KINETICS OF NONADIABATIC H + O + M = OH* + M REACTION: QUANTUM CHEMICAL STUDY

A. V. Pelevkin, B. I. Loukhovitski, and A. S. Sharipov

Central Institute of Aviation Motors, 2 Aviamotornaya Str., Moscow 111116, Russian Federation

Abstract: Multireference quantum chemical calculations are conducted to estimate the rate constant of the nonadiabatic preassociation reaction H + O + $M \leftrightarrows$ OH* + M (M = Ar, N_2) recognized as the major channel of formation of chemiluminescent electronically excited OH* molecules in ignition and combustion of hydrogen. The calculations are performed in wide ranges of temperatures (200–4000 K) and pressures (10^{-3}–10^2 bar). It is shown that the rate constant of this reaction exhibits distinct non-Arrhenius temperature behavior and, moreover, has a complex falloff pressure dependence, with the transition from the third- to the second-order, high-pressure regime occurring at pressures about 10 atm. The obtained dependence on temperature and pressure does not contradict the known experimental data and can be recommended (as a part of the appropriate reaction mechanisms) for further kinetic modeling of OH* chemiluminescence accompanying the high-temperature oxidation of hydrogen and other fuels.

Keywords: hydroxyl radical; electronic excitation; chemiluminescence; nonadiabatic transitions; preassociation; quantum chemistry

DOI: 10.30826/CE24170101 **EDN:** ABPFLX

Figure Captions

Figure 1 Potential energy curves for the bonding ($X^2\Pi$ and $A^2\Sigma^+$; solid curves) and repulsive ($^4\Sigma^-$, $^2\Sigma^-$, and $^4\Pi$; dashed curves) terms of OH molecule obtained at the DW-XMCQDPT2/aug-cc-pV∞Z level of treatment

Figure 2 Temperature dependences of the (R1) reaction rate constant in the second-order dimension at $p = 1$ bar measured in Ar (*a*) and N_2 (*b*) (*1* — [21]; *2* — [22]; *3* — [18]; *4* — [13]; *5* — [15]; *6* — [19]; and *7* — [16]) and adopted in the FFCM-1 model [48] (*8*). Theoretical estimates of the present work under various approximations are provided by curves: I — high-pressure limit; II — $P(v) = P_{\mathrm{nasc}}(v)$; and III — the $k_b(T)$ rate constant is set according to Eq. (2) and the data [23, 24]

Figure 3 The pseudo-second-order (R1) rate constant at $T = 1500$ K vs. bath gas (Ar) pressure, p, calculated (curves) assuming completely thermalized (I), nascent (II), and interpolated (III) $P(v)$ distribution of OH($A^2\Sigma^+, v$) as compared to the available experimental data: *1* — [35]; *2* — [21]; *3* — [22]; *4* — [18]; *5* — [19]; and *6* — [16]

Table Captions

Table 1 The double-Arrhenius second-order $k_{\mathrm{R1}}(T, p = const)$ dependences (in cm^{3}mol^{-1}s^{-1}) for several fixed values of bath gas (M = Ar and N_2) pressure together with the high-pressure limiting rate constant $k^{\infty}_{\mathrm{R1}}(T)$

Table 2 The α_{ij} fitting coefficients for the Chebyshev polynomial representation [49, 50] of the calculated $k_{\mathrm{R1}}(T, p)$ dependence

Acknowledgments

The article was prepared as a part of the implementation of the program for the creation and development of a world-class scientific center called “The Supersonic” (Sverkhzvuk) for 2020–2025 with financial support from the Ministry of Education and Science of Russia (Agreement No. 075-15-2021-605, dated June 24, 2021).

References

1. Golde, M. F. 1976. Chemiluminescence in gases. *Adv. Atom. Mol. Phys.* 11:361–409. doi: 10.1016/S0065-2199(08)60034-2.
2. Vlasov, P. A., T. S. Demidenko, V. N. Smirnov, A. M. Tereza, and E. V. Atkin. 2016. Chemiluminescent emission of CH*, C_2*, OH*, and CO_2* during the ignition of ethane behind reflected shock waves. *Russ. J. Phys. Chem. B* 10:983–990. doi: 10.1134/S1990793116060130.
3. Tereza, A. M., S. P. Medvedev, and V. N. Smirnov. 2019. Experimental study and numerical simulation of chemiluminescence emission during the self-ignition of hydrocarbon fuels. *Acta Astronaut.* 163:18–24. doi: 10.1016/j.actaastro.2019.03.001.
4. Bedard, M. J., T. L. Fuller, Sardeshmukh S., and W. E. Anderson. 2020. Chemiluminescence as a diagnostic in studying combustion instability in a practical combustor. *Combust. Flame* 213:211–225. doi: 10.1016/j.combustflame.2019.11.039.

5. Lytras, I., E. P. Mitsopoulos, E. Dogkas, and P. Koutmos. 2020. Algebraic model for chemiluminescence emissions suitable for using in complex turbulent propane flame simulations. *Combust. Explo. Shock Waves* 56:278–291. doi: 10.1134/S0010508220030041.
6. Kobtsev, V. D., S. A. Kostritsa, A. V. Pelevkin, V. V. Smirnov, A. M. Starik, N. S. Titova, S. A. Torokhov, K. A. Vereshchagin, and S. Y. Volkov. 2019. Ignition and early stage combustion of H_2–O_2 mixture upon the photodissociation of O_2 molecules by UV laser radiation: Experimental and numerical study. *Combust. Flame* 200:32–43. doi: 10.1016/j.combustflame.2018.10.038.
7. Chen, Xinyi, Yiqing Wang, Thorsten Zirwes, Feichi Zhang, Henning Bockhorn, and Zheng Chen. 2021. Heat release rate markers for highly stretched premixed CH_4/air and CH_4/H_2/air flames. *Energ. Fuel.* 35:13349–13359. doi: 10.1021/acs.energyfuels.1c02187.
8. Basevich, V. Ya., and S. M. Frolov. 2007. Kinetics of 'blue' flames in the gas-phase oxidation and combustion of hydrocarbons and their derivatives. *Russ. Chem. Rev.* 76:867–884. doi: 10.1070/RC2007v076n09ABEH003703.
9. Eremin, A. V., M. R. Korshunova, and E. Yu. Mikheyeva. 2019. Influence of flame suppressants on the level of nonequilibrium radiation during ignition of hydrogen–oxygen mixtures behind shock waves. *Combust. Explo. Shock Waves* 55:121–124. doi: 10.1134/S0010508219010143.
10. Panoutsos, C. S., Y. Hardalupas, and A. M. K. P. Taylor. 2009. Numerical evaluation of equivalence ratio measurement using OH* and CH* chemiluminescence in premixed and non-premixed methane–air flames. *Combust. Flame* 156:273–291. doi: 10.1016/j.combustflame.2008.11.008.
11. Sardeshmukh, S., M. Bedard, and W. Anderson. 2017. The use of OH* and CH* as heat release markers in combustion dynamics. *Int. J. Spray Combust.* 9:409–423. doi: 10.1177/1756827717718483.
12. Bauschlicher, C. W., Jr., and S. R. Langhoff. 1987. Theoretical determination of the radiative lifetime of the $A^2\Sigma^+$ state of OH. *J. Chem. Phys.* 87:4665–4672. doi: 10.1063/1.452829.
13. Smith, G., C. Park, and J. Luque. 2005. A note on chemiluminescence in low-pressure hydrogen and methane – nitrous oxide flames. *Combust. Flame* 140:385–389. doi: 10.1016/j.combustflame.2004.11.011.
14. Lauer, M., M. Zellhuber, T. Sattelmayer, and C. J. Aul. 2011. Determination of the heat release distribution in turbulent flames by a model based correction of OH* chemiluminescence. *J. Eng. Gas Turb. Power* 133:121501. doi: 10.1115/1.4004124.
15. Hall, J. M., and E. L. Petersen. 2006. An optimized kinetics model for OH chemiluminescence at high temperatures and atmospheric pressures. *Int. J. Chem. Kinet.* 38:714–724. doi: 10.1002/kin.20196.
16. Kathrotia, T., M. Fikri, M. Bozkurt, M. Hartmann, U. Riedel, and C. Schulz. 2010. Study of the $H + O + M$ reaction forming OH*: Kinetics of OH* chemiluminescence in hydrogen combustion systems. *Combust. Flame* 157:1261–1273. doi: 10.1016/j.combustflame.2010.04.003.
17. Bozkurt, M., M. Fikri, and C. Schulz. 2012. Investigation of the kinetics of OH* and CH* chemiluminescence in hydrocarbon oxidation behind reflected shock waves. *Appl. Phys. B — Lasers O.* 107:515–527. doi: 10.1007/s00340-012-5012-y.
18. Skrebkov, O. V., S. P. Karkach, V. M. Vasil'ev, and A. L. Smirnov. 2003. Hydrogen–oxygen reactions behind shock waves assisted by $OH(^2\Sigma^+)$ formation. *Chem. Phys. Lett.* 375:413–418. doi: 10.1016/S0009-2614(03)00875-3.
19. Donato, N. 2009. OH^* chemiluminescence: Pressure dependence of $O + H + M = OH* + M$. Texas A&M University, Department of Mechanical Engineering, 2009. Master Thesis.
20. Skrebkov, O. V., and S. P. Karkach. 2007. Vibrational nonequilibrium and electronic excitation in the reaction of hydrogen with oxygen behind a shock wave. *Kinet. Catal.* 48:367–375. doi: 10.1134/S0023158407030044.
21. Hidaka, Y., S. Takahashi, H. Kawano, M. Suga, and W. C. Gardiner, Jr. 1982. Shock tube measurement of the rate constant for excited $OH(A^2\Sigma^+)$ formation in the hydrogen–oxygen reaction. *J. Phys. Chem.* 86:1429–1433. doi: 10.1021/j100397a043.
22. Koike, T., and K. Morinaga. 1982. Further studies of the rate constant for chemical excitation of OH in shock waves. *B. Chem. Soc. Jpn.* 55:52–54. doi: 10.1246/bcsj.55.52.
23. Kaskan, W. E. 1959. Abnormal excitation of OH in H_2/O_2/N_2 flames. *J. Chem. Phys.* 31:944–956. doi: 10.1063/1.1730556.
24. Broida, H. P. 1962. Study of electronically excited hydroxyl radicals in the $H + O_3$ atomic flame. *J. Chem. Phys.* 36:444. doi: 10.1063/1.1732528.
25. Davis, M. G., W. K. McGregor, and A. A. Mason. 1974. OH chemiluminescent radiation from lean hydrogen–oxygen flames. *J. Chem. Phys.* 61:1352–1356. doi: 10.1063/1.1682059.
26. Konnov, A. A. 2015. On the role of excited species in hydrogen combustion. *Combust. Flame* 162:3755–3772. doi: 10.1016/j.combustflame.2015.07.014.
27. Skrebkov, O. V., S. S. Kostenko, and A. L. Smirnov. 2020. Vibrational nonequilibrium and reaction heat effect in diluted hydrogen–oxygen mixtures behind reflected shock waves at $1000 < T < 1300$ K. *Int. J. Hydrogen Energ.* 45:3251–3262. doi: 10.1016/j.ijhydene.2019.11.168.
28. Sharipov, A. S., and A. V. Pelevkin. 2019. O reaktsionnoy sposobnosti singletnogo del'ta-kisloroda po otnosheniyu k prosteyshim uglevodorodam [On the reactivity of singlet delta oxygen with respect to the simplest hydrocarbons]. *Goren. Vzryv (Mosk.) — Combustion and Explosion* 12:4–11. doi: 10.30826/CE19120101.
29. Pelevkin, A. V., B. I. Loukhovitski, and A. S. Sharipov. 2021. Reaction of the N atom with electronically excited O_2 revisited: A theoretical study, *J. Phys. Chem. A* 125:8294–8312. doi: 10.1021/acs.jpca.1c05733.
30. Deskevich, M. P., D. J. Nesbitt, and H. J. Werner. 2004. Dynamically weighted multiconfiguration self-consistent

field: Multistate calculations for $F + H_2O \rightarrow HF + OH$ reaction paths. *J. Chem. Phys.* 120:7281–7289. doi: 10.1063/1.1667468.

31. Granovsky, A. A. 2011. Extended multi-configuration quasi-degenerate perturbation theory: The new approach to multi-state multi-reference perturbation theory. *J. Chem. Phys.* 134:214113. doi: 10.1063/1.3596699.
32. Granovsky, A. A. Firefly V. 8.2.0. Available at: http:// classic.chem.msu.su/gran/firefly/index.html (accessed January 11, 2024).
33. Kendall, R. A., T. H. Dunning, Jr., and R. J. Harrison. 1992. Electron affinities of the first-row atoms revisited. systematic basis sets and wave functions. *J. Chem. Phys.* 96:6796–6806. doi: 10.1063/1.462569.
34. Naegeli, D. W., and H. B. Palmer. 1967. Predissociation in the chemiluminescent emission spectrum of OH. *J. Mol. Spectrosc.* 23:44–52. doi: 10.1016/0022-2852(67)90046-X.
35. Ticktin, S., G. Spindler, and H. I. Schiff. 1967. Production of excited $OH(A^2\Sigma^+)$ molecules by the association of ground-state oxygen and hydrogen atoms. *Discuss. Faraday Soc.* 44:218–225. doi: 10.1039/DF9674400218.
36. Parlant, G., and D. R. Yarkony. 1999. A theoretical analysis of the state-specific decomposition of $OH(A^2\Sigma^+, v', N', F_1/F_2)$ levels, including the effects of spin-orbit and Coriolis interactions. *J. Chem. Phys.* 110:363–376. doi: 10.1063/1.478133.
37. Kuznetsov, N. M. 1982. *Kinetika monomolekulyarnykh reaktsiy* [Kinetics of monomolecular reactions]. Moscow: Nauka. 221 p.
38. Harvey, J. N. 2007. Understanding the kinetics of spin-forbidden chemical reactions. *Phys. Chem. Chem. Phys.* 9:331–343. doi: 10.1039/b614390c.
39. Landau, L. D., and E. M. Lifshitz. 1977. *Quantum mechanics: Non-relativistic theory*. New York, NY: Pergamon Press. Vol. 3. 628 p.
40. Fedorov, D. G., and J. P. Finley. 2001. Spin-orbit multireference multistate perturbation theory. *Phys. Rev. A* 64:042502. doi: 10.1103/PhysRevA.64.042502.
41. Matsugi, A. 2018. Collision frequency for energy transfer in unimolecular reactions. *J. Phys. Chem. A* 122:1972–1985. doi: 10.1021/acs.jpca.8b00444.
42. Troe, J. 1977. Theory of thermal unimolecular reactions at low pressures. II. Strong collision rate constants. Applications. *J. Chem. Phys.* 66:4758–4774.
43. Sharipov, A. S., B. I. Loukhovitski, and A. V. Pelevkin. 2023. Diffusion coefficients of electronically excited molecules. *Fluid Dyn.* 58:787–795. doi: 10.1134/S0015462823600943.
44. Brzozowski, J., P. Erman, amd M. Lyyra. 1978. Precision estimates of the predissociation rates of the OH $A^2\Sigma$ state ($v \leq 2$). *Phys. Scripta* 17:507–511. doi: 10.1088/0031-8949/17/5/006.
45. Gray, J. A., and R. L. Farrow. 1991. Predissociation lifetimes of OH $A^2\Sigma^+$ ($v' = 3$) obtained from optical-optical double-resonance linewidth measurements. *J. Chem. Phys.* 95:7054–7060. doi: 10.1063/1.461433.
46. Heard, D. E., D. R. Crosley, J. B. Jeffries, G. P. Smith, and A. Hirano. 1992. Rotational level dependence of predissociation in the $v' = 3$ level of OH $A^2\Sigma^+$. *J. Chem. Phys.* 96:4366–4371. doi: 10.1063/1.462828.
47. Grimme, S. 2012. Supramolecular binding thermodynamics by dispersion-corrected density functional theory. *Chem. — Eur. J.* 18:9955–9964. doi: 10.1002/chem.201200497.
48. Smith, G. P., Y. Tao, and H. Wang. 2016. Foundational Fuel Chemistry Model (FFCM-1), Version 1.0. Available at: https://web.stanford.edu/group/haiwanglab/FFCM1/pages/download.html (accessed January 11, 2024).
49. Kee, R. J., F. M. Rupley, J. A. Miller, *et al.* 2000. Chemkin Collection, Release 3.6. San Diego, CA: Reaction Design Inc..
50. Venkatesh, P. K., A. Y. Chang, A. M. Dean, M. H. Cohen, and R. W. Carr. 1997. Parameterization of pressure- and temperature-dependent kinetics in multiple well reactions. *AIChE J.* 43:1331–1340.

Received November 30, 2023

Contributors

Pelevkin Alexey V. (b. 1993) — junior research scientist, Central Institute of Aviation Motors, 2 Aviamotornaya Str., Moscow 111116, Russian Federation; avpelevkin@ciam.ru

Loukhovitski Boris I. (b. 1979) — Candidate of Science in physics and mathematics, head of sector, Central Institute of Aviation Motors, 2 Aviamotornaya Str., Moscow 111116, Russian Federation; biloukhovitski@ciam.ru

Sharipov Alexander S. (b. 1986) — Candidate of Science in physics and mathematics, head of sector, Central Institute of Aviation Motors, 2 Aviamotornaya Str., Moscow 111116, Russian Federation; assharipov@ciam.ru