JOURNAL OF CATALYSIS 13, 373–384 (1969)

Oxidation of Propylene by Means of SnO_2-MoO_3 Catalysts

II. Hydrogen–Deuterium Exchange between Propylene and Water

J. BUITEN

From the Central Laboratory, Staatsmijnen/DSM, Netherlands

Received September 10, 1968

It has been found that in the presence of SnO_2 covered with MoO_3 and at a temperature of 360°C, propylene and D_2O rapidly exchange hydrogen against deuterium. The distribution of the deuterium over the propylene molecules proved to be approximately binomial. One of the hydrogen atoms in the propylene molecule participated only slightly in the exchange; this must have been the atom bonded to the central carbon atom. Infrared absorption measurements revealed that deuterium appears preferably in the methylene group (as was confirmed by a proton magnetic resonance measurement), and for the greater part in the cis position with respect to the methyl group.

An explanation of the exchange which accounts for the availability of five hydrogen atoms in the propylene molecule for the exchange while being compatible with the above-mentioned preference, is represented by a reversible reaction between propylene and acid surface hydroxyl groups yielding surface-bonded isopropyl groups (or isopropoxy groups, if the surface oxygen atoms are considered to be included). In our view, these groups also constitute the intermediate species in the oxidation of propylene to acetone and acetic acid.

MoO_3 gave a low exchange rate, while SnO_2 proved to hold an intermediate position between MoO_3 and SnO_2/MoO_3. The same applies to the rate of oxidation of propylene.

With SnO_2/MoO_3, isopropyl alcohol was very rapidly dehydrated to propylene at 370°C; also during oxidation of propylene over this catalyst, the off-gas showed the low equilibrium concentration of isopropyl alcohol—even at a very high space velocity. In the dehydration of isopropyl alcohol, MoO_3 showed a fairly high activity. The catalytic action of SnO_2 on isopropyl alcohol, however, was directed almost exclusively towards the oxidative dehydrogenation to acetone. This is one of the arguments to be raised against the view that the above-mentioned isopropyl (isopropoxy) group is also an intermediate in the dehydration of isopropyl alcohol. All experiments were done in the presence of air and water vapor.

INTRODUCTION

In Part I (*1*) it was shown that SnO_2-MoO_3 catalysts owe their activity for the oxidation of propylene by air to the fact that the SnO_2 surface is covered with what might be regarded as a monomolecular layer of MoO_3. This oxidation, which can be carried out at, e.g., 370°C, yields mainly acetic acid and acetone. A condition is that the reaction mixture contains water vapor.

The fact that acetone is formed suggests the following reaction path:

$$\text{propylene} \rightleftarrows \text{isopropyl alcohol} \rightarrow \text{acetone}$$

especially because in the first step (from propylene to isopropyl alcohol and back) water is involved. (As will be shown later, a better representation is

$$\text{propylene} \rightleftarrows \text{I} \rightarrow \text{acetone}$$

where I denotes a surface species related to isopropyl alcohol.) This course of the oxidation of propylene would involve, under the circumstances of the oxidation, exchange of hydrogen and deuterium between propylene (at first C_3H_6) and water (at first D_2O). For this reason several experiments were made to determine the rate of the exchange. Attention was given also to the distribution of the deuterium over the propylene molecules (by mass-spectrometric analysis) and to the position of deuterium in the propylene molecules (by infrared absorption and proton magnetic resonance).

Experiments were also undertaken with introduction of isopropyl alcohol in addition to, or instead of propylene. We further determined the isopropyl alcohol concentrations in various propylene oxidation tests. These concentrations are very small, because at high temperatures the equilibrium between propylene and isopropyl alcohol tends strongly towards propylene.

For comparison, the separate oxides SnO_2 and MoO_3 were also included in the investigation.

EXPERIMENTAL

Normally, the experiments were performed in a reactor of the type described in Part I (*1*).

The test (No. 9, Table 4) for establishing the dehydration rate of isopropyl alcohol at 369°C in the presence of MoO_3-covered SnO_2, was carried out in a special way. In the left-hand leg of the reactor shown in Fig. 1 of Part I (*1*) propylene was oxidized in the usual manner. The reaction gas entered the right-hand leg, where it mixed with a nitrogen flow containing isopropyl alcohol and traversed a bed of 0.1 g of catalyst diluted with 1 g of carborundum particles. We came to this procedure after it had appeared that the use of a simple reactor provided with a small amount of catalyst gave rise to a rather rapid drop of the activity with regard to both the oxidation of propylene and the dehydration of isopropyl alcohol. In spite of all the trouble taken, the cause of this activity drop could not be found. There was, however, ground for supposing that products from the oxidation of propylene prevent deterioration of the catalytic activity. Dehydration of isopropyl alcohol by the above procedure was indeed not hindered by a decrease in activity.

Partly because the experiments were undertaken over a long period, there have been variations in the modes of feeding the liquid reactants and of collecting or analyzing the reaction products. In the tests with MoO_3-covered SnO_2, isopropyl alcohol and acetone were determined in the gas which, after passing through a small condenser, was bubbled through the condensate (kept at 80°C) and, subsequently, led through a reflux condenser. Determination of these compounds, of which only a negligible portion remained in the condensate, was done by means of a gas chromatograph equipped with a gas sampler, a column filled with Carbowax 600 on Chromosorb, and a flame-ionization detector.

The percentages of undeuterated propylene, propylene-d_1, propylene-d_2, etc., in propylene that had been subjected to a hydrogen–deuterium exchange, were determined mass spectrometrically. The electron-accelerating voltage was low (~ 10 V) to prevent fragmentation of the molecules.

The conditions in the experiments with propylene were so chosen that there was only little conversion to oxidation products (see Part I).

The mean total pressure in the catalyst beds was somewhat higher than 1 atm (highest value 1.13 atm with Experiment 8, Table 4).

RESULTS

Exchange Rate and Deuterium Distribution

Table 1 is a survey of the conditions and results of a number of experiments on the H–D exchange between propylene and water vapor. Values are given for the distribution of deuterium in the issuing propylene and for the initial exchange rate. The values mentioned under the experimental mole fractions of C_3H_6, C_3H_5D, $C_3H_4D_2$, etc., in the propylene, denote the mole fractions that would have been found if the distribution of the deuterium atoms over the propylene molecules should be binomial. For the distribution to be binomial, the exchange sites must be equivalent; it is characterized by

$$r_i = \frac{a!}{i!(a-i)!} x^i (1-x)^{a-i} \qquad (1)$$

where a is the number of exchangeable H or D atoms per propylene molecule; r_i, the mole fraction of propylene with i D atoms per molecule ($i = 0, 1, \cdots, a$); x, the

TABLE 1

EXCHANGE OF HYDROGEN AND DEUTERIUM BETWEEN PROPYLENE (INITIALLY C_3H_6) AND WATER VAPOR (INITIALLY D_2O) AT 360°C[a]

Test no.	Catalyst: Type	Catalyst: Surface area (m^2)	Gas flow rate (mole/hr)	$100\,r_{i,\text{expt.}}$ $100\,r_i$ [Eq. (1); $a = 5$] $100\,r_i$ [Eq. (1); $a = 6$]: C_3H_6 ($i = 0$)	C_3H_5D ($i = 1$)	$C_3H_4D_2$ ($i = 2$)	$C_3H_3D_3$ ($i = 3$)	$C_3H_2D_4$ ($i = 4$)	C_3HD_5 ($i = 5$)	C_3D_6 ($i = 6$)	$\frac{x}{x_e}$	Initial exchange rate, u_H (mgram at/m^2 hr)
1	MoO_3[c]	9[g]	0.67	94	6	0.3	0.02	0	0	0	0.018	0.29
				94	6	0.2	0.00	0	0			
				94	6	0.2	0.00	0	0	0		
2	SnO_2[d]	21	0.67	19	39	29	11	2.0	0.16	0.00	0.37	3.4
				20	38	29	11	2.1	0.16			
				21	37	28	11	2.5	0.31	0.015		
3	Mixture of SnO_2 and MoO_3[e]	4.9[h]	1.00	8.4	19	24	24	18	6.9	0.07	0.63	43
				3.5	17	32	31	15	2.8			
				4.3	18	30	28	15	4.0	0.46		
4[b]	Mixture of SnO_2 and MoO_3[e]	4.9[h]	1.00	2.5	11	23	30	24	9.3	0.08	0.75	60
				1.3	9	25	34	24	6.6			
				1.9	11	25	31	22	8.2	1.3		
5	SnO_2 treated with $MoO_2(OH)_2$[f]	4.6	1.00	1.0	3.7	10	23	35	27	<0.1	0.95	≈150
				0.14	1.9	10	28	39	21			
				0.36	3.3	13	27	31	20	5.1		

[a] Partial pressures of propylene, water vapor, and oxygen: 0.06, 0.65, and 0.06 atm, respectively.

[b] Continuation of Test 3.

[c] This catalyst was prepared by applying 1 part by weight of a commercial MoO_3 on 2 parts by weight of carborundum particles of 3-4 mm diam. The catalyst mass (40 g) was used in a reactor of 2-cm il d.

[d] Prepared as SnO_2-A (Part I).

[e] Water was added to commercial SnO_2 and MoO_3 (molecular ratio of these oxides 2:1). The water was evaporated on a steam bath, after which the residue was dried.

[f] This catalyst is comparable with preparation I (Part I); Mo content 0.17% by weight.

[g] Surface area of MoO_3.

[h] Surface area of SnO_2.

fraction of deuterium in the exchangeable hydrogen and deuterium of the propylene. The magnitude of x follows from the experimental mole fractions $r_{i,\text{expt}}$:

$$x = \frac{1}{a}\sum_{i=1}^{a} ir_{i,\,\text{expt}} \tag{2}$$

(Thus, the calculated r_i values are not independent of the experimental ones.) The binomial distributions were calculated for $a = 5$ and $a = 6$. (With $a = 5$, any C_3D_6 present is regarded as not belonging to the propylene.) The initial exchange rate (u_H) is defined as the number of milligram atoms of H (per m^2 of catalyst surface and per hour) that at the beginning of the bed go from propylene (C_3H_6) to water (D_2O), i.e., are exchanged against deuterium. The reason that this definition has been chosen, and the way in which u_H was calculated from the experimental data, are given in the Appendix. In the case of SnO_2/MoO_3, u_H was corrected because of the limited diffusion velocity of the propylene in the catalyst pellets (corrections smaller than 10%). No allowance was made for the fact that a small portion of the propylene is oxidized.

Infrared Absorption and Proton Magnetic Resonance Measurements

Some exchange experiments were carried out with MoO_3-covered SnO_2 (3.5 m^2/g) at 370°C in which x did not assume high values, viz., 0.01, 0.04, 0.06, and 0.20 (in calculating x, a was taken equal to 5). Infrared spectra were taken of the propylene in the issuing gas. These could be interpreted only semiquantitatively.

With $x = 0.04$ and $x = 0.06$, methylene groups with a single deuterium atom (HDC=; D and methyl in the cis position) were roughly twice as frequent as both HDC= (trans) and methyl groups containing deuterium. With $x = 0.01$, the spectrum did not even show more than a signal of HDC= (cis); the irrecognizability of the signals of HDC= (trans) and of H_2DC- may have been partly due to the fact that the extinction coefficients of these groups are considerably smaller than the extinction coefficient of HDC= (cis). On the other hand, in the relatively strongly deuterated propylene with $x = 0.20$, the amount of deuterated methyl groups was comparable with the amount of HDC= (cis), but, as in the other tests, the amount of HDC= (trans) was smaller than that of HDC= (cis). The group $D_2C=$ occurred in the propylenes with $x = 0.06$ and $x = 0.20$, the amount of the latter being twice as large as that in the former. Propylene with D attached to the second carbon atom was absent.

In an exchange experiment carried out at 330°C with a catalyst composed of SnO_2, MoO_3, and SiO_2 (Aerosil), the propylene in the dried issuing gas was condensed at approx. -130°C*. After the tube containing the condensate had been sealed, the proton magnetic resonance was determined at -55°C. The ratio between the numbers of vinyl and methyl H atoms was found to be 0.945. The ratio between the numbers of the methylene H atoms and the H atoms bonded to the second carbon atom could not be determined accurately; the value found was 1.85 ± 0.15. Assuming that there are no D atoms bonded to the second carbon atom (see Discussion section) and using the former ratio of 0.945, one can easily calculate that values above 1.835 for the latter ratio lead to negative numbers of methyl D atoms.

At values from 1.7 (= 1.85 − 0.15) to 1.835, the ratio between the numbers of methylene and methyl D atoms increases from 2.1 to infinity and x varies from 0.089 to 0.033. This range of x values is reasonable (a mass-spectrometric analysis was not done). We may conclude therefore, that this ratio was at least 2. This result is in agreement with the information from infrared absorption.

Dehydration of Isopropyl Alcohol

The conditions and results of some experiments with isopropyl alcohol are given in Table 4. For comparison, values concerning the oxidation of propylene and the exchange are given in Tables 2 and 3. The rates of the dehydration of isopropyl alcohol to propylene, of the oxidation of propylene towards

---

* The attending condensation of O_2 and N_2 must be kept below certain limits.

acetone and acetic acid, and of the exchange reaction, are expressed as rate constants of reactions that are assumed to be first order in the partial pressure of propylene. This assumption seems to be permissible because Tables 2–4 serve only to give a qualitative comparison. (We point out that data at our disposal concerning the dehydration of isopropyl alcohol and the oxidation of propylene, support this assumption.)

As can be seen from the last column in Table 4, the principal reaction in the case of SnO_2 is not the dehydration to propylene, but the oxidative dehydrogenation to acetone. In Experiment 7 in this table 14% of the isopropyl alcohol was converted with a high selectivity into acetone.

TABLE 2

REACTION RATE CONSTANTS FOR OXIDATION OF PROPYLENE[a]

Catalyst			First order reaction rate constant (mmole/m² hr atm)
Type	Surface area (m²)	Temperature (°C)	
MoO_3[b]	6	372°	0.25
SnO_2[c]	9	354°	0.5
SnO_2[d]	9	372°	0.85
SnO_2/MoO_3[e]	14.5	348°	6.5
SnO_2/MoO_3[f]	14.5	372°	7.5

[a] Partial pressures of propylene, water vapor, and oxygen: 0.06, 0.3, and 0.13 atm. Gas flow rate 2.2 moles/hr.

[b] Test 5, Part I, Table 1.

[c] Test 7, Part I, Table 1.

[d] Test 8, Part I, Table 1.

[e] Test 21, Part I, Table 1.

[f] Test 22, Part I, Table 1.

TABLE 3

REACTION RATE CONSTANTS FOR H–D EXCHANGE WITH PROPYLENE[a]

Test no. in Table 1 (this Part)	Catalyst		Gas flow rate (mole/hr)	First order reaction rate constant (mmole/m² hr atm)
	Type	Surface area (m²)		
1	MoO_3	9	0.67	5
2	SnO_2	21	0.67	55
5	SnO_2/MoO_3	4.6	1.00	2500

[a] Partial pressures of propylene (initially C_3H_6), water vapor (initially D_2O), and oxygen: 0.06, 0.65, and 0.06 atm. Temperature 360°C.

The rate constant of the dehydration of isopropyl alcohol was calculated by means of the equations

$$-M\frac{dp_1}{P_g} = M\frac{dp_2}{P_g} = k_1p_1\,ds - k_2p_2\,ds$$

with the solution

$$\frac{p_{1,\mathrm{exit}} - p_{1,\mathrm{equil}}}{p_{1,\mathrm{inlet}} - p_{1,\mathrm{epuil}}} = \exp\left[-\frac{(k_1 + k_2)P_gS}{M}\right] \qquad (3)$$

where k is a rate constant (mmoles/m² hr atm); M, the gas flow through the reactor (millimoles/hr); p, the partial pressure (atm); P_g, the pressure of the reaction gas (atm); s, the surface area of the catalyst in m² (varying from $s = 0$ on the inlet side to $s = S$ on the exit side); S, the total surface area of the catalyst bed (m²); and index 1 indicates isopropyl alcohol, and index 2, propylene).

In Eq. (3) k_2 can be neglected in relation to k_1 and, since K_p is large [see Eq. (4)], $p_{1,\mathrm{equil}}$ need be taken into account only at high degrees of conversion.

The value of the rate constant calculated for Experiment 9 (SnO_2/MoO_3; 369°C) must be considered much too low. A five times larger value, 1.5×10^5 mmoles/m²hr atm, would be much nearer the mark (for argumentation see Table 4, footnote *c*).

The rate constant of the oxidation of propylene was calculated as the number of millimoles of propylene converted towards acetone and acetic acid in the catalyst bed (including half—a somewhat arbitrary choice—of the propylene completely broken down to CO and CO_2), divided by the catalyst surface area (m²) and the partial pressure of propylene (atm) derived from the feed rate. The corresponding quantity for the exchange is u_H divided by the partial pressure of propylene.

Blank runs with reactors containing carborundum alone showed that in the absence of catalyst the dehydration of isopropyl alcohol was negligible and no hydrogen–deuterium exchange took place between propylene and water.

In Experiment 9 (already mentioned above) in which a diluted bed of 0.1 g of MoO_3-covered SnO_2 was used, the dehydra-

TABLE 4
Reaction Rate Constants for Dehydration of Isopropyl Alcohol

Test no.	Catalyst			Temperature (°C)	Gas flow rate (mole/hr)	Initial partial pressures (atm)				First order reaction rate constant (mmole/m² hr atm)	Ratio between yields of acetone and propylene
	Type	Description	Surface area (m²)			C_3H_6	C_3H_7OH	H_2O	O_2		
6	MoO_3	See Table 1, this Part	9	360°	7.6	0	0.055	0.7	0.05	0.15×10^4	0.03
7	SnO_2	3 g of SnO_2-A (see Part I)	9	295°	4.1	0	0.10	0.4	0.10	2^a	30^a
8	SnO_2/MoO_3	0.1 g of MoO_3-covered SnO_2; pellet diam 0.17–0.35 mm; catalyst bed (3 mm diam and 6 mm length) in narrowed portion of reactor	0.35	300°	2.0	0	0.0012	0.35	0.15	$1.5 \times 10^{4\,b}$	0.0035
9	SnO_2/MoO_3	0.1 g of MoO_3-covered SnO_2, diluted with 1 g of carborundum grains; pellet diam of both oxide and carb. 0.17–0.35 mm; diam and length of bed 10 and 8 mm, resp. (apparatus: Fig. 1, Part I)	0.35	369°	2.1	0.06	0.0013	0.3	0.11	$\gg 3 \times 10^{4\,c}$	—
10	SnO_2/MoO_3	As in Test 9, but undiluted (thin layer)	0.35	371°	2.3	0	0.0085	0.35	0.09	$—^d$	0.012

[a] Calculated from an inaccurately measured percentage (0.1 ± 0.05) of propylene in the off-gas.

[b] The value found from the measurement has been raised by 30% to allow for the insufficient transport rate of isopropyl alcohol in and outside the pellets.

[c] The value 3×10^4 was calculated with Eq. (3). Starting from the value found in Test 8 (300°C) and taking 25 kcal/mole as a reasonable value for the activation energy, one gets a much higher result, viz. 1.5×10^5. The latter value is acceptable, whereas the former must be considered much too low because (a) in a relatively short, highly diluted bed with laminar flow, imperfections in the differential equation whose solution is represented by Eq. (3), have a distinct effect if $p_{1,\text{equil}}$ is low, and $p_{1,\text{exit}}$ is comparable in magnitude with $p_{1,\text{equil}}$ (this situation occurred indeed: $p_{1,\text{inlet}} = 1.3 \times 10^{-3}$, $p_{1,\text{equil}} = 7 \times 10^{-6}$, $p_{1,\text{exit}} = 17 \times 10^{-6}$ atm), (b) rate constant k_1 in Eq. (3) is an overall constant whose value in the present test was largely determined by diffusional transport in and outside the catalyst pellets.

[d] Owing to poor contact between gas and catalyst ~20% of the isopropyl alcohol was not converted.

tion of isopropyl alcohol proceeded nearly to equilibrium. Application of a much larger quantity of catalyst must consequently disclose the equilibrium partial pressure of isopropyl alcohol. In a test with 1.4 g of MoO_3-covered SnO_2, the amount of isopropyl alcohol, which was determined in the issuing gas with a measuring error of ~10%, indeed agreed with the equilibrium partial pressure of isopropyl alcohol found from

$$\log_{10} K_p = 7.52 - (2614/T) \qquad (4)$$

where K_p(atm) is the equilibrium constant of the reaction $CH_3CH_2OHCH_3 \rightleftarrows C_3H_6 + H_2O$, and T is the absolute temperature in °K. The constants in this equation were calculated from thermodynamic data for isopropyl alcohol (*2*) and for propylene and water (*3*).

Hydration of Propylene

In experiments with 2 g of catalyst at various space velocities and partial pressures of propylene and water vapor, the equilibrium predicted by Eq. (4) established also from the propylene side. Equilibrium was also reached in a run with a small catalyst charge (0.1 g) possessing a low activity for the oxidation of propylene. A run without a catalyst yielded only a small fraction of the equilibrium amount of isopropyl alcohol.

DISCUSSION

In Table 1 it can be seen that in the presence of an SnO_2-MoO_3 catalyst a remarkably fast exchange of hydrogen and deuterium takes place between propylene and water; comparison of Tables 2 and 3 shows that the ratio between the exchange and oxidation rates is roughly 350.

In considering how the deuterium is distributed over the propylene molecules in the experiments with SnO_2-MoO_3 catalysts (Table 1), we shall at first not take account of the mole fraction of C_3D_6. There appears to exist a moderate agreement between the purely experimental and the calculated (binomial) deuterium distributions. It does not make any considerable difference whether the number of exchangeable hydrogen atoms per C_3H_6 molecule is assumed to be 5 or 6, although it must be remarked that $a = 6$ satisfies better than $a = 5$.

The deviations between the experimental and calculated distributions are, for a large part, of a systematic nature: the experimental distributions are levelled off compared with the calculated ones. This levelling off is probably due to insufficiently rapid diffusion of the propylene molecules in the catalyst pellets.

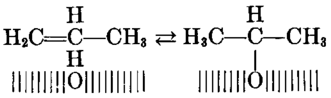
The occurrence of deuterium distributions which may be considered to be binomial proves that during a visit of a propylene molecule to the surface only one hydrogen, or deuterium, atom can be exchanged. (A very rapid exchange between the propylene molecules would also give rise to a binomial distribution. The possibility cannot be excluded but seems improbable.)

A good criterion of the number of exchangeable hydrogen atoms per propylene molecule is the mole fraction of C_3D_6. As appears in Table 1, the purely experimentally determined mole fraction of C_3D_6 obtained with SnO_2-MoO_3 catalysts is much smaller than the mole fraction derived from the binomial distribution, notwithstanding the levelling tendency referred to above. This can be seen the most clearly in the last test, which yielded a calculated mole fraction of 0.05 whereas the experimental value was no more than 0.001. It must be concluded, therefore, that one of the hydrogen atoms in the propylene molecule participates only slightly in the exchange, in other words, that there are five readily exchangeable hydrogen atoms per propylene molecule. The single hydrogen atom bonded to the second (middle) carbon atom must be the hydrogen atom that is difficult to exchange.

What explanation can be advanced for the exchange taking place on SnO_2/MoO_3? Before answering this question we shall first consider the possibility that the exchange reaction coincides with the reaction isopropyl alcohol $\rightleftarrows$ propylene + water proceeding under equilibrium conditions. The rate (in either direction) of this reaction equals $k_1 p_{1,\mathrm{equil}}$, it being supposed that the dehydration is first order in the partial pressure of isopropyl alcohol. For the exchange experiments k_1 can be put equal to 10^5

mmoles/m²hr atm (see Table 4, footnote *c*), while $p_{1,\text{equil}}$ is equal to 1.5×10^{-5} atm (if there is no isotope effect); this gives $k_1 p_{1,\text{equil}} = 1.5$ mmoles/m²hr. This rate is very much smaller than the exchange rates found. The possibility mentioned above consequently is not real.

To account for the exchange we propose a reversible reaction in which propylene and an acid surface hydroxyl group change into an isopropyl group bonded to a surface oxygen atom:



$$\begin{array}{ccc} H_2C{=}\overset{H}{C}{-}CH_3 & \rightleftarrows & H_3C{-}\overset{H}{C}{-}CH_3 \\ \overset{H}{\text{|||||||O||||||||}} & & \overset{|}{\text{|||||||O||||||||}} \end{array} \qquad (5)$$

In an alternative reaction the isopropyl group is not bonded by the oxygen atom of the hydroxyl group, but by another oxygen atom.

It is reasonable to assume that in the presence of D_2O the hydrogen in the surface hydroxyl groups is rapidly substituted for deuterium. The reversible reaction (5) consequently explains the exchange of hydrogen and deuterium between C_3H_6 and D_2O. It also satisfies the requirement that the hydrogen atom bonded to the second carbon atom must be left intact.

The hydrogen atoms of the isopropyl group forming in reaction (5) have equal chances of being released. If one of the methyl groups contains a deuterium atom, the chances that *cis*-propene-1-d_1, *trans*-propene-1-d_1 and propene-3-d_1 will form are in the ratio 1:1:3; a minor secondary kinetic isotope effect might slightly change this ratio. However, the information derived from infrared absorption and proton magnetic resonance shows that at low degrees of deuteration there is a preference for formation of *cis*-propene-1-d_1. The inconsistency can be removed by assuming that the exchange proceeds as follows. The deuterium atom of a reacting surface OD group enters stereospecifically into a bond with the methylene carbon atom of a propylene molecule. (This is quite possible because the orientation of the propylene molecule in relation to the surface and that of the reacting double bond in relation to the atoms to be bonded cannot be arbitrary. Presenting a concrete picture of the configuration of the reacting system is, we think, very much a matter of conjecture.) The further course of the exchange reaction may now go in two directions with approximately equal chances of probability:

(1) One of the two hydrogen atoms bonded to the same carbon atom as the deuterium atom is given off in such a way that *cis*-propene-1-d_1 is formed.

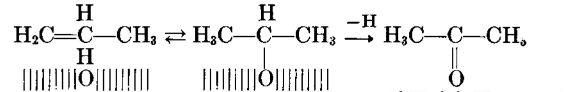
(2) The configuration needed for a stereospecific completion of the exchange reaction is interfered with; this causes formation of the isopropyl group indicated in reaction (5).

If the exchange should be purely stereospecific, it would have to cease upon take-up of either one or two deuterium atoms (the former possibility would arise if introduction of a new deuterium atom would require elimination of the deuterium atom already present). However, this has not been confirmed experimentally. The exchange rates found by us (also in experiments not described in the present paper) are of the same order of magnitude, whatever the degree of deuteration, and the deuterium distributions do not show any sign of discontinuity. The methyl group of propylene has, evidently, sufficient opportunity of reacting. It should be pointed out here that if an H atom is split off from the CH_3 group in $CH_3{-}CH{=}CHD$, two D atoms appear in the methyl group of the propylene produced ($CH_3{-}CH{=}CHD$ changes, via the group $CH_3{-}CH{-}CHD_2$, into $CH_2{=}CH{-}CHD_2$). This explains why at not too low degrees of deuteration the amount of deuterium in methyl groups is comparable with that in methylene groups.

Considering that at low degrees of deuteration, the deuterium finds its way mainly into the methylene group, we may reject all exchange mechanisms according to which the deuterium would first appear in the methyl group. Such mechanisms are the hydrogen switch mechanism of Turkevich and Smith (*4*), and the allyl mechanism which, as proposed by Lake and Kemball (*5*), would take place in the presence of TiO_2. The latter mechanism involves that first a hydrogen atom is abstracted from the methyl group in propylene, so that an allyl group is formed, after which a deuterium atom is restored to this allyl group.

In the oxidation of propylene to acrolein over bismuth molybdate abstraction of hydrogen leading up to an allyl group is the rate-determining step (*6*). This renders it unlikely that a rapid exchange of the hydrogen in propylene against the deuterium in D_2O over any catalyst (and over bismuth molybdate in particular) will go via an allyl mechanism. This conclusion is confirmed by the result of an exchange experiment using a P-containing bismuth molybdate catalyst with 50% by weight of SiO_2. At 370°C the exchange went about 20 times faster than the formation of acrolein (the main product), and in the propylene ($x = 0.017$) only *cis*-propene-1-d_1 could be observed by infrared spectroscopy, as also in the propylene with $x = 0.01$ obtained in one of the experiments with SnO_2/MoO_3. As we see it, the H–D exchange between propylene and water over SnO_2/MoO_3, Bi_2O_3/MoO_3, and TiO_2, must be ascribed to an isopropyl mechanism (which, it should be stated here, was not excluded by Lake and Kemball).

Considering that (a) an SnO_2-MoO_3 catalyst gives a high exchange rate and is characterized by a high activity and selectivity for the oxidation of propylene to acetone and acetic acid, (b) the isopropoxy group in reaction (5) is an appropriate precursor of acetone, (c) hydroxyl groups are involved in reaction (5) and water vapor is needed to ensure proper oxidation of propylene over SnO_2/MoO_3, it may be taken that the isopropoxy group mentioned above is the intermediate in the oxidation of propylene to acetone and acetic acid over SnO_2/MoO_3:



$$H_2C{=}\overset{H}{\underset{\underset{|||||||O|||||||}{H}}{C}}{-}CH_3 \rightleftarrows H_3C{-}\overset{H}{\underset{\underset{|||||||O|||||||}{|}}{C}}{-}CH_3 \xrightarrow{-H} H_3C{-}\underset{\underset{O}{\|}}{C}{-}CH_3 \qquad (6)$$

(CH_3CO_2H upon further oxidation)

There are objections to supposing that the isopropoxy group is also the intermediate in the dehydration of isopropyl alcohol; these will be put forward later.

Exchange also takes place over SnO_2; the rate is much lower than that over SnO_2/MoO_3, although still considerable. In the experiment with SnO_2 (Test 2, Table 1) a binomial deuterium distribution calculated with $a = 5$ agrees very well with the experimental one. The assumption that there are six exchange sites per propylene molecule leads to a less satisfactory agreement; the mole fraction of C_3HD_5 calculated with $a = 6$ is twice as large as that determined experimentally and the small, though detectable, amount of C_3H_6 which should have been present if $a = 6$, could not be observed. Hence, it looks as if the exchange over SnO_2 proceeds along similar lines as over SnO_2/MoO_3.

As to MoO_3, the rate of the exchange is much slower than that observed over SnO_2, and the deuterium distribution may be regarded as binomial. A statement as to the number of exchangeable hydrogen atoms per propylene molecule cannot be given here, in view of the low degree of deuteration reached.

The rate of oxidation of propylene and the exchange rate both increase in the following sequence: MoO_3, SnO_2, SnO_2/MoO_3. It may be taken that scheme (6) is also valid with SnO_2 and MoO_3.

We shall now compare MoO_3, SnO_2, and MoO_3-covered SnO_2 as regards their behavior with respect to isopropyl alcohol. Table 4 shows that the dehydration of isopropyl alcohol proceeds smoothly on MoO_3 and very rapidly on SnO_2/MoO_3. The ratio of the rates of the oxidative dehydrogenation to acetone and the dehydration is small, both for MoO_3 and for SnO_2/MoO_3. With SnO_2 the situation is entirely different. On this oxide, at 295°C, the oxidative dehydrogenation to acetone is the main reaction; dehydration plays only a very subordinate role here. This shows that coverage with MoO_3 completely changes the behavior of SnO_2 with regard to isopropyl alcohol.

It is tempting to regard the isopropoxy group in reaction scheme (6) as also an intermediate in the dehydration and oxidation of isopropyl alcohol. One must expect then that the amounts of acetone and propylene formed from isopropyl alcohol (the formation of acetic acid may be neglected) will be in approximately the same proportion as the rates of the oxidation of propylene towards acetone and acetic acid and the exchange reaction. This condition is not at all satisfied by SnO_2, because of its different behavior referred to above. Also over SnO_2/MoO_3 isopropyl alcohol yields more acetone than might be expected (acetone/propylene = 0.012, Test 10; oxidation rate/exchange rate $\approx 7/2500 = 0.003$). Only with MoO_3 is there a fair agreement [acetone/propylene = 0.03, Test 6; oxidation rate/exchange rate = $0.25/5 = 0.05$ (the differences in the test conditions should be taken into account)]. From the foregoing, and also from the fact that the formation of acetone is, in all cases, attended with much less breakdown to CO and CO_2 than the oxidation of propylene, it follows that isopropyl alcohol cannot be included in reaction scheme (6).

There are, however, good grounds for supposing that the acid OH groups which are assumed to effect the exchange over SnO_2/MoO_3 will also be effective in the dehydration of isopropyl alcohol [for a discussion of possible mechanisms for the dehydration of alcohols over Al_2O_3, see ref. (*7*)]. We are inclined to think that the presence of these groups also has something to do with the circumstance that in the oxidation of propylene over SnO_2/MoO_3 only a relatively small proportion is completely broken down to CO and CO_2.

ACKNOWLEDGMENTS

The author is indebted to Mr. P. M. J. van den Berg, Mr. M. G. P. M. van Montfoort, and Mr. L. H. W. Janssen for performing the experimental work.

APPENDIX

Calculation of the Exchange Rate

It is assumed that the exchange behavior of the hydrogen and deuterium atoms in the propylene molecule is independent of the position and number of these atoms in the molecule. In this connection it is pointed out that a perfectly binomial deuterium distribution is possible (Table 1, test with SnO_2).

As regards water, the degree to which the equilibrium constant K ($= p^2_{HDO}/p_{H_2O}p_{D_2O}$) deviates from the ideal value of 4 is still a matter of discussion (*8*). From the $(G^\circ - E^\circ_0)/RT$ values calculated by Friedman and Haar (*9*) for H_2O, HDO, and D_2O, and from the ΔE°_0 values given by Narten (*10*), it follows that at 360°C $K = 3.8$. This value for the equilibrium constant does not differ appreciably from 4. We consider it a reasonable approximation to suppose that H and D will behave independently also in the water molecule.

When H and D atoms have equal exchange chances—this is not a consequence of the above-mentioned independence—one can easily derive an expression for the exchange rate (u), which, in this case, can be defined as the number of milligram atoms of hydrogen and deuterium per hour and per m^2 of catalyst surface going from propylene to water (or from water to propylene); the nonobservable exchanges (H against H and D against D) also contribute to this rate. If x and y are understood to be the fractions of deuterium in the exchangeable hydrogen and deuterium belonging to propylene and water, respectively, xu denotes the number of milligram atoms of deuterium per hour and per m^2 leaving the propylene and yu the number of milligram atoms of deuterium per hour and per m^2 leaving the water. The difference $yu - xu$ is the rate at which propylene is enriched with deuterium. The exchange under stationary conditions in a fixed bed can consequently be expressed by

$$-P\frac{dx}{ds} = W\frac{dy}{ds} = xu - yu$$

where s is the catalyst surface area (m^2) reckoned from the gas inlet side; P, the flow rate of the exchangeable propylene hydrogen and deuterium (milligram atoms/hr); and W, the flow rate of the water hydrogen and deuterium (milligram atoms/hr). Upon introduction of $\xi = xP$ and $\eta = yW$ this equation can be rewritten as follows:

$$-\frac{d\xi}{ds} = \frac{d\eta}{ds} = \frac{u}{P}\xi - \frac{u}{W}\eta$$

Solution gives

$$\frac{\xi - \xi_e}{\xi_0 - \xi_e} = \frac{x - x_e}{x_0 - x_e} = \exp\left[-\left(\frac{1}{P} + \frac{1}{W}\right)us\right] \quad \text{(A1)}$$

(index 0, beginning of the bed; index e, exchange equilibrium). The equilibrium value of x is given by

$$x_e = C/(P + W), \quad \text{with} \quad C = x_0P + y_0W$$

In this paper x_0 equals 0, and y_0 equals 1, so that $C = W$.

In reality, the *a priori* chance of a "forward" exchange, in which an H atom moves from propylene to water, and a D atom from water to propylene is *smaller* than the chance of a "backward" exchange. Let us denote the respective exchange rates as u_f and u_b (milligram atoms/m² hr). A reasonable assumption is

$$u_f = u_H(1 - x)y \quad \text{and} \quad u_b = u_Dx(1 - y)$$

where u_H and u_D are constants, i.e. are independent of x and y. The above-mentioned inequality of chances involves $u_H < u_D$.

At equilibrium we have $u_f = u_b$ or $u_H(1-x_e)y_e = u_Dx_e(1-y_e)$ or

$$\frac{x_e}{1 - x_e}\bigg/\frac{y_e}{1 - y_e} = \frac{u_H}{u_D} \quad \text{(A2)}$$

Since the deuterium is binomially distributed in propylene (five exchangeable hydrogen atoms per molecule, as was established experimentally) and in water, it follows [see Eq. (1)] that

$$\frac{x_e}{1 - x_e}\bigg/\frac{y_e}{1 - y_e}$$

equals the equilibrium constant E of the reaction

$$\tfrac{1}{5}C_3H_6 + \tfrac{1}{2}D_2O \rightleftharpoons \tfrac{1}{5}CD_2{=}CH{-}CD_3 + \tfrac{1}{2}H_2O$$

i.e.,

$$\frac{x_e}{1 - x_e}\bigg/\frac{y_e}{1 - y_e} = \left[\frac{p^{1/5}_{C_3HD_5}}{p^{1/5}_{C_3H_6}}\bigg/\frac{p^{1/2}_{D_2O}}{p^{1/2}_{H_2O}}\right]_{\text{equil}} = E \quad \text{(A3)}$$

Combination of Eqs. (A2) and (A3) yields

$$u_H/u_D = E \quad \text{(A4)}$$

The value of E can be found by a statistical thermodynamic calculation. If use is made of the Teller-Redlich product rule (*11*) no other molecular data but vibration frequencies are needed for this calculation. As we did not have at out disposal the vibration frequencies of C_3HD_5, whereas those of C_3D_6 were known, we assumed that E is also the equilibrium constant of the reaction

$$\tfrac{1}{6}C_3H_6 + \tfrac{1}{2}D_2O \rightleftharpoons \tfrac{1}{6}C_3D_6 + \tfrac{1}{2}H_2O$$

This assumption implies that, as far as the *equilibrium* is concerned, the hydrogen site at the central carbon atom is equivalent to the other hydrogen sites. Using the product rule referred to above and vibration frequency data for C_3H_6 and C_3D_6 (*12*), and for H_2O and D_2O (*9*), we calculated E for two temperatures. This gave

$E = 0.695$ at 227°C (500°K)
$E = 0.633$ at 360°C (633°K)

When $xu - yu$ is replaced by

$$u_Dx(1 - y) - u_H(1 - x)y$$

the following equation takes the place of Eq. (A1)

$$\frac{x - x_e}{x_0 - x_e}\,\frac{1 + f(x_0 - x_e)}{1 + f(x - x_e)} = \exp\left[-\left(\frac{1}{P} + \frac{1}{W}\right)(1 + q)u_Hs\right] \quad \text{(A5)}$$

with

$$f = \frac{1 - E}{E}\,\frac{P}{P + W}\,\frac{1}{1 + q}$$

and

$$q = \frac{1 - E}{E}\left(2\frac{P}{P + W}x_e + \frac{W - C}{P + W}\right)$$

By combining Eq. (A3) with

$$\frac{P}{P + W}x_e + \frac{W}{P + W}y_e = \frac{C}{P + W}$$

x_e can be calculated.

Eq. (A5) can be reduced to one given by Bolder *et al.* [*13*, Eq. (40)] in a form suiting a homogeneous reaction performed in a closed volume [$\bar{k}t$ is erroneous; it should read $\bar{k}t/N$ (symbols of Bolder *et al.*)].

REFERENCES

1. BUITEN, J., *J. Catalysis* **10,** 188 (1968).

2. CHERMIN, H. A. G., *Petrol. Refiner.* **40,** 234 (1961).

3. LANDOLT-BÖRNSTEIN. "Zahlenwerte und Funktionen," Band II, Teil 4 (6e Aufl.). Springer-Verlag, Berlin-Göttingen-Heidelberg, 1961.

4. TURKEVICH, J., AND SMITH, R. K., *J. Chem. Phys.* **16,** 466 (1948).

5. LAKE, I. J. S., AND KEMBALL, C., *Trans. Faraday Soc.* **63,** 2535 (1967).

6. ADAMS, C. R., AND JENNINGS, T. J., *J. Catalysis* **3,** 549 (1964).

7. KNÖZINGER, H., *Z. Physik. Chem. (Frankfurt)* **48,** 151 (1966); *Z. Angew. Chemie* **80,** 778 (1968).

8. WESTON, R. E., *J. Chem. Phys.* **42,** 2635 (1965).

9. FRIEDMAN, A. S., AND HAAR, L., *J. Chem. Phys.* **22,** 2051 (1954).

10. NARTEN, A., *J. Chem. Phys.* **42,** 814 (1965).

11. HERZBERG, G., "Molecular Spectra and Molecular Structure—Infrared and Raman Spectra of Polyatomic Molecules," p. 231. Prentice-Hall, Englewood Cliffs, New Jersey, 1945.

12. LORD, R. C., AND VENKATESWARLU, P., *J. Opt. Soc. Am.* **43,** 1079 (1953).

13. BOLDER, H., DALLINGA, G., AND KLOOSTERZIEL, H., *J. Catalysis* **3,** 312 (1964).