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The Ammoxidation of Propylene and Isobutene over a Tin–Vanadium–Phosphorus Oxide Catalyst

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Studies have been made of the ammoxidation of propylene and isobutene over a tin oxide–vanadia–phosphorus oxide catalyst. Values of the kinetic parameters based on initial rates are reported for the ammoxidation of the olefins to unsaturated nitriles and to other products. The results are consistent with a mechanism in which the abstraction of an allylic hydrogen from the adsorbed olefins by adsorbed peroxy species is rate determining. The reaction is suggested to occur at Sn^{4+} surface sites from which electron transfer to neighboring vanadium ions is possible.

INTRODUCTION

Studies of the catalytic oxidation of olefins in the presence of ammonia (ammoxidation) have been focused mainly on the reactions of propylene over urania-antimony oxide (*1,2*) or over bismuth molybdate (*3,4*) to reveal many similarities with catalytic oxidation. Over bismuth molybdate, for example, the initial formation of an allylic intermediate is rate determining in both cases, being followed by rapid reactions to yield acrolein (oxidation) or acrylonitrile (ammoxidation). However, the nature of these rapid reactions is still open to doubt. There is good evidence that acrolein reacts readily to produce acrylonitrile (*4,6*), but Seeboth and Heyner (*7*) have concluded that acrylonitrile may also be produced by other routes, involving amine or aldehyde–imine intermediates.

There is also considerable interest in the patent literature in the ammoxidation of isobutene, and a variety of catalysts have been reported (*8–10*). Of these, a combination of tin, vanadium and phosphorus oxides has been reported to be active and selective for the ammoxidation of propylene and isobutene to unsaturated nitriles (*10*). The present studies were initiated to study the kinetics and mechanism of the ammoxidation of these two olefins over this catalyst.

EXPERIMENTAL METHODS

The ammoxidation of propylene and isobutene was studied using a flow system in which a mixture of olefin, oxygen, ammonia, additive and diluent could be passed through a reactor containing between 1 and 10 g of catalyst. Liquid additives were injected into the gas stream at an evaporator by means of a peristaltic pump capable of low flows. The use of a heated mixer minimized pulsations, and the composition and reproducibility of the feed could be estimated by on-line gas chromatography. The gases were passed through a 5 mm i.d. quartz reactor containing the catalyst: measurement of the temperature in the bed confirmed that a constant temperature tin bath maintained the catalyst bed under isothermal conditions (±0.3°C). The effluent gases were then passed through a heated gas sampling valve to a

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trapping system, where hydrogen cyanide and organic nitriles were removed.

Analysis of the reactants and products was completed gas chromatographically, using a Servomex microkatharometer detector associated with three columns arranged in parallel. Permanent gases were separated on a molecular sieve 13X column (30–60 mesh: 10 ft: 20°C). Carbon dioxide, ethylene, propylene and isobutene were separated on a 25 ft column packed with 80–100 mesh Chromosorb P impregnated with 13.5:6.5% bismethoxy ethyl adipate:diethyl hexyl sebacate (20°C). Ammonia, water, hydrogen cyanide, acetonitrile, acrolein, acrylonitrile, methacrolein and methacrylonitrile were separated on Porapak Q (50--80 mesh; 9.5 ft; 135°C), although HCN interfered with the tail of the water peak. Analyses were confirmed on alternative columns and by mass spectrometry. Calibration involved the injection of known amounts of the products: hydrogen cyanide could not be calibrated, and values of peak height on the chromatograph were used to obtain comparative amounts.

Gaseous reactants and products were obtained in the highest available purity from B.O.C. (usually >99%). Liquids, and materials for catalyst preparation, were obtained from B.D.H. Sufficient catalyst was prepared by the method of Sennewald *et al.* (*10*) to allow the use of the same batch throughout the studies. The silica supported vanadium–tin–phosphorus oxide catalyst contained 0.6 wt% V_2O_5, 9.5 wt% SnO_2, 1.7 wt% P_2O_5 and 88.2 wt% SiO_2, corresponding to an atomic ratio of V:Sn:P = 1:9:3.

Samples of fresh and used catalyst gave X-ray diffraction patterns corresponding to the cassiterite, SnO_2, structure. The solid had a bulk density of 0.30 g ml^{-1}, and a specific surface area of 163 m^2 g^{-1}.

The temperature variation across the catalyst bed under reaction conditions was found to be less than 0.2°C. Experiments were carried out at constant contact time, using varying flow rates of identical feed composition. For both propylene and isobutene ammoxidation, the conversions obtained were independent of flow rate, showing that gas phase diffusion was not important. Catalytic activities were also measured using the same amount of catalyst ground to various mesh sizes. No variation could be observed with catalyst of mesh size greater than 10, showing pore diffusion to be unimportant. All subsequent experiments were completed with 20–40 mesh catalyst.

Optimal conditions were established by measuring conversion (defined as the moles of reactant consumed per mole of reactant fed $\times 100\%$) and selectivity (defined as the moles of product per mole of reactant consumed $\times 100\%/\alpha$, where α is the ratio of the number of carbon atoms in the reactant to the number of carbon atoms in the product). Product yields were measured as a function of contact time, defined as the weight of catalyst per unit flow rate (corrected to 25°C), in order to establish the kinetics.

RESULTS

Preliminary experiments showed that the activity of the catalyst dropped by about 5% of the initial value during the first 2 hr of use and thereafter remained constant. No homogeneous reactions could be detected in the absence of catalyst or in the exit lines of the reactor. Gas film diffusion did not affect the kinetics of reaction at the flow rates used.

The ammoxidation of propylene led to the production of acrylonitrile, acetonitrile, acrolein, carbon monoxide, carbon dioxide, nitrogen, hydrogen cyanide and water. The yields of acrylonitrile and acetonitrile were highest at a temperature of ca. 520°C, contact time of ca. 230 g sec $liter^{-1}$ and an oxygen:propylene:ammonia ratio of 2:1:1.75, at which point the yield of acrylonitrile was ca. 35% of the propyl-

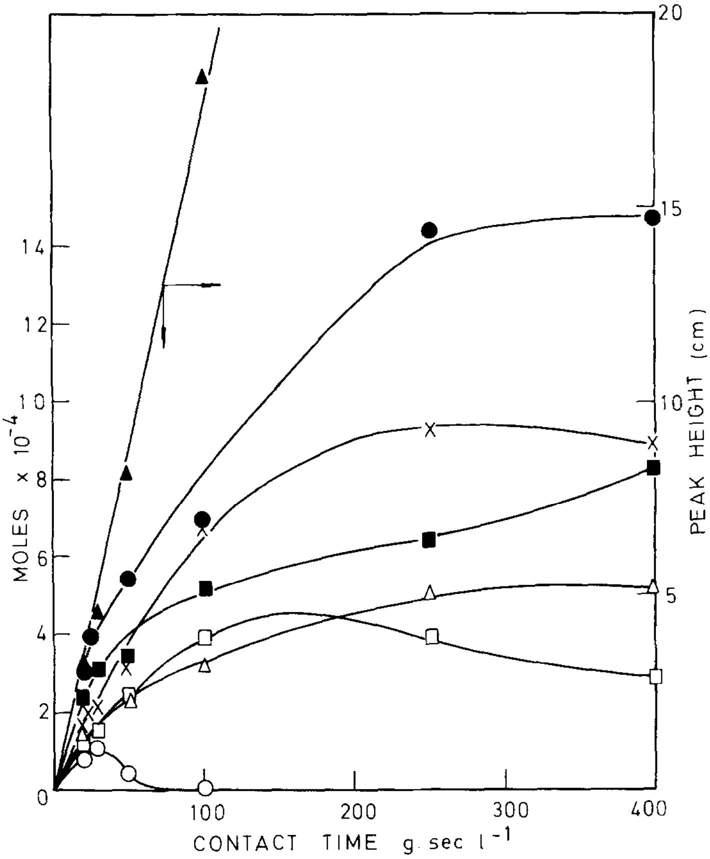

FIG. 1. Products of ammoxidation of propylene as a function of contact time. $(O_2) = (NH_3) = 6.3 \times 10^{-3}$ mol liter^{-1}; $(C_3H_6) = 2.4 \times 10^{-4}$; $T = 550°C$; (x) acrylonitrile; (□) acetonitrile; (○) acrolein; (■) N_2; (●) CO; (△) CO_2; (▲) HCN.

ene fed (ca. 75% on propylene consumed) and that of acetonitrile was ca. 15% of propylene fed.

The kinetics of the ammoxidation of propylene were then examined, using these approximate optima as a guide. Typical plots of yield of products vs contact time are shown in Fig. 1. The dependence of initial rate upon the concentration of reagents was determined by varying the concentration of one reagent in the presence of large and constant concentrations of the others. Plots of log (initial rate) vs log (concentration) gave good straight lines, and the reaction orders obtained by linear least squares analysis are summarized in Table 1, together with the ranges over which they were measured. Activation energies, es-

TABLE 1

KINETIC PARAMETERS FOR THE AMMOXIDATION OF PROPYLENE[a]

Reaction	Orders[b] (±0.02)			Pre-exponential factor	E_A (±0.2 kcal/mol)
	C_3H_6	O_2	NH_3		
Loss of propylene	1.15	1.00	−0.09	2.9×10^8	31.0
1	1.04	0.62	0	1.1×10^7	30.0
2	1.50	0.43	−0.03	1.0×10^6	24.0
3[c]	1.32	0.62	0.43	—	28.0
4	1.89	1.17	−0.20	3.0×10^{12}	40.0
5	1.00	0.77	−0.37	9.7×10^7	37.0
6	0.70	0.41	−0.43	2.1×10^4	29.0

[a] $$\text{propylene} + \text{oxygen} + \text{ammonia} \rightarrow \begin{cases} \text{acrylonitrile} & 1 \\ \text{acetonitrile} & 2 \\ \text{hydrogen cyanide} & 3 \\ \text{carbon monoxide} & 4 \\ \text{carbon dioxide} & 5 \\ \text{nitrogen} & 6 \end{cases}$$

[b] Obtained by varying the concentration of the reagent between 1×10^{-3} and 10×10^{-3} mol liter^{-1} in the presence of an excess of other reagents.

[c] Obtained from chromatographic peak heights.

timated from similar data obtained for the range 480–550°C, are also presented.

Similar experiments were carried out with isobutene. The products of reaction included methacrylonitrile, methacrolein, acetonitrile, carbon monoxide, carbon dioxide, nitrogen, hydrogen cyanide and water. Optimal conditions for the production of methacrylonitrile and methacrolein were found to lie at a temperature of ca. 520°C, contact time ca. 120 g sec liter^{-1} and an oxygen:isobutene:ammonia ratio of 2.5:1:1.2, at which point the yield of the two products was ca. 25% based on isobutene fed (ca. 80% on isobutene consumed).

The kinetics of the ammoxidation of isobutene were then examined as before. A typical product–contact time plot is shown in Fig. 2, and graphs of this type were used to determined the reaction orders reported in Table 2: the range over which the oxygen dependence was determined was limited by the fact that low yields and catalyst deactivation were observed at low oxygen concentrations. Activation energies, also reported in Table 2, were measured for the range 480–550°C.

TABLE 2

KINETIC PARAMETERS FOR THE AMMOXIDATION OF ISOBUTENE[a]

Reaction	Orders[b] (±0.02)			Pre-exponential factor	E_A (±0.5 kcal/mol)
	C_4H_8	O_2	NH_3		
Loss of isobutene	1.00	1.04	0	2.8×10^5	18.0
7	0.51	0.97	0	3.1×10^4	21.0
8	0.54	1.03	0.39	1.2×10^4	16.0
9[c]	1.53	0.27	0.50	—	22.0
10	1.16	1.06	−0.41	3.8×10^8	32.0
11	1.46	0.73	−0.34	1.1×10^7	27.0
12	0	0.83	0.38	3.0×10^2	18.0

[a] $$\text{isobutene} + \text{oxygen} + \text{ammonia} \rightarrow \left\{ \begin{array}{lr} \text{methacrolein} & \\ \quad + \text{methacrylonitrile} & 7 \\ \text{acetonitrile} & 8 \\ \text{hydrogen cyanide} & 9 \\ \text{carbon monoxide} & 10 \\ \text{carbon dioxide} & 11 \\ \text{nitrogen} & 12 \end{array} \right.$$

[b] Obtained by varying the concentration of one reagent between 1×10^{-3} and 10×10^{-3} mol liter^{-1} in the presence of an excess of other reagents.

[c] Obtained from chromatographic peak heights.

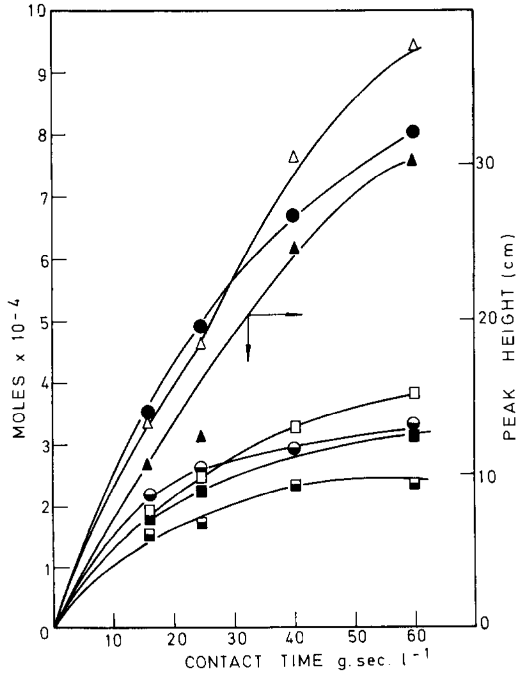

FIG. 2. Products of the ammoxidation of isobutene as a function of contact time. (O_2) = 5.3×10^{-3} mol liter^{-1}; (NH_3) = 6.55×10^{-3} mol liter^{-1}; (C_4H_8) = 3.8×10^{-3} mol liter^{-1}; T = 520°C; (⊖) methacrylonitrile; (⬓) methacrolein; (□) acetonitrile; (●) CO; (△) CO_2; (■) N_2; (▲) HCN.

In both cases, ammoxidation of the olefins in the presence of added products led to no inhibition of the reaction. The addition of nitriles to the oxidizing reagents led to slightly higher yields of hydrogen cyanide. The addition of aldehydes led to increases in the yields of all products except nitrogen: although the mass balances were complicated by polymerization of products, the ammoxidation of the olefins appeared to proceed at the same rate as was observed in the absence of added aldehyde. The absence of product inhibition was confirmed by computer integration of the initial rate laws, which gave good agreement with experimental results at longer contact time: overoxidation of some products in the experimental system was observed (see below).

Experiments were carried out to compare the oxidation, ammoxidation and ammonolysis (reaction with ammonia in the

TABLE 3

COMPARISON OF THE OXIDATION, AMMOXIDATION AND AMMONOLYSIS OF PROPYLENE AND ACROLEIN[a]

Reaction	RH initial ($\times 10^{-4}$)	RH : O_2 : NH_3	RH out ($\times 10^{-4}$)	C_3H_4O ($\times 10^{-4}$)	C_3H_3N ($\times 10^{-4}$)	C_2H_3N ($\times 10^{-4}$)	CO ($\times 10^{-4}$)	CO_2 ($\times 10^{-4}$)	N_2 ($\times 10^{-4}$)	HCN (cm)
Propylene ammoxidation	27.0	1 : 1.75 : 1.8	21.4	0.5	2.5	1.7	2.2	0.9	2.2	6.0
oxidation[b]	27.0	1 : 1.75 : 0	20.4	3.1	—	—	7.4	3.6	—	—
ammonolysis	27.0	1 : 0 : 1.8	26.8	—	Tr	Tr	—	—	0.2	—
Acrolein ammoxidation	11.1	1 : 4 : 4.9	—	1.6	6.6	0.7	5.6	1.9	1.6	17.9
ammonolysis[b]	11.1	1 : 0 : 2.8	—	8.8	1.9	Tr	0.6	0.3	0.1	2.7

[a] $T = 550°C$; contact time, 21.7 g sec liter^{-1}; all units in mol/liter.

[b] Acetaldehyde also produced.

absence of oxygen) of olefins and aldehydes. Typical results are summarized in Table 3: the rate of oxidation is about the same as the rate of ammoxidation and is faster than ammonolysis.

Acrylonitrile was stable to further reaction but methacrylonitrile breaks down fairly slowly to give acetonitrile, CO_2, HCN and N_2. Acrolein reacts readily to form other products, but methacrolein was more stable. Thus, for example, acrolein ammoxidizes readily to produce acrylonitrile (60% at a contact time of 22 g sec liter^{-1}) while methacrylonitrile is produced more slowly from methacrolein (51% at 40 g sec liter^{-1}). On the assumption that most of the nitriles originate from the aldehydes (see below) kinetic comparisons were drawn by combining the yields of methacrolein and methacrylonitrile.

An approximate calibration of the hydrogen cyanide was used to obtain mass balances. With the exception of experiments in the presence of added aldehydes, in which severe polymerization occurred, these mass balances were accurate to within experimental error.

DISCUSSION

Products of the ammoxidation of propylene and isobutene are found to be similar in type, the formation of unsaturated aldehydes and nitriles being accompanied by the production of hydrogen cyanide, carbon oxides and nitrogen (Figs. 1 and 2). The reactions are quite selective; kinetic expressions based on initial rates are summarized in Tables 1 and 2. The reactions were not inhibited by products, although secondary reactions of aldehydes and nitriles were observed.

The retention of the double bond in the aldehyde and nitrile products, and the fact that hydrogen atoms originally in the allylic position are removed to form nitriles, suggests that allylic oxidation is involved in the reaction mechanism. If such a reaction is rate controlling, then the rate of production of aldehydes and nitriles should be comparable with other systems involving allylic hydrogen abstraction. Data are available for the rate of abstraction of allylic hydrogen from olefins by methyl radicals in isooctane solution (*11*) and for the oxidation of olefins over bismuth molybdate, which is rate-controlled by the removal of allylic hydrogen (*4,6,18*). Comparisons are made with the present results in Table 4: relative reactivities were calculated on the basis of the initial rate equations summarized in Tables 1 and 2. Bearing in mind the disparity of the systems and the limited comparison, the agreement is good and supports the suggestion that the abstraction of allylic hydrogen from the olefins is rate determining in ammoxidation over the tin–vanadium–phosphorus oxide catalyst.

Consideration of the proposed reaction mechanism, in conjunction with the in-

TABLE 4

RELATIVE REACTIVITIES OF ALLYLIC HYDROGEN ATOMS

Reactant	No. of primary allylic H atoms	Reactivity per H atom		
		This system 520°C	1[a] 460°C	2 65°C
Propylene	3	0.07	0.07	0.07
Isobutene	6	0.17	0.17	0.17

[a] 1 = oxidation over bismuth molybdate (*18*); 2 = abstraction by Me radicals in isooctane (*11*).

organic chemistry of the catalyst, allows tentative identification of the site of adsorption/reaction. Allylic oxidation requires π-adsorption of the olefin to be followed by hydrogen removal and the transfer of an electron to the catalyst.

$$C_3H_6 + M^{x+} + O^{2-} \rightarrow [C_3H_5\text{-}M]^{x+} + OH^- + e.$$

There is now good evidence that the selectivity of the subsequent oxidation to acrolein depends on the transferred electron migrating from the adsorption site to a second metal center (*12,13*). To be selective, a catalyst should be capable of π-adsorbing olefins and should offer an easy route for delocalization of the electron. Consideration of the inorganic chemistry of the present catalyst shows that both these requirements may be met. The results indicate that the active phase is a solid solution of vanadia in tin oxide, and ESR studies have shown that the structures of these solid solutions are such that electron transfer from Sn^{4+} to V^{4+} is favored (*14,15*). Since Sn^{4+} can π-adsorb olefins, it seems reasonable to suggest that adsorption/reaction centers about the Sn^{4+} ion, with electron transfer to vanadium ions, located at or near the surface, playing an important role in increasing selectivity.

Some confirmation of the above suggestions was obtained by the application of a Langmuir–Hinshelwood treatment to the kinetic results obtained for the production of acrolein plus acrylonitrile from propylene, and methacrolein plus methacrylonitrile from isobutene. If the extraction of allylic hydrogen is rate determining for the production of the unsaturated aldehydes and nitriles, such application can be expected to give some indication as to the species involved. Theoretical models were generated on the basis of many alternative models, but the only equation that was chemically feasible and which gave predictions that agreed with experimental results was based upon a model involving reaction between adsorbed olefin and adsorbed diatomic oxygen both of which compete for the same site:

$$\frac{dP}{dt} = k\,\frac{K_{RH}C_{RH}K_OC_O}{(1 + K_{RH}C_{RH} + K_OC_O)^2},$$

where P = [acrolein plus acrylonitrile] for propylene and [methacrolein plus methacrylonitrile] for isobutene; k is a rate constant and $K_{RH,O}$ and $C_{RH,O}$ are adsorption coefficients and concentrations of olefin and oxygen, respectively. Values of these constants, obtained from the insertion of experimental initial rate data in the above equation are presented in Table 5.

The fact that the adsorption coefficient for isobutene is higher than that of propylene fits in with the mechanism proposed in that the electron donating tendencies of the extra methyl should result in stronger bonding with the surface for the allylic oxidation route. The prediction that the reactive oxygen species is diatomic and competes for adsorption sites also agrees with the proposed mechanism in that peroxy species, O_2^-, have been identified on the surface of tin dioxide (*16*) and have been

TABLE 5

LANGMUIR–HINSHELWOOD PARAMETERS FOR THE AMMOXIDATION OF OLEFINS

Reactant	T (°C)	k (mol g^{-1} sec^{-1})	K_{RH} (liter mol^{-1})	K_O (liter mol^{-1})
Propylene	550	$1.3 \pm 0.2 \times 10^{-2}$	1.0 ± 0.2	83 ± 2
Isobutene	520	$2.7 \pm 0.2 \times 10^{-3}$	240 ± 5	5.7 ± 0.7

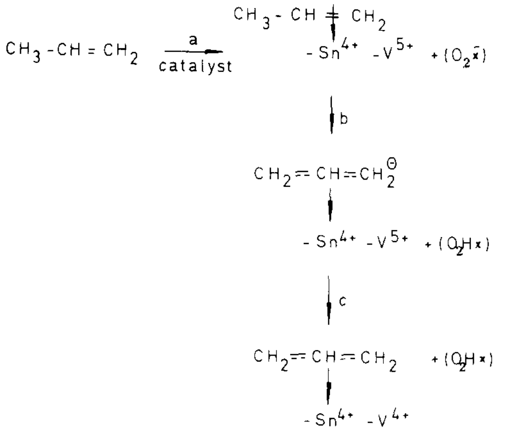

FIG. 3. Sn–V distance in a direction is 3.185 Å (*14*).

suggested to be responsible for the more potent oxidizing capacity of the oxide. Thus the results support and extend a reaction mechanism for the initial stages of ammoxidation, which are summarized as shown in Fig. 3.

The nature of the subsequent fast reaction is much less clear, particularly in that the formation of nitriles has been suggested to involve the further reactions of aldehydes (*6*) and/or of aldehyde–imines (*7*). Comparisons of the oxidation, ammoxidation and ammonolysis of propylene and acrolein (Table 3) show that acrylonitrile could be produced from the ammoxidation of acrolein, but that ammonolysis reactions are unlikely to be important. Acrylonitrile is resistant to secondary oxidation, and at least part of the production of carbon dioxide, hydrogen cyanide and nitrogen would appear to originate from ammoxidation of acrolein.

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