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Mechanism of 1,1-d_2 Propene Oxidation over Oxide Catalysts

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CD_2CHCH_3 was oxidized over bismuth molybdate, tin–antimony mixed oxides, and supported molybdenum and vanadium oxide catalysts. The deuterium retention is high (>90%) in the recovered propene. Percentage retentions of deuterium in the acrolein agree with literature data when bismuth molybdate is used as catalyst. On Sb–Sn–O and supported Mo and V oxides, no isotope effect is noticed for the abstraction of the second hydrogen from the olefin. The slow step of the reaction may therefore be different for the oxidation of propene on Bi–Mo–O and Sb–Sn–O. The ethanal produced by oxidation of CD_2CHCH_3 contains only minor amounts of deuterium, whatever the catalyst used. It is suggested that partial oxidation of propene to acrolein and C–C bond rupture are parallel reactions which involve different intermediates. Possible mechanisms adapted from organic chemistry are presented to explain these findings.

Catalysts such as bismuth molybdates and tin–antimony mixed oxides are widely used for oxidation of propene to acrolein. Because of the industrial importance of this reaction, the mechanism has received considerable attention. The formation of an allylic intermediate in the reaction has been firmly established (*1–5*). However, the central point concerning the mechanism of C–C bond cleavage, which is responsible for the loss of selectivity, is still obscure. Two hypotheses have been proposed. In the first, propene loses successively two hydrogens and the resulting C_3H_4 species undergoes fragmentation (*6*). In the second, a mechanism proceeding through an electrophilic attack on the C=C bond has been proposed (*7*) and some experimental evidence shows that it can operate on supported metallic iridium (*8*). In homogeneous liquid-phase oxidation, this latter mechanism finds broad experimental support (*9*) and has been favored by organic chemists (*10*).

The initial work by Adams and Jennings (*2*) shows that deuterium retention by propene is high on both bismuth molybdate at 723 K and CuO at 633 K. It appears possible therefore to discriminate between the two mechanisms by oxidizing $CD_2{=}CH{-}CH_3$. If C–C bond breakage occurs at the allylic symmetric intermediate, part of the ethanal formed must be deuterated. By contrast, if the ethanal comes from attack at the double bond, only further exchange can introduce deuterium in the molecule. We tried to apply this idea to oxidation catalysts consisting of bismuth molybdate, tin–antimony mixed oxides, and supported molybdenum and vanadium oxides. The first two catalysts are well known for their high selectivity for acrolein production, while Mo/SiO_2 (*11*) and V/SiO_2 (*12*) give fairly good selectivities for ethanal.

EXPERIMENTAL METHODS

Catalysts. A bismuth molybdate sample of composition $2MoO_3–Bi_2O_3$ was prepared by precipitation. After calcination at 723 K its surface area was 4.3 m^2/g. The tin–antimony mixed oxide was characterized by the atomic ratio Sb/Sb + Sn = 0.4. It was prepared by coprecipitation of the chlorides at pH 7. After calcination at 1023 K its surface area was 34 m^2/g.

Supported molybdenum and vanadium

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catalysts were obtained by reacting a solution of $MoCl_5$ or VCl_4 in chloroform with silica or alumina using a procedure first proposed by Chien (*13*). The Mo/SiO_2 sample had a molybdenum content of 2.5 wt% and a surface area of 210 m^2/g. The V/SiO_2 sample contained 0.12 wt% V and its surface area was 180 m^2/g. The silica used as support was a nonporous aerosil from Degussa. The V/Al_2O_3 sample consisted of 0.24 wt% V supported on a 44-m^2/g γ-alumina support. These catalysts were calcined at 723 K in air before use.

Reactants. The labeled propene CD_2CHCH_3 was purchased from Merck, Sharp and Dohme, Canada. The isotopic purity stated by the manufacturer is 98% d_2, and good agreement was found with the mass spectrometric determination performed on the sample. Light propene was purchased from Air Liquide and consisted of 99% C_3H_6. Oxygen and nitrogen from Air Liquide have a purity better than 99.99%.

Procedure. Catalytic experiments were performed using a classical single-pass flow reactor operated at 20–30% conversion. The influence of contact time shows that the rates may still be considered as initial rates, and the selectivities therefore represent initial selectivities.

Comparisons of activities and selectivities were made at standard conditions. A mixture of olefin 90 Torr (1 Torr = 133.3 N m^{-2}), oxygen 90 Torr and nitrogen 570 Torr was stocked in a vessel and circulated over the catalyst bed at a constant flow rate of 20 $cm^3\ min^{-1}$ by a gas-tight circulation pump. The weight of catalyst and the temperature of reaction were adjusted to obtain similar conversions with all the samples investigated.

The labeled propene was introduced by the same procedure, replacing C_3H_6 by the desired reactant. On-line gas chromatographic analysis of the products has been described previously (*11*).

The gases issuing from the reaction were condensed in a trap maintained at 173 K. A significant amount of products could therefore be recovered. The individual products were separated by preparative gas chromatography and collected in NMR tubes filled with $CDCl_3$. These fractions were then analyzed by high-resolution NMR using a XL100 Varian spectrometer. Accumulation allowed well-resolved spectra to be obtained, from which it was possible to deduce the location of deuterium in the molecule.

In some cases, mass spectrometric analysis was employed, using a VG Micromass 70–70F mass spectrometer coupled with a gas-chromatographic separation. The distribution of deuterium in the recovered propene was estimated using the known modes of fragmentation of that molecule. Raw experimental data were corrected for naturally occurring heavy isotopes and for fragmentation according to the method described by Dowie *et al.* (*14*). The reliability of the fragmentation corrections was confirmed by the accuracy with which the fragment peak heights were corrected to zero.

RESULTS

The distribution of products is the same for both labeled and unlabeled propenes on the catalysts investigated and is consistent with literature data. The rates and selectivities for the conversion of propene to acrolein and ethanal are listed in Table 1. As expected, bismuth molybdate and tin–antimony oxides are fairly selective for acrolein, while silica-supported molybdenum and vanadium are fairly selective for ethanal. From these data, only moderate kinetic isotopic effects are noticed. The influence of the partial pressure of oxygen and olefin shows a reaction order close to zero for oxygen and close to one for propene for all the catalysts in the pressure range used here.

The deuterium content of the recovered propene, as obtained from mass spectrometry, is reported in Table 2. The location of deuterium in acrolein and ethanal was de-

TABLE 1

Activities and Selectivities for Propene Oxidation

Catalyst	Temp (°K)	Reactant	Rate of formation[a]		Selectivity (%)		k_H/k_D	
			Acrolein	Ethanal	Acrolein	Ethanal	Acrolein	Ethanal
Sb–Sn–O	688	C_3H_6	6.0	0.73	70	8	0.94	0.92
	688	CD_2CHCH_3	6.4	0.79	74	9		
Mo–Bi–O	678	C_3H_6	35.0	3.5	80	8	1.13	0.83
	678	CD_2CHCH_3	31.1	4.2	71	10		
Mo/SiO$_2$	688	C_3H_6	0.044	0.099	16	36	1.00	1.01
	688	CD_2CHCH_3	0.044	0.098	16	36		
V/SiO$_2$	688	C_3H_6	0.032	0.028	16	14	0.94	1.08
	688	CD_2CHCH_3	0.034	0.026	14	11		
V/AlO$_3$	683	C_3H_6	0.24	0.037	5	1	1.14	0.95
	683	CD_2CHCH_3	0.21	0.039	4	1		

[a] In 10^8 moles sec^{-1} m^{-2}.

termined by NMR by comparing the spectrum of normal compounds with that of the acrolein and ethanal produced in the reaction. The relative intensities of the peaks of the hydrogens in the CHO group and in the methyl and vinyl groups were also compared. The compositions of acrolein and ethanal thus obtained are listed in Tables 3 and 4. Two facts appear clearly:

(i) as expected, deuterium exchange in propene is small, as is necessary for a successful experiment;

(ii) the deuterium content of acetaldehyde remains low.

It was also verified by NMR analysis of the oxidation products of C_3H_6 in the presence of D_2O that the acrolein and ethanal produced in this reaction contained no deuterium, and thus that the heavy water produced in the reaction does not appreciably influence the results.

TABLE 2

Deuterium Content of Propene after Reaction

Catalyst	Recovered propene (%)					
	d_0	d_1	d_2	d_3	d_4	d_5
Mo–Bi–O	6	0	92	2	0	0
Sb–Sn–O	1	0	98	1	0	0
Mo/SiO$_2$	9	1	89	1	0	0
	1	3	96	0	0	0
V/SiO$_2$	8	0	90	2	0	0
V/Al$_2$O$_3$	0	1	97	2	0	0

The oxidation of acrolein on these catalysts is rather slow. Separate experiments show that the conversion to ethanal can be estimated to be less than 5% on Mo- and V-supported catalysts. On Sb–Sn–O, acrolein oxidation yields mainly CO_2 and only traces of ethanal. A similar behavior has been reported for acrolein oxidation on bismuth molybdate (*15*).

DISCUSSION

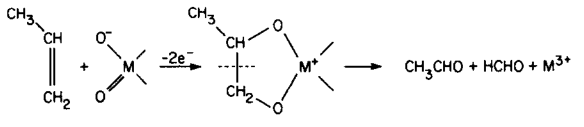
The results concerning the deuterium exchange in propene are consistent with literature data (*2*) since they show that the exchange remains low. Propene is more exchanged on Mo/SiO$_2$ than on Bi–Mo–O or Sb–Sn–O. This may be related to a higher acidity of the former solid since an acidic mechanism could account for the easy exchange of the hydrogen at the CH position yielding d_3 and d_1 propenes from the d_2 reactant.

The lack of a kinetic isotope effect was expected since the initial attack concerns the methyl group. The magnitude of the isotope effect for the abstraction of the second hydrogen can be estimated from the distribution of deuterium in the acroleins produced in the reaction. We can compare the amounts of acrolein CDO and CHO listed in Table 3. The probability of breaking a CH bond rather than a CD bond in the allyl intermediate, which represents this isotope effect, is reflected in the ratio CHO/CDO = k_H/k_D. It appears then that a clear isotope effect is observed on bismuth molybdate, as previously reported by Adams and Jennings (2). The magnitude of this effect $k_H/k_D = 1.63$ is in reasonable agreement with their value of 1.8. However, Bi–Mo–O appears to be a particular case among the catalysts investigated here since the other values are much lower and close to unity. The absence of any isotope effect for the abstraction of the second hydrogen has been previously reported by Cant and Hall (16) for the oxidation of propene over silica-supported rhodium, and was interpreted by the introduction of oxygen into the olefin prior to hydrogen abstraction. The present results suggest that the slow step might not be the same on bismuth molybdate and tin–antimony oxides: on Bi–Mo–O, the abstraction of the second hydrogen would occur before oxygen incorporation, but the reverse would be true on Sb–Sn–O. These differences in the reaction mechanism may be connected with differences in the reducibility of the oxides which would control the relative rates of oxygen incorporation and hydrogen abstraction.

The main objective of this work was to investigate the mechanism of ethanal formation. On that point, NMR gives clear-cut results since all experiments yield ethanal with small deuterium incorporation from the oxidation of CD_2CHCH_3. The absence of any isotope effect ($k_h/k_D = 1$) implies that no CH bond is broken in the slow step of ethanal formation.

The absence of deuterium incorporation in ethanal demonstrates that, in the case of propene, cleavage cannot occur through an allylic symmetric intermediate; therefore selective oxidation of acrolein and C–C bond breakage are parallel reactions at low conversion. At high conversion, successive oxidation of acrolein may occur, but the attack at the double bond, evidenced by Cant and Hall (8) on supported iridium, must be taken into consideration to explain the initial selectivity. It may be pointed out that gas-phase reactions would preferentially consist in oxidation of the methyl group (6) and appear therefore less probable.

A mechanism similar to that proposed for liquid-phase oxidation of alkenes by oxo compounds may be proposed:



Under the conditions of the catalytic reaction, formaldehyde is readily oxidized to CO_2 as well as some of the ethanal. Such a mechanism is in fair agreement with experimental observations since it implies no C–H bond rupture and preserves the identity of the CH_2 moiety.

Ammoxidation of [3-^{13}C]propene on bismuth molybdate yields acetonitrile containing comparable amounts of ^{13}C in the methyl and cyano groups (17), which was interpreted as bond rupture in the allylic intermediate rather than from a breakage in the C=C bond of propene or acrylonitrile. A significant difference would then appear in the mechanism leading to a loss of selectivity between oxidation and ammoxidation. However, it must be taken into account that propene can undergo some isomerization, which was estimated as 15%

TABLE 3

Forms of Acrolein as Determined by NMR

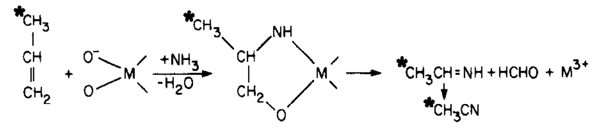
Catalyst	Acrolein (%)	
	$CH_2{=}CH{-}CDO$	$CD_2{=}CH{-}CHO$
Mo-Bi-O	38	62
Sb-Sn-O	51	49
Mo/SiO_2	50	50
	49	51
V/SiO_2	48	52
V/Al_2O_3	53	47

TABLE 4

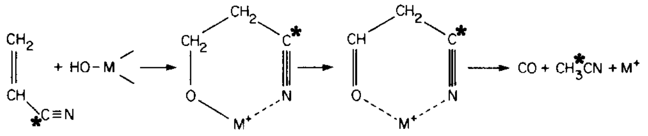
Distribution of Deuterium in the Acetaldehyde Produced by Oxidation of CD_2CHCH_3

Catalyst	Acetaldehyde (%)	
	CH_3CHO	CH_3CDO
Mo-Bi-O	100	—
Sb-Sn-O	90	10
Mo/SiO_2	100	—
	85	15
V/SiO_2	95	5
V/Al_2O_3	88	12

on bismuth molybdate at 723 K (*3*). The observed distribution of ^{13}C could also be accounted for if we assume that acetonitrile is formed by the two paths proposed by Weiss *et al.* (*7*):



from propene[2] and



from acrylonitrile. These reactions have experimental support based on known organic chemistry and can explain the observed labeling of the carbon atoms: it is sufficient to assume that half of the acetonitrile comes from the second reaction if the exchange between terminal carbons is neglected.

This second reaction may be considered at the high conversion (50%) used by Dozono *et al.* (*17*). It is minimized at the lower conversions used here. The disagreement between the present and previous results, therefore, probably lies in the experimental conditions used for the reaction.

In conclusion, the oxidation of CD_2CHCH_3 gives some support to the idea that selectivity for acrolein formation at low conversion is mainly determined by the initial attack on the olefin. This is only partially true for ammoxidation, in which the successive cleavage of acrylonitrile can occur. It must be kept in mind that, at high conversion, heterogeneous or even homogeneous phase oxidation of the products may play a role and decrease the final selectivity.

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[2] Sharpless *et al.* (*18*) have proposed a similar intermediate for vicinal oxamination of olefins by oxo-osmium compounds.

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