

Thermal Chemistry of Dihalopropanes on Ni(100) Single-Crystal Surfaces: Formation of Cyclopropane, Propene, and Propane

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The thermal chemistry of 1,3-diiodopropane, 1-chloro-3-iodopropane, 1-iodopropane, 1-chloropropane, 3-chloropropene, propene, and cyclopropane on Ni(100) surfaces has been studied under ultrahigh vacuum conditions by using temperature-programmed desorption (TPD) and X-ray photoelectron spectroscopy (XPS). Cyclopropane, propene, propane, and hydrogen are all produced by thermal activation of the diiodopropane at low coverages, and iodopropane and molecular desorption are also seen at higher coverages. In contrast with this, only cyclopropane, propene, and chloropropane—but no propane—were observed after thermal activation of 1-chloro-3-iodopropane. Both I 3d and Cl 2p XPS spectra suggest that the adsorption of the dihaloalkanes is molecular below 100 K and that at low coverages both halogen atoms interact directly with the surface. They also point to the fact that the C–I (C–Cl) bonds break between 140 and 180 K in steps that most likely lead to the generation of a three-carbon metallacycle on the surface. These metallacycles may then undergo either intramolecular coupling to form cyclopropane or a dehydrogenation step to generate propenyl groups on the surface, and propenyl moieties, produced either by thermal activation of the metallacycle mentioned above or directly via the surface decomposition of 3-chloropropene, dehydrogenate to propene. Finally, some iodopropyl species are generated at high 1,3-diiodopropane coverages, and those incorporate a surface hydrogen to produce iodopropane (which either desorbs or undergoes a second C–I bond scission to give propyl species, the same as when starting directly with 1-iodopropane). 1-Chloro-3-iodopropane loses an iodine atom first, and some of the resulting 3-chloropropyl yields 1-chloropropane and 3-chloropropene, while the rest reacts further to produce cyclopropane and propene, as in the diiodopropane case. Nevertheless, very little cyclopropane is detected at high 1-chloro-3-iodopropane coverages or in the presence of coadsorbed hydrogen, presumably because the formation of metallacycle species is not favorable in that case. Finally, 1-chloropropane mostly desorbs molecularly and does not yield any hydrocarbon products.

1. Introduction

The reactivity of alkyl halides on metal surfaces has become the subject of interest in recent years because of the ease with which they dissociate upon thermal activation to generate alkyl fragments.^{1,2} By the study of how the resulting alkyl fragments react, a better understanding of the mechanism of heterogeneous catalytic reactions such as Fischer–Tropsch synthesis, reforming, and other alkane conversion processes can be developed.^{3,4}

As part of our continuing studies on the chemistry of alkyl iodides on metal surfaces,^{5–20} and with the goal of characterizing cyclization reactions, here we report results from temperature-programmed desorption (TPD) and X-ray photoelectron spectroscopy (XPS) studies on the adsorption and subsequent thermal decomposition of several C₃ surface intermediates. There has been, to the best of our knowledge, only one previous reported surface science case of a cyclization reaction, that of Zhou and White on Ag(111), where cyclopropane formation was induced by thermal activation of 1-chloro-3-iodopropane.²¹ In addition, there has also been a second report by Bent et al. on the chemistry of some species relevant to this discussion on aluminum surfaces.²² There, the thermal decomposition of several dihalocompounds, including 1,3-diiodopropane, was shown to lead to the formation of the corresponding metallacycles. Those species, which form upon C–I bond scission below 300 K, were characterized by vibrational spectroscopy and were shown to decompose only at temperatures above 400

K and to yield the corresponding olefin. Nevertheless, no cyclization products were detected in these experiments.

In this study, the adsorption and subsequent thermal decomposition of 1,3-diiodopropane and 1-chloro-3-iodopropane were investigated on clean Ni(100) surfaces. The reactions of 1-iodopropane, 1-chloropropane, 3-chloropropene, cyclopropane, and propene on the same surface were also characterized for reference. Briefly, it was found that both dihaloalkanes adsorb molecularly below 100 K but form surface metallacycles upon thermal activation by losing their halogen atoms and that some upright adsorption is induced at higher coverages so that only one of the halogen (iodine) atoms interacts directly with the surface. Cleavage of the C–I (C–Cl) bonds occurs between 140 and 180 K, at which point surface metallacycles and/or either iodopropyl (for 1,3-diiodopropane) or chloropropyl (in the case of 1-chloro-3-iodopropane) groups form on the surface depending on the initial coverage. Cyclization of the metallacyclic groups produces cyclopropane, while β -hydride elimination from the same moiety yields a propenyl intermediate on the surface, a species that can also be generated by the direct thermal activation of 3-chloropropene and that eventually hydrogenates to propene. Hydrogenation of the iodopropyl groups leads to formation of iodopropane, and that molecule either desorbs molecularly or undergoes a C–I bond scission step to form a propyl surface moiety, the same as when starting directly from 1-iodopropane. Propane can then be produced by hydrogenation of either propyl or metallacycle species. In the case of 1-chloro-3-iodopropane, cyclopropane and propene are produced at higher temperatures than those generated by diiodopropane, and desorption of both 1-chloropropane and

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3-chloropropene is also observed at high coverages, but neither cyclopropane nor propane are detected presumably because the formation of the metallacycle species is inhibited in this case. Lastly, neither 1-chloropropene nor cyclopropane decompose thermally on this nickel surface, and propene only dehydrogenates to hydrogen and surface carbon.

2. Experimental Section

The ultrahigh vacuum (UHV) apparatus used in this study has been described in detail previously.^{5,23} Briefly, the main stainless steel chamber is evacuated by a turbomolecular pump to a base pressure of less than 1×10^{-10} Torr and is equipped with instrumentation for temperature-programmed desorption (TPD), X-ray photoelectron (XPS), static secondary ion mass (SSIMS), Auger electron (AES), and ion scattering (ISS) spectroscopies. The details of the experimental procedures used for the TPD and XPS experiments have also been reported previously.^{5,24} TPD data were obtained by using a heating rate of about 10 K/s and by simultaneously recording up to 15 masses in a single experiment with a computer interfaced to the mass quadrupole. The partial pressures in all TPD figures are reported in arbitrary units but can be compared by using the relative intensity bars provided in each frame. XPS spectra were taken by using an aluminum-anode X-ray source and a hemispherical electron energy analyzer set to a constant pass energy corresponding to an overall resolution of about 1.2 eV full-width at half-maximum. The absolute energy scale was calibrated against reported values for the Pt 4f_{7/2} and Cu 2p_{3/2} signals and is accurate to 0.1 eV. The XPS data reported in Figures 8 and 9 were obtained by subtracting the corresponding spectra from the clean nickel surface.

The Ni(100) crystal was cut and polished using standard procedures and cleaned by cycles of oxygen treatment, argon ion sputtering, and annealing until no impurities were detected by either AES or XPS. The 1,3-diiodopropane, 1-chloro-3-iodopropane, 1-iodopropane, 3-chloropropene, and cyclopropane were all purchased from Aldrich (purity 99% or better) and subjected to several freeze–pump–thaw cycles and checked by mass spectrometry before use. Both propene and ultrahigh purity hydrogen were obtained from Matheson Gas products and used as supplied. Exposures of the surface to these gases were done by backfilling of the chamber via leak valves and measured in Langmuirs (1 L = 10^{-6} Torr s, not corrected for ion gauge sensitivities).

3. Results

Figure 1 shows temperature-programmed desorption (TPD) results for 5.0 L of 1,3-diiodopropane (left) and for 5.0 L of 1-chloro-3-iodopropane (right) chemisorbed on Ni(100) surfaces. Only hydrogen (2 amu), cyclopropane and propene (42 amu), and propane (in the case of 1,3-diiodopropane, 44 amu) desorb from the surface at these low coverages. In particular, no propadiene (40 amu), hexene (84 amu), hexane (86 amu), iodoheptane (212 amu), chloropropene (120 amu) or molecular desorption (246 amu) were detected. The formation of allenes is more difficult to test because those compounds are difficult to prepare and are also expected to decompose readily to carbon and hydrogen on the surface, but the data provided no indication that such products were made in these systems either.

At the coverage of 1,3-diiodopropane shown in the left panel of Figure 1 (that resulting from a 5.0 L exposure), a small amount of propane forms at about 110 K and hydrogen desorption is seen at 360 and 430 K. The signal at mass 42, which displays two peaks at about 130 and 190 K, represents the desorption of both cyclopropane and propene (see below).

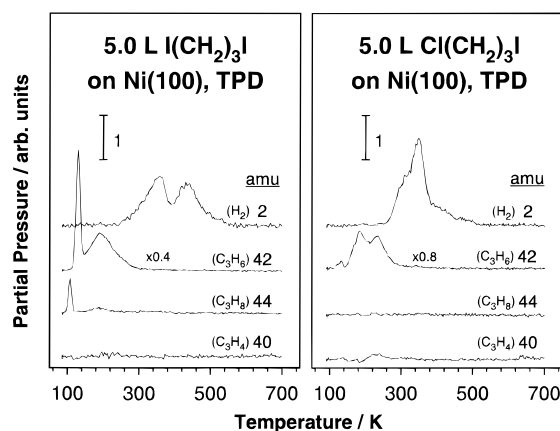


Figure 1. Samples of 2, 40, 42, and 44 amu TPD spectra from Ni(100) surfaces dosed with either 5.0 L of 1,3-diiodopropane (left) or 1-chloro-3-iodopropane (right) at 90 K. The traces correspond to the desorption of H₂, propadiene, cyclopropane and propene, and propane, as discussed in the text. A heating rate of 10 K/s was used in all the experiments reported here.

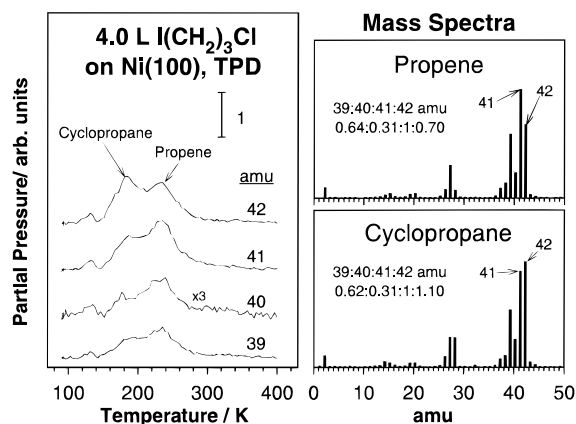


Figure 2. Left: 39, 40, 41 and 42 amu TPD traces from 1-chloro-3-iodopropane on Ni(100). Right: Mass spectra of gaseous propene (top) and cyclopropane (bottom), recorded under the same experimental conditions as in the TPD experiments. The mass spectra were used to determine the contributions of each of the two species to the signal intensities in the raw TPD data. The peak assignment shown in the left panel is the result of this comparison.

In the case of 1-chloro-3-iodopropane, no propane desorption is observed at any exposure, whereas hydrogen desorbs mainly at 350 K (Figure 1, right). Also, the peaks in the 42 amu trace appear at 180 and 235 K, at higher temperatures than in the case of 1,3-diiodopropane, perhaps because the higher strength of the C–Cl bond in the chloro-containing compound inhibits its low-temperature decomposition (see below).

To differentiate between cyclopropane and propene desorption in the TPD of these dihalocompounds, a more careful quantitative analysis of the spectra was performed by comparison with the cracking patterns of the pure products. Figure 2 illustrates this procedure for the case of 1-chloro-3-iodopropane: the left frame shows the TPD traces for 39, 40, 41, and 42 amu, while the two panels on the right display the cracking patterns for pure propene (top) and cyclopropane (bottom) obtained by using the same settings as in the TPD experiments. From these data it is quite straightforward to assign the low- and high-temperature desorption features to cyclopropane and propene, respectively (see also Table 1). Notice in particular the changes in relative intensities in both peaks between the traces for 41 and 42 amu. A similar determination was done for the 1,3-diiodopropane case, where the peak at 130 K was found to correspond to cyclopropane and that around 190 K to propene.

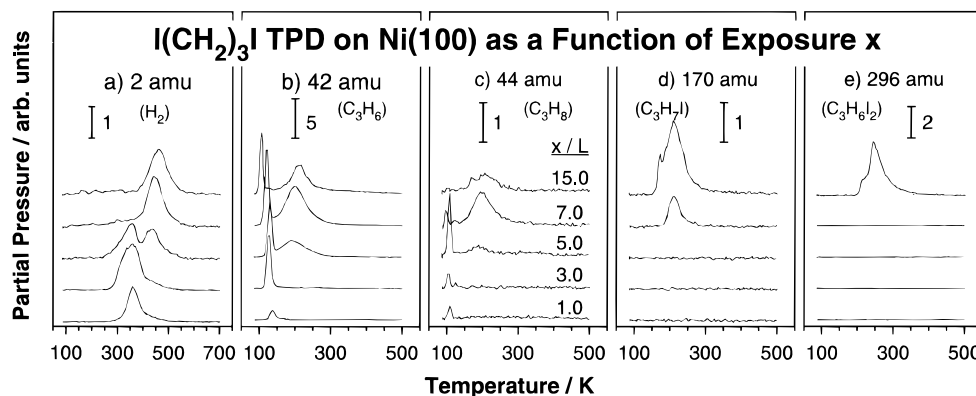


Figure 3. (a) Hydrogen (2 amu), (b) cyclopropane and propene (42 amu), (c) propane (44 amu), (d) 1-iodopropane (170 amu), and (e) 1,3-diiodopropane (296 amu) TPD spectra from 1,3-diiodopropane adsorbed on Ni(100) as a function of initial exposure. All dosings were done at 90 K.

TABLE 1: Peak Intensities (Relative to Those of the 41 amu Signal) for Both the Mass Spectra of Pure Propene and Cyclopropane and the TPD Traces from Experiments with Dihaloalkanes Adsorbed on Ni(100) Surfaces

amu	mass spectra (MS)		temperature-programmed desorption (TPD)			
	propene	cyclopropane	1-chloro-3-iodopropane		1,3-diiodopropane	
			180 K	235 K	130 K	190 K
39	0.64	0.62	0.69	0.66		
40	0.31	0.31	0.36	0.36	0.31	0.31
41	1	1	1	1	1	1
42	0.70	1.10	1.30	0.80	1.10	0.70

The thermal reactions of dihaloalkanes on nickel surfaces were probed further by performing a set of TPD experiments as a function of initial exposure. The results for the case of the 1,3-diiodopropane are summarized in Figure 3. With respect to the desorption of hydrogen (Figure 3a), a single peak is seen about 360 K for $C_3H_6I_2$ doses below 3.0 L, with a yield that doubles as the 1,3-diiodopropane exposure increases from 1.0 to 3.0 L. A new feature about 430 K starts to grow at around 5.0 L at the expense of the low-temperature peak, but the overall yield starts to decrease again compared to that obtained in the 3.0 L case. At 7.0 L and above the hydrogen peak at 360 K disappears completely, and the high-temperature peak becomes larger and shifts to about 480 K. The high temperature of the peaks seen after the high doses suggests that they may be related to the irreversible decomposition of hydrocarbon fragments that form at lower temperatures but survive until heating above 400 K. The overall hydrogen yield is about the same at 1.0 and 15.0 L.

Figure 3b displays the TPD spectra for the 42 amu fragment, which corresponds to the desorption of both cyclopropane and propene (as discussed above). Only cyclopropane formation is observed after a 1.0 L $C_3H_6I_2$ exposure, as indicated by the peak about 135 K. The activation energy of this process was estimated to be about 7 kcal/mol by using Redhead's equation²⁵ and assuming a preexponential factor of 10^{13} s^{-1} . The yield for cyclopropane desorption increases with increasing initial $C_3H_6I_2$ exposure, up to 7.0 L, and the temperature of the desorption maximum shifts down to 105 K at 15.0 L exposure. The contribution due to propene, on the other hand, appears at 190 K and only after a 5.0 L $C_3H_6I_2$ exposure. The activation energy in this case was estimated to be about 12 kcal/mol. The yield for propene production increases while the desorption temperature goes up by 10 K as the initial exposure is varied from 5.0 to 7.0 L of $C_3H_6I_2$, and after a 15.0 L exposure the peak temperature increases further, to about 210 K, but the propene yield decreases again.

Figure 3c shows that a small amount of propane first appears at about 110 K at 1.0 L of $C_3H_6I_2$ in a peak that then grows with increasing initial 1,3-diiodopropane coverage up to 5.0 L. This feature may be associated with the direct decomposition of the dihalocompound, perhaps via the formation of a gas-phase radical,²⁰ but the second desorption peak that starts to grow at higher temperatures (200 K) after a 7.0 L exposure is clearly associated with the surface chemistry of hydrocarbon moieties. The activation energies for propane desorption in the low- and high-temperature regimes are about 6.3 and 12.6 kcal/mol, respectively. Both the low- and high-temperature peaks then decrease in size as the initial dose is increased even further. It is interesting to point out that the propane desorption seen here is very similar to that obtained after adsorption of 1-iodopropane on clean Ni(100), suggesting that both cases may involve a common intermediate.

The desorption of iodopropane upon thermal activation of 1,3-diiodopropane on Ni(100) starts only after exposures above 7.0 L and is seen as an initial peak at 208 K and a small shoulder that grows at 170 K at 15.0 L (Figure 3d). Finally, molecular 1,3-diiodopropane desorption starts above 10.0 L and is seen as a main peak at about 242 K and a shoulder around 215 K (Figure 3e). The size of both molecular peaks increases as the exposure is increased further (not shown), but the low-temperature feature becomes sharper and grows relative to the high-temperature one, suggesting that it may originate from desorption of a condensed layer. A leading edge analysis of this lower-temperature peak gives a value for the sublimation energy of the condensed 1,3-diiodopropane of about 16.0 kcal/mol, very close to that reported in literature.²⁶ The saturation coverage for diiodopropane was estimated to be about 0.2 monolayers by comparing the iodine XPS peak intensity of diiodopropane with that obtained from other known iodoalkanes (see below).

TPD experiments with 1,3-diiodopropane were also done on surfaces predosed with hydrogen. The left panel of Figure 4 summarizes the TPD obtained for the case of 2.0 L of H_2 and 5.0 L of 1,3-diiodopropane coadsorbed at 90 K, in which case only propane, cyclopropane, and hydrogen desorb from the surface. The propane desorption peak (44 amu), centered around 155 K, is much broader than in the case of the clean surface, and the yield is about 5 times larger than without hydrogen coadsorption. The trace for the 42 amu shows that cyclopropane still desorbs at 125 K, even though its yield becomes significantly reduced, but the formation of propene is almost completely inhibited by the presence of surface hydrogen. Lastly, hydrogen desorbs in two stages, around 260 and 370 K. The low-temperature peak, which corresponds to desorption

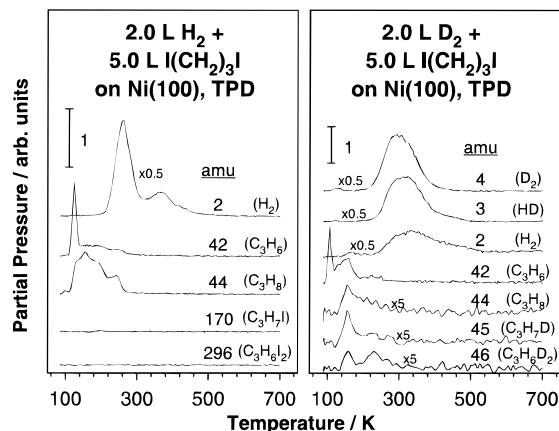


Figure 4. Left: H_2 (2 amu), cyclopropane and propene (42 amu), propane (44 amu), 1-iodopropane (170 amu), and 1,3-diiodopropane (296 amu) TPD spectra from a Ni(100) surface dosed sequentially with 2.0 L of normal hydrogen and 5.0 L of 1,3-diiodopropane. Right: H_2 (2 amu), HD (3 amu), D_2 (4 amu), cyclopropane and propene (42 amu), and propane- d_0 , - d_1 , and - d_2 (44, 45, and 46 amu) TPD spectra from a Ni(100) surface dosed sequentially with 2.0 L of deuterium and 5.0 L of 1,3-diiodopropane.

of the coadsorbed hydrogen, is shifted to lower temperatures because of the repulsive interaction between that hydrogen and the 1,3-diiodopropane, and the high-temperature peak is the result of hydrogen desorption from recombination of H atoms generated by decomposition of the hydrocarbon surface intermediates that form after 1,3-diiodopropane thermal activation. In the case of deuterium preadsorption, the TPD data show the desorption of H_2 , HD, D_2 , propene, cyclopropane, and both normal and partially deuterated propane (Figure 4, right). Consistent with the results with predosed H_2 , hydrogen desorption in this case also occurs at 340 K and is due to decomposition of hydrocarbon moieties, while HD and D_2 originate mainly from the predosed D_2 and desorb at lower temperatures. The hydrogenation of a metallacycle species with two deuterium atoms generates doubly deuterated propane ($\text{C}_3\text{H}_6\text{D}_2$), as seen by small signals around 150 and 230 K in the 46 amu trace, while recombination with one and two hydrogen atoms produces monodeutero and normal propane (responsible for the 150 K peak in the 45 and 44 amu signals), respectively. No iodopropane desorption is observed in any of the hydrogen-predosing cases.

Similar coadsorption experiments were also performed by using high doses of 1-chloro-3-iodopropane in the presence of preadsorbed hydrogen. The left panel of Figure 5 displays the TPD spectra obtained for a saturation dose (12.0 L) of 1-chloro-3-iodopropane on clean Ni(100). At this exposure most of the unsaturated hydrocarbon produced is propene, which desorbs at about 200 K. Small amounts of both 1-chloropropane and 3-chloropropene desorb at about 208 K, but no iodopropane is produced at all, indicating that high-coverage adsorption of the 1-chloro-3-iodopropane is through the iodine atom and that the cleavage of the C—I bond on the surface upon thermal activation is preferred over the C—Cl bond-scission alternative. Molecular desorption is also seen in this case at about 210 K, a temperature slightly lower than that of 1,3-diiodopropane, but neither propane nor propadiene are detected at all at this coverage.

The results from TPD experiment with 4.0 L 1-chloro-3-iodopropane coadsorbed with 2.0 L hydrogen are summarized in the right panel of Figure 5. The main desorption products in this case are hydrogen, propene, and 1-chloropropane, but small amounts of propane and 3-chloropropene are also detected. Propene desorbs at about 173 K and is most probably produced via the decomposition of 3-chloropropene and hydrogenation

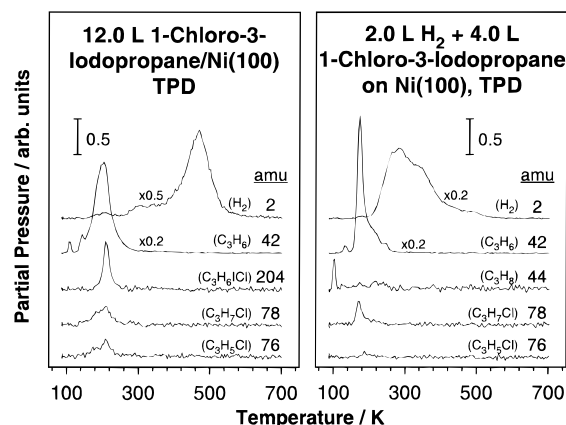


Figure 5. Left: H_2 (2 amu), cyclopropane and propene (42 amu), 3-chloropropene (76 amu), 1-chloropropane (78 amu), and 1-chloro-3-iodopropane (204 amu) TPD spectra from a Ni(100) surface dosed sequentially with 12.0 L of 1-chloro-3-iodopropane at 90 K. Right: H_2 (2 amu), propene (42 amu), propane (44 amu), 3-chloropropene (76 amu), and 1-chloropropane (78 amu) TPD spectra from a Ni(100) surface dosed sequentially with 2.0 L of deuterium and 4.0 L of 1-chloro-3-iodopropane at 90 K.

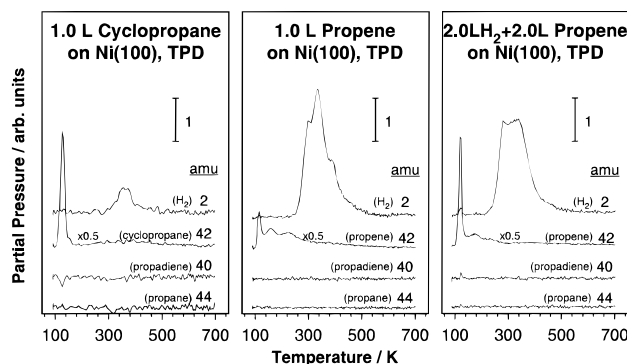


Figure 6. H_2 (2 amu), propadiene (40 amu), cyclopropane and propene (42 amu), and propane (44 amu) TPD spectra from Ni(100) surfaces dosed with 1.0 L of cyclopropane (left), 1.0 L of propylene (center), and 2.0 L of H_2 + 2.0 L of propene (right) at 90 K.

of the resulting propenyl intermediate. This olefin could in principle be also produced by β -hydride elimination from the propyl species generated through partial hydrogenation of metallacycle species, but this is unlikely because studies on surfaces where hydrogen is coadsorbed with 1-iodopropane show that propyl species are readily hydrogenated to propane instead.^{13,27} The formation of metallacycle species must not be important in the 1-chloro-3-iodopropane case because only a very small amount of propane is detected in the TPD experiments. The formation of chloropropane involves recombination of coadsorbed hydrogen with the 3-chloropropyl species on the surface, a hydrogenation step that apparently is more favorable than the dissociation of C—Cl bond in this system because without hydrogen coadsorption no chloropropane formation is observed (Figure 1, right).

Reference TPD experiments with cyclopropane and propene are reported next. The results obtained after dosing 1.0 L of either cyclopropane or propene are summarized in the first two frames of Figure 6. In the case of cyclopropane, only molecular desorption is observed (as a sharp peak at 126 K, left panel of Figure 6), in agreement with the results of previous reports.²⁸ The thermal treatment of cyclopropane when adsorbed alone on clean Ni(100) does not lead to any carbon—carbon activation. The desorption temperature for molecular cyclopropane seen here is slightly lower than that observed for the cyclopropane formed from 1,3-diiodopropane (either with or without hydrogen

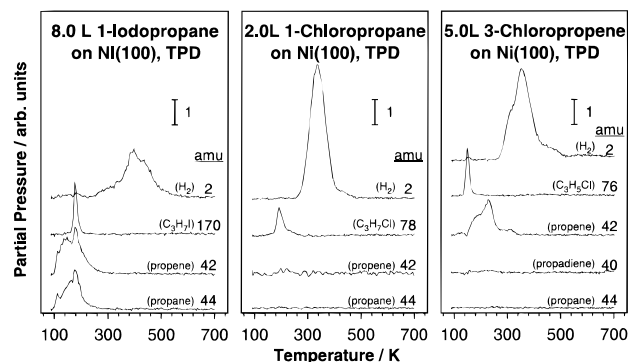


Figure 7. Left: H_2 (2 amu), propene (42 amu), and 1-iodopropane (170 amu) TPD spectra from 8.0 L of 1-iodopropane dosed on Ni(100) at 90 K. Center: H_2 (2 amu), propene (42 amu), propane (44 amu), and 1-chloropropane (78 amu) TPD spectra from 2.0 L of 1-chloropropane dosed on Ni(100) at 90 K. Right: H_2 (2 amu), propadiene (40 amu), propene (42 amu), propane (44 amu), and 3-chloropropene (76 amu) TPD spectra from 5.0 L of 3-chloropropene dosed on Ni(100) at 90 K.

coadsorption), indicating that the detection of cyclopropane in the TPD experiments with dihaloalkanes described above is most likely reaction-limited. The center frame of Figure 6 shows that propene can also desorb molecularly and that no other hydrocarbons (propadiene or propane) are produced.¹¹ The molecular desorption of propene occurs in several stages (110, 155, and 215 K), but some surface dehydrogenation takes place concurrently, as evidenced by the evolution of hydrogen at about 300, 330, and 380 K. Finally, the right panel of Figure 6 displays TPD data for propene dosed on hydrogen-predosed surfaces and again shows hydrogen and propene as the only desorbing products; no hydrogenation to propane was detected here either. Most of the propene coadsorbed with hydrogen desorb around 115 K.

Additional information about the mechanism for the formation of both cyclopropane and propene from the 1,3-dihaloalkanes was obtained by performing TPD experiments with 1-iodopropane, 1-chloropropane, and 3-chloropropene (Figure 7). The left panel of Figure 7 shows the TPD obtained after adsorption of a saturation coverage of 1-iodopropane (8.0 L) on Ni(100) at 90 K. Only hydrogen, molecular 1-iodopropane, propene, and propane desorb from this surface. Hydrogen desorption occurs in a broad temperature range at about 390 K, 1-iodopropane in a sharp peak about 180 K, and both propene and propane as broad features around 130 and 180 K.¹¹ Unlike in the case of 1-iodopropane, the TPD in the center frame of Figure 7 shows that the thermal activation of 1-chloropropane does not generate any desorbing hydrocarbon products, only some hydrogen from total decomposition (which desorbs at about 333 K) and molecular desorption (which occurs around 195 K). With respect to 3-chloropropene, the data in the right panel of Figure 7 show that some propene is produced in two stages around 180 and 230 K and that some hydrogen desorbs at 350 K but that no cyclopropane is formed at all. It is interesting to note that the molecular desorption of 3-chloropropene occurs at 147 K, about 40 K lower than in the case of 1-chloropropane. In addition, the fact that propene is formed from 3-chloropropene but not from 1-chloropropane suggests that the presence of the double bond in 3-chloropropene weakens the C–Cl bond and thus induces its dissociation. The intermediate that results from the carbon–halogen bond scission is most likely a propenyl species (either a σ 3-propen-1-yl moiety or its π -allylic isomer), some of which recombine with surface hydrogen to yield the propene that desorbs between 150 and 250 K. This is consistent with the fact that the C–Cl bond-dissociation energy for

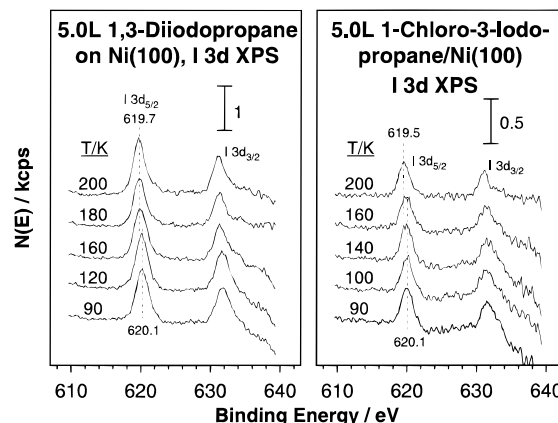


Figure 8. Iodine 3d X-ray photoelectron (XPS) spectra from Ni(100) surfaces dosed with either 5.0 L of 1,3-diiodopropane (left) or 5.0 L of 1-chloro-3-iodopropane (right) at 90 K after annealing to the indicated temperatures.

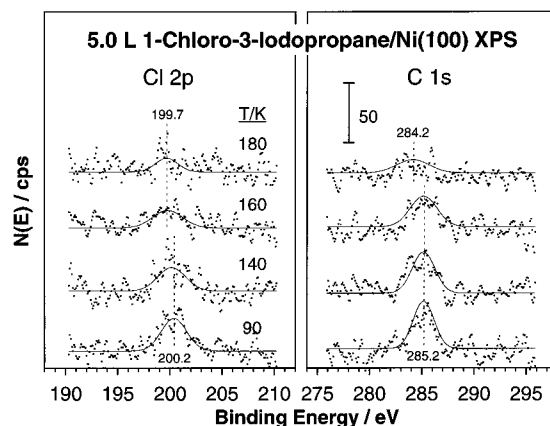
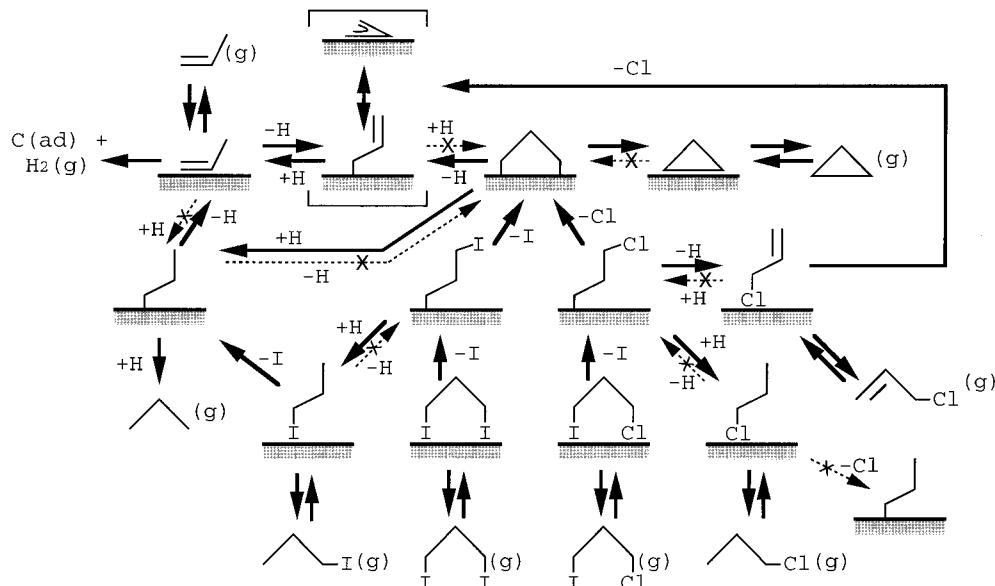


Figure 9. Chlorine 2p (left) and carbon 1s (right) XPS spectra from 5.0 L of 1-chloro-3-iodopropane dosed on Ni(100) at 90 K after annealing to the indicated temperatures. The raw data is shown as dots, whereas Gaussian fits are displayed as solid lines.

3-chloropropene (60 kcal/mol) is about 22 kcal lower than that for 1-chloropropane.²⁹

The initial carbon–halogen bond-cleavage steps in 1,3-diiodopropane and 1-chloro-3-iodopropane were also studied by following the changes in the binding energies of the halogen core electrons with XPS as a function of annealing temperature. Figure 8 displays the I 3d XPS data for 5.0 L of $\text{ICH}_2\text{CH}_2\text{CH}_2\text{I}$ (left) and 5.0 L of $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{I}$ (right). Neither the area nor the shape of the peaks in these figures change in either case by annealing to different temperatures, but the binding energies shift, in the case of the I 3d_{5/2} peak from a value of about 620.1 eV at 100 K, to approximately 619.7 and 619.5 eV after heating to 200 K for 1,3-diiodopropane and 1-chloro-3-iodopropane, respectively. This shift is associated with the scission of the C–I bonds in the adsorbed molecular species¹¹ and occurs around 160 K for 1,3-diiodopropane and at about 180 K for 1-chloro-3-iodopropane. As mentioned before, comparison of the iodine peak areas obtained for surfaces saturated with 1,3-diiodopropane with those of other alkyl iodides¹³ yields a value for the saturation coverage of about 0.2 monolayer in this case.

The left panel in Figure 9 shows Cl 2p XPS spectra from 5.0 L of 1-chloro-3-iodopropane adsorbed on Ni(100) after annealing to the indicated temperatures. Owing to the noise in the raw data, Gaussian fits are also shown in this figure to better highlight the peak maxima. The XPS spectra obtained at 140 K shows a weak signal centered around 200.2 eV, about 0.4 eV lower in value from that observed for molecular 1-chloro-3-iodopropane adsorbed below 100 K. Annealing to higher

SCHEME 1: Interconversion of C₃-Hydrocarbon Intermediates on Ni(100)

temperature (160 K) causes the Cl 2p peak to shift further, to a value of about 199.7 eV, and at higher temperatures (> 180 K) the signal weakens to the point of disappearing under the experiment noise. The corresponding temperature dependence of the C 1s XPS signal is shown in the right panel of Figure 9. The C 1s XPS trace obtained at 90 K shows a peak around 285.2 eV, which is most likely due to nondissociated 3-chloro-1-iodopropane because it is seen at a position between that of iodomethane and chloromethane on Ag(111).³⁰ This peak remains at about the same position after heating to 160 K, but annealing above that temperature results in the disappearance of most of the carbon signal, since a large fraction of the carbon-containing species desorb from the surface (as seen by the TPD data). The small peak that remains after heating to 180 K is centered around 284.2 eV.

4. Discussion

The combined results from the temperature-programmed desorption and X-ray photoelectron spectroscopy experiments reported here provide some detailed information on the thermal chemistry of 1,3-dihaloalkanes on Ni(100). TPD experiments with 1-iodopropane, 1-chloropropane, 3-chloropropene, propene, and cyclopropane were also done in order to get additional insight into the intermediate species involved in the decomposition reactions of the dihaloalkanes. The XPS experiments indicate that below 140 K both 1,3-diiodopropane and 1-chloro-3-iodopropane chemisorb molecularly on the surface because both the I 3d and the Cl 2p binding energies of the adsorbed species are about the same as those reported for nondissociated carbon-halogen bonds in compounds such as iodopropane, iodoethane, and iodomethane.^{6,9,11} However, annealing to temperatures between 160 and 180 K leads to the cleavage of all C-I and C-Cl bonds. Studies with various monohaloalkanes have shown that this is the first decomposition step in such systems and that the activation energy for the dissociation of C-I bonds is only 2–4 kcal/mol.^{8,13} We believe that the same conclusions also apply to the present dihaloalkane cases.

It is not easy to determine if the two carbon-halogen bonds in the dihaloalkanes break sequentially or simultaneously, but a sequential mechanism is suggested by some of the results reported in this work. For one, some iodopropane desorbs in TPD experiments with 1,3-diiodopropane, and likewise, 1-chloropropane is also produced upon thermal activation of 1-chloro-

3-iodopropane, although these reactions are only observed at high coverages. The production of monohaloalkanes from the dihalo reactants not only implies that at least some molecules go through one single C-I bond-scission step and then follow a reductive elimination pathway with surface hydrogen, but also suggests that there is a change in adsorption geometry as the coverage is increased: at low coverages the interaction of the dihalopropane molecules with the surface appears to involve both halogen atoms, but near saturation there is not enough room for such a configuration, and some molecules may therefore be forced to bind in an upright position through only one halogen (the iodine) atom instead. Similar geometrical rearrangements have in fact been seen before with monohaloalkanes.^{13,31,32} In addition, since the C-Cl bond is stronger than the C-I bond (their dissociation energies are on the order of 85 and 55 kcal/mol, respectively³³), it would be expected for the latter to break first in the case of 1-chloro-3-iodopropane. The XPS data are inconclusive on this point, since they indicate that both bonds break between 160 and 180 K, but since only 1-chloropropane (not iodopropane) desorbs in the TPD experiments, the iodine atom must indeed be eliminated first. Moreover, the thermal chemistry of the two dihalocompounds on Ni(100) shows significant differences, a fact that suggests that the higher temperatures needed for the C-Cl bond-scission step lead to a change in the selectivity among the subsequent reactions available to the surface products. Note, however, that once the first C-I bond is broken in the adsorbed 1-chloro-3-iodopropane, the C-Cl bond is then activated and breaks soon afterward.

We believe that the dissociation of both carbon-halogen bonds in the dihaloalkanes on Ni(100) eventually leads to the formation of a surface metallacycle. This same conversion has been reported previously on aluminum single crystals, where the resulting intermediate was isolated and characterized by using vibrational spectroscopy.²² The three-carbon metallacycle then follows a series of conversion steps upon further thermal activation, as summarized in Scheme 1. Several competing reactions are shown there, namely, cyclization to cyclopropane, hydrogenation to propyl and then to propane, and dehydrogenation to propenyl (and eventually to surface carbon). The occurrence of the cyclization reaction on Ni(100) in particular is surprising, since no carbon-carbon coupling steps have been seen in any of the other nickel-based systems studied to date

and because such a reaction is not operational on aluminum single-crystal surfaces either (where propene production is seen instead).²² In the case of 1,3-diiodopropane the cyclization step occurs around 130 K, a temperature that, although low, is still reflective of the energy needed to activate the surface step because molecularly adsorbed cyclopropane desorbs readily below 125 K (Figure 6). Cyclopropane desorption from 1-chloro-3-iodopropane, on the other hand, only occurs around 180 K, presumably because activation of the C–Cl bond requires higher temperatures.

Cyclization steps are common in both organometallic and organic chemistry,^{34,35} and cyclopropane formation from $\text{Cl}(\text{CH}_2)_3\text{I}$ adsorbed on $\text{Ag}(111)$ has also been reported by Zhou and White²¹ (no propene, propane, or iodopropane desorption was seen in that system, though). Several mechanisms have been proposed for these cyclization reactions. One possibility is for an initial C–C bond-breaking step to be followed by insertion of the resulting olefin into the remaining metal–carbene bond.³⁶ However, this mechanism, the basis of metathesis processes, is more typical of early transition metals such as Ti, not late ones such as Pt or Ni, and furthermore, data from our laboratory have shown that CH_3 species (which can dehydrogenate to CH_2 on the surface) do not couple with ethylene on $\text{Ni}(100)$ and also that while 1-iodo-5-hexene do not yield any cyclic products, 1,6-diiodohexane does.³⁷ Lastly, the activation of 3-chloropropene on $\text{Ni}(100)$ generates a propenyl species on the surface but does not form cyclopropane (Figure 7).

Given that dihalopropane precursors were used in the experiments reported in this paper, a second possibility for the formation of cyclopropane on $\text{Ni}(100)$ could be via a concerted reaction on the monohalo intermediate that may form on the surface upon the scission of one of the C–I bonds. This could in fact occur via a $\text{S}_{\text{N}}2$ -type mechanism, the same as in the reaction between methyl iodide and hydrogen adsorbed on $\text{Ni}(100)$.³⁸ However, although cyclopropane formation from 1-chloro-3-iodopropane peaks around 200 K (as Figure 1 shows), the scission of both carbon–halogen bonds appears to occur at much lower temperatures, below 180 K. This suggests that the monohalo intermediate required for the concerted cyclization mechanism being discussed here may not be stable at the temperatures required for that reaction to take place.

A third and more likely mechanism for cyclopropane production in this system is a direct ring closure of the metallacycle species that results from the scission of both carbon–halogen bonds in the original dihalo precursor. The direct formation of cyclopropane is quite common in organometallic chemistry, and extensive work has been done to understand the mechanism of that reaction.³⁴ It has been shown, for instance, that α -deutero- α -phenyl platinacyclobutane can rearrange to produce the α -deutero- β -phenyl platinacyclobutane isomer, apparently by going through a coordinated cyclopropane intermediate.³⁹ In fact, when that platinacyclobutane is treated with Ph_3P , phenylcyclopropane-2- d_1 is produced. A similar isomerization process has also been reported for titanacyclobutane complexes,⁴⁰ and, perhaps more directly connected to our studies, cyclopropane has been produced by both the silver-assisted dissociation of the bromide from (γ -bromopropyl)iron and the dissociation of the phenylmethyl sulfide from (γ -sulfonium-propyl)iron.⁴¹ These latter examples provide support for the idea of a sequential dissociation of 1,3-dihalopropanes on nickel to produce a γ -halopropyl intermediate first and a nickelacyclobutane moiety afterward.

The metallacycle species formed on $\text{Ni}(100)$ can also react via a β -hydride elimination to yield a propenyl surface moiety,

which may adopt either σ 3-propen-1-yl or π η^3 -allyl forms. This step explains the detection of propene, which is most likely produced via the reductive elimination of propenyl groups with surface hydrogen atoms⁴² and which desorbs at about the same temperature as in the case of direct adsorption of low coverages of propene on $\text{Ni}(100)$. The results from TPD experiments with 3-chloropropene, which presumably generates propenyl intermediates (the same as on other metal surfaces^{22,43} and in organometallic complexes^{34,42}), advocate for the ease of the propenyl-to-propene conversion, because low-temperature propene desorption is seen in that case as well (Figure 7). It is conceivable for the nickelacyclobutane intermediate to directly isomerize to propene, but this seems unlikely because (1) the production of propene from dihalopropanes occurs at relatively high temperatures (200–250 K) and (2) a surface intermediate must form concurrently in those systems during the desorption of cyclopropane; otherwise, the conversion would all proceed via this latter route. Since cyclopropane production from 1,3-diiodopropane occurs below 130 K, that intermediate cannot be propene. We propose it to be a propenyl (or allyl) intermediate instead.

The conversion of propenyl to propene on the surface is likely to be reversible, as indicated by the hydrogen–deuterium exchange that takes place when propene is coadsorbed with deuterium on the surface.³⁷ This exchange does not appear to occur via the formation of propyl species on the surface because no propane is detected in TPD experiments with propene, not even in the presence of coadsorbed hydrogen on the surface, and propyl groups, if formed, are known to eliminate easily with hydrogen to form propane.¹¹ Moreover, the reaction of propenyl to propene is apparently more favorable than its conversion back to the metallacycle species because the thermal activation of either 3-chloropropene or propene on the nickel surfaces does not result in the formation of any cyclopropane. The interconversion between propenyl and propene is well-known in organometallic systems.^{34,42}

Finally, the metallacycle species generated from 1,3-diiodopropane can undergo a direct hydrogenation step via the incorporation of an adsorbed hydrogen atom to form propyl fragments on the surface. Those propyl species can subsequently recombine with another hydrogen atom to form propane, which desorb at about 110 K (Figure 3). The dideuteropropane ($\text{C}_3\text{H}_6\text{D}_2$) detected in experiments with coadsorbed deuterium (Figure 4) indicates that such propane is indeed formed by incorporation of two surface hydrogen atoms into the C_3H_6 moiety. Propyl species can also be produced from the iodopropane generated by hydrogenation of 3-iodopropyl on the surface at high coverages. The propyl group produced this way reacts via the same pathways as the propyl group generated from the thermal reaction of 1-iodopropane¹¹ and, in particular, undergoes β -hydride elimination to propene.

Metallacycle species do not appear to form as easily from 1-chloro-3-iodopropane as from 1,3-diiodopropane, particularly at high coverages or in the presence of hydrogen coadsorption. This may be due to the stronger nature of the C–Cl bond. Instead, chloropropyl groups are generated in this case. β -Hydride elimination from this species gives 3-chloropropene, which eventually produces propene (possibly via a propenyl intermediate). Also, hydrogenation of the chloropropyl species generates 1-chloropropane, which, as in the case of the adsorption of molecular 1-chloropropane, does not form any hydrocarbon products at all because it does not generate a propyl group on the surface but simply desorbs molecularly.

The cyclization of alkanes is among the most important of all metal-catalyzed reactions;^{44,45} petroleum reforming, in

particular, is based on the selective promotion of this reaction.⁴⁴ For instance, it is known that *n*-hexane reacts over several transition metals at temperature between 450 and 700 K in the presence of hydrogen to give cyclohexane, methylcyclopentane, benzene, and other isomerization and hydrogenolysis compounds. However, although rhodium, palladium, iridium, and especially platinum catalysts usually display high selectivities for *n*-hexane cyclization to benzene, nickel favors C—C bond-breaking steps instead, and isomerization processes, also typical of platinum-based catalysts, are believed to involve cyclic intermediates as well.⁴⁶ Studies using model single crystals have proven the intrinsic ability of some metals to promote those steps but have fallen short of providing an answer for the unique behavior of platinum in terms of its selectivity for cyclization, aromatization, and isomerization steps.^{47–50} A detailed characterization of the factors that control this ring formation is important for the understanding of the catalytic processes. In our present studies we have shown that C₃ metallacycles derived from dihaloalkanes can in fact be possible intermediates in the cyclization step to form ring structures (cyclopropane) and that this perhaps occurs through a 1,3 C—C direct coupling step. We have also seen that such a step competes with the dehydrogenation to propenyl species and with hydrogenation to propyl and then to propane. It is quite likely for the selectivity in catalytic processes to depend on the relative probabilities for all these pathways.

5. Conclusions

In this report we have shown that the thermal decomposition of 1,3-diiodopropane on Ni(100) surfaces yields cyclopropane, propene, propane, and iodopropane. Decomposition of 1-chloro-3-iodopropane, on the other hand, forms only cyclopropane, propene, and 1-chloropropane, but no propane. A metallacycle intermediate is proposed to be responsible for the formation of all cyclopropane, propene, and propane, while 3-iodopropyl and 3-chloropropyl groups, which seem to be stabilized by high surface coverages, give iodopropane and chloropropane, respectively. With regard to the chemistry seen at low coverages, (1) cyclopropane appears to be produced via a direct C—C coupling of the surface metallacycle, as in organometallic compounds, and to desorb immediately upon formation, (2) β -hydride elimination from the metallacycle intermediate leads to the formation of surface propenyl groups, which can also be generated by direct adsorption of 3-chloropropene on the surface, and recombination of those with hydrogen atoms yields propene, and (3) hydrogenation of one of the metal—carbon bonds in the nickelacyclobutane species produces a propyl surface moiety, which then either dehydrogenate to propene or hydrogenate to propane. In addition, some of the iodopropane made at high coverages decomposes to propyl species on the surface, and those generate additional propane and propene, while chloropropane, which has a stronger carbon—halogen bond, desorbs intact without generating any propyl species (hence, the reason for the absence of any propane formation in that case). Coadsorption of hydrogen with 1,3-diiodopropane was found to increase the yield of propane, presumably because of an enhancement in the hydrogenation of both metallacycle and iodopropyl groups.

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