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Catalytic Oxidation

III. The Mechanism of Ethylene and Propylene Oxidation Over Supported Rhodium and Ruthenium

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The kinetics of ethylene and propylene oxidation over Rh and Ru supported on low area α-alumina were studied and found similar to those reported earlier for the same metals supported on high area silica. The selectivities for product formation were also analogous. The most selective reaction was oxidation of C_3H_6 over Rh at 200°, where substantial amounts of acrolein and acetone were formed. Substitution of deuterium for hydrogen in the olefin methyl-group reduced the rates of these reactions significantly, showing that abstraction of H from this position was involved in the rate-determining steps. The acetones formed from labeled propylenes contained deuterium in all possible positions, but exchange into the product acroleins was minor and confined mainly to the 2-position. The acrolein from CD_3CHCH_2 and CH_3CHCD_2 contained nearly equal amounts of the d_1 and d_2 species, but the unreacted propylene was unisomerized. The absolute values for the deuterium contents showed that the bulk of the acrolein was formed via a symmetric allyl-type intermediate, but that up to 26% of the reaction proceeded with the direct conversion of the methyl group of the olefin into the aldehyde group. The data also showed that the isotope effect for the removal of the second H (or D) from the olefin is minimal. Possible mechanisms to explain these findings are presented.

INTRODUCTION

The literature reveals that a number of oxide systems are selective for the heterogeneous catalytic oxidation of propylene to acrolein (*1*), although only two, Cu_2O and $Bi_2O_3 \cdot xMoO_3$, have been studied in very great detail (*2*). Experiments employing ^{13}C- and ^{14}C-labeled propylenes have established that the reactions proceed via an intermediate in which the two end carbon atoms become equivalent (*3–6*). From the rates of oxidation of various deuterium-labeled propylenes over bismuth molybdate, Adams and Jennings (*7, 8*) concluded that the initial step was the removal of a methyl-hydrogen. Furthermore, the distribution of deuterium in the acrolein produced in their experiments (including Cu_2O catalysts) was consistent with a discrimination isotope effect (k_D/k_H) of 0.55 for abstraction of both the initial D (or H) from the methyl-position and subsequent removal of the second, from either end-carbon. This provided evidence for a symmetric intermediate of the allylic type, a conclusion which has now been widely accepted.

Several oxide systems are known to be good catalysts for oxidation of C_3H_6 to organic compounds other than acrolein. Buiten (*9*) found that acetic acid and acetone were formed during oxidation, in the presence of water vapor, over a monolayer of MoO_3 supported on SnO_2, Moro-oka *et al.* (*10, 11*) reported that acetone alone was

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produced by the same reaction over catalysts containing 10 mole % molybdenum oxide and 90 mole % of either tin oxide or cobalt oxide. The latter authors suggested *(11)* that the reaction involved hydration of the olefin to the secondary alcohol followed by oxidative dehydrogenation to the ketone. However, Buiten *(12)* concluded from a careful investigation using D_2O in the feed that this scheme was not strictly valid for his catalyst system and suggested that a surface compound with the isopropyl structure was an intermediate in the reaction.

The Group VIII noble metals are very active catalysts for olefin oxidation, but in most investigations only trace amounts ($<8\%$) of partially oxidized products have been reported *(13–15)*. In a recent systematic investigation *(16)*, we have shown that the selectivity for partial oxidation is substantial for some of these metals when supported on silica. Ethylene oxidation over Pd and Ir yielded 10–30% acetic acid, and Ir gave 25 to 35% of this product from propylene. Oxidation of propylene over Rh and Ru produced important amounts of both acrolein and acetone. This report presents further data for olefin oxidation over supported Rh and Ru.

EXPERIMENTAL METHODS

All the catalytic experiments reported in this paper were carried out using the flow system described elsewhere *(16)*. The analytical methods, the pretreatment procedures and the purification of gases were also the same, as was the 5% Ru/SiO_2 catalyst used in a few experiments. In all other experiments, approximately 7-g samples of catalysts prepared for us by Engelhard Industries, were used. They consisted of 1.5% of the noble metal deposited on the exterior surfaces of a low area α-alumina (Alcoa T-61, 14–28 mesh, surface area <0.3 m^2 g^{-1}). These catalysts had better heat dissipation characteristics than the metal/silica catalysts and the low surface area of the support minimized product adsorption. However, their metal surface areas were too low to be measured by conventional hydrogen chemisorption techniques so that it was no longer possible to determine specific activities.

The ^{13}C- and deuterium-labeled propylenes were obtained from Merck, Sharp and Dohme of Canada. From the mass spectrum of each, the following amounts of propylenes containing lesser quantities of the label were found to be present.

Major component	Other	%
Propylene-1-^{13}C	C_3H_6	46.5
Propylene-1,1-d_2	C_3DH_5	4.9
Propylene-2-d_1	C_3H_6	2.9
Propylene-3,3,3-d_3	$C_3D_2H_4$	2.8
Perdeuteropropylene	C_3D_5H	5.5

The infrared spectrum (as gas) and the NMR spectrum (in CCl_4 solution) of each deuterated propylene were measured to evaluate the H impurity located at the specified positions. These data were checked against the mass spectrometric analyses. Within the experimental error, agreement was obtained for CD_3CHCH_2, but the CH_3CDCH_2 contained 3%, and the CH_3CHCD_2 1.5% more hydrogen at the labeled position than could be accounted for on the basis of impurities with lower deuterium content. Consequently, some deuterium must be present at nominally unlabeled positions, but its location could not be estimated accurately.

During the tracer experiments, the labeled compounds were introduced at an injection port from a gas-tight syringe (Sage Instruments, Model 234) being driven at a constant rate such that the pressure of the compound introduced exactly duplicated that of the normal reactant flow which had been shut off. Usually, 10 ml (STP) of the labeled compound were added over a 22-min period (giving a pressure of about 7 Torr) and the products formed during the final 5 min were collected, separated by gas chromatography and the distribution of the label was determined mass spectrometrically. The unreacted propylenes were also collected and examined to determine whether any exchange or isomerization had occurred. During co-oxidation experiments, products or possible intermediates were added to the reaction in the same way.

Infrared spectra were recorded with a Beckman IR-12 spectrometer and mass spectra with a Nuclide 6-in. magnetic sector instrument. The mass spectra of deuterated acroleins were taken with both low ionizing voltages (9.5 eV) and under conditions of extensive fragmentation (70 eV). The deuterium distribution was determined from the former after correction, for a small amount of fragmentation ($<5\%$), naturally occurring ^{13}C and starting impurities. From the 70-eV spectra, it was possible in some instances to estimate the relative number of molecules with CDO and CHO groups, using the intensities of peaks with $m/e = 29$ and 30 and those in the region 55 to 60. The procedure was based on the known modes of fragmentation of acrolein as described in the Appendix of Pap. IV in this series (*17*). The distribution of ^{13}C in acrolein formed by oxidation of propylene-1-^{13}C was similarly estimated from its fragmentation spectrum. The high resolution NMR spectra were taken with a Varian-(A-60) spectrometer.

RESULTS

Products. The product distribution for propylene oxidation over Rh/α-Al_2O_3 underwent the changes shown in Fig. 1 during the first few hours on stream. Initially, acetone amounted to about 50% of all propylene consumed, but its rate of formation fell by an order of magnitude during the first hour. The falloff in rate was less pronounced with acetic acid while acrolein and acetaldehyde, and CO_2 and H_2O as well, were produced in nearly constant amounts from the beginning of the reaction. After a few hours, constant selectivities were reached and these are listed in Table 1. These do not differ significantly from our findings with Rh/SiO_2 catalysts (*16*). All kinetics and tracer data were obtained with the catalysts in the lined-out condition.

The distribution of partial oxidation products was constant during the initial stages of C_3H_6 oxidation over Ru/α-Al_2O_3. The selectivities declined in importance relative to total oxidation, however, with the values listed in Table 1 being attained eventually. These were somewhat lower than those found with Ru/SiO_2 (*16*) and only represent pseudo-steady state values. Various procedures (such as very high conversion levels or a complete shutdown in reactant flow) caused further irreversible declines. Moreover, Table 1 shows that Ru and Rh supported on α-Al_2O_3 were quite unselective for C_2H_4 oxidation as were the corresponding silica-supported metals.

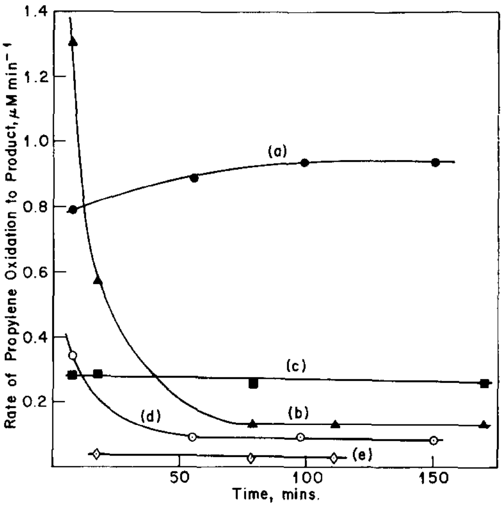


FIG. 1. Variation in product distribution with time during propylene oxidation over Rh/α-Al_2O_3 at 173°. $P_{C_3H_6} = 7$ Torr; $P_{O_2} = 29$ Torr; (a) total oxidation to $CO_2 + H_2O$; (b) oxidation to acetone; (c) oxidation to acrolein; (d) oxidation to acetic acid; (e) oxidation to acetaldehyde.

Kinetics. Approximate relative oxidation rates in the four systems can be derived from the temperatures required to achieve an oxidation rate of 0.5 μM olefin min^{-1} g^{-1} (Table 1). The values for one metal should not be closely compared with the other, however, because the metal surface areas are unknown. As observed with silica-supported metals (*16*), Rh was more active for C_3H_6 than C_2H_4 oxidation, while the reverse was true with Ru.

The temperature dependence of each reaction was determined for each catalyst in the steady state at olefin conversions below

TABLE 1
ACTIVITY AND SELECTIVITY OF Rh AND Ru FOR OLEFIN OXIDATION

	Catalyst and olefin			
	Ethylene		Propylene	
	Rh/α-Al_2O_3	Ru/α-Al_2O_3	Rh/α-Al_2O_3	Ru/α-Al_2O_3
Conditions and results				
Olefin pressure (Torr)	20	21	12	12
Oxygen pressure (Torr)	55	70	46	45
Activation energy (kcal/mole)	26.5 ± 0.2	29 ± 0.4	31.5 ± 2	28 ± 2
Temp for standard activity[a] (°C)	255	211	184	235
Products	Selectivity (% of oxidized olefin)			
Acetaldehyde	<0.1	<0.5	0.5-1.5	1-2
Acetic acid	<0.2	<0.5	4-6	2-6
Acrolein	—	—	10-18	2-5
Acetone	—	—	7-10	2-5
C_3 acids	—	—	<1	<1

[a] Temperature required to achieve rate of 0.5 μM olefin min^{-1} g^{-1}.

20%. Except for C_3H_6 oxidation over Rh/α-Al_2O_3, the apparent activation energies for total oxidation (Table 1) agreed closely with values found for reaction over the same metals supported on silica. Only with the Rh/α-Al_2O_3 catalyst could sufficiently accurate data on the net production rates be obtained to allow Arrhenius plots to be made for the rates of formation of the individual products (products were held-up on the silica support). These temperature dependencies were somewhat dependent upon reactant pressure, however, and the results shown in Fig. 2 are for slightly different conditions than used to collect the data of Table 1. The apparent activation energies (and their standard deviations) corresponding to Fig. 2 were as follows: total oxidation (H_2O), 36.5 kcal $mole^{-1}$, $\sigma = 2.2$; acrolein, 28.4 kcal $mole^{-1}$, $\sigma = 0.8$; acetone, 30.8 kcal $mole^{-1}$, $\sigma = 2.0$; and acetic acid, 33.9 kcal $mole^{-1}$, $\sigma = 4.0$. Although the olefin conversion was low, the significance of the first two values may be questioned, because acrolein (but not acetone or acetic acid) is further oxidized to CO_2 and H_2O, *vide infra.*

The variation in the rate of H_2O formation at low conversions (chiefly from total oxidation) is shown as a function of reactant pressure in Fig. 3. The reactions over Ru/α-Al_2O_3 were less than first order in O_2-pressure and inhibited by olefin. The results for Rh/α-Al_2O_3 deserve special comment. When the O_2-pressure was reduced during C_3H_6 oxidation, the rate increased slowly at first, and then very rapidly below 50 Torr; near 35 Torr, the rate increased

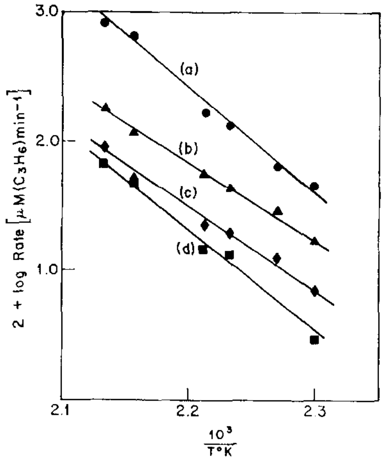


FIG. 2. Effect of temperature on rate of propylene oxidation over Rh/α-Al_2O_3. $P_{C_3H_6} = 24$ Torr; $P_{O_2} = 73$ Torr; (a) oxidation to $CO_2 + H_2O$; (b) oxidation to acrolein; (c) oxidation to acetone; (d) oxidation to acetic acid.

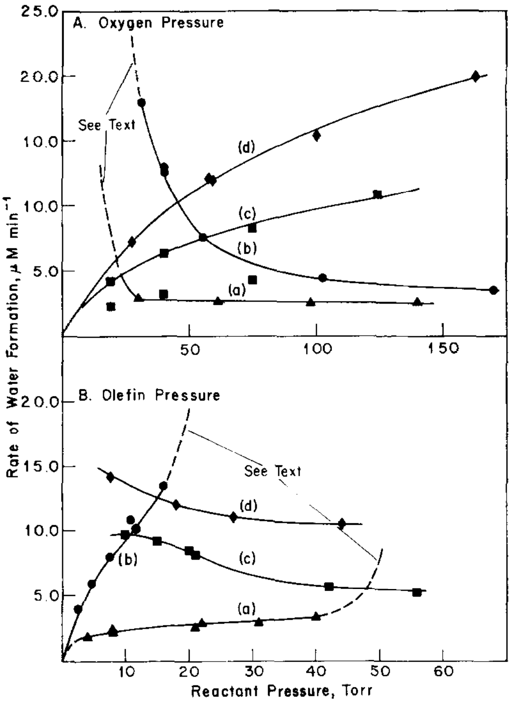


FIG. 3. Dependence of total oxidation rate on reactant pressure: (a) C_2H_4 oxidation over Rh/α-Al_2O_3 at 202°; (b) C_3H_6 oxidation over Rh/α-Al_2O_3 at 184°; (c) C_2H_4 oxidation over Ru/α-Al_2O_3 at 211°; (d) C_3H_6 oxidation over Ru/α-Al_2O_3 at 235°. Fixed reactant pressures as specified in Table 1.

almost vertically with decrease in pressure and total consumption of O_2 resulted. Similar behavior was found for C_2H_4 oxidation; the rate was nearly constant and at a low level between 150 and 30 Torr, but increased extremely rapidly near 25 Torr. The effect of changing olefin pressure was exactly the opposite; very rapid increases in rate occurred for pressures *above* certain limits. It was noticeable that these rapid rate increases took place only when the olefin was in excess of that required for total oxidation. With total consumption of O_2, the selectivity of C_2H_4 oxidation to acetic acid increased from about 0.2 to 5%. With C_3H_6, the yield of acrolein was greatly diminished, although the yields of acetone and acetic acid were little changed. The total consumption of O_2 in this way was not due to loss of control through overheating of the catalyst, since much greater rises in temperature could be tolerated under other conditions.

The dependence of the selectivity for partial oxidation of C_3H_6 on reactant pressures is summarized in Fig. 4. With both Ru and Rh, the ratio of acrolein/acetone was unaffected by these parameters, so these products were summed. With Rh, this sum went through a maximum with pressure of either reactant, the position of which was dependent on the pressure of the other. The most favorable O_2/C_3H_6 ratio was 3:5 under all circumstances, i.e., close to the critical condition. With Ru, highest selectivity for acrolein and acetone formation was achieved with high C_3H_6- and low O_2-pressure; and the same was true of acetic acid formation over Rh.

Tracer studies over Rh/α-Al_2O_3. The olefin pressure used was 7 Torr, ensuring that the reaction was close to first order for this reactant. The relative rates of oxidation of each deuterium-labeled propylene

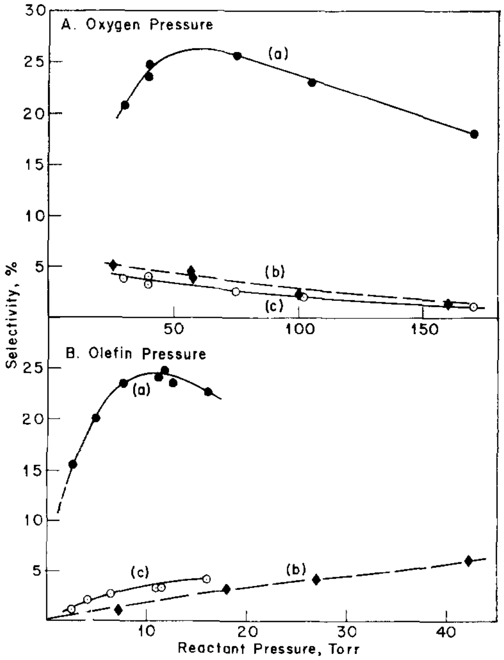


FIG. 4. Variation in selectivity of propylene oxidation with reactant pressures: (a) acrolein + acetone formation over Rh/α-Al_2O_3 at 184°; (b) acrolein + acetone formation over Ru/α-Al_2O_3 at 235°; (c) acetic acid formation over Rh/α-Al_2O_3 at 184°. Fixed reactant pressures as specified in Table 1.

over Rh/α-Al_2O_3 were calculated by normalizing the rate data for the tracer olefins to the rate for C_3H_6 under identical conditions. The results listed in Table 2 are averages of several experiments. For acrolein formation, CD_3CHCH_2 and C_3D_6 were oxidized at about one-third the rate of CH_3CHCD_2, CH_3CDCH_2, and C_3H_6. Thus, a large kinetic isotope effect was operative, but only for deuterium in the methyl group. Oxidation rates to acetone and to $CO_2 + H_2O$ revealed a similar, but less pronounced pattern; again CD_3CHCH_2 and C_3D_6 yielded the least product, but CH_3CHCD_2 oxidation was also significantly slower than C_3H_6 oxidation. The presence of D_2O (or H_2O) in excess of that produced by reaction, led to pronounced reduction in total oxidation relative to partial oxidation, e.g., the selectivity to acrolein was improved, as indicated in the final line of Table 2.

In one experiment, a mixture of C_3H_6, 49.0%; C_3D_5H, 2.5%; and C_3D_6, 48.5% was oxidized and the isotope effect was estimated from a mass spectral analysis of the relative amounts of hydrogen and deuterium in each product. The values obtained, 0.35 for acrolein and 0.54 for acetone, were in excellent agreement with those given in Table 2, which were obtained by direct rate comparison.

Propylenes unoxidized during the above experiment were found to consist of C_3H_6, 47.2%; C_3DH_5, 1.2%; C_3D_5H, 3.4%; and C_3D_6 48.1%. Thus, the overall *intermolecular* hydrogen–deuterium mixing was small, yet significant. Similar results were obtained when specifically deuterated propylenes, unreacted in other experiments, were examined by mass spectrometry. Infrared analysis showed that *intramolecular* transfer was also small (at most 5%). Unreacted propylenes from the oxidation of C_3H_6 (7 Torr) in the presence of D_2O (12 Torr) contained about 3.0% d_1 and <0.7% of more highly deuterated molecules. Extensive intermolecular mixing was found in the acetone, however, as shown in Table 3. Noteworthy was the oxidation of 7 Torr of C_3H_6 in the presence of 10 Torr of D_2O, which produced acetones containing up to and including 6D per molecule in the approximately statistical distribution. This showed that the mechanism for atom scrambling in acetone, when the other propylenes were oxidized, was probably via repeated keto–enol shifts and exchange with D_2O, H_2O, and HDO formed through total oxidation and in acrolein formation. Blank experiments showed that H/D exchange between D_2O and $(CH_3)_2CO$ did not occur in the absence of the catalyst under equivalent conditions, while the final line of Table 3 shows that Rh/α-Al_2O_3 readily facilitated the reaction.

Results of crucial experiments which define the extent and mechanism of exchange processes during acrolein formation are listed in Table 4. Oxidation of an equimolar mixture of C_3H_6 and C_3D_6 gave rise to a mixture of acroleins (line 1) which

TABLE 2

KINETIC ISOTOPE EFFECTS IN PROPYLENE OXIDATION OVER Rh/α-Al_2O_3[a]

	Relative rate constants for reactions leading to		
System	Total oxidation	Acrolein	Acetone
CH_3CHCH_2	1.0	1.0	1.0
CD_3CDCD_2	0.3–0.5[c]	0.35 ± 0.05	0.55 ± 0.05
CH_3CHCD_2	0.65 ± 0.1	0.9 ± 0.05	0.8 ± 0.1
CD_3CHCH_2	0.3–0.5[c]	0.35 ± 0.04	0.55 ± 0.05
CH_3CDCH_2	0.92	1.0	0.97
CH_3CHCH_2/D_2C[b]	0.4–0.6[c]	0.8–0.9	0.6–0.7

[a] Propylene pressure 7 Torr; propylene conversion 20 to 40%.

[b] Oxidation in the presence of 10 Torr D_2O vapor.

[c] Conversion dependent.

TABLE 3

COMPOSITION OF ACETONES FROM REACTIONS OVER 1.5% Rh/α-Al_2O_3

System	Isotopic distribution (mole %)[a] d_0	d_1	d_2	d_3	d_4	d_5	d_6
C_3H_6/C_3D_6	42.7	13.6	3.9	3.9	9.4	12.2	14.1
CD_3CHCH_2	3.4	9.5	25.5	40.3	17.6	3.9	—
CH_3CHCD_2	10.6	26.9	45.9	14.2	2.3	—	—
CH_3CDCH_2	35.1	52.6	11.3	1.0	—	—	—
C_3H_6/D_2O[b]	10.9	15.0	19.1	20.5	18.7	11.7	4.1
Acetone/D_2O[c]	34.8	34.4	19.3	8.0	2.7	0.8	—

[a] Corrected for ^{13}C only.

[b] D_2O added at 10 Torr.

[c] Mole ratio D_2O/CH_3COCH_3 = 5, based on amounts fed.

was only slightly scrambled with respect to H and D. The existence of exchange was, however, found in the oxidation of C_3H_6 in the presence of substantial excesses of D_2O (lines 2, 3, and 4). Examination of the mass spectral fragmentation pattern of the most highly exchanged sample of acrolein (line 4) indicated a composition of: C_2H_3CHO = 41.1%; C_2H_3CDO = 3.8%; C_2H_2DCHO = 51.2%; and C_2H_2DCDO = 3.9%. All the major peaks in the infrared spectrum of this sample were readily interpretable as resulting from an approximately equimolar mixture of CH_2CHCHO and CH_2CDCHO. [An authentic sample of the latter was prepared for comparison purposes by the oxidation of CH_3CDCH_2 over Au where this exchange was minimal (*17*).] Thus, it appeared that the major part of the exchange was taking place at the 2-position, although a small amount also occurred in the aldehyde group. Consideration of the theory of similar exchange processes [e.g., CH_4/CD_4 mixing (*18*)] indicated that the rate of the first-named exchange was 5 to 8 times faster than that of the second.

This was confirmed by oxidation of CH_3CDCH_2 both alone, in which case a considerable amount of acrolein-d_0 was formed (line 5, Table 4), and in the presence of D_2O, which greatly suppressed the loss of the labeled atom (lines 6, 7, and 8).

TABLE 4

COMPOSITION OF ACROLEINS FROM REACTIONS OVER 1.5% Rh/α-Al_2O_3[a]

Propylene	D_2O[c] / acrolein	Isotopic distribution (mole %)[b] d_0	d_1	d_2	d_3	d_4	Max %[d] CDO groups
C_3H_6/C_3D_6	—	67.5	5.4	0.2	5.0	21.7	—
CH_3CHCH_2	50	78.8	21.2	—	—	—	2
CH_3CHCH_2	90	63.9	35.4	0.7	—	—	3.5
CH_3CHCH_2	300	42.8	53.8	3.6	—	—	7
CH_3CDCH_2	—	28.0	72.0	—	—	—	3
CH_3CDCH_2	40	13.1	85.9	1.0	—	—	8
CH_3CDCH_2	160	5.3	92.7	2.0	—	—	8
None	5	94.4	5.6	—	—	—	5

[a] At 195 to 200° with propylene pressure of 7 Torr, the conversion was between 20 and 30%.

[b] From low eV measurements, corrected for fragmentation and ^{13}C content.

[c] Based on D_2O to reactor and acrolein leaving reactor. The ratio (D_2O added)/(H_2O from propylene) was about $\frac{1}{12}$ of these values.

[d] Estimated from fragmentation pattern.

TABLE 5
COMPOSITION OF ACROLEINS FROM REACTIONS OVER 1.5% Rh/α-Al_2O_3[a]

System	Sample no.	Isotopic distribution (mole %)[b] d_0	d_1	d_2	d_3	d_4
CH_3CHCD_2	1	1.0	38.0	54.6	6.3	—
	2	0.9	38.4	54.7	6.0	—
CH_3CHCD_2/H_2O[c]	1	1.0	39.7	56.6	3.9	—
	2	0.8	39.4	56.0	3.9	—
CD_3CHCH_2	1	2.9	43.6	45.7	8.6	—
	2	1.9	43.3	45.6	9.2	—
CD_3CHCH_2/H_2O[c]	1	4.6	49.3	42.1	4.0	—
	2	4.0	50.1	42.8	3.1	—

[a] At 208° with propylene pressure of 7 Torr; the overall conversion was about 35%.

[b] From low eV measurements, corrected for ^{13}C content, fragmentation and starting propylenes with lesser deuterium content except as noted.

[c] Reactant stream saturated with H_2O at 0°C.

The small amount of acrolein-d_2 produced even in the presence of a vast excess of D_2O is indicative of the small extent of exchange with CHO (and $=CH_2$) groups. Thus, our raw data for CD_3CHCH_2 and CH_3CHCD_2 oxidation over Rh (Table 5) must be corrected for exchange at the 2-position. Undoubtedly the production of small amounts of acrolein-d_3 from the latter olefin stems from this process because introduction of H_2O into the feed stream effectively repressed it (Table 5), in agreement with the results in Table 4.

The data of Table 5 were corrected for exchange by assuming that it occurred to the same extent with both acroleins-d_1 and -d_2 and that the amount of acrolein-d_3 was a measure of the extra D incorporated into originally d_2 molecules. The resultant data (Table 6) were also corrected for the presence of some acrolein-d_0. While a small amount of this compound would be expected through replacement of CDO by CHO, its most probable source appeared to lie in our experimental procedure, which involved replacement of the normal reactant stream containing C_3H_6 by one containing the labeled propylene over a 20-min period. If the amount of acrolein formed during this period was insufficient to completely replace the normal acrolein retained by the catalyst, then the sample of acrolein collected over the final stages of the replacement period would contain d_0. The supporting evidence was that low rates of acrolein formation (e.g., CD_3CHCH_2 oxidation compared with that for CH_3CHCD_2) increased the fraction of d_0 molecules and each Sample 2, representing analysis of material collected when a second aliquot of the labeled propylene was oxidized immediately following the first, contained less d_0. Thus, the amounts of d_0 were not truly representative of oxidation of the labeled propylenes, and the analysis of the sample was therefore cal-

TABLE 6
CORRECTED COMPOSITION OF ACROLEINS FORMED BY OXIDATION OF LABELED PROPYLENES OVER Rh/α-Al_2O_3

System	Corrected isotopic distribution (mole %)[a] d_1	d_2
CH_3CHCD_2	42.2	57.8
CH_3CHCD_2/H_2O[b]	41.6	58.4
CD_3CHCH_2	51.9	48.1
CD_3CHCH_2/H_2O[b]	56.4	43.8

[a] Corrected for ^{13}C, fragmentation (<2%), impurities in starting propylenes, exchange at 2 position, and unreplaced d_0 in samples collected.

[b] Reactants saturated with water vapor at 0°C.

culated on a d_0-free basis (Table 6). As had appeared from the raw data, the isotopic distribution in the acrolein produced from CH_3CHCD_2 was similar, but not identical with that formed from CD_3CHCH_2.

The question of how much the distributions were governed by intramolecular movement between the two end carbons was considered. As described elsewhere (*17*), calculations based on the intensities of peaks with *m/e* of 29, 30, and in the region 55 to 60 in the mass spectra measured at 70 eV can be used for this purpose. A detailed analysis was made for the acrolein formed by oxidation of CH_3CHCD_2 in the presence of H_2O. The distribution best fitting the observed spectra was as follows: $CD_2CHCHO = 49.9\%$, $CH_2CHCDO = 36.3\%$ (primary products); $CD_2CDCHO = 3.6\%$, $CH_2CDCDO = 2.2\%$ (formed by exchange at the 2-position); and $CHDCHCDO = 4.5\%$, $CHDCHCHO = 3.3\%$ (resulting from intramolecular movement of some type). Thus, transfer between 1- and 3-positions (which may have occurred in the course of the mass spectral measurements) was <8%, which was only a little greater than observed in the unreacted propylenes, *vide supra*. The fractions of d_1 and d_2 estimated from the above analysis were 41.8 and 58.2%, respectively, which were in excellent agreement with the values given in Table 6.

The oxidation of propylene-1-^{13}C provided confirmation that all acrolein was not formed by a mechanism in which the two end carbon atoms were exactly equivalent. Values for fractional retention of double bond position calculated from the mass spectral data (*17*) are listed in Table 7. A correction has been included for naturally occurring ^{13}C but not for propylene isomerization. The latter was about 3% as determined by infrared measurements in the manner of George (*19*) (see footnote *a* to Table 7). Thus, approximately 60% of acrolein molecules retain the labeled carbon in the terminal olefinic group, in good agreement with the findings for oxidation of the deuterium labeled propylenes. Examination of the mass spectrum of acetone formed by propylene-1-^{13}C oxidation showed that the amount of ^{13}C present at the center carbon was not significantly greater than natural abundance.

TABLE 7

APPARENT OVERALL RETENTION OF DOUBLE BOND POSITION IN ACROLEIN FORMED BY OXIDATION OF PROPYLENE-1-^{13}C OVER Rh[a]

Calculated from peak with *m/e* of	Fractional retention (%)	
	Run 1[b]	Run 2[c]
25	58 ± 10	62 ± 10
26	65 ± 10	74 ± 10
27	69 ± 10	67 ± 5
30[d]	59 ± 5	63 ± 3

[a] The distribution of ^{13}C in the labeled propylene was: starting material: 1-position, 96.6%; 2- and 3-positions, 3.4%; unreacted material: 1-position, 93.5%; 2- and 3-positions, 6.5%.

[b] At 201°, $P_{O_2} = 70$ Torr; $P_{C_3H_6} = 7$ Torr; propylene conversion, 30%.

[c] At 190°, $P_{O_2} = 28$ Torr; $P_{C_3H_6} = 7$ Torr; propylene conversion, 25%.

[d] Corresponds to the $^{13}CHO^+$ fragment. Since all the other *m/e* values contained contributions from *two* fragment ions, calculations based on the *m/e* = 30 value should be the most reliable.

Oxidation of possible intermediates over Rh/α-Al_2O_3. In each case, the compound to be studied was introduced into the normal reactant stream (i.e., containing propylene) and flowed over the catalyst at a temperature such that propylene conversion was small (<3%). The results are summarized in Table 8. Conversion of allyl alcohol was essentially complete under these conditions with acrolein comprising 65% of the product and CO_2 and H_2O the remainder. The latter were probably formed by further oxidation of acrolein, since in a separate test more than 80% of this compound was totally oxidized. Oxidation of both saturated C_3 alcohols was rapid with 1-propanol yielding propionaldehyde and 2-propanol giving acetone. Total oxidation of these compounds was small. Moreover, acetone was unaffected while oxidation of propionaldehyde proceeded very slowly to propionic acid, acetaldehyde, and acetic acid. Acetaldehyde oxidation also yielded mainly

TABLE 8

Co-oxidations Over Rh in the Presence of Propylene[a]

Test compound	Reaction rate (μM min^{-1})	Product distribution (mole % of test compound oxidized) Totally oxidized	Acetaldehyde	Acrolein	Acetone	Acetic acid	Propionaldehyde	C_3 acids
Propylene[b] only	0.5	60	2	25	10	1	<0.1	<1
Allyl alcohol[c]	>6.0	35	—[e]	60	<1	—	<1	—
2-Propanol[c]	4.5	<4	—	—	>95	—	—	—
1-Propanol[c]	4.5	<4	—	—	—	—	>95	—
Propionaldehyde[c]	<0.3	<15	35	—	—	15	—	35
Propylene oxide[c]	<0.4	<20	—	—	—	—	>80	—
Acrolein[c]	1.0	>80	—	—	—	—	—	10
Acetaldehyde[d]	0.7	<30	—	—	—	>70	—	—
Ethylene oxide[d]	<0.1	—	No products detected					
Acetone[c]	<0.1	—	No products detected					

[a] At 179°, P_{O_2} = 70 Torr; $P_{C_3H_6}$ = 7 Torr.

[b] $P_{C_3H_6}$ = 7 Torr, equivalent to 20 μM min^{-1}.

[c] Added at approximately 6.8 μM min^{-1}.

[d] Added at approximately 20 μM min^{-1}.

[e] Amount found did not differ significantly from that formed from C_3H_6 alone.

acetic acid. Propylene oxide and ethylene oxide could be ruled out as intermediates in propylene oxidation over Rh, since both could be passed over the catalyst with the only reaction being isomerization of the former to propionaldehyde.

Tracer studies over Ru/SiO$_2$. Because of poisoning, propylene oxidation over Ru could not be investigated in the same detail as with Rh catalysts. However, two experiments were carried out in which CD_3CHCH_2 was oxidized over a freshly pretreated catalyst (where the greatest yield of partial oxidation products was obtained). Acetone, acrolein, and acetaldehyde, derived from these experiments, were analyzed by mass spectrometry. The results are shown in Table 9.

Both acetone samples were extensively scrambled, although not at equilibrium as the amount of d_3 was considerably in excess of that expected for a statistical distribution. The results for acetaldehyde also indicated that considerable exchange was taking place. The average deuterium content (0.54 and 0.56 in the respective experi-

TABLE 9

Composition of Products of CD_3CHCH_2 Oxidation Over Ruthenium

Compound	Run	Isotopic distribution[c] (mole %) d_0	d_1	d_2	d_3	d_4	d_5	d_6
Acetone	—[a]	4.2	11.2	27.4	46.0	9.8	1.3	—
	—[b]	6.2	13.3	28.3	41.7	8.9	1.6	—
Acrolein	—[b]	3.5	39.4	50.2	6.8	—	—	—
Acetaldehyde	—[a]	8.2	18.3	23.9	47.6	2.0	—	—
	—[b]	8.0	15.3	21.5	53.2	2.0	—	—

[a] At 175°, P_{O_2} = 38 Torr; $P_{C_3H_6}$ = 7 Torr; over 1.0 g of 5% Ru/SiO$_2$ pretreated at 300°.

[b] At 165°, P_{O_2} = 38 Torr; $P_{C_3H_6}$ = 7 Torr; using catalyst as for a.

[c] From low eV measurements, corrected for ^{13}C and starting impurities.

ments) was slightly in excess of that in the starting propylene (0.5), so a tendency did exist for the methyl group to be retained, but the values were much less than that expected for a clean double bond cleavage (0.75). Furthermore, the mass spectral data obtained with higher ionizing voltages showed that the aldehydic position had an appreciable deuterium content (the conclusions of Brinton and Blacet (*20*) were assumed regarding the modes of fragmentation of deuterated acetaldehydes in making these calculations).

As found for Rh, the major portion of the acrolein formed from CD_3CHCH_2 over Ru was d_1 and d_2. However, corrections for exchange processes were not possible because of difficulties in carrying out the necessary blank experiments with this less stable catalyst. For this reason, it was impossible to evaluate the possible significance of the larger percentage of d_2 compared with d_1.

DISCUSSION

The present findings for C_2H_4 and C_3H_6 oxidation over Rh and Ru supported on α-Al_2O_3 are in good agreement with those reported earlier (16) for the silica-supported metals. Activation energies, pressure dependencies, and product distributions were all similar and can therefore be regarded as characteristic of such oxidations under flow conditions. Although Rh was very unselective for C_2H_4 oxidation, it was the most selective group VIII metal for C_3H_6 oxidation, and most of this discussion is concerned with acrolein formation from labeled propylenes by this reaction. The conditions under which these experiments were carried out ensured that the reaction rate was first order in olefin pressure and was inhibited by O_2. Our chief findings were:

1. Acrolein formation from CD_3CHCH_2 or C_3D_6 was much slower than from C_3H_6 or propylenes labeled elsewhere in the molecule. The kinetic isotope effect (k_H/k_D) was about 2.9 compared with theoretical maximum values between 3.3 and 4.0 for the breaking of a C–H relative to a C–D bond at 200° (*21*). Thus, the kinetically slow step must be removal of a methyl hydrogen (or deuterium). In the absence of prior reaction, the species so formed from CD_3CHCH_2 and CH_3CHCD_2 should have the same formal structure, i.e., CH_2CHCD_2. Adams and Jennings (*7*, *8*) have established such a symmetrical intermediate for propylene oxidation over bismuth molybdate; they suggested an adsorbed allylic radical.

2. The chief acroleins produced from the last-named propylenes contained either 1 or 2 D atoms. However, although the necessary corrections for exchange made the product ratios inexact, the d_1/d_2 ratio was not unity, nor always the same. Even the uncorrected data indicated that more d_2 acrolein was formed from CH_3CHCD_2 than from CD_3CHCH_2, which could not be true if *all* oxidation took place via a symmetrical CH_2CHCD_2 intermediate. The data suggest that removal of both hydrogens (or deuteriums) from the same methyl carbon was slightly preferred, and this was supported by the results for $CH_3CH^{13}CH_2$ oxidation.

3. The unreacted olefin did not isomerize extensively nor undergo intermolecular nor intramolecular exchange.

4. Extensive isotopic scrambling occurred in the acetone produced.

The data can be readily interpreted by assuming that the major reaction pathway utilizes the symmetrical allylic radical of Adams and Jennings (*7*, *8*), but that part of the time two hydrogens are removed simultaneously from the methyl group, e.g., by the mechanism suggested by Margolis (*22*):

$$CH_2CHCD_3 + O_2 \longrightarrow CH_2CHCD_2OOD \longrightarrow D_2O + CH_2CHCDO \qquad (1)$$

Of course, other explanations are possible; all that is required is that the identity of the methyl-carbon be conserved part of the time. This could be achieved by forming a formal bond with the surface, or by forming allyl alcohol as an intermediate, since the latter was shown to oxidize selectively to acrolein (Table 8). The larger portion of the acrolein forming reaction, however, involved the symmetric intermediate. A tentative reaction scheme follows. It was derived partly from Adams and Jennings (*7*, *8*) and partly from Mullin and Skirrow (*23*). It is not certain, however, that *all* of the reaction steps are confined to the surface. We assume:

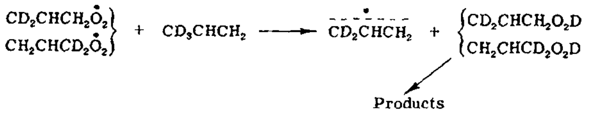
a. Chain initiation;

$$\mathrm{CD_3CHCH_2(g)} \longrightarrow \mathrm{CD_3CHCH_2(ads)} \xrightarrow{\mathrm{O}} \overset{\bullet}{\mathrm{CD_2CHCH_2}} + \cdot\mathrm{OD} \qquad (2)$$

b. Chain propagation;

$$\overset{\bullet}{\mathrm{CD_2CHCH_2}} + \mathrm{O_2} \longrightarrow \mathrm{CD_2CHCH_2\dot{O}_2} + \mathrm{CH_2CHCD_2\dot{O}_2} \qquad (3)$$

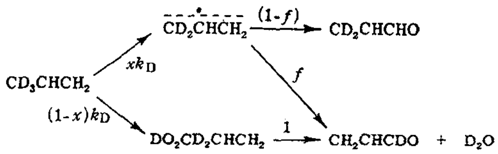
and



$$\left.\begin{matrix}\mathrm{CD_2CHCH_2\dot{O}_2}\\ \mathrm{CH_2CHCD_2\dot{O}_2}\end{matrix}\right\} + \mathrm{CD_3CHCH_2} \longrightarrow \overset{\bullet}{\mathrm{CD_2CHCH_2}} + \left\{\begin{matrix}\mathrm{CD_2CHCH_2O_2D}\\ \mathrm{CH_2CHCD_2O_2D}\end{matrix}\right. \qquad (4)$$

c. Chain termination by further oxidation of intermediate free radicals to CO_2 and H_2O.

Using these ideas together with the experimental data, an analysis can be made of the relative amounts of acrolein produced via symmetrical and unsymmetrical intermediates, respectively. Consider first the reactions of CD_3CHCH_2, i.e.,

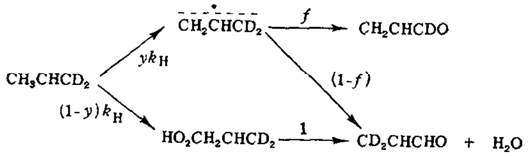


(5),

where x is fraction of the olefin reacting to the symmetric intermediate and f is the fraction of the latter which reacts to form acrolein-d_1; k_D is the rate constant for the reaction of the methyl labeled, d_3, olefin. The ratio of acroleins, d_1/d_2, was (Table 6):

$$\frac{56.4}{43.8} = 1.29 = \frac{1 - x + fx}{(1 - f)x}. \qquad (6)$$

(Values for the experiment with added H_2O were used because exchange with the H on the central carbon with HDO formed in the reaction was repressed in this way.) Similarly for CH_3CHCD_2 we have the scheme:



(7),

where y is defined as for x previously. The ratio d_1/d_2 is then:

$$\frac{41.6}{51.4} = 0.71 = \frac{yf}{y(1 - f) + (1 - y)}. \qquad (8)$$

Equations (6) and (8) can be respectively simplified to

$$(1 - f)x = 0.436, \qquad (9)$$

and

$$fy = 0.415. \qquad (10)$$

Within the present definition of f, x and y (all lying between 0 and 1), Eq. (9) is satisfied only if $0 < f < 0.564$, while Eq. (10) is true only for $0.415 < f < 1$. Since f must satisfy both limits simultaneously, we have $0.415 < f < 0.564$, setting the limits on x and y as $0.74 < x < 1$ and $0.74 < y < 1$.

It should be pointed out that an extreme upper limit for x (or y) would require that y (or x) have the extreme lower limit. However, these extreme combinations would require impossible isotope effects as can be indicated in the following way.

From the schemes (5) and (7) and Table 2 we have that the relative rates of consumption of CD_3CHCH_2 and CH_3CHCD_2 is given by

$$\frac{xk_D + (1-x)k_D}{yk_H + (1-y)k_H} = \frac{k_D}{k_H} = \frac{0.35}{0.90} = 0.39, \quad (11)$$

while the relative rates of allyl radical and hydroperoxide formation are, respectively,

$$\frac{xk_D}{yk_H} = \frac{0.39x}{y}, \quad (12)$$

and

$$\frac{(1-x)k_D}{(1-y)k_H} = \frac{0.39(1-x)}{(1-y)}. \quad (13)$$

The two quotients represent the kinetic isotope effects for the two modes of reaction of the olefin and can be expected to be between 0.25 and 1.3, the theoretical limits at the temperature employed (*21*). (Actually we would expect the isotope effects in hydroperoxide formation to be close to 1.) Hence we have

$$0.25 < \frac{0.39x}{y} < 1.3 \text{ and}$$

$$0.25 < \frac{0.39(1-x)}{1-y} < 1.3.$$

The first set of inequalities is satisfied by all values of x and y within the previous limits, but the second set is true only for $x < 0.83$ and $y < 0.92$. Thus, the only reasonable limits for these parameters are $0.74 < x < 0.83$ and $0.74 < y < 0.92$, thus setting the final limits on f as $0.45 < f < 0.525$.

This value for f (0.49 ± 0.04) implies that removal of either an H or a D from the symmetric intermediate is equally likely, which contrasts with the results of Adams and Jennings (*7, 8*) on oxide catalysts where the isotope effect in this second abstraction was equal to that found in the first abstraction from the olefin. The addition of O_2 to either end of the allyl radical [Eq. (3)] is equally probable. This is one way that the isotope effect for the removal of the second H or D from the molecule can be avoided, but it probably is not unique. Our values for x and y show that no more than 26% of the acrolein is formed by the minor pathway. Thus, the overall percentage of reaction which proceeds with retention of configuration cannot exceed 63%, i.e., 26% plus half the remaining 74%. This agrees well with the results obtained with the ^{13}C-labeled propylene (Table 7) where the overall percentage of acrolein produced with apparent retention of double bond position was 59 ± 5 and 63 ± 3% from the most reliable results for the two runs.

The isotope effects in formation of acrolein and $CO_2(+H_2O)$ were quite similar (Table 2), thus suggesting the same rate-determining step is involved, and also that the latter compounds form via successive oxidation of the former. The co-oxidation experiments detailed in Table 8 substantiate this hypothesis. A radical mechanism is also attractive in explaining the anomalous features of the pressure dependencies. The peculiar orders near the critical runaway condition could reflect a rapid change in chain length in a way analogous to that observed near the explosion limits in the gas phase. To the extent that the kinetics of ethylene oxidation over Rh are similar to those for propylene oxidation, the same instability of surface species can be inferred.

The products of gas phase oxidation of propylene in a flow system were found by Kamiya (*24*) to be acetaldehyde, 34%; propylene oxide, 24%; acrolein, 12%; and allyl alcohol, 5%. Only small amounts of the first two compounds are observed during oxidation over Rh while the data of Table 8 reveal that the metal is not very active in their further oxidation. This does not rule out radical processes, however, since the active surface could still facilitate total oxidation, or prevent formation, of radicals which lead to these products while favoring paths which lead to acrolein and acetone.

Because of rapid exchange processes, it

was impossible to assess whether or not the reaction mechanism would leave the product acetone with the same six hydrogens (or deuteriums) found in the starting propylenes. In the absence of such mixing, it would be quite possible for the observed isotope effect to be much closer to that found for acrolein, in which case the same rate-determining step could be inferred. Several radical mechanisms could be written, but there is no information to favor one or another. Acetone was not formed by isomerization of propylene oxide, since Rh/α-Al_2O_3 was not very active for this process and yielded propionaldehyde. Nor do we think it is formed via hydration to isopropanol and subsequent dehydrogenation because H_2O was available in limited amounts only through concurrent total oxidation and the acetone yield relative to acrolein fell when additional water was incorporated in the feed.

The similarity in product distribution would suggest that Ru acts in a similar manner to Rh for olefin oxidation. However, the deuterium contents in the acroleins formed from CD_3CHCH_2 over the two metals differed, so this may not be strictly true. The pressure dependencies differed also. Because of mixing reactions, one cannot be sure that acetaldehyde and acetic acid are produced during propylene oxidation over Ru in the same manner we have shown for Ir (*25*), i.e., by clean cleavage of the C=C bond.

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