

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet HO_x_VOC50

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This data sheet updated: 29th October 2007 (with no revisions of the preferred values).

HO + CH₃CN → products

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(2.1 \pm 0.3) \times 10^{-14}$	295 ± 2	Poulet et al., 1984	DF-EPR
$(8.6 \pm 1) \times 10^{-14}$	393		
$6.28 \times 10^{-13} \exp(-1030/T)$	250-363	Kurylo and Knable, 1984	FP-RF
$(1.94 \pm 0.37) \times 10^{-14}$	298		
$1.1 \times 10^{-12} \exp[-(1130 \pm 90)/T]$	256-388	Hynes and Wine, 1991	PLP-LIF (a)
$(2.48 \pm 0.38) \times 10^{-14}$	298		

Comments

- (a) No definitive evidence for a pressure dependence of the rate coefficient for the HO + CH₃CN reaction was observed over the pressure range 61-933 mbar (46-700 Torr) of N₂ diluent or 40-840 mbar (30-630 Torr) of He diluent. In the presence of O₂, the HO radical decays were non-exponential indicating regeneration of HO radicals.

Preferred Values

$k = 2.2 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (1 bar).

$k = 8.1 \times 10^{-13} \exp(-1080/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 250-390 K at 1 bar.

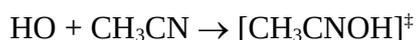
Reliability

$\Delta \log k = \pm 0.15$ at 298 K.

$\Delta(E/R) = \pm 200$ K.

Comments on Preferred Values

The preferred 298 K rate coefficient is a unweighted average of the rate coefficients of Poulet et al. (1984), Kurylo and Knable (1984) and Hynes and Wine (1991). The temperature dependence is the mean of those determined by Kurylo and Knable (1984) and Hynes and Wine (1991). Hynes and Wine (1991) observed no definitive evidence for a pressure dependence of the rate coefficient for the HO + CH₃CN reaction in N₂ or He diluent over the pressure ranges 61-933 mbar (46-700 Torr) or 40-840 mbar (30-630 Torr), respectively. In the presence of O₂, the HO radical decays were non-exponential (Hynes and Wine, 1991), indicating regeneration of HO radicals. Combined with analogous data for the reactions of HO radicals with CD₃CN [for which the rate coefficient was pressure dependent over the pressure range 53-923 mbar (40-692 Torr) of N₂ diluent] and of DO radicals with CH₃CN and CD₃CN (Hynes and Wine, 1991), it appears that the initial HO radical reaction proceeds by H-atom abstraction from the CH₃ group and HO radical addition to the CN group (Hynes and Wine, 1991).



Subsequent reactions of the addition adduct in the presence of O₂ then lead to the regeneration of HO radicals. In view of the possibility of a pressure dependence of the 298 K rate coefficient at low total pressures ≤0.1 bar (Hynes and Wine, 1991), the preferred values are only applicable to atmospheric pressure.

Tyndall et al. (2001) have observed the formation of formyl cyanide, HC(O)CN, from reaction of HO radicals with CH₃CN at atmospheric pressure of synthetic air using FTIR spectroscopy, and a formation yield of HC(O)CN of 40 ± 20% was obtained. The details of the reaction mechanism, including that for formation of HC(O)CN, are presently not known.

References

- Poulet, G., Laverdet, G., Jourdain, J. L. and Le Bras, G.: J. Phys. Chem., 88, 6259, 1984.
Kurylo, M. J. and Knable, G. L.: J. Phys. Chem., 88, 3305, 1984.
Hynes, A. J. and Wine, P. H.: J. Phys. Chem., 95, 1232, 1991.
Tyndall, G. S., Orlando, J. J., Wallington, T. J. and Hurley, M. D.: J. Phys. Chem. A, 105, 5380, 2001.

- Recommendation
- ▲ Poulet et al. (1984)
- ▼ Kurylo and Knable (1984)
- Hynes and Wine ((1991)

