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# Interplay Between Bromine and Iodine in Oxidative Dehydrogenation

Kunlun Ding,<sup>[a]</sup> Horia Metiu,<sup>[a]</sup> and Galen D. Stucky\*<sup>[a]</sup>

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 "C<sub>3</sub>H<sub>6</sub>+C<sub>3</sub>H<sub>7</sub>I", and iodine is too expensive for industrial deployment. Bromine is a more reactive oxidant, however, less

selective towards C<sub>3</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>7</sub>Br. We show here that using bromine/iodine mixtures with low iodine content (no greater than 20%) results in up to 80% of "C<sub>3</sub>H<sub>6</sub>+C<sub>3</sub>H<sub>7</sub>X" 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).<sup>[1]</sup> However, in both the SC and FCC processes, propylene is produced as a by-product and the selectivity and yields are always low.<sup>[2]</sup> 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.<sup>[1]</sup>

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<sup>[3]</sup>). 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.<sup>[2,4]</sup> 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<sup>®</sup> process developed by Lummus and the Oleflex<sup>™</sup> process developed by UOP.<sup>[4]</sup> 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.<sup>[2,5]</sup> 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<sup>[2,5,6]</sup>, 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.<sup>[7]</sup> The resulting hydrogen halides can be oxidized back to halogens and recycled.<sup>[7,8]</sup> Among the halogens, F<sub>2</sub> is inappropriate because of its high reactivity and the unfavorable thermodynamics for its use in a halogenation-dehydrohalogenation process. Similarly, Cl<sub>2</sub> reactions with alkanes are always fast and non-selective, and under some conditions an explosion may occur.<sup>[9]</sup> I<sub>2</sub> reacts selectively, but relatively slowly, with propane at low temperatures to produce propyl iodides and propylene. High propylene yields can be achieved with stoichiometric I<sub>2</sub> and propane feeding.<sup>[10]</sup> However, this reaction is only thermodynamically favorable at high temperatures (Figure S1). Furthermore, since a stoichiometric reaction of I<sub>2</sub> with propane is needed, the recycling efficiency of the relatively expensive I<sub>2</sub> greatly limits the potential industrial application of this process.<sup>[11]</sup> Figure S1 summarizes the thermodynamics and energy profiles of propane halogenation reactions. Compared to Cl<sub>2</sub> and I<sub>2</sub>, Br<sub>2</sub> 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-C<sub>3</sub>H<sub>6</sub>Br<sub>2</sub>.<sup>[7]</sup> Consequently, single-pass propane conversion, using present technology, has limited utility.

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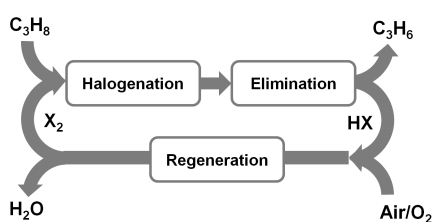


Figure 1. Illustration of halogen-mediated propane to propylene process.

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.<sup>[8b]</sup> 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 “C<sub>3</sub>H<sub>6</sub>+C<sub>3</sub>H<sub>7</sub>X” (X = Br, I). The C<sub>3</sub>H<sub>7</sub>X 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 C<sub>3</sub>H<sub>7</sub>Br or C<sub>3</sub>H<sub>6</sub>. 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 I<sub>2</sub>, 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-C<sub>3</sub>H<sub>7</sub>Br, but with a low conversion (10%). Significant amounts of polybrominated products, mainly 2,2-C<sub>3</sub>H<sub>6</sub>Br<sub>2</sub>, appear at reaction temperatures above 573 K (reactions 1 – 5). When the reaction temperature is further increased to 673 K, C<sub>3</sub>H<sub>7</sub>Br and 2,2-C<sub>3</sub>H<sub>6</sub>Br<sub>2</sub> start to decompose, giving C<sub>3</sub>H<sub>6</sub> and CH<sub>2</sub>=CBrCH<sub>3</sub> (reactions 6 and 7). CH<sub>2</sub>=CBrCH<sub>3</sub> further decomposes to C<sub>3</sub>H<sub>4</sub> (allene and propyne) at even higher reaction temperature (reaction 8). As the reaction temperature is increased, the selectivity for “C<sub>3</sub>H<sub>6</sub>+C<sub>3</sub>H<sub>7</sub>Br” drops first and then slightly increases and finally reaches a constant value of approximately 70%. Plotting the “C<sub>3</sub>H<sub>6</sub>+C<sub>3</sub>H<sub>7</sub>Br” selectivities against the propane conversions, one can see that the maximum “C<sub>3</sub>H<sub>6</sub>+C<sub>3</sub>H<sub>7</sub>Br” yield is less than 50% (Figure 3).

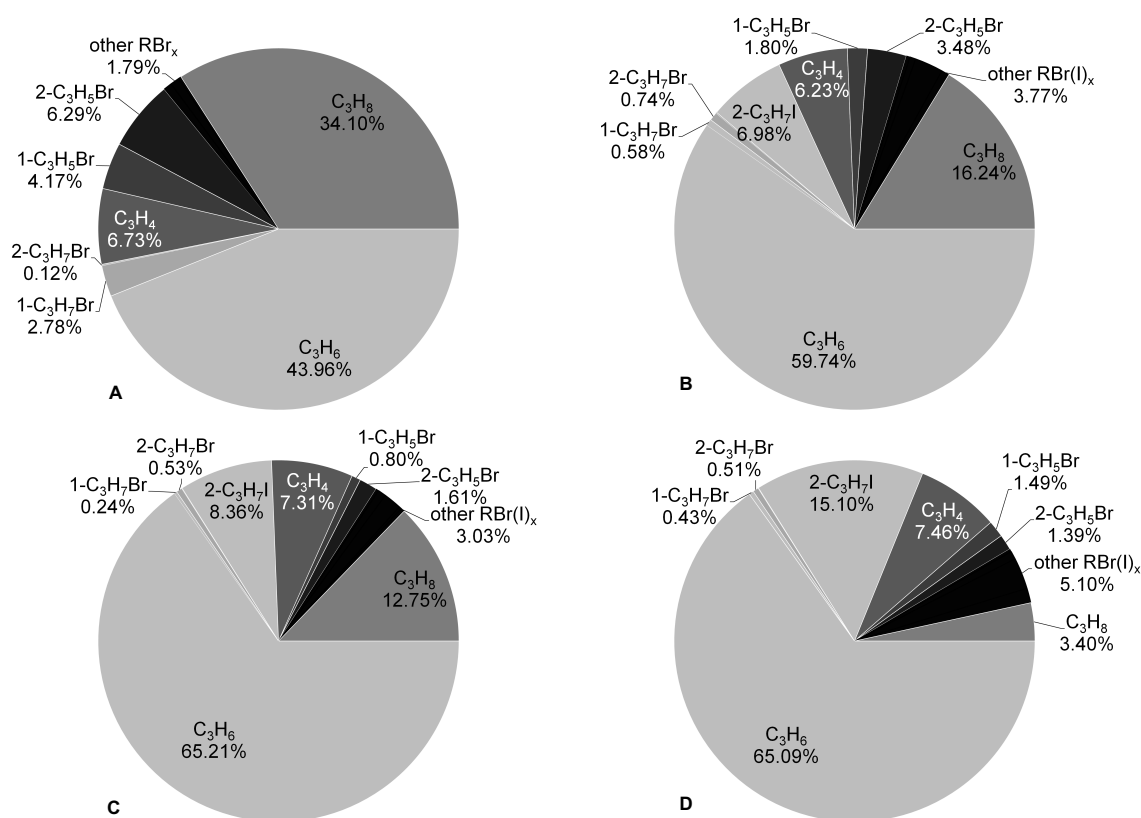
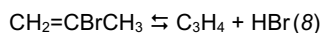
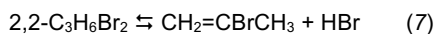
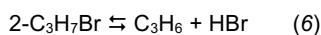
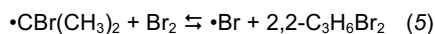
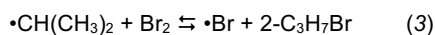
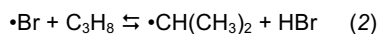
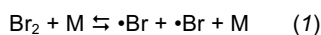


Figure 2. Product distributions of the “C<sub>3</sub>H<sub>8</sub>+Br<sub>2</sub>” reaction (A) without I<sub>2</sub> at 773 K; (B) with I<sub>2</sub>/Br<sub>2</sub> mole ratio of 1/9 at 773 K; (C) with I<sub>2</sub>/Br<sub>2</sub> mole ratio of 1/9 at 798 K; (D) with I<sub>2</sub>/Br<sub>2</sub> mole ratio of 2/8 at 798 K. Residence time = 8 s, C<sub>3</sub>H<sub>8</sub>:Br<sub>2</sub>:Ar mole ratio = 7:7:47, C<sub>3</sub>H<sub>8</sub> input = 7.9 mmol. (All the pie charts are on a mole carbon basis.)



In order to produce high-purity  $\text{C}_3\text{H}_6$  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.<sup>[7]</sup> Furthermore, compared to halocarbons,  $\text{C}_3\text{H}_6$  is difficult to efficiently separate from  $\text{C}_3\text{H}_8$ . 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  $\text{CH}_2\text{Br}_2$  in methane bromination. As we described in our previous work<sup>[8]</sup>, the presence of  $\text{CH}_2\text{Br}_2$  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  $\text{CH}_2\text{Br}_2$  and  $\text{C}_3\text{H}_8$ , producing  $\text{CH}_3\text{Br}$  and  $\text{C}_3\text{H}_6$ .<sup>[8b]</sup> Iodine can also improve the methane conversion and  $\text{CH}_3\text{Br}$  selectivity in the methane bromination process, as iodine catalyzes the reaction between  $\text{CH}_2\text{Br}_2$  and  $\text{CH}_4$ , producing more  $\text{CH}_3\text{Br}$ .<sup>[8c]</sup>

Inspired by the iodine catalysis effect in the methane bromination process, we expected that similar chemistry should exist in the  $\text{C}_3\text{H}_8$  bromination process. We studied next the influence of iodine in the  $\text{C}_3\text{H}_8$  bromination process. We kept the  $\text{C}_3\text{H}_8/\text{Br}_2$  molar ratio equal to 1 and varied the  $\text{I}_2/\text{Br}_2$  ratio, reaction temperature, and residence time. The results are given in Figures 2 to 4 and S3 to S5. With an  $\text{I}_2/\text{Br}_2$  ratio of 1/9, the conversions of  $\text{C}_3\text{H}_8$  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  $\text{I}_2$  (Figure 3A). Further increasing the reaction temperature leads to dramatic differences in the  $\text{C}_3\text{H}_8$  conversions and “ $\text{C}_3\text{H}_6+\text{C}_3\text{H}_7\text{X}$ ” selectivities with and without  $\text{I}_2$ . As we mentioned above, both  $\text{C}_3\text{H}_8$  conversion and “ $\text{C}_3\text{H}_6+\text{C}_3\text{H}_7\text{X}$ ” selectivity reach constant values above 723 K without  $\text{I}_2$ . Interestingly, and in contrast, in the presence of  $\text{I}_2$ , both  $\text{C}_3\text{H}_8$  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  $\text{C}_3\text{H}_8$  is converted with “ $\text{C}_3\text{H}_6+\text{C}_3\text{H}_7\text{X}$ ” selectivity of 71% without  $\text{I}_2$ , while in the presence of  $\text{I}_2$  (with an  $\text{I}_2/\text{Br}_2$  ratio of 1/9), 84% of the  $\text{C}_3\text{H}_8$  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  $\text{C}_3\text{H}_8$  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  $\text{I}_2$ , and  $\text{C}_3\text{H}_4$  as a major side-product.

Increasing the  $\text{I}_2/\text{Br}_2$  ratio from 1/9 to 2/8 leads to a higher conversion of  $\text{C}_3\text{H}_8$  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  $\text{C}_3\text{H}_8$  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  $\text{I}_2/\text{Br}_2$  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  $\text{I}_2$  is well above 80%.

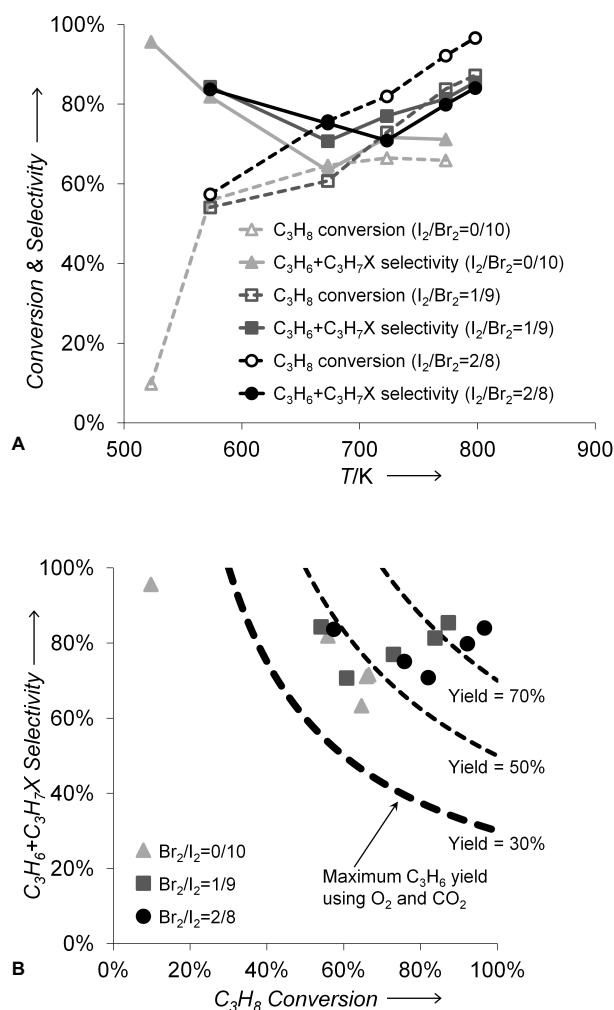


Figure 3. (A) Temperature-dependent  $\text{C}_3\text{H}_8$  conversions and “ $\text{C}_3\text{H}_6+\text{C}_3\text{H}_7\text{X}$ ” selectivities of the “ $\text{C}_3\text{H}_8+\text{Br}_2$ ” reaction with different mole ratios of  $\text{I}_2/\text{Br}_2$ . (B) “ $\text{C}_3\text{H}_6+\text{C}_3\text{H}_7\text{X}$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

In order to explore the origin of the iodine promoting effects in the  $\text{C}_3\text{H}_8$  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  $\text{C}_3\text{H}_8$ . 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  $\text{C}_3\text{H}_8$ . (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  $\text{C}_3\text{H}_4$  in high conversions at higher temperatures with or without a heterogeneous catalyst, but the  $\text{C}_3\text{H}_8$  conversion remains lower than 10%. As we stated above, iodine effectively catalyzes the reaction between  $\text{CH}_2\text{Br}_2$  and  $\text{C}_3\text{H}_8/\text{CH}_4$ .<sup>[8b,8c]</sup> Iodine mainly abstracts bromine from  $\text{CH}_2\text{Br}_2$ , 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  $\text{C}_3\text{H}_8$  (Figure S8). However, the conversion of  $\text{C}_3\text{H}_8$  is lower than that in the “ $\text{CH}_2\text{Br}_2+\text{C}_3\text{H}_8$ ” system using the same amount of  $\text{I}_2$ .<sup>[8b]</sup> Although we do not have the exact bond dissociation energy

(BDE) of the C–Br bonds in 2,2-C<sub>3</sub>H<sub>6</sub>Br<sub>2</sub>, we estimate that the value is somewhat close to that of CH<sub>2</sub>Br<sub>2</sub> (~66kcal/mol).<sup>[12]</sup> From our previous work<sup>[8b]</sup> we have determined that bromine atom abstraction by iodine radicals requires a high temperature (773 K in case of CH<sub>2</sub>Br<sub>2</sub>). However, such a high reaction temperature leads to the decomposition of 2,2-C<sub>3</sub>H<sub>6</sub>Br<sub>2</sub>, producing CH<sub>2</sub>=CBrCH<sub>3</sub>. Since the C–Br bond in CH<sub>2</sub>=CBrCH<sub>3</sub> has a much higher BDE (~80kcal/mol), the bromine abstraction becomes even harder. This explains the lower conversion of C<sub>3</sub>H<sub>8</sub> in “2,2-C<sub>3</sub>H<sub>6</sub>Br<sub>2</sub>+C<sub>3</sub>H<sub>8</sub>” system compared to that in “CH<sub>2</sub>Br<sub>2</sub>+C<sub>3</sub>H<sub>8</sub>” system.

The influence of residence time on the C<sub>3</sub>H<sub>8</sub> 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 C<sub>3</sub>H<sub>8</sub> conversion and “C<sub>3</sub>H<sub>6</sub>+C<sub>3</sub>H<sub>7</sub>X” selectivity. From the product distributions one can clearly see that the percentage increases of “C<sub>3</sub>H<sub>6</sub>+C<sub>3</sub>H<sub>7</sub>X” are approximately equal to the percentage decreases of “C<sub>3</sub>H<sub>8</sub>+C<sub>3</sub>H<sub>5</sub>Br”. This can be ascribed to the iodine-catalyzed C<sub>3</sub>H<sub>8</sub> reaction with C<sub>3</sub>H<sub>5</sub>Br (Figure S8). The iodine-catalyzed C<sub>3</sub>H<sub>8</sub> reaction with C<sub>3</sub>H<sub>5</sub>Br giving C<sub>3</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>7</sub>X is one of the reasons for the higher C<sub>3</sub>H<sub>8</sub> conversions and “C<sub>3</sub>H<sub>6</sub>+C<sub>3</sub>H<sub>7</sub>X” selectivities of C<sub>3</sub>H<sub>8</sub> bromination in the presence of I<sub>2</sub>.

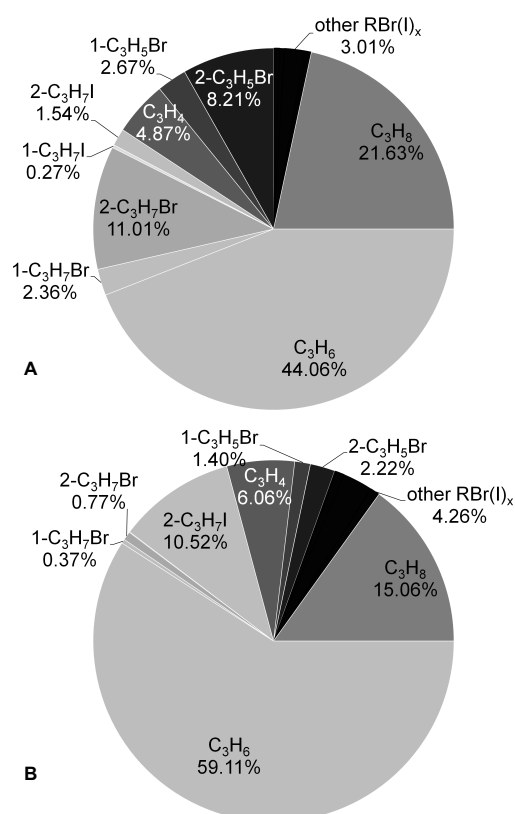
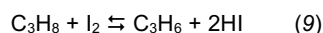


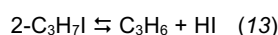
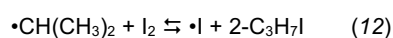
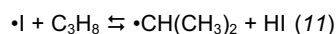
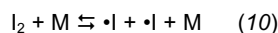
Figure 4. Product distributions of the “C<sub>3</sub>H<sub>8</sub>+Br<sub>2</sub>” reaction with I<sub>2</sub>/Br<sub>2</sub> mole ratio of 1/9, at 1.3 s (A) and 16 s (B). T = 773 K, C<sub>3</sub>H<sub>8</sub>:Br<sub>2</sub>:Ar mole ratio = 7:7:47, C<sub>3</sub>H<sub>8</sub> input = 7.9 mmol. (All the pie charts are on a mole carbon basis)

It should be noted that the contribution of 2-C<sub>3</sub>H<sub>7</sub>Br decreases with reaction temperature and residence time, while the contribution of 2-C<sub>3</sub>H<sub>7</sub>I goes in the opposite direction (Figures 2 and S3 to S5). Since 2-C<sub>3</sub>H<sub>7</sub>I decomposes faster than 2-C<sub>3</sub>H<sub>7</sub>Br, it

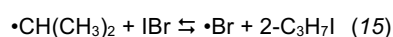
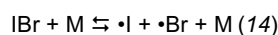
is not reasonable that 2-C<sub>3</sub>H<sub>7</sub>I remains in the outlet stream while 2-C<sub>3</sub>H<sub>7</sub>Br does not. The most likely explanation is that the observed 2-C<sub>3</sub>H<sub>7</sub>I in the outlet stream was formed in the cooling region between the reactor and NaOH/organic bi-phase trap, through the addition of HI to C<sub>3</sub>H<sub>6</sub>. The amount of 2-C<sub>3</sub>H<sub>7</sub>I is proportional to the concentrations of HI and C<sub>3</sub>H<sub>6</sub> and residence time in the cooling region. Higher temperature accelerates reaction 9 in the forward direction so that more HI and 2-C<sub>3</sub>H<sub>7</sub>I are formed.



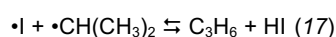
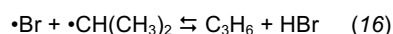
If Br<sub>2</sub> is not present, the above reaction is accomplished via the following elementary reactions:



Since the •Br-radical abstraction of hydrogen from C<sub>3</sub>H<sub>8</sub> is several orders of magnitude faster than the abstraction of hydrogen from C<sub>3</sub>H<sub>8</sub> by the •I radical,<sup>[8b]</sup> reaction 11 does not make a significant contribution if Br<sub>2</sub> is present. Instead, reaction 2 is the main route for the generation of the •CH(CH<sub>3</sub>)<sub>2</sub> radical. After the •CH(CH<sub>3</sub>)<sub>2</sub> radical is formed, it can be trapped both by Br<sub>2</sub> and I<sub>2</sub>, giving 2-C<sub>3</sub>H<sub>7</sub>Br and 2-C<sub>3</sub>H<sub>7</sub>I respectively, which further decomposes into C<sub>3</sub>H<sub>6</sub>. 2-C<sub>3</sub>H<sub>7</sub>I decomposes faster than 2-C<sub>3</sub>H<sub>7</sub>Br. In addition to Br<sub>2</sub> and I<sub>2</sub>, 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.<sup>[13]</sup> For this reason, 2-C<sub>3</sub>H<sub>7</sub>I instead of 2-C<sub>3</sub>H<sub>7</sub>Br is more likely to be formed when reacting the •CH(CH<sub>3</sub>)<sub>2</sub> radical with IBr (reaction 15).



Another possible way for the •CH(CH<sub>3</sub>)<sub>2</sub> radical to evolve into C<sub>3</sub>H<sub>6</sub> is by reacting •CH(CH<sub>3</sub>)<sub>2</sub> radical with •Br and •I radicals, as shown in reactions 16 and 17.<sup>[10b,14]</sup> These two aspects, the trapping of •CH(CH<sub>3</sub>)<sub>2</sub> radical by I<sub>2</sub> and IBr to form 2-C<sub>3</sub>H<sub>7</sub>I (reaction 12 and 15) and the dehydrogenation of •CH(CH<sub>3</sub>)<sub>2</sub> radical by •I radical to form C<sub>3</sub>H<sub>6</sub> (reaction 17), both contribute to the acceleration of C<sub>3</sub>H<sub>6</sub> formation with the addition of I<sub>2</sub>.



We know that the main side-reaction of C<sub>3</sub>H<sub>8</sub> bromination is the consecutive bromination of 2-C<sub>3</sub>H<sub>7</sub>Br to 2,2-C<sub>3</sub>H<sub>6</sub>Br<sub>2</sub>. The introduction of I<sub>2</sub> into the bromine halogenation process accelerates the formation of C<sub>3</sub>H<sub>6</sub>, which is in competition with the formation of 2,2-C<sub>3</sub>H<sub>6</sub>Br<sub>2</sub>. The result is a higher “C<sub>3</sub>H<sub>6</sub>+C<sub>3</sub>H<sub>7</sub>X” selectivity.

## Conclusion



In conclusion, we have studied C<sub>3</sub>H<sub>8</sub> dehydrogenation by bromine with and without the presence of iodine. A small amount (I<sub>2</sub>/Br<sub>2</sub> ratio no more than 2/8) of I<sub>2</sub> results in up to 80% single-pass "C<sub>3</sub>H<sub>6</sub>+C<sub>3</sub>H<sub>7</sub>X" 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.<sup>[10,15]</sup>

## Experimental Section

The reactions were conducted in an atmospheric pressure glass tube reactor system, which is identical with that in our previous work.<sup>[8a, 8b]</sup> The configuration of the reaction system is shown in Figure S9. C<sub>3</sub>H<sub>8</sub>, HBr and Ar flow rates were controlled by mass flow controllers. I<sub>2</sub> was dissolved in Br<sub>2</sub> or 2,2-C<sub>3</sub>H<sub>6</sub>Br<sub>2</sub> 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<sub>3</sub>H<sub>5</sub>Br and C<sub>3</sub>H<sub>7</sub>Br (HP-PLOT Q and DB-624, Agilent); (2) gaseous hydrocarbon C<sub>1</sub>-C<sub>6</sub> (Select Al<sub>2</sub>O<sub>3</sub> MAPD, Varian); and (3) liquid halocarbon products (DB-17, Agilent). All the experiments reported here have carbon balances of 95-105%.

## Acknowledgements

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

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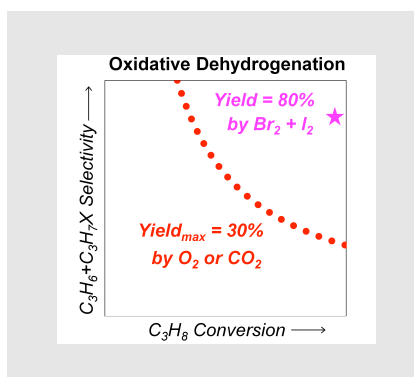
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## Entry for the Table of Contents

### 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.



Kunlun Ding, Horia Metiu, and Galen D. Stucky\*

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**Interplay Between Bromine and Iodine in Oxidative Dehydrogenation**