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$$\mathbf{O(^3P) + CN(X^2\Sigma^+) \rightarrow N(^4S) + CO(X^1\Sigma^+)} \quad \mathbf{(1)}\ \Delta Hr^{298} = -\ 322.4\ \text{kJ mol}^{-1} \quad \textit{(Baulch et al., 2005)}$$

$$\mathbf{\rightarrow N(^2D) + CO(X^1\Sigma^+)} \quad \mathbf{(2)}\ \Delta Hr^{298} = -\ 92.3\ \text{kJ mol}^{-1} \quad \textit{(Baulch et al., 2005)}$$

Rate Coefficient Data ($k = k_1 + k_2$)

k / cm^3 molecule^{-1} s^{-1}	T / K	Reference	
Rate Coefficient Measurements			
$k = (10.5\pm5.8)\times10^{-11} \cdot \exp(-1200\pm350)/T)$	570-687	Boden and Thrush, 1968	(2)
$k = 2.0\times10^{-11}$	298	Schacke et al. 1974	(3)
$k = 2.0\times10^{-11}$	298-387	Albers et al. 1975	(4)
$k = 1.7\pm0.7\times10^{-11}$	298	Schmatjko and Wolfrum, 1977	(5)
$k = 1.8\times10^{-11}$	295	Schmatjko and Wolfrum, 1978	(6)
$k = 3.1\ (+2.6/-1.3)\times10^{-11}$	2000	Louge and Hanson, 1984	(7)
$k = 13.0 \cdot \pm2.6$	3000-4500	Davidson et al., 1991	(8)
$k = 3.69\pm0.75\times10^{-11}$	298	Titarchuk and Halpern, 1995	(9)
Theory			
$k = 4.35\times10^{-11}\cdot(T/298)^{0.46}\cdot\exp(-364/T)$	300-5000	Cobos, 1996 (Statistical)	(10)
$k = 1.42\times10^{-10}\cdot(T/298)^{0.13}\cdot\exp(-5.3/T)$	5-400	Andersson, 2003 (QCT)	(11)
$k = 8.69\times10^{-10}\cdot(T/300)^{0.17}/ (5+3\exp(-288/T)+\exp(-326/T)$	15-400	Klippenstein, 2011 (TST)	

Comments

There have been several scattered measurements of the rate coefficients for this reaction. We believed that the determinations at room temperature (3-6,9) are the more accurate. Studies (3-6) all used a combined discharge flow/flash photolysis method (O-atoms from discharge through He/O_2 mixture, CN radicals were produced from photolysis of C_2N_2) and O atomss (in excess /CN) by microwave discharge. These measurements seem reliable but the authors give few details on how they measure/estimate the [O] atom concentration. Moreover, they have to deal with CN vibrational relaxation and secondary N + CN reaction, with N issued from O + CN. In the paper by Albers et al. (4), they report a T-independent rate coefficient for O + CN. But their value of the rate coefficient for CN + O_2 (which should be much easier to determine than those for O + CN) reaction is a factor of about 2.5 smaller than the currently accepted – and very well determined – value, casting some doubt on their measurements on O + CN. Study (9) used a double photolysis technique (CN from BrCN and O(^{3}P) from SO_2 or N_2O, CN being detected directly by LIF). In this last study the O-atom concentrations were estimated from the estimated photon flux and the absorption cross-sections. This method, using absolute cross section absorption of precursor, is not straightforward. However, we attach more weight to this last determination and we estimate an "average" value of the experimental rate coefficient at room temperature equal to k(298K) = 3 × 10^{-11} cm^3 molecule^{-1} s^{-1}. No measurements of low-temperature rate coefficients have been reported.

It should be noted that both channels are exothermic and allowed by spin-orbit correlation rules. The fact that more surfaces correlate with the reactants than pass adiabatically to the products, suggests that the rate coefficient should be lower than a simple collisional estimate. Reaction (2) to CO($^1\Sigma^+$) + N(^{2}D) on doublet surfaces is likely to proceed through strongly bound states of NCO ($X^2\mathbf{\Pi}$, $A^2\Sigma^+$, $B^2\mathbf{\Pi}$) and is likely to be favoured over reaction (1) via quartet surfaces to CO($^1\Sigma^+$) + N(^{4}S). (On these surfaces, there is no initial 'pairing' of electrons from each of the radical reactants.) This conclusion is supported by theoretical work by Abrahamsson *et al.* (12) which suggests that there is a substantial barrier on the lowest quartet surface – at least for linear configurations. Previous ab-initio calculations from the same team (11) using two potential energy surfaces corresponding to electronic states of $^2A'$ and $^2A''$ symmetry lead to potential barriers on both surfaces for the nonlinear approach of O toward CN. This makes the rate of reaction decrease with decreasing temperature below 200 K. Moreover, it is almost exclusively N + CO that is formed due to the C + NO channel being endothermic by about 1.2 eV. This means that trajectories entering (near-) collinearly into the CNO minimum emerge as nonreactive in most cases. Quasi-classical trajectory calculations lead to a rate that is constant not in good agreement with most experimental rate coefficients (fig 10 of Andersson et al. (11)):

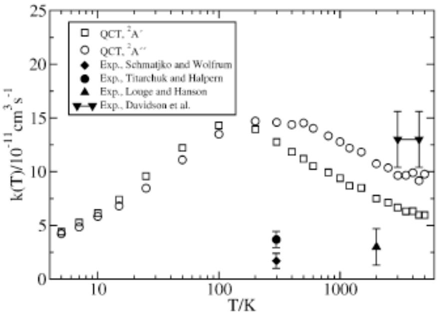

Figure 10. Total thermal rate coefficients for the O + CN reaction. Open symbols correspond to calculated rate coefficients for the $^2A'$ and $^2A''$ surfaces, and filled symbols correspond to experimental results (refs 35−38).

As pointed by the authors, is it likely that the theoretical rate coefficients for the O + CN presented in the paper are too high in the low-temperature regime. So the T dependence of this reaction is difficult to estimate. There is likely a competition between two opposite effects: increase at low temperature due to the rather strong, attractive, long-range forces between the dipole moment of CN and the quadrupole moment of O(^{3}P) atoms and the presence of a barrier for the nonlinear approach of O toward CN, which decreases the rate coefficient at low temperature (the electronic degeneracy factor due to O_J population varying only from 0.30 at 300 K to 0.40 at 10K). The statistical works of Cobos (10) seems not to be reliable as he found a barrier leading to an unexpected very low rate coefficient at low temperature. In 2011 Stephen Klippenstein performed (for this datasheet) TST calculations leading to k(CN+O) = $1.68\times10^{-10}T^{1/6}$ [2/(5+3exp(-288/T)+exp(-326/T)], in relatively good agreement with Anderson *et al.* calculations (11), and so notably higher than experimental determinations. No clear explanation has been found to explain this difference.

For the branching ratio between (1) and (2), Wolfrum et al have determined a N(^{2}D)/N(^{4}S) branching ratio of 5.7 using a bi-modal CO(v) distribution. They interpret the bi-modal distribution in terms of different energy distribution pathways for the two N(^{2}D) and N(^{4}S) channels, with the distribution for the N(^{4}S) channel being inverted and non-statistical. This measurement is questionable as first the quadruplet surfaces are supposed to be repulsive, and also because their directly measurement of a N(^{2}D)/N(^{4}S) branching ratio of 25 using VUV absorption (using discharge lamp) is very different, and no convincing explanation is provided (they suggest that N(^{4}S) reacts with C_2N_2 but but in general N(^{2}D) has a higher reactivity than N(^{4}S)). However, as the radiative lifetime of the ^{2}D excited state of N atoms is *ca.* 26 hours (A ~ 7.4×10^{-6} s^{-1}), spontaneous radiation will be the main loss process for N(^{2}D) where the gas density is less than *ca.* 10^6 cm^{-3} (as in most regions of the ISM).

Preferred Values

Total rate coefficient (10 – 300 K)

$k_1 + k_2 = 5\times10^{-11}$ **cm^3 molecule^{-1} s^{-1}**

Branching Ratios

$k_1 / (k_1 + k_2) =$ **0.15**

$k_2 / (k_1 + k_2) =$ **0.85**

Reliability

$F_0 = 3$, $g = 0$

Comments on Preferred Values

It's difficult to recommend an overall rate coefficient as the experimental rate coefficients are scattered at 298 K and the two calculations are 3 to 10 times higher than the experimental values. As we don't see any evidence to choose a particular value, we propose an intermediate value between experimental and theoretical ones of 5.0×10^{-11} cm^3 molecule^{-1} s^{-1} with an uncertainty of a factor of 3 for the entire range between 10 and 300 K.

References

DL Baulch, CT Bowman, CJ Cobos, RA Cox, T Just, JA Kerr, MJ Pilling, D Stocker, J Troe, W Tsang, RW Walker, J Warnatz: J. Phys. Chem. Ref. Data 34 (2005) 757-1397.
(2) JC Boden, BA Thrush: Proc. R. Soc. London, Ser. A 305 (1968) 107-23.
(3) H Schacke, KJ Schmatjko, J Wolfrum.: Ber Bunsenges. Physik. Chem. 77 (1973) 248.
(4) AA Albers, K Hoyermann, H Schacke, KJ Schmatko, J Wolfrum: Proc. 15th Symps. (Intl) Combust. (1975) 765.
(5) KJ Schmatjko, J Wolfrum: Symposium (International) on Combustion 16 (1977) 819-27.
(6) KJ Schmatjko, J Wolfrum: Ber. Bunsen-Ges. Phys. Chem. 82 (1978) 419-28.
(7) MY Louge, RK Hanson: Int. J. Chem. Kinet. 16 (1984) 231-50.
(8) DF Davidson, AJ Dean, MD DiRosa, RK Hanson: Int. J. Chem. Kin. 23 (1991) 1035-50.
(9) TA Titarchuk, JB Halpern: Chem. Phys. Lett. 232 (1995) 192-96.
(10) CJ Cobos: React. Kinet. Catal. Lett. 57 (1996) 43-47.
(11) S Andersson, N Markovic, G Nyman: J. Phys. Chem A. 107 (2003) 5439-47.
(12) E Abrahamsson, S Andersson, G Nyman, N Markovic: Chem. Phys. 324 (2006) 507-14.