

Kinetics and Mechanisms of the Gas-Phase Reactions of the NO₃ Radical with Organic Compounds

Roger Atkinson

Statewide Air Pollution Research Center, University of California, Riverside, CA 92521

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A substantial data base concerning the rate constants for the gas-phase reactions of the nitrate (NO₃) radical with organic compounds is now available, with rate constants having been determined using both absolute and relative rate methods. To date, the majority of these kinetic data have been obtained at room temperature using relative rate techniques utilizing both the reactions of the NO₃ radical with other organic compounds and the equilibrium constant for the NO₃ + NO₂ ⇌ N₂O₅ reactions as the reference reaction. In this article, the literature kinetic and mechanistic data for the gas-phase reactions of the NO₃ radical with organic compounds (through late 1990) have been tabulated, reviewed and evaluated. While this available data base exhibits generally good agreement and self-consistency, further absolute rate data are needed, preferably as a function of temperature. Most importantly, mechanistic and product data for the reactions of the NO₃ radical with organic compounds need to be obtained.

Key words: atmospheric chemistry; nitrate radical; organic compounds; reaction kinetics; reaction mechanisms.

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TABLE 8. Rate constants k and temperature-dependent parameters, $k = Ae^{-B/T}$, for the gas-phase reactions of the NO_3 radical with oxygen-containing organic compounds

Oxygenate	$10^{12} \times A$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	B (K)	k ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	at T (K)	Technique	Reference
Formaldehyde			$(5.89 \pm 0.48) \times 10^{-16}$	298 ± 1	RR [relative to $K_5(\text{NO}_3 + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_5)$ $= 3.41 \times 10^{-11} \text{ s}^a$	Atkinson <i>et al.</i> ³⁹
			5.6×10^{-16}	298 ± 2	S-A	Cantrell <i>et al.</i> ⁴⁰
			$(8.7 \pm 0.6) \times 10^{-16}$	298 ± 2	RR [relative to $K_5(\text{NO}_3 + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_5)$ $= 3.41 \times 10^{-11} \text{ s}^a$	Cantrell <i>et al.</i> ⁴⁰
			$(7.9 \pm 1.7) \times 10^{-16b}$	295 ± 2	RR [relative to $K_5(\text{NO}_3 + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_5)$ $= 5.00 \times 10^{-11} \text{ s}^a$	Hjorth <i>et al.</i> ⁶⁰
Acetaldehyde			$(2.54 \pm 0.64) \times 10^{-15}$	300	RR [relative to $K_5(\text{NO}_3 + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_5)$ $= 2.65 \times 10^{-11} \text{ s}^a$	Morris and Niki ⁵⁸
			$(2.44 \pm 0.52) \times 10^{-15}$	298 ± 1	RR [relative to $K_5(\text{NO}_3 + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_5)$ $= 3.41 \times 10^{-11} \text{ s}^a$	Atkinson <i>et al.</i> ³⁹
			$(3.15 \pm 0.60) \times 10^{-15}$	299 ± 1	RR [relative to $K_5(\text{NO}_3 + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_5)$ $= 3.00 \times 10^{-11} \text{ s}^a$	Cantrell <i>et al.</i> ⁴¹
			$(1.26 \pm 0.16) \times 10^{-15}$	264	F-LIF	Dlugokencky and Howard ⁹²
			$(2.74 \pm 0.33) \times 10^{-15}$	298		
			$(5.27 \pm 0.63) \times 10^{-15}$	332		
	1.44 ± 0.18	1860 ± 300	$(1.00 \pm 0.12) \times 10^{-14}$	374		
Acrolein			$(1.11 \pm 0.17) \times 10^{-15}$	298 ± 2	RR [relative to $k(\text{ethene})$ $= 2.05 \times 10^{-16} \text{ s}^a$	Atkinson <i>et al.</i> ⁹⁹
Crotonaldehyde			$(5.12 \pm 0.17) \times 10^{-15}$	298 ± 2	RR [relative to $k(\text{propene})$ $= 9.45 \times 10^{-15} \text{ s}^a$	Atkinson <i>et al.</i> ⁹⁹
Methanol			$\leq 6 \times 10^{-16}$	298 ± 2	FP-A	Wallington <i>et al.</i> ⁵⁷
			$(2.1 \pm 1.1) \times 10^{-16}$	294	DF-A	Canosa-Mas <i>et al.</i> ⁹⁰
			$(4.61 \pm 0.92) \times 10^{-16}$	323		
			$(6.8 \pm 2.7) \times 10^{-16}$	348		
			$(1.29 \pm 0.49) \times 10^{-15}$	373		
			$(3.11 \pm 0.84) \times 10^{-15}$	423		
			$(2.51 \pm 0.45) \times 10^{-15}$	428		
	$1.25^{+1.16}_{-0.61}$	2562 ± 241	$(6.32 \pm 1.35) \times 10^{-15}$	473		
Ethanol			$\leq 9 \times 10^{-16}$	298 ± 2	FP-A	Wallington <i>et al.</i> ⁵⁷
2-Propanol			$\leq 2.3 \times 10^{-15}$	298 ± 2	FP-A	Wallington <i>et al.</i> ⁵⁷
Dimethyl ether			$\leq 3 \times 10^{-15}$	298 ± 2	FP-A	Wallington <i>et al.</i> ⁵⁶
Tetrahydrofuran			$(4.90 \pm 0.28) \times 10^{-15}$	296 ± 2	RR [relative to $k(\text{trans-2-butene})$ $= 3.89 \times 10^{-13} \text{ s}^a$	Atkinson <i>et al.</i> ⁶⁷
Furan			$(1.44 \pm 0.02) \times 10^{-12}$	295 ± 1	RR [relative to $k(\text{trans-2-butene})$ $= 3.88 \times 10^{-13} \text{ s}^a$	Atkinson <i>et al.</i> ¹⁰²

TABLE 15. Rate constants k for the gas-phase reactions of the NO_3 radical with organic radicals

Organic Radical	$10^{12} \times k$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	at T (K)	Technique	Reference
$\text{CH}_3\text{O}\cdot$	2.3 ± 0.7	298	MP-A	Crowley <i>et al.</i> ¹³⁷

*et al.*¹⁴² obtained rate constants for the reaction of the NO_3 radical with $\text{CH}_3\text{CH}_2\text{CCl}=\text{CH}_2$ of $(1.73 \pm 0.31) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 299 K and $(2.2 \pm 0.6) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 ± 1 K, respectively (the latter reevaluated using the presently recommended value of K_5). A product study at room temperature and atmospheric pressure of air of the NO_3 radical reactions with $\text{CH}_3\text{CH}_2\text{CCl}=\text{CH}_2$, $\text{CH}_3\text{CHClCH}=\text{CH}_2$, $\text{CH}_3\text{CH}=\text{CHCH}_2\text{Cl}$ and $\text{CH}_3\text{CH}=\text{CClCH}_3$ was also carried out¹⁴².

3. Conclusions and Atmospheric Implications

A substantial data base concerning the rate constants for the gas-phase reactions of the NO_3 radical with organic compounds is now available, with rate constants having been determined using both absolute and relative rate methods. To date, the majority of these kinetic data have been obtained at room temperature using relative rate techniques utilizing both the reactions of the NO_3 radical with other organic compounds and the equilibrium constant K_5 for the $\text{NO}_3 + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_5$ reactions as the reference reaction. However, despite significant uncertainties in the equilibrium constant K_5 , the available data base exhibits generally good agreement and self-consistency. Clearly, further absolute rate data are needed, preferably as a function of temperature, before the NO_3 radical reactions can be viewed as being on as firm a base as are the corresponding OH radical reactions.⁸⁷ As for the reactions of the OH radical with organic compounds,^{85,87} there is a general lack of mechanistic and product data available for the reactions of the NO_3 radical with organic compounds.

From the ambient tropospheric NO_3 radical concentration data presented by Atkinson *et al.*,³² the geometric mean maximum NO_3 radical mixing ratio over continental areas is ~ 35 ppt (with a two standard deviations spread of an order of magnitude). Since for a given 12-hr nighttime period the average NO_3 radical concentration is less (sometimes significantly less^{13,14,16,17}) than the maximum, a 12-hr average nighttime NO_3 radical concentration in the tropospheric boundary layer over continental areas of $\sim 5 \times 10^8 \text{ molecule cm}^{-3}$ (20 ppt) appears reasonable. This 12-hr average nighttime NO_3 radical concentration is ~ 300 higher than the global tropospheric 12-hr average OH radical concentration of $1.5 \times 10^6 \text{ molecule cm}^{-3}$ derived from the atmospheric concentration and emissions data for 1,1,1-trichloroethane (CH_3CCl_3).¹³⁸ Thus, since reaction with the OH radical is a major, if not dominant, daytime chemical loss process for organic compounds in the troposphere,⁸⁹ the rate constants for the NO_3 and OH radical reactions must be in

the ratio $k_{\text{NO}_3}/k_{\text{OH}} > 10^{-3}$ for the NO_3 radical reaction with a given organic compound to be significant as a tropospheric loss process.

The NO_3 radical reactions are then potentially significant as a tropospheric loss process for the thiols and alkyl sulfides, the alkenes other than ethene and the 1-alkenes (hence including the monoterpenes and compounds such as acenaphthylene and acephenanthrylene), the hydroxy-substituted aromatic hydrocarbons, and certain other specific compounds such as styrene, acenaphthene, azulene and dimethyl selenide. In particular, since the daytime NO_3 radical concentrations may approach the daytime OH radical concentrations under certain NO_x concentration conditions (see Sec. 1), those organic compounds for which the NO_3 radical reaction rate constants are comparable to, or exceed, the OH radical reaction rate constants (for example, 2,3-dimethyl-2-butene, α -phellandrene, α -terpinene, terpinolene, pyrrole, azulene, dimethyl selenide, and *o*-, *m*- and *p*-cresol) may undergo significant reaction during daytime hours with the NO_3 radical in addition to reaction with the OH radical and/or O_3 .

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