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Heterogeneous Catalytic Isotopic Exchange of Benzylic Compounds in Solution

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Isotopic exchange reactions of bibenzyl and benzylic derivatives with deuterium (D_2) and tritium (T_2) gas, catalyzed by Pd/C, have been performed in solution. Catalyst pre-washed with the reacting gas showed improved H/D or H/T exchange. In aprotic solvents such as dioxane, ethyl acetate, and cyclohexane, 3.1 to 3.5 D atoms were exchanged under standard conditions in 1 h, while in benzene 1 D atom was exchanged. D atoms adsorbed on the catalyst surface were rapidly replaced by H from methanol, diluting the D_2 gas phase. Compounds containing O or N atoms enhanced the rate of exchange, while S atoms inhibited the catalyst activity. The H/D exchange obeyed pseudo-first order kinetics when D_2 gas was used in large excess. When T_2 gas replaced D_2, a substantial decrease in rate of exchange was observed, due to the slower dissociative chemisorption of T_2 on the catalyst surface. The results indicated that this exchange process occurred through two simultaneous mechanisms. The breaking of the C–H bond appeared to be the rate-determining step.

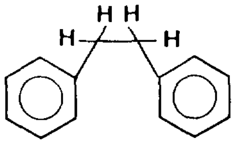
INTRODUCTION

The isotopic exchange reaction between hydrogen atoms of organic molecules and gaseous deuterium or tritium occurring on the surface of transition metals has been widely covered in the literature (1). This chemical process is closely related to the activation of the C–H bond which is fundamental in many reactions in heterogeneous catalysis.

Most of the research (2) deals with two phase reactions proceeding between the metal (as a foil or dispersed on alumina) and the reacting molecule in the vapor phase. These simple systems are convenient for an understanding of the basic processes relating to the C–H bond activation, the reactant–metal bond, the isotopic exchange mechanism, and the isotopic exchange kinetic effect.

Few papers on isotopic exchange in solution have been published (3–5), since these reactions are performed in a three-phase system: a solid phase (catalyst), a liquid phase (organic reactant dissolved in solvent), and a gaseous phase (hydrogen, deuterium, or tritium). These are usually performed in laboratories familiar with catalytic labelling (6a, 7). However, besides a few examples of exchange performed on some benzylic compounds (6a), to the best of our knowledge no work has been published on a systematic study of the parameters influencing such a three-phase exchange system.

We report here on the catalyzed isotopic exchange, in solution, between a dissolved organic reactant (hereafter termed the substrate) and deuterium or tritium gas. Bibenzyl was taken as the model and 10% palladium on carbon was used as catalyst.



bibenzyl

EXPERIMENTAL

General

Ultraviolet spectra were recorded on a Gilford 2600 spectrophotometer, NMR spectra on a Varian EM 360 spectrometer, and MS spectra on a Varian MAT 44 mass spectrometer. Radiochemical and chemical purity were determined by radiochromatogram scanning of thin-layer chromatography plates (tlc) on a Berthold LB 2722 Duenschicht Scanner II; total and specific activity were measured on a Packard Tri-Carb A 2030 liquid scintillation analyzer. Reagents of analytical grade were commercial samples from Aldrich (USA), solvents and tlc plates were from Merck (Germany), palladium on activated charcoal was from Fluka (Switzerland), deuterium (D_2) gas was from Matheson (USA), and tritium (T_2) gas was from Radium Chemie (Switzerland).

Deuterations and Tritiations

The experiments were performed on a vacuum manifold, as previously described (8).

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Preparation of the Catalyst

A 10-ml reaction vessel containing 25 mg of 10% Pd/C catalyst was connected to the manifold and air evacuated. A pressure of 160 Torr D_2 or T_2 gas was introduced at room temperature and the catalyst was vigorously agitated with a magnetic stirrer for 30 min with D_2 and for 24 h with T_2. The gas was then evacuated and replaced by a fresh pure D_2 or T_2 gas aliquot. This operation was repeated three times before using the catalyst in a deuterium or tritium exchange experiment. No difference in efficiency of exchange was observed whether the catalyst is prewashed with D_2 under solvent (dioxane, ethyl acetate) or dry.

Typical Experiment

0.1 mmol (18.2 mg) bibenzyl dissolved in 0.5 ml dioxane was added to the dry catalyst in the reaction vessel which was then reconnected to the vacuum manifold. The solution was frozen by cooling with liquid nitrogen and evacuated to a residual pressure of 10^{-2} Torr. After 0.6 mmol of D_2 gas was transferred into the reaction system, the temperature of the solution was allowed to return to room temperature, developing an initial pressure of 640 Torr. The suspension was vigorously stirred for 2 h and, thereafter, 5 ml dioxane was added. The catalyst was separated by filtration and the solution was evaporated to dryness. The residual solid was dissolved in $CDCl_3$ for NMR analysis.

Gas Sampling for Mass Spectra Analysis

An additional 5-ml vessel with a vacuum stopcock was attached to the manifold, air evacuated, isolated from the system by the stopcock, and maintained under vacuum. After the reaction had been stopped and frozen, the vessel was reconnected and a sample of the residual gas collected.

Experiments Using Dioxane-d_8 as Solvent

In the cases where the substrates were liquids, dioxane-d_8 was used as solvent, allowing direct NMR analysis.

Radioactivity Units

Use will be made of the following units: Becquerel (Bq) = 1 disintegration/sec; Terabecquerel (TBq) = 10^{12} Bq; Curie (Ci) = 3.7×10^{10} disintegrations/sec = 3.7×10^{10} Bq.

RESULTS AND DISCUSSION

D_2 Pressure Effect

The following results were determined by ^{1}H-NMR, where the integrated ratio peaks of aliphatic versus aromatic hydrogens gave a measure of relative deuterium enrichment of the aliphatic carbons (Table 1). This is based on the assumption that aromatic hydrogens are not exchanged (6a,b), and thus their peak can be taken as an internal standard. This assumption was confirmed by mass spectra, which showed that no more than 0.07% of the aromatic moiety was part of the isotopic exchange process.

In a first run of experiments, we found that a systematic increase of the deuterium pressure resulted in a similar proportional increase of the hydrogen–deuterium exchange in bibenzyl up to 300 Torr. Above this pressure, a steady decrease in the concentration of deuterium in the molecule was observed (Table 1, entries 1–5). These results are most probably due to some additional contribution from hydrogen atoms adsorbed on the catalyst surface, providing dilution of D_2 gas.

Hydrogen Adsorbed on Catalyst

Analysis of the hydrogen content of the commercial 10% Pd/C used in this work gave 0.8% (w/w) of H_2. This percentage represents 0.2 mmol of H for 25 mg catalyst, while the usual amounts of bibenzyl (0.1 mmol) in our experiments contained 0.4 mmol of exchangeable aliphatic atoms. Even prolonged pre-heating of the catalyst under high vacuum was not able to expel the hydrogen atoms adsorbed on its surface (5).

One may expect that an increase in D_2 gas would enhance the exchange of the hydrogen atoms adsorbed (9) on the catalyst surface, resulting in the isotopic dilution of the reaction gaseous phase. In addition, these released hydrogen atoms would easily react with the bibenzyl molecules already adsorbed on the catalyst surface. The combination of an increase in D_2 pressure and the presence of H atoms on the catalyst surface has an additive effect, resulting in lowering the expected deuterium incorporation in bibenzyl as observed (Table 1). To overcome this undesired dilution, we attempted to "pre-wash" the catalyst with D_2 prior to performing the reaction. After washing three times for 30 min with fresh D_2 gas fractions whilst stirring, the total catalyst hydrogen expelled (H_2 and HD as determined by mass spectra analysis) found in D_2 gas (Table 1, entries 6–8) corresponded to the amount initially found (0.2 mmol H) on the catalyst surface.

In experiments performed with pre-washed catalyst, a correlation was observed (Table 1, entries 9–11) between the efficiency of H–D exchange on the catalyst surface and the incorporation of deuterium in bibenzyl. An increase of D_2 pressure resulted in essentially complete exchange (within ±5% analytical error) of the aliphatic hydrogens (entry 11).

From Table 1 (entries 3 and 5), it appears that the hydrogen adsorbed on the catalyst surface lowers the

TABLE 1

Effect of Unwashed and Pre-washed Catalyst on Isotopic Ratio D/H in Gaseous Phase and on D/H Exchange in Bibenzyl

Entry	Number of washes	Isotopic gas composition (%) after reaction: H_2	HD	D_2	H	D	Initial pressure (Torr)[a]	H atoms exchanged[b]
1	0	—	—	—	—	—	160	1.2
2	0	—	—	—	—	—	300	2.0
3	0	—	—	—	—	—	480	1.9
4	0	—	—	—	—	—	480	1.9[c]
5	0	—	—	—	—	—	640	1.6
6	1	35.0	43.0	22.0	56.5	43.5	160	—
7	2	7.0	34.0	59.0	24.0	76.0	160	—
8	3	3.0	26.0	71.0	16.0	84.0	160	—
9	1	37.0	44.0	19.0	59.0	41.0	300	2.5
10	3	24.0	47.0	29.0	47.0	53.0	300	3.1
11	3	7.5	33.0	60.0	24.0	76.0	640	4.0

Note. Experimental conditions were as follows. Entries 1–5: unwashed catalyst, 25 mg 10% Pd/C; solvent, 0.5 ml dioxane; substrate, 18.2 mg (0.1 mmol) bibenzyl; reaction time, 2 h. Entries 6–8: wash of catalyst, 25 mg; no solvent; room temperature; wash time, 30 min./wash, each wash performed with fresh D_2 gas. Entries 9–11: 25 mg pre-washed catalyst; solvent, 0.5 ml dioxane; substrate, 18.2 mg (0.1 mmol) bibenzyl; reaction time, 2 h.

[a] Entries 1–5 and 9–11 include solvent vapor pressure.

[b] Accuracy of ±5%.

[c] Reaction time, 24 h.

isotopic exchange. On the other hand, when pre-washed catalyst is used, having D atoms adsorbed on its surface, the isotopic H–D exchange is also lowered if the gaseous phase is H_2 or N_2 (Table 2, entries 5–7). The results (entries 6 and 7) indicate that the adsorbed D atoms make a minor direct contribution to the exchange (5–10%), but their presence has a crucial function in the exchange mechanism. These D-activated species react in the reductive elimination step (10) with the chemisorbed bibenzyl, giving the final deuterated product.

TABLE 2

Isotopic Exchange in Bibenzyl

Entry	Time (min)	Gas	H atoms exchanged[a] (C_{ex})	$\ln \frac{C_0}{C_0 - C_{ex}}$
0	0	D_2	0.0	0
1	1	D_2	1.0	0.29
2	15	D_2	2.0	0.69
3	30	D_2	2.3	0.85
4	60	D_2	3.5	2.08
5	120	D_2	4.0	∞
6	120	N_2	0.2	0.05
7	120	H_2	0.4	0.11
8[b]	15	H_2	0.5	0.13
9[b]	30	H_2	0.55	0.15
10[c]	30	H_2	0.3	0.08

Note. Experimental conditions were as follows. Catalyst, 25 mg 10% Pd/C, pre-washed with deuterium; solvent, 0.5 ml dioxane; substrate, 18.2 mg (0.1 mmol) bibenzyl; gas pressure, 640 Torr, including solvent vapor pressure; room temperature.

[a] Accuracy of ±5%.

[b] Deuterated bibenzyl, 0.1 mmol, containing 3.4 D atoms/molecule.

[c] Tritiated bibenzyl, 0.1 mmol, containing 2.5 T atoms/molecule, 2.66 TBq/mmol (72 Ci/mmol).

Solvent Effect

The H–D exchange between bibenzyl and D_2 gas, catalyzed by pre-washed Pd/C, was performed in different solvents (Table 3) and the results were compared after 1 h of reaction.

When aprotic solvents (dioxane, ethyl acetate, cyclohexane) were used, only small differences were found. A quantity of 3.1 to 3.5 H atoms were replaced by D atoms (entries 1–3). When the solvent contained a hydroxyl group (methanol), the D incorporation dropped to 1.65 H atom. This may be explained by a fast competitive D exchange between the H atoms of CH_3OH and the H atoms of bibenzyl (3, 4, 11). The hydroxylic H atoms exchange with the D atoms adsorbed on the catalyst surface and, therefore, the isotopic exchange of the benzylic positions is performed with "diluted" deuterium. To confirm this effect, CH_3OH was replaced by CH_3OD and the apparent H–D exchange was enhanced to 3.4 atoms (entry 5), giving the same exchange value as that for the aprotic

TABLE 3

Solvent Effect on Isotopic Exchange in Bibenzyl

Entry	Solvent	H atoms exchanged	Isotopic gas composition (%) after reaction: H_2	HD	D_2
1	Dioxane	3.3	9.3	32.6	58.2
2	Ethyl acetate	3.5	6.0	28.2	65.8
3	Cyclohexane	3.1	19.0	38.0	43.0
4	Methanol	1.6	51.7	18.8	29.5
5	Methanol d_1	3.4	1.1	4.7	94.1
6	Benzene	1.0	1.0	11.1	87.9

Note. Experimental conditions were as follows. Pre-washed catalyst, 25 mg 10% Pd/C; solvent, 0.5 ml; substrate, 18.2 mg (0.1 mmol) bibenzyl; D_2 pressure, 640 Torr including solvent vapor pressure; reaction time, 1 h; room temperature.

solvents. A small solvent contribution to the H/D benzylic exchange was observed when dioxane-d_8 was used with benzylamine (Table 4, entries 4 and 5). Benzene was found to be a less efficient solvent, an effect which can be attributed to the π-complex formed between the benzene ring and the catalyst. It is known that an adsorbed benzene molecule covers 8 Rh atoms on the surface of a rhodium catalyst (12, 13). It is possible that a similar coverage capacity occurs with Pd. In addition, of all the solvents used, D_2 has the lowest solubility in benzene (14–16), providing a small concentration of D atoms on the active sites of the catalyst.

TABLE 4

Isotopic Exchange as a Function of Benzylic Derivative

Entry	Substrate	H atoms exchanged	H exchanged[a] (%)
1	Bibenzyl	3.3	82.5
2	Benzyl alcohol	1.0	50
3	Benzyl alcohol[b]	2.0	100
4	Benzylamine[b]	1.6	80
5	Benzylamine[b,c]	0.3	15
6	Dibenzylamine[b]	3.5	87.5
7	Dibenzyl sulfide	0.0	0
8	Dibenzyl ether	4.0	100
9	Benzyl cyanide	—	0
10	2-Phenylbutyric acid	0.6[d]	15
11	4-Benzyl pyridine	0.2	10
12	Diphenylmethane	1.0	50
13	Phenylacetic acid	0.8	40

Note. Experimental conditions were as follows. Pre-washed catalyst, 25 mg 10% Pd/C; solvent, 0.5 ml dioxane; substrate, 0.1 mmol; D_2 gas pressure, 640 Torr including solvent vapor pressure; reaction time, 1 h, room temperature.

[a] Accuracy of ±5%; the active hydrogen atoms of -OH, -NH, and NH_2 groups are not included in this column.

[b] 0.5 ml dioxane-d_8.

[c] Gas used was N_2.

[d] 0.3 H exchanged in benzylic position and 0.3 H in side chain.

Substrate Structure

Under our optimal experimental conditions (pre-washed catalyst, high D_2 pressure), a time of 1 h was chosen *arbitrarily* to compare the different reacted molecules. The influence of the atom bonded to the benzylic moiety may be determined from Table 4.

A large atom like sulfur, with an electronegativity of 2.44, inhibits the catalyst activity (entry 7) which may be due to a strong binding to the palladium surface. Small atoms, such as oxygen and nitrogen, having a high electronegativity compared to the carbon atom (C = 2.5, O = 3.5, N = 3.07), enhance the isotopic exchange (entries 3, 4, and 8).

This enhancement may be related to a partial positive charge borne by the aliphatic carbons which favors a nucleophilic-like attack of the D atoms by weakening the C–H bond. Trials performed with benzylamine and dibenzylamine dissolved in dioxane-d_8 (entries 4 and 6), where the H atoms bonded to N were already exchanged by the solvent (total disappearance of the H signal of $-NH_2$ in NMR spectra), also showed a higher exchange of the benzylic hydrogen atoms with D_2 gas than those of bibenzyl.

It is accepted (1g) that the lone electron pair of N is transferred to the metal, forming a π–d bond. From our results, it seems that this bond has a weak poisoning effect on the catalyst, in disagreement with other published results (2f, 4, 11). The π-allyl complex rapidly formed between the benzylic moiety and the Pd atoms, due to the low activation energy required (2e, 17), favors the isotopic exchange. The presence of a bulky group (entry 10), a

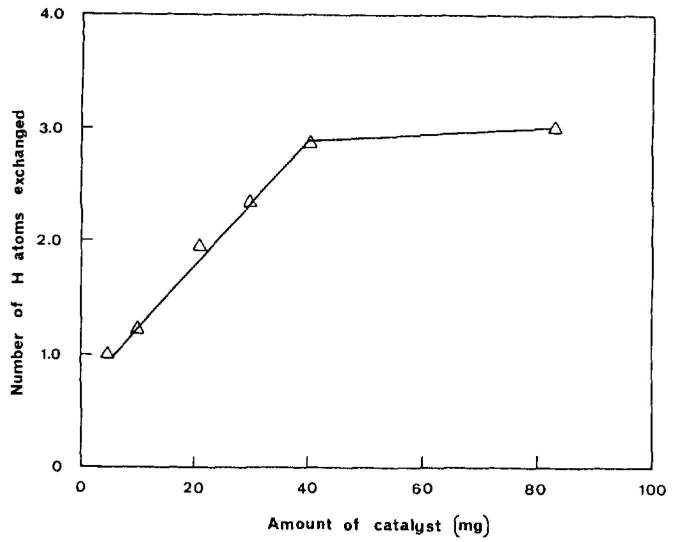

FIG. 1. H/D exchange in bibenzyl vs amount of catalyst. Experimental conditions were as follows. Catalyst pre-washed with D_2, 0.5 ml dioxane, 18.2 mg (0.1 mmol) bibenzyl, D_2, 640 Torr; reaction time, 30 min; room temperature.

strong π-bond (entries 9 and 11), or a hydroxyl group (entries 2 and 13) strongly affect the isotopic exchange.

Effect of Catalyst Amount

The isotopic exchange between the aliphatic hydrogens of bibenzyl and D_2 gas was found to be rate dependent on the amount of catalyst (Fig. 1). This dependence is first order in catalyst in the range 5–40 mg. Above 40 mg Pd/C and 30 min reaction time, the slope of the number of H atoms exchanged levelled off and remained constant up to 81 mg, leading to H/D equilibrium.

We found that even 5 mg of Pd/C has the same exchange efficiency as 25 mg; the only difference is in the rate of reaction where, in the case of 5 mg, 3.3 of the 4 hydrogens were exchanged after 48 h, while only 1 h was needed to obtain the same exchange effect with 25 mg catalyst.

Profile of Bibenzyl Isotopic Exchange

The exchange was measured by ^{1}H-NMR integration of the aliphatic peak as a function of time (Table 2, entries 1–5). A large excess (threefold) of D_2 gas was introduced in the reaction in order to provide pseudo-first order conditions, and also to minimize the dilution of surface deuterium, due to the contribution of hydrogen atoms expelled from bibenzyl.

The data for entry points 1–4 (t = 1 min to t = 60 min) follow first order kinetics, i.e., the plot of ln $\{C_0/(C_0 - C_{ex})\}$ versus t, where C_0 = initial "concentration" of exchangeable aliphatic hydrogens (four atoms) and C_{ex} is the number of H atoms exchanged at time t, is approximately linear, with a rate constant of 2.41×10^{-2} min^{-1}. However, during the initial minute (t = 0 to t = 1 min), the rate is much faster, indicating that two mechanisms occur simultaneously. The first one corresponds to the attack of D atoms formed by the dissociative adsorption of D_2 gas on bibenzyl. This very fast exchange, occurring during the short initial time (within 1 min) which was not exactly measured, looks similar to a conventional radical or associative π-complex reaction (7). The second, slower one, where three adjacent carbons participate, is a dissociative π-complex mechanism. The π-complex intermediate, first formed by the benzene rings of bibenzyl, transforms into a π-allyl complex, which facilitates the exchange of the aliphatic hydrogen atoms (1f, 18–21). A molecular model of bibenzyl shows that a preferred spatial configuration is obtained when one phenyl ring is co-planar to the catalyst surface and the close benzylic function is also oriented toward the surface catalyst. Such a configuration will facilitate the formation of this π-allyl intermediate.

Isotope Effect

From our experiments with D_2, where 4 H atoms were exchanged (Table 2, entry 5), we had expected with T_2 the same exchange effect, providing a specific activity of about 4.2 TBq/mmol (116 Ci/mmol). However, we obtained a relatively low specific activity (1.02 TBq, 27.5 Ci/mmol) corresponding to 1 H atom exchanged (Table 5). In a repeat experiment, the catalyst was pre-washed with tritium for 24 h because of the slow reaction exchange between H and T (21, 22), and after performing a 2-h reaction, a specific activity of 1.27 TBq/mmol (34.4 Ci/mmol) was measured. When the reaction was continued overnight instead of for 2 h (with a tritium pre-washed catalyst, as usual), a specific activity of 3.77 TBq/mmol (102 Ci/mmol), equivalent to the incorporation of 3.5 T atoms, was reached. These results indicate that the dissociative chemisorption of tritium on the catalyst surface has a regulating effect on the rate of reaction, probably due to a slower adsorption of T on the catalyst surface when compared to D adsorption. In further trials, the exchange of deuterated bibenzyl with H_2 gas (Table 2, entries 8 and 9) provided an exchange of only 0.5 D atom and 0.55 D atom after 15 min and 30 min, respectively. This effect was emphasized by an exchange reaction performed between tritiated bibenzyl (1.95 TBq, 1.8 T atoms) and hydrogen gas, giving 0.3 atom of tritium exchanged after 30 min (entry 10). The breaking of the C–D (or C–H or C–T) bond seems to be the slow step and, most probably, is rate-determining for this isotopic exchange reaction.

TABLE 5

Tritium Exchange in Bibenzyl

Entry	Reaction time (h)	Spec. activ. TBq/mmol	(Ci/mmol)	T incorp. (atoms)	Yield (%)
1	2	1.02	(27.5)	0.95	23.7
2	2[a]	1.27	(34.4)	1.18	29.7
3	20[a]	3.77	(102.0)	3.52	88.0

Note. Experimental conditions were as follows. Pre-washed catalyst with tritium, 25 mg 10% Pd/C; solvent, 0.5 ml dioxane; substrate, 18.2 mg (0.1 mmol) bibenzyl; tritium gas pressure, 640 Torr, including solvent vapor pressure; room temperature.

[a] Catalyst pre-washed three times with tritium for 24 h.

CONCLUSIONS

Pd/C is an efficient catalyst in isotopic exchange between D_2 or T_2 gas and aliphatic hydrogen atoms for dissolved benzyl derivatives. Pre-washing the catalyst with the isotopic gas enhances the incorporation of D or T atoms. The reaction is linearly dependent on the catalyst amount. The reaction is solvent dependent. The hydroxyl function of CH_3OH solvent competes with the substrate for the surface D atoms. O and N hetero-atoms attached to the benzylic moiety enhance the exchange, while a S atom inhibits the reaction.

An isotope effect can be detected, indicating that the breaking of the C–H (or C–D or C–T) bond is the rate-determining step in the H/D or H/T exchange reaction.

The exchange occurs through two simultaneous mechanisms.

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