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The Mechanism of the Oxidation of Propene to Acrolein over Antimony–Tin Mixed Oxide Catalysts

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The oxidation of propenes such as $^{13}CH_2{=}CH{-}CH_3$, $CH_2{=}CH{-}CD_3$, *cis*-$CHD{=}CD{-}CH_3$, and $CH_2{=}CH{-}CH_3$ was studied over Sb_6O_{13}, SnO_2, and Sb–Sn mixed oxide catalysts. The results with $^{13}CH_2{=}CH{-}CH_3$ and $CH_2{=}CH{-}CD_3$ were consistent with a π-allyl intermediate. The isotope effect for allylic hydrogen abstraction was 1/0.55 (k_H/k_D) over the Sb–Sn oxide catalysts, indicating that this is the slowest step in the formation of acrolein as with other catalyst systems. The oxidation of $CHD{=}CH{-}CH_3$ did not exhibit a marked isotope effect for the second hydrogen abstraction. This is inconsistent with a fast π-allyl to σ-allyl equilibration process or the irreversible π-allyl to σ-allyl conversion observed over other metal oxide catalysts. The absence of an isotope effect is similar to oxidations over rhodium. The roles of Sn and Sb ions in the oxidation are also discussed.

INTRODUCTION

Sb–Sn oxide is one of the active catalysts for the partial oxidation and ammoxidation of olefins (*1, 2*). Several studies of such catalyst systems using labeled propenes have been reported. Godin *et al.* (*3*) have concluded that oxidation over a Sb–Sn oxide catalyst proceeds via a π-allyl intermediate by using $^{13}CH_2{=}CH{-}CH_3$. Portefaix *et al.* (*4*) have reported that little or no isotope effect is observed for the abstraction of the second hydrogen over a Sb–Sn oxide catalyst using $CD_2{=}CH{-}CH_3$. Keulks *et al.* (*5*) have found an isotope effect for the first hydrogen abstraction and little or no isotope effect for the second hydrogen abstraction over U–Sb oxide catalysts. Similar results have been reported for the ammoxidation of propylene by Burrington *et al.* (*6*).

The oxidation of stereolabeled propene to acrolein has been studied previously by one of the authors over Bi–Mo oxides, Cu_2O, Rh/Al_2O_3, and unsupported Rh catalysts (*7, 8*). With Bi–Mo oxide catalysts (*7*), a deuterium discrimination isotope effect in the second hydrogen abstraction was confirmed, indicating a rapid conversion between π-allyl and σ-allyl intermediates. With Cu_2O catalysts (*7, 8*), an irreversible conversion of π-allyl to σ-allyl species was proposed and a deuterium isotope effect in the second hydrogen abstraction was explained through this mechanism. Another oxidation mechanism without an isotope effect in the second hydrogen abstraction was observed with rhodium catalysts (*7*). Such work demonstrated the usefulness of studies with a partially deuterated vinyl group ($CHD{=}CH{-}CH_3$) to distinguish between these three types of processes and prompted this study.

Many workers have studied the structure and properties of Sb–Sn oxides (*1, 2*). One of the authors (T.O.) has reported (*9*) that Sb oxide is present as noncrystalline Sb(III) and Sb(V) oxides dispersed on SnO_2, whose surface proportions depend on the particle size of SnO_2; high rates and selectivities to acrolein were obtained at a surface ratio of about Sb/Sn = 1/2 to 1/3.

In this work, labeled propenes such as $CH_2{=}CH{-}CD_3$, *cis*-$CHD{=}CD{-}CH_3$, and

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$^{13}CH_2$=CH–CH_3 were used to study the oxidation mechanism. The oxidations were done over Sb_6O_{13}, SnO_2, and Sb–Sn oxide catalysts. The results for these catalysts are compared with each other and with other systems such as the Bi–Mo oxides and Cu_2O. The oxidation mechanism and the roles of Sb and Sn oxide ions are also discussed.

METHODS

Sb–Sn oxide catalysts were prepared by a coprecipitation method as described in Ref. (*9*). Type A catalysts were prepared by coprecipitation from an aqueous solution of $SnCl_4$ and $SbCl_5$. Type B catalysts were prepared from $SnCl_2$ and $SbCl_5$. A notable difference between the A and B catalysts was in the particle size of the SnO_2. Sb(30 at. %)–Sn–oxide(A) and Sb(10%)–Sn–oxide(B) (hereafter Sb(30)Sn–O and Sb (10)Sn–O) showed a maximum activity in acrolein formation as the Sb content was varied and were used in the present study. The preparation of SnO_2 and Sb_6O_{13} is also described in Ref. (*9*).

The catalytic oxidations of propene were carried out in a closed circulation system (ca. 1000 cm^3). The reaction products such as acrolein, acetaldehyde, CO_2, and CO were analyzed by gas chromatography. The reactants CH_2=CH–CD_3 (99%), *cis*-CHD=CD–CH_3 (96.7%), and $^{13}CH_2$=CH–CH_3 (99%) were obtained from MSD Canada, Ltd. CH_2=CH–CH_3 and O_2 were obtained from cylinders (99%).

Microwave spectroscopy was used to determine the relative amounts of the isotopic acrolein products using a Hewlett–Packard 8460A spectrometer. Three to five sets of rotational transitions were compared and the peak intensities were converted into molar ratios. The 4_{04}–3_{03}, 4_{14}–3_{13}, and 4_{13}–3_{12} transitions were mainly used. The procedure is described elsewhere (*7, 8, 10*). This was not a sufficiently large set of transitions to obtain very high precision for the samples containing three to four isotopic species, but the precision in the isotopic ratios (±5 to ±10%) in Tables 2–6 is sufficient to provide useful insights on the reaction processes.

RESULTS AND DISCUSSION

Catalytic activity. Typical reaction conditions and results for the oxidation of propene are given in Table 1. The oxidation rates over Sb_6O_{13} were very low, its activity being 1000 times smaller than that over Sb–Sn oxide catalysts. The selectivity to acrolein on Sb–Sn oxide catalysts was ca. 80%. The activity over SnO_2 was two to three times higher than that over Sb–Sn oxide catalysts while selectivity to acrolein was very low. The results are the same as those published previously (*9, 11*).

Oxidation of CH_2=CH–CH_3 and CH_2–CH–CD_3. An equimolar mixture of CH_2=CH–CH_3 and CH_2=CH–CD_3 was oxidized by the catalysts. As shown in Table 2, the ratios of CH_2=CH–CHO/(CH_2=CH–CDO + CD_2=CH–CHO) were about 1/0.6 for Sb_6O_{13} and 1/0.55 for the Sb–Sn oxide catalysts. Table 3 shows the results for the oxidation of $^{13}CH_2$=CH–CH_3 over Sb(30)–Sn–O and SnO_2 catalysts. The ratio of $^{13}CH_2$=CH–CHO/CH_2=CH–^{13}CHO for Sb(30)–Sn–O was nearly 1. This indicates that both terminal carbon atoms are oxidized with equal probability. Thus, the ratio of CH_2=CH–CHO/(CH_2=CH–CDO + CD_2=CH–CHO) gives the initial deuterium isotope effect for acrolein formation over Sb–Sn oxide catalyst, i.e., the abstraction of the allylic hydrogen is the slow step in acrolein formation, the same as published previously for other oxide catalysts (Table 4). The amounts of CH_2=CH–CDO and CD_2=CH–CHO were equal (within experimental uncertainty) and indicate that the second H(D) abstraction occurs with little or no isotope effect. Portefaix also found little or no isotope effect when using CD_2=CH–CH_3 (*4*).

With SnO_2, equal amounts of $^{13}CH_2$=CH–CHO and CH_2=CH–^{13}CHO were produced upon oxidation of $^{13}CH_2$=CH–CH_3 as shown in Table 3. This indicates that the attack of oxygen occurs with equal

TABLE 1

Typical Reaction Conditions and Characteristics of the Catalysts

	Sb_6O_{13}	Sb(30)–Sn–O[a]	Sb(10)–Sn–O[b]	SnO_2
Surface area (m^2/g)	28	83	24	8.9
Catalyst used (g)	1.5	0.036–0.05	0.125	0.022–0.033
Reactant pressure (Torr)[c]				
Propene	15	15	15	15
O_2	30	30	30	15
Reaction temp. (°C)	400	400	400	400
Propene conversion (%)	0.8	20	10	11
Rate, C_3 reacted				
($\mu mol\ m^{-2}\ min^{-1}$)	0.002–0.003	2.5–3	2.6–3.5	5.5–10
Selectivity to acrolein (%)	40–60	80	70	10–20

[a] Sb–Sn mixed oxide, 30 at.% Sb, preparation A; see Methods.
[b] Sb–Sn mixed oxide, 10 at.% Sb, preparation B; see Methods.
[c] 1 Torr = 133.3 Pa.

probability at both terminal carbon atoms of the π-allyl intermediate. The ratio of CH_2=CH–CHO/(CH_2=CH–CDO + CD_2=CH–CHO) in Table 2 is ca. 1/0.8, which is different from those over Sb_6O_{13} and Sb (30)–Sn–O (1/(0.6–0.55)). Deuterium substitution might be expected to retard the oxidation of deuterated species and lead to increases in their amounts relative to the normal species as observed in Table 2.

Oxidation of cis-CHD=CD–CH$_3$. In order to obtain more complete information on the second hydrogen abstraction step, as pointed out in the introduction, the oxidation of *cis*-CHD=CD–CH_3 was studied. The formation of the π-allyl intermediate (CHD–CD–CH_2) should lead to four acrolein species; see Scheme 1. Within experimental uncertainty, the results over Sb_6O_{13} and the two Sb–Sn–O catalysts (Table 5) gave ratios for ACR-2-d_1 : ACR-*trans*-2,3-d_2 : ACR-*cis*-2,3-d_2 of essentially 1 : 1 : 1 while a slight excess of ACR-1,2-d_2 was produced. Over SnO_2 the amounts of ACR-2-d_1 and ACR-1,2-d_2 increased a little more.

It was shown in previous work (*7, 8*) that the ratio ACR-2-d_1 : ACR-1,2-d_2 : *cis*-ACR-2,3-d_2: : *trans*-ACR-2,3-d_2 depends on the catalyst. With a Bi–Mo oxide catalyst (*7*), the ratio should be approximately 0.5 : 1 : 1 : 1 since the terminal hydrogens and deuterium of the allyl species have equal probability of abstraction except for a deuterium isotope effect. This implies a fast equil-

TABLE 2

Relative Amounts of Acrolein Obtained from the Oxidation of CH_2=CH–CH_3 and CH_2=CH–CD_3 over Various Catalysts[a]

	CH_2=CH–CHO	CH_2=CH–CDO	CD_2=CH–CHO
Sb(30)–Sn–O	1.00	0.27	0.28
Sb(10)–Sn–O	1.00	0.26	0.27
Sb_6O_{13}	1.00	0.28	0.30
SnO_2	1.00	0.42	0.32–0.39

[a] Experimental conditions are nearly the same as those in Table 1. CH_2=CH–CH_3 : CH_2=CH–CD_3 = 1 : 1.

TABLE 3

Relative Amounts of [^{13}C]-Acrolein from Oxidation of $^{13}CH_2{=}CH{-}CH_3$ over SnO_2 and Sb(30)–Sn–Oxide[a]

Catalyst	$^{13}CH_2{=}CH{-}CHO$	$CH_2{=}CH{-}^{13}CHO$
Sb(30)–Sn–O[b]	1.00	0.96
SnO_2[c]	1.00	1.00

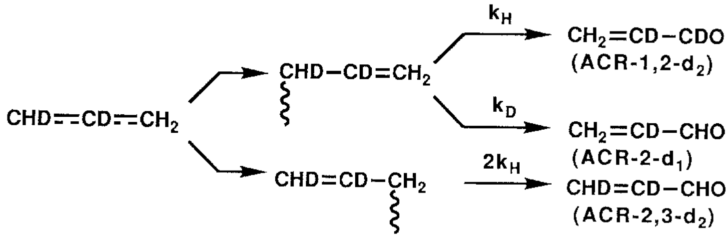
[a] Temperature 400°C; $^{13}CH_2{=}CH{-}CH_3$, 99%.
[b] $P(C_3H_6)$ = 14.5 Torr and $P(O_2)$ = 30 Torr; propene conversion 2.4%, and acrolein selectivity 71%.
[c] $P(C_3H_6)$ = 11 Torr and $P(O_2)$ = 16 Torr, conversion 12%, and selectivity 25%.

ibration between π-allyl and σ-allyl species. With Cu_2O (*7, 8*), the ratio should be 0.5 : 1.5 : 1 : 1, which originates from an irreversible conversion of the π-allyl to a σ-allyl intermediate and a deuterium isotope effect for abstraction at the CHD end. With Rh/Al_2O_3 and Rh metal (*7*), little or no isotope effect is observed for the second hydrogen abstraction and the ratios should be nominally 1 : 1 : 1 : 1. The results over Sb_6O_{13} and the Sb–Sn–O catalysts are very different from those over Bi–Mo oxides and Cu_2O but are more in line with those over Rh where no isotope effect in the second abstraction is observed. The small excess in the amount of ACR-1,2-d_2 (and in ACR-2-d_1 over SnO_2) appears significant. It may be associated with the unique deuterium substitution at the aldehyde moiety in ACR-1,2-d_2 and the sensitivity of this site to an isotope effect in subsequent oxidation of acrolein to CO and CO_2. Such a process would certainly increase the amount of ACR-1,2-d_2 over poor selectivity catalysts like SnO_2. Evidence for such a process was noted in Table 2 for the results over SnO_2. The higher amounts of ACR-1,2-d_2 might also arise from a subtle inverse isotope effect, whereby the second H-abstraction from the CHD end of the allyl species occurs faster than that from the CH_2 end. This situation is reminiscent of the inverse deuterium kinetic secondary isotope effects observed in many addition reactions to double bonds which accelerate reaction rates as deuterium substitution increases (see Ref. (*15*) for an illustration and further

TABLE 4

Comparison of the Primary Isotope Effect in the Oxidation of Propene to Acrolein

Catalyst	Temp.	Deuterated propene	Rate ratio	Ref.
Bi–Mo–O	450°C	C_3H_6	1.0	Adams and Jennings (*12*)
		C_3D_6	0.55	
U–Sb–O	400°C	C_3H_6	1.0	Keulks *et al.* (*5*)
		$CH_2{=}CD{-}CD_3$	0.48	
Au/Support	265°C	C_3H_6	1.0	Cant and Hall (*13*)
		$CH_2{=}CH{-}CD_3$	0.4	
Rh/Al_2O_3	180°C	C_3H_6	1.0	Cant and Hall (*14*)
		$CH_2{=}CH{-}CD_3$	0.35	
Sb–Sn–O	400°C	C_3H_6	1.0	This work
		$CH_2{=}CH{-}CD_3$	0.55	



SCHEME 1.

references). A speculative explanation would entail a complex interplay of zero point energy differences for reactants and transition states as the CH_2 vs CHD ends transform to products. Another example of an inverse effect has been observed by Amenomiya and Pottie (*16*) who reported that the loss of H and D from deuterated ethanes in their mass spectrometric fragmentation depends on the amount of deuterium in the ethane, i.e., the loss of H increases with D substitution.

Apart from the subtle details which lead to preference for ACR-2-d_1 and ACR-1,2-d_2, and which remain cloudy, the primary mechanistic information from the oxidation of CHD=CH–CH_3 is that the second H-abstraction step resembles oxidations over Rh, where little or no isotope effect is observed, rather than over Bi–Mo oxides and copper oxide. The absence of an isotope effect is curious. It implies conversion of the π-allyl species to acrolein in a manner consistent with statistical loss of H and D uninfluenced by isotope effects. Possible interpretations in the case of Rh have been discussed (*7*). Perhaps the proximity of H or D to an active site, which occurs randomly, is an important factor. One possibility involves less symmetric surface σ-allyl intermediates as discussed in Ref. (*7*).

Isomerization of cis-CHD=CD–CH_3. Table 6 shows the results of any isomerization of propene during the oxidation reactions. With Sb_6O_{13}, the rate is very low, but CH_2=CD–CH_2D species are formed. This indicates that the isomerization proceeds via a π-allyl mechanism. On the other hand, with SnO_2 and Sb(30)–Sn–O catalysts, only *trans*-CHD=CD–CH_3 is formed. On SnO_2 the isomerization seems to proceed via a π-bond fission mechanism. On a Sb(30)–Sn–O catalyst, it should also take place on the Sn oxide sites. These facts indicate that tin ions

TABLE 5

Relative Acrolein Formation Rates in the Oxidation of *cis*-CHD=CD–CH_3 over Various Catalysts[a]

	(ACR-*trans* 2,3-d_2)	(ACR-*cis* 2,3-d_2)	(ACR-2-d_1)	(ACR-1,2-d_2)
Sb_6O_{13}	1.00	0.99	0.97	1.18
Sb(30)–Sn–O	1.00	1.00	1.11	1.28
Sb(10)–Sn–O	1.00	1.00	1.17	1.36
SnO_2	1.00	0.91–1.04	1.24–1.40	1.35–1.47

[a] Experimental conditions are the same as those in Table 1.

TABLE 6

Extent of Isomerization of Unreacted *cis*-CHD=CD–CH_3 upon Oxidation at 400°C

$P(C_3')$ (Torr)	Reaction[a] time (min)	Exchange rate (μmol m^{-2} min^{-1})	(D)(H)C=C(D)(CH_3) (*cis*)	(D)(H)C=C(CH_3)(D) (*trans*)	(H)(H)C=C(CH_2D)(D) (sym)[b]	(H)(H)C=C(CH_2D)(D) (asym)[c]
SnO_2						
16	8	40	1.00	0.20	0	0
7.5	12	19	1.00	0.23	0	0
Sb(30)–Sn–O						
15	12	2.6	1.00	0.36	0	0
8	12	1.6	1.00	0.20	0	0
Sb_6O_{13}						
15	70	0.011	1.00	0.03	0.007	0.012

[a] Experimental conditions are nearly the same as those in Table 1.
[b] Methyl deuterium in carbon skeleton plane.
[c] Methyl deuterium out of carbon plane.

TABLE 7

Reaction Orders and Rate Constants in the Oxidation of Propene over Various Catalysts at 400°C (from Ref. *9*)

Catalyst (Sb at.%)	Reaction orders		Rate constants		
	C_3H_6	O_2	k_1[a]	k_2[b]	k_2/k_1
Sb_6O_{13}	1	0	0.004	0.1	25
Sb(10)–Sn–O[c]	0.3	0.5	7.7	5	0.6
Sb(50)–Sn–O[d]	0.3	0.4	6.3	3.7	0.6
SnO_2	0	0.4–0.5	$\gg k_2$	3–8	~0

[a,b] Calculated from the equation $R = k_1k_2p(C_3H_6)p(O_2)^{1/2}/(k_1p(C_3H_6) + k_2p(O_2)^{1/2})$; R is rate in μmol/min m² (C_3H_6 reacted). Pressure ranges: $P(C_3H_6)$ = 0.8–8 kPa and $P(O_2)$ = 0.8–8 kPa.

[c] Prepared by method B. See Methods.

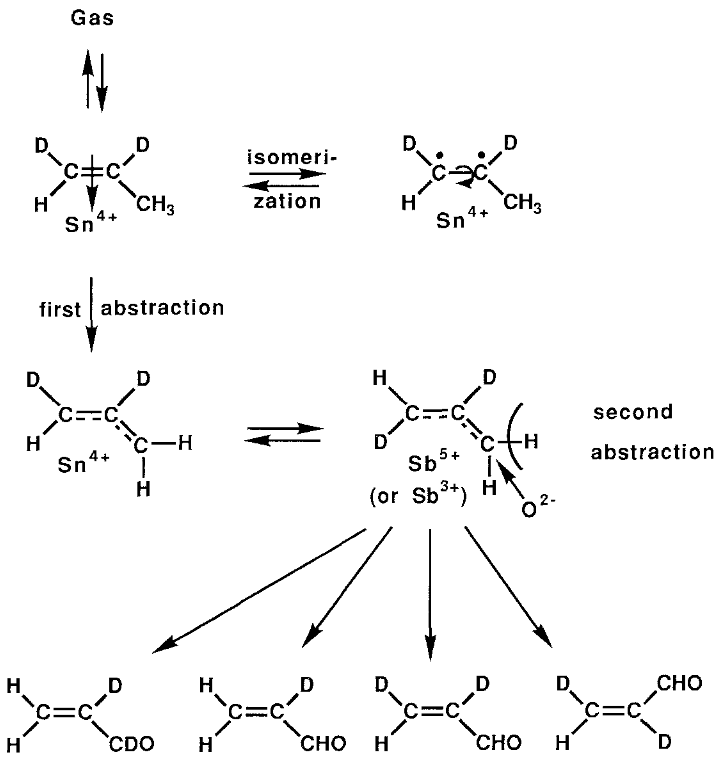
[d] Prepared by method A. See Methods.

interact more readily with propene than antimony ions.

Oxidation mechanism and catalyst composition. Grasselli *et al.* (*6, 17, 18*) have proposed that Sb^{3+}–O and Sb^{5+}–O moieties are responsible for π-allyl formation and oxygen insertion, respectively. Volta *et al.* (*19*) proposed that the surface Sb^{3+}–Sb^{5+} couples produced on SnO_2 which contains Sb ions as a solid solution are responsible for partial oxidation. McAteer (*20*) suggested that acidic sites (Sn^{4+}) and basic sites (Sb^{3+}) are necessary for butene oxidation. A similar model has also been proposed by Berry (*21*).

As reported previously, lattice oxygen is responsible for the propene oxidation over Sb–Sn oxide catalysts (*9, 22, 23*). Ono *et al.* (*9*) have analyzed the kinetic results using a simple redox mechanism as shown in Table 7. With Sb_6O_{13}, the oxidation is first order in propene while with Sb–Sn oxide catalysts the order is 0.3–0.5 in both propene and oxygen. The kinetics are drastically changed by the addition of Sn oxides. The rate constants become ca. 1000 times larger for k_1 and 50 times for k_2 in comparison with those on Sb_6O_{13}. Thus, the reduction step (k_1) is greatly promoted by the addition of Sn oxides. According to the results of Table 2, the slow step on a Sb–Sn oxide catalyst is also the hydrogen abstraction from $-CH_3$. The promoter action of this step seems to originate from the presence of Sn ions (Scheme 2). This seems to be supported by the strong interaction between tin ions and propene as evidenced by the *cis–trans* isomerization reaction. As far as the reduction–oxidation mechanism is concerned, the rate for abstraction of the first hydrogen is nearly equal to that for reoxidation by gaseous oxygen on Sb–Sn oxide catalysts.

The second hydrogen abstraction may occur on both Sb and Sn oxide ions. However, the acrolein selectivity will not become high if that step takes place solely on Sn ions. Furthermore, the reaction process on Sb (30)–Sn–O is the same as that on Sb_6O_{13} but different on SnO_2, as evidenced by the oxidation of CH_2=CH–CH_3 and CH_2=CH–CD_3 mixtures (Table 2). Thus, the conversion of the π-allyl species to acrolein seems to take place on Sb ions (Scheme 2). Workers at ICI (*24–26*) have proposed that a highly disordered Sb–Sn–O provides a suitable structure for oxidation reactions and that a favorable surface Sb/Sn ratio is roughly 1/3. Similar results have been found also by Ono *et al.* (*9*) as described in the Introduction. A bifunctional mechanism where both Sb and Sn ions participate seems to be in operation.



SCHEME 2.

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