Unimolecular reaction of methyl isocyanide (CH_3NC) to acetonitrile (CH_3CN): A high-level theoretical study

Thanh Lam Nguyen, James H. Thorpe, and John F. Stanton

Quantum Theory Project, Department of Chemistry and Physics, University of Florida, Gainesville, FL 32611 (USA).

The isomerization of methyl isocyanide to acetonitrile is a textbook unimolecular reaction, which was experimentally studied in detail (for an extensive range of temperatures and pressures in the fall-off region) by Rabinovitch and coworkers more than 50 years ago [1,2]. On the basis of constructed models and statistical Rice-Ramsperger-Kassel-Marcus (RRKM) theory, Rabinovitch and coworkers were able to satisfactorily reproduce their measured rate constants in the fall-off region, thus validating RRKM theory [1]. However, such kinetics calculations (using man-made models for transition state structural and vibrational parameters) are very empirical and unsatisfactory. In 1980, Schaefer and coworkers [3] used SCF/DZ+P theory to obtain *ab initio* rovibrational parameters for stationary points and an activation energy of 43.7 kcal/mol, 5.3 kcal/mol higher than the experimental value of 38.4 kcal/mol. Using these SCF rovibrational parameters and the experimental activation energy, Hase [3] computed thermal rate constants at the high-pressure limit with transition state theory (TST). The theoretical results were about 50% higher than the experiment [3]. Theoretical data in the fall-off region were not available for comparison.

In this work, for the first time, thermal rate constants for the title reaction are computed from first principles for a wide range of temperatures and pressures in order to construct fall-off curves using high-level calculations. The potential energy surface was first constructed using the HEAT-345Q protocol [4-6], followed by solving a two-dimensional master equation to obtain k(T,P), where microcanonical rate constants, k(E,J), were computed using the SCTST/VPT2 approach [7-10]. The calculated activation energy is 38.25 ± 0.25 kcal/mol, in excellent agreement with the experimental value of 38.4 kcal/mol. Thermal rate constants calculated at the high-pressure limit for three temperatures (199.4, 230.4, and 259.8 ^{o}C) agree well (within 10%) with experiment. The experimental fall-off curves can be reproduced nearly perfectly using

an average energy of 2000 cm^{-1} transferred per collision in a downward direction [2,11] (see Figure 1 below).

[1] F. W. Schneider and B. S. Rabinovitch, *J. Am. Chem. Soc.* **84**, 4215-4230 (1962).
[2] F. J. Fletcher, B. S. Rabinovitch, K. W. Watkins, and D. J. Locker, *J. Phys. Chem.* **70**, 2823-2833 (1966).
[3] P. Saxe, Y. Yamaguchi, P. Pulay, and H. F. Schaefer III, *J. Am. Chem. Soc.* **102**, 3718-3723 (1980).
[4] A. Tajti, P. G. Szalay, A. G. Csaszar, M. Kallay, J. Gauss, E. F. Valeev, B. A. Flowers, J. Vazquez, J. F. Stanton, *J. Chem. Phys.* **121**, 11599-11613 (2004).
[5] Y. J. Bomble, J. Vazquez, M. Kallay, C. Michauk, P. G. Szalay, A. G. Csaszar, J. Gauss, J. F. Stanton, *J. Chem. Phys.* **125**, 064108-1 (2006).
[6] M. E. Harding, J. Vazquez, B. Ruscic, A. K. Wilson, J. Gauss, J. F. Stanton, *J. Chem. Phys.* **128**, 114111 (2008).
[7] W. H. Miller, Faraday Discuss **62**, 40-46 (1977).
[8] I. M. Mills, Vibration-Rotation Structure in Asymmetric- and Symmetric-Top Molecules. In Molecular Spectroscopy: Modern Research; Rao, K. N.; Mathews, C. W., Ed.; Academic Press: New York **Vol. 1**, 115 (1972).
[9] T. L. Nguyen, J. F. Stanton and J. R. Barker, Chem Phys Lett **499** (1-3), 9-15 (2010).
[10] T. L. Nguyen, J. F. Stanton and J. R. Barker, J Phys Chem A **115** (20), 5118-5126 (2011).
[11] S. C. Chan, B. S. Rabinovitch, J. T. Bryant, L. D. Spicer, T. Fujimoto, Y. N. Lee, and S. P. Pavlou, *J. Phys. Chem.* **74**, 3160-3175 (1970).

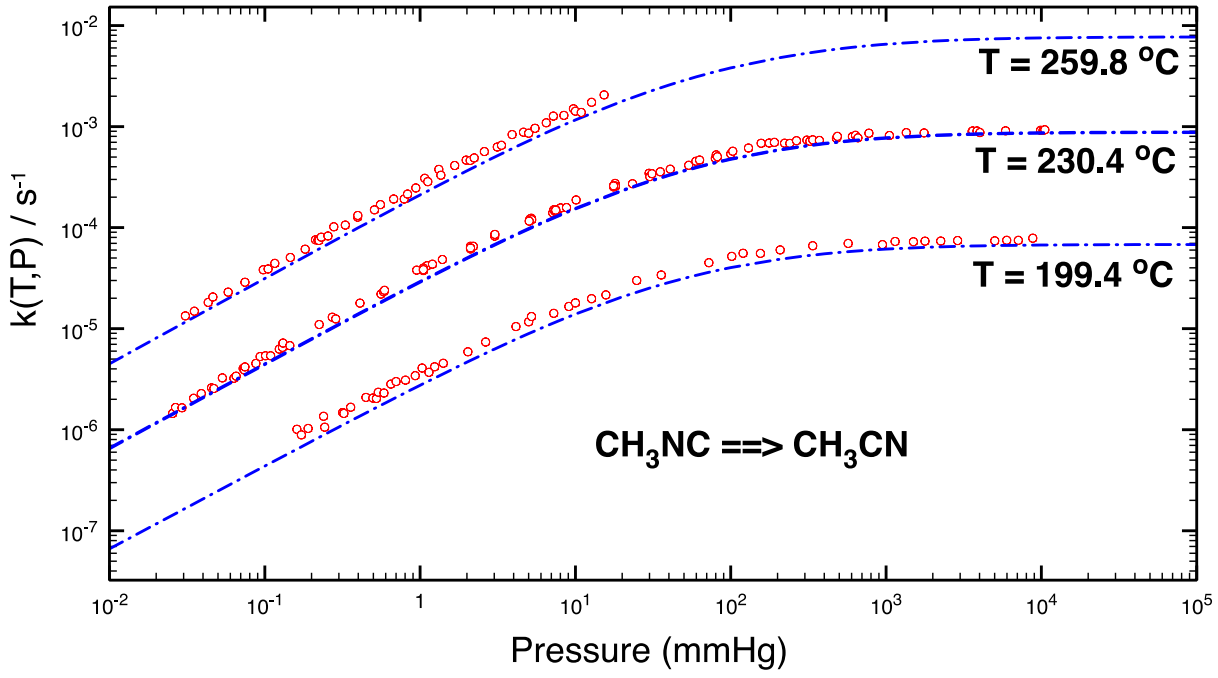

Figure 1: Fall-off curves for the isomerization of CH_3NC to CH_3CN: symbols are experiment; dash-dot lines are theory.