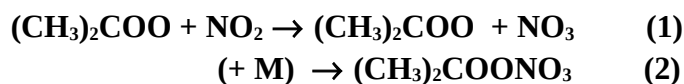


## IUPAC Subcommittee on Gas Kinetic Data Evaluation – Data Sheet CGI\_20

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The citation for the preferred values in this data sheet is: IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, <http://iupac.pole-ether.fr>.

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### Rate coefficient data ( $k = k_1 + k_2$ )

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp /K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(2.3 \pm 2.5) \times 10^{-12}$	293	Chhantyal-Pun, et al., 2017	PLP-PIMS(a)
$(2.1 \pm 0.3) \times 10^{-12}$ (for $(\text{CD}_3)_2\text{COO}$ )	293		

### Comments

(a)  $(\text{CH}_3)_2\text{COO}$  (acetone oxide) was produced by the reaction of  $(\text{CH}_3)_2\text{Cl} + \text{O}_2$ .  $\text{CH}_3\text{CHI}$  was generated by 248-nm laser photolysis of 2,2-diiodopropane,  $(\text{CH}_3)_2\text{Cl}_2$ , at 293 K and 4 Torr, in a large excess of  $\text{O}_2$ . The reacting mixture was monitored by  $\text{tT}$  tunable synchrotron PIMS at  $m/z = 74$  which was used to measure time-dependence of  $[(\text{CH}_3)_2\text{COO}]$  in the gas phase. The kinetics of decay was used to determine the rate constants. ~~A However large background signal a persistent background~~ at  $m/z = 74$  prevented reliable measurement of the rate coefficient. ~~for the reaction of  $(\text{CH}_3)_2\text{COO}$  with  $\text{NO}_2$  from the slope of the first order decay plots of  $(\text{CH}_3)_2\text{COO}$  in the presence of excess known concentrations of  $\text{NO}_2$ . The derived  $k$  values had a 95% uncertainty bound larger than the value of the second-order rate coefficient itself. The~~ The cited result,  $(2.3 \pm 2.5) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ , should therefore be interpreted as an upper limit value of the rate coefficient of  $k((\text{CH}_3)_2\text{COO} + \text{NO}_2) \leq 5 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ . However, in the case of  $(\text{CD}_3)_2\text{COO}$  the background had a negligible effect, allowing accurate measurement of its rate coefficient for reaction with  $\text{NO}_2$ .

### Preferred Values

Parameter	Value	T/K
$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$2.1 \times 10^{-12}$	293
<i>Reliability</i>		
$\Delta \log k$	0.3	293

Comments on Preferred Values

The reported measurements on the overall reaction of  $(\text{CH}_3)_2\text{COO}$  with  $\text{NO}_2$  suffer from interference from a background but the rate coefficient for the deuterated form,  $(\text{CD}_3)_2\text{COO}$ , is similar to that for both *syn*- and *anti*- $\text{CH}_3\text{CHOO}$  reacting with  $\text{NO}_2$ :  $k(\text{CH}_3\text{CHOO} + \text{NO}_2) = (2 \pm 1) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$  reported by Taatjes et al.(2013), which is the basis of the IUPAC recommendation for overall  $k(\text{CH}_3\text{CHOO} + \text{NO}_2) = (2 \pm 1) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , for both conformers (data sheet: CGI\_17). A rate coefficient of similar magnitude for the reaction of  $\text{CH}_2\text{COO}$  with  $\text{NO}_2$  was obtained by Stone et al.(2014), who measured a  $k$  value of  $(1.5 \pm 0.5) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ , independent of pressure in the range 25 – 300 Torr. (data sheet: CGI\_17). The earlier value of reported by Weltz et al. (2012), who also used PIMS to measure  $k(\text{CH}_2\text{COO} + \text{NO}_2)$  was higher but had a larger experimental uncertainty. The overall body of data appears to show that all carbonyl oxides react with  $\text{NO}_2$  with similar rates

The products of the reactions of Criegee intermediates with  $\text{NO}_2$  are usually presumed to be  $\text{NO}_3$  and a carbonyl compound (in this case acetone). Attempts to measure  $\text{NO}_3$  products from the reaction of  $(\text{CD}_3)_2\text{COO}$  with  $\text{NO}_2$  failed, as have similar attempts for other carbonyl oxide reactions with  $\text{NO}_2$ . However there are several possible association channels leading to an addition complex, and eventual nitrate production observed in ozonolysis experiments may result from further reaction of this complex.

### References

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