

# IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation – Data Sheet oRCIOx41

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$$\Delta H^\circ = -107 \text{ kJ mol}^{-1}$$

## Low-pressure rate coefficients Rate coefficient data

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$(3.8 \pm 1.8) \times 10^{-29} [\text{O}_2]$	298	Moore and Carr, 1990	FP-MS (a)
$(5.0 \pm 1.0) \times 10^{-29} (T/298)^{-6.2} [\text{O}_2]$	248-324	Wu and Carr, 1991	FP-MS (b)

## Comments

- (a)  $\text{CF}_2\text{ClO}_2$  radicals generated by flash photolysis of  $\text{CF}_2\text{ClBr}$  in the presence of  $\text{O}_2$  and detected by MS. Measurements over the pressure range 1.3-13 mbar, extrapolated with  $F_c = 0.6$  and  $k_\infty = 5.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 298 K.
- (b) As comment (a).  $F_c = 0.78 \exp(-T/569)$ , i. e.,  $F_c(298) = 0.46$ , and  $k_\infty = 4.5 \times 10^{-12} (T/298)^{-2.5} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  used for extrapolation.

## Preferred Values

$$k_0 = 5.0 \times 10^{-29} (T/298)^{-6.2} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range 250-320 K.}$$

### Reliability

$$\Delta \log k_0 = \pm 0.3 \text{ at 298 K.}$$

$$\Delta n = \pm 2.$$

### Comments on Preferred Values

The pressure dependence in the investigated pressure range fits well to that observed at higher pressures for the reverse dissociation by Köppenkaströp and Zabel (1991) and the theoretical modellings by Destriau and Troe (1990) and by Caralp et al. (1988). Uncertainties of the used  $F_c = 0.46$  at 298 K do not much influence the values of the derived  $k_0$ . Therefore the values from Wu and Carr (1991) are our preferred values, assuming equal values of  $k_0$  for the bath gases  $\text{O}_2$  and  $\text{N}_2$ .

## High-pressure rate coefficients Rate coefficient data

$k_{\infty}/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/ Comments
<i>Absolute Rate Coefficients</i>			
$5.2 \times 10^{-12}$	298	Moore and Carr, 1990	(a)
$4.5 \times 10^{-12} (T/298)^{-2.5}$	248-324	Wu and Carr, 1991	(b)

### Comments

- (a) As comment (a) for  $k_0$ .  
(b) As comment (b) for  $k_0$ . The measurements were performed so far from the high pressure range that extrapolations were uncertain.

### Preferred Values

$$k_{\infty} = 6.3 \times 10^{-12} (T/298)^{-0.7} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range 250-320 K.}$$

#### Reliability

$$\Delta \log k_{\infty} = \pm 0.3 \text{ at 298 K.}$$

$$\Delta n = \pm 0.5.$$

#### Comments on Preferred Values

The unusually large negative temperature coefficient of  $k_{\infty}$  derived by Wu and Carr (1991) signals problems with the falloff extrapolations. For this reason it appears safer to employ the falloff curves for  $\text{CF}_2\text{ClO}_2\text{NO}_2$  dissociation from Köppenkastrop and Zabel (1991), which were studied over a ten times larger pressure range extending up to higher pressures. Doing this, the preferred value is derived which is consistent with our preferred data for  $\text{CF}_3\text{O}_2 + \text{NO}_2$ . As for the reverse reaction,  $F_c = 0.30$  is recommended.

### References

- Caralp, F., Lesclaux, R., Rayez, M.-T., Rayez, J.-C. and Forst, W.: J. Chem. Soc. Faraday Trans. 2, 84, 569, 1988.  
Destriau, M. and Troe, J.: Int. J. Chem. Kinet., 22, 915, 1990.  
Köppenkastrop, D. and Zabel F.: Int. J. Chem. Kinet., 23, 1, 1991.  
Moore, S. M. and Carr, R. W.: J. Phys. Chem., 94, 1393, 1990.  
Wu, F. and Carr, R. W.: Int. J. Chem. Kinet., 23, 701, 1991.