

Kinetics of a Criegee intermediate that would survive high humidity and may oxidize atmospheric SO₂

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Criegee intermediates are thought to play a role in atmospheric chemistry, in particular, the oxidation of SO₂, which produces SO₃ and subsequently H₂SO₄, an important constituent of aerosols and acid rain. However, the impact of such oxidation reactions is affected by the reactions of Criegee intermediates with water vapor, because of high water concentrations in the troposphere. In this work, the kinetics of the reactions of dimethyl substituted Criegee intermediate (CH₃)₂COO with water vapor and with SO₂ were directly measured via UV absorption of (CH₃)₂COO under near-atmospheric conditions. The results indicate that (i) the water reaction with (CH₃)₂COO is not fast enough ($k_{\text{H}_2\text{O}} < 1.5 \times 10^{-16} \text{ cm}^3 \text{ s}^{-1}$) to consume atmospheric (CH₃)₂COO significantly and (ii) (CH₃)₂COO reacts with SO₂ at a near-gas-kinetic-limit rate ($k_{\text{SO}_2} = 1.3 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$). These observations imply a significant fraction of atmospheric (CH₃)₂COO may survive under humid conditions and react with SO₂, very different from the case of the simplest Criegee intermediate CH₂OO, in which the reaction with water dimer predominates in the CH₂OO decay under typical tropospheric conditions. In addition, a significant pressure dependence was observed for the reaction of (CH₃)₂COO with SO₂, suggesting the use of low pressure rate may underestimate the impact of this reaction. This work demonstrates that the reactivity of a Criegee intermediate toward water vapor strongly depends on its structure, which will influence the main decay pathways and steady-state concentrations for various Criegee intermediates in the atmosphere.

atmospheric chemistry | Criegee intermediate | SO₂ oxidation | chemical kinetics

Unsaturated hydrocarbons are emitted into the atmosphere in large quantities from either human or natural sources. Ozonolysis of unsaturated hydrocarbons produces highly reactive Criegee intermediates (CIs) (1), which may (i) decompose to radical species like OH radicals or (ii) react with a number of atmospheric species, for example, with SO₂ to form SO₃ and with NO₂ to form NO₃ (2, 3). The SO₂ oxidation by CIs has gained special attentions because the SO₃ product would be converted into H₂SO₄, an important constituent of aerosols and acid rain (4–8). For example, Mauldin et al. (4) have speculated that Criegee intermediate reactions with SO₂ may account for the discrepancy between the observed and modeled concentrations of H₂SO₄ in a boreal forest region, where various alkenes are emitted by trees.

Recently, Welz et al. (2) demonstrated an efficient method to prepare a CI in a laboratory by the reaction of iodoalkyl radical with O₂ (for example, CH₂I + O₂ → CH₂OO + I). This method can produce a CI of high enough concentration that allows direct detection. With photoionization mass spectrometry (PIMS) detection, Welz et al. (2) measured the rate coefficients of the simplest CI (CH₂OO) reactions with SO₂ and NO₂. Notably, these new rate coefficients, confirmed by a few later investigations (9–11), are orders of magnitude larger than those previously used (12, 13) in atmospheric models (e.g., MCM v3.3, available at mcm.leeds.ac.uk/MCM/browse.htm?species=CH2OO), suggesting a greater role of CIs in atmospheric chemistry. This result also indicates previous ozonolysis analyses may be affected by complicated and partly unknown side reactions and may contain errors in some of the reported rate coefficients.

Typical water concentration in the troposphere (1.3×10^{17} to $8.3 \times 10^{17} \text{ cm}^{-3}$ at the dew point of 0–27 °C) is orders of magnitude higher than those of atmospheric trace gases like SO₂, NO₂, and volatile organic compounds (VOC) (on the order of 10^{12} cm^{-3} or less). Although it has been shown that CIs may react very fast with SO₂, NO₂, and organic acids (2, 3, 14), the reactions of CIs with atmospheric water vapor would still strongly influence the fates and concentrations of atmospheric CIs (see Fig. 1 for a simplified schematic). As expected, the reactivity of CIs toward water vapor would govern the modeling results of atmospheric H₂SO₄ formation from CIs (8, 15, 16).

However, there had been discrepancies about the reactivity of CIs toward water. Whereas studies (17–20) using C₂H₄ ozonolysis as a CH₂OO source show substantial reactivity of CH₂OO toward water vapor, despite a large scatter (10^{-17} to $10^{-12} \text{ cm}^3 \text{ s}^{-1}$) in the reported rate coefficient, other studies (2, 10, 21) using the CH₂I+O₂ reaction as a CH₂OO source reported negative observation for the CH₂OO reaction with water vapor.

More recently, Chao et al. (22) and Berndt et al. (23) investigated the reaction of CH₂OO with water vapor using the CH₂I+O₂ reaction and the C₂H₄ ozonolysis as their CH₂OO sources, respectively. Both groups observed clear second-order kinetics with respect to the concentration of water and concluded that reaction with water dimer predominates in the decay of CH₂OO under atmospheric conditions and that previous studies may require some reinterpretations. The reported rate coefficient of the CH₂OO reaction with water dimer is large, about $7 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ (22), leading to extremely fast decay rate of CH₂OO under typical tropospheric conditions (Table 1).

Taatjes et al. (3) and Sheps et al. (24) have reported that the *anti*-form of methyl-substituted CI (CH₃CHOO, R¹ = H in Fig. 1) reacts with water vapor much faster than the *syn*-form (R¹ = CH₃ in Fig. 1) does. Quantum-chemical investigations (25–27) as well as studies of alkene ozonolysis (20, 28) also indicate that the structure of a CI strongly influences its reactivity toward water vapor. If one type of CI reacts slowly with water vapor but reacts quickly with

Significance

Ozonolysis of alkenes produces highly reactive Criegee intermediates. Whereas water dimer efficiently scavenges the simplest Criegee intermediate CH₂OO in the troposphere, this study clearly demonstrates that water vapor does not react with dimethyl substituted Criegee intermediate (CH₃)₂COO, at least not fast enough to significantly consume (CH₃)₂COO in the troposphere. On the other hand, (CH₃)₂COO reacts with SO₂ three times faster than CH₂OO does, indicating Criegee intermediates of a structure similar to (CH₃)₂COO are potential candidates for an efficient oxidant in the atmospheric SO₂ oxidation.

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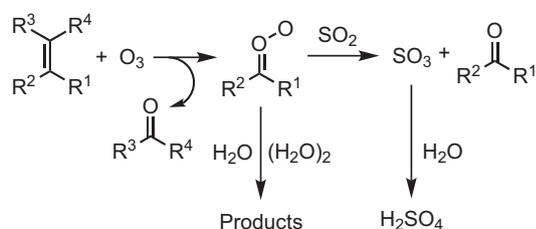


Fig. 1. Reaction scheme showing competitions for CIs between reactions with water (monomer and dimer) and with SO₂.

SO₂, these CIs may accumulate to higher concentrations and have higher probability to oxidize atmospheric SO₂. Table 1 shows selected rate coefficients for relevant CI reactions and the effective first-order decay rate coefficients (k_{eff}) of small CIs under an atmospheric condition.

As will be discussed in detail in *Discussion and Conclusions*, the steady-state concentration of a particular CI would depend on its formation rate and effective decay rate coefficient; its impact on the SO₂ oxidation would further depend on its concentration and reaction rate coefficient with SO₂. Experimental results (Table 1) show that CH₂OO and *anti*-CH₃CHOO react with water vapor very quickly (3, 22–24). Thus, their steady-state concentrations would be too low to have a significant impact in SO₂ oxidation under typical atmospheric conditions, as shown in modeling results (15, 16). On the other hand, previous experimental data for *syn*-CH₃CHOO (3, 24) are not precise enough to determine its main decay pathways in the atmosphere.

Quantum-chemistry (25–27) calculations predicted that the *anti*-form of CIs (CIs with R¹ = H in Fig. 1, including CH₂OO) react with water vapor very quickly and that the *syn*-form of CIs (CIs with R¹ ≠ H in Fig. 1, including dialkyl-substituted CIs) react slowly with water vapor. Here, steric hindrance of the alkyl group may account for the structure dependence in the reactivity. However, due to uncertainty in the calculated rate coefficients, it is unclear about the main decay channels of the *syn*-CIs in the atmosphere. For example, some theoretical investigation (29) shows that the reactions of water vapor with *syn*-CIs may still be fast enough (with a large uncertainty) to efficiently scavenge atmospheric *syn*-CIs, whereas some other calculations (25) suggest that these reactions are too slow to consume *syn*-CIs significantly. If the latter is

the case, *syn*-CIs may have higher steady-state concentrations in the troposphere and may still play an important role in the SO₂ oxidation; otherwise the steady-state concentrations of *syn*-CIs would still be low due to their fast consumption by reactions with water vapor (unless their sources are significantly larger than current estimation) and we might need to find another candidate for the unknown oxidant [oxidant X in the work by Mauldin et al. (4)] in the SO₂ atmospheric chemistry.

To shed some light on this important issue, we performed direct kinetic measurements of the reactions of dimethyl-substituted CI, (CH₃)₂COO, with water vapor and with SO₂ under near-atmospheric conditions. By introducing the water reactant at high concentrations, the rate coefficient of (CH₃)₂COO reaction with water can be better constrained. In contrast with the fast reaction of CH₂OO with water dimer, this result shows that the relative probabilities of (CH₃)₂COO reactions with SO₂ and with water vapor are comparable in the troposphere, so water alone would not completely scavenge (CH₃)₂COO, suggesting CIs of similar structures may play a more important role in the atmospheric oxidation of SO₂.

Results

Fig. 2A shows time-resolved difference absorption spectra recorded in the (CH₃)₂CI₂/O₂ pulsed photolysis system, in which the laser pulse defines delay time $t = 0$. The photodissociation of the (CH₃)₂CI₂ precursor produces (CH₃)₂CI radicals; (CH₃)₂COO was formed through the reaction of (CH₃)₂CI + O₂ → (CH₃)₂COO + I (30). At $t = 50 \mu\text{s}$, a strong absorption band peaked at 330 nm was observed, which decays with the delay time. At very long delay time (e.g., 2,000 μs), a negative difference absorption signal peaked at 296 nm was observed, which corresponds to the depletion of the (CH₃)₂CI₂ precursor. Fig. 2B shows the spectra recorded at a very similar condition but adding SO₂ gas to scavenge CIs. The absorption signal in Fig. 2B consists mainly of the depletion of (CH₃)₂CI₂ and a small amount of IO [a byproduct, likely from I + (CH₃)₂COO → IO + (CH₃)₂CO]. Other possible species in the absorption cell are SO₃ and acetone, which absorb rather weakly in the studied wavelength region [the absorption cross-sections σ for the relevant species are $\sigma(\text{SO}_3) < 1 \times 10^{-21} \text{ cm}^2$, $\sigma(\text{acetone}) < 5 \times 10^{-20} \text{ cm}^2$, and $\sigma \sim 10^{-17} \text{ cm}^2$ for a CI] (30, 31). Following the established method of spectral analysis in similar systems (22, 31–33), the absorption band of (CH₃)₂COO can be obtained from the difference between the spectra in Fig. 2A and B and is shown in Fig. 2C. The resultant spectrum of (CH₃)₂COO is slightly broader

Table 1. Reported bimolecular rate coefficients k and effective first-order rate coefficients ($k_{\text{eff}} = k[\text{Coreactant}]$) for simple CI reactions with H₂O, (H₂O)₂, and SO₂ at a given atmospheric condition

CI	Coreactant	[Coreactant]/cm ⁻³	$k/\text{cm}^3\text{s}^{-1}$	$k_{\text{eff}}/\text{s}^{-1}$	Reference
CH ₂ OO	H ₂ O	5.4×10^{17}	$<1.5 \times 10^{-15}$	<810	(22)
	(H ₂ O) ₂	6.0×10^{14}	6.5×10^{-12}	3,900	(22)
	SO ₂	1.2×10^{12}	3.9×10^{-11}	47	(2)
<i>anti</i> -CH ₃ CHOO	H ₂ O	5.4×10^{17}	1.0×10^{-14}	5,400	(3)
			2.4×10^{-14}	13,000	(24)
	SO ₂	1.2×10^{12}	6.7×10^{-11}	80	(3)
<i>syn</i> -CH ₃ CHOO	H ₂ O	5.4×10^{17}	$<4 \times 10^{-15}$	$<2,200$	(3)
			$<2 \times 10^{-16}$	<110	(24)
	SO ₂	1.2×10^{12}	2.4×10^{-11}	29	(3)
(CH ₃) ₂ COO	H ₂ O	5.4×10^{17}	$<1.5 \times 10^{-16*}$	$<81*$	This work
	(H ₂ O) ₂	6.0×10^{14}	$<1.3 \times 10^{-13*}$	$<78*$	This work
	SO ₂	1.2×10^{12}	1.3×10^{-10}	160	This work

The assumed concentrations of H₂O and SO₂ correspond to a relative humidity RH = 70% and a SO₂ mixing ratio of 50 ppb at 298 K and 1 atm. Only data from direct kinetic measurements are selected.

*The rate constant of the H₂O reaction with (CH₃)₂COO is obtained by assuming the rate constant of the (H₂O)₂ reaction with (CH₃)₂COO is zero and vice versa (SI Appendix, Table S2); thus, these two effective decay rates should not be added together.

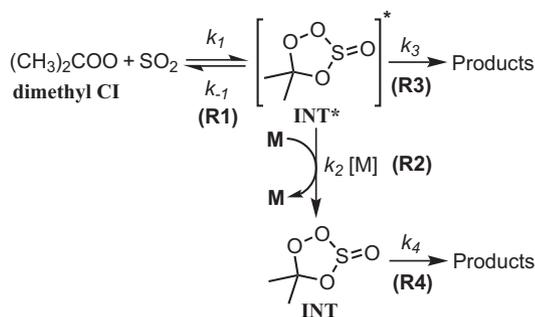


Fig. 6. Proposed mechanism for CI reaction with SO_2 .

and an alkene); k_{decay} would be the summation of the effective decay rate constants k_{eff} of all possible decay pathways; k_{therm} is the thermal decomposition rate coefficient; $k_{\text{H}_2\text{O}}$, k_{w_2} , k_{SO_2} , and k_{NO_2} are the bimolecular rate coefficients of CI reactions with H_2O , $(\text{H}_2\text{O})_2$, SO_2 , and NO_2 , respectively. The k_{therm} for $(\text{CH}_3)_2\text{COO}$ has been reported recently to be $3 \pm 0.4 \text{ s}^{-1}$ at 293 K (34) with a significant temperature dependence (28).

Considering the possible concentrations of H_2O and SO_2 in the troposphere, we can evaluate the effective decay rate constants of simple CIs by water reaction and by SO_2 reaction. As shown in Table 1, the consumptions of CH_2OO and *anti*- CH_3CHOO by water (including monomer and dimer) are extremely fast, $>10^3 \text{ s}^{-1}$, predominating in their k_{decay} . The very large k_{decay} would result in very low steady-state concentrations for these CIs, limiting their roles in oxidizing other atmospheric species like SO_2 and NO_2 (see Eqs. 7–9).

On the other hand, the reaction of $(\text{CH}_3)_2\text{COO}$ with H_2O is much slower, such that the water reaction would not limit the $(\text{CH}_3)_2\text{COO}$ concentration in the troposphere anymore. In addition, the rate coefficient of $(\text{CH}_3)_2\text{COO}$ reaction with SO_2 is larger than those of other known CI reactions with SO_2 , indicating a greater role of $(\text{CH}_3)_2\text{COO}$ in the atmospheric SO_2 oxidation. In other words, there is a strong structure dependence in the CI oxidation of SO_2 . For $(\text{CH}_3)_2\text{COO}$, its k_{decay} is smaller and its k_{SO_2} is larger, such that the SO_2 oxidation rate by $(\text{CH}_3)_2\text{COO}$ is faster in comparison with those for CH_2OO and *anti*- CH_3CHOO , assuming similar formation rates (see Eq. 9). In addition, for a CI with small $k_{\text{H}_2\text{O}}$ and k_{w_2} , its k_{therm} would be another important factor that also influences its $[\text{CI}]_{\text{ss}}$ and oxidation capacity. A related issue is that the thermal decomposition of *syn*-CIs [including $(\text{CH}_3)_2\text{COO}$] may form OH radicals through a 1,4 H-migration process (30), which may be an important non-photolytic OH source in the troposphere. Again, structure dependence of k_{therm} for various CIs would need further investigation.

Previous studies of ozonolysis of 2,3-dimethyl-2-butene (tetramethyl ethylene, $\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{R}^4 = \text{CH}_3$) (20, 28, 34) have provided some information about the $(\text{CH}_3)_2\text{COO}$ reactions with H_2O and with SO_2 . But, the results are far from consistency. First, the reported k_{SO_2} are on the order of $10^{-13} \text{ cm}^3 \text{ s}^{-1}$ (34), much smaller than the value determined from the direct kinetic measurement (Table 1). A similar situation also happens for smaller CIs like CH_2OO and CH_3CHOO (12, 13, 35), suggesting there might be some systematic issues in the ozonolysis experiments. Very recently, Newland et al. (20) measured the removal of SO_2 in the presence of alkene–ozone systems and concluded that the SO_2 removal displays a clear dependence on relative humidity for all four alkene ozonolysis systems [ethene (to form CH_2OO), *cis*-2-butene (to form CH_3CHOO), *trans*-2-butene (to form CH_3CHOO), and 2,3-dimethyl-2-butene (to form $(\text{CH}_3)_2\text{COO}$)], confirming a significant reaction for stabilized CIs with H_2O . However, Berndt et al. (28) investigated the H_2SO_4 formation as a function of $[\text{H}_2\text{O}]$ in similar ozonolysis reactions and reported quite different values. The results for $(\text{CH}_3)_2\text{COO}$ are summarized in Table 2. The result by Newland et al. is not consistent with the results of Berndt et al. and this work. The reason for this

discrepancy may originate from the complexity of the ozonolysis experiments, in which it is difficult to fully quantify the side reactions during the long reaction time.

It is important to note that the reactivity of a particular CI toward water vapor strongly depends on its structure. Table 1 indicates that a methyl group substitution for R^1 may alter the rate coefficient by orders of magnitude. Although ozonolysis experiments (20, 28, 34) have also shown a trend for the structure dependence, the magnitude of the reactivity difference is much smaller than what is observed in the direct kinetic measurements (Table 1). In addition, the ozonolysis experiments cannot distinguish the *anti*- and *syn*- conformers of CIs, which have quite different reactivity.

The results summarized in Table 1 give direct evidence that the reaction of water with $(\text{CH}_3)_2\text{COO}$ is greatly hindered by the methyl group at the R^1 position. Interestingly, methyl substitution seems to enhance the reactivity of CIs toward SO_2 . One can imagine that CIs with more complicated substitution groups may also react with water slowly but react with SO_2 quickly, similar to $(\text{CH}_3)_2\text{COO}$. Such CIs may be the candidate for the oxidant X in the SO_2 oxidation, an important issue raised recently (4).

Considering that much of the VOC emissions consist of a large variety of alkenes, ranging from simple alkenes like C_2H_4 and C_3H_6 to bigger alkenes like isoprene, monoterpenes, sesquiterpenes, etc., various CIs are expected to form in the atmospheric ozonolysis reactions. To assess the impact of the CI+ SO_2 reaction class on the atmosphere, it is critical to know the atmospheric concentration of CIs. As mentioned above, it requires the relevant rate coefficients to estimate the atmospheric concentration of a CI. Water is the third most abundant molecule in the air. The reactions of CIs with water are crucial in determining the concentrations and fate of the CIs. The slow rates of water reactions with $(\text{CH}_3)_2\text{COO}$ or with similar CIs are very difficult to measure, but very important in estimating the concentrations of those CIs and thus the oxidizing capacity of the atmosphere.

Materials and Methods

The experimental setup has been described in detail elsewhere (22, 32). In brief, $(\text{CH}_3)_2\text{COO}$ was generated from photolysis of a gaseous mixture consisting of $(\text{CH}_3)_2\text{Cl}_2$, O_2 , and buffer gas (N_2) at 248 nm (KrF excimer laser) via the established preparation method: $(\text{CH}_3)_2\text{Cl}_2 + h\nu \rightarrow (\text{CH}_3)_2\text{Cl} + \text{I}$; $(\text{CH}_3)_2\text{Cl} + \text{O}_2 \rightarrow (\text{CH}_3)_2\text{COO} + \text{I}$ (2, 30). $(\text{CH}_3)_2\text{COO}$ was monitored via its strong UV absorption (30). Continuous probe light went through the photolysis reactor (25 or 20 mm inner diameter, 76 cm long) six or eight times to enhance the absorption signal.

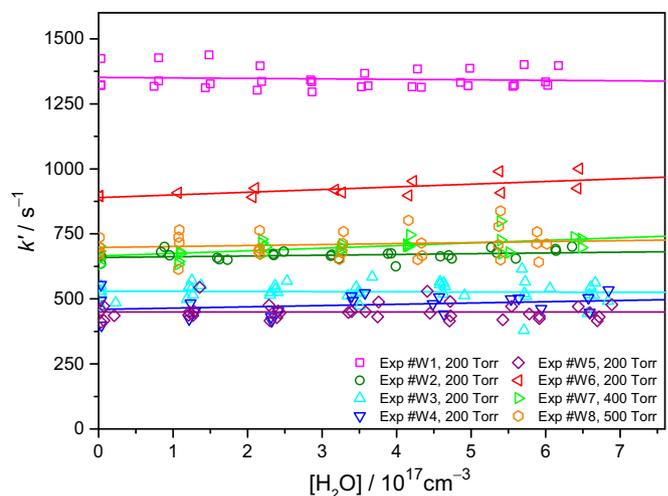


Fig. 7. Pseudo-first-order rate coefficient of $(\text{CH}_3)_2\text{COO}$ as a function of $[\text{H}_2\text{O}]$. Solid lines are linear fit to the data of each experiment. There are 223 data points (see *SI Appendix, Table S2* for the experimental conditions).

Table 2. Ratio of the rate coefficients of (CH₃)₂COO reactions with H₂O and with SO₂, $k_{\text{H}_2\text{O}}/k_{\text{SO}_2}$

$k_{\text{H}_2\text{O}}/k_{\text{SO}_2}$	Method	Reference
$<1.2 \times 10^{-6}$	Absolute direct kinetic measurements of (CH ₃) ₂ COO	This work
$<4 \times 10^{-6}$	Relative measurements of the H ₂ SO ₄ product	Berndt et al. (28)
$(8.7 \pm 2.5) \times 10^{-5}$	Relative measurements of the SO ₂ and O ₃ consumptions	Newland et al. (20)

Spectral Measurements. Transient absorption spectra of the reaction system were measured with a continuous broadband light source (Energetiq, EQ-99) and a time-gated ICCD spectrometer (Andor, SR303i and DH320T-18F-03). The light source was projected to the entrance of the absorption cell by an achromatic lens (Thorlabs ACA254-100-UV). To enhance the absorption signal, the probe light was reflected eight times through the photolysis reactor by a spherical mirror ($R = 1$ m, Thorlabs, CM750-500-F01) and a SiO₂ prism. The probe beam and the photolysis beam were overlapped collinearly in the photolysis reactor. For the ICCD measurement, the reference spectrum was recorded 200 μs before the photolysis pulse. Transient spectra at delay times 50, 100, 150, 200, 250, 300, 500, 1,000, and 2,000 μs were recorded.

Kinetics Measurements. Absorption signal at 340 nm was measured in real time by using a balanced photodiode detector (Thorlabs, PDB450A) and a bandpass filter (Edmund Optics, 65129, 10-nm OD4 band pass filter) and the same light source. A time-dependent transmittance change ($<1\%$) was observed after the photolysis pulse even without adding any sample. This background did not depend on [H₂O], or on [SO₂]. It can be subtracted by performing a background run under the same experimental condition except adding (CH₃)₂Cl₂. The presented data are after the background subtraction.

[SO₂] Measurements. The SO₂ concentration was adjusted by controlling the amount of SO₂ in buffer gas with mass flow controllers (Brooks, 5850E or

5800E) and monitored by its UV absorption (190–330 nm) with a D₂ lamp (Ocean Optics, D-2000) and a spectrometer (Ocean Optics, Maya2000 Pro).

Relative Humidity Measurements. The relative humidity was adjusted by controlling the mixing ratio of dry and moisturized buffer gases with mass flow controllers (Brooks, 5850E or 5800E) and monitored with a humidity sensor (Rotronic, HC2-S). The temperature for measuring the water reaction was controlled at 298.2 ± 0.5 K.

Precursor Preparation. The precursor, (CH₃)₂Cl₂, was synthesized following a reported method (36). In brief, acetone was added to hydrazine monohydrate (80 °C, >1 h) to obtain acetone hydrazone (CH₃)₂C=NNH₂. Saturated solution of iodine in ethyl ether was added to acetone hydrazone (at room temperature), which is mixed with ethyl ether and triethylamine, to obtain the final product. The structure of the synthesized (CH₃)₂Cl₂ was checked with H-NMR spectroscopy [(CH₃)₂Cl₂: 3.00 ppm (6H, s, Me) in CDCl₃] (37).

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