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THE MECHANISM OF THE CATALYTIC HYDROGENATION OF α, β UNSATURATED CARBONYL COMPOUNDS—V[1]

TRITIUM ISOTOPE EFFECTS

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Abstract—The isotope effects of the hydrogenation of some α,β-unsaturated carbonyl compounds with H_2/HT in the presence of different catalysts have been determined. The isotope effects depend on both catalyst and substrate. In general the size decreases in the order Pt > Pd > Rh > tris(triphenylphosphine) rhodium chloride. For the hydrogenation of dimethyl acrylate the isotope effects shown by Pt, Pd and Rh agree reasonably well with maximum calculated values assuming a reversible hydrogen addition to the β carbon and an irreversible addition to the α position. For the hydrogenation of fumarate another mechanism seems to be valid.

ACCORDING to the preceding communication,[1] knowledge of isotope effects is required to understand the intramolecular isotope distribution and mechanism of hydrogenation of α,β-unsaturated carbonyl compounds. No such information seems to be available. Isotope effects have been even excluded.[2]

METHODS

The isotope effects were determined in 2 ways.

1. Stepwise degradation of the hydrogenation products,[1] especially butyric acid obtained by hydrogenation of crotonic acid ethyl ester and isovaleric acid by hydrogenation of dimethylacrylic ethyl ester in the presence of Pt, Pd, Rh, or tris(triphenylphosphine) rhodium chloride. Dimethylacrylic acid was selected as there is no H-atom in β position, and therefore no hydrogen shift to the α position can occur.[1]

The tritium content in the α or β position was compared with the tritium content of one gram atom of the hydrogenation gas.

2. *Radio gaschromatographic analysis*. During a hydrogenation, aliquots were taken and parts of these analysed radio gaschromatographically.[3, 4] The specific radio activity could be determined from the amounts of hydrogenated and non-hydrogenated compound and tritium activity. The tritium content in the substrates due to exchange reactions could be subtracted from the tritium content produced by hydrogenation. (Table 2.) Dimethyl fumarate, dimethyl maleate, methyl crotonate and for comparison 4-methyl cyclohexene were hydrogenated and the so called mean isotope effect determined. The hydrogenation gas was always used in large excess.

RESULTS

In Table 1 the isotope effects of tritium addition to the α and β positions of isovaleric acid and the tritium content in the Me groups caused by exchange reactions are

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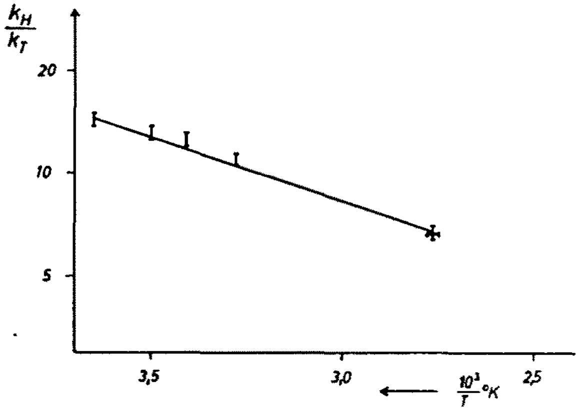


FIG. 1 Temperature dependence of the Isotope effect of the hydrogenation of fumaric acid dimethyl ester with platinum at 0·0; 12·5; 20·5; 32·0 and 88°. Reciprocal absolute temperature versus logarithm of the isotope effect.

TABLE 1. ISOTOPE EFFECTS OF THE HYDROGEN ADDITION AT C-2 AND AT C-3 IN THE HYDROGENATION OF DIMETHYLACRYLIC ACID WITH H_2/HT.

Catalyst	C-2	C-3	T-Content of the methyl groups[a]
Pt[b]	9·9 ± 2·8	1·5 ± 0·1	11
Pd[c]	3·6 ± 0·2	0·8 ± 0·1	58
Rh[d]	2·15 ± 0·16	1·05 ± 0·05	55

[a] Given as per cent. The T-Content of one gram atom hydrogen = 100%.

[b] according to Adams.

[c] 10% Pd on charcoal (E. Merck, Darmstadt).

[d] 5% Rh on charcoal (Engelhard catalyst).

given. The isotope effects in the β positions are in all three cases small. However, in the α position there is an isotope effect of ca. 10 in the hydrogenation with Pt. The isotope effect caused by Pd is substantially smaller, and still smaller for Rh.

In Table 2 the mean isotope effects in the hydrogenation of different compounds with Pt, Pd and the homogeneous catalyst tris(triphenylphosphine) rhodium chloride are given. The isotope effects are dependent on both catalyst and substrate. The largest isotope effects occur in the hydrogenation with Pt and range between 13 for fumaric acid and 3 to 4 for 4-methylcyclohexene. The difference between fumaric and maleic acid is especially remarkable. The effects with Pd are substantially smaller, but here there is also a significant difference between fumaric and maleic acid although there is no difference between fumaric acid and 4-methylcyclohexene. The isotope effects in hydrogenations with tris(triphenylphosphine) rhodium chloride are very small with carbonyl compounds and inverse with 4-methylcyclohexene.

The isotope effects in the hydrogenation of tetrolic acid to *cis*-crotonic acid its isomerization and/or further hydrogenation are given in Table 3. The isotope effects for tritium addition to an α, β C≡C triple bond are similar to those which were

TABLE 2. MEAN ISOTOPE EFFECTS OF THE HYDROGENATION WITH H_2/HT AND DIFFERENT CATALYSTS.

Catalyst	Compound	Percentage hydrogenation	Mean isotope effect	$\frac{\text{T-Content of olefin}}{\text{T-Content of product}} \times 100$
Pt	Fumaric acid[a]	20	13·1[b] ± 1·4[c]	no exchange
Pt	Fumaric acid	59	12·5 ± 1·2	no exchange
Pt	Fumaric acid	100	12·5 ± 0·8	—
Pd	Fumaric acid	11	1·7 ± 0·2	no exchange
Pd	Fumaric acid	100	1·7 ± 0·1	no exchange
Tris-(triphenylphosphine)-rhodium chloride	Fumaric acid	17	1·14 ± 0·12	no exchange
Pt	Maleic acid	19	7·8 ± 0·5	no exchange
Pt	Maleic acid	51	6·6 ± 0·5	no exchange
Pt	Maleic acid	100	6·4 ± 0·3	—
Pd	Maleic acid	9	2·6 ± 0·4	no exchange
Pd	Maleic acid	60	2·5 ± 0·2	3 ± 1
Pt	Crotonic acid	6	4·2 ± 0·6	2 ± 1
Pt	Crotonic acid	38	4·5 ± 0·4	12 ± 2
Pd	Crotonic acid	9	2·5 ± 0·3	4 ± 1
Pd	Crotonic acid	58	2·4 ± 0·2	20 ± 2
Tris-(triphenylphosphine)-rhodium chloride	Crotonic acid	15	1·0 ± 0·1	no exchange
Tris-(triphenylphosphine)-rhodium chloride	Crotonic acid	30	0·96 ± 0·07	no exchange
Tris-(triphenylphosphine)-rhodium chloride	Crotonic acid	100	1·01 ± 0·05	no exchange
Pt	4-Methyl-cyclohexene	13	3·8 ± 1·0	17 ± 2
Pt	4-Methyl-cyclohexene	17	3·1 ± 0·8	7 ± 1
Pd	4-Methyl-cyclohexene	8	1·6 ± 0·5	6 ± 2
Pd	4-Methyl-cyclohexene	28	1·7 ± 0·5	12 ± 2
Pd	4-Methyl-cyclohexene	100	1·7 ± 0·3	—
Tris-(triphenylphosphine)-rhodium chloride	4-Methyl-cyclohexene	18	0·7 ± 0·08	1 ± 0·5
Tris-(triphenylphosphine)-rhodium chloride	4-Methyl-cyclohexene	42	0·68 ± 0·07	5 ± 1

[a] All acids were hydrogenated as methyl or ethyl esters.

[b] Average of 3–4 measurements.

[c] Average deviation from the mean.

observed in the hydrogenation of a double bond with Pt or Pd. Here also the values for Pt are substantially higher.

The temperature dependence of the isotope effect in the hydrogenation of dimethyl fumarate with Pt is shown in Fig. 1. A plot of the logarithm of the isotope effect against the reciprocal of the absolute temperature gives a straight line. The difference in activation energy for H and T with Pt calculated from the temperature dependence is 1·42 kcal/mole. Finally the pressure dependence of the isotope effect of the hydro-

TABLE 3. AVERAGE ISOTOPE EFFECT OF THE HYDROGENATION OF TETROLIC ACID ETHYL ESTER WITH H_2/HT AND Pd OR Pt

	Tetrolic acid ester (%)	Hydrogenation products in percent			Mean isotope effect	Mean isotope effect
		Isocrotonic acid ester	Crotonic acid ester	Butyric acid ester	Tetrolic acid Isocrotonic acid	"Crotonic acid" Butyric acid
Pd	80	17	1	2	2·0 ± 0·2	1·8 ± 0·4
	65	31	2	3	1·9 ± 0·2	1·6 ± 0·3
	31	59	4	6	1·9 ± 0·2	1·7 ± 0·3
Pt	88	7	1	3	5·2 ± 0·8	4·4 ± 0·9
	76	14	2	6	5·1 ± 0·7	4·1 ± 0·8
	59	24	7	10	5·0 ± 0·5	4·0 ± 0·6

TABLE 4. PRESSURE DEPENDENCE OF THE MEAN TRITIUM ISOTOPE EFFECT OF THE HYDROGENATION OF FUMARIC ACID DIMETHYL ESTER WITH Pt

Pressure (atm)	0·6	3	4	6	25
Isotope effect	12·8 ± 1·1	12·6 ± 1·2	10·6 ± 0·9 10·1 ± 0·9	12·1 ± 1·0	10·4 ± 0·9

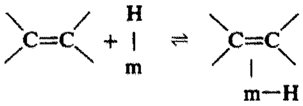
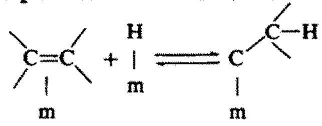
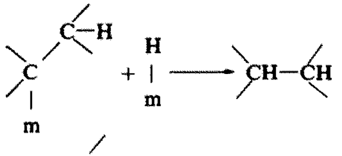
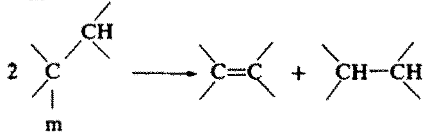
genation of dimethyl fumarate with Pt with H_2/HT between 0·5 and 25 atm was studied. As shown in Table 4, the isotope effect is not dependent on pressure in this range.

DISCUSSION

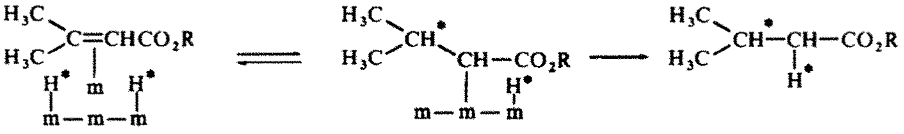
Table 5 shows the calculated maximum isotope effects for the individual steps of the catalytic hydrogenation according to the scheme of Horiuti and Polanyi[5] and a mechanism suggested by Bond.[6] The calculations are given in the appendix.

The addition of the olefin to the hydrogen/hydrogen isotope loaded surface can, at most, only lead to a small isotope effect. There is no indication that the step is rate determining. Hydrogen diffusion has only been considered as the rate determining step by Bittner *et al.*[7] in the hydrogenation of oleic acid with Pd and H_2/HT and by Augustine *et al.*[8] under special experimental conditions. Bittner *et al.*[7] found an isotope effect of about 1. The isotope effect for step 2 (Table 5) should be between $\sqrt{2}$ and $\sqrt{3}$ depending on whether the diffusion of H_2 and HT molecules or H and T atoms is considered. If the equilibrium of hydrogen adsorption on the catalyst surface occurs before the rate determining step, then the equilibrium isotope effects in Table 5 are to be expected. Hydrogen adsorption in the hydrogenation of ethylene with nickel at −23° was considered as the rate determining step by Miyahara.[9] No isotope effect was found. Rennard and Kokes[10] considered step 4 or 5 (Table 5) in the deuteration of ethylene and propylene at −78° with $PdD_{0·24}$ as rate determining. They found $k_H/k_D = 0·5$. If step 4 were irreversible and rate determining, a maximum isotope effect of 10 for Pt, ca. 4 for Pd, and 2·8 for Rh would be calculated for the rupture of the metal-hydrogen bond. (Appendix.) However, the calculated isotope effect is inverse if an equilibrium is reached. Miyahara,[9] Rennard and Kokes,[10] and Laidler[11] consider step 5 to be rate determining. According to Miyahara[9] there is no isotope effect in the hydrogenation of ethylene with D_2 and nickel at 28°.

TABLE 5. CALCULATED MAXIMUM TRITIUM ISOTOPE EFFECTS FOR THE INDIVIDUAL STEPS OF HYDROGENATION

Step	Reaction	Kind of isotope effect expected	Calculated Pt	Pd	Rh
1		secondary	~1	~1	~1
2	Hydrogen diffusion	kinetic	1·5	1·5	1·5
3	$H_2 + MH^* \rightleftharpoons HH^* + MH$	equilibrium	1·2	1·4	1·9
4		kinetic or equilibrium	10 0·6	4 0·4	2·8 0·3
5		kinetic	10	4	2·8
6		kinetic	17	17	17

The calculated maximum isotope effects for step 5 are the same as for step 4 if this were irreversible. For step 6 the maximum isotope effect is independent of the catalyst. If the isotope effect is determined by the difference in zero point energy in the transition state, it can depend on the substrate and the metal and take up values which are smaller than the maxima. The disproportion formulated in step 6 cannot be completely eliminated owing to the found isotope effects, yet these can be more readily understood in terms of the mechanism of Horiuti and Polanyi.[5] Thus in the case of dimethyl acrylate where only the α-adsorbed alkyl occurs (see preceding paper[1]) we formulate the steps:



I II III

The isotope effects found for tritium addition to the α-position of dimethylacrylic acid agree reasonably well with the maximum calculated values (Tables 1, 5 and Appendix). This means that the hydrogen addition in this position (transition II → III) is rate determining and that the transition state is near the point of half rupture of the bond. If the equilibrium isotope effect of hydrogen adsorption (step 3) at the values found plays a role, then the value of this equilibrium isotope effect is smallest for Pt at 1·2, and largest for Rh at 1·9. The isotope effect of hydrogen addition at the β

position is small. For Pd it is slightly inverse. The comparison of calculated and found values supports a back reaction II → I, without the thermodynamic equilibrium being fully established. The isotope effects in the α and β positions confirm the scheme of Horiuti and Polanyi[5] and the suggestion of Smith *et al.*[12] in which the intermediate in the hydrogenation of α, β-unsaturated carbonyl compounds is an α adsorbed alkyl and which then irreversibly goes over to the saturated compounds. They further show that the isotope effect is principally responsible for the asymmetry in the hydrogenation of α, β-unsaturated carbonyl compounds with Pt. In the hydrogenation with Pd or Rh dilution effects can play a significant role.[2]

Another mechanism must be suggested for the hydrogenation of dimethyl fumarate with Pt. There is an isotope effect of 12–13 for the addition of both H-atoms. Even for the hypothetical limiting case where the addition of an H-atom occurs with an infinite isotope effect, a value of 6–6·5 is obtained for the addition of the other hydrogen. This value still corresponds to a kinetic isotope effect. This can be best explained by two consecutive irreversible additions or one simultaneous addition of two H-atoms. This suggestion is supported by the fact that during the hydrogenation no hydrogen on the fumaric acid is exchanged (Table 2). The reversible addition of an H-atom to the adsorbed olefin leading to the formation of a labelled fumaric acid would be noticeable, because of the suggested equilibrium[13] between the adsorbed olefin and that in solution. Carboxy groups exert a stabilizing effect on olefinic bonds during reduction. For example, 1,2-dimethylcyclohexene yields only 80% *cis* product over Pt[14] but 1,2-dicarbomethoxycyclohexene yields 100% *cis* product under the same conditions.[15]

Although the isotope effect of the hydrogenation of dimethyl maleate with Pt is only about half as large as with fumaric ester, the same conclusions can be valid. But a two step mechanism may be possible too.

The temperature dependence of the isotope effect in the hydrogenation of fumaric ester shows that in the region 0° to 80° no change in the rate determining step occurs. We find that the isotope effects in the hydrogenations with tris(triphenylphosphine) rhodium chloride is $k_H/k_T = 0{\cdot}7\text{–}1{\cdot}14$. This agrees satisfactorily with the values found for cyclohexene and *cis* and *trans*-2-methylpent-3-ene.[16, 17] Owing to the higher donor effect of deuterium and tritium[18] the electron density of the central atom in the complex[16, 17] will be increased, so that the olefin can be preferentially added. This leads to an inverse isotope effect.

CALCULATION OF THE ISOTOPE EFFECTS

Only stretching modes were taken into account. The following wave numbers (cm^{-1}) were used for calculation: $W_{H_2} = 4405$[19], $W_{HT} = 3598$[19]; $W_{CH} = 3019$[20], $W_{CD} = 2220$[20]; $W_{PtH} = 2110$[21], $W_{PtD} = 1460$[21]; $W_{RhH} = 2100$[16], $W_{RhD} = 1800$[16]; $W_{PdH} = 2035$. $W_{PdD} = 1755$ was estimated by the difference of the heats of adsorption of H_2 and D_2 on Pd.[22] The values calculated for deuterium were converted for tritium by the equation

$$\frac{k_H}{k_D} = \left(\frac{k_H}{k_T}\right)^{1,442} \tag{1}$$

derived by Swain *et al.*[23]

The isotope effects for the equilibrium of step 3 (Table 5) were calculated by the equation:

$$K = \frac{W_{\mathrm{HH}^{*}}}{W_{\mathrm{H}_2}} \times \frac{W_{m\mathrm{H}}}{W_{m\mathrm{H}^{*}}} \times \exp\left\{\frac{hc}{2kT}\left[(W_{\mathrm{H}_2} - W_{\mathrm{HH}^{*}}) - (W_{m\mathrm{H}} - W_{m\mathrm{H}^{*}})\right]\right\} \tag{2}$$

where m means metal
W = stretching mode of the bonds
h = Planck's constant
k = Boltzmann's constant
c = velocity of light
T = absolute temperature

For the equilibrium isotope effect of step 4 the same equation was used but instead of the difference $W_{\mathrm{H}_2} - W_{\mathrm{HT}}$ the difference $W_{\mathrm{CH}} - W_{\mathrm{CT}}$ was substituted.

To calculate the maximum kinetic isotope effects, i.e. "half separation" of the hydrogen in the transition state of step 4, 5 or 6 (Table 5) we used the simple equation

$$\frac{k_1}{k_2} = \frac{k_{\mathrm{H}}}{k_{\mathrm{H}^{*}}} = \exp\frac{hc}{2kT}(W_{\mathrm{H}} - W_{\mathrm{D}}) \tag{3}$$

which is derived from the equation given by Eyring and Cagle[24]

$$\frac{k_1}{k_2} = \frac{\sinh u_{1/2}}{\sinh u_{2/2}} \text{ with } u = \frac{hc}{kT}(W_{\mathrm{H}} - W_{\mathrm{D}}) \tag{4}$$

using the approximation $\sinh(x) = e^{x/2}$.

TABLE 6. CONDITIONS OF GAS CHROMATOGRAPHIC SEPARATION

Substances for separation[a]	Column 2 m	Temp °C	Flow rate ml/min N_2	Retention Time min.
Dimethyl fumarate	Polyethylene glycol[b]	125°	25	40
Dimethyl succinate	Polyethylene glycol[b]			55
Dimethyl maleate	Polyethylene glycol[b]			70
Ethyl butyrate	Polyethylene glycol[b]	85°	15	18
Ethyl iso crotonate	Polyethylene glycol[b]			32
Ethyl trans crotonate	Polyethylene glycol[b]			44
Ethyl tetrolate	Polyethylene glycol[b]			70
Methylcyclohexane	Silicon grease	50°	10	16
4-Methylcyclohexene	42 S 5,57[c]			19

[a] Solvent ethyl acetate or benzene.
[b] Perkin–Elmer type 42 S 12,14.
[c] Perkin–Elmer type 42 S 5,57.

EXPERIMENTAL

Most of the experimental details are given in the preceding paper.[1]

Comparison of the specific radioactivity of the hydrogenation gas and the different hydrogen positions of the products: The steel flask with T-labelled hydrogen was connected with a quartz tube filled with freshly oxidized copper oxide. The tube was flushed with N_2 and heated to 550° and then the labelled hydrogen was slowly led into the tube. The water formed was quantitatively collected in a cold trap. After two combustions the water from the 3rd, 4th and 5th combustions was taken and analyzed by liquid scintillation counting. Each sample was analyzed twice and the mean of the six values so obtained was $3{\cdot}12 \pm 0{\cdot}07{\cdot}10^7$ dpm/mM. The labelled products were degraded and the radioactivity measured as described.[1]

Radio gaschromatography.[3,4] The equipment used was that of Laboratorium Prof. Dr. Berthold, Wildbad and Bodenseewerk Perkin–Elmer Co. GmbH, Überlingen Germany. The conditions of gaschromatography are shown in Table 6.

For simultaneous determination of the tritium activity the efluents of the column were split in the ratio 1:10. One part went into the flame ionization detector and nine parts into a U-shaped reaction tube which was heated to 600° and filled with a cracking and hydrogenation catalyst.[4] Hydrogen was introduced into the reactor at the rate of 20 ml/min. Methane (20 ml/min) was led into the outcoming gas flow, which went through a flow counter operating in the proportional region of 10 or 80 ml volume.

The response of the flame ionization detector was calibrated every day by injecting known concentrations of the different compounds into the gas chromatograph. The efficiency of the radioactivity was determined by using standard tritium labelled toluene which was also used for calibration of the liquid scintillation counter.

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