

# CHEMICAL IONIZATION BY OXIDATION OF *n*-HEXANE AND DIMETHYL KETONE IN REFLECTED SHOCK WAVES

P. A. Vlasov, O. B. Ryabikov, V. N. Smirnov, D. I. Mikhailov, and Yu. P. Petrov

N. N. Semenov Federal Research Center for Chemical Physics of the Russian Academy of Sciences, 4 Kosygin Str., Moscow 119991, Russian Federation

**Abstract:** Chemical ionization is the process of formation of charged particles as a result of energy release during the formation of a new chemical bond in chemical reactions between neutral components. Chemical ionization is most often observed in the processes of hydrocarbon combustion. Measurements of ionization current in internal combustion engines are of great practical interest. To understand the correlation of the type of ionization signal and the processes proceeding in the combustion chamber of the engine and to reduce the time and cost required for debugging electronic engine control systems, it is necessary to build detailed kinetic mechanisms of chemical ionization and to conduct detailed kinetic calculations with their help. Most experiments on chemical ionization were carried out in flames with obvious limitations: the composition of the mixture cannot be changed in an arbitrarily wide range of concentrations of fuel and oxidant, investigate pyrolysis processes, arbitrarily change the temperature and pressure, it is impossible to dispose of the transfer processes and gradients of temperature and reactive components. Experiments in shock tubes in the reflected shock waves are free from all the above disadvantages. In the present experiments, electric currents to electrically isolated and uninsulated cylindrical probes were recorded, to which a negative potential of  $-9\text{ V}$  was applied. From the processing of total current profiles to conducting probes, the concentration profiles of free electrons in a chemically reacting mixture of acetone and *n*-hexane with oxygen were determined. At the same time, two additional signals were simultaneously recorded: chemiluminescence signals of electronically excited  $\text{OH}^*$  radicals ( $\lambda_1 = 308\text{ nm}$ ) and radiation absorption signals at a wavelength of  $\lambda_2 = 216\text{ nm}$  by  $\text{CH}_3$  radicals, which are precursors of  $\text{CH}$  radicals, directly involved in the chemical ionization of the formation of primary positive ions and free electrons:  $\text{CH} + \text{O} = \text{CHO}^+ + e^-$ . The main goal of the present work was to experimentally study the kinetics of chemical ionization during the oxidation of various mixtures of *n*-hexane and acetone with oxygen in reflected shock waves using a shock tube technique and to build a unified kinetic model of the chemical ionization process based on the experimental results obtained.

**Keywords:** ionization sensor; chemionization; thermionization; internal combustion engines; combustion process; kinetic model of chemionization; detailed kinetic modeling; reflected shock waves

**DOI:** 10.30826/CE19120403

## Acknowledgments

This work was performed within the framework of the Program of Fundamental Research of the Russian Academy of Sciences on the research issue of FRCCP RAS No. 47.16.

## References

1. Frolov, S. M., V. S. Aksenov, K. A. Avdeev, A. A. Borisov, V. S. Ivanov, A. S. Koval, S. N. Medvedev, V. A. Smetanyuk, F. S. Frolov, and I. O. Shamshin. 2013. Rabochiy protsess impul'sno-detonatsionnoy gorelki na prirodnom gaze [Working process of a pulsed detonation burner operating on natural gas]. *Goren. Vzryv (Mosk.) — Combustion and Explosion* 6:90–97.
2. Aravin, G. S. 1951. Ionizatsiya plameni i plamennykh gazov v usloviyakh bomby i dvigatelya [The ionization in flames and combustion products in bomb and engine]. Moscow: ICP USSR AS. PhD Thesis. 157 p.
3. Andersson, I. 2002. Cylinder pressure and ionization current modeling for spark ignited engines. Linköping University. PhD Thesis.
4. Shaikin, A. P., P. V. Ivashin, and A. D. Deryachev. 2017. Issledovanie vzaimosvyazi toka ionizatsii i maksimal'nogo indikatornogo davleniya pri sgoranii benzovozdushnoy smesi, obogashchennoy vodorodom [The study of interrelationship of ionization current and maximum indicated pressure during the combustion of hydrogen rich gasoline–air mixture]. *Vektor nauki TGU [Vector of Science of TSU]* 39(1):30–35. doi: 10.18323/2073-5073-2017-1-30-35.
5. Reinmann, R., A. Saitzkoff, B. Lassesson, and P. Strandh. 1998. Fuel and additive influence on the ion current. SAE Paper No. 980161.
6. Eriksson, L., L. Nielsen, and J. Nytomt. 1996. Ignition control by ionization current interpretation. SAE Paper No. 960045.
7. Nielsen, L., and L. Eriksson. 1998. An ion-sense engine fine-tuner. *IEEE Contr. Syst.* 18(5):43–52.
8. Eriksson, L. 1999. Spark advance modeling and control.

- Linköping University. PhD Thesis. 207 p.
9. Reinmann, R., A. Saitzkoff, F. Mauss, and M. Glavmo. 1997. Local air–fuel ratio measurements using the spark plug as an ionization sensor. SAE Paper No. 970856.
  10. Wilstermann, H. 1999. Wechselspannungszündung mit integrierter Ionenstrommessung als Sensor für die Verbrennungs- und Motorregelung. University Fridericiana of Karlsruhe. PhD Thesis.
  11. Saitzkoff, A., R. Reinmann, T. Berglind, and M. Glavmo. 1996. An ionization equilibrium analysis of the spark plug as an ionization sensor. SAE Paper No. 960337.
  12. Calcote, H. F. 1957. Mechanisms for the formation of ions in flames. *Combust. Flame* 1(3):385–403.
  13. Schofield, K. 2008. The enigmatic mechanism of the flame ionization detector: Its overlooked implications for fossil fuel combustion modeling. *Prog. Energy Combust.* 34:330–350.
  14. Lawton, J., and F. J. Weinberg. 1969. *Electrical aspects of combustion*. Clarendon Press. 355 p.
  15. Lewis, B., and G. Elbe. 1987. *Combustion, flames and explosions of gases*. 3rd ed. Academic Press Inc. 731 p.
  16. Brown, R. C., and A. N. Eraslan. 1988. Simulation of ionic structure in lean and close-to-stoichiometric acetylene flames. *Combust. Flame* 73(1):1–21.
  17. Agafonov, G. L., D. I. Mikhailov, V. N. Smirnov, A. M. Tereza, P. A. Vlasov, and I. V. Zhiltsova. 2016. Shock tube and modeling study of chemical ionization in the oxidation of acetylene and methane mixtures. *Combust. Sci. Technol.* 188(11-12):1815–1830.
  18. Burcat, A., E. Olchanski, and C. Sokolinski. 1996. Kinetics of hexane combustion in a shock tube. *Israel J. Chem.* 36:313–320.
  19. Curran, H. J., P. Gaffuri, W. J. Pitz, C. K. Westbrook, and W. R. Leppard. 1995. Autoignition chemistry of the hexane isomers: An experimental and kinetic modelling study. SAE Paper No. 1995-95-2406.
  20. Tsuboi, T., K. Ishii, and S. Tamura. 2001. Thermal oxidation of acetone behind reflected shock wave. *T. Jpn. Soc. Mech. Eng.* 67:2797–2804.
  21. Pichon, S., G. Black, N. Chaumeix, M. Yahyaoui, J. M. Simmie, H. J. Curran, and R. Donohue. 2009. The combustion chemistry of a fuel tracer: Measured flame speeds and ignition delays and a detailed chemical kinetic model for the oxidation of acetone. *Combust. Flame* 156:494–504.
  22. Akih-Kumgeh, B., and J. M. Bergthorson. 2011. Ignition of C<sub>3</sub> oxygenated hydrocarbons and chemical kinetic modeling of propanal oxidation. *Combust. Flame* 158(10):1877–1889.
  23. Chong, Ch. T., and S. Hochgreb. 2011. Measurements of laminar flame speeds of acetone/methane/air mixtures. *Combust. Flame* 158(3):490–500.
  24. Singh, H. B., D. O'Hara, D. Herlth, W. Sachse, D. R. Blake, J. D. Bradshaw, M. Kanakidou, and P. J. Crutzen. 1994. Acetone in the atmosphere: distribution, sources, and sinks. *J. Geophys. Res.* 99:1805–1819.
  25. Yujing, M., and A. Mellouki. 2000. The near-UV absorption cross sections for several ketones. *J. Photochem. Photobiol. A* 134(1-2):31–36.
  26. Vlasov, P. A., I. V. Zhiltsova, V. N. Smirnov, A. M. Tereza, G. L. Agafonov, and D. I. Mikhailov. 2018. Chemical ionization of *n*-hexane, acetylene, and methane behind reflected shock waves. *Combust. Sci. Technol.* 190(1):57–81.
  27. Agafonov, G. L., V. N. Smirnov, and P. A. Vlasov. 2011. Shock tube and modeling study of soot formation during the pyrolysis and oxidation of a number of aliphatic and aromatic hydrocarbons. *P. Combust. Inst.* 33:625–632.
  28. Gaydon, A. G., and I. R. Hurle. 1963. *The shock tube in high-temperature chemical physics*. London: Chapman and Hall. 307 p.
  29. Chang, P. M., L. Talbot, and K. J. Touryan. 1975. *Electric probes in stationary and flowing plasmas: Theory and application*. Berlin – Heidelberg – New York: Springer-Verlag. 150 p.
  30. Alekseev, B. V., and V. A. Kotel'nikov. 1988. *Zondovyy metod diagnostiki plazmy* [Probe method in plasma diagnostics]. Moscow: Energoatomizdat. 238 p.
  31. Vlasov, P. A. 2000. Probe methods of diagnostics of chemically reacting dense plasma. *Plasma diagnostics*. Eds. A. A. Ovsyannikov and M. F. Zhukov. Cambridge International Science Publishing, CISP. Ch. 12. 299–337.
  32. Calcote, H. F., and I. R. King. 1955. Studies of ionization in flames by means of Langmuir probes. *P. Combust. Inst.* 5:423–434.
  33. King, I. R., and H. F. Calcote. 1955. Effect of probe size on ion concentration measurement in flames. *J. Chem. Phys.* 23:2203–2204.
  34. Aravin, G. S., Yu. K. Karasevich, P. A. Vlasov, I. L. Pankrat'eva, and V. A. Polyanskii. 1981. Use of electric probes for studying the parameters of a dense unsteady plasma with chemical reaction. *15th Conference (International) on Phenomena in Ionized Gases Proceedings*. Minsk. 957 p.
  35. Vlasov, P. A., Yu. K. Karasevich, I. L. Pankrat'eva, and V. A. Polyanskii. 2008. Metody issledovaniya kinetiki ionizatsii v udarnykh volnakh [Research techniques of the ionization kinetics in shock waves]. *Physical-Chemical Kinetics in Gas Dynamics* 6:1–32. Available at: [www.chemphys.edu.ru/pdf/2008-12-25-001.pdf](http://www.chemphys.edu.ru/pdf/2008-12-25-001.pdf) (accessed November 29, 2019).
  36. Agafonov, G. L., V. N. Smirnov, and P. A. Vlasov. 2010. Shock-tube and modeling study of soot formation during pyrolysis of propane, propane/toluene and rich propane/oxygen mixtures. *Combust. Sci. Technol.* 182:1645–1671.
  37. Agafonov, G. L., I. V. Bilera, P. A. Vlasov, Yu. A. Kolbanovskii, V. N. Smirnov, and A. M. Tereza. 2015. Soot formation during the pyrolysis and oxidation of acetylene and ethylene in shock waves. *Kinet. Catal.* 56(1):12–30.
  38. Wang, H., X. You, A. V. Joshi, S. G. Davis, A. Laskin, F. Egolfopoulos, and C. K. Law. 2007. USC Mech Version II. High-temperature combustion reaction model of H<sub>2</sub>/CO/C<sub>1</sub>–C<sub>4</sub> compounds. Available at: [http://ignis.usc.edu/USC\\_Mech\\_II.htm](http://ignis.usc.edu/USC_Mech_II.htm) (accessed May 2007).

39. Wang, H., E. Dames, B. Sirjean, D. A. Sheen, R. Tangko, A. Violi, J. Y. W. Lai, F. N. Egolfopoulos, D. F. Davidson, R. K. Hanson, C. T. Bowman, C. K. Law, W. Tsang, N. P. Cernansky, D. L. Miller, and R. P. Lindstedt. September 19, 2010. A high-temperature chemical kinetic model of *n*-alkane (up to *n*-dodecane), cyclohexane, methyl-, ethyl-, *n*-propyl and *n*-butyl-cyclohexane oxidation at high temperatures. JetSurF version 2.0. Available at: <https://web.stanford.edu/group/haiwanglab/JetSurF/JetSurF2.0/> (accessed November 29, 2019).
40. Chen, B., H. Wang, Zh. Wang, J. Han, A. Alquaity, H. Wang, N. Hansen, and S. Sarathy. 2019. Ion chemistry in premixed rich methane flames. *Combust. Flame* 202:208–218.
41. Sato, K., and Y. Hidaka. 2000. Shock-tube and modeling study of acetone pyrolysis and oxidation. *Combust. Flame* 122(3):291–311.
42. Davidson, D. F., S. C. Ranganath, K.-Y. Lam, M. Liaw, Z. Hong, and R. K. Hanson. 2010. Ignition delay time measurements of normal alkanes and simple oxygenates. *J. Propul. Power* 26:280–287.
43. Lam, K.-Y. 2013. Shock tube measurements of oxygenated fuel combustion using laser absorption spectroscopy. Stanford, CA: Stanford University. PhD Thesis.
44. Frank, P., K. A. Bhaskaran, and Th. Just. 1986. Acetylene oxidation: The reaction  $C_2H_2 + O$  at high temperatures. *P. Combust. Inst.* 21:885–893.
45. Zhang, K., C. Banyon, C. Togbe, Ph. Dagaut, J. Bugler, and H. Curran. 2015. An experimental and kinetic modeling study of *n*-hexane oxidation. *Combust. Flame* 162:4194–4207.
46. Becker, K. H., D. Kley, and R. J. Norstrom. 1969.  $OH^*$  chemiluminescence in hydrocarbon atom flames. *P. Combust. Inst.* 12:405–413.

Received November 20, 2019

## Contributors

**Vlasov Pavel A.** (b. 1955) — Doctor of Science in physics and mathematics, leading research scientist, N. N. Semenov Federal Research Center for Chemical Physics of the Russian Academy of Sciences, 4 Kosygin Str., Moscow 119991, Russian Federation; National Research Nuclear University MEPhI (Moscow Engineering Physics Institute), 31 Kashirskoe Sh., Moscow 115409, Russian Federation; iz@chph.ras.ru

**Ryabikov Oleg B.** (b. 1943) — Candidate of Science in physics and mathematics, research scientist, N. N. Semenov Federal Research Center for Chemical Physics of the Russian Academy of Sciences, 4 Kosygin Str., Moscow 119991, Russian Federation; zaslonko@chph.ras.ru

**Smirnov Vladimir N.** (b. 1950) — Doctor of Science in physics and mathematics, chief research scientist, N. N. Semenov Federal Research Center for Chemical Physics of the Russian Academy of Sciences, 4 Kosygin Str., Moscow 119991, Russian Federation; vns1951@yandex.ru

**Mikhailov Dmitrii I.** (b. 1994) — research scientist, N. N. Semenov Federal Research Center for Chemical Physics of the Russian Academy of Sciences, 4 Kosygin Str., Moscow 119991, Russian Federation; mihalych2006@mail.ru

**Petrov Yurii P.** (b. 1944) — senior research scientist, N. N. Semenov Federal Research Center for Chemical Physics of the Russian Academy of Sciences, 4 Kosygin Str., Moscow 119991, Russian Federation; iz@chph.ras.ru