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Metal-Catalyzed Intramolecular Hydrogen Shift during Hydrogenation and Exchange of Methyl Vinyl Ketone

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The hydrogenation and exchange of methyl vinyl ketone were studied over palladium, platinum, and rhodium catalysts by nuclear magnetic resonance spectroscopy and mass spectrometry. The unsymmetrical addition of deuterium across the C–C double bond resembles results for α,β-unsaturated esters and is explained by a modified classical mechanism involving an intramolecular hydrogen shift.

Recently we postulated an intramolecular hydrogen shift to account for unsymmetrical addition of deuterium to the C–C double bonds of certain α,β-unsaturated esters (*1*, *2*). A critical part of the postulate was participation of oxygen, and to test this we initiated investigations of other systems. We wish to report that our first such study discloses a similar occurrence in the α,β-unsaturated ketone system.

EXPERIMENTAL

Neat methyl vinyl ketone (MVK) (Monomer-Polymer Laboratories) was hydrogenated at 28–30° under 1 atm deuterium (General Dynamics 99.5% D_2) over 5% Rh/C, 5% Pt/C, and 5% Pd/C catalysts (Englehard) in a constant pressure apparatus similar to those previously described (*3*). Reaction mixtures were filtered after reduction and subjected to gas-liquid chromatographic (GLC), nuclear magnetic resonance (NMR), and, in two cases, mass spectral (MS) analyses. In certain experiments the butanone was purified by GLC before NMR and MS analyses. GLC analyses and purification were accomplished on an 8-ft by ¼-inch Carbowax 20-M column at 85°C and 120 ml/min He flow rate. NMR spectra were obtained on a Varian A-60 spectrometer.

Percentage compositions of reaction mixtures were determined by comparing areas under GLC tracings as measured by a standard ball and disc integrater (Disc Instruments, Inc.). No corrections were applied to the integrated areas since standard mixtures could be analyzed with reasonable accuracy (about 2%) and this was not critical.

The average of at least five integrations was obtained for each NMR spectrum. Using the methyl group as a three-proton standard the number of hydrogens and deuteriums in each position of the ethyl group was determined (Fig. 1). The error was ±0.07 deuterium and MS analyses revealed no exchange in the methyl group (Table 3). Samples were diluted with CCl_4.

MS analyses were performed by Mr. J. Neuzil of the Institute of Gas Technology with the instrument and procedure previously described (*4*).

RESULTS

The most reliable experiments are shown in Table 1. They represent less than half of the experiments performed because polymerization of starting material makes this system difficult to study.

MVK was purified by distillation. This apparently removes the polymerization inhibitor because slow polymerization occurs and the concentration of polymer increases

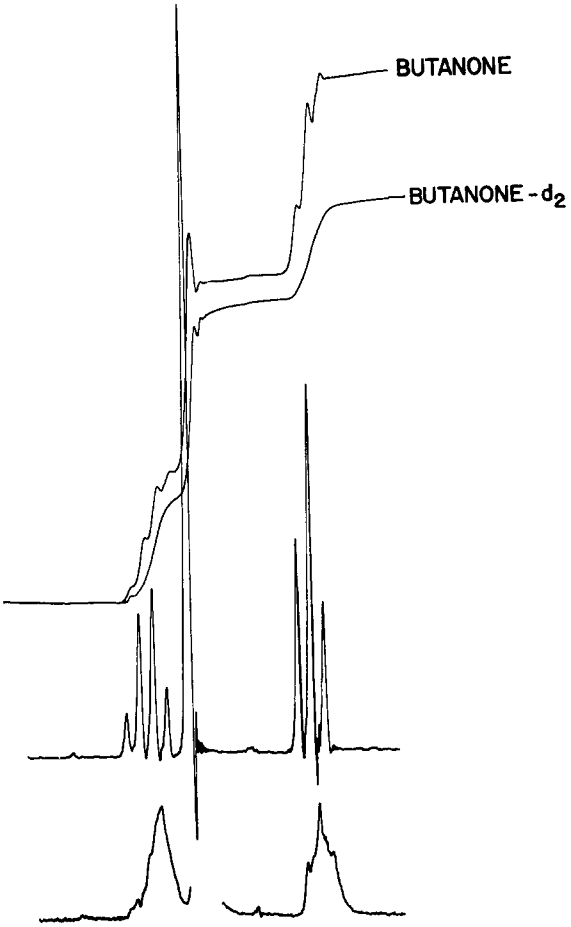


FIG. 1. Comparison of NMR spectra and integrals of light butanone and butanone-d_2. Increasing magnetic field is to the right.

upon storage. The NMR spectrum of the polymer overlaps with the upfield portion of the ethyl group in butanone (Fig. 1). This increases the areas of the ethyl portion more than that of the methyl portion, which is used as a standard. Since the amount of deuterium is obtained by difference, the amount of deuterium in the ethyl is lowered. An example can be shown with Exps. 6C and 6E on rhodium (not in Table 1), which were run 5 days and 6 months, respectively, after distillation. The former adsorbed only 80% of the theoretical amount of deuterium and the latter only 40%. GLC analyses of each showed 100% butanone but NMR analyses revealed only 1.66 deuteriums (0.44 in α, 1.22 in β) in butanone from 6C and only 1.06 (0.24 in α, 0.82 in β) from 6E. Clearly the polymer was not detected by GLC but was by NMR.

Polymer interference can be removed by purification of butanone before NMR or MS analysis. However, the point could be raised that if polymerization also occurs during reduction, some exchanged olefin will polymerize and remove deuterium from the system. This will lower the amount of deuterium found in the purified product because deuterium will be distributed between polymer and butanone. To remove this objection, we have excluded all experiments in which there was substantially less than two deuteriums per GLC-purified butanone at 100% reduction. Since no appreciable H_2–D_2 exchange occurs in these and similar experiments (*4*) there should be a maximum of two deuteriums per mole-

TABLE 1
DEUTEROGENATIONS OF METHYL VINYL KETONE (MVK)

			GLC analyses			NMR analyses of butanone	
Expt.[a]	Catalyst/g	MVK (g)	Butanone	MVK	Butanol	α	β
2F	Rh/0.0205	0.774	100.0	0	0	0.58	1.37
3F	Rh/0.0212	1.040	75	25	0	0.50	1.12
3G	Rh/0.0206	0.774	100.0	0	0	0.65	1.33
10C	Rh/0.0269	0.793	93.0	6.0	0	0.53[b]	1.32[b]
10F	Pd/0.0198	0.777	99.0	0	0	0.42	1.52
						0.38[c]	1.56[c]
14B	Pd/0.0278	5.596	9.5	90.5	0	0.08	0.24
						0.12[c]	0.50[c]
10E	Pd/0.0214	0.621	99.0	0	0	0.35	1.58
3C	Pt/0.0208	1.0	77.5	18.7	3.6	0.63	0.67
						0.44[c]	0.98[c]
						0.62[d]	1.38[d]
5D	Pt/0.0235	1.30	93.4	1.5	5.1	0.66[c]	1.06[c]
						0.76[d]	1.24[d]
10G	Pt/0.0194	0.755	90.0	2.0	8.0	0.63	0.59

[a] The number is the MVK distillation batch and the letter is the run using that batch; e.g., 10C is the third hydrogenation with batch 10; 10F, the sixth . . . .

[b] Same analysis before and after GLC purification.

[c] GLC purified before analysis.

[d] These are the above numbers which have been normalized to an average deuterium content of 2.0.

cule. Our qualitative observation is that there was most polymerization over rhodium and least over palladium, i.e., the most experiments excluded were over rhodium and the least were over palladium.

Reductions over the platinum catalyst yielded some butanol in addition to butanone. In Exps. 3C and 5D but not in 10G GLC separations were performed to eliminate butanol and unreacted MVK from the reaction mixtures. For 5D the comparison of separated to unseparated product shows major interference at the β position but not at the α position. On this basis we include the 10G α position in the table even though it was not GLC purified.

Reactions are fastest on palladium and slowest on rhodium, and the rates on each catalyst vary according to the time lapse between methyl vinyl ketone distillation and reduction. When distillation occurs just prior to reduction, rates are fastest. However, it should be emphasized that deuterium distributions, the results of competitive rates, are not greatly influenced by the overall rate, e.g., compare Expts. 2F, 3G, and 10C with relative rates of approximately 1:1:2. Therefore, the mechanistic aspects disclosed by these experiments should not be influenced by factors which effect the overall rate.

Several hydrogenations were carried out to different percentages of completion and the components separated and analyzed. Because of overlap in the complex ABC splitting pattern of the vinylic hydrogens it was not possible to determine the extent of exchange in each of the olefinic positions of recovered MVK; however, there was exchange in those positions (0.63 D's in Expt. 14B). Decoupling experiments may solve this problem, but we made no attempt to perform such experiments. Two partial reduction experiments which are not considered accurate enough to be included in Table 1 are 3J: 14% butanone over Rh/C, $\alpha = 0.25$, $\beta = 1.05$; and 4C: 24% butanone over Rh/C, $\alpha = 0.25$, $\beta = 1.08$. Results from mass spectral analyses of Expts. 10F and 14B are shown in Table 2.

Several new substances, about 1%, appeared early in the gas chromatograms of the reaction mixtures and some attempts were made to identify them. A number of

TABLE 2
MASS SPECTRAL RESULTS FOR BUTANONE FROM EXPTS. 10F AND 14B

14B 9.5% reduction	10F 99% reduction
d_0[a] 46.4%	15.5%
d_1 35.2%	24.0%
d_2 13.9%	24.8%
d_3 3.5%	22.1%
d_4 1.1%	12.5%
d_5 0.02%	1.0%
d_6 0.00%	0.03%
Avg. D[b] 0.78	1.95

[a] d_0 represents molecules containing no deuteriums; d_1, 1; d_2, 2; . . .

[b] Average number of deuteriums per molecule.

known compounds were tested but none had retention times equal to the new compounds. We excluded the possibility of external contaminants, but trapped samples evaporated rapidly on warming to room temperature and we did not pursue the search further.

DISCUSSION

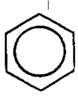
The NMR data reveal unsymmetrical addition of deuterium to the C–C double bond. For comparison, data are presented in Table 3 for methyl acrylate and styrene. Over Pd/C it is clear that MVK yields results similar to methyl acrylate but different from styrene, which has no oxygen function. Over Pt/C and possible Rh/C the reverse is true, so the deuterium distribution is not only sensitive to the structure of the compound but also to the nature of the metal surface.

The mass spectral data (Table 2) furnish another type of information. Virtually no exchange occurs in the methyl group, and one of the five positions of the ethyl group exchanges only slowly. The first fact supports our use of the methyl group as an internal standard, the second fact, when considered with the NMR data, points to the α hydrogen in MVK as difficultly exchangeable.

The small average deuterium content and the large amount of d_0 at 9.5% reaction (Expt. 14B, Table 2) reveal that an olefin exchange reaction is occurring which replaces deuterium with hydrogen on the surface and stores deuterium in desorbed MVK. This is supported by NMR findings of 0.63 D's in the recovered MVK, a 21% exchange if all three hydrogens exchange but 31.5% if only β hydrogens exchange.

More can be learned from mass spectra by performing mathematical manipulations on the data. One such treatment (*4*) converts an experimental deuterium distribution into a distribution that would be expected if the surface contained 100% deu-

TABLE 3
COMPARISONS ON DIFFERENT CATALYSTS

		Rh/C	Pt/C	Pd/C
CH_2	$C(H,D)_3$	1.55[a]	1.52[b]	1.69[b]
$\Vert$	$\vert$			
CH →	$C(H,D)_2$	0.49[a]	0.50[b]	0.34[b]
$\vert$	$\vert$			
CO_2CH_3	CO_2CH_3			
CH_2	$C(H,D)_3$	1.33	1.38	1.56
$\Vert$	$\vert$			
CH →	$C(H,D)_2$	0.65	0.62	0.38
$\vert$	$\vert$			
$COCH_3$	$COCH_3$			
CH_2	$C(H,D)_3$	—	1.32[b]	1.41[b]
$\Vert$	$\vert$			
CH →	$C(H,D)_2$	—	0.68[b]	0.58[b]
$\vert$	$\vert$			
				

[a] Reference 2.

[b] G. V. Smith and J. A. Roth, unpublished data.

terium at all times during the reaction. We have developed a computer program for performing this calculation and the results are shown in Table 4.

TABLE 4

Comparison of Experimental and Computed Values for Butanone from Expts. 10F and 14B

	14B (9.5% reduction)			10F (99% reduction)		
	$d_{ex}{}^{a}$	N^{b}	$d_{calc}{}^{c}$	$d^{e}{}_{x}{}^{a}$	N^{b}	$d_{calc}{}^{c}$
0	46.4		18.4	15.5		5.0
1	35.2		46.1	24.0		23.7
2	13.9	88.4	31.0	24.8	43.2	35.6
3	3.5	0.4	3.5	22.1	2.5	22.1
4	1.1	10.8	1.1	12.5	47.7	12.5
5	0.02	0.4	0.02	1.0	6.6	1.0
Surface-D[d]		55			68	
α-D[e]		0.12			0.38	
β-D[e]		0.50			1.56	

[a] Experimental deuterium distribution, % (from Table 2).

[b] Essentially the N values are weighting factors for binomial expansions such that the sums of the d's match, as closely as possible, the experimental d's:

$$\begin{array}{llllllll}
N_2\,(H+D)^2 = N_2\,(H^2 & +\,2H\,D & +\,D^2) & & & \\
N_3\,(H+D)^3 = N_3\,(H^3 & +\,3H^2D & +\,3H\,D^2 & +\,D^3) & & \\
N_4\,(H+D)^4 = N_4\,(H^4 & +\,4H^3D & +\,6H^2D^2 & +\,4H\,D^3 & +\,D^4) & \\
N_5\,(H+D)^5 = N_5\,(H^5 & +\,5H^4D & +\,10H^3D^2 & +\,10H^2D^3 & +\,4HD^4 & +\,D^5) \\
\qquad\qquad\qquad\quad d_0 & d_1 & d_2 & d_3 & d_4 & d_5
\end{array}$$

Values of H and D (H + D = 1) are substituted into the expansions and a value of N_5 is selected for perfect fit of d_5; N_4 is selected for perfect fit of d_4; N_3 for d_3; and N_2 is $100 - (N_3 + N_4 + N_5)$. New values of H and D are substituted until minimum error is obtained between calculated and experimental values of d_0, d_1, and d_2.

[c] Deuterium distribution calculated from N's, %.

[d] Percent D of (H,D) on surface; value used to calculate N's.

[e] Number of deuteriums in position by NMR (from Table 1).

Deuterium distributions calculated from N's do not perfectly match experimental distributions. That no computed set of N's can produce a perfect match indicates the mechanism to be more complex than a mere equilibration of certain positions with the surface pool of hydrogen and deuterium, (H,D).

Large N_2 and N_4 suggest existence of two kinds of butanone—butanone in which two and butanone in which four positions have interacted with the surface enough times to give them the same deuterium/hydrogen ratio as the surface. Butanone formed by the addition of one (H,D) to the α and β positions would give N_2. Exchange of the two terminal positions before reduction would account for N_4.

It is difficult to understand by an exchange–addition process how an unsymmetrical deuterium distribution could occur if 88.4% of the molecules have done nothing more than add (H,D) across the double bond (Table 4). It is equally difficult to explain why butanone contains less α-D than surface-D. One could argue that the calculated surface-D is high, and at 9.5% reaction it may be high since there are only 0.78 D's in the butanone, i.e., if each position picked up the surface-D there would be 2(0.55) or 1.10 D's in the butanone. However, at 99% reaction the surface-D is certainly not high yet it is still approximately twice α-D. That the surface-D rises only slightly during 9.5% and 99% reaction suggests an early establishment of a steady state.

A successful mechanism must explain the following facts: (1) there is much more β-D than α-D in butanone; (2) there is rapid exchange at β positions but no exchange at the α position; (3) there is a

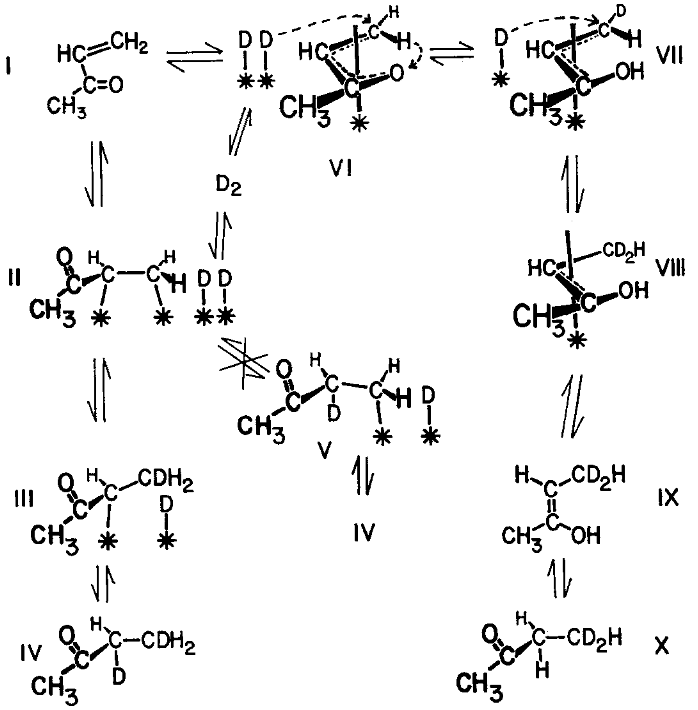


FIG. 2. Suggested mechanistic scheme. Asterisks represent points of attachment to the metal surface.

higher surface-D than α-D; (4) the MVK results resemble methyl acrylate results and not styrene results over Pd/C, but over Pt/C and possibly Rh/C the reverse is true.

Explanations for (1) and (2) could be rationalized by the classical half-hydrogenated state mechanism (*5*). Fact (3) and possibly (4) can be explained by an intramolecular hydrogen shift. A possible mechanism is shown in Fig. 2.

Path I–IV represents the classical "half-hydrogenated state" mechanism; I to III to I exchanges the β positions and if V is not formed, the α position will not exchange. Scheme VI–X enriches the α position in hydrogen if prior β exchange does not occur. Since MVK most closely resembles methyl acrylate over palladium it seems reasonable to assume that at least one of the steps in the sequence I–VI–IX has a higher activation energy relative to sequence I–IV over platinum and rhodium than it does over palladium. This meshes with published ideas on formation of π-bonded species on various catalysts (*6*).

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