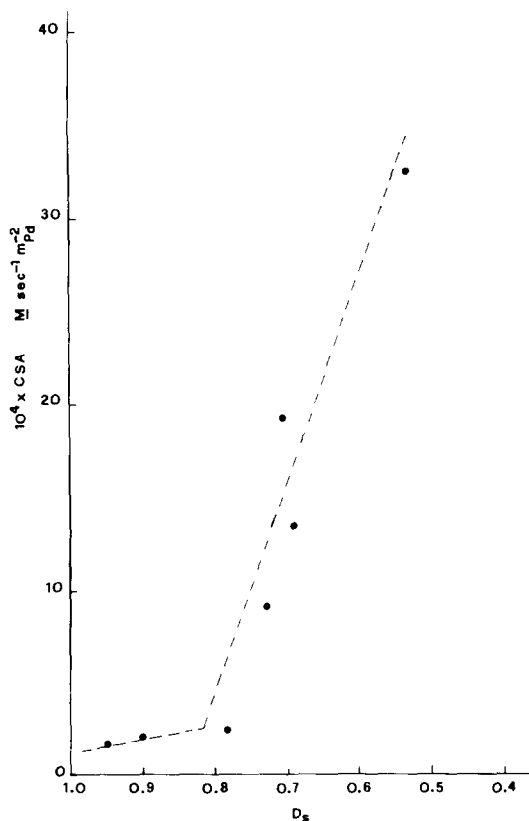


FIG. 5. Dependence of the catalytic specific activity, CSA, on degree of Pd metal dispersion.

the substrate concentration is that nitrobenzene is strongly adsorbed on the Pd surface; this is found in some well-documented records where similar results have been interpreted in the same way (2). Thus, the dependence of CSA on the degree of Pd dispersion may not be related to nitrocompound coordination, but rather to  $H_2$  activation which constitutes the rate determining step.

Recently reported XPS experiments have demonstrated that the nitro group of nitrobenzene adsorbed on metallic film dissociates, leaving oxygen on the metallic surface (6). The thickness of the resulting oxide layer has been estimated at 4–5 Å. This fact cannot be disregarded in our discussion; within the assumption that the Pd catalysts under kinetic conditions behave in a manner similar to that of the nickel and iron

catalysts of (6), the catalysts constituted of clusters with averaged diameter in the range 10 to 15 Å, once reacted with nitrobenzene, should be regarded as Pd oxide- $C_6H_5N(ads)$ .

At variance with this case, since Pd metal particles  $\geq 50$  Å show well-defined crystallographic features, the occurrence of substrate-metallic surface interaction only along preferential geometrical planes may be envisaged, as demonstrated in a number of cases (25). This leads to different activity of the catalysts constituted of Pd clusters, with respect to those constituted of Pd particles  $\geq 50$  Å. Indeed, the almost total absence of crystalline features for catalysts of type A (11) compels us to surmise an unusual structural condition for the smaller Pd particles or, in any case, a progressive crystalline organization related to the progressive increase of particle diameter. The characterization of catalyst F is representative in this regard. The WAXS pattern obtained is shown in Fig. 6; the volume crystallite distribution function (26) leads to a crystallite averaged diameter of 50 Å, while SAXS analysis indicates a value of 29 Å. The latter agrees with the results of chemisorption analysis, suggesting that a considerable fraction of noncrystalline Pd escapes

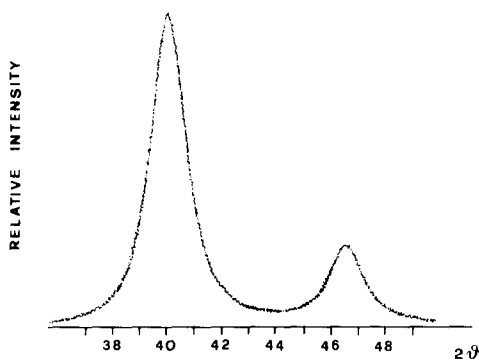


FIG. 6. 111 and 200 peak profile for catalyst F. Background due to glass scattering has been recorded in parallel and matched against the catalyst data. Intensity was collected in  $0.02^\circ$  steps in the range  $35$ – $50^\circ$ . Instrumental conditions: divergence slit  $2^\circ$ ; graphite monochromato; PHA acceptance 40%; X Cu target tube operated at 2 KW.



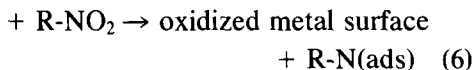
WAXS measurements and that the crystalline fraction of Pd loading refers only to the largest metallic particles.

Finally, the particle dimension dependent role of the Pd hydride phase has recently been stressed in hydrogenation processes (11, 27, 28). A larger content of dissolved H<sub>2</sub> in the larger particles and the easier reversibility of the  $\alpha$ -Pd  $\rightarrow$   $\beta$ -Pd hydride reaction may, to some extent, facilitate the reduction of the metallic surface oxidized by the nitro group dissociation.

### Effects of Substrate Nature

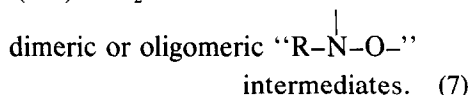
In general, nitrocompounds are quite strong coordinating agents toward metals (29, 30); therefore, it seems unlikely that changes in the nature of the organic group may induce such differences in coordinating the metal as to justify a different hydrogenation mechanism. In the hypothesis of a unique metal-nitrocompound interaction of the type

Pd metal surface



the quite different stability between alkyl and aryl nitrenes (31, 32) may effectively differentiate the kinetic behavior of nitrocompound hydrogenation. C<sub>6</sub>H<sub>5</sub>-N may be stable enough to be directly hydrogenated to aniline, accounting for the kinetic pattern of nitrobenzene reduction. Interestingly, nitrosobenzene hydrogenation carried out with catalysts E and F at 25°C and 1 atm P<sub>H<sub>2</sub></sub> was still independent of substrate concentration and about 100 times faster than nitrobenzene hydrogenation at 90°C. This fact agrees with reaction (6); in fact a less severe oxidation of the metallic surface may be envisaged with a concomitant increase in catalytic activity.

In the cases of Et-NO<sub>2</sub> and t-Bu-NO<sub>2</sub>, the nitrocompound may be involved in the stabilization of the corresponding nitrene intermediates according to the reaction



The tentative formulation of dimeric or oligomeric "R-N-O-" intermediates is consistent with nitrene reactivity; reaction (7) parallels the deoxygenation of nitroso and nitro compounds with phosphines where nitrene intermediate reacts further with the phosphine to give condensation products (33). The hydrogenation of the "R-N-O-" species may positively compete with t-Bu-NO<sub>2</sub> consumption according to reactions (6) and (7); therefore, the exponential profile of percent t-Bu-NO<sub>2</sub> concentration vs time is not surprising, since reaction (6) becomes inhibited or poisoned.

In conclusion, nitroalkane hydrogenation appears to involve, as a crucial point, direct oxygen transfer from the nitro group to the metallic surface, so that the fundamental step consists in the reduction of the oxidized metallic surface rather than hydrogen transfer to nitrogen. This approach finds a leading precedent in the XPS study on nitrobenzene-metallic film interaction (6), in the reaction of oxygen transfer from nitrobenzene to phosphine in Ni(phosphine)<sub>4</sub> complexes (34) where, as in our case, the proposed intermediate involves a net increase in the oxidation state of the metal ion.

### ACKNOWLEDGMENT

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