Supplementary Information

Chain-propagation, chain-transfer, and hydride-abstraction by cyclic carbocations on water surfaces

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Experimental Setup

Experimental setup was essentially the same as that used in our previous work. 1 Here, we briefly describe it and show some specific features on the experiments. The unsaturated cyclic hydrocarbon gas was flowed into the spraying chamber by buffer N2 at a known flow rate (5–500 mL min⁻¹) through Teflon tubing located near the grounded nebulizer. The vapor pressures of 97, 67, 32, 88, 31, 35, 36 and 28 Torr for cyclohexa-1,3-diene (1,3-c-h), cyclohexa-1,4-diene (1,4-c-h), 1-methylcyclohexa-1,4-diene (1-m-1,4-c-h), cyclohexene (c-h), 1-methylcyclohexene (1-m-c-h), 3-methylcyclohexene (3-m-c-h), 4-methylcyclohexene (4-m-c-h) and toluene (tol), respectively, at 298 K were taken from the literatures. 2–5

The pH-adjusted aqueous microjets flow coaxially with the sheath through which the
nebulizer gas N₂(g) is injected at a high velocity. Upon hitting the surface of the microjet, a gas molecule either becomes protonated by the microjet or rebounds into the gas phase.⁶–¹¹ The concentration of the hydrocarbon in the reaction chamber is determined by its vapor pressure and a dilution factor, that is derived from the ratio of carrier gas (5–500 mL min⁻¹) to the flow rate of the drying gas (12 L min⁻¹). The typical conditions used in the present experiments were as follows: drying nitrogen gas flow rate 12 L min⁻¹; drying nitrogen gas temperature: 613 K; inlet voltage: −3.5 kV relative to ground; fragmentor voltage: 60 V.

The carbocation products that we observed via mass spectrometry are generated when the gaseous hydrocarbon/N₂ stream collides with the aqueous microjet just after it is sprayed from the grounded nozzle. We have shown evidences that the species that we monitor are produced by the reaction of the gases with the intact microjets, rather than with the small, highly concentrated nanodroplets formed by Coulombic explosions.⁹,¹⁰,¹¹–¹³ Also, it has been found the polarization of the initial microjets does not affect the observed kinetics and products.¹¹,¹²,¹⁴,¹⁵ The lack of any signals corresponding to protonated products in the mass spectra of 1 mM isoprene dissolved in a 1:1 v/v water−acetonitrile at pH values of 1.9–4.3¹⁶ proves that the observed reactions occur on the gas side rather than on the bulk side of the interface. Further experimental details could be found in our previous publications.⁶,¹⁷¹¹,¹⁴,¹⁸,¹⁹

**Product Signal Intensities as a Function of pH**

Our previous studies showed hydrocarbons whose proton affinities are larger than that of gaseous water (165 kcal mol⁻¹) are protonated on the surface of microjets at bulk pH < 4–5.¹⁸,²⁰ Proton affinities of the tested species are listed in Table S1 to be compared with typical signal intensities of products observed from the microjets at pH = 2.2 ± 0.4. Because proton affinities are unavailable for 1-m-c-h, 3-m-c-h, and 4-m-c-h, the values are
determined by our quantum calculations. The proton affinities are determined by considering isomerization after H$^+$ addition to C=C double bonds in quantum calculations. These results show that signal intensities of propagating carbocations are almost independent from proton affinities and the stable forms of carbocations. Figure S4 shows the signal intensities of the carbocationic oligomers as a function of bulk pH. The signals for both $(1,3\text{-c-h})_n\text{H}^+$ and $(\text{c-h})_n\text{H}^+$ follows a sigmoidal-like titration curve. Suppression and decrease in the signal intensities at smaller pH were observed. In our previous reports, protonated products produced by PT from $(\text{H}_3\text{O})^+(\text{H}_2\text{O})_{n<4}$ were observed only when the microjets were acidic (bulk pH < 4-5), and followed similar sigmoidal curves.\textsuperscript{16,21,22} The present and previous results are consistent with the observation that the water surface is positively charged only at bulk pH values of less than about 4–5.\textsuperscript{14,15,23–26} The mass-spectral signal intensity for $(1,3\text{-c-h})_2\text{H}^+$ at pH = 0.69 was ~30% lower than that at pH = 2.26, which might be explained by competitive adsorption of larger $(1,3\text{-c-h})_n\text{H}^+$ oligomers ($n \geq 4$) on the air–water interface; these oligomers should have increasingly larger interfacial affinities.\textsuperscript{17} The larger oligomer products, although formed in small yields, may become predominant on the surface by replacing smaller products. Alternatively, an increase in the concentration of Cl$^-$ as a result of adding HCl to the solution might induce a suppression or a decrease in the signals for the products. We notice that adding a 10 mM NaCl to a solution depressed the signal for $(\text{ISO})_2\text{H}^+$ by ~44% under the similar experimental conditions, whereas it did not influence the chain-growth processes.\textsuperscript{1}

**Quantum-Chemical Calculations for the Carbocationic Reactions**

The initial proton-transfer (PT) reactions (Table S2), alcohol-formation reaction (Table S3), and dimerization pathways, including intramolecular hydrogen-atom transfer (Schemes S1–
were investigated through quantum chemical calculations at the CBS-QB3//ωB97X-D/6-311++G(d,p) level of theory$^{27-29}$ by using the program Gaussian 09.$^{30}$ The zero-point-energy-corrected ground-state energies are reported here.

**Intramolecular Hydrogen-Atom Transfer in (1-m-c-h)H$^+$, (3-m-c-h)H$^+$ and (4-m-c-h)H$^+$**

Figures 3 and S5 show the positive-ion mass spectra during the uptake of 1-m-c-h, 3-m-c-h, and 4-m-c-h on a D$_2$O microjet (pD = 2.05); the spectra consistently demonstrate the occurrence of hydride abstraction (HA) and subsequent monomer addition. Quantum chemical calculations of the relative energies of protonated methylecyclohexane isomers and their isomerization transition states (Scheme S1) in the gas-phase suggested that intramolecular hydrogen-atom transfer proceeds smoothly, resulting in the formation of a tertiary carbocation, which is the initial protonated form of (1-m-c-h)H$^+$. These are consistent with the observation that the mass signal intensity as a function of exposure of the three isomers exhibited a similar trend, as shown in Figures 4 and S6.

Quantum chemical calculations indicated that 1-m-c-h, 3-m-c-h, and 4-m-c-h dimerize without energetic barriers as shown in Scheme S2. Note that here we ignore the effects of solvation by water. Hydride abstraction was also calculated to be barrierless, as shown in Scheme S3.

**Termination Reactions**

As discussed in our previous paper,$^1$ the reaction of carbocations with water molecules yielding alkyl alcohols could be a major termination process in cationic polymerization.$^{31}$

\[
RH^+ + (H_2O)_m \text{ (liq)} \rightarrow RH-OH + H^+(H_2O)_{m-1} \text{ (liq)} \quad \text{(RS1)}
\]

The lacks of protonated alcohols and oxocarbenium intermediates$^{32}$ in the mass spectra imply the contribution of water termination processes is negligible under the present condition (e.g., water is less available at the interface). Although our theoretical calculations
show that the alcohol formation from the hydrated carbocations \( m \geq 3 \) and water is energetically accessible (Table S3), there is no experimental evidence for this at the air–water interface. The absence of such termination products would stem from a much less density of water molecules at topmost layers of the interface.

We previously confirmed that chloride anions (from HCl) do not affect the extent of oligomerization by adding excess NaCl to the microjets.\(^1\)

\[
\text{R}_n\text{H}^+ + \text{Cl}^- \text{(int)} \rightarrow \text{R}_n\text{H–Cl (int)}
\] (RS2)

Under the present experimental conditions, chain transfer (CT) and/or HA will be the most important termination processes in the chain growth of carbocations (see the main text).

**Chain Propagation of 1,4-c-h and 1-m-1,4-c-h**

Several pathways for the oligomerization of 1,4-c-h can be proposed, as shown in Scheme S4. One pathway involves intramolecular hydrogen-atom transfer to form a stable carbocation (Scheme S4a). Another involves the addition of a monomer to activated C\(^+\) without intramolecular hydrogen-atom transfer. Whereas the trimer was observed at \( E_{1,4-c-h} = 9.2 \times 10^{10} \) molecules cm\(^{-3}\) s, an increase in exposure up to \( E_{1,4-c-h} = 9.2 \times 10^{11} \) molecules cm\(^{-3}\) s did not result in the formation of larger oligomers, suggesting that the bulky nature of \((1,4-c-h)_3\text{H}^+\) might hinder further propagation. Our quantum chemical calculations showed that intramolecular hydrogen-atom transfer proceeds without a significant energetic barrier. The most stable carbocation of \((1,4-c-h)_2\text{H}^+\) is formed after intramolecular hydrogen-atom transfer resulting in conjugative resonance. When a neutral 1,4-c-h molecule adds to the stabilized \((1,4-c-h)_2\text{H}^+\) ion, the activated C\(^+\) site is surrounded by bulky hexagons forming the conjugative resonance of the tertiary C\(^+\) sites, which, through steric hindrance, prevent further chain propagation (Scheme 1B). The scheme is consistent with the absence of \((1,4-c-h)_4\text{H}^+\) even at the larger exposure. Similarly, intramolecular hydrogen-atom transfers
in \((1\text{-m-1,4-c-h})_2H^+\) result in a carbocation with conjugative resonance at the tertiary C\(^+\) sites (Scheme 1C), which is consistent with our experimental results, i.e., the absence of \((1\text{-m-1,4-c-h})_3H^+\) signals in the mass spectrum. This explains why \(1\text{-m-1,4-c-h}\) has a lower ability to undergo oligomerization than \(1,4\text{-c-h}\), despite the electron-donation effect of the methyl group.

**Chain Propagation of 1,3-c-h**

If intramolecular hydrogen-atom transfers are feasible for \((1,3\text{-c-h})_2H^+\), the carbocation will be stabilized through the formation of the same carbocation as that of the \((1,4\text{-c-h})_2H^+\). However, this scheme would stop chain propagation at the trimer, as observed for \(1,4\text{-c-h}\). This strongly suggests that intramolecular hydrogen-atom transfer does not occur in \((1,3\text{-c-h})_nH^+\). Quantum chemical calculations showed an energy barrier of 10 kcal mol\(^{-1}\) for the hydrogen-atom transfer from the initial adduct (Scheme S4b). \(1,3\text{-c-h}\) inherently contains conjugated C=C double bonds, leading to a carbocation with resonant stabilization when a monomer is added. Formation of hydrogen bonds with conjugative \(\pi\)-electron possibly enhances the oligomerization of \(1,3\text{-c-h}\) by interrupting the intramolecular hydrogen-atom transfer.

**Reaction Mechanisms for 1-m-c-h, 3-m-c-h and 4-m-c-h**

Whereas the uptake of c-h on microjets resulted in dimerization, the dimer cations of \(1\text{-m-c-h}, 3\text{-m-c-h}, \text{ and } 4\text{-m-c-h}\) were not observed, implying that intramolecular hydrogen-atom transfer to form tertiary carbocations proceeds faster than monomer addition to the active C\(^+\) site, and is preferentially followed by a HA reaction. Consistently, an increase in the electron density at a C=C double bond of a neutral monomer is known to control the ability of a molecule to undergo oligomerization in bulk organic solutions.\(^{33,34}\) However, electrophilic attack by the tertiary carbocation on the \(\pi\)-bond of a neutral monomer is rather
restricted by the presence of a methyl group in the cases of 1-m-c-h, 3-m-c-h, and 4-m-c-h. When the carbocation approaches the nucleophile, the overlapping π-electrons will be involved in the reaction processes while the π-electrons locate perpendicularly to the plane of the cyclic hexagon. The HA reaction, which proceeds through a σ-electron process, will be less sensitive to the angle of approach.

Protonation of Tol

In the experiments with toluene (tol, M = 92), we found that protonated toluene (tol)H⁺ (m/z = 93) is successfully formed by the PT reactions (Figure S3G), whereas (tol)2H⁺ (m/z = 185) is not formed by the CP reaction. There is also no evidence for HA reactions yielding benzyl cation (C₆H₅CH₂⁺) that could isomerize to a tropylium ion (C₇H₇⁺) (m/z = 91), which would have a resonance-stabilized structure. The lack of CP and HA reactions implies that toluene is not an efficient π- or (H−)-donor at the air–water interface. Our results are consistent with a previous report on the lower nucleophilicity of toluene in dichloromethane solution.35 Also, aromatic compounds are generally much less reactive towards oxidants (electrophiles) such as ozone than are alkenes in the gas-phase.36,37 The HA reaction of 1-m-1,4-c-h results in the formation of isomeric carbocations of (tol)H⁺ with various methyl positions. Because the HA-induced carbocation of 1-m-1,4-c-h reacted with a neutral 1-m-1,4-c-h to form an oligomeric product, we conclude that alkenes (such as 1-m-1,4-c-h) are more reactive nucleophiles than are aromatic compounds (such as tol) at the air-water interface. It is known that the delocalized π-electrons of the aromatic ring of tol create a quadrupole moment with a partial negative charge above both aromatic faces and a partial positive charge around the periphery.38,39 We infer that this feature would inhibit the access of (tol)H⁺ to the methyl group of tol for HA reactions.
Other reaction products

We note non-negligible peaks at m/z = M + 16 and m/z = M + 32 appear in the experiments of 1,4-c-h (Fig. S3A). These species are likely oxidation products by oxygen molecules in the solution or reagent impurity, since the experiments are performed in the reaction chamber under anoxic condition with purged N₂ gas. Interestingly, peaks at m/z = M - 1 + 16 = M + 15 (HA-induced species + 16) appear in the experiments of 3-m-c-h, 4-m-c-h, and c-h (Figs. S3C, D, E), that may have the same origin.

It is also noted that multiply charged products, e.g., (1,3-c-h)ₙH⁺ₙ⁺, were not seen in our experiments. For example, if (1,3-c-h)₃H⁺ (m/z = 241) is further protonated, the peak (1,3-c-h)₃H₂⁺ at m/z = (241 + 1)/2 = 121 should have appeared, at variance with our observation (Fig. 3A in main text). The lack of such species may be explained by the fact that the concentrations of gaseous reactant are always larger than that of H⁺ at the topmost layers of interface. This result is also consistent with the Eley-Rideal mechanism, that is, the observed reactions occur only when reactant (g) collides to the surface.

Estimation of Reaction Efficiency of Chain Propagation

As previously reported in the case of isoprene,¹ here we estimate the reaction efficiency to account for the observed chain propagation of 1,3-c-h up to the n = 6 oligomer. The reaction efficiency is defined as the ratio of the number of successful chain propagations to the total number of collisions of activated carbocations on the surface. By assuming collision-controlled growth based on an Eley–Rideal (ER) mechanism, in which 1,3-c-h(g) is directly supplied from the gas-phase to an activated carbocation on the water surface under the largest [1,3-c-h(g)] (97 Torr) conditions, 1,3-c-h(g) gases impact on the water surface with a flux 2.75 × 10²⁶ m⁻² s⁻¹. The number of 1,3-c-h(g) molecules that collide with an activated carbocation (1,3-c-h)H⁺ in an area of water surface of 1 × 10⁻¹⁸ m² in the present
exposure time \( \sim 1 \times 10^{-5} \) s is derived to be \( 2.8 \times 10^3 \). Here we assumed that an area of \( \sim 1 \) nm\(^2\) is the distance in which \((1,3\text{-c-h})_n\text{H}^+\) reacts with a neutral molecule at the water surface. Because the reaction efficiency of the observed chain propagation depends on the structure of the neutral monomer \(1,3\text{-c-h}\), rather than on the terminal molecular structure of the active carbocation,\(^{34}\) we also assumed that the chain propagation for \((1,3\text{-c-h})_n\text{H}^+\) is independent from the degree of oligomerization. Thus, the reaction efficiency for chain propagation is estimated to be \( \geq 2.1 \times 10^{-3} \) to account for the observed formation of \((1,3\text{-c-h})_6\text{H}^+\). The introduced \(1,3\text{-c-h}(g)\) with buffer \(\text{N}_2 [0.5 \text{ L min}^{-1} \text{ for } (1,3\text{-c-h})_6\text{H}^+ \text{ formation}]\) would be diluted by the drying \(\text{N}_2 (12 \text{ L min}^{-1})\) by up to \( \sim 24 \) times. These conditions yield a reaction efficiency for chain propagation of \( \sim 0.05 \).

The formation of large oligomers results from the CP reaction with a probability of \(10^{-2}–10^{-1}\) for molecular collision, which is significantly larger than the uptake coefficient for the initial proton transfer of \( \sim 10^{-6} \).\(^{16}\) This estimate suggests that the initial proton-transfer reaction is a rate-determining step for the cationic oligomerization under the experimental conditions.

**SI References**


5. Environmental Protection Agency, [https://comptox.epa.gov/dashboard](https://comptox.epa.gov/dashboard), 01/08/2018


Figure S1. Relative signal intensities of (1,3-c-h)_nH^+ (n = 1-4) to the sum of the signals as a function of the capillary voltage (V), in experiments performed on H_2O microjets at pH = 2.04 with (A) exposure of 1.3 \times 10^{11} and (B) 1.3 \times 10^{12} molecules cm^{-3} s. Symbols of squares, circles, blue triangles, and magenta triangles correspond to (1,3-c-h)_nH^+ (n = 1, 2, 3, 4), respectively. Positive ion mass spectra as a function of capillary voltage are shown in (C) and (D). Note the product distributions are found to be independent from capillary voltage values.
Figure S2. Positive ion mass spectra as a function of drying gas temperature obtained from experiments performed on H$_2$O microjets at pH = 2.04 with at $E$(1,3-c-h) = $1.3 \times 10^{12}$ molecules cm$^3$ s$^{-1}$. 
Figure S3. Positive-ion mass spectra in the absence (gray) or presence (other colors) of gaseous (A) 1,4-c-h, (B) 1-m-c-h, (C) 3-m-c-h, (D) 4-m-c-h, (E) c-h, (F) 1-m-1,4-c-h, and (G) tol on water microjets at pH = 2.03 ± 0.02. Molecular masses of the monomer (M) are also shown. The signals correspond to $R_nH^+ [m/z = (n \times M) + 1]$ are labeled by their $n$ values. Other signals including HA-induced products are labeled by their $m/z$. 
Figure S4. Signal intensities as a function of bulk pH in experiments performed on \( \text{H}_2\text{O} \) microjets exposed to (A) 1,3-\( \text{c-h} \)(g) at \( E = 1.3 \times 10^{11} \) molecules cm\(^{-3}\) s, and (B) c-\( \text{h} \)(g) at \( E = 2.4 \times 10^{11} \) molecules cm\(^{-3}\) s.
Figure S5. Positive-ion mass spectra with $m/z$ ranges of 93–101 and 188–196 on D$_2$O microjets at pH = 2.05 in the presence of gaseous 3-m-c-h (A and B, respectively) and 4-m-c-h (C and D, respectively) at different concentrations.
**Figure S6.** Evolutions of the positive-mass signals at $m/z = 95, 97,$ and 191 as a function of exposure of (A) $3\text{-m-c-h}(g)$ and (B) $4\text{-m-c-h}$ on H$_2$O microjets of pH = 2.05. The $E$ values are estimated from the equilibrium vapor pressure of c-h.
**Figure S7.** Positive-ion mass spectra of D₂O microjets at pD = 2.04 in the absence (gray) and the presence (purple) of gaseous 1,4-c-h. (A) - (C) shows specific m/z regions of the spectra for RₙH⁺ and RₙD⁺ (n = 1–5). The m/z 243 signal in (C) appeared in the absence of 1,4-c-h would come from background impurity.
Figure S8. Positive-ion mass spectra at \( m/z = 90–100 \) (A) and 185–195 (B) in the presence of 1-m-1,4-c-h(g) on microjets of H\(_2\)O (black lines) at pH = 2.02 and on D\(_2\)O (pink lines) at pD = 2.03. The exposure value was estimated to be \( 4.2 \times 10^{11} \) molecules cm\(^{-3}\) s.
**Figure S9.** Positive-ion mass spectra of (A) pent-1-ene, (B) pent-2-ene, and (C)–(F) penta-1,4-diene at various concentrations on H₂O microjets at pH = 2.77 for (A) and (B) or pH = 1.70 for (C)–(F). Mass spectra at m/z = 65–75 (C), 133–143 (D), 200–210 (E), and 268–278 (F) are shown.
Scheme S1. Relative energies of protonated methyl-cyclohexene isomers. The values correspond to the energies relative to that of the tertiary carbocationic form in units of kcal mol\(^{-1}\); values shown in parenthesis are those for the transition states, showing that intramolecular hydrogen-atom transfer proceeds smoothly.
Scheme S2. Calculated hydride-abstraction pathways of (A) 1-m-c-h, (B) 3-m-c-h, and (C) 4-m-c-h. The values shown are the energies relative to that of the initial form in units of kcal mol⁻¹, showing that monomer addition and intramolecular hydrogen-atom transfer proceed smoothly.
Scheme S3. Dimerization pathways of (A) 1-m-c-h, (B) 3-m-c-h, and (C) 4-m-c-h calculated by the quantum chemical calculation; these were not observed in the experiments. The values shown are the energies relative to that of the initial form in units of kcal mol\(^{-1}\), and the values in parenthesis are those for the transition states, showing that the monomer addition and the intramolecular hydrogen-atom transfer proceed smoothly.
Scheme S4. Relative energy changes of carbocations of 1,3-c-h and 1,4-c-h on the dimerization and subsequent intramolecular hydrogen-atom transfers, derived by the quantum chemical calculation. The values shown are energies relative to the energy of the initial separated form of the monomer cation and neutral molecule in units of kcal mol\(^{-1}\), and the values in parenthesis are those for the transition states.
Table S1. Gas-phase proton affinities,\textsuperscript{40} propagating cationic forms are compared with the sum of R\textsubscript{n}H\textsuperscript{+} signals on H\textsubscript{2}O microjet at $E = (0.4 - 1.2) \times 10^{12}$ molecules cm\textsuperscript{-3} s. Since proton affinities are unavailable for 1-m-c-h, 3-m-c-h, and 4-m-c-h, the values determined by our quantum calculations are listed in parentheses.

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Proton affinity (kcal mol\textsuperscript{-1})</th>
<th>Stable cation</th>
<th>Signal (ion counts)</th>
</tr>
</thead>
<tbody>
<tr>
<td>isoprene</td>
<td>198 (195)</td>
<td>tertiary</td>
<td>$\sim 2 \times 10^6$</td>
</tr>
<tr>
<td>buta-1,3-diene</td>
<td>187 (187)</td>
<td>secondary</td>
<td>$\sim 2 \times 10^6$</td>
</tr>
<tr>
<td>1,3-c-h</td>
<td>200 (197)</td>
<td>secondary</td>
<td>$\sim 5 \times 10^5$</td>
</tr>
<tr>
<td>penta-1,4-diene</td>
<td>(192)</td>
<td>secondary</td>
<td>$\sim 3 \times 10^5$</td>
</tr>
<tr>
<td>1,4-c-h</td>
<td>200</td>
<td>secondary</td>
<td>$\sim 7 \times 10^4$</td>
</tr>
<tr>
<td></td>
<td>(179→197)$^a$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-m-1,4-c-h</td>
<td>(191)</td>
<td>tertiary</td>
<td>$\sim 1 \times 10^5$</td>
</tr>
<tr>
<td>c-h</td>
<td>187 (184)</td>
<td>secondary</td>
<td>$\sim 1 \times 10^4$</td>
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<td>(182)</td>
<td>secondary</td>
<td>$\sim 6 \times 10^4$</td>
</tr>
<tr>
<td>pent-2-ene</td>
<td>(181)</td>
<td>secondary</td>
<td>$\sim 6 \times 10^4$</td>
</tr>
<tr>
<td>1-m-c-h</td>
<td>(194)</td>
<td>tertiary</td>
<td>$\sim 3 \times 10^4$</td>
</tr>
<tr>
<td>3-m-c-h</td>
<td>(183→196)$^a$</td>
<td>tertiary\textsuperscript{b}</td>
<td>$\sim 1 \times 10^4$</td>
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<tr>
<td>4-m-c-h</td>
<td>(182→196)$^a$</td>
<td>tertiary\textsuperscript{b}</td>
<td>$\sim 8 \times 10^3$</td>
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<tr>
<td>tol</td>
<td>187</td>
<td>tertiary</td>
<td>$\sim 6 \times 10^3$</td>
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\textsuperscript{a} Just after addition of H\textsuperscript{+} to C=C double bonds (left value), 1,4-c-h, 3-m-c-h, and 4-m-c-h can be further stabilized by intramolecular hydrogen-atom transfer (right value). \textsuperscript{b} Via the isomerization.
**Table S2.** Enthalpy of the initial proton-transfer reaction $R + H^+(H_2O)_m \rightarrow RH^+ + (H_2O)_m$ estimated by the quantum chemical calculation. Immediately after an addition of $H^+$ to C=C double bonds, $1,4$-c-h, $3$-m-c-h, and $4$-m-c-h can be further stabilized by intramolecular hydrogen-atom transfers. The values calculated after intramolecular hydride transfers are listed in parentheses. Note that a considerable level of solvation ($m > 3$) turns the reactions endothermic.

<table>
<thead>
<tr>
<th>Reactant</th>
<th>$m = 1$</th>
<th>$m = 2$</th>
<th>$m = 3$</th>
</tr>
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<tbody>
<tr>
<td>c-h</td>
<td>-20</td>
<td>11</td>
<td>24</td>
</tr>
<tr>
<td>1,3-c-h</td>
<td>-33</td>
<td>-2</td>
<td>11</td>
</tr>
<tr>
<td>1,4-c-h</td>
<td>-15 ($-33$)</td>
<td>16 ($-2$)</td>
<td>29 (11)</td>
</tr>
<tr>
<td>1-m-c-h</td>
<td>-30</td>
<td>1</td>
<td>13</td>
</tr>
<tr>
<td>3-m-c-h</td>
<td>-19 ($-32$)</td>
<td>12 ($-1$)</td>
<td>25 (12)</td>
</tr>
<tr>
<td>4-m-c-h</td>
<td>-18 ($-32$)</td>
<td>13 ($-1$)</td>
<td>25 (12)</td>
</tr>
</tbody>
</table>

**Table S3.** Enthalpy of the alcohol-formation reaction $RH^+ + (H_2O)_m \rightarrow R-OH + H^+(H_2O)_{m-1}$ estimated by the quantum chemical calculation. With solvation ($m > 4$), the alcohol-formation reactions become fully exothermic.

<table>
<thead>
<tr>
<th>Reactant</th>
<th>$m = 2$</th>
<th>$m = 3$</th>
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</thead>
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<tr>
<td>(c-h)H$^+$</td>
<td>11</td>
<td>$-14$</td>
</tr>
<tr>
<td>(1,3-c-h)H$^+$</td>
<td>26</td>
<td>1</td>
</tr>
<tr>
<td>(1-m-c-h)H$^+$</td>
<td>21</td>
<td>$-5$</td>
</tr>
</tbody>
</table>