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Temperature-Dependent Kinetics of the Reaction of the Criegee Intermediate CH_2OO with Pyruvic Acid

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Abstract

The kinetics of the reaction between formaldehyde oxide (CH_2OO) and pyruvic acid ($\text{CH}_3\text{COCO}\text{OH}$) has been investigated. Laser flash-photolysis-transient absorption spectroscopy measurements over the range $T = 275\text{--}375$ K were used to measure T -dependent bimolecular rate constants. The rate constants show non-Arrhenius behavior, initially increasing and subsequently decreasing with T . A maximum value of $(21.4 \pm 1.1) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ was observed at 325 K. At room temperature (296 K), the rate constant was measured to be $(19.5 \pm 1.0) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$, which is in line with the value expected for reaction of CH_2OO with a substituted carbonyl and significantly smaller than typical values for reactions with carboxylic acids. Various pathways have been characterized by *ab initio* calculations at the CBS-QB3 level for reaction of CH_2OO with the two lowest-energy conformers of pyruvic acid, labelled Tc and Tt. Both conformers can undergo 1,3-dipolar cycloaddition reactions at either carbonyl group to form secondary ozonides via submerged barriers. The presence of an internal H-bond in the more stable Tc conformer has a significant impact on reactivity, inhibiting the alternative 1,2-addition/insertion and 1,4-addition reaction pathways involving the OH or COOH groups, respectively, that occur more readily for the less stable Tt conformer and form hydroperoxymethylpyruvate ester. The unusual T dependence of the measured rate constants is attributed to the increasing thermal population of the less stable Tt conformer at higher T , and the availability of additional reaction pathways.

Introduction

Criegee intermediates (carbonyl oxides, R_1R_2COO , CIs) typically react rapidly with carboxylic acids ($RCOOH$), with room temperature rate constants that approach or exceed the gas-kinetic collision limit.¹⁻³ In the troposphere, reaction with carboxylic acids, which may be found with mixing ratios of a few ppb,⁴ may be competitive with water dimer, the major reactive sink for the simplest CI, formaldehyde oxide (CH_2OO). Carboxylic acids react with CIs via a direct barrierless 1,4-addition mechanism (also referred to as a 1,4-insertion)⁵ to form hydroperoxide esters.

The kinetics of the reactions between photochemically-produced CIs with carboxylic acids ($RCOOH$) have been studied directly using a variety of experimental methods.⁶⁻¹² At room temperature, rate constants are generally $k_{RCOOH} > 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ and are affected by the substituents on both the CI and the acid. Previously measured values for $CH_2OO + RCOOH$ reactions are compiled in Table S1 in Supporting Information. Acetic acid ($R = CH_3$) reacts faster than formic acid ($R = H$), while fluorinated carboxylic acids ($R = CF_3$) react faster still. Similarly, the rate constants for reactions of larger CIs such as acetaldehyde oxide (CH_3CHOO) or acetone oxide ($(CH_3)_2COO$) with carboxylic acids are larger than those of CH_2OO .⁹ Temperature-dependent measurements are scarcer, but where available they show a weak negative dependence with $-(E_a/R) \approx 200\text{--}700 \text{ K}$.^{7,11} Chhantyal-Pun et al.⁹ have developed a structure-activity relationship (SAR) for $CI + RCOOH$ reactions using a dipole capture model in which the kinetics are controlled by long-range attractive (dipole-dipole) forces.

A significant outlier in the dipole capture SAR is the reaction of CH_2OO with pyruvic acid ($CH_3COCOOH$, PyrA), an α -ketoacid, for which the room temperature rate constant $k_{PyrA} = (20 \pm 2) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ is an order of magnitude smaller than for other carboxylic acids.⁹ The discrepancy has been attributed to the presence of an internal hydrogen bond in the most stable conformer of PyrA, labelled Tc, which inhibits the typically barrierless 1,4-addition mechanism that leads to the formation of hydroperoxymethylpyruvate ester (hydroperoxymethyl-2-oxopropanoate, HPMP). The

Tc conformer lies ~ 2 kcal mol⁻¹ below the Tt conformer, and is strongly favored at room temperature.^{13–20} The structures of the low energy Tt and Tc conformers of PyrA are shown in Figure 1. 1,3-dipolar cycloaddition reactions to form secondary ozonides (SOZs) can occur at the carbonyl groups of both conformers.^{21–24} Recently, we have explored the reaction kinetics of CH₂OO with a range of substituted carbonyls and experimentally demonstrated that reactivity is controlled by the electron-withdrawing or electron-donating character of the substituents.^{25–28} The reactivity trend can be understood using frontier molecular orbital theory,^{29–31} in which electron-withdrawing substituents lower the energy of the C=O π^* orbital and are activating, while electron-donating

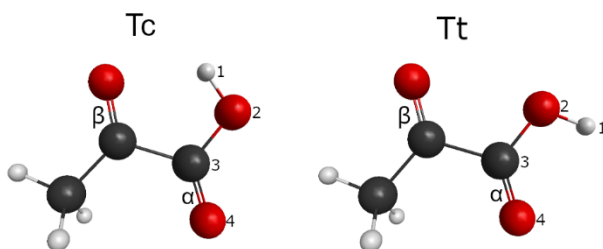


Figure 1: Low-energy Tc and Tt conformers of pyruvic acid. The carbonyl groups are labelled α (acid) and β (acetyl). Numbers 1–4 indicate the atoms directly participating in the 1,2-addition/insertion and 1,4-addition reaction mechanisms.

substituents have the opposite effect and are deactivating.

Here, we describe laser flash photolysis transient absorption spectroscopy measurements quantifying the temperature-dependent kinetics of the reaction between CH₂OO and PyrA over the range 275–375 K. FTIR measurements are used to quantify the temperature-dependent equilibrium constant for interconversion between the Tc and Tt conformers. Complementary CBS-QB3 calculations characterize stationary points on the reaction energy and free energy surfaces, showing the existence of multiple reaction pathways for each conformer.

Experimental and Computational Methods

a. Experimental Methods

Kinetics experiments were carried out using laser flash photolysis transient absorption spectroscopy in a temperature-controlled flow reactor that has been described in detail previously.^{26,27} Briefly, CH₂OO is produced by laser photolysis of diiodomethane (CH₂I₂) in the presence of excess O₂. Reactant concentrations are determined from transient absorption spectra using pulsed UV LEDs. Complementary temperature-dependent FTIR measurements are used to determine the relative populations of the two PyrA conformers.

The 266 nm output of an Nd:YAG laser is used to photolyze CH₂I₂, with typical fluences of around 5 mJ cm⁻². Dichroic mirrors steer the photolysis beam through the reactor and long-pass filters ($\lambda < 315$ nm) protect other instrumentation from residual laser light. Reactant concentrations are determined from absorption spectra using a pulsed UV LED centered at 365 nm, providing spectral coverage in the range 355–390 nm. The 300 ns LED pulses are counter-propagated relative to the laser through the flow cell and dispersed in a spectrograph. Transient absorption spectra were recorded at ten delays after photolysis with $\Delta t = 20$ –2000 μ s to determine CH₂OO concentrations. Each transient spectrum involved a total accumulation of 400 pre-photolysis reference and post-photolysis signal spectra, which were acquired by cycling over the delay set four times to minimize potential systematic errors introduced by drifting conditions. Absorbance due to excitation to the S₁ ($n\pi^*$) band of PyrA falls within the LED output range,³² so it was possible to monitor its concentration *in situ*. Absorption spectra were derived from 100 signal spectra taken with PyrA present directly after each kinetics measurement and 100 reference spectra obtained with no PyrA present and otherwise equivalent flow conditions.

Experiments were performed at a total pressure of 83–88 Torr, with the gas mixture comprising

$[\text{CH}_2\text{I}_2] = 1 \times 10^{15} \text{ cm}^{-3}$, $[\text{O}_2] = 2 \times 10^{17} \text{ cm}^{-3}$, $[\text{PyrA}] = (0.5\text{--}2) \times 10^{15} \text{ cm}^{-3}$, and balance $[\text{N}_2] = 2 \times 10^{16} \text{ cm}^{-3}$. PyrA and CH_2I_2 were introduced by a flow of N_2 via smog bubblers held in a water bath at 295 K to ensure that the vapor pressure remained constant (~ 1 Torr for both chemicals). PyrA flow concentrations were controlled using a range of choked-flow orifices, with all other flow rates held constant. All experiments were performed with pseudo-first order conditions of excess PyrA, with concentrations at least two orders of magnitude greater than that of the peak measured concentrations of CH_2OO . The flow reactor temperature was varied over the range 275–375 K, with a precision of better than 1 K, as measured on two thermocouples. All chemicals were used as supplied: O_2 (Airgas, UHP 4.4), N_2 (Airgas, industrial grade), CH_2I_2 (Sigma Aldrich, 99%) and PyrA (Fisher Scientific, >97%).

The temperature-dependent relative populations of the two PyrA conformers were determined in separate FTIR spectroscopy measurements of the headspace above the liquid taken using a JASCO 4700 spectrometer. Approximately 1 cm^3 of liquid PyrA was deposited in a 9 cm long sample cell fitted with ZnSe windows. The temperature of the cell was varied over the range 295–365 K using insulated heating tape (Briskheat) and monitored with a K-type thermocouple.

b. Computational Methods

Electronic structure calculations on the available reaction pathways were performed with the *Gaussian 16*³³ and *GAMESS*^{34,35} software packages. Initial optimization and orbital energy calculations were carried out with B3LYP/cc-pVDZ. Thermodynamic energies were further refined with the CBS-QB3 compound method,³⁶ which has been shown to provide reliable thermochemistry at modest computational cost.^{37–39} Cartesian coordinates and images of the optimized geometries of the transition states as well as the full CBS-QB3 energy output can be found in the Supporting Information. Intrinsic reaction coordinate (IRC) calculations confirmed the transition state structures correspond to the anticipated minima along the potential energy surface. Additional

calculations were performed using the MP2 and B3LYP methods with various basis sets (cc-pVDZ, cc-pVTZ, aug-cc-pVDZ, aug-cc-pVTZ) to characterize the relative energies, harmonic frequencies, and IR intensities of the Tc and Tt conformers of PyrA.

Results

The kinetics of the $\text{CH}_2\text{OO} + \text{PyrA}$ reaction was studied over the temperature range 275–375 K at a total pressure of 83–88 Torr. Complementary FTIR measurements were performed to quantify the temperature-dependent equilibrium constant for interconversion between the Tc and Tt conformers and determine their thermal populations.

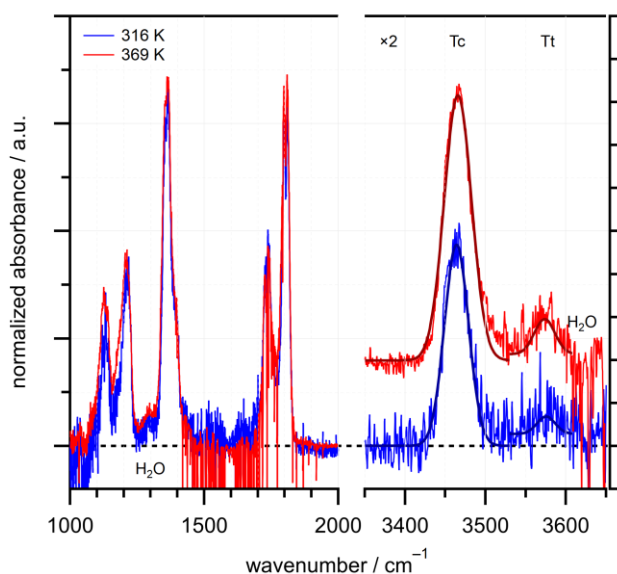


Figure 2: Normalized FTIR spectra of PyrA taken at 316 K (blue) and 369 K (red). Absorbance in the high frequency region has been scaled by a factor of 2 and the higher temperature spectrum offset vertically for clarity. The ν_1 OH stretch bands of the Tc and Tt conformers are observed at 3465 and 3577 cm^{-1} , respectively, and are overlaid by Gaussian fits. Sharp features near 1600 cm^{-1} and 3600 cm^{-1} are due to H_2O transitions, which are imperfectly subtracted.

a. Conformer Equilibrium

IR spectra of gas-phase PyrA were collected at four temperatures ranging from 316–369 K; Figure 2 shows examples of the spectra collected at $T = 316$ K and 369 K. Bands in the 1000–2000 cm^{-1} region are essentially unaffected by temperature. In contrast, while the OH stretching band of the major Tc conformer is evident at 3465 cm^{-1} at all temperatures, that of the Tt conformer at 3577 cm^{-1} becomes stronger as the temperature increases. The results are consistent with previous measurements that have also shown a ~ 100 cm^{-1} red-shift of the OH stretch frequency in the Tc conformer.^{20,40} Relative Tt and Tc populations were determined by fitting the OH stretch bands to Gaussian functions and used to obtain temperature-dependent equilibrium constants $K(T)$ for $\text{Tc} \rightleftharpoons \text{Tt}$ interconversion, given by Equation 1:

$$K = \frac{[\text{Tt}]}{[\text{Tc}]} = \frac{A_{\text{Tt}}I_{\text{Tc}}}{A_{\text{Tc}}I_{\text{Tt}}} \quad \text{E1}$$

where A_x is the area of the band and I_x is the calculated IR intensity. Figure 3 shows a van't Hoff plot of $\ln K$ against $1/T$, from which the standard enthalpy and entropy changes can be determined according to Equation E2:

$$\ln K = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad \text{E2}$$

Absent any IR intensity correction, an unweighted linear fit of the experimental data returns $\Delta H^\circ = +2.0 \pm 0.3$ kcal mol⁻¹, which is in good agreement with previous values determined experimentally.^{13,17} The CBS-QB3 calculations predict a slightly larger value of $\Delta H^\circ = +2.6$ kcal mol⁻¹, which in turn agrees with the results of CCSD(T)/CBS calculations reported by Church et al.⁴¹

We note, following Schellenberger et al.¹³ that the correction applied to the relative IR intensities of

the Tc and Tt bands affects the value of ΔS° . The unweighted fit based solely on the experimental integrated band intensities returns a value $\Delta S^\circ = 0.9 \pm 0.8 \text{ cal K}^{-1} \text{ mol}^{-1}$. Figure S1 and Table S2 in Supporting Information compile IR intensities for the Tt and Tc OH stretches calculated using the B3LYP and MP2 methods with several basis sets, and Table S3 compiles calculated thermodynamics

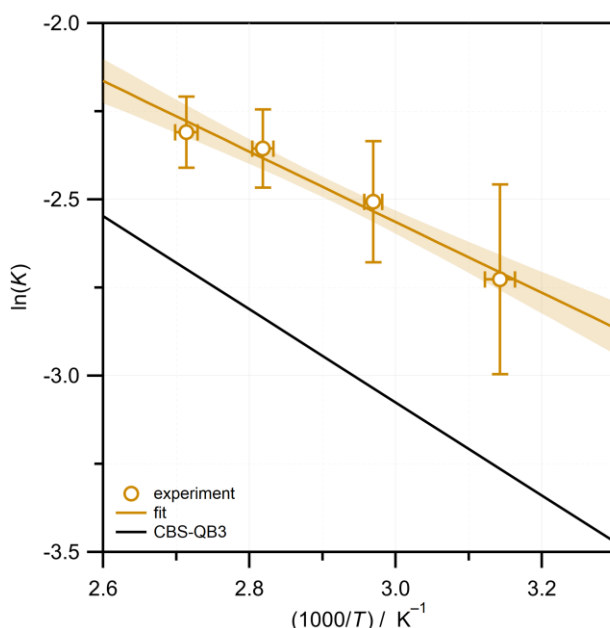


Figure 3: van't Hoff plot for the equilibrium between Tc and Tt conformers determined from FTIR spectra acquired over the temperature range 316–369 K. Solid line is a linear fit to the experimental data. Error bars are 1σ uncertainties obtained from the variation among repeated measurements. The shaded area represents a 1σ confidence band for the linear fit. Computational values (black) are extracted from the results of CBS-QB3 calculations.

values. In general, the H-bonded Tc conformer is calculated to have the greater IR intensity, with the Tc:Tt ratio decreasing as the size of the basis set is increased. The MP2 ratios are systematically lower than B3LYP. The DFT method is expected to calculate intensities more reliably.⁴² The choice of method and basis set shifts the van't Hoff plot vertically upwards by $\ln(I_{\text{Tc}}/I_{\text{Tt}})$. The calculated ratios

suggest that ΔS° should be offset upwards by 0.6–1.2 cal K⁻¹ mol⁻¹. We use the IR intensity values from the B3LYP/aug-cc-pVTZ calculations, which gives $\Delta S^\circ = 1.6 \pm 0.8$ cal K⁻¹ mol⁻¹, and $\Delta G^\circ = 1.5 \pm 0.4$ kcal mol⁻¹ at 298 K. The results of the van’t Hoff analysis are compiled in Table 1, with 1 σ statistical uncertainties derived from the linear fit. The relative populations of the Tc and Tt conformers, derived from the van’t Hoff analysis of the experimental IR spectra and the CBS-QB3 calculations are summarized in Figure S2 in Supporting Information. The fractional population of the Tc conformer decreases from $f_{Tc} \approx 0.95$ to 0.85 across the 275–375 K temperature range spanned in the kinetics measurements.

We note here that the fractional populations of the Tc and Tt conformers at a given temperature in the flow reactor will be the same as in the FTIR apparatus, provided thermal equilibrium is also established in the former. We have applied canonical transition state theory to calculate the unimolecular rate constants for isomerization using Equation 3:

$$k = \frac{k_B T}{h} \exp\left(-\frac{\Delta^\ddagger G^\circ}{RT}\right) \quad \text{E3}$$

where $\Delta^\ddagger G^\circ$ is the free energy barrier for interconversion. At the CBS-QB3 level and 298 K, we calculate $\Delta^\ddagger G^\circ = +12.0$ kcal mol⁻¹ for the forward reaction (Tc $\rightarrow$ Tt) and +9.9 kcal mol⁻¹ for the reverse (Tt $\rightarrow$ Tc). Room temperature isomerization rate constants are therefore $k_{Tc \rightarrow Tt} = 8.0 \times 10^3$ s⁻¹ and $k_{Tt \rightarrow Tc} = 2.9 \times 10^5$ s⁻¹, and we expect thermal equilibrium to be approached within a few μ s. This timescale can be considered as an upper limit, as this simple application of transition state theory has neglected the effect of tunneling, which is known to allow interconversion at very low temperatures.^{20,43}

Table 1: Experimental and calculated thermodynamic values for the conversion of Tc to Tt. Experimental values were obtained from the van’t Hoff plot shown in Figure 3, and use B3LYP/aug-cc-pVTZ IR band intensities. The standard Gibbs energy is

evaluated at 298 K, assuming no T dependence in the standard enthalpies and entropies. The calculated values were obtained at the CBS-QB3 level.

	experiment	CBS-QB3
$\Delta H^\circ / \text{kcal mol}^{-1}$	$+2.0 \pm 0.3$	$+2.62$
$\Delta S^\circ / \text{cal K}^{-1} \text{mol}^{-1}$	$+1.6 \pm 0.8$	$+1.76$
$\Delta G^\circ / \text{kcal mol}^{-1}$	$+1.5 \pm 0.4$	$+2.10$

b. CH₂OO + Pyruvic Acid Kinetics

Kinetics measurements of the CH₂OO + PyrA reaction were performed as described previously.^{25–28} CH₂OO was produced in the flow cell by 266 nm photolysis of CH₂I₂ in the presence of excess O₂. Transient absorption spectra over the range 355–390 nm were collected at ten photolysis-probe delays using a pulsed LED. The transient absorption spectra were fit to a linear combination of CH₂OO and IO cross sections to derive time-dependent concentrations using Beer’s law. Peak [CH₂OO]₀ values, observed at ~20 μs after photolysis, were ~7×10¹² cm⁻³ and depended only minimally on [PyrA]. The same kinetic model, as used previously to describe the loss of CH₂OO,^{25–28} accounts for second order self-reaction ($k_{\text{self}} = 7.8 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$)²⁶ and pseudo-first order loss due to reaction with excess PyrA and other background reactions ($k_{\text{loss}} = k_{\text{bgd}} + k_{\text{PyrA}}[\text{PyrA}]$), according to Equation E4:

$$[\text{CH}_2\text{OO}]_t = \frac{k_{\text{loss}}[\text{CH}_2\text{OO}]_0}{k_{\text{loss}} \exp(k_{\text{loss}}t) - 2k_{\text{self}}[\text{CH}_2\text{OO}]_0[1 - \exp(k_{\text{loss}}t)]} \quad \text{E4}$$

PyrA concentrations were determined from absorption spectra acquired at the end of each kinetics run. Signal spectra were obtained immediately following the kinetics measurement (absent photolysis), followed by reference spectra acquired without PyrA but with all other gas flows constant. Figure 4(a) shows examples of PyrA spectra obtained using different choked-flow orifices

obtained at room temperature (296 K). The spectra are fit to PyrA absorption cross section data taken from the JPL evaluation⁴⁴ to determine the *in situ* concentration of PyrA in the flow reactor for the preceding kinetics run. It is assumed that [PyrA] remained constant during each run, which was verified by separate time-dependent measurements such as those as shown in Figure S3 in

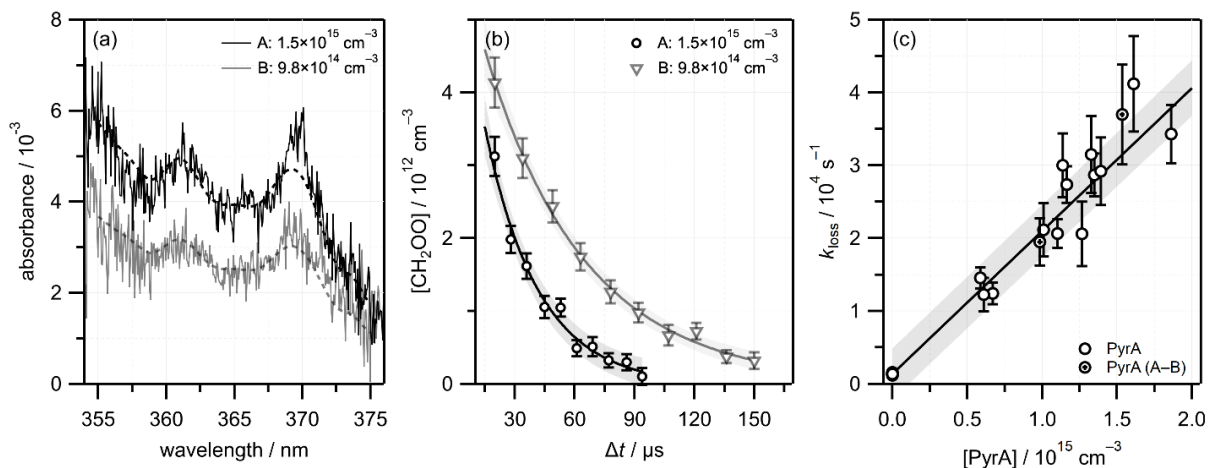


Figure 4: Typical experimental data, acquired at 295 K. (a) PyrA absorption spectra measured *in situ* directly after each kinetics experiment at two different concentrations (labelled A and B). Dashed lines show the fits of the PyrA cross-section to the spectra. (b) $[\text{CH}_2\text{OO}]_t$ profiles for the PyrA concentrations corresponding to A and B, along with fits to the kinetic model described in the text. (c) Pseudo-first order plot of k_{loss} against [PyrA]. The specific data points corresponding to time profiles A and B in panel (b) are highlighted. Error bars represent 1σ statistical uncertainties from fits of the experimental data and shaded areas represent 1σ confidence bands in the fits.

Supporting Information. Variation in [PyrA] over a 10 min period, typical for a single kinetics measurement, is around 2%.

The rate of $[\text{CH}_2\text{OO}]$ decay increases in the presence of higher concentrations of PyrA, as shown by

the time profiles in Figure 4(b), which were obtained at 296 K. Loss rates k_{loss} were determined by fitting the $[\text{CH}_2\text{OO}]_t$ time profiles to Equation E4, while holding the value of k_{self} fixed. The complete set of k_{loss} values obtained from repeated measurements at room temperature with varying $[\text{PyrA}]$ is shown in Figure 4(c). A linear fit of the data returns a room temperature bimolecular rate constant $k_{\text{PyrA}} = (19.5 \pm 1.7) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ for the reaction of CH_2OO with PyrA. The background loss rate is k_{bgd}

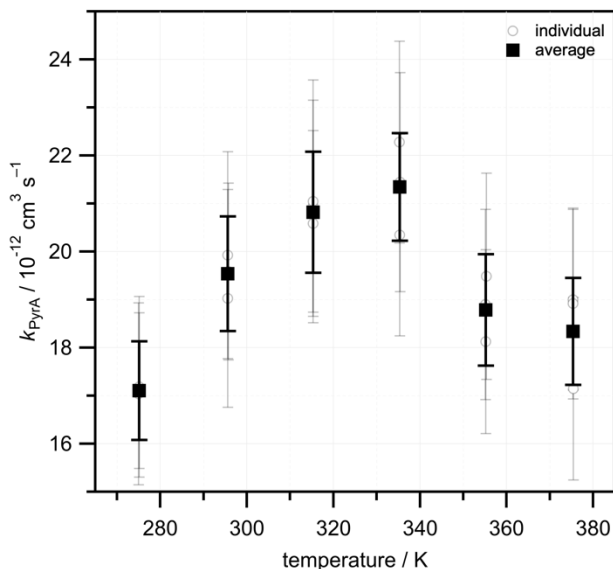


Figure 5: Temperature-dependent bimolecular rate constants for the reaction of CH_2OO with PyrA. Individual kinetics runs (gray, open circles) and weighted average values (black, filled squares) are shown. Error bars are 1σ statistical uncertainties in the pseudo-first order fits (gray) or the weighted averages (black).

$= 1370 \pm 80 \text{ s}^{-1}$, which is in reasonable agreement with the expected rate due to room temperature reaction of CH_2OO with residual I atoms produced by photolysis or the $\text{CH}_2\text{I} + \text{O}_2 \rightarrow \text{CH}_2\text{OO} + \text{I}$ reaction.⁴⁵

An additional factor that may influence the observed kinetics is the presence of products PyrA photolysis. PyrA has an absorption cross section of $7 \times 10^{-21} \text{ cm}^2$ at the photolysis wavelength of 266

nm, which corresponds to excitation of the S_2 state.⁴⁴ While PyrA photodissociation has not been studied directly at this wavelength, experiments performed using excitation at 248 nm,⁴⁶ and to the S_1 state at longer wavelengths^{32,47} suggests the final products are carbon dioxide (CO_2) and acetaldehyde (CH_3CHO), formed with near unit quantum yield. The decarboxylation mechanism is believed to involve primary production of methylhydroxycarbene (MHC, $CH_3\dot{C}OH$), which subsequently isomerizes to the more stable CH_3CHO . CO_2 is unreactive towards CH_2OO and consequently will have no effect on the observed kinetics, but CH_3CHO is known to react with CH_2OO with a room temperature rate constant of $\sim 1.2 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$.^{28,48-51} Based on the experimental laser fluence and the PyrA cross section, we estimate only $\sim 0.005\%$ of the PyrA is photolyzed. If we assume that MHC promptly isomerizes to CH_3CHO , then we anticipate it to be present with concentrations $< 2.0 \times 10^{11} \text{ cm}^{-3}$. At these low concentrations, its contribution to the rate of CH_2OO loss would be negligible at $< 0.24 \text{ s}^{-1}$. The kinetics of MHC reactions with CH_2OO have not been measured, but even assuming a gas kinetic rate constant ($\sim 10^{-10} \text{ cm}^3 \text{ s}^{-1}$), its contribution to CH_2OO loss or consumption of PyrA would be insignificant. Alternative reactions with, for example O_2 , are also unlikely to play a role as recent work has suggested that the related hydroxymethylene ($H\dot{C}OH$) species reacts slowly with O_2 .⁵²

Equivalent temperature-dependent measurements were made at 20 K intervals across the range 275–375 K. The complete set of rate constants for the reaction of CH_2OO with PyrA is shown as a function of temperature in Figure 5 and the values of k_{PyrA} and k_{bgd} are listed in Table 2. The dependence of the bimolecular rate constants on temperature is modest but non-Arrhenius. Values of k_{PyrA} first increase from $17 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ at 275 K, reach a maximum of $22 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ at 335 K, then decrease as temperature is increased further. The quoted 1σ uncertainties in the rate constants are based on the weighted averages of repeated pseudo-first order kinetics measurements at each temperature, where the individual uncertainties were derived from propagating uncertainties in the concentration of PyrA (estimated to be $\sim 8\%$) and statistical uncertainties from the fits.

Table 2: Temperature-dependent rate constants k_{PyrA} and observed background loss rates k_{bgd} for the reaction of CH_2OO with pyruvic acid (PyrA). Errors are derived from uncertainties in the weighted average of three independent measurements at each temperature.

T / K	$k_{\text{PyrA}} / 10^{-12} \text{ cm}^3 \text{ s}^{-1}$	$k_{\text{bgd}} / \text{s}^{-1}$
275	17.1 $\pm$ 1.0	1480 $\pm$ 90
296	19.5 $\pm$ 1.2	1370 $\pm$ 80
315	20.8 $\pm$ 1.3	1080 $\pm$ 80
335	21.4 $\pm$ 1.1	920 $\pm$ 80
355	18.8 $\pm$ 1.2	930 $\pm$ 80
375	18.3 $\pm$ 1.1	650 $\pm$ 80

c. Computational Results

PyrA is a multifunctional organic molecule and consequently can react with CH_2OO via several pathways, all of which are exothermic by 40–50 kcal mol⁻¹. We explicitly consider three classes of reaction, characterizing the entrance channel van der Waals complexes (vdW), transition states (TSs), and products at the CBS-QB3 level: 1,4-addition across the CI by the carboxylic acid –COOH moiety, 1,2-addition across the CI involving only the –OH group, and 1,3-dipolar cycloaddition at either of the C=O sites. The primary products of the 1,3-dipolar cycloadditions are 1,2,4-trioxolane SOZs, while the 1,4-addition and 1,2-addition/insertion reactions form the hydroperoxide ester HPMP, with similar exothermicities. The presence of the internal H-bond in the Tc conformer is significant as it inhibits the 1,4-addition and 1,2-addition/insertion pathways, reducing the overall reactivity. The analogous 1,2-addition/insertion pathway was also found to be inhibited in reactions of CH_2OO with hydroxyketones with internal H-bonds.²⁷

For each PyrA conformer there are eight 1,3-dipolar cycloaddition pathways for reaction with CH_2OO ,

all of which involve the reactants approaching with near-parallel heavy atom planes. Reaction can take place at either C=O group; the planar CH₂OO can approach with either face oriented towards

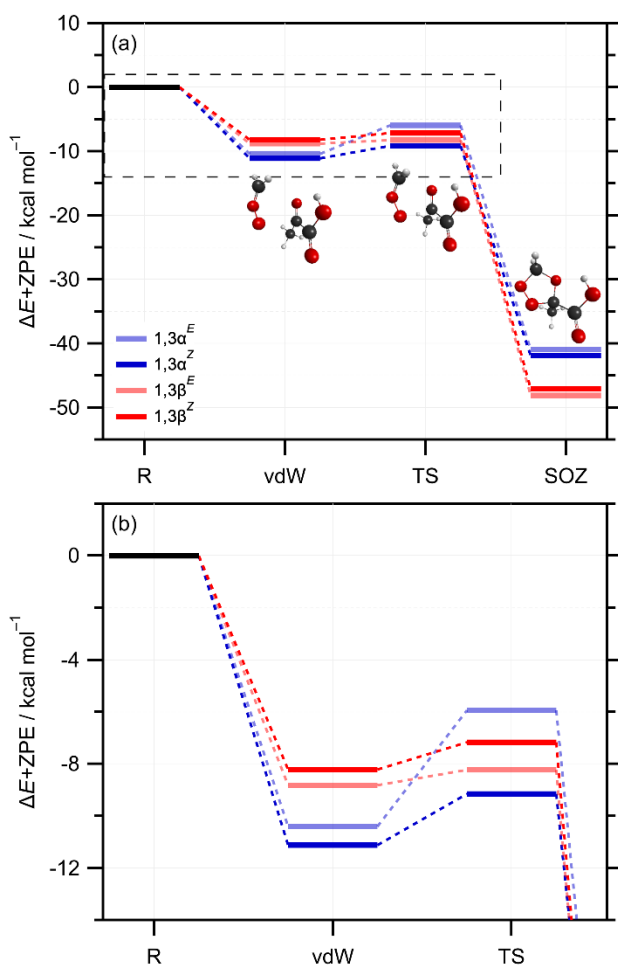


Figure 6: Calculated zero-point corrected energy profiles at 0 K for the 1,3-dipolar cycloaddition reactions of CH₂OO with the Tc conformer of PyrA, calculated at the CBS-QB3 level. (a) Full range, (b) is an expanded view of the region enclosed by the dashed box. The labels α and β correspond to reaction at the acid or acetyl C=O group, respectively; E/Z superscripts indicate the orientation of CH₂OO relative to the C=O substituents, as described in the text. Structures of the entrance channel complex (vdW), transition state (TS), and secondary ozonide product (SOZ) are shown for the 1,3 β^E pathway.

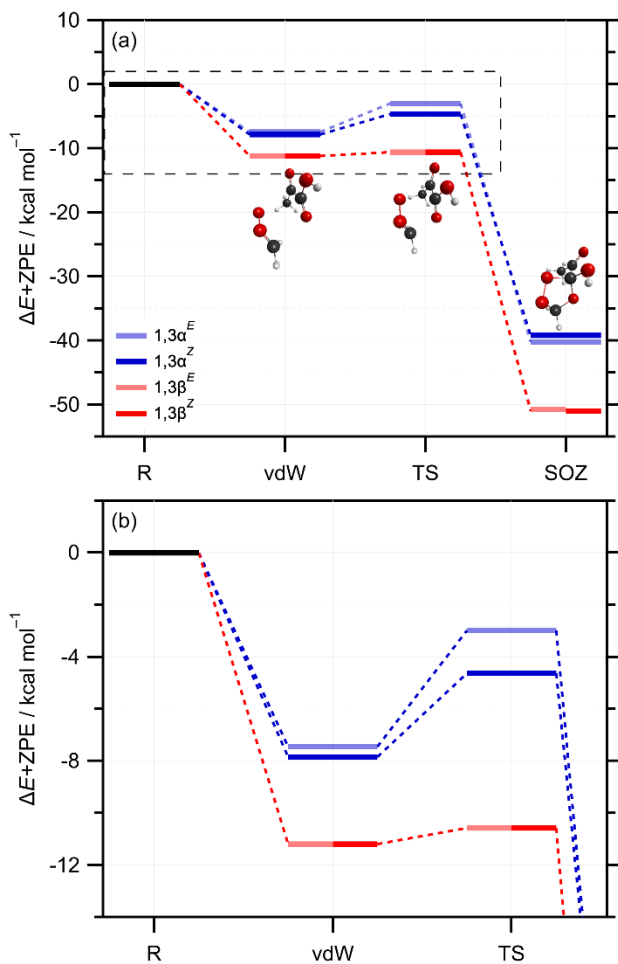


Figure 7: Calculated zero-point corrected energy profiles at 0 K for 1,3-dipolar cycloaddition reactions of CH₂OO with the Tt conformer of PyrA, calculated at the CBS-QB3 level. (a) Full range, (b) is an expanded view of the region enclosed by the dashed box. The labels α and β correspond to reaction at the acid and acetyl C=O group, respectively; E/Z superscripts indicate the orientation of CH₂OO relative to the C=O substituents, as described in the text. Structures of the entrance channel complex (vdW), transition state (TS), and secondary ozonide product (SOZ) are shown for the 1,3 α^E pathway.

PyrA; and reaction can take place at either face of the PyrA. The carboxylic acid and acetyl C=O groups are labelled α and β , respectively, and reaction at each site leads to distinct SOZs that are structural

isomers. Reaction at the β C=O is more exothermic than reaction at the α C=O by ~ 6 kcal mol $^{-1}$ for the Tc conformer and ~ 10 kcal mol $^{-1}$ for the Tt conformer. The CH₂OO orientation is specified based on whether the central O atom is oriented towards (*Z*) or away from (*E*) the higher priority carbonyl substituent group. For reaction at the α site, the acetyl group is prioritized over the alcohol; for reaction at the β site, the carboxylic acid group is prioritized over the methyl.⁵³ The *E/Z* pathways lead to conformers of the respective α SOZ and β SOZ with differently puckered rings, which are separated by small energy gaps of ~ 1 kcal mol $^{-1}$. Finally, reaction can also occur at the reverse face of PyrA, leading to the production of enantiomers of the various SOZs with identical energies.

Entrance channel vdW complexes and TSs have been characterized for four of the eight 1,3-dipolar cycloaddition pathways available for each PyrA conformer. The enantiomeric reverse face reactions are energetically identical by symmetry. Both vdW complexes and TSs are characterized by near-parallel heavy atom planes in both reactants, consistent with the interactions between the π systems that participate in the cycloaddition. The vdW complexes are lower in energy than the reactants by ~ 7 – 12 kcal mol $^{-1}$, with a typical separation of ~ 2.6 Å (the distance between the atoms that will form the new C–O bonds in the SOZ, where $r_{\text{CO}} \approx 1.4$ Å). For the Tc conformer, the $\alpha^{E/Z}$ vdW complexes are lower in energy than the $\beta^{E/Z}$ vdW complexes, while the reverse is true for Tt. From the vdW complexes, the cycloaddition TSs are reached by closing the intermolecular separation to ~ 2.1 Å, which results in small, submerged barriers of 0.5–4.5 kcal mol $^{-1}$. For both Tc and Tt, the TS barrier energies increase in the order $\beta^Z < \beta^E < \alpha^Z < \alpha^E$. The zero-point corrected energy profiles ($\Delta E + \text{ZPE}$ at 0 K) are shown for the 1,3-dipolar cycloaddition reactions of the Tc conformer in Figure 6. Representative structures of the vdW complex, TS, and product SOZ are shown for the β^E pathway; the others are in Supporting Information. Figure 7 shows the analogous energy profiles for the Tt conformer, with representative structures for the α^E pathway. The corresponding free energy profiles (ΔG at 298 K) are presented in Figure S4 and Figure S5 in Supporting Information. The calculated energies and free energies are also compiled in Table 3.

Table 3: Relative energies, including zero-point contributions($\Delta E + \text{ZPE}$) at 0 K and free energies (ΔG) at 298 K calculated at the CBS-QB3 level for 1,3-dipolar cycloaddition pathways of the $\text{CH}_2\text{OO} + \text{PyrA}$ reaction.

Conformer	Pathway	$\Delta E + \text{ZPE} [\Delta G] / \text{kcal mol}^{-1}$		
		vdW	TS	SOZ
Tc	$1,3\alpha^E$	-10.4 [+0.5]	-5.9 [+6.6]	-41.0 [-28.1]
	$1,3\alpha^Z$	-11.1 [-0.1]	-9.2 [+3.0]	-41.9 [-29.0]
	$1,3\beta^E$	-8.8 [+2.3]	-8.2 [+4.3]	-48.1 [-35.0]
	$1,3\beta^Z$	-8.2 [+2.6]	-7.2 [+5.2]	-47.0 [-33.8]
Tt	$1,3\alpha^E$	-7.5 [+3.2]	-3.0 [+9.6]	-40.3 [-27.3]
	$1,3\alpha^Z$	-7.9 [+2.7]	-4.6 [+8.1]	-39.2 [-26.1]
	$1,3\beta^E$	-11.2 [+0.4]	-10.6 [+2.3]	-50.8 [-37.6]
	$1,3\beta^Z$	-11.2 [+0.4]	-10.6 [+2.4]	-51.0 [-37.8]

The 1,2-addition and 1,4-addition pathways lead to HPMP products and involve, in most instances, H-bonded entrance channel vdW complexes. For the minor Tt conformer, the OH group is freely available to participate in H-bonding and/or reaction, while for the major Tc conformer, formation of an external H-bond with CH_2OO inevitably disrupts the internal H-bond and can facilitate Tc/Tt isomerization. The CBS-QB3 energy profiles ($\Delta E + \text{ZPE}$ at 0 K) are shown in Figure 8 with the corresponding free energy profiles (ΔG at 298 K) shown in Figure S6 in Supporting Information. Energy and free energy values for the reaction pathways are compiled in Table 4.

Table 4: Relative energies, including zero-point contributions($\Delta E + \text{ZPE}$) at 0 K and free energies (ΔG) at 298 K calculated at the CBS-QB3 level for the 1,2-addition/insertion and 1,4-addition pathways of the $\text{CH}_2\text{OO} + \text{PyrA}$ reaction.

$\Delta E + \text{ZPE} [\Delta G] / \text{kcal mol}^{-1}$

Conformer	Pathway	vdW	TS	HPMP
Tc	1,4	-9.1 [+1.1]	-0.7 [+9.5]	-40.8 [-29.5]
Tt	1,2	-8.9 [+0.2]	-3.5 [+8.3]	-44.6 [-32.8]
	1,4		-8.9 [+0.2]	-43.3 [-31.6]

We have identified three distinct H-bonded vdW complexes (shown in Figure 8 and in Supporting Information) between CH₂OO and Tc PyrA, which have energies 7–9 kcal mol⁻¹ below the separated reactants and differ primarily in the relative orientation of the CH₂OO. The Tc-*trans* (abbreviated to Tc-t) complex features both constituents in a coplanar geometry with a *trans* arrangement of the heavy atoms adjacent to the (approximately collinear) O–H---O axis. Rotation about this same axis to give a dihedral angle of ~70° between the heavy atom planes of PyrA and CH₂OO leads to the lowest energy Tc-*perp* (Tc-p) complex via a small energy barrier (TS_{t/p}). Subsequent rotation about the internal inertial *a*-axis of the CH₂OO constituent converts Tc-p into the higher energy Tc-*perp'* (Tc-p') complex via TS_{p/p'}. The coplanar Tc-*cis* (Tc-c) geometry is a saddle point, which converts between equivalent, mirrored Tc-p arrangements. Energy barriers for interconversion between the complexes with retention of the Tc arrangement in PyrA are < 1 kcal mol⁻¹ above the higher energy complex. In contrast, the only H-bonded vdW complex identified for the Tt conformer has a near coplanar Tt-*trans* (Tt-t) arrangement (defined as before and shown in Figure 8) and a binding energy that is similar to the Tc-t complex. The Tt-t complex can be formed from the Tc-p' complex via TS_{Tc/Tt} in which the OH group of PyrA rotates out of the heavy atom plane, analogous to the interconversion TS located for an isolated PyrA molecule. The presence of the H-bond with the terminal O atom of CH₂OO lowers the energy barrier for Tc/Tt interconversion from 12.3 kcal mol⁻¹ for isolated PyrA to only 5.0 kcal mol⁻¹ for the PyrA-CH₂OO complex. Complexes involving PyrA and OH radical have also been shown to lower the barrier to Tc/Tt interconversion.⁴¹

No stable complexes were identified for Tt PyrA in which the CH₂OO was in a *perp* or *cis* orientation; all geometry optimizations ultimately converged on *cis*-HPMP, the primary product of the 1,4-addition reaction, which can subsequently isomerize over a negligible energy barrier (0.2 kcal mol⁻¹) to form the slightly more stable *trans*-HPMP conformer. The existence of a stable Tt-t species implies the presence of a small barrier to reaction from that vdW minimum. The zero-point corrected

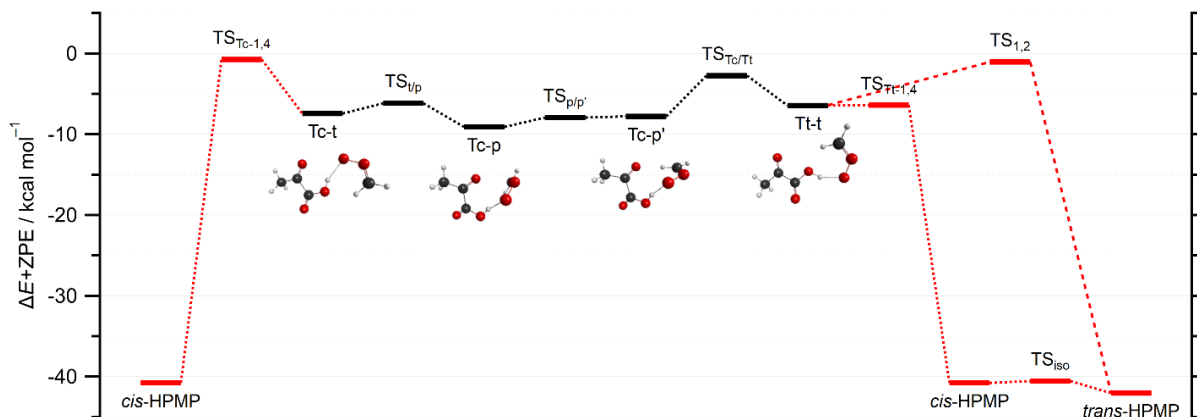


Figure 8: Calculated zero-point corrected energy profiles at 0 K for the 1,2-addition/insertion and 1,4-addition reactions of CH₂OO with the Tc and Tt conformers of PyrA, calculated at the CBS-QB3 level. Reactions to form HPMP products are shown in red, H-bonded entrance channel complexes in black. Dotted lines connect stationary points for isomerization or isomerization/reaction paths, dashed lines connect stationary points for conventional reaction paths, as discussed in the text.

energy of TS_{Tt-1,4} is found to be nearly identical to that of the Tt-t complex, confirming that the 1,4-addition reaction is effectively barrierless, even if the Tt-t region of the PES is sampled. The geometry of TS_{Tt-1,4} (shown in Supporting Information) can be best described as having a Tt-p orientation –the heavy atom planes are no longer near-coplanar, but have a dihedral angle of ~75°, as in the Tc-p vdW complex, while the OH bond length of 1.00 Å remains almost unchanged from its value in the Tt-t

vdW complex. That is, $\text{TS}_{\text{Tt-1,4}}$ is a reactant-like TS that is effectively associated with an isomerization that should lead to another vdW complex conformer, but one that is unstable and collapses directly to the *cis*-HPMP product. The TS for the 1,2-addition/insertion pathway ($\text{TS}_{1,2}$ shown in Supporting Information), which leads to the more stable *trans*-HPMP product by retaining the arrangement of the C=O groups, is also reached from the entrance channel Tt-t vdW complex. $\text{TS}_{1,2}$ involves a more significant re-orientation of the CH_2OO constituent, a slight rotation of the OH out of the PyrA heavy atom plane, and is a much more product-like TS than $\text{TS}_{\text{Tt-1,4}}$. Relative to the Tt-t complex, the O–H distance has extended to 1.56 Å from 1.00 Å while the H---O distance has decreased from 1.71 Å to 1.01 Å.

Finally, an isomerization/reaction TS has been identified for the 1,4-addition pathway that leads to *cis*-HPMP from the Tc-t complex, which is labelled $\text{TS}_{\text{Tc-1,4}}$. As with the analogous $\text{TS}_{\text{Tt-1,4}}$ stationary point, $\text{TS}_{\text{Tc-1,4}}$ describes primarily an isomerization between Tc and Tt that is mediated by the presence of the CH_2OO . The geometrical changes relative to the Tc-t complex primarily involve out-of-plane rotation of the OH bond to give a Tp arrangement, with simultaneous re-orientation of the CH_2OO to allow direct formation of *cis*-HPMP. $\text{TS}_{\text{Tc-1,4}}$ is also highly reactant-like, with the OH bond length of 1.00 Å remaining almost identical to that of the Tc-t vdW complex. The higher energy of +6.7 kcal mol⁻¹ relative to Tc-t is consistent with the corresponding barrier for interconversion between Tc-p' and Tt-t (5.0 kcal mol⁻¹), and significantly lower than the equivalent barrier for isolated PyrA.

Discussion

The room temperature rate constant obtained in this work for the $\text{CH}_2\text{OO} + \text{PyrA}$ reaction of $k_{\text{PyrA}} = (19.5 \pm 1.2) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ agrees well with the value of $(20 \pm 2) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ reported previously by Chhantyal-Pun et al.⁹ Typically, the room temperature bimolecular rate constants for the reactions of CH_2OO (and larger CIs) with a range of carboxylic acids are significantly larger, approaching or

exceeding the gas-kinetic limit.^{8,9,11,12} In the few cases where the effect of temperature has been explored, the rate constants show a weak negative dependence.^{7,11} The magnitude and temperature-dependence of the rate constants for CI + RCOOH reactions result from the barrierless 1,4-addition mechanism, for which the kinetics are largely controlled by long-range attractive interactions. The SAR for CI + RCOOH reactions, developed by Chhantyal-Pun et al.⁹ using a dipole-capture model, allows rate constants to be estimated using only the reduced mass of the collision pair and their dipole moments, calculated at the B3LYP/aug-cc-pVTZ level. The SAR predicts a room temperature rate constant for the CH₂OO + PyrA reaction of $k_{\text{PyrA}} = 3.8 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, almost 20 times larger than the observed value. As will be discussed further below, this ratio is broadly consistent with the fractional population of the Tt conformer at room temperature. Conformer-dependent reactivity of PyrA has been discussed previously in the context of reaction with the OH radical,⁴¹ although the H-atom abstraction mechanism in that reaction is different.

The value of k_{PyrA} at room temperature is much closer to what would be expected for 1,3-dipolar cycloaddition reactions between CH₂OO and α -dicarbonyls such as biacetyl (BiAc) or acetylpropionyl (AcPr), for which values of $k \approx 10 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ have been measured.^{25,26} Recently, we have proposed SARs in which the reactivity trend for CI + R₁R₂CO cycloaddition reactions can be explained by the electron-donating or electron-withdrawing character of the R₁, R₂ substituents.^{25-28,54} The effect can be rationalized by considering the energy gap ΔE_s between the frontier molecular orbitals that participate in the cycloaddition,²⁹⁻³¹ specifically the unoccupied π^* orbital of the carbonyl and the n(p_C-p_O) orbital of the CI. Substituents that are electron-withdrawing lower the energy of the π^* orbital and decrease ΔE_s , resulting in greater reactivity.²⁷ Electron-donating substituents have the opposite effect of raising the π^* orbital energy and are deactivating.

Alternatively, Hammett substituent constants can be used to estimate the relative reactivity for 1,3-dipolar cycloaddition at the α (acid) and β (acetyl) carbonyls. Previously, we have shown that the

para position Hammett constants (σ_p) correlate with measured rate constants of CH₂OO for a range of carbonyl species.^{25,54} Consistent with the FMO treatment above, electron withdrawing groups (relative to an H-atom substituent; $\sigma_p = 0$) characterized by $\sigma_p > 0$ are activating and electron donating substituents characterized by $\sigma_p < 0$ are deactivating. However, a limitation of this approach is that it cannot distinguish between the Tt and Tc conformers as both species will have identical substituent constants.

For reaction at the α C=O, the substituents are OH and CH₃CO, which have σ_p values of -0.37 and +0.50, respectively.⁵⁵ Similarly, the substituents on the β C=O are CH₃ and COOH, which have $\sigma_p = -0.17$ and +0.45, respectively.⁵⁵ Both carbonyls have one activating ($\sigma_p > 0$) and one deactivating substituent ($\sigma_p < 0$), although the sum $\Sigma\sigma_p > 0$ for reaction at both carbonyl sites, indicating carbonyl groups that are activated relative to formaldehyde ($\Sigma\sigma_p = 0$). The weighted average of previous measurements of the rate constant for the CH₂OO + HCHO reaction is $k_{\text{HCHO}} = 3.9 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$,^{28,56} which is around five times smaller than k_{PyrA} , qualitatively consistent with the Hammett analysis approach. Based on a previously determined SAR between $\ln k$ and $\Sigma\sigma_p$ for a range of CH₂OO + R₁R₂CO reactions,⁵⁴ the rate constants for reaction at the α and β carbonyls are predicted to be similar, with values of 3.4×10^{-12} and $5.6 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$, respectively. The predicted overall rate constant of $9 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ is just under half the room temperature value obtained experimentally. Table 5 summarizes the Hammett σ_p values and predicted rate constants.

Table 5: Hammett substituent constants and predicted rate constants for 1,3-dipolar cycloaddition between CH₂OO and PyrA at α and β C=O sites. The predicted rate constant is given by $\ln k = -(26.8 \pm 0.4) + (3.3 \pm 0.5)\Sigma\sigma_p$.⁵⁴

Reaction site	R ₁ , R ₂	$\sigma_{p,R_1}, \sigma_{p,R_2}, \Sigma\sigma_p$	$k / 10^{-12} \text{ cm}^3 \text{ s}^{-1}$
α	OH, CH ₃ CO	-0.37, +0.50, +0.13	3.4 $\pm$ 1.5
β	CH ₃ , COOH	-0.17, +0.45, +0.28	5.6 $\pm$ 2.5

The FMO SAR allows a more quantitative and species-specific prediction of the relative reactivity at both C=O sites and for both conformers. Empirically, we have found a negative linear correlation between $\ln k$ and the orbital energy gap ΔE_s , as defined above, for a range of $\text{CH}_2\text{OO} + \text{R}_1\text{R}_2\text{CO}$ reactions.^{25–28,54} Orbital energy gaps for the $\text{CH}_2\text{OO} + \text{PyrA}$ system, calculated at the B3LYP/aug-cc-pVTZ level are compiled in Table 6, along with the predicted rate constants based on the linear correlation reported in Enders et al.²⁸ Based on the FMO SAR, cycloaddition at the β C=O site dominates for both the Tc and Tt conformers, with predicted rate constants of 19×10^{-12} and $11 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$, respectively. The value for the major Tc conformer is in excellent agreement with the experimental value. In contrast, the α C=O site is predicted to be relatively unreactive for both conformers, with $<0.04 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$. This prediction is at odds with the Hammett analysis as well as the CBS-QB3 results (discussed further below) that suggest reaction at the α C=O site should be important.

Table 6: Frontier molecular orbital energy gap evaluated at B3LYP/aug-cc-pVDZ level and predicted bimolecular rate constants for reactions of CH_2OO with Tc and Tt conformers of PyrA. The predicted rate constant is given by $\ln k = -(17.5 \pm 0.2) - (1.66 \pm 0.03)\Delta E_s$.²⁸

Conformer	Reaction site	$\Delta E_s / \text{eV}$	$k / 10^{-12} \text{ cm}^3 \text{ s}^{-1}$
Tc	α	8.07	0.037±0.009
	β	4.31	19.0±3.5
Tt	α	8.18	0.030±0.008
	β	4.61	11.7±2.2

The relative energies of the various reaction pathways for both conformers of PyrA were also evaluated at the CBS-QB3 level of theory. For the Tc conformer, these calculations show the 1,3-dipolar cycloaddition at the α site to have the lowest energy TS (see Figure 6 and Table 3) indicating this pathway is likely the major reaction channel. The impact of the orientation of CH₂OO approach (*E/Z*) depends on both PyrA conformer and reaction site. The largest effect is found for reaction at the α C=O site of Tc PyrA, where the α^Z TS is > 3 kcal mol⁻¹ lower than the α^E TS. Reaction at the β C=O site is less affected by the *E/Z* orientation, with TS energy differences < 1 kcal mol⁻¹ for both the Tc and Tt conformers. By comparison, calculations by Long et al. characterizing the cycloaddition of CH₂OO at the carbonyl group of formic acid found the TS energy to be -0.5 kcal mol⁻¹ at the same level of theory used here.⁵⁷ The complexes and transition states are significantly lower in energy for both Tc and Tt conformers of PyrA, which is likely due to additional stabilization from conjugation with the β carbonyl group and the intramolecular hydrogen bond.

The TS energies for 1,3-dipolar cycloaddition at the β C=O of the Tt conformer are significantly lower than at the α C=O site (see Figure 7 and Table 3), reversing the order observed for the Tc conformer. Reaction of the Tt conformer is also less affected by the *E/Z* orientation of CH₂OO, where the TS energy difference is only ~1.5 kcal mol⁻¹ for reaction at the α C=O site. This shift highlights the influence of the intramolecular hydrogen bond on the relative reactivity of the carbonyl groups of the Tc and Tt conformers. Furthermore, the availability of the OH hydrogen in the Tt conformer opens up the 1,4-addition channel where simultaneous hydrogen abstraction by the terminal O atom of CH₂OO and C–O bond formation between the CI carbon and the carboxylic acid oxygen results in the formation of *cis*-HPMP. Previous work on formic acid has shown the 1,4-addition reaction to be direct and barrierless.^{57,58} With the exception of the isomerization/reaction mechanisms described earlier, no significant entrance channel complexes or TSs could be located for the 1,4-addition reaction of CH₂OO with Tt PyrA at the CBS-QB3 level which uses the B3LYP/6-311G(2d,d,p) method for geometry optimizations, or using other DFT methods with several different basis sets. We note that

a very small TS barrier of only ~ 0.1 kcal mol⁻¹ relative to the entrance channel vdW complex has been identified for the CH₂OO + HNO₃ reaction which proceeds via the same mechanism to form hydroperoxymethylnitrate (HPMN).^{59,60} The TS energy for the nitric acid reaction was obtained from single point CCSD(T)/aug-cc-pVTZ calculations at geometries optimized using CCSD/cc-pVDZ or B3LYP/aug-cc-pVTZ calculations. The presence or absence of a barrier in 1,4-addition reactions may depend on the computational method used.

The 1,2-addition/insertion pathway leading to *trans*-HPMP is only possible for the Tt conformer, although it is unlikely to be competitive. Previous calculations for the reaction of CH₂OO with the OH group of formic acid reported that the relative energy of the TS for the analogous pathway is -1.3 kcal mol⁻¹ (CBS-QB3; ΔE at 298 K).⁵⁷ This value is > 2 kcal mol⁻¹ higher than the energy of TS_{1,2} found here, where $\Delta E + \text{ZPE}$ at 0 K = -3.5 kcal mol⁻¹ (see Table 3). Hydroxyketones have an analogous 1,2 addition/insertion pathway. Cornwell et al. found barrier heights of $+2.2$ and -0.5 kcal mol⁻¹ (CBS-QB3; $\Delta E + \text{ZPE}$ at 0 K) for 1,2-addition/insertion of CH₂OO with hydroxyacetone and hydroxybutanone, respectively.²⁷ Overall, the relative energies of the Tt conformer of PyrA suggest that its reactivity is primarily governed by the barrierless 1,4-addition, followed by 1,3-cycloaddition at the β C=O site. In contrast, 1,3-dipolar cycloaddition at the α C=O and 1,2-addition at the -OH group are expected to make a negligible contribution to the reactivity.

The bimolecular rate constants for the CH₂OO + PyrA reaction shown in Figure 5 and compiled in Table 2, clearly do not follow an Arrhenius T dependence. Overall, $k_{\text{PyrA}}(T)$ values vary only by $\sim 25\%$ across the 100 K experimental temperature range, reaching a maximum near 335 K. Also changing with temperature are the fractional populations of the Tc and Tt conformers, which the *ab initio* calculations show can react via different mechanisms. While the dominant Tc conformer is restricted to reacting with CH₂OO via the 1,3-dipolar cycloaddition mechanism, the minor Tt conformer, which becomes increasingly prevalent as T increases, can additionally react via the barrierless 1,4-addition

pathway. Between 275 K and 375 K, the fractional population of Tt-PyrA increases from 0.06 to 0.13, as shown in Figure S2 in Supporting Information. As noted above, the SAR developed by Chhantyal-Pun et al. for CI + RCOOH reactions predicts a room temperature rate constant of $3.8 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ for the 1,4-addition reaction $\text{CH}_2\text{OO} + \text{PyrA}$. If the reaction were exclusively due to the low population Tt conformer, the *apparent* bimolecular rate constant would be $29 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$, close to the value predicted by the 1,3-dipolar cycloaddition SAR for the dominant Tc conformer, and in line with the experimental results. We therefore expect that both conformers contribute similarly to the overall loss of CH_2OO at room temperature; the anticipated rate constant for the 1,3-dipolar cycloaddition reaction of dominant (95%) Tc conformer is ~ 20 times smaller than the expected rate constant for the 1,4-addition reaction of the minor (5%) Tt conformer.

To assess the relative contributions of Tt and Tc to the overall reactivity across the experimental temperature range we define the effective rate constant $k_{\text{PyrA}}^{\text{eff}}$ in terms of f_{Tc} and f_{Tt} , the fractional populations of Tc and Tt, and the total rate constants k_{Tc} and k_{Tt} , summed over the various reaction pathways for each conformer, as shown in Equation E5. Each term in Equation E5 is temperature dependent, as the conformer populations and rate constants will change as the thermal energy changes.

$$k_{\text{PyrA}}^{\text{eff}} = f_{\text{Tc}}k_{\text{Tc}} + f_{\text{Tt}}k_{\text{Tt}} \quad \text{E5}$$

For the Tc conformer, we consider only 1,3-dipolar cycloaddition, while the 1,4-addition dominates for the Tt conformer. Expressing the fractional populations of Tc and Tt in terms of the T-dependent equilibrium constant K leads to Equation E6.

$$k_{\text{PyrA}}^{\text{eff}} = \frac{k_{\text{Tc}} + Kk_{\text{Tt}}}{1 + K} \quad \text{E6}$$

To estimate $k(T)$ for the 1,3-dipolar cycloaddition reactions of CH_2OO with Tc and Tt conformers, we

use an Arrhenius expression based on the room temperature values predicted by the empirical FMO SAR (shown in Table 6) and an estimated $-E_a/R = 1200$ K, which is typical for this class of reaction and leads to a negative T dependence.^{26–28,50,51,56,61–65} Rate constants for 1,4-addition reactions between CH_2OO and carboxylic acid also show a weak negative T dependence,^{7,11} and $k(T)$ is estimated in the same way using $-E_a/R = 400$ K and the room temperature value from the Chhantyal-

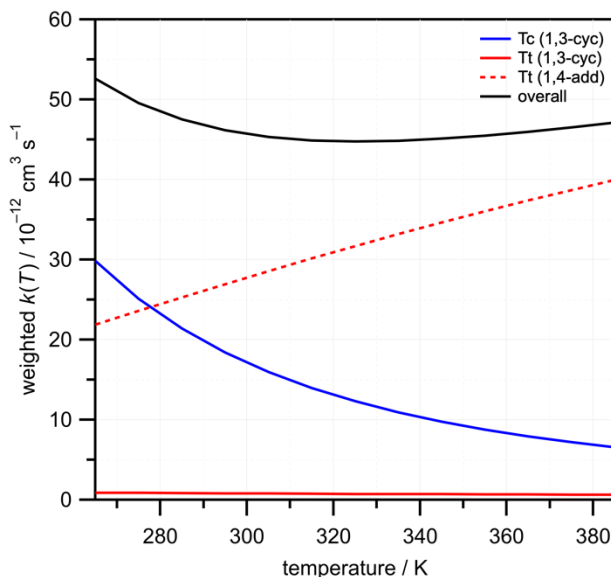


Figure 9: Temperature dependence of rate constants for reactions of CH_2OO with the Tc (blue) and Tt (red) conformers of PyrA, weighted by their fractional populations. Estimates of Arrhenius pre-exponential factors and activation energies are described in the text. The temperature dependence of the overall effective rate constant (black) is also shown.

Pun et al. SAR.⁹ Figure 9 shows the overall $k_{\text{PyrA}}^{\text{eff}}(T)$ value across the experimental temperature range as predicted by Equation E6. Also shown are the individual $k_{\text{Tc}}(T)$ and $k_{\text{Tt}}(T)$ components for the different reaction pathways, each weighted by the fractional populations of each conformer. The $\text{CH}_2\text{OO} + \text{Tt-PyrA}$ reaction is dominated by the 1,4-addition mechanism at all temperatures. The effective rate constant $k_{\text{PyrA}}^{\text{eff}}(T)$ shows a modest dependence on temperature, as observed

experimentally, but the magnitude is overestimated and the curvature is positive.

Conclusions

We have measured the temperature-dependent rate constant $k_{\text{PyrA}}(T)$ for the $\text{CH}_2\text{OO} + \text{PyrA}$ reaction across the temperature range 275–375 K using a laser flash photolysis, transient absorption spectroscopy technique. The value of $k_{\text{PyrA}}(T)$ was found to vary only modestly (<30%), reaching a maximum near 335 K, and decreasing at higher and lower temperatures. At room temperature, the measured rate constant of $19 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ is in good agreement with previous measurements. The value is an order of magnitude smaller than values typically observed for $\text{CH}_2\text{OO} + \text{RCOOH}$ 1,4-addition reactions ($k_{\text{RCOOH}} \geq 100 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$) but in line with the value expected for a 1,3-dipolar cycloaddition reaction $\text{CH}_2\text{OO} + \text{R}_1\text{R}_2\text{CO}$, where the substituents R_1 and R_2 have a net electron-withdrawing (activating) effect. CBS-QB3 calculations suggest that the major Tc conformer reacts primarily via the cycloaddition pathway at the acid C=O, while the minor Tt conformer reacts primarily via the barrierless addition pathway typical of RCOOH with a smaller contribution from the cycloaddition reaction at the acetyl C=O. The variation of the observed rate constant with temperature is likely due to the T -dependent populations of the Tc and Tt conformers and the relative significance of different reaction pathways, although the observed behavior cannot be described by only three reaction pathways. Additional measurements capable of detecting and distinguishing the SOZs and HPMP products are required to identify and quantify branching between competing reaction pathways. Further work modelling the temperature dependent behavior of the $\text{CH}_2\text{OO} + \text{PyrA}$ reaction system with software packages such as *MESMER* or *Multiwell* is of interest

Supporting Information

Compilation of rate constants for $\text{CI} + \text{RCOOH}$ reactions; conformer equilibrium calculations and fractional populations; reactant concentration stability; CBS-QB3 reaction free energy profiles and

stationary point Cartesian coordinates.

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