

02.1;06.1

## The features of acetylene pyrolysis in an atmosphere of inert gases in a cyclic compression reactor

© S.A. Vasiljev<sup>1</sup>, B.S. Ezdin<sup>1</sup>, L.V. Yanshole<sup>2</sup>, Yu.V. Pakharukov<sup>3</sup>, V.V. Kalyada<sup>1</sup>, F.K. Shabiev<sup>3</sup>

<sup>1</sup> Novosibirsk State University, Novosibirsk, Russia

<sup>2</sup> International Tomography Center, Siberian Branch of Russian Academy of Sciences, Novosibirsk, Russia

<sup>3</sup> Tyumen State University, Tyumen, Russia

E-mail: s.vasilev3@nsu.ru

Received November 23, 2022

Revised December 15, 2022

Accepted December 15, 2022

The pyrolysis of acetylene was studied experimentally in a cyclic compression reactor in an atmosphere of buffer inert gases (argon, neon, helium). A significant difference in the thermodynamic conditions for the complete pyrolysis of the precursor for various buffer gases was revealed. The reaction products of acetylene in neon and helium contained up to 20% of the part soluble in organic solvents. The study of the ethanol-soluble part of the product using time-of-flight mass spectrometry with matrix-assisted laser desorption/ionization made it possible to distinguish even and odd branches in the spectrum of substances by the number of carbon atoms. A mechanism is proposed for the formation of larger particles by merging smaller ones.

**Keywords:** cyclic compression reactor, acetylene pyrolysis, buffer inert gas, growth mechanism, carbon nanoparticles.

DOI: 10.21883/TPL.2023.02.55375.19436

The process of pyrolysis of hydrocarbons has a considerable application potential (clean gaseous hydrogen fuel, carbon nanoparticles) in various fields [1–3].

A piston–cylinder compression reactor is a convenient instrument for pyrolysis of hydrocarbons (specifically, acetylene). High temperatures needed for pyrolysis are established in the vicinity of the top dead center (TDC) piston position due to compression of the gas volume. An additional temperature effect is achieved in adiabatic compression of a mixture of hydrocarbons diluted with a monatomic gas.

The process of thermal decomposition of acetylene into hydrogen and soot was examined in such reactors [4,5]. Hydrogen and carbon nanoparticles with a mean size of approximately 40 nm were the primary reaction products.

The authors of [6] performed hydrocarbon pyrolysis in an inert gas (Ar, Ne, He) atmosphere under pressures up to 11 MPa and calculated temperatures  $T = 1500–2000$  K. An almost complete pyrolysis of hydrocarbons to molecular hydrogen and carbon nanoparticles was noted.

Experiments were carried out in a cyclic piston–cylinder compression reactor that was described in detail in [7,8]. Acetylene was used as a precursor. Argon, neon, and helium were buffer gases. Gaseous reactor products were analyzed with an UGA-200 universal gas analyzer. Data on the degree of acetylene decomposition are presented in the table.

Substances soluble in organic solvents were found among the products of pyrolysis of acetylene in neon and helium. Solvents were discolored to yellow. A mass loss of 15–18% was found after dissolution of the product in ethanol with subsequent solution separation by centrifugation and drying

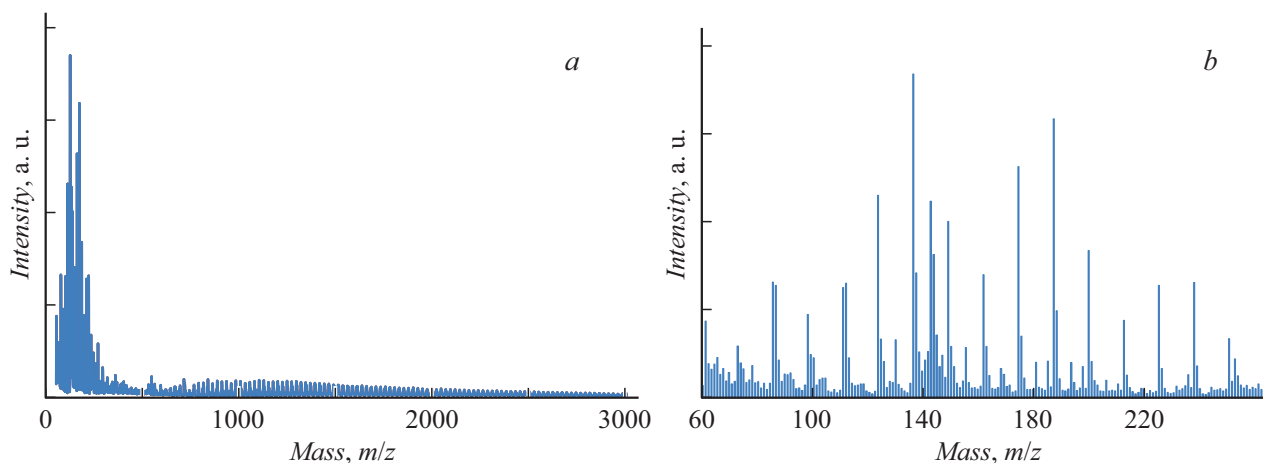
of the residue. The products of acetylene pyrolysis in argon did not have a soluble component.

The presence of a large number of various substances in soluble pyrolysis products was established by X-ray diffraction analysis, chromatography–mass spectrometry, nuclear magnetic resonance, and IR and UV spectrometry; however, the substances were not identified definitively by these methods.

The most comprehensive data were provided by time-of-flight mass spectrometry with matrix-assisted laser desorption/ionization (MALDI-TOF MS), which was performed at the Center of Collective Use „Mass spectrometric investigations“ Shared Equipment Center of the Siberian Branch of the Russian Academy of Sciences with the use of an Ultraflex III (Bruker Daltonics, Germany) MALDI-TOF/TOF spectrometer. Samples were deposited onto a standard polished metal target (MTP Bruker Daltonics) without any added matrix. Measurements were performed 3–5 min after the deposition of a sample onto a target (immediately after the solvent evaporation). Mass spectra of positive ions were recorded in the 30–4500  $m/z$  range. The product of pyrolysis of 10% acetylene in 90% neon under a pressure of 5.5 MPa was used for measurements. The solvent was ethanol (HPLC grade, J.T. Baker). Substances dissolved in ethanol and, possibly, suspended in it were subjected to examination. Figure 1 presents an example mass spectrum for this sample. A considerable fraction of substances in the spectrum is missing from the NIST database. This database contains 1209 hydrocarbon compounds in the range of 60–590 u. A total of 381 masses within this range (i.e., around 65%) lack corresponding chemical substances, but these peaks are present in the spectrum (Fig. 1, b).

Degree of acetylene decomposition (in %) under different pressures in a reactor for various buffer gases (their concentration in the mixture is also indicated)

Buffer gas	Buffer gas content, %	Pressure at TDC			
		5 MPa	7 MPa	10 MPa	11 MPa
Argon	90.0	96	—	—	—
Neon	72.0	91	96	97	98
Helium	96.4	—	—	84	90



**Figure 1.** *a* — MALDI-TOF mass spectrum of products of acetylene pyrolysis in neon; *b* — fragment of this spectrum within the 60–250  $m/z$  range.

A continuous distribution of signals with a distance of 12 u, which corresponds to a single carbon atom, between monoisotopes is seen in the spectrum. The spectrum also features two components with even and odd possible numbers of carbon atoms.

Figure 2 presents the results of processing of spectra corresponding to even and odd numbers of carbon atoms. The following approximations of experimental data are also plotted in the same figure:

$$I(N_C) \sim \exp\left(-\frac{(\ln N_C - 13.6)^2}{283}\right) / (N_C \cdot 11.9\sqrt{2\pi}) + \sin(2.2 \ln N_C + 2.15)/(165 \ln N_C), \quad (1)$$

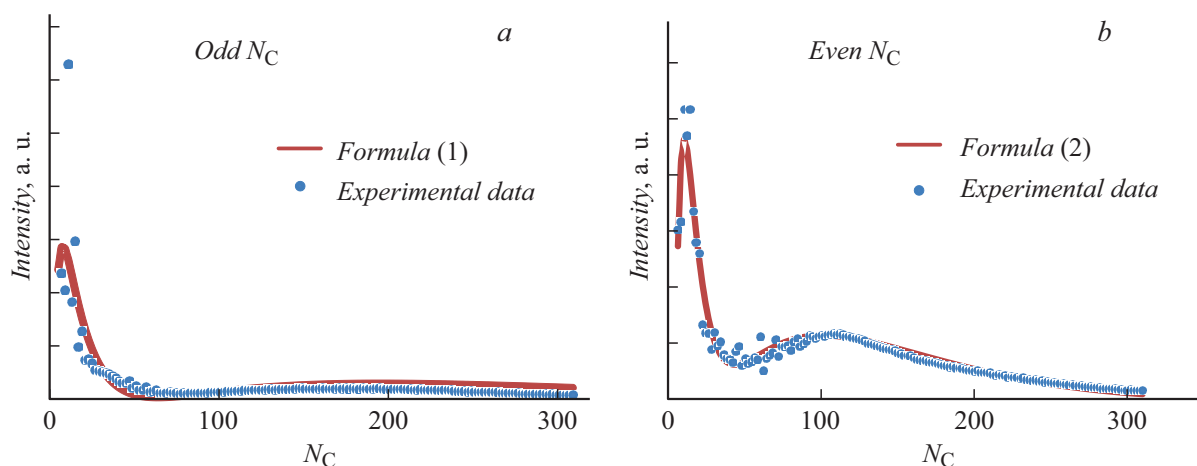
$$I(N_C) \sim \exp\left(-\frac{(\ln N_C - 15.4)^2}{66}\right) / (N_C \cdot 5.75\sqrt{2\pi}) + \sin(2.8 \ln N_C + 0.72)/(620 \ln^2 N_C). \quad (2)$$

Here,  $N_C$  is the number of carbon atoms.

Root-mean-square differences between formulae (1) and (2) the experimental data for odd and even  $N_C$  are 5.5% and 3.5%, respectively. The first term in these formulae represents a lognormal distribution that is indicative of a dependence of random-value factors. This distribution should be observed if lower-mass clusters are involved in the formation of higher-mass ones (i.e., if carbon clusters may form by incorporating both individual carbon atoms

and already formed carbon clusters). We started the search for a dependence characterizing the experimental data with the assumption of lognormality of distribution over masses, since a distribution of this kind has already been observed for carbon nanoparticles [9]. However, a well-pronounced harmonic dependence was obtained after subtraction of a lognormal distribution from the experimental data for even  $N_C$  and normalization to  $\ln(N_C)^2$ . Normalization to  $\ln N_C$  was required for odd  $N_C$ . The first maximum is at  $N_C = 10$  and 11 for even and odd  $N_C$ . It may correspond to a planar structure (two  $C_6$  rings, which have two common  $sp^2$ -hybridized carbon atoms in the former case and one common  $sp^3$ -hybridized carbon atom in the latter case). Three  $C_6$  rings may correspond to the  $N_C = 14$  and 15 peaks. The  $N_C = 108$  and  $N_C \sim 175$ –185 maxima for even and odd  $N_C$ , respectively, apparently correspond to bulk structures.

We attribute the difference in results of pyrolysis of acetylene in different buffer gases to substantially non-equilibrium exchange processes between buffer gas atoms and precursor molecules. Owing to a high concentration of buffer gas, the work on compression of a gas mixture is converted primarily into the internal energy of a buffer gas and is then transferred via collisional processes to precursor molecules. The kinetic energy acquired by precursor molecules in collisions with buffer gas atoms is redistributed over the degrees of freedom of precursor



**Figure 2.** Plots of integrated intensities of mass-spectrum peaks for odd (a) and even (b) numbers of carbon atoms.

molecules. Equilibrium is achieved first in translational and rotational degrees of freedom [10]. The processes of filling of vibrational degrees of freedom with subsequent dissociation of precursor molecules are the most important for chemical reactions. Tens of thousands of collisions of molecules and atoms of comparable masses ( $C_2H_2$  in Ar or Ne) and many times more collisions of molecules with atoms of light buffer gases ( $C_2H_2$  in He) are needed to fill vibrational levels. For example, the time of vibrational relaxation for nitrogen at a temperature of 1500 K is estimated at  $2 \cdot 10^{-4}$ – $3.8 \cdot 10^{-3}$  s [11]. This is the time lag between the temperature of vibrational degrees of freedom of a precursor and the buffer gas temperature. In helium, the time lag is even more significant. Owing to this lag, the state of precursor molecules needed for dissociation may be established only within a fairly short time interval (or not be established at all). Specifically, the time interval of pyrolysis of helium is much shorter than the one in argon.

In our view, the presence or lack of substances soluble in organic solvents is also attributable to differences in thermodynamic conditions between buffer gases. MALDI-TOF mass spectra revealed that the soluble component contains carbon clusters with a relatively low number of carbon atoms and that these clusters are involved in the formation of larger clusters. We believe that this process proceeds further, inducing the formation of carbon nanoparticles. While the characteristic times in argon are sufficiently long for pyrolysis of precursor molecules with subsequent nanoparticle growth, the time intervals in helium are too short for nanoparticle growth. The process ends with the formation of nanoparticle nuclei, which are regarded in the present study as the main constituent of the soluble component.

Neon as buffer gas assumes an intermediate position between helium and argon. Although the atomic weights of neon, argon, and acetylene are comparable, the collision cross sections of neon and argon atoms differ significantly (by a factor of 4.5); at the same time, the Bohr radii of gas

atoms [12] suggest that these cross sections for neon and helium are almost equal. A neon atom collides once within a time interval in which argon, being two times heavier, undergoes several collisions. Therefore, as in the case with helium, the temperature of vibrational levels of precursor molecules in neon may lag behind the temperature in argon, although the lag itself is much smaller in magnitude than the one corresponding to helium. The temperature range in helium is significantly restricted and may be insufficient for pyrolysis and subsequent synthesis of carbon clusters under certain conditions, while pyrolysis and synthesis reactions in neon and argon may still remain viable under the same conditions.

Owing to its high enthalpy of formation, acetylene turned out to be a universal precursor for pyrolysis in a cyclic compression reactor in an atmosphere of light helium and heavier neon and argon. We managed to achieve a nearly complete decomposition of acetylene into carbon and hydrogen within the operating pressure range of the reactor (5–11 MPa) both in argon and in lighter neon and helium. The significant difference in physical conditions needed for pyrolysis of hydrocarbons in different buffer gases was explained in the context of specific features of non-equilibrium processes of heat-exchange between a buffer gas and a precursor.

Products of reaction in neon and helium contained a significant amount of substances soluble in organic solvents. MALDI-TOF MS allowed us to characterize the soluble component of products of acetylene pyrolysis in neon.

A lognormal mass distribution of carbon particles was used as a basis for the proposed mechanism of formation and growth of carbon clusters, which are assumed to expand by incorporating smaller clusters.

## Funding

Experiments on synthesis and examination of the properties of carbon nanomaterials were supported financially by the Ministry of Science and Higher Educa-

tion of the Russian Federation (project 075-15-2020-797 (13.1902.21.0024)).

### Conflict of interest

The authors declare that they have no conflict of interest.

### References

- [1] H. Filik, A.A. Avan, Arab. J. Chem., **13**, 6092 (2020). DOI: 10.1016/j.arabjc.2020.05.009
- [2] R. Kour, S. Arya, S.-J. Young, V. Gupta, P. Bandhoria, A. Khosla, J. Electrochem. Soc., **167**, 037555 (2020). DOI: 10.1149/1945-7111/ab6bc4
- [3] D. Maiti, X. Tong, X. Mou, K. Yang, Front. Pharmacol., **9**, 1401 (2019). DOI: 10.3389/fphar.2018.01401
- [4] M.S. Vlaskin, V.M. Zaichenko, P.V. Belov, A.V. Grigorenko, A.I. Kurbatova, A.V. Eremin, V.E. Fortov, Theor. Found. Chem. Eng., **55**, 315 (2021). DOI: 10.1134/S0040579521020135.
- [5] Yu.V. Fedoseeva, K.M. Popov, G.A. Pozdnyakov, V.N. Yakovlev, B.V. Sen'kovskiy, L.G. Bulusheva, A.V. Okotrub, J. Struct. Chem., **58**, 1196 (2017). DOI: 10.1134/S002247661706018X
- [6] B. Ezdin, Yu. Pakharukov, V. Kalyada, F. Shabiev, A. Zarvin, D. Yatsenko, R. Safargaliev, A. Ichshenko, V. Volodin, Catal. Today, **397**, 249 (2022). DOI: 10.1016/j.cattod.2021.09.024
- [7] B. Ezdin, D. Yatsenko, V. Kalyada, A. Zarvin, A. Ichshenko, A. Nikiforov, P. Snytnikov, Data Brief, **28**, 104868 (2020). DOI: 10.1016/j.dib.2019.104868
- [8] B.S. Ezdin, V.V. Kalyada, D.A. Yatsenko, A.V. Ischenko, V.A. Volodin, A.A. Shklyayev, Powder Technol., **394**, 996 (2021). DOI: 10.1016/j.powtec.2021.09.032
- [9] B.S. Ezdin, S.A. Vasiljev, D.A. Yatsenko, V.E. Fedorov, M.N. Ivanova, V.V. Kalyada, Yu.V. Pakharukov, F.K. Shabiev, A.E. Zarvin, Sib. Fiz. Zh., **17** (3), 29 (2022) (in Russian). DOI: 10.25205/2541-9447-2022-17-3-29-46
- [10] A.I. Bechina, E.V. Kustova, Vestnik St. Petersburg Univ. Math., **52**, 81 (2019). DOI: 10.3103/S1063454119010035.
- [11] V.N. Komarov, O.Yu. Polyanskii, Uch. Zap. TsAGI, **9** (5), 120 (1978) (in Russian).
- [12] J.B. Mann, *Atomic structure calculations II. Hartree-Fock wave functions and radial expectation values: hydrogen to lawrencium*, report (New Mexico, 1968).