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Halogen-Mediated Oxidative Dehydrogenation of Propane

Using Iodine or Molten Lithium Iodide

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Abstract. We studied propylene production by the reaction of propane with oxygen in the presence of gaseous I₂ which works as a gas-phase catalyst. I₂ is either introduced as a gas in the mixture of propane and oxygen, or it is produced when propane and oxygen come in contact with molten LiI or a mixture of molten LiI and LiOH. The single-pass propylene yields obtained in both types of experiments are ~64%, at 500 °C and propane partial pressure of 0.1 atm. The main role of I₂ is to initiate chain reactions that lead to the formation of a propyl iodide intermediate that decomposes to form propylene. Another important intermediate is HI, which reacts very rapidly with oxygen to regenerate I₂ and prevent oxygen from attacking the hydrocarbons.

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Keywords. Oxidative dehydrogenation, propane, molten salt, iodine, LiI, LiOH, halogen

1 Introduction

Propylene is a side product in refineries, whose main product is gasoline. The demand for gasoline is high in the summer and low in the winter and this causes disruptive seasonal variations in the propylene supply. Propylene is also a side product in ethylene production, by steam reforming of naphtha or gas oil, and the demand for propylene is growing faster than that for ethylene, which again causes supply limitations.

Furthermore, ethylene producers are switching to ethane steam reforming, which produces no propylene. To respond to these multiple supply constraints, the industry developed “propylene on demand” processes whose goal is the production of propylene through the dehydrogenation of propane [1]:

These processes have a number of common shortcomings. Reaction 1 is equilibrium-limited and to shift equilibrium to higher, single-pass propane conversion one works at high temperature (between 550 °C and 650 °C) and low propane pressure. The latter is achieved either by creating vacuum or by diluting the feed with steam, which are both expensive. The reaction produces coke which poisons the catalyst and for some processes more time is spent on decoking the catalyst than on producing propylene. The reaction is highly exothermic which adds substantially to the cost of the process. The single-pass yield is at most 55%, depending on the process.

In principle many of these shortcomings can be alleviated by performing oxidative dehydrogenation (ODH), a process in which oxygen or CO₂ are added to the feed, in the hope that with the appropriate catalyst they will react *selectively* with the hydrogen produced by the dehydrogenation reaction (1). This shifts the equilibrium of the dehydrogenation reaction towards higher propane conversion, makes the net reaction exothermic (if oxygen is used) and it is likely to prevent coke formation. Extensive research based on this idea has yet to find a commercially viable catalyst [2-4].

In this article we report experiments that study a different procedure for performing oxidative dehydrogenation of propane, which we call halogen-mediated oxidative dehydrogenation (HM-ODH). Formally this is described by the reaction network outlined below. Instead of reacting the hydrogen formed in reaction (1) with oxygen, we react it with a halogen X₂ according to

HX formed in this reaction is cheaper than X₂ and the market for it is limited. To recover the halogen from HX one performs a Deacon-like reaction

The sum of the reactions (1)-(3) is

which is the oxidative dehydrogenation of propane. Since the free energy is a function of state, the scheme described by reactions (2)-(4) is thermodynamically equivalent to ODH. The only possible advantage of HM-ODH must come from kinetics.

This idea was implemented [5-7] by bringing a mixture of alkane and oxygen in contact with molten LiI. The reaction of LiI with oxygen produced I₂, which then reacted, in gas phase, according to the formal scheme (2)-(4). It is not known whether the liquid LiI surface is a catalyst, or a source of I₂, or both. This procedure is able to convert a large number of hydrocarbons to alkenes with a remarkably high yield [5,6].

The use of a molten salt may appear unusual, but there has been quite a bit of work over years exploring the use of molten salts as catalysts [8-12] or as promoters [13-23]. Molten salts have high heat capacity and heat conductivity [24-27,12] which is helpful in preventing hot spots in oxidation reactions. They are also good solvents, so it is easy to “dope” them to modify their catalytic chemistry. Unfortunately, molten salts,

halogens, and halogen hydrides are corrosive and this is a serious concern for commercial applications of molten salts or of HM-ODH.

In the present article we examine the gas phase reaction of propane with oxygen and I₂, as well as the reaction of propane and oxygen with molten LiI. The goal is to produce propylene with high yield and to clarify some aspects of the mechanism. While the gas-phase reaction of propane with iodine has been examined before [28,29], we are not aware of any studies that examined the gas-phase reaction of propane with I₂ in the presence of oxygen.

By improving our understanding of I₂-mediated ODH using molten LiI we have found conditions for which we achieve 80% propane conversion and 84% selectivity to propylene, at 500 °C. This performance is better than that of the current dehydrogenation processes and of the prior ODH experiments. Halogen-mediated chemistry, in the presence of oxygen, has the potential to improve substantially the conversion of alkanes to alkenes. The main impediment is the cost of corrosion resistant equipment.

2 The reaction mechanism

To facilitate a better understanding of the experimental results we discuss first the HM-ODH reaction mechanism. When the reaction is performed with propane, O₂ and molten lithium iodide there are two parallel reaction networks: one taking place in the gas that is in contact with the melt, and another involving the melt.

2.1 The mechanism of the gas-phase reactions. While no previous work has studied the reaction of propane, I₂ and O₂ in the gas, there is quite a bit of information about various parts of the reaction network to allow us to propose a plausible reaction mechanism. It is generally accepted [30-34] that the reactions of halogens with H₂ or alkanes are chain reactions. When iodine is used, the chain initiation is the dissociation of I₂,

One essential advantage of using I₂ is that it dissociates at lower temperature than other halogens. The iodine atom reacts with propane to make a propyl radical and HI,

This is the rate-limiting step when the halogen is I₂. The propyl radical reacts with I₂

to make propyl iodide, which eliminates HI to form the propylene:

We have not listed all possible reactions: some form radicals and do not terminate the chain; others will form products that we did not observe in experiments.

The effect of oxygen is relatively easy to explain. Our experiments show almost none of the products of hydrocarbon oxidation. This can happen because the reaction of O_2 with HI

is much faster than the reaction of oxygen with any of the organic compounds present in the system [35]. The high rate of this reaction is beneficial in three ways. 1. The rapid consumption of O_2 prevents the oxidation of the hydrocarbons. 2. The rapid consumption of HI prevents its reaction with propylene (the reverse of reaction (8)) or the propyl radical (the reverse of reaction (6)). 3. Reaction (9) converts cheap HI into I_2 , which can be recycled back into the reactor. The high rate of reaction (9) is one of the reasons why the use of I_2 is preferred over that of Br_2 or Cl_2 , whose acids are oxidized more slowly.

The mechanism proposed above does not include a role for water, which is produced by the HM-ODH reaction. Our experiments have shown that adding water to the feed does not have a substantial effect on the propylene yield. It is very likely that the propyl radical reacts with water to make propane and OH. This is not a favorable event but OH will react with propane to make water and propyl. Therefore, the presence of water does not stop chain propagation. Similarly, the iodine atom can react with water to make HI and OH, but OH will react with another HI to make water and I, which continues the chain reaction. Since OH is a very aggressive radical, it will react with propane to make a propyl radical and water, or with HI to make an I radical and water; these reactions continue the chain and therefore water does not play an important role in the process. We also find that very little CO_x is formed, in spite of the presence of water, which indicates that steam reforming of the hydrocarbons or of the propyl iodide is a minor reaction under the conditions used here.

2.2 Reactions involving molten LiI. LiI reacts with the gaseous oxygen according to [5-7,36]

The gaseous I₂ formed in this way reacts with a mixture of gaseous propane and O₂ according to the reactions (5)-(10). These reactions produce HI and it has been proposed [5-7,36] that HI reacts with Li₂O according to

We propose that this is a minor reaction since LiI, like many other molten salts, is extremely hygroscopic [12,24,25,27,26] and, in addition, the HM-ODH process generates water. As a result, Li₂O(s), formed by reaction (11), reacts with the water present in the salt to form LiOH. This reacts with HI to recover the LiI consumed by reaction (11):

The formation of LiOH, rather than of Li₂O, is convenient because the hydroxide is soluble in the molten LiI, while the oxide is not.

If all goes according to the chemical equations given above, there is no net consumption of I₂ or LiI; the net reaction is the oxidative dehydrogenation Eq. 4, with I₂ and LiI being “catalysts”. In practice, however, one cannot avoid losing some iodine-containing compounds from the reactor and the iodine lost in this way needs to be recovered and recycled.

3 Experimental Methods

The molten salt reactor used in this work is shown in Fig. 1. It is a 15-cm-long quartz tube having a diameter of 1.25 cm, surrounded by a heating block. The gas and molten salt temperature is controlled by quartz-sleeved thermocouples. The gases (O₂ and C₃H₈, or O₂, C₃H₈, and I₂) are introduced in the reactor through a gas sparger (a 2-mm quartz tube with a medium Pyrex frit). The gaseous I₂ is produced in a sublimation cell that contains a mixture of solid I₂ and silica. Mass controllers are used for gas delivery. All plumbing exposed to I₂ or HI was constructed from quartz, polytetrafluoroethylene (PTFE), or polyetheretherketone (PEEK) to avoid corrosion. A convection oven was constructed around the reactor and the sublimation cell, to prevent the condensation of gaseous iodine. The salt was dried in flowing Ar at 110 °C for 3 hours, after loading in the reactor, and care was taken to minimize exposure of the LiI salt to air before loading. Constant propane partial pressure was maintained in all experiments unless otherwise noted.

In one mode of operation, the tube that introduces gases to the reactor was positioned directly over the surface of the salt (1/16 square inch salt surface area) so that the gases did not bubble through the liquid salt, but instead flowed over the surface. The gas space above the salt was also heated to maintain a known gas-phase volume and a known salt surface area. Some mixing in the gas-phase is likely due to the way the gas was introduced.

In retrospect we have realized that this reactor is not the best design. As we explained earlier in this article HI consumes rapidly the oxygen and prevents the oxidation of the hydrocarbons. It is therefore important that one uses a mixing reactor so that the feed entering the reactor encounters the HI produced by reaction. The reactor described in Fig. 1 achieves this but only partially. A better design would introduce oxygen gradually along the reactor so that the O₂ concentration is never higher than that required by the stoichiometry of the reaction $2 \text{HI} + \frac{1}{2} \text{O}_2 \rightarrow \text{I}_2 + \text{H}_2\text{O}$.

The gas-phase reactions between propane, iodine, and oxygen were studied using the reaction vessel used for molten salt experiments, except that the reactor contained no salt.

Fig. 1 Molten salt reactor used for iodine-mediated oxidative dehydrogenation of propane. The gas-phase reaction was performed in the same reactor with the salt removed.

To investigate I_2 -mediated ODH using molten LiI (no I_2 in the gaseous feed), we flow oxygen and propane over the surface of the molten salt. We have also investigated the effect of $LiOH$ as an oxidant for HI , by using molten LiI to which we added $LiOH$, or by using $LiOH$ dissolved into an “inert” molten salt (1:1 KCl - $LiCl$). We call these salts inert because they do not react with oxygen to produce chlorine; however, they do cause propane reactions. We use a mixture of chlorides (e.g. KCl - $LiCl$) to lower the melting temperature since neither chloride alone melts at the temperatures used in this work. There is always some loss of I_2 , which may leave the reactor as I_2 , C_3H_7I , or HI , so the

amount of LiI decreases in time. However, this decrease is slow and we found that the propylene yield was constant for 20 hours.

The gas leaving the reactor was scrubbed with 1M KI solution, for removal of I₂ and HI, before sampling the gas composition with online GC or a differentially-pumped mass spectrometer (SRS RGA 200) operating at < 10⁻⁵ torr. In some experiments, a liquid trap with CDCl₃ was added between the reactor and the KI solution to capture condensable hydrocarbons and other compounds for ¹H NMR analysis (Bruker Advance DMX500MHz spectrometer).

4 Results and Discussion

4.1 Halogen-mediated ODH in the gas phase using I₂(g) and O₂(g). To examine the role of gas-phase iodine we performed two experiments: in one, propane reacted with oxygen in the absence of iodine; and in the other, propane reacted with a mixture of oxygen and iodine. No molten salt was present in either experiment. Except for the presence or the absence of I₂(g), the reaction conditions in the two experiments were the same.

The bar graph at the left-hand side of Fig. 2 shows the product yields for the reaction of C₃H₈ with oxygen, in the gas phase (in the absence of I₂) at 500 °C. The propane partial pressure was 0.1 atm and that of oxygen was 0.05 atm; they have the molar ratio required by the stoichiometry of the reaction $\text{C}_3\text{H}_8 + \frac{1}{2} \text{O}_2 \rightarrow \text{C}_3\text{H}_6 + \text{H}_2\text{O}$. The estimated space time was 90 seconds and the total standard cubic centimeter per minute (sccm) was 5. The yield of propylene was ~16%, which is rather low compared to any of the existing processes. Oxygen conversion was 100%, which suggests that if the oxygen concentration in the feed were higher, the selectivity would be worse. The black vertical bar indicates the missing carbon in the carbon balance. To protect the mass spectrometer and/or the gas chromatograph, we trap all iodine-containing compounds prior to their reaching the detector. Therefore, some of the missing carbon can be propyl iodide. In one experiment we bubbled the effluent through CDCl₃ and performed NMR experiments, which detected 2-iodopropane and 1-iodopropane (see Fig. S1 in Electronic Supplementary Material). Benzene is a possible product but none was detected by NMR. A black deposit was observed on the walls of the reactor when gas-phase experiments

were performed, or floating on the molten salt when this was used. We suggest that the majority of missing carbon is likely to be in the black deposit or in propyl iodide.

The bar graph at the right-hand side of Fig. 2 shows the product yield for the reaction of propane with oxygen in the presence of I_2 . The molar ratios of the compounds in the feed were $C_3H_8:O_2:I_2 = 1:0.5:0.5$. In the presence of iodine the propylene yield is ~63%; the production of carbon oxides and of cracking products is reduced substantially. Oxygen conversion was 100%. The amount of water produced in this reaction was not monitored and because of this Fig. 2 shows only carbon-containing products.

Fig. 2 Comparison between the yields of the gas-phase reaction of propane with oxygen without iodine (left) and with O_2 and I_2 (right). When iodine was absent, the molar ratios were $C_3H_8:O_2 = 0.1:0.05$. When iodine was present, $C_3H_8:O_2:I_2 = 0.1:0.05:0.05$. In both cases the space time was 90 seconds, the temperature was 500 °C, the total flow was 5 sccm, the total pressure was 1 atm, and the inert gas was Ar.

Both iodine and oxygen need to be present for high propylene yields. If only iodine is present, the conversion is low; if only oxygen is present, the selectivity is low.

One of the disadvantages of propane dehydrogenation performed industrially is that it is equilibrium-limited; the halogen-mediated process (which is thermodynamically equivalent to oxidative dehydrogenation) is not.

The small amount of CO_x in the effluent indicates that C_3H_8 , C_3H_6 , and $2-C_3H_7I$ do not react with oxygen when I_2 is present. We propose that this happens because the reaction of O_2 with the HI formed during the HM-ODH reaction is much faster than the

reaction of O_2 with the hydrocarbon. This rapid consumption of oxygen diminishes hydrocarbon oxidation. To test whether this is indeed the case we examined the reaction of C_3H_8 , C_3H_6 , and $2-C_3H_7I$ with O_2 at 400 °C and 500 °C, in the absence of I_2 , in the reactor used to obtain the data shown in Fig. 2. The results (hydrocarbon and oxygen conversion and selectivity to CO and CO_2) are shown in Table 1. The molar ratio O_2 :hydrocarbon of 0.05:0.1 was the same as that used for the experiments that produced the data shown in Fig. 2. No salt was present, argon was used as an inert gas, space time was 90 seconds, and the conversion of O_2 was complete (at a temperature of 500 °C). Clearly in the absence of I_2 , propane, propylene, and propyl iodide are oxidized until all oxygen has been converted.

These findings provide a suggestion for a better reactor design. In the present work we introduce propane, I_2 , and O_2 into the reactor. There is no HI at the entrance of the reactor since this is produced by the reaction of I_2 with propane as the gases move along the reactor. Therefore, close to the entrance of the reactor the hydrocarbon is not “protected” from oxidation by the reaction of O_2 with HI. A better design would introduce oxygen gradually, along the reactor, so that in each reactor region the molar concentration of O_2 should be half the local molar concentration of the HI (produced by the reaction of I_2 with propane). It is very likely that the high yield obtained in our reactor is due to the mixing, by the flow, of the products with the incoming feed.

In the right-hand side of Fig. 3 we show how propane conversion, propylene selectivity, and propylene yield depend on the oxygen-to-propane ratio when the I_2 :propane molar ratio was held constant at 0.5. In the absence of oxygen, I_2 hardly reacts with propane and selectivity to propylene is poor (mostly cracking and coking). We explored further the dependence of propylene conversion for the reaction of propane with I_2 (in the absence of oxygen) and the results are shown in Fig. S3. The propylene yield increases when the ratio of I_2 to propane increases.

When oxygen is added, the conversion and the selectivity to propylene increase. There is a maximum propylene yield when the molar ratio $C_3H_8:O_2 = 0.5$, which is the stoichiometric ratio for the reaction $C_3H_8 + 1/2 O_2 \rightarrow C_3H_6 + H_2O$. The oxygen conversion is 100%, regardless of the propane-to-oxygen ratio (we varied the molar ratio of O_2 to propane ratio from 0 to 2). This means that adding O_2 beyond the $O_2:C_3H_8$ ratio

of 0.5:1.0 increases conversion, but it degrades selectivity so that propylene yield is lowered.

Fig. 3 Propane conversion (green), propylene selectivity (blue) and propylene yield (orange) at a temperature of 500 °C, a space time of 90 seconds, a flow rate of 5 sccm, partial pressure of propane = 0.1 atm, with argon used to maintain constant total pressure of 1 atm. The data on the left were taken in the presence of mixture of molten LiI and LiOH in the molar ratio of 1:1 (the reactor configuration is shown in the inset), with no I₂ in the gaseous feed. The data on the right were taken in the absence of the molten salt and with I₂ in the gas feed in the molar ratio I₂:C₃H₈ = 0.5:1. In both cases oxygen conversion was complete.

It seems slightly mysterious that propane conversion in the presence of I₂ and the absence of O₂ is so low and that adding oxygen increases both conversion and selectivity. There is however a simple explanation. When oxygen is absent, I₂ reacts with propane to form propylene and HI but the equilibrium $C_3H_8 + I_2 \rightleftharpoons C_3H_6 + 2 HI$ favors propane formation. When oxygen is present, the reaction $2HI + 1/2O_2 \rightarrow I_2 + H_2O$ is very fast [33]. Because of this both HI and O₂ are rapidly consumed: HI is prevented from reacting with propylene and oxygen is prevented from reacting with the hydrocarbons. Both effects are beneficial for the propylene yield.

4.2 HM-ODH using LiI(l) and a solution of LiOH(l) in molten LiI(l)

4.2.1 HM-ODH with a molten mixture of LiI and LiOH, at 500 °C. We carried out HM-ODH by flowing gaseous propane and oxygen (no I₂ was present in the gaseous feed) over the surface of a mixture of molten LiI and LiOH. Oxygen reacts with the molten iodide and produces I₂(g):

Water is included in this reaction because it is always present in the system: it is produced by the HM-ODH reaction and some of it is retained in the molten salt, which is very hygroscopic. It is possible that Li_2O is formed first and this reacts with water to form LiOH . Li_2O is insoluble in molten LiI and we did not see the formation of a solid in the system. We assume therefore that the formation of LiOH is rapid. The variation of propane conversion, propylene yield, and propylene selectivity with the oxygen-to-propane ratio are shown in the left side of Fig. 3. In this case the only I_2 present in the system is that produced by the oxidation of the salt.

The mixture of propane and oxygen (no I_2 is present in the gaseous feed) is introduced in the reactor through a frit that is close to the surface of a bed of molten mixture of LiI and LiOH of molar ratio of 1. The reactor is shown schematically in the inset in Fig. 3. The LiOH was added for two reasons: it is formed during the HM-ODH process and it reacts with HI to yield LiI and water. The gas flows into the surface of the molten salt and then turns around and flows into the head space, which contains O_2 , propane, and the I_2 produced by the reaction of oxygen with LiI . The area of the salt surface in contact with the reactant gas is 1/16 square inch. The space time in the system is 90 seconds (this includes the space time in the head space above the salt). The contact time of the gas with the salt is very short as compared to the space time in the head space.

Given the short contact time of the gases with the salt (as compared to the space time of the gases in the head space), it is difficult to decide between two possibilities: 1. Propane reacts with the molten salt or with some intermediates produced by the exposure of the salt to oxygen (LiIO , LiIO_3 are possibilities); 2. The salt is merely a source of I_2 and HM-ODH takes place entirely in the gas phase. One difference between the two experiments (Figure 3) is that when the molten salt is used, the maximum yield is obtained at an oxygen-to-propane ratio of one, while in the absence of the salt the maximum yield is obtained for $\text{O}_2:\text{C}_3\text{H}_8 = 0.5$. To some extent this is expected because when the I_2 is produced by the reaction of O_2 with LiI , some oxygen is used to oxidize the salt and the remainder reacts with HI in the gas phase.

The experiments whose results are presented in Fig. 4 were done in order to determine whether the molten LiI provides a sufficient amount of I_2 to the gas. We

determine this by performing HM-ODH with LiI:LiOH melt with and without I₂ in the gaseous feed. The bar graph on the left side of Fig. 4 shows the composition of the effluent for a gas feed of C₃H₈ and O₂ in the molar ratio 1:0.5, partial pressure of propane of 0.1 atm, and total pressure of 1 atm. The propylene yield is very high (~65%), very little CO_x is produced, and very little carbon is unaccounted for.

Fig. 4. The product yields obtained by flowing propane and oxygen over the surface of a mixture of molten LiI and LiOH (in the molar ratio 1:1) in the reactor shown between the bar charts. (Left) the product yields when no I₂ was present in the gas entering the reactor; (Right) the product yields when iodine was added to the gas feed in the molar ratio, I₂:C₃H₈ = 0.5. In both experiments the surface of the melt was 1/16 square inch, the space time in the space above the salt was 90 seconds, the temperature was 500 °C, the partial pressure of propane was 0.1 atm and that of oxygen was 0.05 atm, total flow rate was equal to 5 sccm.

The results in the right side of Fig. 4 were obtained by adding I₂ to the gaseous feed (C₃H₈ + ½O₂ + ½I₂) that is flowed over molten LiI:LiOH. The presence of additional I₂ (besides that produced by oxygen reacting with LiI) hardly makes any difference. This indicates that the molten salt can produce all the I₂ needed for HM-ODH, in spite of the fact that the area of the molten salt in contact with the gas is small.

We cannot measure the amount of gas-phase iodine produced by the oxidation of LiI. However we can use the oxygen balance to obtain an estimate. The water in the effluent must come from either HI combustion or hydrocarbon combustion. The amount of water produced by hydrocarbon combustion can be estimated from the amount of CO_x detected. Knowing this and the total amount of water in the effluent, we calculate the water formed by the oxidation of HI, hence the amount of HI produced. Assuming that all I_2 was converted to HI, we estimate that the partial pressure of I_2 in the head space above the molten salt was ~ 0.055 atm. This is roughly equal to the amount introduced into the gas feed in the experiment in which the molten salt was not present (Figure 2). It is therefore not surprising that the propylene yields are very similar in the two experiments. However, it is surprising that the reaction of oxygen with the molten salt produces sufficient I_2 in the gas in spite of the small surface area and the short contact time.

4.2.2 The effect of salt and gas composition at 400 °C. Industrial propane dehydrogenation is performed at temperatures near 600 °C because thermodynamic equilibrium favors higher yields at higher temperature. Going above 600 °C causes too much cracking. We have already shown that HM-ODH gives better propylene yields at a lower temperature (500 °C). We have observed that the reaction between oxygen, propane, and iodine can be detected as low as 370 °C (Fig. S5). Here we explore the performance at 400 °C. The measurements described below were performed by bubbling the gaseous feed through three inches of molten salt (a schematic of the reactor is shown in the inset of Fig. 5a). The space above the melt was also three inches long and the reaction took place in the bubbles traveling through the salt, perhaps at the surface of the salt, and in the gas phase above the salt. The total space time was 30 seconds (this includes the time the bubbles traveled through the salt and the time spent in the space above the reactor). The bubbles rise through the salt very rapidly and much of the space time is spent in the head space. Using a stop-flow experiment to estimate the gas hold-up in the reactor informs us that 3 seconds were spent in the bubbles rising through the salt and 27 seconds in the space above the salt. Fig. 5a gives results obtained in the absence of oxygen in the gas; those in Fig. 5b correspond to having propane and oxygen in 1:0.5 molar ratio.

The experiments whose results are reported in the bar graphs a_1 and b_1 of Fig. 5 correspond to the reaction of propane with I_2 (1:1 molar ratio), in the absence (a_1) or the presence (b_1) of oxygen, when no salt is present in the reactor. The bar graphs are practically identical, telling us that, at this temperature, it makes no difference whether oxygen is present in the feed or not. The propylene yield is very low (~8%).

The results shown in the bar graphs a_2 and b_2 were obtained in the presence of a 1:1 mixture of molten LiCl/KCl; we used this mixture of salts because neither pure salt will melt at 400 °C. Chlorides were chosen because they do not react, at this temperature, with oxygen to produce chlorine and therefore there should be no halogen-mediated ODH. In a_2 the gas contained I_2 and propane, and in b_2 it contained propane, I_2 , and oxygen. We find that the presence of the melt degrades selectivity: more CO_x and missing carbon are produced than in the case when no salt was present (a_1 and b_1). Since the salt is very hygroscopic we suggest that water is present and some steam reforming takes place, which explains the presence of CO_x in the feed. This is confirmed by experiments in which we passed propane and argon through a bed of molten LiCl/KCl and found that CO is produced for about 4 hours, after which the reaction slows down as the salt runs out of water (Fig. S2).

The results shown in a_3 of Fig. 5 indicate that not much happens when we bubble propane through a 1:1 mixture of molten LiI/LiOH in the absence of I_2 or O_2 in the gas; the conversion is minimal. Note that the difference in the propylene yield between a_3 and b_3 is substantial. Adding oxygen greatly increases the propylene yield because O_2 reacts with LiI and generates gaseous I_2 . It is interesting to compare b_2 (I_2 in the gas but LiCl/KCl in the melt) with b_3 (no I_2 in the gaseous feed but LiI/LiOH in the melt). Replacing LiCl/KCl with LiI/LiOH leads to a higher propylene yield, even though in both cases I_2 was present. However, in one case I_2 was introduced with the gaseous feed and in the other it was produced by the oxidation of LiI. One is tempted to suggest that the presence of LiI is beneficial beyond serving as a source of I_2 . However, the difference between b_2 and b_3 may be due to the fact that more I_2 is produced in b_3 . The results presented in a_4 show that adding I_2 while the melt is LiI/LiOH improves the propylene yield as compared to a_3 , where no gaseous I_2 was present in the feed (but it was produced from LiI). The addition of oxygen to the gaseous mixture of I_2 and propane increases the

propylene yield further (compare b_4 with either a_4). The yield is also increased if I_2 is added to oxygen and propane flowed over LiI/OH (compare b_3 to b_4).

It appears that at 400 °C the presence of oxygen in the gas and of LiI/LiOH in the melt and the addition of I_2 to the gaseous feed lead to the highest propylene yield. The highest propylene yield is obtained when the salt is LiI/LiOH and the gas contains O_2 , I_2 , and propane. However, the best yield obtained at 400 °C is well below that obtained at 500 °C.

Based on the results presented in Fig. 5, it is proposed that the propylene yield at 400 °C is controlled by I_2 concentration in the gas, and the propylene yields vary as shown below

In the absence of oxygen, LiI does not produce I_2 and the propylene yield is lower than that obtained in all other experiments (Fig. 5).

Fig. 5 The role of oxygen and of the molten salt. The only difference between the experiments in part (a) and part (b) is that the former were performed in the absence of oxygen while oxygen was added to the latter. (a₁) I₂:C₃H₈:Ar = 0.5:1:8.5 reacted in the empty reactor (no salt was present); (b₁) I₂:C₃H₈:O₂:Ar = 0.5:1:0.5:8 reacted in the empty reactor. (a₂) the reaction described at a₁ was performed in the presence of molten LiCl/KCl; (b₂) the reaction in b₁ was performed in the presence of molten LiCl/KCl. (a₃) C₃H₈:Ar = 1:9 reacted in the presence of LiI/LiOH; (b₃) C₃H₈:O₂:Ar = 1:0.5:8.5 reacted in the presence of LiI/LiOH. (a₄) C₃H₈:I₂:Ar = 1.0:0.5:8.5 reacted in the presence of LiI/LiOH; (b₄) I₂:C₃H₈:O₂:Ar = 0.5:1:0.5:8 reacted in the presence of LiI/LiOH. The reactor for (a) and (b) is shown in the inset, the height of the molten salt was 3 inches and that of the head space was 3 inches. The total pressure was 1 atm, space time was 30 seconds, the molar ratio of LiI:LiOH was 1:1 and the temperature was 400 °C.

4.2.3 The effect of space time at 400 °C. We have also examined the effect of space time on the HM-ODH reaction performed in gas phase. The longest standard -space time we were able to achieve in our reactor was 1.5 minutes based on standard feed conditions. The results are shown in Fig. 6 where longer space times give higher propylene yields and higher carbon oxide yields at 400 °C. We find that the propylene yield increases with the space time. In spite of the long space time, not all O₂ is converted at 400 °C. This is not the case at 500 °C, when under the same conditions and at a space time of 90 second the propylene yield was ~64%, all oxygen was converted, and relatively fewer unwanted products (CO_x, C1+C2 and missing carbon) were produced.

Fig. 6 The reaction yields for HM-ODH in gas phase, at a temperature of 400 °C as a function of space time. No molten salt was present; I₂:O₂:C₃H₈:Ar = 0.5:0.5 :1:8; 400 °C; total pressure 1 atm.

4.2.4. The role of propyl iodide. C₃H₇I is an intermediate in the proposed mechanism. For this reason we investigated briefly the chemistry of C₃H₇I under the reaction conditions used in the present work. In the mechanism proposed here we have assumed that C₃H₇I decomposes easily into HI and propylene. We have also assumed that the presence of oxygen aids the decomposition by oxidizing HI and preventing its reaction with C₃H₆. In Fig. 7 we show the results of temperature-programmed reaction for a feed of 2-C₃H₇I:Ar = 0.15:1.0. The space time was 90 seconds. We find that the decomposition of 2-C₃H₇I starts at ~ 300 °C and its rate increases rapidly as the temperature goes up. Around 400 °C this trend is reversed and the amount of propyl

iodide escaping from the reactor increases. The main net reactions taking place in this experiment are $\text{C}_3\text{H}_7\text{I} \rightleftharpoons \text{C}_3\text{H}_6 + \text{HI}$ and $\text{C}_3\text{H}_7\text{I} + \text{HI} \rightleftharpoons \text{C}_3\text{H}_8 + \text{I}_2$. Thermodynamic calculations indicate that at equilibrium, the conversion of propyl iodide should increase monotonically from room temperature to 500 °C, which indicates the observed trend is not due to thermodynamics and so must be due to kinetics. The results shown in Fig. 7 can be explained by assuming that the pre-exponentials in the rate constants of the backward reactions are larger than those of the forward reactions, which means that at higher temperatures the backward reactions become faster than the forward the forward reactions. We note that propane formation is a secondary reaction and therefore the amount of propane cannot exceed the amount of propylene, unless additional reactions are invoked. This interpretation is correct only if we assume that propylene does not react with HI while the effluent travels between the reactor and the mass spectrometer (or the GC). The carbon balance decreases as the temperature increases; this is due, at least in part, to the formation of coke which occurs above 350 °C. Solid black residue was observed in the reactor after the experiment. These results emphasize the importance of oxygen in the HM-ODH reaction: it removes HI and this hinders the recombination of HI with propylene.

Fig. 7. Temperature-programmed reaction in which 0.15:1 $\text{C}_3\text{H}_7\text{I}:\text{Ar}$ was flowed into an empty reactor as the temperature was ramped linearly in time. The total gas-phase space time was 90 seconds.

4.2.5 Combustion reactions, coking, carbon accumulation, and stability. In all experiments described here we observe secondary reactions due in which the hydrocarbons are partially oxidized. In order to test the extent of partial oxidation for

propane, propylene, and propyl iodide (an intermediate), we fed each hydrocarbon with oxygen into the reactor under the conditions described in the caption of Table 1.

Propane is relatively inert towards oxygen at both temperatures, while propylene reacts more rapidly, and iodopropane reacts even more rapidly. The only desirable oxygen reaction in the gas phase is with HI, and there is sufficient time for propylene and iodopropane oxidation if HI is not present. A proper balance between the amount of oxygen and that of HI is essential for obtaining high propylene yields.

Table 1. Partial oxidation for different hydrocarbons that are present in the HM-ODH process.

O₂:hydrocarbon = 0.5:1; hydrocarbon partial pressure 0.1 atm; total pressure 1 atm (the inert gas was Ar), no salt was present, and the space time was 90 seconds.

Reactants	Temperature	Hydrocarbon conversion	O ₂ conversion	Selectivity to CO	Selectivity to CO ₂
O ₂ + Propane	400 °C	8%	2%	1%	0%
O ₂ + Propane	500 °C	44%	100%	28%	4%
O ₂ + Propylene	400 °C	20%	65%	80%	2%
O ₂ + Propylene	500 °C	49%	100%	75%	6%
O ₂ + 2-Iodopropane	400 °C	40%	98%	28%	6%
O ₂ + 2-Iodopropane	500 °C	45%	100%	26%	9%

Propane is relatively inert towards oxygen at both temperatures, while propylene reacts more rapidly, and iodopropane reacts even more rapidly. The only desirable oxygen reaction in the gas phase is with HI, and there is sufficient time for propylene and iodopropane oxidation if HI is not present. A proper balance between the amount of oxygen and that of HI is essential for obtaining high propylene yields.

Coke has also been observed in the salt. When a mixture of propane and oxygen is bubbled through any of the salts we tested, carbon accumulates and was observed as a black residue on the salt surface. We assume that the main source of carbon is CO disproportionation reaction that can form carbon and CO₂. To test this we ran 10% CO in argon through LiI and saw large amounts of black solid formed. It is interesting to note that floating coke on the surface of the melt could make continuous coke removal possible in a large-scale process.

Often, the presence of a large surface area affects the kinetics of chain reactions [37]. This does not happen in the present work: when the reactor was packed with large amounts of broken quartz, gas-phase HM-ODH was not affected (Fig. S4). One possible explanation is that one of the compounds (or intermediates) involved in the gas-phase reaction binds to the quartz surface and blocks the sites where the radicals could bind and recombine.

Ideally no iodine leaves the reactor: and all I_2 reacts with propane and all HI reacts with the lithium oxide or with oxygen and no propyl iodide is present in the effluent. It is not clear that this could be achieved through good reactor design. Our reactor was not designed to capture all of the iodine containing compounds, the system is depleted of LiI. We ran under conditions where it would take several days to deplete the salt of iodine, and no deactivation was observed. To examine the depletion of LiI we performed experiments in which a very thin layer of molten LiI was supported on SiO_2 and a mixture of propane and oxygen were flowed through this bed in a plug flow reactor. After approximately 15 minutes of steady performance (Fig S6), the rate of reaction decayed and conversion became very low: the LiI layer was converted to Li_2O . The amount of oxygen consumed during the experiment indicates all of the LiI is consumed and activity is maintained almost until all LiI was consumed.

5 Conclusions

Iodine is an efficient gas-phase catalyst for oxidative dehydrogenation of propane. High ODH yields to propylene were achieved by using iodine either generated *in-situ* from LiI or added as a gas to the propane and oxygen feed. These two versions provided nearly equivalent yields, which were higher than those achieved by ODH on solid catalysts or by the industrial dehydrogenation processes in the absence of oxygen.

In the gas phase, propane conversion increases with increased oxygen concentration, and the propylene yield is highest when the propane to O_2 ratio is 1:0.5, which corresponds to the stoichiometry of the reaction $C_3H_8 + \frac{1}{2} O_2 \rightarrow C_3H_6 + H_2O$.

When molten LiI or a mixture of molten LiI and LiOH is used as a source of I_2 , the reaction of oxygen with LiI is rapid and produces sufficient I_2 so that addition of I_2 to the feed does not increase the propylene yield.

We propose that the high rate of the reaction of oxygen with HI is the main reason for the high propylene yield. Rapid consumption of oxygen by HI prevents the oxidation of the hydrocarbons. Rapid consumption of HI by oxygen prevents the reaction of HI with propyl iodide to make propane and I₂, as well as the reaction of HI with propylene to make propyl iodide. In the present experiments O₂ was introduced in the feed (with propane) and HI was produced as the reaction proceeded along the reactor. The ratio of oxygen to HI is too high in the first half of the reactor and too low in the second half. The reason for high alkene yields when molten LiI is used is likely to be gas-phase I₂-mediated ODH using iodine sourced from the salt. However, the contact time with the molten salt is much shorter than the space time in the gas so we cannot rule out that some reactions, besides the oxygen reaction with LiI, take place at the liquid surface.

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Conflict of Interest: The authors declare that they have no conflict of interest.

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