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A Comparison of the Single Turnover and Standard Solution Phase Techniques in Alkene Deuterations

The Single Turnover (STO) procedure for investigating catalysts and catalytic reactions has been shown to be useful as a means of characterizing dispersed metal catalysts (*2*). Beyond that, however, it is also a valuable tool in evaluating catalytic reactions such as the room-temperature deuterium exchange on alkanes (*3*) as well as determining the effect of competitive adsorption of a solvent in a catalytic hydrogenation (*4*). While there is a correlation between the vapor-phase STO results and solution-phase data in comparing hydrogen presaturated and nonpresaturated catalysts in alkene hydrogenation (*5*), it was felt that a more definitive comparison between the results obtained using these two techniques was warranted. Since there is an extensive literature concerning the deuterium addition and exchange with alkenes both in the vapor phase and in solution (*6*) it was considered that this would be an appropriate reaction to use in a direct comparison of a solution-phase catalytic reaction with one run using the STO procedure.

EXPERIMENTAL

Materials. The catalysts used were aged 5% Pt/C and 5% Pd/C obtained from Engelhard Industries, the same catalysts were used in previous work (*1*, *7*). The methylcyclopentene was obtained from Aldrich Chemical Company, distilled, and degassed before use. The deuterated ethanol (EtOD), obtained from Aldrich, was +99.5 atom% D and was used as received. The D_2, obtained from Matheson, was at least 99.5% pure and was passed through a Deoxo unit, a drying tower, and a filter before use.

The *Solution-phase deuterations* were run as previously described (*7*) using 25 mg of catalyst, 10 ml of EtOD solvent, and 0.25 ml of methylcyclopentene. The deuteration was run to 25% completion and a sample extracted for injection into a gas chromatograph (6 ft., 20% Carbowax-20 on Chromosorb P at room temperature, and a 30-ml/min He carrier gas flow rate) interfaced with a VG Industries Spectralab 200 quadrupole mass spectrometer utilizing a 16-channel specific mass detector to provide digital readout and continuous recording of the partial pressures of species with *m*/*e* values of 84 to 96. The background was subtracted from these values and they were then corrected for natural isotopic abundance. Repetitive analyses showed that the deuterium composition data were reproducible to ±1%. These data are listed in Tables 1 and 2.

The *Single turnover deuterations* were run using the apparatus and gas purification procedures described previously (*2*, *4*). The catalyst, 5 mg, was placed in the reactor tube and swept with oxygen-free He for 30 min. A 100-μl pulse of D_2 was passed over the catalyst followed by the injection of 1 μl of methylcyclopentene into the carrier gas stream through a septum containing Tee upstream from the catalyst sample (*4*). Another 100-μl pulse of D_2 completed the STO sequence which was repeated several times. The products were analyzed by an onstream GC/MS as described above.

In the solvent-modified STO procedure the catalyst was first saturated by the injec-

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TABLE 1

Deuterium Distributions Obtained with a Pt/C Catalyst

	STO	Solvent-modified STO	Solution
d_0[a]	20	12	12
d_1	24	16	18
d_2	23	20	23
d_3	15	18	19
d_4	9	14	16
d_5	5	9	12
d_6	1	5	
d_7	1	3	
d_8		2	
d_{ave}	1.4	2.8	2.5

[a] $m/z = 84$ (d_0) through 92 (d_8).

tion of 3 μl of degassed EtOD through the septum. This was followed after 1 min by the STO sequence described above.

RESULTS AND DISCUSSION

Methylcyclopentene (**1**) was deuterated over 5% Pt/C and 5% Pd/C in EtOD using a procedure identical to that previously used for the solution-phase deuteration of methylcyclohexene. **1** was also deuterated over these same catalysts using the vapor-phase Single Turnover procedure. Both reactions were run at room temperature. In the STO sequence the catalyst was placed in a tubular reactor and saturated with a pulse of D_2 followed by the injection of a small amount of **1** into the carrier gas stream flowing over the catalyst. **1** was converted to deuterated methylcyclopentane (**2**) only by reaction with the D_2 adsorbed on the catalyst surface (excess D_2 was not present) and the product was then analyzed by on-stream GC/MS.

The deuterium compositions of **2** obtained from each of these reactions, after correction for natural isotopic abundance, are listed in Tables 1 and 2. Data on the deuterium composition of **1** recovered from these reactions are not included because in the STO procedure **1** is present in considerable excess and the deuterium incorporation data is masked by the large amount of undeuterated material present in the reaction mixture.

These data show that the deuterium composition of **2** obtained by solution-phase deuteration is different from that formed using the standard STO procedure. Over Pt the STO sequence gives more of the lighter deuterated material while in solution more d_4 and d_5 species are produced and the product has a considerably higher d_{ave}. The opposite is seen with Pd. In solution the product is primarily d_0 with little polydeuterated material present and a low d_{ave}. In the standard STO sequence over Pd more of the polydeuterated species are formed. It would appear, then, that data obtained with the standard STO sequence cannot be directly related to solution-phase catalytic reactions.

We have recently shown, however, that exposure of Pt and Pd catalysts to alcohol vapor prior to an STO reaction sequence results in a marked modification of the reaction characteristics of these catalysts (*4*). This change has been explained by the adsorption of alcohol molecules on the different types of active sites present on the catalyst which, in turn, changes the number of

TABLE 2

Deuterium Distributions Obtained with a Pd/C Catalyst

	STO	Solvent-modified STO	Solution
d_0[a]	29	54	60
d_1	22	26	27
d_2	15	10	9
d_3	10	3	3
d_4	7	0	1
d_5	5	0	
d_6	3	0	
d_7	3	3	
d_8	2	3	
d_9	1		
d_{10}	1		
d_{11}	1		
d_{ave}	2.2	1.0	0.6

[a] $m/z = 84$ (d_0) through 95 (d_{11}).

surface orbitals available for adsorption of the reactants and, thus, modifies the catalyst reactivity. Since this same kind of surface interaction can be occurring in solution-phase reactions it was felt that a more appropriate STO comparison with the solution-phase deuteration of **1** would be one which is run on a catalyst which had been previously saturated with the solvent vapor. This was accomplished by first injecting a small amount of degassed EtOD into the carrier gas stream passing over the catalyst in the reactor. After waiting a sufficient time for the excess alcohol to be swept from the system the standard D_2–**1**–D_2 STO reaction sequence was run. The data obtained from these reactions are also listed in Tables 1 and 2 and show that with both Pt and Pd catalysts pretreatment with EtOD before the STO deuteration of **1** gave **2** with deuterium compositions very similar to those obtained over the same catalyst in solution. About the only appreciable difference is the presence of somewhat more of the more highly deuterated species in the products obtained from the STO procedure. With the deuterium distribution observed in deuterium exchange on cyclopentane over Pt catalysts determined by the type of active sites present (*3*) and the presence of alcohol modifying the nature of the active sites present on the catalyst (*4*) these data indicate that the EtOD-modified catalyst surface is the determining factor in the deuterium distribution regardless of whether the reaction is run in the vapor phase or in solution.

Thus, at least with Pt and Pd catalysts, the STO procedure can realistically be used to evaluate catalytic processes, even those run in solution. The only qualification in the use of the STO sequence for study of catalytic reactions normally run in solution is that the catalyst must first be modified by exposure to solvent vapors before running the STO sequence.

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