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# $N(^4S) + CN(^2\Sigma^+) \rightarrow C(^3P) + N_2(^1\Sigma_g^+)$ $\Delta H^o_{298}(1) = -191.4$ kJ mol$^{-1}$ *(Baulch* et al.*, 2005)*

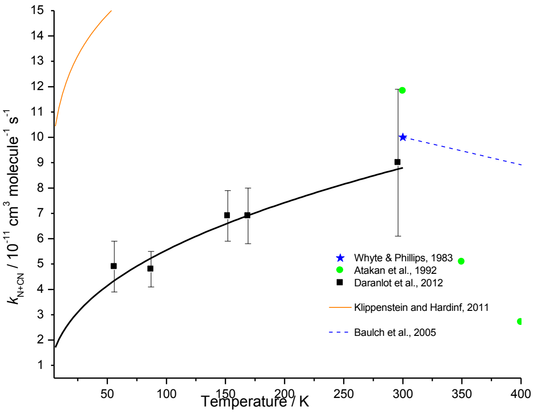
## Rate Coefficient Data *k*

| $k$ / cm$^3$ molecule$^{-1}$ s$^{-1}$ | $T$ / K | Reference | Comments |
|---|---|---|---|
| *Rate Coefficient Measurements* | | | |
| $1.0 \times 10^{-10}$ | 300 | Whyte & Phillips, 1983 | |
| $3.24 \times 10^{-13} \exp(1770/T)$ | 300-534 | Atakan *et al.*, 1992 | |
| $8.8 \times 10^{-11} (T/300)^{0.42}$ | 56-296 | Daranlot *et al.*, 2012 | |
| *Reviews and Evaluations* | | | |
| $9.8 \times 10^{-10} T^{-0.40}$ | 300-3000 | Baulch *et al.*, 2005 (p. 1139) | |
| $3.0 \times 10^{-10}$ | 298-2500 | UMIST database | |
| $3.0 \times 10^{-10}$ | all temperatures | OSU website | |
| *Theory* | | | |
| | 300-2500 | Moskaleva & Lin, 2001 | |
| $2.0 \times 10^{-10} (T/300)^{0.18}$ | 10-400 | Klippenstein & Harding, 2011 | |
| | 50-300 | Ma *et al.*, 2012 | |

## Comments

The reactants correlate with triplet and quintet states, the products with only triplet states. As the reactants are only in S and Σ states there is no spin orbit coupling. Therefore, there is a constant electronic degeneracy factor of *ca.* 3/8. The three measurements of the rate coefficient at 298 K agree well. However, Atakan *et al* (2) suggests what seems like an extraordinarily steep negative dependence with *T*. L. B. Harding performed (for this datasheet) CASPT2(10e,9o)/CBS scans of the potential energy surface for this reaction. These calculations suggest that there is no barrier to formation of either NCN (exothermic by 435 kJ/mol) or CNN (also exothermic by 337 kJ/mol). Furthemore, the saddlepoint for transformation from NCN to CNN is well below the N + CN energy. So the reaction likely proceeds via addition to form both NCN and CNN followed by dissociation from the CNN complex to C + NN. However, even though very exothermic, either the isomerization or the dissociation could provide some sort of dynamical bottleneck especially at higher *T*.

S. Klippenstein performed long-range TST calculations (using CASPT2(8,8)/CBS potentials and so including not only dispersion but also contributions from the dipole induced-dipole and other terms) leading to (including the 3/8 term from electronic degeneracy) $k(\mathrm{CN+N}) = 2.0 \times 10^{-10} (T/300)^{1/6}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, which is about twice the experimental determinations (1 and $1.1 \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$) at room temperature. The CRESU data by Daranlot *et al.* (3) obtained at low temperature present a more pronounced positive temperature dependence. The rate constants were determined relative to those of the N+OH reaction. Ma *et al.* (5) have performed quantum capture calculations on a new two-dimensional potential energy surface to calculate low-temperature rate constants for the N + CN reaction. These rate constants present a positive temperature dependence in reasonably good agreement with the experimentally determined relative rate values of Daranlot *et al.* (3).



## Preferred Values

*Rate coefficient (10 – 300 K)*

$\boldsymbol{k}$ **(T) = $8.8\times10^{-11}$ $(T/300)^{0.42}$ $cm^3$ $molecule^{-1}$ $s^{-1}$**

*Reliability*

**$F_0 = 1.4$ ; $g = 1.5$**

## 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.

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