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Interplay Between Bromine and Iodine in Oxidative Dehydrogenation

Kunlun Ding,^[a] Horia Metiu,^[a] and Galen D. Stucky^{*[a]}

Oxidative dehydrogenation is a promising way to produce olefins, diolefins and aromatics. However, the product yield is limited by the consecutive oxidation of the product to oxygenated products. The highest yield reported for propane oxidative dehydrogenation is only about 30%. Alternatively, halogens can be used as oxidants in oxidative dehydrogenations. Although the iodine process is highly selective, it requires very high reaction temperatures (~ 900 K) to give a good yield of "C₃H₆+C₃H₇I", and iodine is too expensive for industrial deployment. Bromine is a more reactive oxidant, however, less

selective towards C₃H₆ and C₃H₇Br. We show here that using bromine/iodine mixtures with low iodine content (no greater than 20%) results in up to 80% of "C₃H₆+C₃H₇X" single-pass yield at moderate reaction temperatures (< 800 K). The results are promising for developing a low temperature on-purpose propylene technology. Furthermore, the underlying chemistry might be extended to the synthesis of many other commercially desirable unsaturated hydrocarbons.

Introduction

Most of the current propylene production is via steam cracking (SC) and fluidic catalytic cracking (FCC).^[1] However, in both the SC and FCC processes, propylene is produced as a by-product and the selectivity and yields are always low.^[2] The availability of ethane as a major component of natural gas at natural gas prices has attracted many ethylene producers to utilize ethane instead of naphtha as the feedstock in steam crackers. As a result, the ratio of propylene/ethylene produced from steam crackers continues to decline. At the same time, driven by the expanding polypropylene market, the demand ratio of propylene/ethylene is increasing. For these reasons, it becomes increasingly important to develop on-purpose propylene production technologies that offer higher propylene/ethylene production ratios.^[1]

Propane dehydrogenation has long been thought to be an ideal route for propylene production because of the theoretical high propylene selectivity and low capital investment, as well as the independence of the propylene production cost to naphtha price. Propane is commercially available from two major sources, petroleum refining and natural gas processing (natural gas usually contains 1-4% of propane by volume^[3]). Compared to methane and ethane, propane is more easily transported. For this reason, most of the propane produced is used as a fuel for industrial and domestic heating. However, propane dehydrogenation is limited by thermodynamics, so that very high reaction temperatures on the order of 1000 K are required to give a high single-pass propane conversion.^[2,4] Hence, the separation of the resulting hydrogen and unreacted propane from propylene becomes an issue. Despite these disadvantages, several propane dehydrogenation processes have been commercialized, including the Catofin® process developed by Lummus and the Oleflex™ process developed by UOP.^[4] Theoretically, introducing an oxidant can drive the reaction to be more thermodynamically favorable. However, the highest propylene yield reported for propane oxidative dehydrogenation (ODH) is only about 30%, mainly due to the consecutive oxidation of propylene to oxygenated products.^[2,5] The oxidative dehydrogenation

pathways to produce diolefins and aromatics suffer from the same issue. Although many different catalysts, promoters and alternative oxidants have been studied^[2,5,6], a commercially viable breakthrough has yet to be achieved. The chemistry described in this work is a new pathway that increases the previous best yield of ~30% for propane conversion to propylene to ~80%.

One possible alternative is to produce propylene through a halogen route, as illustrated in Figure 1. Propane reacts readily with halogens, producing propyl halides. A subsequent elimination process produces propylene and hydrogen halides.^[7] The resulting hydrogen halides can be oxidized back to halogens and recycled.^[7,8] Among the halogens, F₂ is inappropriate because of its high reactivity and the unfavorable thermodynamics for its use in a halogenation-dehydrohalogenation process. Similarly, Cl₂ reactions with alkanes are always fast and non-selective, and under some conditions an explosion may occur.^[9] I₂ reacts selectively, but relatively slowly, with propane at low temperatures to produce propyl iodides and propylene. High propylene yields can be achieved with stoichiometric I₂ and propane feeding.^[10] However, this reaction is only thermodynamically favorable at high temperatures (Figure S1). Furthermore, since a stoichiometric reaction of I₂ with propane is needed, the recycling efficiency of the relatively expensive I₂ greatly limits the potential industrial application of this process.^[11] Figure S1 summarizes the thermodynamics and energy profiles of propane halogenation reactions. Compared to Cl₂ and I₂, Br₂ reactions with propane are more feasible. However, in order to resolve the polyhalogenation selectivity issue in gaseous alkane bromination processes, a higher propane to bromine ratio is required in order to avoid the formation of 2,2-C₃H₆Br₂.^[7] Consequently, single-pass propane conversion, using present technology, has limited utility.

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Figure 1. Illustration of halogen-mediated propane to propylene process.

In our previous efforts to solve the dibromomethane selectivity issue that exists in the bromine based methane conversion to petrochemicals process, we discovered that iodine could efficiently catalyze the reaction between propane and dibromomethane, highly selectively producing propylene and methyl bromide.^[8b] Thereby, we proposed a low-cost, integrated on-purpose propylene technology using methane and propane as feedstocks. However, the overall propylene yield is limited by the methyl bromide-to-propylene conversion, which is analogous to the methanol-to-propylene process. In order to reduce the complexity as well as the potential capital cost of the propylene production, we aimed at using propane alone as the feedstock.

In this paper, we report a dual halogen process for the high yield, single-pass conversion of propane to “C₃H₆+C₃H₇X” (X = Br, I). The C₃H₇X that is formed is readily converted to propylene. The selectivity is significantly improved by the presence of even small amounts of iodine. This is a low temperature (< 800 K)

process that avoids all of the issues described above when either bromine or iodine is the sole halogenation agent. We show how the interplay between bromine and iodine plays an important role in oxidative dehydrogenation.

Results and Discussion

Ideally, a propane-to-bromine molar ratio of 1 is required to convert all the propane to C₃H₇Br or C₃H₆. For this reason we fixed the propane-to-bromine molar ratio to 1 in our studies. We initially carried out control experiments on propane bromination without I₂, with the results being given in Figures S2, 2A, and 3. Propane conversion with bromine alone increases with reaction temperature and finally reaches a constant value of approximately 66%. At 523 K, propane is highly selectively converted to 2-C₃H₇Br, but with a low conversion (10%). Significant amounts of polybrominated products, mainly 2,2-C₃H₆Br₂, appear at reaction temperatures above 573 K (reactions 1 – 5). When the reaction temperature is further increased to 673 K, C₃H₇Br and 2,2-C₃H₆Br₂ start to decompose, giving C₃H₆ and CH₂=CBrCH₃ (reactions 6 and 7). CH₂=CBrCH₃ further decomposes to C₃H₄ (allene and propyne) at even higher reaction temperature (reaction 8). As the reaction temperature is increased, the selectivity for “C₃H₆+C₃H₇Br” drops first and then slightly increases and finally reaches a constant value of approximately 70%. Plotting the “C₃H₆+C₃H₇Br” selectivities against the propane conversions, one can see that the maximum “C₃H₆+C₃H₇Br” yield is less than 50% (Figure 3).

Figure 2. Product distributions of the “C₃H₈+Br₂” reaction (A) without I₂ at 773 K; (B) with I₂/Br₂ mole ratio of 1/9 at 773 K; (C) with I₂/Br₂ mole ratio of 1/9 at 798 K; (D) with I₂/Br₂ mole ratio of 2/8 at 798 K. Residence time = 8 s, C₃H₈:Br₂:Ar mole ratio = 7:7:47, C₃H₈ input = 7.9 mmol. (All the pie charts are on a mole carbon basis.)

In order to produce high-purity C_3H_6 using only bromine as a halogenation reactant, $\text{C}_3\text{H}_7\text{Br}$ needs to be separated out of the stream and then fed into another reactor.^[7] Furthermore, compared to halocarbons, C_3H_6 is difficult to efficiently separate from C_3H_8 . For this reason, 573 K seems to be the best bromination temperature. Unfortunately, at this temperature the formation of $2,2\text{-C}_3\text{H}_6\text{Br}_2$ reduces the carbon and bromine efficiencies for the overall process.

The formation of $2,2\text{-C}_3\text{H}_6\text{Br}_2$ is similar to the formation of CH_2Br_2 in methane bromination. As we described in our previous work^[8], the presence of CH_2Br_2 is one of the main obstacles hindering the industrial application of a bromine based gas-to-liquid technology. We found that small amounts of iodine could effectively catalyze the reaction between CH_2Br_2 and C_3H_8 , producing CH_3Br and C_3H_6 .^[8b] Iodine can also improve the methane conversion and CH_3Br selectivity in the methane bromination process, as iodine catalyzes the reaction between CH_2Br_2 and CH_4 , producing more CH_3Br .^[8c]

Inspired by the iodine catalysis effect in the methane bromination process, we expected that similar chemistry should exist in the C_3H_8 bromination process. We studied next the influence of iodine in the C_3H_8 bromination process. We kept the $\text{C}_3\text{H}_8/\text{Br}_2$ molar ratio equal to 1 and varied the I_2/Br_2 ratio, reaction temperature, and residence time. The results are given in Figures 2 to 4 and S3 to S5. With an I_2/Br_2 ratio of 1/9, the conversions of C_3H_8 and selectivities for “ $\text{C}_3\text{H}_6+\text{C}_3\text{H}_7\text{X}$ ” at low reaction temperatures (573 and 673 K) are similar to results obtained in the absence of I_2 (Figure 3A). Further increasing the reaction temperature leads to dramatic differences in the C_3H_8 conversions and “ $\text{C}_3\text{H}_6+\text{C}_3\text{H}_7\text{X}$ ” selectivities with and without I_2 . As we mentioned above, both C_3H_8 conversion and “ $\text{C}_3\text{H}_6+\text{C}_3\text{H}_7\text{X}$ ” selectivity reach constant values above 723 K without I_2 . Interestingly, and in contrast, in the presence of I_2 , both C_3H_8 conversion and “ $\text{C}_3\text{H}_6+\text{C}_3\text{H}_7\text{X}$ ” selectivity increase with reaction temperature. At 773 K, only 66% of C_3H_8 is converted with “ $\text{C}_3\text{H}_6+\text{C}_3\text{H}_7\text{X}$ ” selectivity of 71% without I_2 , while in the presence of I_2 (with an I_2/Br_2 ratio of 1/9), 84% of the C_3H_8 is converted with a “ $\text{C}_3\text{H}_6+\text{C}_3\text{H}_7\text{X}$ ” selectivity of 81%. Further increasing the temperature to 798 K leads to a C_3H_8 conversion of 87% with the “ $\text{C}_3\text{H}_6+\text{C}_3\text{H}_7\text{X}$ ” selectivity of 85% in the presence of I_2 , and C_3H_4 as a major side-product.

Increasing the I_2/Br_2 ratio from 1/9 to 2/8 leads to a higher conversion of C_3H_8 with almost the same selectivity for “ $\text{C}_3\text{H}_6+\text{C}_3\text{H}_7\text{X}$ ”, while the trends of these two factors as a function of the reaction temperature are similar. A C_3H_8 conversion of 97%

with a “ $\text{C}_3\text{H}_6+\text{C}_3\text{H}_7\text{X}$ ” selectivity of 84% was achieved at 798 K with the I_2/Br_2 ratio of 2/8. The “ $\text{C}_3\text{H}_6+\text{C}_3\text{H}_7\text{X}$ ” selectivities are plotted against propane conversions in Figure 3B, and one can see that the maximum “ $\text{C}_3\text{H}_6+\text{C}_3\text{H}_7\text{X}$ ” yield in the presence of I_2 is well above 80%.

Figure 3. (A) Temperature-dependent C_3H_8 conversions and “ $\text{C}_3\text{H}_6+\text{C}_3\text{H}_7\text{X}$ ” selectivities of the “ $\text{C}_3\text{H}_8+\text{Br}_2$ ” reaction with different mole ratios of I_2/Br_2 . (B) “ $\text{C}_3\text{H}_6+\text{C}_3\text{H}_7\text{X}$ ” selectivities plotting against C_3H_8 conversions. Residence time = 8 s, $\text{C}_3\text{H}_8:\text{Br}_2:\text{Ar}$ mole ratio = 7:7:47, C_3H_8 input = 7.9 mmol.

In order to explore the origin of the iodine promoting effects in the C_3H_8 bromination process, we carried out several control experiments. We first focused on the reaction between $2,2\text{-C}_3\text{H}_6\text{Br}_2$ and C_3H_8 . Our control experiments on “ $2,2\text{-C}_3\text{H}_6\text{Br}_2+\text{C}_3\text{H}_8$ ” show that $2,2\text{-C}_3\text{H}_6\text{Br}_2$ is too reactive compared to C_3H_8 . (Figures S6 and S7) $2,2\text{-C}_3\text{H}_6\text{Br}_2$ quickly decomposes into $\text{CH}_2=\text{CBrCH}_3$ and C_3H_4 in high conversions at higher temperatures with or without a heterogeneous catalyst, but the C_3H_8 conversion remains lower than 10%. As we stated above, iodine effectively catalyzes the reaction between CH_2Br_2 and $\text{C}_3\text{H}_8/\text{CH}_4$.^[8b,8c] Iodine mainly abstracts bromine from CH_2Br_2 , while bromine abstracts hydrogen from $\text{C}_3\text{H}_8/\text{CH}_4$. Introducing a small amount of iodine ($\text{I}_2/2,2\text{-C}_3\text{H}_6\text{Br}_2$ mole ratio of 3/97) certainly accelerates the reaction between $2,2\text{-C}_3\text{H}_6\text{Br}_2/\text{CH}_2=\text{CBrCH}_3$ and C_3H_8 (Figure S8). However, the conversion of C_3H_8 is lower than that in the “ $\text{CH}_2\text{Br}_2+\text{C}_3\text{H}_8$ ” system using the same amount of I_2 .^[8b] Although we do not have the exact bond dissociation energy

(BDE) of the C–Br bonds in 2,2-C₃H₆Br₂, we estimate that the value is somewhat close to that of CH₂Br₂ (~66kcal/mol).^[12] From our previous work^[8b] we have determined that bromine atom abstraction by iodine radicals requires a high temperature (773 K in case of CH₂Br₂). However, such a high reaction temperature leads to the decomposition of 2,2-C₃H₆Br₂, producing CH₂=CBrCH₃. Since the C–Br bond in CH₂=CBrCH₃ has a much higher BDE (~80kcal/mol), the bromine abstraction becomes even harder. This explains the lower conversion of C₃H₈ in “2,2-C₃H₆Br₂+C₃H₈” system compared to that in “CH₂Br₂+C₃H₈” system.

The influence of residence time on the C₃H₈ bromination process was also studied. Changing the residence time is equivalent to changing the size of the reactor and keeping the flow constant. It can be seen in Figures 4 and S5 that a longer residence time leads to slightly higher C₃H₈ conversion and “C₃H₆+C₃H₇X” selectivity. From the product distributions one can clearly see that the percentage increases of “C₃H₆+C₃H₇X” are approximately equal to the percentage decreases of “C₃H₈+C₃H₅Br”. This can be ascribed to the iodine-catalyzed C₃H₈ reaction with C₃H₅Br giving C₃H₆ and C₃H₇X is one of the reasons for the higher C₃H₈ conversions and “C₃H₆+C₃H₇X” selectivities of C₃H₈ bromination in the presence of I₂.

Figure 4. Product distributions of the “C₃H₈+Br₂” reaction with I₂/Br₂ mole ratio of 1/9, at 1.3 s (A) and 16 s (B). T = 773 K, C₃H₈:Br₂:Ar mole ratio = 7:7:47, C₃H₈ input = 7.9 mmol. (All the pie charts are on a mole carbon basis)

It should be noted that the contribution of 2-C₃H₇Br decreases with reaction temperature and residence time, while the contribution of 2-C₃H₇I goes in the opposite direction (Figures 2 and S3 to S5). Since 2-C₃H₇I decomposes faster than 2-C₃H₇Br, it

is not reasonable that 2-C₃H₇I remains in the outlet stream while 2-C₃H₇Br does not. The most likely explanation is that the observed 2-C₃H₇I in the outlet stream was formed in the cooling region between the reactor and NaOH/organic bi-phase trap, through the addition of HI to C₃H₆. The amount of 2-C₃H₇I is proportional to the concentrations of HI and C₃H₆ and residence time in the cooling region. Higher temperature accelerates reaction 9 in the forward direction so that more HI and 2-C₃H₇I are formed.

If Br₂ is not present, the above reaction is accomplished via the following elementary reactions:

Since the •Br-radical abstraction of hydrogen from C₃H₈ is several orders of magnitude faster than the abstraction of hydrogen from C₃H₈ by the •I radical,^[8b] reaction 11 does not make a significant contribution if Br₂ is present. Instead, reaction 2 is the main route for the generation of the •CH(CH₃)₂ radical. After the •CH(CH₃)₂ radical is formed, it can be trapped both by Br₂ and I₂, giving 2-C₃H₇Br and 2-C₃H₇I respectively, which further decomposes into C₃H₆. 2-C₃H₇I decomposes faster than 2-C₃H₇Br. In addition to Br₂ and I₂, IBr is also likely present during the propane dehydrogenation reaction (reaction 14). It has been shown that the reaction between a radical and an interhalogen molecule XY (ICl, BrCl and IBr) will always favor attack on the less electronegative atom of XY.^[13] For this reason, 2-C₃H₇I instead of 2-C₃H₇Br is more likely to be formed when reacting the •CH(CH₃)₂ radical with IBr (reaction 15).

Another possible way for the •CH(CH₃)₂ radical to evolve into C₃H₆ is by reacting •CH(CH₃)₂ radical with •Br and •I radicals, as shown in reactions 16 and 17.^[10b,14] These two aspects, the trapping of •CH(CH₃)₂ radical by I₂ and IBr to form 2-C₃H₇I (reaction 12 and 15) and the dehydrogenation of •CH(CH₃)₂ radical by •I radical to form C₃H₆ (reaction 17), both contribute to the acceleration of C₃H₆ formation with the addition of I₂.

We know that the main side-reaction of C₃H₈ bromination is the consecutive bromination of 2-C₃H₇Br to 2,2-C₃H₆Br₂. The introduction of I₂ into the bromine halogenation process accelerates the formation of C₃H₆, which is in competition with the formation of 2,2-C₃H₆Br₂. The result is a higher “C₃H₆+C₃H₇X” selectivity.

Conclusion

In conclusion, we have studied C_3H_8 dehydrogenation by bromine with and without the presence of iodine. A small amount (I_2/Br_2 ratio no more than 2/8) of I_2 results in up to 80% single-pass " $C_3H_6+C_3H_7X$ " yield at 798 K. The yields presented here are much higher than those reported in the traditional ODH processes, which are no greater than 30%. Compared to the less-selective bromine process and the high-temperature, also expensive, iodine process, a dual halogen process using bromine and iodine together displays the advantages of both halogens. The results are particularly promising for developing a low-temperature on-purpose, high-yield propylene technology. Furthermore, the underlying chemistry might be extended to the high yield synthesis of many other unsaturated hydrocarbons, including olefins, diolefins, and aromatics.^[10,15]

Experimental Section

The reactions were conducted in an atmospheric pressure glass tube reactor system, which is identical with that in our previous work.^[8a, 8b] The configuration of the reaction system is shown in Figure S9. C_3H_8 , HBr and Ar flow rates were controlled by mass flow controllers. I_2 was dissolved in Br_2 or 2,2- $C_3H_6Br_2$ and delivered by syringe pump. The liquid reactant was vaporized in the head space of the reactor. The effluent stream from the reactor was passed through a fritted glass bubbler trap containing organic solution (10 wt% octadecane in hexadecane) and 4M NaOH solution, all remaining gaseous product were collected in a gas bag after passing through a final base trap (4M NaOH solution) to prevent any residual HBr/HI from entering the bag. For most of the experiments, reactions were run for half an hour with all the products collected and analyzed. The products were analyzed with three GCs equipped with flame ionization detectors and capillary columns, which measured: (1) gaseous halocarbons including C_3H_5Br and C_3H_7Br (HP-PLOT Q and DB-624, Agilent); (2) gaseous hydrocarbon C_1-C_6 (Select Al_2O_3 MAPD, Varian); and (3) liquid halocarbon products (DB-17, Agilent). All the experiments reported here have carbon balances of 95-105%.

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Keywords: on-purpose propylene • dual halogen • bromine • iodine • oxidative dehydrogenation

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Entry for the Table of Contents

FULL PAPER

A single-pass " $C_3H_6 + C_3H_7X$ " yield above 80% was achieved in propane oxidative dehydrogenation using bromine and iodine together as oxidants. This dual-halogen process is promising for the synthesis of many other unsaturated hydrocarbons, including olefins, diolefins, and aromatics.

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