Quantification of Hydroxycarbonyls from OH−Isoprene Reactions

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Atmospheric oxidation of isoprene initiated by the hydroxyl radical OH plays an important role in tropospheric ozone formation,[1] but its mechanism remains uncertain. For example, a major fraction of the carbon from the OH−isoprene reaction has not been quantified, largely due to analytical difficulties in detecting and quantifying the reaction products. The OH−isoprene reaction occurs by OH addition to the >C=C< bonds to form four possible hydroxyalkyl radicals, which subsequently react with oxygen molecules to form hydroxyperoxy radicals.[2] Addition of O_2 occurs only at the carbon β to the OH position for internal OH addition, but takes place at two centers (β or δ to the OH position) for terminal OH addition. The reaction of hydroxyperoxy radicals with NO leads to formation of β- or δ-hydroxyalkoxy radicals or organic nitrates.[3] The δ-hydroxyalkoxy radicals possess both (*E*) and (*Z*) configurations (Scheme 1).

The alkoxy radicals are key intermediates in isoprene oxidation reactions.[4,5] Hydroxyalkoxy radicals may potentially undergo decomposition, isomerization, or reaction with O_2.[5] Quantum chemical calculations have shown relatively small barriers to C−C bond cleavage between the α and β carbons, indicating that unimolecular dissociation of the β-hydroxyalkoxy radicals represents the dominant process.[4,6] Decomposition of the β-hydroxyalkoxy radicals leads to the formation of methyl vinyl ketone (MVK) and methacrolein (MACR), along with formaldehyde. In contrast, the decomposition barriers of the δ-hydroxyalkoxy are significantly higher, rendering this pathway implausible.[4,6] Except for the alkoxy radical II_*E*, H-migration of the δ-hydroxyalkoxy radicals occurs readily via a 1,5 H-shift to form double hydroxy radicals,[7] which then react to form C4 ($C_4H_6O_2$) or C5 ($C_5H_8O_2$) hydroxycarbonyls (Scheme 1). The likely fate of radical II_*E* is reaction with O_2 to form a C5-hydroxycarbonyl. Several experimental studies identified and quantified the products of the OH-initiated isoprene oxidation in the presence of NO. As summarized in Table 1, the yields of MVK, MACR, and 3-methyl furan (possibly formed from cyclization and loss of H_2O from C5-hydroxycarbonyls)[9b] are 29−36%, 21−25%, and 4.4%, respectively.[8,9] In addition, the measured yields of the alkyl nitrates range from 4% to 14%.[9] Hence, the quantified products account for 60−70% of the isoprene carbon balance. Hydroxycarbonyls from isoprene reactions have been observed but have not been quantified;[10] it has been postulated that hydroxycarbonyls likely account for the missing products of the isoprene reactions.[10b]

We conducted an experimental study of the hydroxycarbonyls arising from the OH-initiated oxidation of isoprene. The experimental procedures were similar to those in our previous investigation;[11] the OH−isoprene reactions were simulated in a high-pressure turbulent flow reactor. The hydroxycarbonyls were detected and quantified by proton-transfer reaction mass spectrometry (PTR-MS). The PTR-MS technique has been described previously.[12] Briefly,
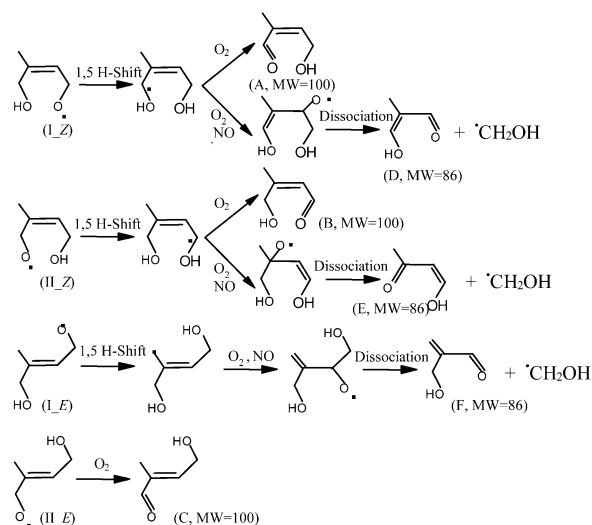
Scheme 1

Table 1. Product Yields (%) from OH-Initiated Oxidation of Isoprene in the Presence of NO

product	previous work	this work[a]
MVK	$29 \pm 7,$[b] $36 \pm 4,$[c] $32 \pm 5,$[d] 44 ± 6[e]	55 ± 6
MACR	$21 \pm 5,$[b] $25 \pm 3,$[c] $22 \pm 2,$[d] 28 ± 4[e]	
organic nitrate	$8-14,$[b] $8-12,$[e] 4.4 ± 0.8[f]	
3-methyl furan	$<2,$[e] 4.4 ± 0.6[g]	
C5-hydroxycarbonyl		19.3 ± 6.1
C4-hydroxycarbonyl		3.3 ± 1.6
C5-carbonyl		8.4 ± 2.4

[a] The yield represents the sum of all isomers, and the top value corresponds to the sum of MVK and MACR yields. Experimental conditions: $[C_5H_8] = (0.4-6) \times 10^{12}$ molecule cm^{-3}, $[NO] = (0.4-4) \times 10^{12}$ molecule cm^{-3}, $[O_2] = (5-7) \times 10^{15}$ molecule cm^{-3}, and $[OH] = (5-10) \times 10^{10}$ molecule cm^{-3}. The typical reaction time is about 0.05 s. [b] From ref 8a. [c] From ref 8b. [d] From ref 8c. [e] From ref 9b. [f] From ref 9a. [g] From ref 8d.

the proton-transfer reaction $R + H_3O^+ \rightarrow RH^+ + H_2O$ converted a small fraction of the reagent H_3O^+ ions into protonated product ions RH^+ which were then detected by the MS system. This method allows quantification of chemical species without the necessity of calibration, provided that the proton-transfer reaction rate constant is available.[12] The PTR-MS method hence is advantageous because of the difficulty to obtain the authentic standards of hydroxycarbonyls. We derived the hydroxycarbonyl yield (*Y*) according to

$$Y (\%) = k_{iso}/k_{car} \times \Delta S_{car}/\Delta S_{iso} \qquad (1)$$

where k_{car} and k_{iso} are the ion−molecule rate constants for the proton-transfer reactions between hydroxycarbonyls and H_3O^+ and between isoprene and H_3O^+, respectively. $\Delta S_{car}/\Delta S_{iso}$ is the ratio of the protonated hydroxycarbonyl produced to the protonated
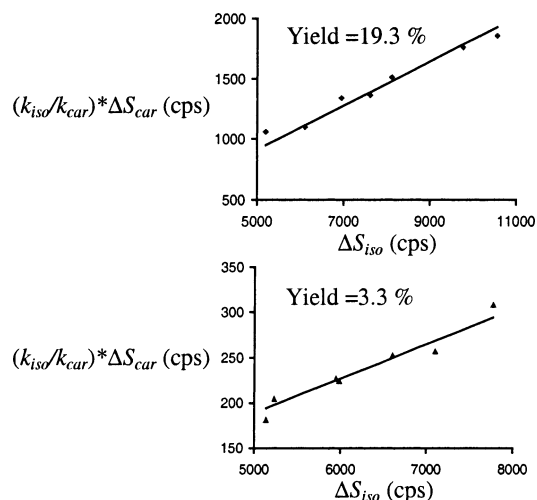
Figure 1. Plot of k_{iso}/k_{car} ΔS_{car} versus ΔS_{iso} for C5 (top) and C4 (bottom) hydroxycarbonyls. The slope of the line corresponds to the yield.

isoprene reacted (as the isoprene concentration is successively varied). The ion−molecule reaction rates between H_3O^+ and hydroxycarbonyls were determined using the average-dipole-orientation (ADO) theory,[13] which has been validated for accuracy for many hydrocarbons and oxygenated organic species.[12,14] Calibration showed an excellent agreement between the isoprene concentrations estimated from the known volumetric mixing ratio of the gas standard in the flow reactor and measured by the PTR-MS method (within 10%).

Figure 1 depicts single ion monitoring (SIM) of protonated C5- ($C_5H_9O_2^+$, $m/e = 101$) and C4-hydroxycarbonyls ($C_4H_7O_2^+$, $m/e = 87$) versus protonated isoprene. The ion−molecule reaction rate constants determined from the ADO theory are 3.9×10^{-9}, 3.7×10^{-9}, and 1.9×10^{-9} cm^3 s^{-1} for C5-, C4-hydroxycarbonyls (averaged over all isomers), and isoprene, respectively. Table 1 lists the experimental yields of C5- and C4-hydroxycarbonyls, with the values of (19.3 ± 6.1)% and (3.3 ± 1.6)%, respectively, measured at a flow reactor pressure of about 100 Torr and at a temperature of 298 ± 2 K. Each value represents an average of more than 10 measurements at various experimental conditions (Table 1). The uncertainty reflects both random error due to data scattering and systematical error (± 25%) related to the ion−molecule rate constants and possible fragmentation of the proton-transfer reactions.

The measurements of the relative yields between C4- and C5-hydroxycarbonyl unravel intriguing mechanistic features of the consecutive degradation pathways of the δ-hydroxyalkoxy radicals. In the mechanism illustrated in Scheme 1, the product of 1,5 H-shift of the (Z) form of alkoxy radicals I and II corresponds to an allylic radical with two plausible pathways. One pathway involves hydrogen abstraction from the α-hydroxy group by O_2 to yield a C5-hydroxycarbonyl. The other is expected to lead to formation of a peroxy radical by O_2 addition (not shown) and then, by NO to NO_2 conversion, to an alkoxy radical. The expected decomposition of the resulting alkoxy radical forms a C4-hydroxycarbonyl. The dominance in the formation of C5- over C4-hydroxycarbonyls suggests that O_2 hydrogen abstraction from the α-hydroxy group dominates over O_2 addition for the double hydroxy radical. Facile hydrogen abstraction of the α-hydroxy radical is explained because of the weak bond adjacent to the electron-rich carbon, and is supported by experimental evidence.[15] On the other hand, the measured yield of about 3% for the C4-hydroxycarbonyls is likely

attributed to alkoxy radical I_E. The distinction between C4- and C5-hydroxycarbonyls is crucial for modeling tropospheric O_3, because the C4-hydroxycarbonyl pathway involves an additional conversion of NO to NO_2.[7a]

We also identified another mass peak at $m/e = 85$ and assigned it to protonated C5-carbonyl C_5H_8O, which likely corresponds to the unsaturated carbonyl formed from cyclization of the OH−isoprene adducts of internal OH addition.[16] We estimated a yield of (8.4 ± 2.4)% for this species, consistent with the recent suggested formation of these species following OH addition to internal C atoms and confirming the small fraction of OH addition at these sites.[2a]

Quantification of the carbonyls enables the carbon closure to the OH−isoprene system. As shown in Table 1, the sum of the measured carbonyl yields and the averaged literature yields of MVK, MACR, 3-methyl furan, and organic nitrates accounts for about 97% of the total reacted isoprene, with a combined experimental uncertainty of about ± 10%. Those carbonyls hence constitute the major portion of the previously missing carbons.

Finally, this work demonstrates the application of PTR-MS for quantification of products of hydrocarbon reactions, which should have profound impacts on elucidation of the chemistry of atmospheric hydrocarbons.

Supporting Information Available: Mass spectra and additional yield measurements (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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