Mechanism of Palladium-Catalyzed Transfer Hydrogenolysis of Aryl Chlorides by Formate Salts[1]

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Chlorotoluene was hydrodehalogenated using formic acid and its salts in the presence of palladium-on-carbon (10% Pd/C). The hydrogen-donating ability of formate salts was found to depend on the counterion of the formates. The activity decreased in the order: $Cs^+ \approx K^+ > NH_4^+ > Na^+ > NHEt_3^+ > Li^+ > H^+$. The addition of a base such as ammonium acetate to HCOOH accelerated the hydrogenolysis reaction rate establishing that $HCOO^-$ ion is essential for the reaction to proceed. Similarly, addition of a potassium salt to lithium formate increased the rate, again suggesting the importance of the counterion. Hydrogenolysis experiments using molecular hydrogen revealed that HCl formed during the reaction deactivated the catalyst but did not poison it completely. Kinetic studies showed that the rate of hydrodechlorination by the transfer process was independent of the substrate (2-chlorotoluene) concentration. Both hydrogen donor (HCOONa) and the catalyst (10% Pd/C) exhibited first order dependence. Based on the kinetic data and the observed isotope effect, a mechanism has been proposed involving abstraction of formyl hydrogen by the catalyst as the *rate-limiting step*. The rate expression derived was $R = k'$ [HCOONa][Pd/C]. At higher concentrations of hydrogen donor, the dissociation of HCOONa was affected and as a consequence the rate expression changed to $R = k'\alpha$[HCOONa][Pd/C], where α is the *degree of dissociation* of HCOONa.

Introduction

Catalytic transfer hydrogenation/hydrogenolysis is an important synthetic technique in organic chemistry.[2] In contrast to traditional hydrogenation wherein molecular hydrogen is used, this method is more advantageous and less cumbersome due to the fact that it can be achieved at ambient conditions with simple experimental setup. This technique is applicable to numerous functional groups including halo, nitro, cyano, allyl, and benzyl groups as well as aldehydes, ketones, and olefins.[2]

Halogen is often introduced to mask the reactivity at a given position of a molecule during complex organic synthesis; its selective removal precedes the isolation of the final product.[3] In addition, it has been shown that hydrogenolysis of haloaromatics by labeled transfer agents is a very mild and potentially effective method for preparing selectively deuterated or tritiated organic molecules, including biomolecules.[4] These dehalogenation reactions can be achieved in many ways including chemical, electrochemical, and catalytic methods.[3] Among catalytic methods, catalytic transfer hydrogenolysis (CTH) has been utilized by many researchers in the past because of its simplicity and efficiency. A number of hydrogen donors including HCOOH,[5] HCOOLi,[6] HCOONa,[7] HCOOK,[7f,8] $HCOONH_4$,[9] $HCOONHEt_3$,[10] polymethylhydrosiloxane,[7d] indoline,[11] tetrahydroquinoline,[11] methanol,[12] ethanol,[13] 2-propanol,[14] benzyl alcohol,[15] and sodium hypophosphite[16] proved successful in the presence of both heterogeneous (e.g., Pd/C, Raney Ni) and homogeneous (e.g., $PdCl_2(PPh_3)_2$, $Pd(PPh_3)_4$) catalysts. Among these hydrogen donors, formic acid and its salts occupy a special place since the ease of hydrogen donation is higher than with most donors. This is owing to the fact that a stable molecule such as CO_2, which has a very large negative enthalpy of formation ($\Delta H^\circ_{f,298} = -393.51$ kJ mol^{-1}), is released from the hydrogen donor. In other words, these formates possess a carbon that can function as a hydride donor under irreversible conditions.

Recent studies have demonstrated that formate salts are superior to formic acid as hydrogen donors. For

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example, Anwer and Spatola[17] reported that numerous benzyl protecting groups were rapidly and efficiently cleaved using ammonium formate catalytic transfer hydrogenation (AF-CTH). They found under similar conditions, the rate of debenzylation is negligible with HCOOH. Wiener *et al.*[18] also observed that potassium formate was better than sodium formate which in turn was better than formic acid as donors for nitrotoluene reduction. Having noticed that formate salts are better hydrogen donors than other transfer agents, we felt it important to evaluate the hydrogen-donating efficiencies of this class of hydrogen donors. In addition, elucidation of the mechanisms of these transfer hydrogenation reactions is of great significance since these techniques are gaining considerable interest and importance both in laboratory and in industry. Unfortunately mechanistic studies on these reactions are very scarce. The only report on the mechanism of hydrodechlorination of aryl halides by a formate salt (HCOOK) appeared recently which emphasizes the adsorption of the donors on the catalyst as the *rate-determining step*.[8] This proposed mechanism was based on a series of experimental observations on a three-phase (liquid-liquid-solid) catalytic system.

The present study reports for the first time a comparative evaluation of the efficiencies of various formate salts as hydrogen donors and a detailed mechanism of transfer hydrogenolysis of aryl chlorides. HCOONa was chosen as a representative donor for kinetic studies since we have been interested in using ^{2}HCOONa and ^{3}HCOONa for preparing labeled compounds. 2-Chlorotoluene was selected as substrate, though 4-chlorotoluene gave similar results. This choice was based on the purity of 2-chlorotoluene which was >99%.

Results and Discussion

The Hydrodechlorination Reaction. The hydrodechlorination reaction of aryl halides in the presence of formic acid or formate salts can be written as

$$\mathrm{ArCl + HCOOM \rightarrow ArH + MCl + CO_2} \quad (1)$$

where M is H, alkali metals, NH_4, $NHEt_3$, etc.

The above reaction is generally catalyzed by transition metals such as palladium under mild conditions. It is important to emphasize here that formic acid and its salts decompose catalytically in the *absence* of hydrogen acceptor (in this case, ArCl) according to eqs 2–4, which are practically irreversible in open reaction vessels. In the case of alkali metal formates, solvent (generally water or alcohol) takes part in the reaction to form bicarbonate species (eq 3) where M is alkali metal.

$$\mathrm{HCOOH \rightarrow H_2 + CO_2} \quad (2)$$

$$\mathrm{HCOOM + H_2O \rightarrow H_2 + CO_2 + OH^- + M^+ \rightarrow H_2 + MHCO_3} \quad (3)$$

$$\mathrm{HCOONH_4 \rightarrow H_2 + CO_2 + NH_3} \quad (4)$$

In view of this, one can envisage at least three possible reaction pathways for transfer hydrogenolysis of aryl halides in the *presence* of the above hydrogen donors: (i) formate decomposition precedes hydrodechlorination reaction; that is, hydrogenolysis of aryl halide is accomplished via a *dehydrogenation–hydrogenation* route, (ii) decomposition of formate also occurs during the hydrogenolysis reaction in a parallel path liberating H_2, and (iii) formyl hydrogen exclusively transfers to the acceptor molecule via catalyst surface resulting in dechlorination.

Using molecular hydrogen as a reductant, it is shown that the first possibility is eliminated, since the rate of dechlorination is much slower with H_2 gas. The absence of $NaHCO_3$ in the product and the near stoichiometric nature of the reaction suggest that the parallel reaction is almost absent when HCOONa is used as hydrogen donor. Hence, the hydrogenolysis reaction appears to be entirely a transfer process. This supports the fact that the hydrogen transfer from hydrogen donor to an acceptor is thermodynamically more favored instead of being evolved as molecular hydrogen. Control experiments in which the catalyst was omitted indicated that the uncatalyzed reaction is totally absent at 20 °C. Also, the reaction did not proceed in the absence of HCOONa signifying that the ethanol is not a good hydrogen donor under these conditions.

Activation of the Catalyst. The catalyst (10% Pd/C), though it is supplied in the reduced form, can pick up oxygen and other gases/vapors present in ambient air during storage and handling. This might limit the activity of the catalyst to some extent. One might argue that physisorbed or chemisorbed gases at room temperature may not pose any problem. But we have shown earlier that the catalytic activity of Pd/C is improved significantly when it is activated before the addition of hydrogen acceptor.[9b] For example, complete dechlorination of 4-chlorotoluene occurred in less than 15 min at room temperature when ammonium formate was added to the 5% Pd/C catalyst prior to the introduction of the substrate, while the same took about 90 min when the donor was added after the substrate. In view of this, we have activated the catalyst with the hydrogen donor for 30 s to avoid any induction period as a result of adsorbed impurities which might affect the accuracy of initial rate measurements. During this activation period, copious liberation of hydrogen and carbon dioxide was noticed indicating the decomposition of the formic acid or its salts.[19] We presume that during this activation process many of the surface impurities are removed and more catalytic sites are exposed.

The order of addition of the reagents may also play an important role in these reactions. After experimenting with different possibilities, we selected the following standard protocol. Hydrogen donor was first dissolved in a solvent, catalyst was then added, followed by a 30 s delay for activation of the catalyst by the donor, and finally the substrate was added. The analysis of the evolved gases during the hydrodechlorination reaction revealed that very small amounts of H_2 gas (0.1 mL min^{-1}) were formed via side reaction (decomposition). The rate of this parallel reaction is found to decrease with reaction time; in other words, it is proportional to the formate concentration. The formate loss via this process is considered negligible (<1% of total formate used) as inferred from the net amount of hydrogen liberated. To compensate for the loss of formate salts during both

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(19) Decomposition (dehydrogenation) of formic acid is much slower than its salts.

activation process and via side reaction(s), a 20% excess of donor was used.

Hydrogen-Donating Abilities of Various Formate Salts. We[17] and others[18] have shown that salts of formic acid are much better hydrogen donors than formic acid. This is the main reason why formate salts, rather than formic acid, have been employed for transfer hydrogenolysis of various functional groups in the literature. In spite of the wide use of formate salts as hydrogen donors, there has been no systematic study to date describing the efficiencies of various formates. We have, therefore, selected some of the most common and easily accessible salts of formic acid such as HCOOLi, HCOONa, HCOOK, HCOOCs, $HCOONH_4$ and $HCOONHEt_3$ and studied their relative activities. Some of these formate salts are either commercially unavailable or hygroscopic in nature. In order to obtain quantitative results, the assay of formate salts should be accurately known. This condition demands that hygroscopic salts need thorough drying before use. Also, the laboratory made formates (e.g., HCOOLi, HCOOCs, and $HCOONHEt_3$) should match the purity and other characteristics with the commercial samples in order to obtain a meaningful comparison among these formate salts. To avoid such variance, all formate salts were prepared starting from the same "lot" of formic acid. After preparing all the formate salts, a comparison was made, for instance, between the laboratory made aqueous HCOONa and the dried commercial sample of HCOONa (Matheson Coleman & Bell, reagent grade) which gave identical activity results for hydrodechlorination of 2-chlorotoluene.

Palladium supported on activated carbon (10% Pd/C) was chosen as the catalyst. This choice was based on our earlier findings[9b] that Pd/C was far superior to other supported catalysts such as Pd/Al_2O_3, Pd/kieselguhr, $Pd/BaSO_4$, and $Pd/CaCO_3$. From the same study, ethanol was found to be one of the best solvents for the hydrodechlorination reaction. Therefore, a mixed solvent system containing ethanol ($EtOH:H_2O$ 88:12), which can bring both substrate and the water-soluble hydrogen donor into solution, was utilized in this study. Under these conditions, the reaction can be classified as a *true* liquid-phase heterogeneous catalytic system involving two condensed phases. When 2-chlorotoluene (0.20 M), formic acid or its salts (0.24 M), and 10% Pd/C (0.20 g) were mechanically stirred under inert atmosphere at 20 °C, the hydrogen-donating abilities of the Group 1A formates followed the order $Cs^+ \approx K^+ > Na^+ > Li^+ > H^+$. The time-conversion profiles for all the formates are presented in Figure 1. For each hydrogen donor, the reaction was repeated to arrive at the initial rates, which are given in Table 1.

The arguments, which are plausible explanations for the observed activities of Group 1A formates, run as follows. The separation of the formate ion from its cation, which is necessary for the ionization of alkali metal formates, depends on both the polarity of the bond and the internuclear distance between the oxygen(s) of the formate and the alkali metal ion. It is well authenticated that the greater the polarity of the bond, the greater the ease of ionization. Assuming equal polarities of the O–M bond in HCOOM, where M is H, Li, Na, K, Cs, the ease of separation of ions is greatly influenced by the initial distance between their centers of charge. The equal polarity assumption is logical since all alkali metal hydroxides are categorized as strong bases. Cation size increases on passing down the periodic group, and consequently the internuclear distance between O–M increases with increasing atomic number. The degree of dissociation of the formates and thus the donor activity will follow the order: HCOOCs > HCOOK > HCOONa > HCOOLi > HCOOH.

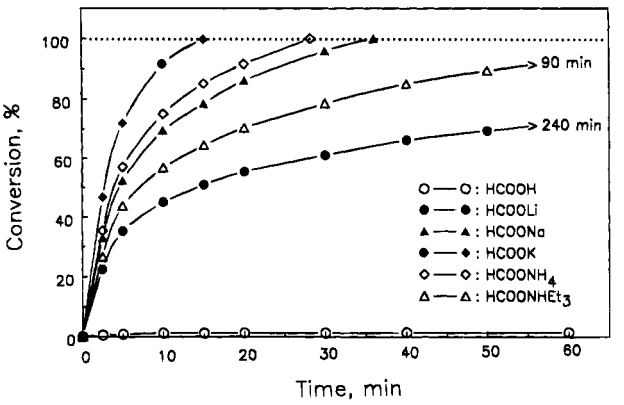

Figure 1. Reaction profiles for transfer hydrogenolysis of 2-chlorotoluene in the presence of various hydrogen donors. Time-conversion plot for HCOOCs, which is similar to HCOOK, is omitted for clarity. Reaction conditions: 2-chlorotoluene (5 mmol, 0.20 M), hydrogen donor (6 mmol, 0.24 M), catalyst (10% Pd/C, 0.20 g), solvent (88% ethanol, 25 mL), and temperature (20 °C).

Table 1. Initial Rates of Transfer Hydrogenolysis for Various Formate Salts[a]

hydrogen donor	initial rate × 10^3, mol L^{-1} min^{-1}	100% conversion time, min
HCOOH	0.71	∞
HCOOLi	31.4	240
HCOONa	46.2	36
HCOOK	65.4	17
HCOOCs	60.2	18
$HCOONH_4$	49.5	28
$HCOONHEt_3$	37.3	90

[a] Reaction conditions: 2-chlorotoluene (5 mmol, 0.20 M), formate salt (6 mmol, 0.24 M), catalyst (10% Pd/C, 0.20 g), ethanol (22 mL), water (3 mL), and temperature (20 °C).

Table 2. Ionic Size and Electronegativities of Group 1A Elements and Their Cations

Group 1A element	size, Å		electronegativity	
	element	cation	element[a]	cation[b]
H	0.37	negligibly small	2.1	7.47
Li	1.34	0.6	1.0	2.53
Na	1.54	0.95	0.9	2.44
K	1.96	1.33	0.8	2.12
Rb	2.11	1.48	0.8	2.04
Cs	2.25	1.69	0.7	1.95

[a] Pauling scale. [b] Electronegativities of cations calculated from atomic stability ratios.

Accordingly, the degree of dissociation of the formate salts should increase with the ionic size of the Group 1A elements. As can be seen in Figure 1, the observed activity results for various formates agree very well with this hypothesis. A quantitative correlation, however, can be obtained with the use of ionic radii values of Group 1A elements. For reference, the ionic sizes (Å) of these ions are presented in Table 2. A plot of initial reaction rates versus ionic radii (Figure 2) has demonstrated that the relation is indeed quite striking up to K^+. Beyond this, some other factors such as slower diffusion of reactants may be offsetting this dissociation advantage, therefore not reflected in initial reaction rates. In other words, the rate of diffusion of reactants within the pore

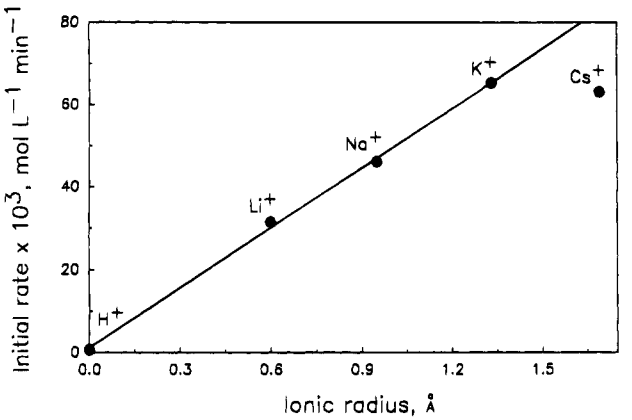

Figure 2. Influence of counterion of alkali metal formates on the hydrogen-donating ability.

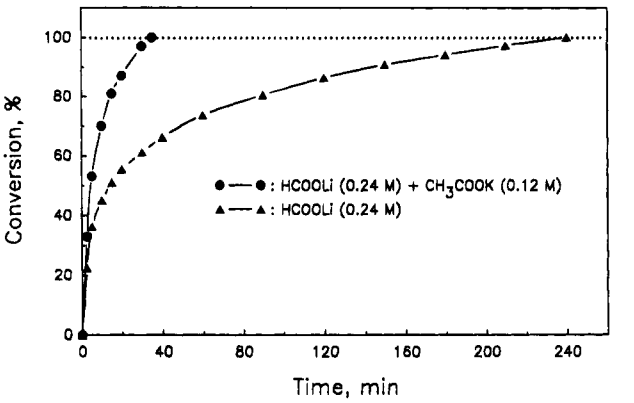

Figure 3. Effect of potassium ion on the hydrogen-donating efficiency of HCOOLi. Reaction conditions: as in Figure 1.

structure is slower than the reaction rate. Electronegativity of the Group 1A elements did not yield any meaningful correlation with the initial rates.

As previously noted, Wiener *et al.* compared the efficiencies of HCOOH, HCOONa, and HCOOK as hydrogen donors.[18] They observed that HCOOK is significantly more active than sodium formate while the free acid is practically inactive for nitrotoluene reduction. The difference in activity between the two salts was attributed to the higher solubility of $KHCO_3$ (4 M at 35 °C) as compared with $NaHCO_3$ (1 M at 35 °C). Their understanding is that the lower solubility of $NaHCO_3$ indirectly reduced the activity by partially covering the catalyst surface.

The other formate salts used in this comparative study are $HCOONH_4$ and $HCOONHEt_3$. Their observed activities are ranked as follows: $HCOONH_4$ > $HCOONHEt_3$ > HCOOH. As mentioned earlier, the polarity of the O–N bond and the size of the cation are the two important properties which can be used to rationalize the observed activity results. From the strength of the corresponding bases, viz., NH_3 (pK_a = 9.25), Et_3N (pK_a = 10.72), one would expect $HCOONHEt_3$ to show greater activity as O–N bond polarity is expected to be higher for the stronger base. The size effect also dictates that $HCOONHEt_3$ would display higher activity. But the observed results do not fit this scenario. Apparently, the cation size comparison is not valid in these two instances (NH_4^+ and $NHEt_3^+$) where steric hindrance predominates in the latter case. It is believed that the steric factor may be neutralizing the polarity advantage. Therefore, the ease of adsorption of formate ion on palladium surface may be hindered when the counterion is much bulkier ($NHEt_3^+$).

To further demonstrate the importance of counterion and also show the influence of added counterion of different size, an experiment of transfer hydrogenolysis was performed wherein a salt of potassium, viz., CH_3COOK, was added to HCOOLi (eq 5). The time-conversion plots for reactions with and without the addition of potassium salt are depicted in Figure 3. From the kinetic data, it was inferred that the initial rate has increased from 31.4 × 10^{-3} mol L^{-1} min^{-1} for HCOOLi to 46.1 × 10^{-3} mol L^{-1} min^{-1} when 3 mmol of CH_3COOK was added. The initial rate value for HCOOK is 65.4 × 10^{-3} mol L^{-1} min^{-1}.

$$HCOOLi + CH_3COOK \rightleftharpoons HCOOK + CH_3COOLi \quad (5)$$

Formic Acid as Hydrogen Donor. As shown in Figure 1, formic acid is a very poor hydrogen donor for the hydrodehalogenation of 2-chlorotoluene. The conversion levels did not exceed 2% even after 240 min. If the availability of formate ions is a limitation, then one should observe a steady increase in conversion with time, however little it may be. The time–conversion profile looks as if one of the products, viz., HCl, has poisoned the catalyst irreversibly. But it has been documented in the literature[20] that HCl has only a deactivating influence on the catalyst. Therefore, it is quite common to add bases such as alkali or alkaline metal hydroxides, acetates, alkoxides, amines, and ammonia during dechlorination using molecular hydrogen to scavenge HCl and accelerate the reaction.

In contrast to the present results, there are also examples of hydrodechlorination of aryl halides with HCOOH. In a recent report,[5a] HCOOH has been utilized for dechlorination of several chloro compounds in boiling dimethylformamide. The removal of HCl at the reaction temperature of 153 °C or the likely presence of dimethylammonium formate (formed from dimethylamine, a decomposition product of DMF) may have contributed to this accomplishment. In another example, HCOOH in DMF was successfully used for hydrodechlorination in the presence of Pd/C at 50–60 °C; in this example, the substrate had two amine groups which apparently served as scavengers for HCl.[5b]

In our experiments, we first examined the effect of addition of a base to the HCOOH system. Ammonium acetate was selected for solubility reasons. The reactions in the presence of ammonium acetate are written as follows:

$$HCOOH + CH_3COONH_4 \rightleftharpoons HCOONH_4 + CH_3COOH \quad (6)$$

$$ArCl + HCOONH_4 \rightarrow ArH + CO_2 + NH_4Cl \quad (7)$$

It can be seen from the Figure 4 that when ammonium acetate (6 mmol) was added after 30 min, the reaction took 90 min for completion. However, when it was added initially, the hydrogenolysis reaction proceeded to 100% conversion in 30 min. The calculated initial rates for these two situations are 37.5 × 10^{-3} mol L^{-1} min^{-1} and

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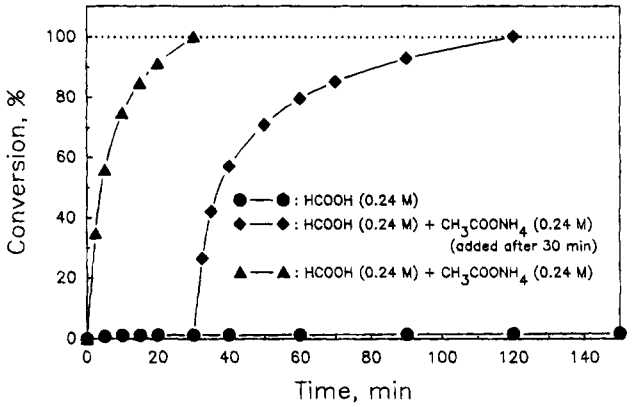

Figure 4. Effect of ammonium acetate on hydrodechlorination of 2-chlorotoluene by HCOOH. Reaction conditions: as in Figure 1.

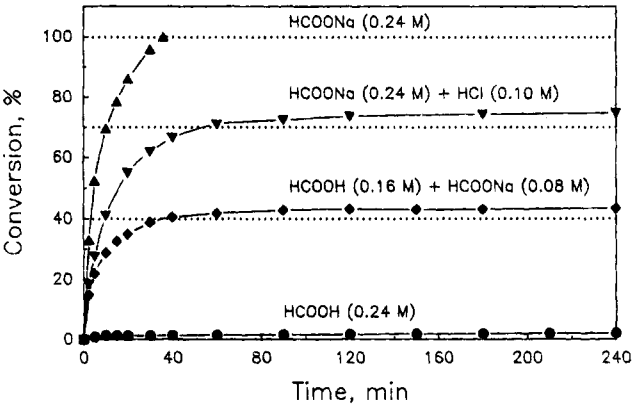

Figure 5. Effect of HCOONa on the hydrogen-donating ability of HCOOH and the influence of HCl on the catalytic activity. Reaction conditions: as in Figure 1.

48.7×10^{-3} mol L^{-1} min^{-1}, respectively. The decreased rate in the former case may be explained if it is assumed that HCl formed during the initial 30 min partially deactivated the catalyst.

It has been hypothesized that insufficient activation of the catalyst by HCOOH might be one of the reasons for low conversion. The basis for this postulate is that the activation of the catalyst by HCOOH is considered slower than the formate salts. To verify this premise, the ensuing experiment was realized. A mixture of HCOONa (0.08 M) and HCOOH (0.16 M) was used so that *HCOONa-activated catalyst* could help transfer hydrogen from HCOOH to the aryl halide. The results presented in Figure 5 clearly demonstrate that this is not the case. The reaction rate was high as long as HCOONa (equivalent to 40% conversion) was present in the medium. Once it was consumed, the rate of the reaction dropped and reached a plateau. Beyond the 40% conversion limit, HCOOH took part in the reaction and as a result HCl was formed (pH decrease). From these results, it is concluded that HCl equivalent to 2% conversion of aryl halide appears to be the threshold concentration to suppress the transfer hydrogenolysis by formic acid.

The above results prompted us to examine the effect of *added* HCl on catalytic activity. To achieve this goal, a test kinetic run was made in which HCl was added to a solution of sodium formate (Figure 5). Such a study proved to be not very informative since HCOONa (a salt of a weak acid and a strong base) reacts with HCl (strong

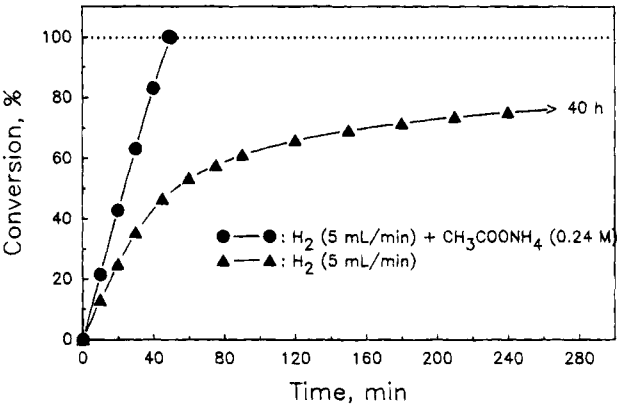

Figure 6. Hydrogenolysis of 2-chlorotoluene using molecular hydrogen. Reaction conditions: 2-chlorotoluene (5 mmol, 0.20 M), solvent (88% ethanol, 25 mL), catalyst (10% Pd/C, 0.20 g), temperature (20 °C), and H_2 flow (5 mL/min).

acid) to form HCOOH and NaCl. This was reflected in the kinetic profile. As indicated above, once HCOONa is depleted (in this case, the resultant HCOONa is equivalent to 70% conversion), the rate fell sharply. This experiment generated additional information but not the one we anticipated in the first place, i.e., whether or not HCl poisons the catalyst. As a result, an alternative hydrogenolysis experiment wherein HCl would be generated during the reaction was designed to fulfill the objective. One such reaction is the traditional catalytic hydrogenolysis using molecular hydrogen.

Hydrogenolysis of 2-Chlorotoluene. We wished to obtain quantitative information on the influence of liberated HCl on the hydrogenolysis rate and also to monitor the change in reaction rate when HCl is trapped with a base (CH_3COONH_4). The kinetic results of the hydrogenolysis reaction are depicted in Figure 6. As seen from the figure, the liberated HCl did have a negative influence on the catalyst but did not poison the catalyst completely. It is inferred that the deactivating effect was proportional to concentration of HCl formed. The reaction took 40 h for completion with an initial rate of 2.6×10^{-3} mol L^{-1} min^{-1}. The pH of the final solution was found to be approximately one. On the other hand, the addition of 6 mmol of CH_3COONH_4 enhanced the reaction rate dramatically, and the reaction time was reduced to 50 min with an initial rate of 4.3×10^{-3} mol L^{-1} min^{-1}. This clearly confirms that H^+ ion retards the palladium's capability toward the activation of H_2. The same may be true for $HCOO^-$ ion activation. Having demonstrated the influence of H^+ (HCl) on the catalyst, we next selected another important catalytic system, viz., hydrogenolysis of the C–O bond, to obtain further insights into the mechanism of these reactions.

Transfer Hydrogenolysis of Benzyl Acetate. We were curious to comprehend what happens when HCOOH is used as a hydrogen donor for a reaction in which strong acid such as HCl is not formed as a product. One such reaction is the hydrogenolysis of benzyl acetate as shown in eq 8. Can this system provide enough formate ions for the reaction to proceed?

$$PhCH_2OCOCH_3 + HCOOH \rightarrow PhCH_3 + CH_3COOH + CO_2 \quad (8)$$

The answer to the above question is yes. Indeed, HCOOH is capable of providing enough $HCOO^-$ ions

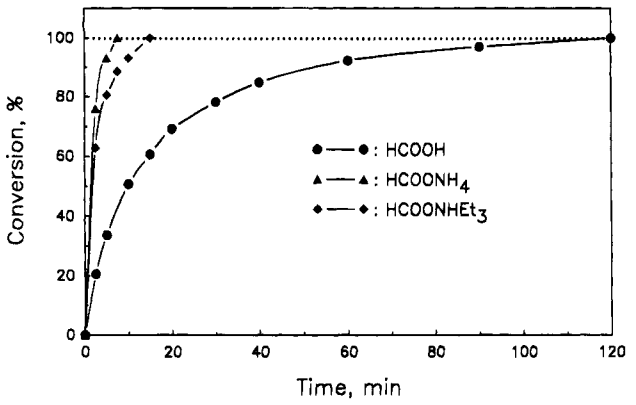

Figure 7. Kinetic profiles for transfer hydrogenolysis of benzyl acetate by HCOOH, $HCOONH_4$, and $HCOONHEt_3$. Reaction conditions: benzyl acetate (5 mmol, 0.20 M), hydrogen donor (6 mmol, 0.24 M), catalyst (10% Pd/C, 0.20 g), solvent (88% ethanol, 25 mL), and temperature (20 °C).

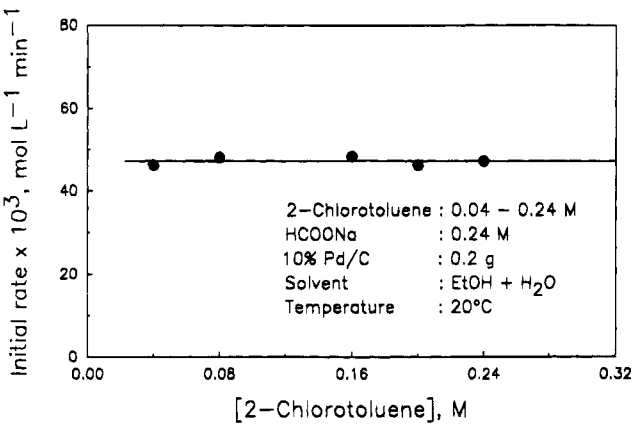

Figure 8. Dependence of the initial rate on the concentration of substrate (2-chlorotoluene).

under these experimental conditions (Figure 7). Though the equilibrium concentration of formate ions is smaller (6.5×10^{-3} M if it were aqueous solution), they can be replenished via dissociation as they are consumed. The initial rate of this reaction is 23.9×10^{-3} mol L^{-1} min^{-1}. For comparison, the above reaction was performed independently using ammonium formate and triethylammonium formate as hydrogen donors. The time–conversion profiles as depicted in Figure 7 and the calculated initial rates of 85.7×10^{-3} mol L^{-1} min^{-1} and 70.6×10^{-3} mol L^{-1} min^{-1}, respectively, further substantiate the importance of formate ions in these reactions.

The above described series of experiments have provided us a wealth of information on the general behavior of the catalytic system in question. It is unequivocally shown that (i) $HCOO^-$ ion is an important precursor for the reaction, (ii) HCl deactivates the catalyst but does not poison it completely, and (iii) HCl, being a strong acid, suppresses the dissociation of formic acid thereby depleting the concentration of $HCOO^-$ ions. After acknowledging these facts, the more specific kinetic data on hydrodechlorination of 2-chlorotoluene, viz., reaction order with respect to each reactant, was attempted by changing the variables such as the concentration of substrate, hydrogen donor, and the catalyst.

Reaction Order Determination. As seen from Figure 8, the initial rate of hydrodechlorination of 2-chlorotoluene using sodium formate and 10% Pd/C catalyst is independent of the substrate concentration in the range

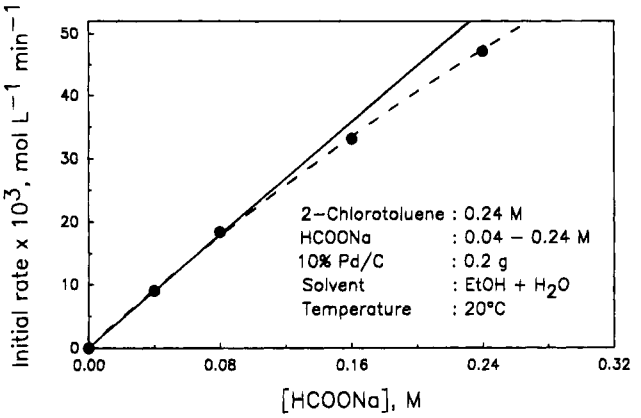

Figure 9. Dependence of the initial rate on the concentration of hydrogen donor (HCOONa).

examined. This zero order dependence demonstrates that either adsorption of substrate or surface reaction is a fast step and occurs after the *rate-determining step*. It is proved independently that decomposition of sodium formate to hydrogen and $NaHCO_3$ on the catalyst surface (eq 3) is arrested immediately after introduction of chloroaromatics. This suggests that the hydride on the catalyst surface is more reactive toward chloroaromatics than either water or alcohol. But once all chloroaromatics are consumed, the liberation of hydrogen again resumes if excess hydrogen donor is present in the system.

The plot of initial rate of reaction versus the initial concentration of hydrogen donor (HCOONa) is shown in Figure 9. The reaction rate followed a linear relationship with the concentration of HCOONa over the range 0.0–0.08 M. At higher concentrations the linearity is no longer held. The deviation from linearity may be a result of the diminished supply of formate ions; i.e., the concentration of free $HCOO^-$ species is not equivalent to the concentration of HCOONa when [HCOONa] > 0.08 M. At the same time, we can not rule out the possibility that $NaHCO_3$ formed during the initial activation process may be responsible for this deviation.

The dependence of the initial rate on the concentration of catalyst is essential to establish the reaction order. The catalyst being a supported heterogeneous catalyst, the total amount of palladium present in the catalyst does not represent the real concentration since only surface metal atoms are active for catalysis. Therefore, the number of active sites (number of surface metal atoms) were calculated using the XRD technique. The X-ray powder diffraction profile, which was used to compute the integral line width and hence mean crystallite size is shown in Figure 10. After accounting for instrumental line broadening, the crystallite size was determined using the Scherrer equation.[21] The calculated average crystallite size and the percent metal dispersion are 5.3 nm and 17%, respectively. The plot of initial rate versus the amount of catalyst (number of active sites) is displayed in Figure 11. The first order dependence indicated that the overall reaction rate is proportional to the total number of active sites on the catalyst. Based on the kinetic results, no catalyst poisoning by the reagents was observed.

Isotope Effect. Isotopic techniques have become vital in mechanistic studies of many chemical reactions,

(21) Klug, H. P.; Alexander, L. E. *X-ray Diffraction Procedures*; Wiley: New York, 1954.

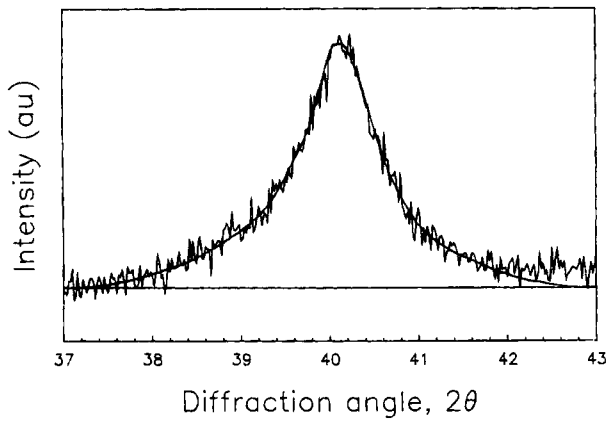

Figure 10. X-ray powder diffraction profile of the Pd(111) peak of 10% Pd/C catalyst.

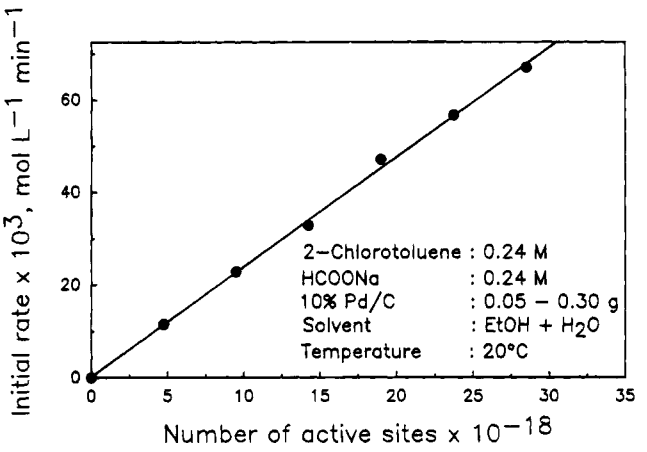

Figure 11. Dependence of the initial rate on the amount of catalyst (number of active sites).

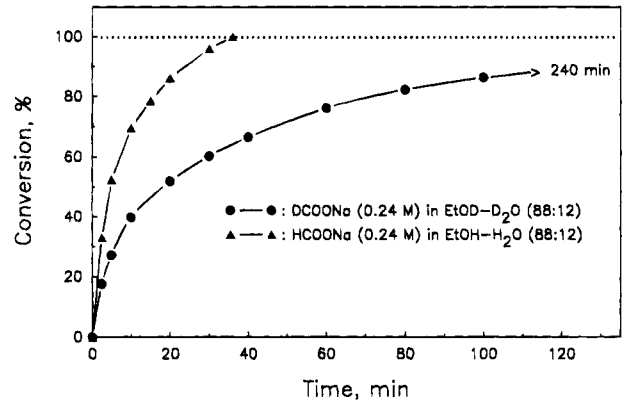

Figure 12. Effect of DCOONa on the rate of transfer hydrogenolysis of 2-chlorotoluene. Reaction conditions: as in Figure 1.

particularly heterogeneous catalysis, where the reaction mechanisms are more complex in nature. Therefore, experiments were designed to understand the mechanism with the aid of isotopically labeled hydrogen donors. To achieve this goal, kinetics of transfer hydrogenolysis of 2-chlorotoluene by HCOONa–EtOH–H_2O and DCOONa–EtOD–D_2O were performed under the same conditions employed elsewhere in this study (Figure 12). From the initial rates obtained, 46.2×10^{-3} mol L^{-1} min^{-1} and 24.7×10^{-3} mol L^{-1} min^{-1}, respectively, the primary kinetic isotope effect was calculated to be 1.87. This result suggests that the transfer of formyl hydrogen of the donor

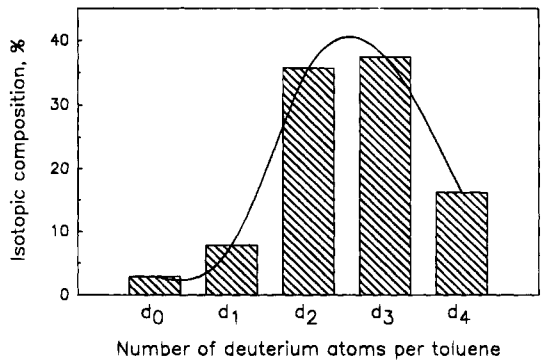

Figure 13. Deuterium isotope distribution in toluene formed during transfer hydrogenolysis of 2-chlorotoluene by DCOONa.

onto the catalyst surface is the *rate-determining step* in the overall process. This observation substantiated our earlier findings[4] on hydrodechlorination of Boc-D-*p*-ClPhe using $HCOONH_4$ and $DCOONH_4$. A similar conclusion had been made by Azran *et al.* for the homogeneous catalytic transfer hydrogenation of benzylideneacetophenone by formic acid using a polymer-based $IrCl(CO)(PPh_3)_2$ catalyst.[22]

Wiener *et al.*[18] found that a kinetic isotopic effect was absent when HCOOK–H_2O was replaced by DCOOK–D_2O during nitrotoluene reduction. They concluded that the scission of the formyl C–H and the water O–H bonds were not part of the *rate-limiting step* in the overall process. The main reason for not observing the isotope effect in their case could be the use of a triphasic (liquid/liquid/solid) system which complicates the kinetics. Nevertheless, the same authors[23] had earlier reported that the isotopic effect was substantial (k_H/k_D = 23.8) in the case of decomposition of sodium formate (HCOONa–H_2O vs DCOONa–D_2O) catalyzed by 5% Pd/C at 35 °C. They suggested that participation of both formate ion and water in the rate-determining step is the reason for the large isotope effect. These results are in agreement with our findings that the catalytic decomposition of HCOONa was very facile at 20 °C while decomposition of DCOONa was much slower with a long induction period.

The product (toluene) analysis by GC-MS revealed that benzylic hydrogens are very labile on the surface of palladium. The amount of deuterium in the product was calculated to be far in excess of the principal source of deuterium, viz., DCOONa. Figure 13 shows the extent of deuterium incorporation in the product. In addition to the expected monodeuterated product (2-deuteriotoluene), di-, tri-, and tetradeuterated toluenes were formed. The latter products were produced as a result of exchange reactions between benzylic hydrogens and solvent deuteriums assisted by the Pd surface. It was shown that uncatalyzed exchange between toluene and EtOD/D_2O was not facile at reaction conditions. The product distribution in the case of 4-chlorotoluene was similar to 2-chlorotoluene. During hydrodehalogenation of aromatic halides under basic conditions, a side reaction, viz., coupling is frequently observed. When HCOONa was used as hydrogen donor, this side reaction was completely absent as evident from HPLC analysis results. On the other hand, the coupling product (2,2′-dimethylbiphenyl) was formed in less than 0.5% when DCOONa was used.

(22) Azran, J.; Buchman, O.; Orchin, M.; Blum, J. *J. Org. Chem.* **1984,** *49,* 1327.
(23) Wiener, H.; Sasson, Y.; Blum, J. *J. Mol. Catal.* **1986,** *35,* 277.

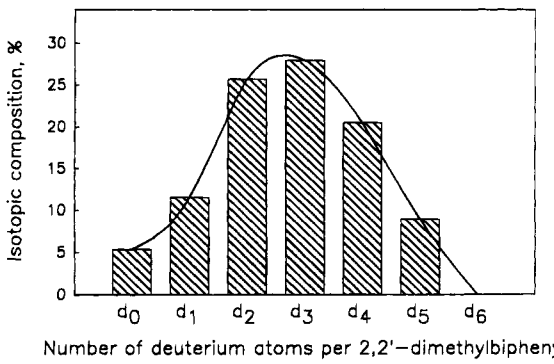

Figure 14. Deuterium isotope distribution in 2,2'-dimethylbiphenyl formed during transfer hydrogenolysis of 2-chlorotoluene by DCOONa.

The GC-MS analysis of this compound yielded a product of composition as shown in Figure 14.

Mechanism. It is apparent that formate ion is the active species in the transfer hydrogenolysis process. Sodium formate, the source for formate ion, does not seem to dissociate completely into $HCOO^-$ and Na^+ ions in 88% ethanol especially at high concentrations. Therefore, the dissociation of the sodium formate is considered as the first step of this transfer hydrogenolysis mechanism (eq 9).

The second step in the process may be the adsorption of $HCOO^-$ onto the palladium metal surface (eq 10). This adsorption leads to dissociative chemisorption resulting in PdH^- and CO_2 (eq 11). The active PdH^- then reacts with aryl chloride to form arene and Cl^-. Since carbon dioxide is a poor adsorbate, it leaves the surface and escapes into the gas phase. In the absence of any hydrogen acceptor, the hydride or hydride like species picks up a proton from either water or ethanol to form H_2 which can also leave the catalyst and eventually the liquid phase since the solubility of H_2 is limited. The hydroxide ion (in the case of water) combines with CO_2 to form bicarbonate. The evolution of H_2 and the formation of $NaHCO_3$ (pH increase) support the above mechanistic pathway. In the case of HCOOH or $HCOONH_4$ or $HCOONHEt_3$, the hydride ion combines with H^+ or NH_4^+ or $NHEt_3^+$ depending on the donor to produce H_2. These are precisely the mechanisms of decomposition of formic acid and its salts on most transition metals (eqs 2–4).

The observed kinetic isotopic effect suggests that the dissociative chemisorption of formate (eq 11) is the *rate-determining step* in the overall process. The zero order dependence of the substrate shows that adsorption (eq 12) as well as reaction (eq 13) of 2-chlorotoluene occur in fast steps. These equations have been represented as individual stages; however, there appears to be no reason for not considering them as a single step. The nucleophilic character of H^- coupled with the high affinity of Na^+ toward Cl^- probably make the reaction between PdH^- and 2-chlorotoluene instantaneous. Wiener *et al.* have emphasized the role of water in these reactions and have proposed HCO_3^- as a surface intermediate.[8] From our results, it is clear that water does not act as a hydrogen donor. Thus, it is unlikely that HCO_3^- is an intermediate in these reactions.

The chemisorbed hydrogen (Pd–H) can exhibit H^-, H, or H^+ behavior depending on the environment such as reactants and process conditions. There is evidence in the literature that it displays either H^- or H^+ character in the liquid phase. For example, during hydrodehalogenation of chlorotoluenes, H^- like behavior is obvious.[1,2d] In the case of coupling reactions in the presence of a strong base such as an alkali metal hydroxide, H^+ is removed from PdH^- leaving two electrons on the surface of the metal cluster. These electrons are responsible for radical chemistry witnessed in the coupling reaction of bromobenzene to yield biphenyl in the presence of HCOONa and Pd/C.[24]

From the kinetic data, the following mechanism has been proposed for the hydrodechlorination of 2-chlorotoluene by HCOONa under the catalytic influence of 10% Pd/C. The catalyst is denoted as Pd^0 for convenience.

$$HCOONa \overset{K_1}{\rightleftharpoons} HCOO^- + Na^+ \quad (9)$$

$$Pd^0 + HCOO^- \overset{K_2}{\rightleftharpoons} Pd(HCOO^-)_{ad} \quad (10)$$

$$Pd(HCOO^-)_{ad} \xrightarrow[k]{\text{slow}} PdH^- + CO_2 \quad (11)$$

$$PdH^- + ClC_6H_4CH_3 \xrightarrow{\text{fast}} PdH^-(ClC_6H_4CH_3)_{ad} \quad (12)$$

$$PdH^-(ClC_6H_4CH_3)_{ad} \xrightarrow{\text{fast}} Pd^0 + C_6H_5CH_3 + Cl^- \quad (13)$$

Rate expressions have been derived based on this mechanism. Sodium formate, being an electrolyte, dissociates completely into $HCOO^-$ and Na^+ ions at low concentrations ($\leq$0.08 M) and hence concentration of $HCOO^-$ is equal to the initial concentration of HCOONa.

$$\text{rate} = k[Pd(HCOO^-)_{ad}] \quad (14)$$

$$[Pd(HCOO^-)_{ad}] = K_2[Pd^\circ][HCOO^-] \quad (15)$$

$$\therefore \text{rate} = kK_2[Pd^0][HCOO^-] = kK_2[Pd^0][HCOONa]_0 \quad (16)$$

At higher concentrations of HCOONa (>0.08 M), incomplete dissociation of HCOONa into $HCOO^-$ and Na^+ ions is presumed. For the sake of clarity, the *degree of dissociation* (α) of sodium formate which is related to dissociation constant K_1 is taken into consideration.

$$\text{rate} = k[Pd(HCOO^-)_{ad}] \quad (17)$$

$$[Pd(HCOO^-)_{ad}] = K_2[Pd^0][HCOO^-] \quad (18)$$

$$[HCOO^-] = \alpha[HCOONa]_0 \quad (19)$$

$$\therefore \text{rate} = k\alpha K_2[Pd^0][HCOONa]_0 \quad (20)$$

The *degree of dissociation*, which is a function of concentration, becomes unity as concentration tends to zero. Therefore, at low concentrations of sodium formate, eq 20 inverts to eq 16. The above rate expressions are

(24) (a) Bamfield, P.; Quan, P. M. (Imperial Chemical Industries Ltd), Ger. Offen. 2,540,740, 1976. (b) Bamfield, P.; Quan, P. M. *Synthesis* **1978,** 537. (c) Shimizu, S.; Sasaki, Y.; Hirai, C. *Bull. Chem. Soc. Jpn.* **1990,** *63,* 176.

consistent with our experimental observations and hence the validity of the mechanism is supported.

Conclusions

Catalytic transfer hydrogenation/hydrogenolysis using formate salts is a versatile technique useful for a wide variety of functional groups including aryl chlorides. The hydrogen-donating abilities of formate salts have been shown to depend on the counterion. In the case of alkali metal formates the activities increased linearly with ionic size. But $HCOONH_4$ was found to be a better hydrogen donor than $HCOONHEt_3$. Here, the polarity of the O–N bond, which depends on the basicity of the corresponding base does not explain the observed results. Presumably, the steric hindrance exerted by the bulkier $NHEt_3^+$ ion hinders the adsorption of formate on palladium surface rendering it less active. The poor hydrogen-donating ability of formic acid toward aryl chlorides is partly attributed to the deactivating effect of the reaction product HCl on the catalyst. The major factor, however, is the suppression of the HCOOH dissociation by a strong acid HCl (the common ion effect) depleting the concentration of $HCOO^-$ ions. It is undoubtedly shown that $HCOO^-$ is the active species during hydrogenolysis and not HCOOH. This finding has an important fundamental significance, which helps to rationalize the nature of formate ion interaction with metal surfaces. The activation of undissociated HCOOH by the solid metal catalyst appears to be forbidden at ambient conditions. The kinetic data and the isotope effect demonstrate that scission of the formyl C–H bond is the *rate-determining step*. The hydride or hydride-like species formed on the Pd surface reacts with the substrate in a fast step resulting in the desired hydrogenolysis reaction.

Experimental Section

Materials. 2-Chlorotoluene (Aldrich, 99+%), 4-chlorotoluene (Aldrich, 98%), formic acid (Aldrich, 95–97%), LiOH (Mallinckrodt Chemical Works, purified), NaOH (J. T. Baker, Analyzed Reagent), KOH (J. T. Baker, Analyzed Reagent), CsOH (Aldrich), ammonium hydroxide (Fisher Scientific, 28–30%), absolute ethanol (Aaper Alcohol and Chemical Co.), EtOD (Aldrich, >99.5 atom % D), D_2O (Aldrich, 99.7 atom % D), DCOONa (MSD Isotopes, 99 atom % D), and catalyst (Aldrich, 10% Pd/C) were used as obtained. Triethylamine (Aldrich, >99%) was purified by distillation.

Analysis. HPLC analysis was performed on a Hitachi 655A-11 liquid chromatograph equipped with a UV monitor (655A), LC controller (L-5000), and an integrator (D-2000). The Vydac C_{18} on silica (5 μm) column (250 mm x 4.6 mm) and acetonitrile–water (60:40) as eluent were employed. The relative response factors for the reactant (2-chlorotoluene) and the product (toluene) at 254 nm were determined by injecting known amounts of these compounds. These factors were used to calculate the true conversion values. GC-MS analyses were carried out using cross-linked methyl silicone 12 m × 0.2 mm with 0.33 μm thickness column with Hewlett Packard 5890 series II gas chromatograph and 5971A mass selective detector.

X-Ray Diffraction. About 40 mg of 10% Pd/C catalyst was supported on a zero-background holder and powder diffraction spectrum was obtained with a Rigaku diffractometer Model D/Max-B using Ni-filtered Cu Kα radiation at 40 kV and 35 mA. Line broadening analysis (LBA) was employed to determine the crystallite size of the supported metal. The instrumental line broadening was calculated from the quartz XRD profile.

Preparation of Formate Salts. To a known amount of the aqueous solution of formic acid (Aldrich, 95–97%) were added alkali metal hydroxides or ammonium hydroxide or triethylamine while stirring and cooling. The addition was continued until the pH read 7. The total concentration of formate salts was in the range of 30–40 wt %.

Transfer Hydrogenolysis of 2-Chlorotoluene. To a 100-mL three-necked round-bottomed flask equipped with a gas inlet and a septum arrangement were added the aqueous solution of formate salts (6 mmol), water (total volume: 3 mL), 17 mL of absolute ethanol, and a stir bar. The flask was placed in a water bath to maintain the temperature of 20 °C. The solution was deaerated with nitrogen gas for 15 min (N_2 flow rate: 60 mL/min). The flow was reduced to 5 mL/min and 0.20 g of 10% Pd/C was added to the solution. After 30 s, a solution of 2-chlorotoluene (5 mmol) in 5 mL of deaerated ethanol was injected into the flask and the reaction was followed. The stirring rate was kept constant for all the experiments. Aliquots of 200 μL were withdrawn using a hypodermic syringe at regular intervals, quenched, filtered, and assayed using reversed-phase high-performance liquid chromatography (RP-HPLC) at 254 nm. For initial rate determination, the samples from the reaction vessel were withdrawn in quick intervals ensuring that the conversions were less than 20%. From the time versus conversion curves, initial rates were determined from the gradient of the linear part.

Transfer Hydrogenolysis of Benzyl Acetate. The procedure followed was similar to that of 2-chlorotoluene.

Hydrogenolysis of 2-Chlorotoluene. To a 100-mL three-necked round-bottomed flask equipped with a gas inlet and a septum arrangement were added 3 mL of water, 17 mL of absolute ethanol, and a stir bar. The flask was placed in a water bath to maintain the temperature of 20 °C. The solution was deaerated with hydrogen gas for 15 min (H_2 flow rate: 60 mL/min). The flow was reduced to 5 mL/min, and 0.20 g of 10% Pd/C was added to the solution. After 2 min, a solution of 2-chlorotoluene (5 mmol) in 5 mL of deaerated ethanol was injected into the flask and the reaction was followed. Aliquots of 200 μL were withdrawn using a hypodermic syringe at regular intervals, quenched, filtered, and analyzed using RP-HPLC at 254 nm.

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