Catalytic Behavior of Group VIII Transition Metals in the Deuterium–Acrolein Reaction

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The catalytic reactions between acrolein and deuterium over all the Group VIII transition metals were studied by microwave spectrometry. A high catalyst selectivity in the exchange reaction, in which hydrogen is replaced by deuterium in acrolein, was found. Over Rh, Pd, Ir, Ru, and Ni, hydrogens situated on the β carbon were quasi-selectively exchanged while over Pt, Os, and especially Co, an additional exchange of the aldehydic hydrogen took place. Over Fe, the hydrogen situated on the α carbon and the aldehydic hydrogen were exchanged equally. An attempt is made to relate the nature of the exchange to hydrogenation, decarbonylation, and hydrogenolysis and several reaction mechanisms are proposed in addition to the classical Horiuti–Polanyi mechanism, which is restricted to hydrogenation of the C–C double bond.

INTRODUCTION

In the exchange and hydrogenation of olefins and of ketones, similar mechanisms have been proposed to explain the addition of deuterium to the C–C double bond and to the C–O double bond, and the multiple exchange on vicinal carbon atoms. The mechanisms proposed are interconversion between monoadsorbed and diadsorbed species and the formation of a π-allylic species that is delocalized on three carbon atoms for the hydrocarbons, and on two carbon atoms and one oxygen atom for the oxo compounds (*1, 2*). Aldehydes are known to react differently from ketones; on palladium, in the presence of deuterium gas, the carbonyl group is not deuterated, but either the aldehydic hydrogen is exchanged (*3*) or ether is formed, depending on the experimental conditions (*4*); in the absence of hydrogen or deuterium and at higher temperature, decarbonylation takes place (*4*). We thought that it would be interesting to study the influence of the aldehyde group (CHO) on the hydrogenation of the C–C double bond and vice versa in α,β-unsaturated aldehydes.

In the case of α,β-unsaturated ketones, the hydrogenation of cyclopentenone (*5*)

and methyl vinyl ketone (*6*) have been studied. In order to account for unsymmetrical addition of deuterium across the C–C double bond, Smith and Deany (*6*) proposed, in addition to the Horiuti–Polanyi mechanism, an intramolecular hydrogen shift.

We report here the result of a study of the exchange reaction and hydrogenation in acrolein, the simplest α,β-unsaturated aldehyde, over Group VIII transition metals. Microwave spectrometry and nuclear magnetic resonance (NMR) were used to locate the deuterium atoms in the molecules.

METHODS

Apparatus and Procedure

The catalytic reactions were carried out in an all-glass, grease-free flow system at atmospheric pressure. The catalyst was isothermal and isobaric. A small amount of reactant (ca. 2.5 mg) was used for each run and was carried through the reactor at a constant partial pressure (5 Torr) by deuterium gas. A catharometer, installed in the flow line between the injector device and the reactor, allowed the pressure to be recorded as a function of time ($P = f(t)$), and gave a curve closely approximating a

square-wave pulse. The reaction products issuing from the reactor were collected in a trap during the plateau of the curve of $P = f(t)$. It was verified with a second catharometer, installed between the reactor and the trap, that all the product had been ejected from the reactor; this meant that no polymerization had occurred. Then, after the various molecules had been analyzed and separated by gas–liquid chromatography (glc), their mass, microwave, or nuclear magnetic spectra were recorded.

Materials

Acrolein was purchased from Merck and propanal from Fluka (purum grade). The acrolein was used just after purification by gas–liquid chromatography. Deuterium gas, from Air Liquide, of 99.4% isotopic purity, was passed through molecular sieves before use.

The supported metal catalysts were prepared by impregnating pumice with a metal salt solution. Pumice, in granular form (Prolabo), was crushed, washed, and sifted (35–40 mesh). This carrier was used instead of alumina on which acrolein reacts at room temperature. It was checked in control experiments that, up to 200°C, pumice treated in the same way as metal catalysts did not catalyze acrolein reactions. The preparation of 10% Fe,Co,Ni/pumice catalysts from nitrate salts was already described (7). Temperatures of calcination and reduction are reviewed below:

Fe(NO$_3$) $\cdot$ 9H$_2$O (Merck) calcined 12 h at 350°C and reduced 20 h by H$_2$ at 400°C,
Co(NO$_3$) $\cdot$ 6H$_2$O (Merck) calcined 12 h at 500°C and reduced 20 h by H$_2$at 450°C,
Ni(NO$_3$) $\cdot$ 6H$_2$O (Prolabo) calcined 12 h at 600°C and reduced 20 h by H$_2$ at 400°C.

Ten percent Ru,Rh,Pd,Ir,Pt, and 0.1% Os supported on pumice were prepared from aqueous solutions of chloride salts; chlorides of Group VIII noble metals are known to be easily reduced (8). After impregnation, metal/pumice was dried either at 100°C overnight or by desiccating for Ir,Ru, and Os to avoid the decomposition of iridium chloride or the formation of volatile oxides of ruthenium and osmium. Then the catalysts were reduced by H$_2$ during 20 h at temperatures indicated below:

[(NH$_4$)$_2$Ru]Cl$_6$ $\cdot$ $\frac{3}{2}$H$_2$O (Johnson Matthey) reduced at 350°C,
[(NH$_4$)$_2$Rh]Cl$_5$ $\cdot$ H$_2$O (Johnson Matthey) reduced at 350°C,
PdCl$_2$ (Johnson Matthey) reduced at 350°C,
[(NH$_4$)$_2$Os]Cl$_6$ (Johnson Matthey) reduced at 200°C,
IrCl$_4$ (Caplain St. Andre) reduced at 200°C,
H$_2$PtCl$_6$ (Johnson Matthey) reduced at 200°C.

Before each run, the metal/pumice catalyst was pretreated by passing a hydrogen flow over it at reduction temperature for 12 h followed by deuterium flow for 2 h to remove any hydrogen retained on the catalyst.

Gas Chromatography

The reaction products (hydrocarbons, propanal, acrolein, propanol, and allyl alcohol) were separated on a 5 m × ¼ in. 10% Carbowax 20 M firebrick column operating at 40°C under 480 Torr hydrogen pressure. The reactant product was purified on the same column and was used just afterward. The various hydrocarbons (ethane, ethylene, propane, and propene) were then analyzed on a 0.3 m × ¼ in. silica column operating at 20°C under 350 Torr nitrogen pressure.

Mass Spectrometry

The mass spectrometry analysis was performed with a CH7 Varian–Mat apparatus operating with 70-V electrons, a trap current of 300 μA and resolution of 1000. The usual corrections were made for natural isotopes and for the first C–H, C–D fragmentation which corresponds to fragmentation at the aldehydic hydrogen (9); the other C–H fragments were small enough to be neglected. In order to account for the isotopic effect of C–H, C–D fragmentation, the mass spectrum of CH_3–CH_2–CDO formed by the exchange of propanal on palladium was recorded and the fragmentation deduced:

$$\frac{C_3H_5O^+}{C_3H_6O^+} = 0.32, \qquad \frac{C_3H_5O^+}{C_3H_5DO^+} = 0.154.$$

In mass spectra of propanal formed by deuteration of acrolein, corrections for fragmentation were made by using the C–H and C–D fragmentation ratio from d_6, d_5, d_4, and d_3 molecules and the C–H fragmentation ratio from d_2 and d_1. In acrolein the C–D fragmentations were considered equivalent.

Microwave Spectrometry

The microwave measurements were carried out with a conventional 50 kHz square-wave stark microwave spectrometer (10). The deuterated propanal mixture formed by catalytic deuteration of acrolein gave us an inextricable microwave spectrum. The microwave spectrum was very dense for pure normal molecules. A fortiori, when several isomers for mono-, di-, tri-, and tetra-deuterated species were present, no reliable quantitative measurements could be made. However, the microwave analysis of a deuterated propanal sample coming from a deuterium–propanal exchange reaction on palladium allowed the monodeuterated species to be identified unquestionably as a CH_3–CH_2–CDO species.

In contrast, the spectrum of deuterated acrolein could be analyzed precisely; deu-terated species were detected when they constituted as little as 0.3% of the total product. The complete *trans*–acrolein structure was analyzed by Cherniak and Costain (11). The rotational constants of the four monodeuterated and dideuterated (CHD=CH—CDO) species have been published. From those, one could predict, using Kraitchman's equations, the rotational constants of any dideuterated species and then the transition frequencies within 2 MHz.

For analysis measurements, the adsorption cell, a 5-m-long double X-band waveguide, was cooled to $-60°C$; a 100-μA crystal current and 15-mTorr gas pressure were used.

The composition of the deuterated acrolein was determined quantitatively by measuring the intensities of the rotational lines; for this calculation, the areas of the peak corresponding to the $1_{01} \leftarrow 0_{00}$ transition for various species were multiplied by a correction coefficient (proportional to the square root of the product of the rotational constants, multiplied by the square of the frequency; the dipole moments were considered equal for the various species). The frequencies and correction coefficients are listed in Table 1.

Nuclear Magnetic Resonance Spectrometry

Proton NMR spectrometry cannot give the hyperfine deuterium distribution, but it can reveal the deuterium content of each carbon group in propanal (CH_3–CH_2–CHO). NMR spectrometry demands ten times as much product as does microwave analysis. Propanal was therefore analyzed in reactions in which acrolein was almost completely reduced. No further chromatographic separation was done because an impurity containing an ethyl group and an acid group was introduced into propanal when it was passed through a Carbowax column; this impurity interfered in the NMR spectrum. No such compound was detected by mass spectrometry. The NMR

TABLE 1

Frequencies and Relative Correction Coefficients of Various Deuterated Acrolein Species

Species[a]	Frequencies	Correction coefficients
d_0	8902.23	1.000
1-d_1	8813.96	0.886
2-d_1	8801.54	0.877
3-d_1	8577.25	0.838
4-d_1	8342.2	0.817
3,4-d_2	8068.7	0.691
2,3-d_2	8465.59	0.742
2,4-d_2	8256.73	0.721
1,2-d_2	8710.2[b]	0.785
1,3-d_2	8257.8[b]	0.724
1,4-d_2	8494.3[b]	0.752

[a] d_0, d_1, and d_2 mean that the species were respectively non-, mono-, or dideuterated, while the numbers preceding d specify which hydrogen atom (see Fig. 1) was replaced by a deuterium atom.
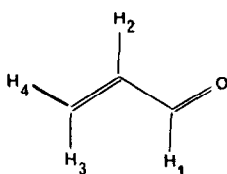
[b] Calculated values.

FIG. 1. Labeling of H atoms in acrolein.

spectra were obtained on a Cameca spectrometer working at 250 MHz.

RESULTS

Exchange Reaction

Table 2 summarizes the results of hydrogen–deuterium exchange in acrolein used as the starting reactant: the reaction conditions and the mass and microwave spectrometric data are shown. In the mass spectra, we never found more deuterated molecules than dideuterated ones. The location of the deuterium in a monodeuterated molecule depends very much on the catalyst. External double-bond hydrogens were very selectively exchanged on iridium, rhodium, and palladium and were predominant on nickel and ruthenium. Besides this reaction, an aldehydic hydrogen was exchanged on cobalt especially, and on platinum and osmium. Iron was inactive at 25°C, but at 85°C internal double-bond hydrogen and aldehydic hydrogen were nearly equally exchanged while external double-bond hydrogen exchange was negligible. On rhodium and palladium, dideuterated species were produced in sufficient amounts to be analyzed; of dideuterated species, only 3,4-d_2 was found. It is of interest that a major part of the d_2 species was formed by multiple exchange.

TABLE 2

Isotopic Analysis of Acrolein

Run	Metal	Weight (mg)	Flow rate (μl/min)	Temperature (°C)	Mass spectra			Microwave spectra				
					d_0	d_1	d_2	1-d_1	2-d_1	3-d_1	4-d_1	3,4-d_2
1	Fe	1000	0.34	85	98.1	1.8	0.1	42	48	<5	<5	not examined
2	Co	600	0.12	25	94.2	5.5	0.3	72	6	11	11	not examined
4	Os	1000	0.07	25	97.8	2.1	0.1	60	<4	18	18	not examined
6	Os	1000	0.15	100	91.2	7.9	0.9	40	—	30	30	not examined
8	Pt	1000	1.5	25	98.6	1.1	0.4	23	3	37	37	not examined
10	Pt	200	1.7	95	95.7	3.6	0.7	31	—	34	35	not examined
11	Ir	500	0.18	25	92.8	6.7	0.5 (0.12)[a]	1	1	49	49	not examined
13	Ni	200	0.74	25	98.2	1.6	0.2 (0.01)[a]	<5	<5	45	45	not examined
18	Ru	500	0.5	25	94.6	5.0	0.3 (0.07)[a]	<5	<5	45	45	not examined
21	Rh	50	1	25	79.3	14.7	6 (0.66)[a]	0	0	50	50	100
23	Pd	50	1.98	25	91.6	6.5	1.9 (0.12)[a]	0	0	50	50	100
24	Pd	200	0.62	25	74.4	18.8	6.8 (1.19)[a]	0	0	50	50	100
26	Pd	5	1.76	95	93.7	5.1	1.2 (0.07)[a]	0	0	50	50	100

[a] Calculated d_2 if simple exchange reaction is assumed (statistical distribution of d_0, d_1, and d_2 with two exchangeable atoms).

Hydrogenation, Decarbonylation, and Hydrogenolysis

Besides the exchange reaction in the starting reactant (acrolein), there were hydrogenation and, to a lesser extent, decarbonylation and hydrogenolysis of the C–O bond: the results are listed in Table 3. Deactivation takes place more or less rapidly, depending on the catalyst. However, as the reaction product distribution has been checked to be independent of the reaction time, and therefore of the total conversion, this phenomenon is no longer considered; the reported results correspond to a conversion, averaged over the time of reaction. On each metal, hydrogenation of the C–C double bond, yielding propanal, was the most rapid reaction. Depending on the catalyst, propanol appeared simultaneously with or just after propanal, or else it did not appear at all. To illustrate this point, the percentage of propanol as a function of hydrogenation conversion was plotted (Fig. 2).

In spite of some irreproducibility in product distributions, as can be seen on osmium and cobalt, mean curves could be drawn, and extrapolation to zero conversion allows some conclusions about the behavior of the catalyst to be drawn in regard to the exchange results. On the metals catalyzing the terminal hydrogen exchange (such as palladium, rhodium, nickel, iridium, and ruthenium), only the C–C double bond was initially hydrogenated; when the conversion increased propanol was still negligible except on ruthenium. Otherwise, on cobalt, osmium, and platinum, catalysts on which the aldehyde hydrogen was exchanged, propanol was formed simultaneously with propanal. Decarbonylation was always a minor reaction. It did not take place on palladium even at a high hydrogenation conversion. On the other metals, comparison of the ethane–ethylene formation at about 20% hydrogenation conversion shows that on cobalt, rhodium, and ruthenium, decarbonylation occurred to a significant extent, whereas it was negligible on nickel and platinum and was still very small on iridium. The C–O hydrogenolysis yielding propane–propene took place only on platinum at 25°C and on osmium at 100°C. Only on these two metals did allyl alcohol appear in the hydrogenated products.

Propanal Analysis

A mass spectrum analysis was made for deuterated propanal and the results are reported in Table 4. The d_2 maximum was slightly less pronounced on rhodium and palladium; the d_3 and, to a lesser extent, d_4 molecules were formed on all the catalysts. The distribution did not change
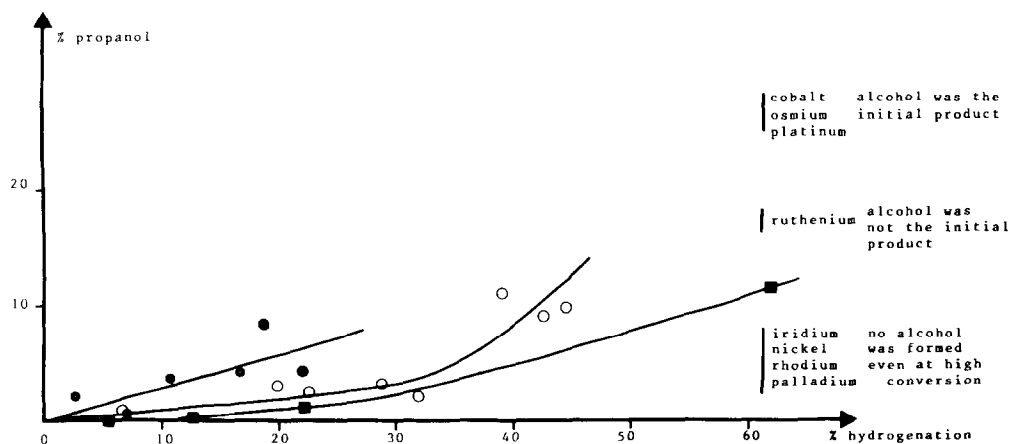

FIG. 2. Propanol as a function of hydrogenation. ◑, Osmium; ○, platinum; ●, cobalt; ■, ruthenium.

TABLE 3

Hydrogenation, Decarbonylation, and Hydrogenolysis of Acrolein

Run	Metal	Weight (mg)	Flow rate (μl/min)	Temperature (°C)	Propanal	Propanol	Allyl alcohol	Propane Propene	Ethane Ethene	Overall conversion[a]	Exchange[b] (%)
2	Co	600	0.12	25	10.5	8.2	—	c	c	18.7	5.8
3		600	0.15	25	17.6	4.3	—	c	0.27 {37 / 63}	22.1	c
4	Os	1000	0.07	25	2.5	2.1	c	c	c	4.6	2.3
5		1000	0.15	25	5.3	0.1	є	—	0.05 {95 / 5}	5.5	a
6		1000	0.15	100	32	9.2	1.3	c	c	42.5	8.8
7		1000	0.30	100	47.7	15.8	3.5	0.28 {40 / 60}	0.44 {60 / 40}	67.6	c
8	Pt	1000	1.5	25	34.4	9.9	є	c	c	44.3	1.4
9		200	0.3	25	19.4	2.4	0.6	0.21 {85 / 15}	0.03 {70 / 30}	22.6	c
11	Ir	500	0.18	25	14.2	—	—	c	c	14.2	7.2
12		1000	0.37	25	24.4	—	—	—	0.07 {68 / 32}	24.5	c
13	Ni	200	0.74	25	64.6	—	—	c	c	64.6	1.8
14		100	0.30	25	80.9	1.4	—	—	0.06 {80 / 20}	82.4	c
15		50	0.30	25	8.2	—	—	—	0.02 {87 / 13}	8.2	c
16	Ru	200	0.30	25	2.4	—	—	—	0.01 {20 / 80}	2.4	c
17		400	0.30	25	12.5	0.5	—	—	0.16 {68 / 32}	13.1	c

TABLE 3—Continued.

Run	Metal	Weight (mg)	Flow rate (μl/min)	Temperature (°C)	Propanal	Propanol	Allyl alcohol	Propane Propene	Ethane Ethene	Overall conversion[a]	Exchange[b] (%)
18	Ru	500	0.5	25	20.7	1.1	—	c	c	21.8	5.4
19		500	0.12	25	50.4	11.6	—	c	c	62	15.4
20	Rh	10	0.30	25	25.5	0.2	—	—	$0.15\begin{cases}84\\16\end{cases}$	25.8	c
21		50	1.00	25	46.6	0.2	—	c	a	46.8	20.7
22		30	0.30	25	53	0.8	—	—	$0.31\begin{cases}90\\10\end{cases}$	54.1	c
24	Pd	200	0.62	25	83	—	—	—	a	83	25.6
25		30	0.30	25	56.1	—	—	—	<0.002	56.1	c

[a] Sum of hydrogenation, decarbonylation and hydrogenolysis products.
[b] $(100 - d_0)$ in acrolein mass spectra.
[c] Not examined.

significantly when the conversion increased, as is seen in the runs on nickel and palladium; no more than two deuterium atoms entered into the molecules even at 80% hydrogenation conversion. This seems to indicate that *no consecutive propanal exchange* occurred. It was, indeed, found that, under the same experimental conditions, deuterium–propanal exchange took place to a very small extent (Table 5), while at 65°C three hydrogen atoms were exchanged; the aldehydic hydrogen, was preferentially exchanged (see run 31, Table 5, for which the location of the deuterium was checked by microwave spectrometry), and as is well known to happen in deuterium–ketone exchange (*1, 12*) on palladium, two hydrogen atoms situated on the carbon atom in α of carbonyl were then exchanged. This multiple exchange was not observed in the experiments of Teillet and Cornet (Table 5). This could be due to a difference of dispersion in their palladium/pumice catalyst. The location of deuterium in propanal formed by acrolein deuteration was studied by NMR for a run catalyzed by palladium in a reaction that produced a high hydrogenation conversion (Table 6). This analysis shows that the two deuterium atoms entering into the molecule during the addition process were not distributed equivalently on the methyl and methylene groups. The ratio of deuterium on methyl to that on methylene carbons (2.7) was even higher than the statistically calculated ratio (1.5). On the other hand, the aldehydic hydrogen was extensively exchanged. This confirms that aldehydic exchange took place on the surface during the step in which deuterium was added at the C–C double bond.

DISCUSSION

Exchange of External Hydrogens: $CX_2{=}CH{-}CHO$ ($X = H, D$)

To explain this preferentially exchanged position on the C–C double bond, it is tempting to propose a classical Horiuti–
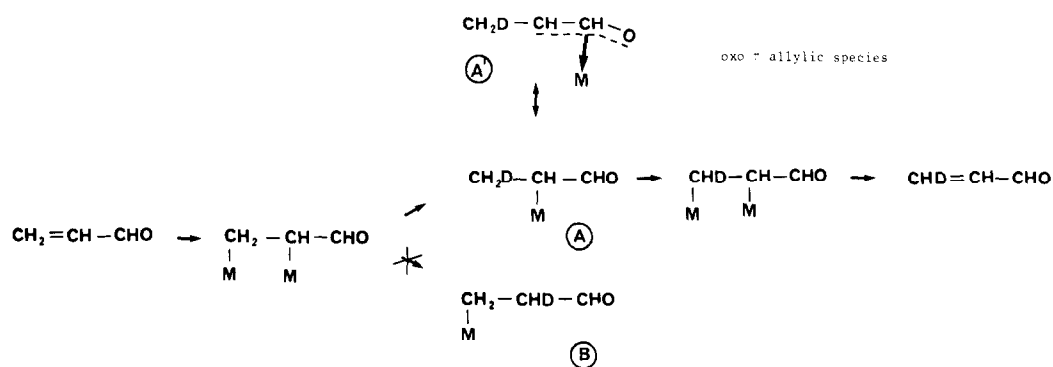
TABLE 4

Deuteration of Acrolein: Results of Mass-Spectral Analysis for Propanal

Run	Metal	Propanal (%)	d_0	d_1	d_2	d_3	d_4	d_5	d_6	$\Sigma_{i=1}^{6} i d_i / 100$
1	Fe 100°C	2.9	4.7	5.3	55.2	30.8	3.4	0.6	—	2.2_5
2	Co	10.5	3.9	8.5	65	19.4	2.6	0.5	—	2.0_9
4	Os	2.5	5.4	12.4	59.2	16.3	5.5	1	0.1	2.0_7
6	Os 100°C	32	4.3	7.8	59.8	20.7	6.1	1.1	0.1	2.2_0
8	Pt	34.4	3.5	8.5	73.7	11.1	3	0.4	—	2.0_3
10	Pt 95°C	29.7	3.5	5.4	62.7	20.6	6.7	1.0	—	2.2_4
11	Ir	14.2	7.6	16.2	64.8	9.6	1.9	—	—	1.8_2
29	Ni	22.8	4	9.8	70.6	13	2.4	0.2	—	2.0_0
13	Ni	64.6	3.5	6.8	74.9	12.5	2	0.3	—	2.0_3
18	Ru	20.7	6.1	7.6	52.9	25	7.1	1.3	—	2.2_3
21	Rh	46.6	9.6	16.2	33.8	25.0	12.1	3.0	0.3	2.2_4
27	Pd	4.8	17.6	24.3	36.6	13.4	8.1	—	—	1.7_8
24	Pd	83	12.4	18.4	32.5	22.2	11.2	2.8	0.5	2.1_2
26	Pd 95°C	31.7	7.8	17.8	46.4	19.3	7.9	0.7	—	2.0_3
28	Pd 100°C	100	6.2	10.7	44.9	25.2	11.6	1.4	—	2.3_0

Polanyi type of mechanism, in which selectivity operates in the formation of the half-hydrogenated state (Scheme 1). Species A would be formed preferentially to species B because A would be stabilized by formation of an oxo π-allylic complex: such a species would explain the participation of the oxygen atom in this mechanism and the difference between butene (13) and acrolein exchange on various catalysts.

An oxo π-allylic species was introduced first by Cornet and Gault (1) to explain the exchange of hydrogen atoms situated α to the carbonyl group in cyclopentanone. So, if such a species A were formed from acrolein, the hydrogen atom attached to carbon 2 would be exchanged. However, this is never the case: only $CD_2{=}CH—CHO$ is formed. This mechanism is therefore rejected as an explanation of the exchange reaction of acrolein. Smith and Deany (6), in the methyl vinyl ketone (MVK) exchange reaction, noted the presence of β exchange in MVK on palladium,

$$CH_2D-CH-CH{\searrow}O$$
Ⓐ
M

oxo π allylic species

$$CH_2D-CH-CHO \longrightarrow CHD-CH-CHO \longrightarrow CHD=CH-CHO$$
M   Ⓐ   M   M

$$CH_2=CH-CHO \longrightarrow CH_2-CH-CHO \quad{\nearrow}{\ast}$$
M   M

$$CH_2-CHD-CHO$$
M
Ⓑ

Scheme 1

TABLE 5

Deuterium–Propanal Exchange on Palladium Pumice

Run	Metal	Weight (mg)	Flow rate (μl/min)	Tempera-ture (°C)	d_0	d_1	d_2	d_3	d_4	d_5	d_6
30	Pd 10%	200	0.62	25	97.5	2.2	0.3	—	—	—	—
31	Pd 10%	500	0.5	65	47.3	39.2	8.1	5.4	—	—	—
32	Pd 10%	1000	0.5	65	14.5	39.4	19	26.2	—	—	—
	Pd 2%[a]	3300	8.3	60	14.2	83.7	1.3	0.9			

[a] In the work of J. Teillet and D. Cornet (3)—NMR analysis showed 100% deuterium atoms on aldehydic hydrogen.

which they explained by invoking a mechanism similar to that drawn above (Scheme 1), but they did not justify the preferential direction of the reaction and they did not then introduce the oxo π-allylic species. However, they proposed an additional mechanism, namely, an intramolecular 1–4 hydrogen shift, in order to explain why more β-D than α-D was introduced into butanone during the addition of deuterium. We think that the latter mechanism could also explain the β exchange reaction in acrolein (Scheme 2).

Interconversion between species C and E followed by desorption would indeed give species CX_2=CH—CHO (X = H, D). Unfortunately it was not possible to analyze precisely the microwave spectra of the deuterated propanal and to come to a conclusion about the formation of the CD_2H–CH_2–CHO species, but the high deuterium

content of methyl in comparison with that of methylene in propanal is well explained by assuming that this mechanism, as well as the classical Horiuti–Polnyi mechanism, participates in the deuteration process.

In homogeneous catalysis, Hendrix *et al.* (14) reported finding evidence of a π-allyl hydroirontricarbonyl complex (I) involved in the rearrangement of allyl alcohol by $Fe(CO)_5$:
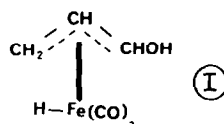
Such a reaction intermediate (I) is similar to the π-allylic species E that we assume was formed.

The behavior of catalysts would depend upon the stability of species E. If it is very stable, multiple exchange of terminal hy-
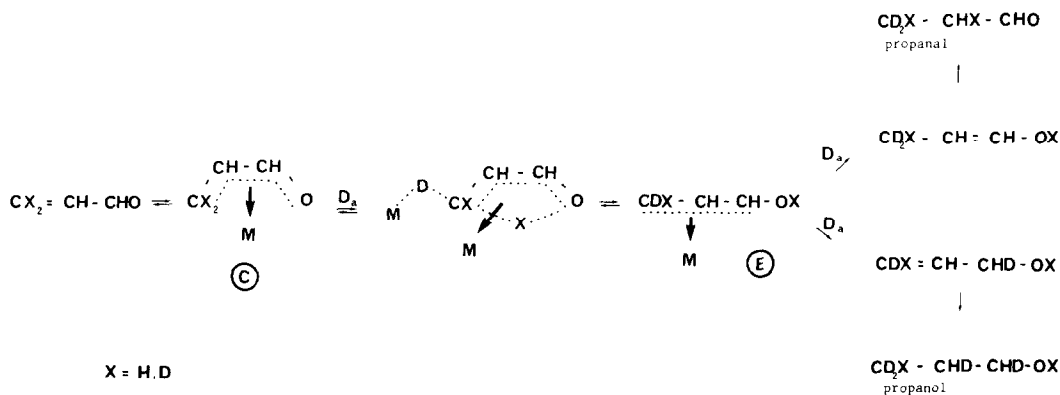
SCHEME 2

TABLE 6

NMR Results for Propanal, from Deuteration of
Acrolein on Palladium at 80% of Reduction

	d_0	d_1	d_2	d_3	d_4	d_5	d_6
Mass spectra	13	20.6	33.5	21.6	9.4	1.7	0.2

$\Sigma_i \, idi = 2$

Distribution of these two deuterium atoms

NMR analysis	CH$_3$	CH$_2$	CHO
	1.2	0.45	0.35

drogen atoms in acrolein is observed: this occurs on palladium, rhodium, ruthenium, and nickel. When species E is less stable, it is readily hydrogenated to give propanol and propanal, and in that case the exchange of terminal hydrogen atoms becomes a minor reaction in comparison with other reactions; this case is observed on platinum, osmium, and cobalt.

Exchange of the Aldehydic Hydrogen and Decarbonylation

The aldehydic hydrogen was exchanged mainly on cobalt and osmium, and to a small extent on platinum. This implies a dissociative mechanism that would involve the same reaction intermediates that Tsuji and Ohno (15) introduced to explain the mechanism of carbonylation and decarbonylation in homogeneous catalysis (Scheme 3).
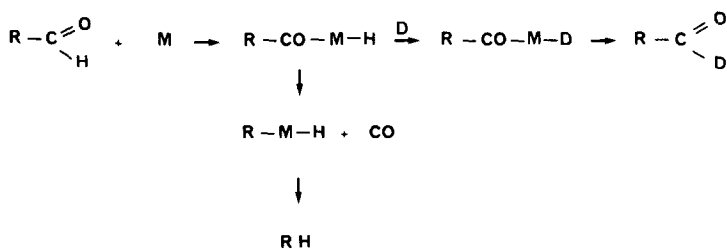
It is of interest that the aldehyde exchange is favored on cobalt, which is the best catalyst among the transition metals for decarbonylation and is known in homogeneous catalysis to be the catalyst of choice in oxosynthesis (16).
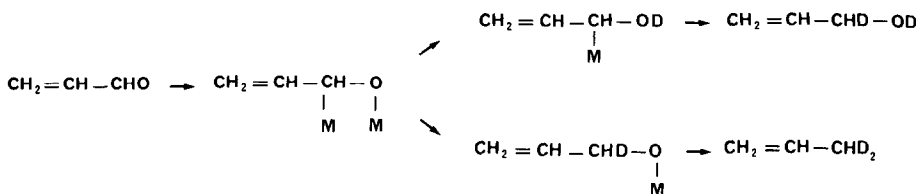
C–O Bond Hydrogenolysis

Kemball and Stoddart (12) already noted the exceptional ability of platinum, in comparison with palladium, rhodium, tungsten, and nickel, to induce fission of the C–O bond in acetone, cyclopentanone, and cyclohexanone. This role was confirmed in the hydrogen–acrolein reaction and extended to osmium. If the formation of allyl alcohol is related to hydrogenolysis, as it seems to be, the same intermediate reactions could be involved. The common step would be the associative adsorption of a carbonyl group followed by the formation of two half-hydrogenated intermediates; the one bonded to a carbon atom would yield alcohol, and the other, bonded to an oxygen atom, would break the C–O bond (Scheme 4).

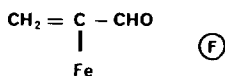## Reactions with Iron as a Catalyst

The low catalytic activity observed in the deuterium–acrolein reaction on iron has already been found in butadiene hydrogenation and was attributed to carburation of the catalyst (17). However, the exchange of acrolein on this metal is very peculiar; it is the only Group VIII metal that gives a noticeable exchange on carbon 2 in addition to an exchange of the aldehydic hydrogen. This type of exchange is similar to that observed in 1-butene (18), in which only the internal hydrogen is replaced. It can be interpreted by assuming a similar mechanism involving a vinylic dissociative species F.


SCHEME 3

$$CH_2 = CH - CHO \quad \longrightarrow \quad \underset{\substack{| \\ M}}{CH_2 = CH} - \underset{\substack{| \\ M}}{CH} - O$$

$$CH_2 = CH - CH - OD \quad \longrightarrow \quad CH_2 = CH - CHD - OD$$
$$\underset{M}{|}$$

$$CH_2 = CH - CHD - O \quad \longrightarrow \quad CH_2 = CH - CHD_2$$
$$\underset{M}{|}$$

SCHEME 4

$$CH_2 = \underset{\substack{| \\ Fe}}{C} - CHO \qquad \textcircled{F}$$

CONCLUSION

The results presented in this paper show that when deuterium and acrolein react on a metal catalyst, in addition to the classical Horiuti–Polanyi mechanism, which leads only to C–C double-bond hydrogenation, several other mechanisms compete on the surface, depending on the catalyst. First the mechanism of Smith and Deany involving an intramolecular hydrogen shift and the formation of a π-allylic species E,

$$\underset{M}{CH_2 \cdots \overset{\displaystyle CH}{\underset{\displaystyle |}{\diagup}} \cdots CHOH}$$
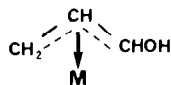
took place over all Group VIII transition metals except iron; when species E was stable, the mechanism led to exchange of the hydrogens situated on the β carbon, and when it was unstable the mechanism led to hydrogenation of species E into propanol. Second, dissociative adsorption of the aldehydic carbon atom occurred mainly on cobalt and, to a lesser extent, on platinum, osmium, and iron, leading to the exchange of the aldehydic hydrogen, and decarbonylation. Next, associative adsorption on the carbonyl group, which could lead to either the formation of allyl alcohol or hydrogenolysis of the C–O bond occurred only on platinum and osmium. Finally, dissociative vinyl adsorption on the internal C–C double-bond carbon took place only on iron.

ACKNOWLEDGMENTS

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