

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet ROO_35

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RCHOO + O₃ → RCHO + 2O₂	(1)
RCHOO + H₂O → products	(2)
RCHOO + CO → products	(3)
RCHOO + HCHO → products	(4)
RCHOO + C₂H₄ → products	(5)
RCHOO + NO → RCHO + NO₂	(6)
RCHOO + NO₂ → RCHO + NO₃	(7)
RCHOO + SO₂ → products	(8)
RCHOO + HCOOH → products	(9)
RCHOO + CH₃CHO → secondary ozonide	(10)
RCHOO → products	(11)
RRCOO → products	(12)

(R=H or CH₃)

Rate coefficient data

k/cm ³ molecule ⁻¹ s ⁻¹	Criegee intermediate	Temp /K	Reference	Technique/Comments
Relative Rate Coefficients				
k ₂ /k ₈ = (6.1 ± 0.3) × 10 ⁻⁵	CH ₃ CHOO	295	Calvert et al., 1978 ¹	(a)
k ₁ :k ₃ :k ₄ :k ₅ :k ₈ = 2.5 × 10 ⁻³ : 1.8 × 10 ⁻³ :2.5 × 10 ⁻¹ : 2.5 × 10 ⁻³ :1.0	CH ₂ OO	296	Su, Calvert and Shaw, 1980 ²	RR-FTIR (b)
k ₂ /k ₈ = (2.3 ± 1) × 10 ⁻⁴	CH ₂ OO	298	Suto, Manzanares and Lee, 1984 ³	(c)
k ₇ /k ₈ = (1.4 ± 0.4) × 10 ⁻²	CH ₂ OO	298	Manzanares, Suto and Lee, 1987 ⁴	(d)
k ₂ /k ₈ = (8.3 ± 3.6) × 10 ⁻⁴	CH ₂ OO	298	Becker, Bechara and Brockmann, 1993 ⁵	RR-FTIR/ TDLS (e)
k ₂ /k ₈ = (4.1 ± 2.2) × 10 ⁻⁴	(CH ₃) ₂ COO	298	Becker, Bechara and Brockmann, 1993 ⁵	RR-FTIR/ TDLS (f)
k ₂ /k ₉ = 7.1 × 10 ⁻⁵	CH ₂ OO	298	Neeb et al., 1997 ⁶	RR-FTIR/ HPLC (g)
Absolute Rate Coefficients				
k ₁₀ = 1.0 × 10 ⁻¹²	CH ₃ CHOO	~298	Fenske et al., 2000 ⁷	FT-FTIR (h)
k ₁₁ = 76 s ⁻¹	CH ₃ CHOO	~298	Fenske et al., 2000 ⁷	(i)
k ₁₂ = 6.4 s ⁻¹ (measured at ca. 130 mbar)	(CH ₃) ₂ COO	298	Kroll et al., 2001 ⁸	LIF (j)
k ₂ < 4.0 × 10 ⁻¹⁵	CH ₂ OO	298	Weltz et al., 2012	PLP-PIMS(k)
k ₆ < 6.0 × 10 ⁻¹⁴	CH ₂ OO	298		
k ₇ = 7.0 ^(+3,-2) × 10 ⁻¹²	CH ₂ OO	298		
k ₈ = (3.9±0.7) × 10 ⁻¹¹	CH ₂ OO	298		

Comments

- (a) Derived from a reanalysis of the data of Cox and Penkett⁸ from a study of the aerosol formation from SO₂ in the presence of O₃-O₂-*cis*-2-C₄H₈ mixtures at atmospheric pressure. In this system the Criegee intermediate involved is believed to be CH₃CHOO.
- (b) FTIR study of the C₂H₄-O₃ reaction in the presence of O₂-N₂ mixtures at a total pressure of 920 mbar and with added CO, HCHO, or SO₂. Relative rate coefficients derived from a computer simulation of reactant consumption and product formation, based on a mechanism of 20 elementary reactions.
- (c) Flow system involving C₂H₄-O₃-SO₂-H₂O mixtures in which H₂SO₄ aerosol concentrations were monitored by scattered UV light. Relative rate coefficients obtained from the dependencies of the aerosol formation on the concentrations of O₃, SO₂, and H₂O.
- (d) Similar study to that of comment (c), with the inclusion of the effect of added NO₂ on the formation of the H₂SO₄ aerosol.
- (e) Study of the C₂H₄-O₃ reaction in the presence of 1 bar of synthetic air with and without added SO₂; H₂O₂ yields were measured by tunable diode laser absorption spectroscopy or by FTIR spectroscopy.
- (f) Same study as for comment (e) with (CH₃)₂C=C(CH₃)₂ as the reactant.
- (g) Reaction carried out in a 570 L spherical glass reactor. Hydroxymethyl hydroperoxide (HMHP) concentrations monitored by HPLC and formic acid concentration by FTIR. Formation of HCOOH from HMHP shown to be due, in part, to heterogeneous processes. k_2/k_9 was derived by fitting [HCOOH] and [HMHP] as a function of time to a reaction scheme and using values of $k(\text{O}_3 + \text{C}_2\text{H}_4) = 1.6 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, $k(\text{CH}_3\text{OO} + \text{H}_2\text{O}) = 1 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and assuming that 47% of the Criegee biradicals are stabilized.
- (h) Reaction studied in an atmospheric pressure flow-tube. An excess of acetaldehyde was added to the reaction mixture through a sliding injector such that all thermalised CH₃CHOO, post-injector, was converted to secondary ozonide (SOZ). SOZ was detected by FTIR. The temperature of the study was not reported.
- (i) Unimolecular decomposition rate coefficient obtained relative to the reaction with acetaldehyde from a numerical analysis of the flow-tube data.
- (j) OH observed by LIF in flow-tube experiments. The unimolecular rate coefficient was calculated by assuming that at 100 Torr the observed formation of HO, over timescales of 100's to 1000's of ms, is due to the thermal decomposition of stabilised dimethylcarbonyl oxide.
- (k) CH₂OO (formaldehyde oxide) was produced by the reaction of CH₂I + O₂. CH₂I was generated by 248-nm laser photolysis of diiodomethane, CH₂I₂, at 298 K and 4 torr, in a large excess of O₂. The reacting mixture was monitored by tunable synchrotron photoionization mass spectrometry, which allowed characterisation of the PIMS over the region 9.5 – 11.5 eV, and time-resolved direct detection of CH₂OO at $m/z = 46$. The first order decay in the presence of measured concentrations of reactant gas was used to determine the rate constants.
- (l) As note (k) but using 1,1 diiodoethane photolysis to produce CH₃CHOO (acetaldehyde oxide) which was monitored by PIMS.

Preferred Values

Parameter	Reaction	Value	T/K
k_2 /cm ³ molecule ⁻¹ s ⁻¹	CH ₂ OO + H ₂ O	< 4.0 x 10 ⁻¹⁵	298
k_6	CH ₂ OO + NO	< 6.0 x 10 ⁻¹⁴	
k_7	CH ₂ OO + NO ₂	7.0(⁺³ ₋₂) x 10 ⁻¹²	
k_8	CH ₂ OO + SO ₂	(3.9±0.7) x 10 ⁻¹¹	
<i>Reliability</i>			
$\Delta \log k$		± 0.3	298

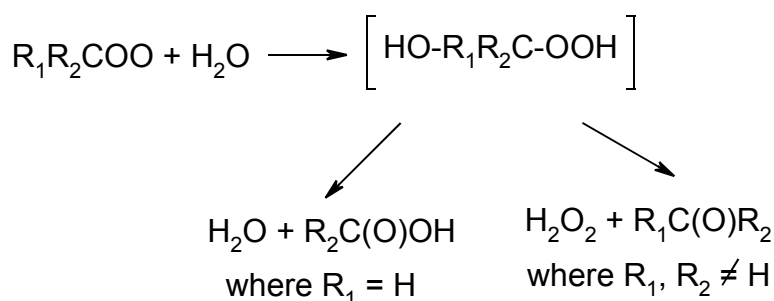
Comments on Preferred Values

Vibrationally excited Criegee intermediates or biradicals, [RCHOO][‡], are produced from the reactions of O₃ with alkenes.¹¹ These species decompose unimolecularly to give molecular or radical products or undergo collisional deactivation to yield thermally equilibrated Criegee intermediates, RCHOO. In our previous evaluation, IUPAC, 2003¹⁰ we considered the kinetic and other information relating to the bimolecular reactions that have been proposed for these thermally equilibrated Criegee intermediates. It was concluded that relative rate measurements for reactions of Criegee intermediates with H₂O, NO₂, SO₂, RCHO and RC(O)OH are the only experimental basis on which to assess the rates of these reactions. No recommendation was made for rate data and it was suggested that for most tropospheric conditions the only effective reaction of the biradicals is likely to be that with H₂O. Recent direct measurements of rate coefficients for CH₂OO reactions cited above change this situation.

The recent direct photoionization mass spectrometric detection of formaldehyde oxide (CH₂OO) as a product of the reaction of CH₂I with O₂, has enabled direct laboratory determinations of CH₂OO kinetics (Welz et al., 2012). The rate constants for CH₂OO reactions with SO₂ and NO₂ appear to be accurately determined and provide a basis for a recommendation. The reactions of CH₂OO proved unexpectedly rapid. The upper limit for reaction with water is above literature estimates of the rate constant (ref 12) and tends to confirm the established models. On the other hand, the reaction with NO is two orders of magnitude slower than literature estimates, based on estimates of the energetics of the proposed reaction pathway RCHOO + NO → RCHO + NO₂. (ref 2). These results imply a substantially greater role of carbonyl oxides in models of tropospheric sulfate and nitrate chemistry than previously assumed.

In deriving the relative rate coefficients it was necessary to assume that all the RCHOO Criegee intermediates have equal reactivity. Recent results reported from experimental work using the PLP-PIMS technique indicates that the high reactivity extends to e.g., CH₂OO and CH₃CHOO. Further experimental verification for higher RCOO species would allow the earlier relative rate studies to be put on an absolute basis.

There is little direct experimental evidence on the products of RCHOO reactions. Where the products are stated these have largely been suggested on the basis of analogy with related reactions. Work of Neeb *et al.*²⁴ shows that the reaction of the CH₂OO Criegee intermediate with H₂O leads initially to hydroxymethyl hydroperoxide (HOCH₂OOH). The HOCH₂OOH may then decompose to HCOOH and H₂O but the extent to which this occurred by heterogeneous processes in the system used by Neeb *et al.*²⁴ is uncertain. Hydroperoxides have been found in a number of other O₃-alkene studies²⁵⁻²⁷ and are suggested to arise in a similar way, by direct interaction of the Criegee intermediate with H₂O. In addition to the expected formation of carboxylic acids from the reactions of the biradicals with H₂O, recent studies of the reactions of O₃ with *trans*-2-butene,^{5,25,26} isoprene^{24,25} and monoterpenes^{25,26,27} have reported varying amounts of H₂O₂ product. Since the yields of H₂O₂ were considerably enhanced by the presence of H₂O, it was proposed that H₂O₂ was formed in a direct reaction involving Criegee intermediates. Thus these observations may be rationalised in terms of the following reactions:



For the reaction of CH₂OO with H₂O, H₂O₂ formation is a minor pathway.

Reaction of R₁R₂COO Criegee intermediates with aldehydes leads to the formation of the corresponding ozonides,^{7,30,31,32} i.e., R₁R₂COO + R₃CHO → R₁R₂COOCH(O)R₃. However, the formation of ethene ozonide has not been observed in the reaction of CH₂OO with HCHO or in the O₃-ethene reaction.^{2,13,15,31} The proposal that the reaction of the CH₂OO Criegee intermediate with HCHO leads to HOCH₂OCHO^{2,13,15,31,33} has now been shown to be incorrect. The spectrum observed in the CH₂OO-HCHO reaction and assigned to HOCH₂OCHO is now known to belong to HOOCH₂OCHO,^{34,35} which is formed by the reaction of the CH₂OO Criegee intermediate with HCOOH.

Tobias and Ziemann³⁶ have determined rate coefficients for the reactions of the CH₃(CH₂)₁₁CHOO Criegee intermediate with acids, aldehydes and alcohols relative to the reaction with H₂O. The following rate coefficient ratios were obtained (H₂O = 1): methanol, 22; 2-propanol, 50; formaldehyde, 2700; and heptanoic acid, 17000.

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