

The Kinetics of the Reaction of Cyclopentadienyl Radical with NO₂

Vadim D. Knyazev

Department of Chemistry, The Catholic University of America, Washington, DC, USA

knyazev@cua.edu

The reaction of the C₅H₅ (cyclopentadienyl) radical with nitrogen dioxide



was studied in the 305 – 800 K temperature range at low densities of helium bath gas ((3-12)×10¹⁶ atoms cm⁻³). Cyclopentadienyl radicals were produced by the pulsed, 248-nm laser photolysis of cyclopentadiene¹ and their decay was subsequently monitored in time-resolved experiments using photoionization mass spectrometry. Experiments were conducted under pseudo-first order conditions with NO₂ in large excess over C₅H₅. Concentrations of C₅H₅ were kept low ([C₅H₅]₀ = (0.5 – 2.6)×10¹¹ molecules cm⁻³) to ensure that radical-radical reactions had negligible rates in comparison with the rate of reaction 1. Experiments were performed to establish that the decay constants did not depend on the initial radical concentration or the photolyzing laser intensity. The values of the bimolecular rate constant k_1 determined in this study demonstrate a strong negative temperature dependence (Figure 1), which can be represented by the following modified Arrhenius expression:

$$k_1(T) = 1.16 \times 10^6 T^{-5.66} \exp(-1603 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (\text{I})$$

This strong decrease of the rate constant with temperature is not dissimilar to that observed in another radical-radical reaction with the participation of the cyclopentadienyl radical, that of C₅H₅ self-reaction,¹ where the rate constant decreased by an order of magnitude between 300 and 600 K. The rate constants demonstrate no dependence on pressure within the experimental range. Formation of product at the mass of 81 was observed in reaction 1; this ion signal was attributed to C₅H₅O. Reaction potential energy surface was studied using quantum chemistry and the mechanism was analyzed.

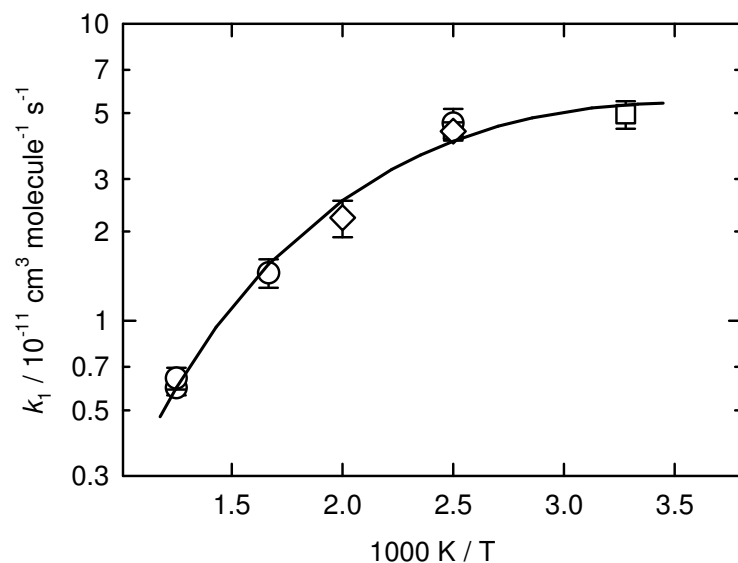


Figure 1. The temperature dependence of the rate constant of reaction 1. Different symbols (squares, circles, and diamond) represent different bath gas densities (3×10¹⁶, 6×10¹⁶, and 12×10¹⁶ molecules cm⁻³, respectively). The line is the fit of eq. I.

References

- (1) Knyazev, V.D.; Popov, K.V. *J. Phys. Chem. A* **2015**, 7418–7429.