

Oxidation of Propene by Means of SnO₂-MoO₃ Catalysts

III. Kinetic Hydrogen Isotope Effects

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A mixture of 8.9% of propene-2-*d* (CH₂=CD-CH₃) and 91.1% of ordinary propene was oxidized over an SnO₂-MoO₃ catalyst (at 370°C and 1 atm; air and water vapor present; continuous flow). The percentage of propene-2-*d* in the nonconverted propene (2/3 of the initial quantity) was 10.8. It is concluded that ordinary propene reacts about 2.2 times faster than propene-2-*d*.

In another test, ordinary propene was first supplied and then propene-2-*d*; the degree of conversion was rather low. The formation of acetone, acetic acid, acetaldehyde and maleic acid was attended by kinetic isotope effects; those relating to acetone and acetic acid differed appreciably, but the average was 1.8, smaller than the 2.2 cited above. The difference must be due to a partly rate-determining step, which does not manifest itself in the isotope effect when the two propenes are introduced as a mixture. Kinetic experiments suggest that this step is one of those enabling oxygen to take part in the oxidation process and also that the large difference between the isotope effects involved in the formation of acetone and acetic acid is to be ascribed to the behavior of the oxygen.

Experiments have also been undertaken with propene in which most of the methyl- and methylene-hydrogen atoms had been replaced by D atoms (the percentage of CD₂=CH-CD₃ in this propene was 55). These runs formed part of a series performed with all four combinations of deuterated propene and ordinary propene, on the one hand, and D₂O and H₂O on the other. On introduction of deuterium into the propene, the collective rate of formation of acetone, acetic acid and acetaldehyde remained unchanged, but decreased upon a change-over from H₂O to D₂O. This can be explained by means of a reaction model in which propene is chemisorbed in the form of isopropyl groups.

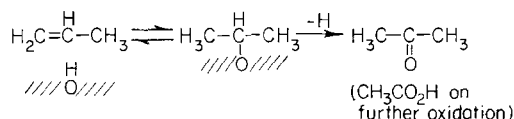
There was no kinetic isotope effect in the formation of acrolein (a byproduct) from propene-2-*d*, but one was observed from propene whose methyl and methylene groups had been deuterated, in agreement with the literature. The mechanisms responsible for the formation of acetone and related substances, on the one hand, and acrolein, on the other, differ widely, but they agree on the point that in both of them abstraction of a hydrogen atom constitutes the primary oxidation step.

Using other catalysts for oxidizing propene to acetone and acetic acid (i.e., V₂O₅ and Fe₂O₃-MoO₃), a kinetic isotope effect was noted when the H atom bound to the second carbon atom of the propene was replaced by a D atom.

INTRODUCTION

In Part I of this series (1) it was demonstrated that SnO₂ covered with a monomolecular layer of MoO₃ directs the oxidation of propene (in the presence of molecular oxygen and water vapor) to acetic acid and acetone. In Part II (2), we related this oxidation to the exchange of H and D between propene and water vapor, and proposed a

reaction mechanism in which an isopropyl group bound to a surface oxygen atom plays the leading role:



A typical feature of the mechanism is the

abstraction of the hydrogen atom bound to the middle carbon atom of the isopropyl group; this constitutes the first irreversible step. It may be expected therefore that a comparison of the rates of oxidation of propene-2-*d* ($\text{CH}_2=\text{CD}-\text{CH}_3$) and ordinary propene will exhibit the existence of a kinetic isotope effect. To check this, we did two experiments, one with a mixture of propene-2-*d* and ordinary propene, and one, comprising two runs, with each of the two propenes separately.

Furthermore, we did a series of experiments to study the effects (on the rate of oxidation of propene, the product distribution and the rate of exchange of H and D between propene and water vapor) of the replacement of the methyl- and methylene-hydrogen by deuterium and of the use of D_2O instead of H_2O .

$\text{SnO}_2\text{-MoO}_3$ was used as a catalyst in all cases. However, runs with propene-2-*d* not mixed with ordinary propene were carried out also on $\text{Fe}_2\text{O}_3\text{-MoO}_3$ and V_2O_5 ; the results achieved with these catalysts are included in this article.

METHODS

Apparatus

The experiments were conducted in the continuous flow-type reactor described earlier (1). Water was supplied by means of a saturator.

Separating volatile products from the condensate was done in the same way as in Part II (2). The apparatus used for this purpose is shown in Fig. 1; it may be regarded as a simple unit for continuous rectification, being composed as it is of a reboiler (the hot-condensate part) and a dephlegmator (the reflux condenser). The amount of acetone retained in the condensate was calculated with $(A/a)/(w/W)$, which is a kind of relative volatility, being taken equal to 16. (A , the amount of acetone leaving the apparatus; a , the amount of acetone retained in the condensate; w , the amount of water vapor leaving the condensate held at 80°C ; W , the amount of condensate; "amount" = moles/unit time.) The value found, in no case more than 5% of the

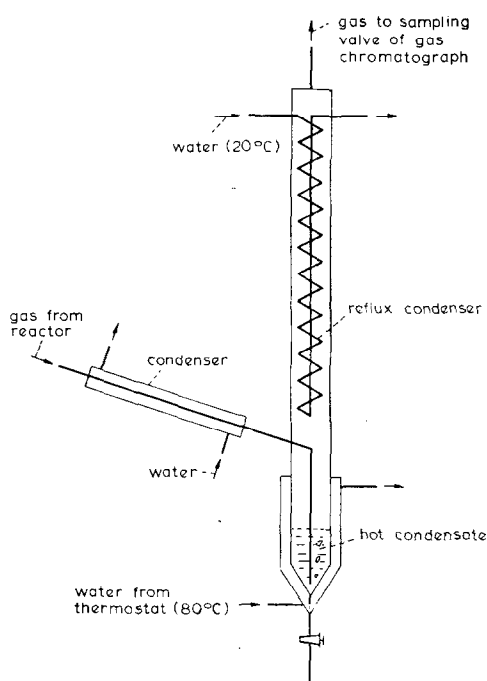


FIG. 1. Apparatus for separating volatile products from condensate.

quantity of acetone produced, was taken into account in determining the total acetone output. The amounts of acetaldehyde and acrolein could be neglected.

The duration of a run was as a rule between 1 and 2 hr.

Analysis

For the methods used in determining the acids, CO and CO_2 , and the deuterium distribution in propene, reference is made to Parts I and II (1, 2).

The more volatile components were determined by means of a gas chromatograph equipped with a gas sampling valve, a column filled with Carbowax 600 on Chromosorb and a flame ionization detector.

A difficulty was that the gas-chromatographic peaks of deuterated acetone and acrolein deviated from normal peaks, so that it was not possible to use the peak heights in uncorrected form. The retention time of nearly completely deuterated acrolein appeared to be 3.75% longer than that of ordinary acrolein; owing to this the peaks of partly deuterated acrolein showed an ir-

regular shape. We therefore adopted the following approach. In four chromatograms representative of the four cases in Table 2A we determined the acrolein peak areas (corrected for the tail of the acetone peak) and their ratios to the corresponding peak heights as measured from the minimum between acetone and acrolein. By means of these ratios, which diverged by a factor of at most 1.65, the peak heights in other chromatograms we converted to peak areas. It was assumed that the peak areas are independent on the degree of deuteration.

Acetone did not yield peaks of an irregular shape, but special tests revealed that the peak height of perdeutero-acetone is 12% larger than that of an equal molar amount of ordinary acetone, and that the retention time of perdeutero-acetone is 2.25% shorter than that of ordinary acetone. The increase of this peak height is due to the joint effect of a stronger signal of the flame ionization detector and a decrease of the retention time. We considered it worthwhile to calculate to what degree these factors influence the peak height of partially deuterated acetone. To this end the peak for partially deuterated acetone was derived as follows from the function $y_0[t]$, which represents the recorder signal as function of time t for ordinary acetone:

$$y = \sum_{i=0}^6 \{(1 + 0.0158i) / (1 - 0.00375i)\} b_i y_0[t / (1 - 0.00375i)],$$

where y = magnitude of the recorder signal and $b_i = \{6! / i!(6 - i)!\} f^i (1 - f)^{6-i}$ (f = fraction of hydrogen replaced by deuterium). It is seen that this equation holds with $f \rightarrow 0$ and $f \rightarrow 1$: in the former case $y = y_0[t]$, in the latter we have

$$y = \{(1 + 0.0948) / (1 - 0.0225)\} \times y_0[t / (1 - 0.0225)] = 1.12 y_0[t / 0.9775].$$

We furthermore assumed that an H-D-exchange equilibrium establishes during the passage of acetone through the condensate. The following values of f , representative of the cases 2, 3 and 4 in Table 2A, were estimated: 0.16, 0.785 and 1, respectively; in case 1, $f = 0$. The shape of the function y was known from a photographic magnifi-

cation of an ordinary acetone peak. It appeared that peak heights calculated with $f = 0.16$ and $f = 0.785$ deviated distinctly from those calculated by linear interpolation between $f = 0$ and $f = 1$.

No corrections were made for acetaldehyde.

Preparation of Propenes Containing D

The preparation of propene-2-d (from α -methyl acrylic acid via 2-Br-propene) was carried out by the method of Norris *et al.* (3). The product was stored in a stainless steel cylinder. Mass-spectrographic analysis showed that it contained 0.8% of C_3H_6 . A proton magnetic resonance measurement gave only two simple peaks, one for $=CH_2$ and one for $-CH_3$, the areas of which were in the correct proportion.

Propene containing much D in its methyl and methylene groups was made by exchange of H and D between propene and D_2O [see Part II (2)] over SnO_2 covered with MoO_3 . The exchange reaction was performed at 370°C in the presence of air. The gas issuing from the reactor was passed in succession through:

1. Three water-filled washing bottles in which carbonyl compounds were retained [see Part I, p. 191 (1)];
2. A molecular sieve (for drying);
3. A vessel cooled at $-80^\circ C$ and containing activated carbon previously heated at $500^\circ C$ in a nitrogen stream (for adsorption of propene).

The propene was desorbed from the activated carbon by raising the temperature, caught in a cold trap and thence transmitted to a stainless steel cylinder. The exchange was carried out in two steps. In the first 38% of the methyl and methylene H atoms were replaced by D. After the second step the percentage composition of the propene was: d_0 , 0.1; d_1 , 0.3; d_2 , 2.1; d_3 , 9.8; d_4 , 32.5; d_5 , 54.8; d_6 , 0.4.

RESULTS

Experiment with a Mixture of Propene (C_3H_6) and Propene-2-d

One of our experiments was done with a mixture of ordinary propene and propene-

2-*d*. The composition of this mixture was 91.1% *d*₀, 8.9% *d*₁. The percentage *d*₁ had been chosen rather low, to minimize the disturbing effect of the reaction *d*₁ → *d*₀ [see Eq. (1)]. The mixture was oxidized under similar conditions as mentioned in Table 1; this time, however, a much larger amount of catalyst was used, viz., 10 g. Here, too, a monomolecular layer of MoO₃ was applied by passing water vapor containing MoO₂(OH)₂ through the catalyst bed at 450°C (1). Calculation from the amounts of the various oxidation products showed that 34% of the mixture had been converted. The selectivities were: acetone, 3.5%; acetic acid, 55%; acetaldehyde, 4.5%; maleic acid, 8%; acrolein, 3.5%; acrylic acid, 2.5%; total breakdown, 23%.

That an isotope effect is indeed involved here appears from the difference between the mass-spectrographically determined *d*₁-percentages for the original propene mixture and the propene in the reaction gas; these percentages amounted to 8.9 and 10.8, respectively. (A series of three washing bottles each filled with a 2% sodium hydroxide solution and placed in ice, were used

to keep carbon dioxide and organic vapors out of the reaction gas sample.)

The results of this experiment have been used as a basis for deriving the value of a constant α , which is defined as the ratio of the chances with which a C₃H₆ molecule and a propene-2-*d* molecule will be oxidized to products in the group characterized by acetone and acetic acid which depend for their formation on the occurrence of a kinetic isotope effect. Anticipatory to the results of Table 1, we shall proceed from the assumption that acrolein and acrylic acid (with proportional amounts of completely broken-down propene added to them) are the only products whose formation is not governed by the isotope effect. The ratio of the chance with which the oxidation of a C₃H₆ molecule will go towards the latter products to the chance with which it will be oxidized to the former is called ϵ (considered as a constant). Furthermore, the effect of replacing the D atom of propene-2-*d* by an H atom has to be accounted for. This is done by introducing a constant δ , which is defined as the ratio of the chance with which a propene-2-*d* molecule will be transformed into C₃H₆

TABLE 1
KINETIC ISOTOPE EFFECTS IN THE OXIDATION OF PROPENE OVER SnO₂-MoO₃^a

	Product	Ordinary propene (μ moles) converted to product (per m ² and per hr)	Propene-2- <i>d</i> (μ moles) converted to product (per m ² and per hr)	Ratio (kinetic isotope effect)
Acetone group	Acetone	69	28	2.4
	Acetic acid	88	60	1.5
	Acetaldehyde	24	13	1.8
	Maleic acid	9.3	5.6	1.7
	Combustion ^b	20	8	2.5
	Sum	210	115	1.8
Acrolein group	Acrolein	47	49	1.0
	Acrylic acid	8.3	8.5	1.0
	Combustion ^b	5.7	4.2	1.4
	Sum	61	61	1.0

^a Catalyst: 2 g of SnO₂ (3.5 m²/g; particle size, \approx 0.5 mm) covered with MoO₃ (MoO₂(OH)₂) (a layer of MoO₃ crystals was present before the catalyst bed) at 450°C and diluted with 4 g of carborundum (particle size \approx 0.5 mm). Temperature, 370°C; pressure, 1 atm; partial pressures of air, water vapor and either C₃H₆ or CH₂=CD-CH₃: 0.6, 0.35 and 0.05 atm. Gas feed rate, 0.9 mole/hr.

^b The amounts of combustion products inevitably formed together with acetic acid, acetaldehyde and maleic acid are not included. It is assumed that proportional amounts of the total combustion may be assigned to the acetone group and the acrolein group.

TABLE 2
EFFECT OF DEUTERIUM PRESENT IN PROPENE AND/OR WATER ON THE RATES OF FORMATION OF
SOME COMPOUNDS AND ON THE RATE OF EXCHANGE OF H AND D^a

A. RESULTS OF EXPERIMENTS

Case	Components of feed gas beside O ₂ and N ₂	Mean deuterium fraction in		Rate of formation (μmole/m ² hr)					Standard exchange rate, <i>w</i> _H ^c (μgramat/m ² hr)
		Propene \bar{x}	Water \bar{y}	Acetone	Acetaldehyde	Acetic acid	Acetone + acetaldehyde + acetic acid	Acrolein	
I	C ₃ H ₆ and H ₂ O	0	0	101	22	98	221	56	
II	Deuterated propene ^b and H ₂ O	0.60	0.11	121	20	77	218	43	30300
III	C ₃ H ₆ and D ₂ O	0.28	0.89	72	14	82	168	47	42000
IV	Deuterated propene ^b and D ₂ O	0.91	0.99	83	12	63	158	31	33400

B. VALUES OF THE CONSTANTS IN $^{10}\text{LOG RATE} = a + b\bar{x} + c\bar{y}$

	<i>a</i>	<i>b</i>	<i>c</i>
Acetone	2.00	+0.16	-0.23
Acetaldehyde	1.35	-0.04	-0.23
Acetic acid	1.99	-0.17	-0.04
Acetone + acetald. + acetic acid	2.34	0.00	-0.15
Acrolein	1.75	-0.24	-0.05
Exchange	4.57	-0.18	+0.11

^a Catalyst: 1 g of SnO₂ (specific area, 3.5 m²/g; particle size, ≈0.25 mm) covered with MoO₂(OH)₂ at 450°C; a layer of MoO₃ crystals was present before the catalyst bed. Temp, 370°C; pressure, 1.1 atm; partial pressures: propene, 0.03; water, 0.2; O₂, 0.2; N₂, 0.7 atm; gas feed rate, 1.3 mole/hr.

^b Composition: *d*₀, 0.1; *d*₁, 0.3; *d*₂, 2.1; *d*₃, 10; *d*₄, 32; *d*₅, 55; *d*₆, 0.4%.

^c Calculated with Eq. (A5), ref. (2).

to its total chance of reacting. Solution of a set of equations in which these constants appear resulted in:

$$^{10}\text{lg}\{(R_{\text{ex}} - \delta/m)/(R_{\text{in}} - \delta/m)\} = m \text{ } ^{10}\text{lg}(1 - X_1) \quad (1)$$

$$\epsilon = Y''/\{Y' + (m + \delta)X_1/(R_{\text{in}} + 1)\} \quad (2)$$

$$\alpha = (m + 1)/[1 - \{\delta + (m + \delta)\epsilon\}] \quad (3)$$

where

m a parameter;

*R*_{in} *d*₀/*d*₁ ratio before reaction (at the reactor inlet);

*R*_{ex} *d*₀/*d*₁ ratio after reaction (at the reactor exit);

*X*₁ total degree of conversion for *d*₁;

Y' degree of conversion to products of

the acetone group for the mixture of *d*₀ and *d*₁;

Y'' degree of conversion to products of the acrolein group for the mixture of *d*₀ and *d*₁;

the degrees of conversion are expressed as fractions.

The values of *R*_{in}, *R*_{ex}, *X*₁, *Y'* and *Y''* follow directly from the experimental data. If δ is known, *m* can be calculated by means of Eq. (1). The value of ϵ then follows from Eq. 2, so that α can be calculated with Eq. 3.

An indication as to the magnitude of δ was obtained in the second step of the preparation of highly deuterated propene. The percentage of *d*₆ rose during this step from about 0.01 to about 0.4. As an approximation

(which is justified, as the d_6 percentage is much smaller than that following from a binomial distribution), the fraction of the propene molecules in which the H atoms bound to the middle carbon atom are replaced by D atoms can be put equal to the ratio of the percentages of d_6 and d_5 . This ratio was $0.4:54.8 = 0.007$. The fraction of the propene molecules which, at the same time, reacted to oxygenated products was found to be 0.065. These numbers relate to a situation in which H is exchanged against D. Therefore, the quotient $0.007:(0.065 + 0.007)$, which is equal to 0.1, can be considered only as the order of magnitude of δ . On the other hand, an increase of the C_3H_6 content was not observed in an experiment with nearly pure propene-2-*d* containing 0.8% C_3H_6 (this is the experiment the results of which are given in Table 1); in view of measuring errors, an increase corresponding to a δ value of 0.05 can, however, not be excluded.

α was calculated for three values of δ , viz., 0, 0.05 and 0.1; the results are given below:

δ	ϵ	α
0	0.0786	2.15
0.05	0.0784	2.29
0.1	0.0781	2.45

2.2 seems to be a probable value for α .

*Comparative Experiment with Propene (C_3H_6) and Propene-2-*d**

First, a run was made with ordinary propene. This was followed by a run with propene-2-*d*. At the end, it was checked by means of ordinary propene if the catalyst activity and selectivity had not essentially changed in the meantime. The degrees of conversion of both propenes were less than 10%. The rates of formation of the various products and groups of products are given in Table 1, both with ordinary propene and propene-2-*d*. It is seen that the rate with ordinary propene and that with propene-2-*d* differ distinctly for several products (particularly for acetone), whereas for acrolein and acrylic acid they are approximately equal. The ratios of the rates represent the kinetic isotope effects in the formation of various

products. They are given in the last column of Table 1 and are discussed below.

Experiments with Highly Deuterated Propene

The runs with highly deuterated propene (DP) formed part of a series performed with either ordinary propene (HP) or DP, plus either H_2O or D_2O . The runs were arranged in four sets of three each. The third run in each set was a repetition of the first, while the second differed from the first and the third in that either HP was replaced by DP, or H_2O by D_2O . The survey below makes this more clear.

- Set 1. HP replaced by DP in 2nd run, H_2O present in all 3 runs;
- Set 2. HP replaced by DP in 2nd run, D_2O present in all 3 runs;
- Set 3. H_2O replaced by D_2O in 2nd run, HP present in all 3 runs;
- Set 4. H_2O replaced by D_2O in 2nd run, DP present in all 3 runs.

The results of every set represent the difference between two of the following cases: case I: HP, H_2O ; case II: DP, H_2O ; case III: HP, D_2O ; case IV: DP, D_2O (e.g., case I arises in the first and the third run of set 1, case II in the second run of set 1). This setup of the experiments ensured that the influence of changes in catalytic activity would be as small as possible.

The rates of formation of acetone, acetaldehyde, acetic acid and acrolein were determined for every run (this is not quite true with regard to acetic acid; see below). Besides, the standard rate u_{H} of the H-D-exchange between propene and water [for definition and calculation see Part II (2)] was calculated from mass-spectrographic data, except of course when deuterium was absent. The rates measured in the first and the third run of every set were averaged (the differences between these two runs were always small); in the case of acetic acid averaging took place automatically, for this acid was determined in the combined condensates obtained from the first and the third run. The difference between the logarithm of the rate in the second run and the logarithm of the average rate in the first and third runs was calculated for every set.

For every type of rate (e.g., the rate of formation of acetone), the sum of the differences provided with the correct sign [symbolically written as $-(\text{II} - \text{I}) + (\text{IV} - \text{III}) + (\text{III} - \text{I}) - (\text{IV} - \text{II})$], would be zero if there were no disturbances. In fact, the sum deviated from zero, viz., by 0.022 for acetaldehyde and by 0.034 for acrolein; incidentally, no deviation was found for acetone. In the case of acetaldehyde and acrolein, every term of the sum was corrected by an equal amount to make the sum equal to zero. Summation of the differences was not possible for the rate of formation of acetic acid, as the value of the rates determined in the first and third runs of set 2 had to be rejected for being absurd, nor for the exchange rate u_{H} , as this rate could not be determined in the first and third runs of both sets 1 and 3 (D was absent).

The rates given in Table 2A have been so selected that for every product:

1. The differences between the logarithms of the rates equal those measured in the four sets of runs and if possible corrected to zero sum;
2. The arithmetic mean of the logarithms of the rates equal the arithmetic mean of the logarithms of the rates actually measured.

Table 2A does not give information on the combustion of propene and the formation of maleic acid and acrylic acid, as the data concerned were not consistent.

The deuterium fractions x and y in propene and water, respectively, change within the reactor. The mean fractions (\bar{x} and \bar{y}) were calculated from $\bar{x} = x_e + l_x$ and $\bar{y} = y_e + l_y$ where x_e and y_e are equilibrium fractions [for the calculation of x_e and y_e see Part II (2)] and l_x and l_y are the logarithmic means of $x_{\text{inlet}} - x_e$ and $x_{\text{exit}} - x_e$ and of $y_{\text{inlet}} - y_e$ and $y_{\text{exit}} - y_e$, respectively. The values of \bar{x} and \bar{y} varied only little over similar runs; the values mentioned in Table 2A are average values.

To calculate the effects of complete replacement of H by D in propene and water it was assumed that, for every type of rate, the logarithm of the rate is a linear function of \bar{x} and \bar{y} , i.e.,

$$^{10}\log \text{rate} = a + b\bar{x} + c\bar{y}$$

For the formation of each product, e.g., acetone, there exist four rate values (corresponding to the cases I, II, III and IV) and four pairs of values for \bar{x} and \bar{y} . So, four equations (to be referred to as I, II, III and IV) are available for determining the three constants a , b and c . For calculating the constants we used Eq. (I), Eq. (II) minus Eq. (III), and Eq. (IV). [As regards the exchange reaction, Eq. (I) was missing, so that a , b and c had to be solved from Eqs. (II, III and IV).] The values found for a , b and c are given in Table 2B. If the linear relationship between $^{10}\log \text{rate}$, \bar{x} and \bar{y} is justified, the values of a , b and c must be in conformity also with the separate Eqs. (II and III). It appeared that in the cases II and III $a + b\bar{x} + c\bar{y}$ was always smaller than $^{10}\log \text{rate}$. The deviations (necessarily the same in both cases) were 0.012 for acetone, 0.007 for acetaldehyde, 0.003 for acetic acid, 0.011 for acetone + acetaldehyde + acetic acid, and 0.035 for acrolein; the last deviation is rather large.

The values of b and c in Table 2B approximately represent the change in rate occurring when x and/or y change from 0 to 1. They show a great diversity. It is interesting to note that effects are found not only when D is introduced into propene (see values of b), but also when D_2O is used instead of H_2O (see values of c).

DISCUSSION

General Considerations. Isotope Effect in the Experiment with a Mixture of Propene (C_3H_6) and Propene-2-d

We have done an experiment with ordinary propene and propene-2-d separately and one with a mixture of the two. The magnitude of the kinetic isotope effect in these experiments is influenced in different ways by reaction steps other than those in which the isotope reacts (the latter step will, for brevity, be referred to as the isotope step).

When the two propenes are both present in the reaction mixture, they tend to compete with each other. *For the isotope effect to manifest itself completely then, the isotope step*

need not be rate determining. What is only necessary is that the isotope step (which may be regarded as fully irreversible) is not preceded by other steps in which propene, or species derived from it, take part, unless these species are in equilibrium both with each other and with that involved in the isotope step. The complete isotope effect cannot be measured if the rates of the forward and backward reactions in the slowest preceding step are no longer very fast relative to the rate of the isotope step.

When ordinary propene and deuterated propene are allowed to react separately (under identical conditions), *the complete kinetic isotope effect will be observed only if the isotope step is fully rate determining.* In principle, any one step in the complex of steps involved in the oxidation of propene may be partly rate determining and, in consequence, tend to obscure the isotope effect.

If the species (I) undergoing the isotope step is formed by chemisorption of propene (P), it is seen that the degree to which the magnitude of the isotope effect is influenced by the reversible step $P \rightleftharpoons I$ depends on whether the two propenes are reacted separately or in mixed form. An extreme case is encountered when I occurs on practically all available surface sites and, at the same time, the reaction $I \rightarrow P$ is very slow compared with the isotope reaction. If under these conditions the two propenes are both present, the ratio between the degrees of occupation of the two I's will assume such a value that the difference in reactivity between the I's is cancelled out and, in consequence, no isotope effect is observed. On the other hand, a propene that is reacted separately will occupy the whole of the catalyst surface (in the extreme case mentioned); there will then be no difference in degree of occupation between the species derived from ordinary propene and that derived from propene-2-d, so that the kinetic isotope effect manifests itself completely (provided there is no other step that is partly rate determining).

The species undergoing the isotope step is probably an isopropyl group bound to a surface oxygen atom and formed by addition

of a hydrogen atom (proton) from a hydroxyl group to propene (2). This chemisorption is reversible in view of the fact that propene and heavy water vapor are capable of exchanging H and D atoms. This exchange proceeds very rapidly. Certain observations reported in Part II suggest that the exchange goes only partly via formation of complete isopropyl groups. Nevertheless, this part of the exchange will still be fast compared with the isotope step. It is likely, therefore, that in the experiment with the mixture of the two propenes the complete (or nearly complete) isotope effect has been measured. This is confirmed by the fact that in the experiment with separate propenes a smaller effect has been found (this point is further elucidated below).

The magnitude of the isotope effect may be estimated as follows. Assume that the increase in activation energy connected with replacement of H by D equals the decrease in zero-point energy of the stretching vibration of the bond to be ruptured. The bond in question is that between the middle carbon atom of an isopropyl group and the protium atom attached to it. The vibration frequency of this bond may in good reason be put equal to that of the bond between a protium atom and a tertiary carbon atom of a saturated hydrocarbon. For an H atom the latter vibration frequency can be put equal to 2890 cm⁻¹ (4), but this value differs only slightly from that of other C-H bonds in saturated hydrocarbons. For a D atom the frequency of the corresponding vibration may, to a good approximation, be taken equal to $2890/\sqrt{2}$ cm⁻¹. The decrease in zero-point energy connected with replacement of H by D, consequently equals $(Nhc/2) \times 2890 \times (1 - 1/\sqrt{2})$ (where N denotes the Avogadro number, h is Planck's constant, and c the light velocity), which corresponds to 1.210 kcal/mole. This means that the reaction rate at 370°C changes by a factor 2.58. (The factor calculated as the ratio of vibrational partition functions is hardly greater (2.60), which shows that the excited vibration states of the bond in question make only a very minor contribution to the kinetic isotope effect.)

A calculation as set forth above is based on

many simplifying assumptions; hence the measured kinetic isotope effect may differ considerably from that derived from simple theory (5). In view of this, the agreement between the measured effect (about 2.2) and the predicted value (2.6) may well be considered satisfactory.

Discussion of the Views of Moro-oka et al.

An additional remark to be made concerns an aspect of the experiment with a mixture of ordinary propene and propene-2-*d*. This experiment yielded remarkably little acetone, but much acetic acid, owing to the fact that acetone, as we have demonstrated in separate experiments, is easily oxidized to acetic acid on a $\text{SnO}_2/\text{MoO}_3$ catalyst. Acetone (either in gaseous form or in the form it has before desorption) is the primary oxidation product, and acetic acid the secondary one.

An entirely different view is that held by Moro-oka *et al.* (6-9) who also conducted the oxidation of propene towards formation of acetone by means of various catalysts, including $\text{SnO}_2/\text{MoO}_3$. These workers hold (8) that acetic acid, which in their experiments with $\text{SnO}_2/\text{MoO}_3$ at 115-220°C (8, 9) is obtained as a by-product, owes its formation to the propene double bond being attacked by active oxygen present on the catalyst surface. We consider it unlikely, however, that the mechanism of the acetic acid formation at the lower temperatures used by the above-mentioned authors should differ from that at 370°C.

Further, the way in which they account for the ketone formation (8) is not in conformity with our views. They postulate that an olefin is hydrated into an alcohol which, by oxidative dehydrogenation, is then transformed into a ketone. This view seems to be correct, because the results of experiments in which use was made of H_2^{18}O lead up to the conclusion that the oxygen atom in acetone should originate from water vapor (10). However, Moro-oka and co-worker's experiments with propene and isopropyl alcohol as well as ours (2) indicate that isopropyl alcohol is not an intermediate in the oxidation of propene. Arguments supporting this conclusion are given below.

1. As can be seen in Table 8 of Ref. (8), runs with isopropyl alcohol at partial pressures of 0.02, 0.04 and 0.09 atm and 135°C yield approximately 2.5 ml of gaseous acetone/ml of catalyst and per hour. Table 1 of Ref. (8) shows that the amount of acetone formed from propene at 0.20 atm partial pressure and under otherwise identical conditions is much larger (6.2 ml) although the partial pressure of isopropylalcohol cannot have been higher than 0.005 atm (which is the equilibrium partial pressure).

2. That isopropyl alcohol is not an intermediate appears even more clearly from our runs at appreciably higher temperatures. At these temperatures the amount of isopropyl alcohol present beside the propene is only extremely small (equilibrium pressure of the order of 10^{-5} atm). Further, as appears from table 4 of Ref. (2), the conversion of isopropyl alcohol goes predominantly towards propene, and only to a minor degree towards acetone. This leads to the conclusion that isopropyl alcohol, notwithstanding its extremely high reaction rate, contributes only little towards the total amount of acetone formed in the oxidation of propene.

*Isotope Effects in the Comparative Experiment with Propene (C_3H_6) and Propene-2-*d**

Let us now consider the kinetic isotope effects that occur when propene and propene-2-*d* are reacted separately. Table 1 shows that these effects arise in the production of acetone, acetic acid, acetaldehyde, maleic acid and in the totally destructive consumption of propene, but not in the production of acrolein and acrylic acid. The first mentioned compounds may be looked upon as a group (further referred to as the acetone group), the formation mechanism of which is essentially different from that of the latter compounds (likewise taken as a group).

The kinetic isotope effect in the acetone group amounts to 1.8, which is distinctly lower than the factor of 2.2 for the experiment with a mixture of ordinary propene and propene-2-*d*. Inhibition effects of products as the cause of this difference would seem improbable. The step $\text{P} \rightleftharpoons \text{I}$ mentioned in the beginning of the Discussion can only give rise to an isotope effect of the same value as

that found in the experiment with a mixture, or a larger value. The cause of the decrease of the isotope effect must, therefore, be sought in the presence of some step that is partly rate determining. This step presumably forms part of the reaction in which reduced sites of the catalyst surface are supplied with oxygen or, more generally, of the reaction in which the oxygen molecule is transformed into a state (mono- or diatomic) in which it can take up the H or the D atom. This view is based on the observation made in kinetic experiments (carried out in the author's laboratory) that the reaction rate of propene undergoes a moderate acceleration upon an increase of the partial oxygen pressure.

Table 1 shows highly diverse isotope effects for the products of the acetone group. The effect is smallest for acetic acid (1.5), whereas high values have been found for acetone (2.4) and the products formed by total breakdown (approx 2.5; for the calculation see Table 1). Besides, the CO_2/CO ratio was 0.26 in the run with $\text{C}_3\text{H}_5\text{D}$ and 0.40 in that with C_3H_6 . In other words, an increase of the amount of propene converted (caused by replacement of D by H) gives rise to selectivity changes within the group. This was also observed in the kinetic experiments referred to above; here, too, we noted an increase of the acetone/acetic acid ratio, the selectivity for total breakdown and the CO_2/CO ratio when the amount of propene converted per unit time was increased (by raising the partial pressure of propene) and the partial pressures of water vapor and oxygen and the space velocity were kept constant.

We are thus confronted with the remarkable phenomena (i) that upon an increase in oxygen consumption the reaction requiring the relatively largest amount of oxygen, i.e., the total oxidation of propene to H_2O and CO_2 , gains in significance; (ii) that the increase in the aggressiveness of oxygen (in whatever form this element may react) caused by the larger oxygen consumption tends to lower the selectivity for acetic acid, but not that for acetone (in the experiment of Table 1 the selectivity for acetone even appeared to increase). All this once more

demonstrates the importance of the "oxygen side" of the oxidation of propene. Our present knowledge does not yet enable us to make reasonable suggestions as to a reaction mechanism that might account for the above observations.

With regard to maleic acid, we wish to point to the remarkable feature that this acid (maleic anhydride under the reaction conditions), with four carbon atoms in its molecule, invariably forms during oxidation of propene over $\text{SnO}_2/\text{MoO}_3$. It would seem to us that this acid is formed on the catalyst surface as a result of the condensation of groups containing two C atoms, and a subsequent oxidation reaction. The kinetic isotope effect in the formation of maleic acid would then, in essence, be the isotope effect in the formation of the above-mentioned groups. So far, no indications have been obtained showing that acetaldehyde should be the parent substance of maleic acid.

Isotope Effects Occurring in the Application of V_2O_5 and $\text{Fe}_2\text{O}_3/\text{MoO}_3$

We now interrupt the discussion for a moment to disclose some results which, although not covered by the title of the present article, are yet relevant to the subject in hand.

A systematic investigation on 15 oxides (mainly oxides of transition elements), both in their original form and upon treatment with a stream of water vapor containing $\text{MoO}_2(\text{OH})_2$, disclosed that V_2O_5 (without MoO_3), Fe_2O_3 (with MoO_3) and ZrO_2 (with MoO_3) can also be employed for oxidizing propene to acetone and acetic acid in the presence of water vapor; it appeared, however, that with ZrO_2 (with MoO_3) a considerable proportion of the propene (e.g., as much as 30% of the amount converted) underwent total combustion. [The usefulness of the system $\text{Fe}_2\text{O}_3/\text{MoO}_3$ is also reported by Moro-oka *et al.* (6, 9) and Pralus, Figueras and Mourgues (11).] As to the first two catalysts we again searched for a kinetic isotope effect upon replacement of ordinary propene by propene-2-d.

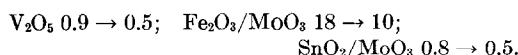
The preparation of the catalysts was as follows:

V_2O_5 : evaporating an ammonium vanadate

solution until dryness, and heating the residue overnight at 450°C;

$\text{Fe}_2\text{O}_3/\text{MoO}_3$: precipitating iron hydroxide from a solution of ferric nitrate by addition of ammonia, washing the precipitate by decantation, evaporating until dryness, heating the residue at 500°C for 4 hr, granulating, and finally passing 1.7 kg of water vapor saturated with $\text{MoO}_2(\text{OH})_2$ through a bed of 1.5 g of the granules at 450°C.

The runs with V_2O_5 were conducted at 220°C, those with $\text{Fe}_2\text{O}_3/\text{MoO}_3$ at 270°C. Since earlier kinetic experiments with V_2O_5 had brought out a distinct influence of the partial oxygen pressure, pure oxygen (instead of air) was used in the experiment with V_2O_5 , in order to suppress the partly rate-determining effect of reactions on the oxygen side as much as possible; in the case of $\text{Fe}_2\text{O}_3/\text{MoO}_3$ this was deemed unnecessary. In the runs with either of these two catalysts, the ratio between the amounts of ordinary propene and propene-2-*d* oxidized per unit time could be regarded as the kinetic isotope effect, because the degree of conversion was relatively low and hardly any acrolein and acrylic acid were formed. The values found were 2.3 in the runs with V_2O_5 and 2.2 in those with $\text{Fe}_2\text{O}_3/\text{MoO}_3$. This shows that it is not only on $\text{SnO}_2/\text{MoO}_3$ where the rate is determined predominantly by the abstraction of the hydrogen atom from the second carbon atom. The behavior of the two catalysts was also similar to that of $\text{SnO}_2/\text{MoO}_3$ as regards the change in the acetone/acetic acid ratio upon replacement of ordinary propene by propene-2-*d*:



This analogy did not exist with regard to the selectivity for total combustion and the CO_2/CO ratio.

Isotope Effects in Experiments with Highly Deuterated Propene

Let us now turn to the results of experiments in which deuterated or nondeuterated propene (with H in either case being bound to the second carbon atom) and deuterated or nondeuterated water vapor were supplied to the reactor. These results are compiled in

Table 2A and B. Again, let us first consider the acetone group in its entirety (the combination of acetone, acetic acid and acetaldehyde may be looked upon as an adequate representation of this group). As can already be seen, rather vaguely, in Table 2A and, with much more clarity, in Table 2B, introduction of deuterium into the propene molecule (at the first and the third carbon atom) has no effect on the rate with which propene is oxidized to products of the acetone group. This may seem obvious in view of the fact that abstraction of the hydrogen atom bonded to the second carbon atom constitutes the step by which the rate of oxidation of propene to products of the acetone group is mainly determined. Yet, we are confronted here with something special, since: (a) the occurrence of a secondary kinetic isotope effect would not be inconceivable, and (b) the surface concentration of the isopropyl groups and, hence, the oxidation rate might, quite possibly, depend on the deuterium content of the propene (this is elucidated in the following discussion of a reaction model).

On the other hand, replacement of H_2O by D_2O does have an influence on the rate with which propene is oxidized to products of the acetone group.

Variations in the deuterium contents of both propene and water each have an influence on the standard rate of the exchange reaction.

Reaction model. In an effort to give a consistent explanation of the above-mentioned phenomena, we designed a reaction model with the following characteristics.

1. The surface hydroxyl groups and the water vapor are in equilibrium with each other, a situation characterized by:

$$\begin{aligned} \vartheta_{\text{OH}} &= K_{\text{H}}(p_{\text{H}_2\text{O}})^{1/2} = K_{\text{H}}(p_{\text{w}})^{1/2}(1 - y) \\ &= f_{\text{H}}(1 - y), \\ \vartheta_{\text{OD}} &= K_{\text{D}}(p_{\text{D}_2\text{O}})^{1/2} = K_{\text{D}}(p_{\text{w}})^{1/2}y = f_{\text{D}}y, \end{aligned}$$

where ϑ_{OH} and ϑ_{OD} are the surface concentrations of OH and OD; K_{H} and K_{D} , equilibrium constants (this implies that the occupied part of the surface is negligible compared with the free part); $p_{\text{H}_2\text{O}}$, $p_{\text{D}_2\text{O}}$ and

p_w , the partial pressures of H₂O, D₂O and water (in whatever form), respectively; y , the ratio between the number of D atoms and the number of H and D atoms in water vapor; and f_H and f_D , quantities defined by the equations.

2. Propene is chemisorbed as isopropyl groups (see the reaction equation given in the Introduction) while the rates of chemisorption r_H (reaction with OH groups) and r_D (reaction with OD groups) are equal to:

$$r_H = k'_H p \vartheta_{OH}, \quad r_D = k'_D p \vartheta_{OD}$$

where k'_H and k'_D are constants and p is the partial pressure of propene. The degree of deuteration of the propene is assumed to have no effect on k'_H and k'_D .

3. The rate of desorption of propene ($s_{H,i}$ in case an isopropyl group with i D atoms releases an H atom, and $s_{D,i}$ if it releases a D atom) is given by:

$$s_{H,i} = \{(6 - i)/6\} k''_H r_i \vartheta_{is}, \quad s_{D,i} = (i/6) k''_D r_i \vartheta_{is}$$

where k''_H and k''_D are constants, r_i is the fraction of the isopropyl groups with i D atoms per group, and ϑ_{is} denotes the surface concentration of isopropyl groups. The r_i 's satisfy a binomial distribution.

This model was elaborated for a stationary state since this exists in every point of a catalyst bed through which a continuous flow is passed. For convenience sake we assumed that no oxidation takes place. The calculations resulted in the following equation for ϑ_{is} :

$$\Theta \{1 + (\rho - 1)(z + 5x)/(\Theta + 5)\} = \rho \quad (4)$$

where $\Theta = k''_D \vartheta_{is} / \{k'_H f_H p (1 - y) + k'_D f_D p y\}$, $\rho = k''_D / k''_H$, $z = \sigma y / \{1 + (\sigma - 1)y\}$ (with $\sigma = k'_D f_D / k'_H f_H$), and $x =$ fraction of the D atoms in propene. It appears from this equation that ϑ_{is} normally depends on both x and y .

A much simpler situation arises if $k''_H = k''_D (= k'')$, i.e., if ρ equals unity. In that case Θ , too, is equal to 1, so that

$$\vartheta_{is} = (k'_H f_H p / k'') \{1 + (\sigma - 1)y\}. \quad (5)$$

In the event $\rho = 1$, the model provides a simple expression also for the rate r_e of the exchange of H and D between water vapor

and propene caused by the adsorption and desorption of propene,

$$r_e = (5/6) k'_H f_H p \{\sigma(1 - x)y - x(1 - y)\} \quad (6)$$

An equation similar to that above has been used for calculating the standard rate of exchange u_H [with Eq. (A5), ref. (2)],

$$r_e = u_H(1 - x)y - u_D x(1 - y).$$

If propene is assumed to oxidize at a rate proportional to ϑ_{is} , Eq. (5) predicts that the rate of oxidation is independent of x , but dependent on y . This is exactly what we have found experimentally with regard to oxidation of propene to the whole assembly of products of the acetone group. From the value of c (Table 2B) it follows that the ratio of the rates of oxidation at $y = 1$ and $y = 0$ equals 0.71. According to Eq. (5), this ratio is equal to σ . From Eq. (6) it follows that σ is the equilibrium constant of the exchange (if $\rho = 1$); at 370°C its value equals 0.63 [see Part II (2)]. The slight difference with the above-mentioned value of 0.71 can be accounted for by the fact that the abstraction of the central H atom from the isopropyl group is not completely rate determining. Hence, as far as the oxidation is concerned, the experimental results are in good agreement with the reaction model on the condition that k''_H and k''_D are equal. [Equality of k''_H and k''_D implies that the desorption of isopropyl groups resulting in formation of propene is not attended by an isotope effect. This can be explained by assuming that the activation energy of the desorption is essentially the energy needed for transforming an isopropyl group into a carbonium ion. A similar situation occurs in the elimination of hydrogen halide from organic halides in the gas phase (12); the rate of this elimination is independent of the bond strength of the hydrogen atom to be split off.] The exchange data can, however, not be reconciled with the equality of k''_H and k''_D according to which the standard rate of exchange u_H must be constant. However, u_H depends on both x and y . (One might rightly object therefore to calculating the numerical values of u_H in such a way as if u_H were a constant. However, we did not

see any other practicable way of approach.) In addition, the nature of this dependence (expressed in the values of b and c in Table 2B) can be explained by the reaction model only if $k''_{\text{D}}/k''_{\text{H}}$ is equal to 2.4 (being much larger than 1, this value is not acceptable). However, it must be borne in mind here that, as demonstrated in Part II, a considerable part of the exchange reaction does not lead up to formation of an isopropyl group; it might be that this type of exchange is a concerted reaction in which both the protium atom arriving in and that departing from the propene molecule are involved.

Selectivity changes within the acetone group occur also in the experiments represented in Table 2A and B. In the first place, the transition from ordinary to deuterated propene is marked by an increase of the acetone/acetic acid ratio, with the amount of acetone plus acetic acid formed per unit time remaining substantially constant. Calculated from the values of b for acetone and acetic acid, the increase is slightly larger than a factor 2 [$0.16 - (-0.17) = 0.33$; antilog $0.33 = 2.1$]. It is evidently caused by a kinetic isotope effect in the oxidation of acetone to acetic acid (the term "acetone" is meant to include also acetone in the pre-desorbed state): in this oxidation protium atoms must be abstracted from the acetone, which is more difficult to realize with D atoms than with H atoms; a factor of about 2 would not seem unreasonable.

Second, there is the decrease of the acetone/acetic acid ratio that marks the transition from ordinary to heavy water. This decrease, calculated from the c values for acetone and acetic acid, is slightly larger than a factor 1.5. It is due mainly to a decrease of the production of acetone; judged from the value of c , the production of acetic acid decreases only slightly. It is difficult to explain this phenomenon.

With acetaldehyde the situation is much the same as that sketched for the acetone group as a whole. We point out, however, that there is little certainty with regard to the accuracy of the acetaldehyde determination (the gas-chromatographic peaks for acetaldehyde appeared on the tail of the

propene peak; the influence of deuteration on peak height has not been established).

Finally, a few words on the occurrence of a kinetic isotope effect in the formation of acrolein (this compound is obtained in minor quantities, together with a little acrylic acid, during oxidation of propene over $\text{SnO}_2/\text{MoO}_3$). It has been found that the production of acrolein remains virtually unchanged when the H atom bonded to the second carbon atom of propene is replaced by a D atom (Table 1), but decreases by a factor of approx 1.75 (following from the value of b for acrolein in Table 2B) when the H atoms, bound to the first and third carbon atoms, are replaced by D atoms. This is in conformity with the generally accepted view that the oxidation of propene to acrolein over oxidic catalysts starts with abstraction of a hydrogen atom from the methyl group of propene (13). Oxidizing propene over bismuth molybdate at 450°C , Adams and Jennings (14) found that the rate constants measured with C_3H_6 and C_3D_6 were in the ratio 1.8:1.

The mechanisms responsible for the formation of acetone and related substances, on the one hand, and acrolein and acrylic acid, on the other, differ widely, but they agree on the point that in either of them abstraction of a hydrogen atom constitutes the primary oxidation step.

ERRATUM

The remark at the end of the Appendix of Part II (2) to the effect that a symbol N should have been omitted in an equation derived by Bolder, Dallinga and Kloosterziel (15) is unjustified. As appears from definitions given on page 319 of their article, the quantity N is included in \bar{k} .

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