Kinetic Isotope Effect in the Ammoxidation of Propane over an Alumina Supported Vanadium Antimony Oxide Catalyst

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Deuterium labeling experiments indicate that two parallel pathways occur in the ammoxidation of propane over an alumina supported vanadium antimony oxide based catalyst, one in which the rate determining step involves hydrogen abstraction from the secondary carbon and the other in which it involves hydrogen abstraction from a primary carbon. Experiments show that d_0-propane reacts faster than both 2,2-d_2-propane (observed $k_H/k_D = 1.7$) and 1,1,1,3,3,3-d_6-propane (observed $k_H/k_D = 1.1$), indicating that abstraction from the secondary carbon occurs 12–15 times more rapidly than the abstraction from a primary carbon. Scrambling of hydrogen and deuterium in acrylonitrile precluded the use of products in the rate analysis; the percentage of deuterated propane in reacted vs unreacted gas mixtures was used to determine the relative rates of reaction between the propanes used. Two different reaction feed mixtures, one with excess ammonia and oxygen compared to propane and one with excess propane compared to ammonia and oxygen, were used in order to ensure that high selectivities to propylene plus acrylonitrile were achieved and that the most selective pathway, not one leading to waste production, was being observed. © 1996 Academic Press, Inc.

INTRODUCTION

Activation of unsaturated hydrocarbons to produce derivative chemicals has been of both technical and economic interest in recent years. At present, most of these chemicals are made from olefins but substitution with paraffins would result in substantially lower feedstock costs. The challenge of selectively activating paraffins using heterogeneous catalysis stems from the higher C–H bond dissociation energies of lower paraffins as compared to olefins. Despite this energy barrier, much progress has been made in the use of paraffins as feedstocks for production of chemicals as evidenced by the commercialization of the selective oxidation of *n*-butane to maleic anhydride.

Conversion of propane to acrylonitrile offers a potentially economically attractive alternative to acrylonitrile production via propylene ammoxidation because of the exi-sting and projected price differential between propane and propylene. An understanding of the kinetics and mechanism of paraffin oxidation in general and propane ammoxidation in particular is useful in the identification of catalysts and process conditions which will selectively yield acrylonitrile from propane. Despite the usefulness of such investigations, little mechanistic work on the selective ammoxidation of propane has been reported.

An overall kinetic scheme in which the formation of acrylonitrile proceeds via propylene and acrolein intermediates over a gallium antimony oxide catalyst was proposed by Osipova and Sokolovskii (1), but they did not give any kinetic arguments for this mechanism. Minow *et al.* (2) established that acrylonitrile is formed via intermediate propylene over V_2O_5–SiO_2, MoO_3–SiO_2, and Bi_2O_3–MoO_3–SiO_2 catalyst systems by measuring product accumulation as a function of propane conversion. More recently, Centi *et al.* proposed a kinetic scheme in which acrylonitrile is formed both from propane directly and via a propylene intermediate over alumina supported vanadium antimony oxide catalysts (3). None of these reports a reaction mechanism based on isotope labeling.

Several attempts have been made to probe the nature of the initial interaction between propane and selective oxidation catalysts. Osipova and Sokolovskii compared the rates of propane and isobutane ammoxidation over gallium antimonate based catalysts and concluded that hydrogen abstraction as a proton from a primary carbon site to form a carbanion intermediate is the rate determining step in propane ammoxidation (4, 5). Centi and Trifiro concluded that selective oxidation of small paraffins (C_2–C_7) occurs via a concerted mechanism over vanadium phosphate catalysts (6). Neither of these studies directly probed the rate determining step, however. The results from both studies are consistent with more than one possible mechanism.

The present study uses selectively deuterated propanes in order to identify the carbon–hydrogen bonds broken in the rate determining step for propane ammoxidation over an alumina supported vanadium antimony oxide based catalyst which had been identified previously as a selective

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catalyst for the ammoxidation of propane to acrylonitrile (7).

Competitive reactions in which nondeuterated and selectively deuterated propanes are simultaneously reacted are used to eliminate ambiguities regarding catalyst aging and exact ratios of propane to the other reactants. While this method does not allow for direct measurement of rate constants for each of the deuterated propanes, the ratio of each to nondeuterated propane is sufficient for evaluating whether the C–H bond in any given position is broken during the rate determining step.

EXPERIMENTAL

Catalyst Preparation

Preparation of 50% $VSb_{3.5}P_{0.5}WO_x$–50% Al_2O_3 has been described previously (7). Antimony trioxide powder was added to a hot solution of ammonium vanadate in water and the resulting slurry refluxed overnight. Solutions of ammonium meta-tungstate and dibasic ammonium phosphate were added to the solution followed by the addition of a suspension of hydrated alumina (Catapal SB) in water. After partial evaporation, the mixture became too thick to stir. It was transferred to an evaporating dish and dried overnight at $120°C$. The dried material was heat treated at $350°C$ for 5 h, screened to $-20 + 35$ mesh particle size, and then calcined at $610°C$ for 3 h.

Pulse Experiments Using Selectively Deuterated Propanes

Deuterated propanes and propylenes were obtained from MSD Isotopes, Inc., and used without further purification. The purity of these gases (at.% D) is 1,1,1,3,3,3-d_6-propane, 96.9%; 2,2-d_2-propane, 97.5%; d_8-propane, 99.5%; 1,1-d_2-propylene, 99.6%; 2-d_1-propylene, 97.6%; and 3,3,3-d_3-propylene, 99.2%.

The pulse microreactor studies were carried out in an assembly, described previously (8), that allowed measured amounts of reactant gases to flow over the catalyst and then into a gas chromatograph interfaced to a mass spectrometer. For these studies, 0.27–0.28 g (0.27–0.28 cc) of catalyst was placed in a stainless steel microreactor equipped with a preheat leg and heated to $470°C$ in a molten salt bath. Helium was flowed over the catalyst at 24 cc/min and 1.87 cc (measured at $22°C$) of the feed gases were injected into the helium stream. These feed gases consisted of a mixture of mole ratios of either 1 propane/1 NH_3/2 O_2/4 N_2 or 5 propane/1 NH_3/2 O_2. The higher propane feed mixture was used to obtain higher selectivities to acrylonitrile plus propylene, ensuring that the most selective pathway, not one leading to waste production, is being probed. The propane portion of the feed consisted of a mixture of approximately 50% nondeuterated propane and 50% of a deuterated propane. Each pulse was prepared by filling a syringe with the appropriate amount of a selectively deuterated propane and then adding the appropriate amount of a preanalyzed mixture (regulated through mass flow controllers) of nondeuterated propane, ammonia, oxygen, and nitrogen. One-half of each pulse was passed through a blank tube and analyzed to ascertain overall composition and percentage of propane containing deuterium; the other half was passed over the catalyst and analyzed for product distribution and percentage of unreacted propane containing deuterium. Each experiment was repeated at least three times in order to ensure reproducibility.

Analysis of the effluent and feed gases was carried out using a Varian 3700 gas chromatograph equipped with a thermal conductivity detector. The entire pulse was injected onto the columns. The column system consists of a 6 ft $\times$ 1/8″ stainless steel Super Q column in parallel with a set of columns consisting of a 6 ft $\times$ 1/8″ stainless steel mole sieve 13X column (45/60 mesh) in parallel with a 30 ft $\times$ 1/8″ stainless steel column packed with 23% SP-1700 on 80/100 Chromosorb PAW. The flow through each column is 25 cc/min. The Super Q column is inside the Varian 3700 oven and is temperature programmed starting at $100°C$ for 5 min, increasing to $150°C$ at $10°C$/min, and then remaining at $150°C$ for 6 min. The other two columns are in a temperature controlled box outside the Varian 3700 and are run isothermally at $60°C$. Separation and analysis of propane, propylene, acrylonitrile, acrolein, acetonitrile, CO, CO_2, O_2, and N_2 were carried out using this system.

After passing through the thermal conductivity detector, a slipstream of the gas corresponding to the propane retention time was sent to a Hewlett-Packard 5970B mass selective detector. Samples of nondeuterated propane and each of the deuterated propanes were used as standards for the fragmentation patterns for these gases.

Experiments to Test for Hydrogen/Deuterium Scrambling

In order to determine if the deuterium is scrambling with the hydrogen atoms in the propane or the products formed during the ammoxidation of propane, experiments were carried out in which the products and unreacted propane were collected in a cold NMR tube after passing over the catalyst and then analyzed using proton nuclear magnetic resonance spectroscopy. Selectively deuterated propylene was also passed over the catalyst and collected for NMR analysis to determine the extent of scrambling in this product. Both dry ice/cyclohexanone baths and liquid nitrogen were used to cool the cold finger because when liquid nitrogen was used acrylonitrile appeared to freeze in the needle directing the products into the NMR tube and was not observed in the NMR spectra.

The products collected were dissolved in deuterated chloroform. Proton NMR spectra were obtained on a Varian Associates VXR-400 using a $90°$ pulse and a 15-s delay.

RESULTS

NMR Experiments

When 2,2-d_2-propane is fed over the catalyst, deuterium in the acrylonitrile appears to have scrambled to all the carbon sites. No scrambling is observed in the propane or propylene, however. An accurate integration for the protons on the methyl group of propylene could not be obtained because of the presence of peaks from the protons in water (a by-product of the reaction) in the same area of the NMR spectrum. Coupling of protons, or the lack thereof, is used to determine if protons are present in all of the positions of the propane, propylene, and acrylonitrile.

When deuterated propylenes are fed over the catalyst (2-d_1-, 3,3,3-d_3-, or 1,1-d_2-propylene) no scrambling between the C_2 position and the C_1 or C_3 positions is observed for propylene. Scrambling between the C_1 and C_3 positions does occur. However, the acrylonitrile formed exhibits complete scrambling in each case.

Pulse Experiments

Table 1 shows the propane conversion and propylene and acrylonitrile selectivities obtained under each of the conditions described under Experimental. In each case, a high selectivity to propylene plus acrylonitrile was desired since these represent selective products. Under low propane feed conditions, higher selectivity to propylene is observed for 2,2-d_2-propane than for the propanes containing deuterium on primary carbons. Acrylonitrile selectivity is the same for all of the propane samples. Carbon balances were between 96 and 102%.

Calculations

Matrix algebra was used to determine the percentage of the propane which is nondeuterated and deuterated in both the feed gas and the effluent gas mixtures. In each case, four m/e values from the mass spectrum were used in the calculation, two of which are large for nondeuterated propane and small for the deuterated propane and two of which are large for the deuterated propane and small for the nondeuterated propane. The specific values used were $m/e = 40$, 41, 43, and 46 for the mix with $C_3H_6D_2$, $m/e = 39$, 42, 44, and 49 for the mix with $C_3H_6D_2$, and $m/e = 39$, 42, 44, and 52 for the mix with C_3D_8. From these results in combination with the total propane conversion obtained from gas chromatography, the fractional conversions of the nondeuterated and deuterated propanes were determined.

Because scrambling was observed in the acrylonitrile, products could not be used to determine the extent of nondeuterated vs deuterated propane conversion. However, no scrambling was observed in the unreacted propane after passing over the catalyst. Propane conversion was therefore calculated by subtracting the moles of propane in the effluent (determined by gas chromatography) from the moles of propane in the feed. Since the fraction of propane which was deuterated is known for both the feed gas mixture and the effluent mixture, the fractional conversion of nondeuterated propane and deuterated propane could be determined.

Rate constants for the reactions of nondeuterated and deuterated propanes were calculated using the equation $k_{propane} = -\ln(1 - \text{fractional conversion}_{propane})/\text{contact time}$. The assumption of a plug flow reactor model implied by this equation is justified by the large ratio (17–17.5) of pulse size at reaction temperature to the size of the catalyst bed. Since ratios of rate constants for only simultaneously reacted propanes are calculated, the assumption of pseudo-first-order is appropriate. Other factors in the rate equation will appear in both the numerator and the denominator of the ratio, canceling each other out. The assumption that fractional conversion is equal to the rate constant is not used in this case because the conversions are too high for this to be a good approximation. The ratios of the rate constants (k_H/k_D) are given in Table 2. The theoretical values of k_H/k_D assuming hydrogen abstraction from either primary or secondary carbons, calculated using

$$\frac{k_H}{k_D} = \exp\left\{ \frac{hc}{2kT} \left(\bar{\nu}_{k_H} - \bar{\nu}_{k_D} \right) \right\},$$

where c is the velocity of light, and $\bar{\nu}$ is the wavenumber (9) of the stretching frequency of the bond assumed to be broken (10, 11), are also given in Table 2.

DISCUSSION

As seen in Table 2, a deuterium isotope effect is observed for both 2,2-d_2-propane and 1,1,1,3,3,3-d_6-propane. Although the k_H/k_D of 1.7 for 2,2-d_2-propane is clearly significant, the k_H/k_D of 1.1 for 1,1,1,3,3,3-d_6-propane cannot be treated as insignificant. The C–H bond energies are 98 and 95 kcal mol^{-1}, respectively, for the primary and

TABLE 1

Distribution of Selective Products in Pulse Experiments

Feed gas composition	Deuterated propane fed	% Propane conversion	% Acrylo-nitrile selectivity	% Propylene selectivity
Low propane	2,2-d_2-propane	30–32	24–26	20–28
	1,1,1,3,3,3,-d_6-propane	35–45	27–30	8–11
	C_3D_8	32–33	30–32	8–11
High propane	2,2-d_2-propane	18–22	3–9	54–60
	1,1,1,3,3,3,-d_6-propane	25–28	4–6	40–53
	C_3D_8	18–20	4–6	53–59

Note. Low propane, mole ratio of 1 hydrocarbon/2 NH$_3$/3 O$_2$/6.6 N$_2$/3 H$_2$O. High propane, mole ratio of 5 hydrocarbon/1 NH$_3$/2 O$_2$/1 H$_2$O.

TABLE 2

Relative Rates of Deuterated and Nondeuterated Propane

Deuterated propane used	k_H/k_D experiment	Theoretical k_H/k_D for abstraction from	
		Primary carbon	Secondary carbon
2,2,-d_2			
Low propane	1.7	0.99	2.02
High propane	1.7		
1,1,1,3,3,3,-d_6			
Low propane	1.1	2.04	0.98
High propane	1.1		
C_3D_8			
Low propane	2.0	2.04	2.03
High propane	2.4		

Note. Low propane, mole ratio of 1 hydrocarbon/2 NH$_3$/3 O$_2$/6.6 N$_2$/3 H$_2$O. High propane, mole ratio of 5 hydrocarbon/1 NH$_3$/2 O$_x$/1 H$_2$O. Theoretical k_H/k_D values calculated from CH$_3$ degenerate stretching and CH$_2$ anti-stretching frequencies: CH$_3$CH$_2$CH$_3$, 2962 cm^{-1}, 2910 cm^{-1}; CH$_3$CD$_2$CH$_3$, 2974 cm^{-1}, 2182 cm^{-1}; CD$_3$CH$_2$CD$_3$, 2227 cm^{-1}, 2929 cm^{-1}; CD$_3$CD$_2$CD$_3$, 2224 cm^{-1}, 2181 cm^{-1}, respectively (9).

secondary positions on propane. Since these values are close, parallel pathways, one with secondary hydrogen abstraction and one with primary hydrogen abstraction as the rate determining steps, can be envisioned. The following equations for the observed k_H/k_D, derived following the method of Melander (10), would apply for propane deuterated at the primary and secondary positions, respectively,

$$\left(\frac{k_H}{k_D}\right)_{obs} = \frac{6k_1k_H + 2k_2k_H}{6k_1k_D + 2k_2k_H}$$

and

$$\left(\frac{k_H}{k_D}\right)_{obs} = \frac{6k_1k_H + 2k_2k_H}{6k_1k_H + 2k_2k_D},$$

where k_1 and k_2 represent the portions of the rate constants that vary with position for C–H bond breaking at primary and secondary sites, respectively, k_H and k_D are the theoretical factors in the rate constants differentiating between protons and deuterons in a given position, and $(k_H/k_D)_{obs}$ is the observed k_H/k_D.

When the results obtained in this series of experiments are evaluated using these equations and the calculated k_H/k_D values given in Table 2 are substituted for the theoretical factors in the rate constants after both the numerators and the denominators have been divided by k_D to allow for the use of ratios rather than absolute theoretical values, the abstraction of a hydrogen from the secondary carbon is calculated to occur 12–15 times more rapidly than abstraction of a hydrogen from a primary carbon. This value is reasonable based on the stability of radical intermediates of propane. In the case of chlorination of propane, a reaction which proceeds through propyl radicals, the products

are 45% 1-chloropropane and 55% 2-chloropropane. This indicates that secondary hydrogen abstraction is occurring 3–4 times more rapidly than primary hydrogen abstraction. For bromination, 97% 2-bromopropane is formed, indicating that secondary hydrogen abstraction is occurring about 97 times more rapidly than primary hydrogen abstraction. This large ratio is due to the low reactivity of the bromine molecules. Thus, the observed secondary to primary abstraction ratio of 12–15 for the ammoxidation of propane on these catalyst surfaces appears to be a reasonable value.

In addition to these data, the data in Table 1 show more propylene formation from 2,2-d_2-propane and higher selectivity to propylene plus acrylonitrile under low propane feed conditions than for the propanes which contain deuterium in the primary positions. This indicates that in the pathway where abstraction of hydrogen from the secondary carbon is rate determining, abstraction from the primary carbon after the rate determining abstraction may compete with C–C bond breaking to form waste products, mostly CO and CO$_2$, under propane ammoxidation conditions. Substitution of deuterium for hydrogen on the primary carbons appears to slow the rate of this abstraction sufficiently to make the rate of waste production more competitive under these conditions. Under the high propane feed conditions, the lower oxygen partial pressure as compared to propane is likely to inhibit the production of carbon oxides from propane. The data are also consistent with the interpretation that a direct route from propane to acrylonitrile, without a propylene intermediate, is favored by the secondary pathway in which the primary hydrogen abstraction is rate limiting.

These results are in apparent contradiction to the work of Osipova and Sokolovskii (5), where they conclude that a hydrogen is abstracted from a primary carbon in the rate determining step. This conclusion is based on general principles of organic reaction chemistry. H· or H⁻ abstraction to form a radical or carbonium ion intermediate, respectively, is more facile at a tertiary carbon than at a secondary carbon site. Thus, the rate of these abstraction reactions leading to ammoxidation would be expected to be greater for isobutane than for propane. In contrast, proton abstraction to form a carbanion intermediate is most facile at a primary carbon site, and would be expected to proceed more rapidly on an unbranched hydrocarbon than on a branched chain hydrocarbon. Since these workers observe a higher rate for propane conversion than isobutane conversion, they conclude that the rate determining step for propane ammoxidation over the gallium antimonate based catalyst system is proton abstraction from a methyl group.

However, statistical factors are not included in calculation of the relative rates performed by these workers. It is necessary to take into account, for example, the presence of two hydrogens on the secondary carbon of propane compared to only one on the tertiary carbon of isobutane.

TABLE 3

Comparison of Rates of Propane and Isobutane Conversion over $GaSb_3Ni_{1.5}PO_x$ at 550°C

Hydrocarbon	Hydrocarbon conversion (%)	Absolute rate of hydrocarbon conversion[a]	Rate assuming H-abstraction from C_2 carbon[a]	Rate assuming H-abstraction from primary carbon[a]
Propane	0 (Extrapolated)	5.6	2.8	0.93
	10	4.7	2.4	0.78
Isobutane	0 (Extrapolated)	4.3	4.3	0.48
	10	3.5	3.5	0.39

Note. Source: Osipova, Sokolovskii, Kinet. Katal. 20, 510 (1979).
[a] Rates in 10^{-11} molecules/cm²/sec.

If statistical factors are included, the results are consistent with the rate determining step being hydrogen abstraction either from the secondary carbon of propane and the tertiary carbon of isobutane or from the primary carbon of either molecule, as Table 3 shows. In addition, it should be recognized that a lower rate for isobutane ammoxidation compared to propane ammoxidation may be due in part to steric effects that impede interaction and coordination of isobutane with the catalyst surface.

Adsorption studies of propane on gallium antimony oxide catalysts display an increase in methylene groups on the surface as adsorption temperature is increased from 25 to 400°C (5). Sokolovskii *et al.* interpret these data as confirmation that hydrogen is abstracted from primary carbons, leaving a greater number of CH_2 groups on the surface. Careful examination of their data, however, indicates that when a reaction mixture of propane, oxygen, and ammonia is preadsorbed on the surface, the increase in adsorbed methylene groups is greatly reduced. Additionally, the adsorption temperature is 150°C lower than the reaction temperature for propane ammoxidation. It is, therefore, not clear that the observed adsorption bands are from intermediates in the propane ammoxidation mechanism.

Centi *et al.* propose a concerted mechanism for small paraffins under oxidation conditions (6). As noted above, ammonia may be involved in the hydrogen abstraction step for the ammoxidation reaction of propane over vanadium antimony based catalysts. This could easily result in a different mechanism for the ammoxidation reaction than for the corresponding oxidation reaction. More importantly, a concerted mechanism indeed may be at work for *n*-butane where the two methylene groups have comparable C–H

bond strengths, while in contrast, propane is more likely to react via a hydrogen abstraction from the single methylene group followed by removal of a hydrogen from a primary carbon in a subsequent step.

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