

The spectroscopic study of methane and cyclohexane transformation products in a glow discharge

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Formation of products in a glow discharge in the medium of argon with small additives (0.2–0.8 mole %) of methane and cyclohexane both with and without oxygen additives (up to 2 mole %) at a pressure of $\sim 10^{-1}$ Torr has been studied by the method of matrix IR-spectroscopy. A number of stable and labile electrically neutral intermediates have been fixed in the formed products, which allowed conclusions on methane and cyclohexane reactions proceeding in cold plasma at a low pressure. In particular, methane decay reversibility in cold plasma conditions and cyclohexane tendency to cycle decay are shown; evidences of the nonradical mechanism of formation of lower alkenes and olefin from cyclohexane in these conditions are obtained.

Introduction

At present, mechanisms and kinetics of radical-chain reactions of organic compounds in non-equilibrium conditions of electric-discharge plasma are under active study, first of all, because of the search for new nontraditional methods for hydrocarbon material processing. The majority of related works are devoted to the study of C₁–C₄ gas hydrocarbon transformation, mainly, methane. Transformation reactions of these hydrocarbons are characterized by low selectivity, which makes difficulties for their study. There are no data on mechanisms and kinetics of elementary reactions for C₆ and higher hydrocarbons.

One of the main approaches to the study of kinetics and mechanisms of chemical reactions in electric discharges is mathematical simulation. Reliable modeling requires the knowledge of the plasma composition. Such data can be obtained with the help of direct spectroscopic diagnostics.

In this work, the results are presented on the study of hydrocarbon material transformation in glow discharge plasma by means of direct spectroscopic registration of instable intermediates along with stable decay products by the matrix IR-spectroscopy technique. The technique was successfully used earlier for analyzing intermediates, originating in a microwave discharge.^{1–3}

Experiment

Experiments were carried out at a matrix-isolation setup consisting of a vacuum cryostat with a copper mirror base inside, cooled to ~ 10 K by the microcryogenic system of the closed cycle Displex CSW-208R (APD Cryogenics Inc.), reaction mixture

preparation system, and vacuum system. The cryostat pressure was measured with PMI-2 (10^{-4} – 10^{-7} torr) and PMT-2 (10^{-1} – 10^{-4} torr) gage heads. During the experiments, the cryostat pressure was about 10^{-5} torr while sputtering matrices (10^{-6} torr before and after the sputtering). The base temperature was measured with a silicon diode DT-470-SD12, attached to the base, and controlled by a temperature controller Lake Shore, Model 330-11 (Lake Shore Cryotronics, Inc.). The reaction mixture, consisting of Ar, hydrocarbon, and oxygen, passed through a quartz tube, vacuum-tight attached to the cryostat. The mixture pressure in the tube was measured with the gage head PMT-2 and maintained at $\sim 10^{-1}$ torr.

A glow discharge in the reaction mixture was ignited with the help of electrodes made of thin alfol, wound around the quartz tube. An alternating voltage of 2–15 kV with the 500–2000 Hz frequency was fed to the electrodes from a high-voltage pulse generator. The active discharge power was 1–4 W.

The used mixtures were prepared according to the standard pressure method¹ and contained 0.2–0.8 mole % of hydrocarbon (CH₄ or *c*-C₆H₁₂) and 0–2 mole % of oxygen in argon. The matrices were sputtered to the cool copper base, about 80 mm distant from the boundary of glow plasma region. IR spectra were recorded by the IR-spectrometer IFS-113v Bruker within 4000–400 cm⁻¹ interval with a 1 cm⁻¹ resolution.

Results and discussion

Methane experiments

The typical spectrum of discharge products in the Ar–CH₄ mixture is shown in Fig. 1. Characteristic absorption frequencies of the considered products are given in Table 1.

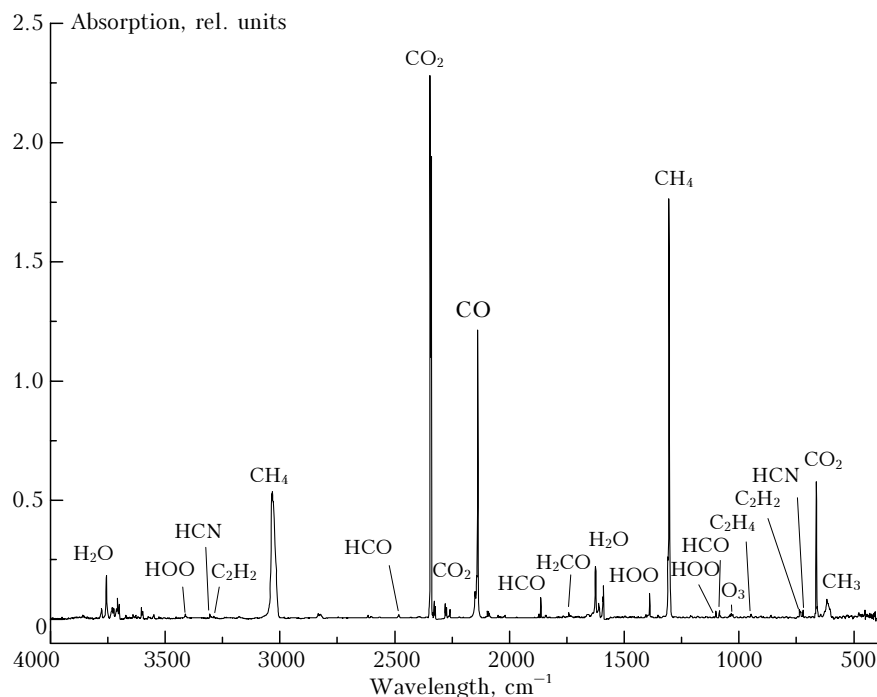


Fig. 1. Matrix IR spectrum (10 K) of discharge products (10–15 kV, 1 kHz) in the Ar–CH₄ (0.8 mole %) mixture, the amount of CH₄ passing through the reactor is 0.25 mmole.

Table 1. IR-bands recorded in the experiment and identical for the Ar–CH₄ and Ar–CH₄–O₂ mixtures

Wavelength, cm ⁻¹	Assignment	Wavelength, cm ⁻¹	Assignment	Wavelength, cm ⁻¹	Assignment
3777	H ₂ O	2834	–	1441	C ₂ H ₄
3756	H ₂ O	2798	H ₂ CO	1389	HOO
3731	–	2483	HCO	1335	C ₂ H ₂
3723	–	2345	CO ₂	1310	CH ₄
3711	H ₂ O	2339	CO ₂	1306	CH ₄
3707	–	2327	–	1299	CH ₄
3700	–	2322	–	1101	HOO
3603	–	2280	¹³ CO ₂	1086	HCO
3597	–	2274	¹³ CO ₂	1035	O ₃
3413	HOO	2259	–	948	C ₂ H ₄
3306	HCN	2139	CO	737	C ₂ H ₂
3289	C ₂ H ₂	1872	NO	735	C ₂ H ₂
3037	CH ₄	1864	HCO	731	C ₂ H ₂
3033	CH ₄	1742	H ₂ CO	721	HCN
3028	CH ₄	1624	H ₂ O	663	CO ₂
3021	CH ₄	1608	H ₂ O	661	CO ₂
2864	H ₂ CO	1590	H ₂ O	617	CH ₃

As is evident from the Table 1 and Fig. 1, the main methane decay products (IR matrix spectrum of methane is described in Ref. 4 in detail) in the absence of oxygen are acetylene⁵ and ethylene,⁶ which are recombination products of CH radical and CH₂ methylene.³ Along with these products, formation of a noticeable amount of methyl radical CH₃ was recorded^{7,8}; its formation was noticeably higher at small degrees of methane transformation, i.e., at lower frequencies and electrode voltages. This fact well agrees with an idea of methyl radical formation at the beginning stages of methane chemical transformation in low-temperature plasma

and its following destruction.⁹ The ethane, being the product of methyl radicals, was not recorded.

The pressure increase in the cryostat in a discharge indicated the formation of molecular hydrogen, non-condensable into the matrix. There always is some amount of water,¹⁰ oxygen, nitrogen, and carbon dioxide in the reaction mixture (less than 0.01 mole % of oxygen is present in the used vacuum system) due to the presence of micro-leakages in any vacuum system and the desorption of adsorbed gases from surfaces of the vacuum system and cryostat. The presence of oxygen and nitrogen has determined while discharging the formation of noticeable

amounts of carbon dioxide¹¹ and monoxide,^{12,13} as well as hydrogen cyanide¹⁴ and trace amounts of formaldehyde H_2CO [Ref. 15] (Table 1). Hydrogen cyanide is formed due to reaction of excited nitrogen molecules with CH radical, and the formaldehyde is a product of molecular and/or atomic oxygen with methylene.³ In addition, formation of H_2O [Ref. 16] and HCO [Refs. 17 and 18] radicals and ozone¹⁹ was noted. The formation of H_2O radicals indicates the presence of atomic hydrogen and/or oxygen in the reaction system.¹⁶

An addition of oxygen to the reaction mixture totally suppressed the formation of acetylene and HCN and decreased the ethylene yield, which is the evidence of the active trapping of CH radicals by oxygen-containing particles and less active trapping of CH_2 . Methyl radical bands were not revealed in the recorded spectra. At the same time, an essential intensity enhancement of H_2O and CO_2 bands of HOO and HCO radicals, as well as the formaldehyde. An amount of CO in the matrix was virtually invariable, evidently, due to its fast oxidation to CO_2 .

Thus, the carried out experiments allow the conclusion that the used experimental approach is quite promising for direct spectroscopic identification of highly reactive intermediates of the hydrocarbon transformation processes in a glow discharge.

Cyclohexane experiments

Before the discharge experiments, the matrix IR spectrum of cyclohexane (*c*- C_6H_{12}) was recorded.

The spectrum totally agrees with those earlier described^{20,21} for the mixture of “bath” and “chair” conformers (Fig. 2, Table 2). A glow discharge in the Ar-*c*- C_6H_{12} (0.3–0.4%) mixtures resulted in formation of quite complicated mixture of products at 50% conversion of *c*- C_6H_{12} . The degree of cyclohexane transformation slightly increased with enhancing voltage or discharge frequency. The main products were acetylene⁵ and ethylene,^{5,6} along with which formation of smaller amount of allene ($\text{H}_2\text{C}=\text{C}=\text{CH}_2$),²² methyl acetylene ($\text{CH}_3\text{C}\equiv\text{CH}$),²² and methane⁴ was recorded.

The above set of products indicates deep cyclohexane destruction in experimental conditions. Formation of a noticeable amount of methane is the evidence of secondary reactions of neutral or charged CH_n ($n = 2, 3$) particles with molecular or atomic hydrogen, present in the reaction mixture. In the experiments, a weak band of CH_3 radical^{7,8} was also recorded at 617 cm^{-1} and hypothetically a band of allyl radical ($\text{H}_2\text{C}=\text{CHCH}_2$)^{22,23} at 801 cm^{-1} (Fig. 3), which is evident from some enhancement of diallyl (hexa-1.5-diene) band intensity²³ while annealing matrices (35–40 K) with simultaneous band disappearance at 801 cm^{-1} due to allyl radical dimerization in diffusing in the soft matrix. In addition, there were observed weak bands of HOO [Ref. 16] and HCO [Refs. 17 and 18] radicals, bands of stable oxygen-containing products: CO_2 [Ref. 11], CO [Refs. 12 and 13], H_2CO [Ref. 15], and H_2O [Ref. 10], as well as HCN [Ref. 14] resulting from occurrence of trace atmospheric gases in the discharge zone and the matrix due to setup micro-leakages.

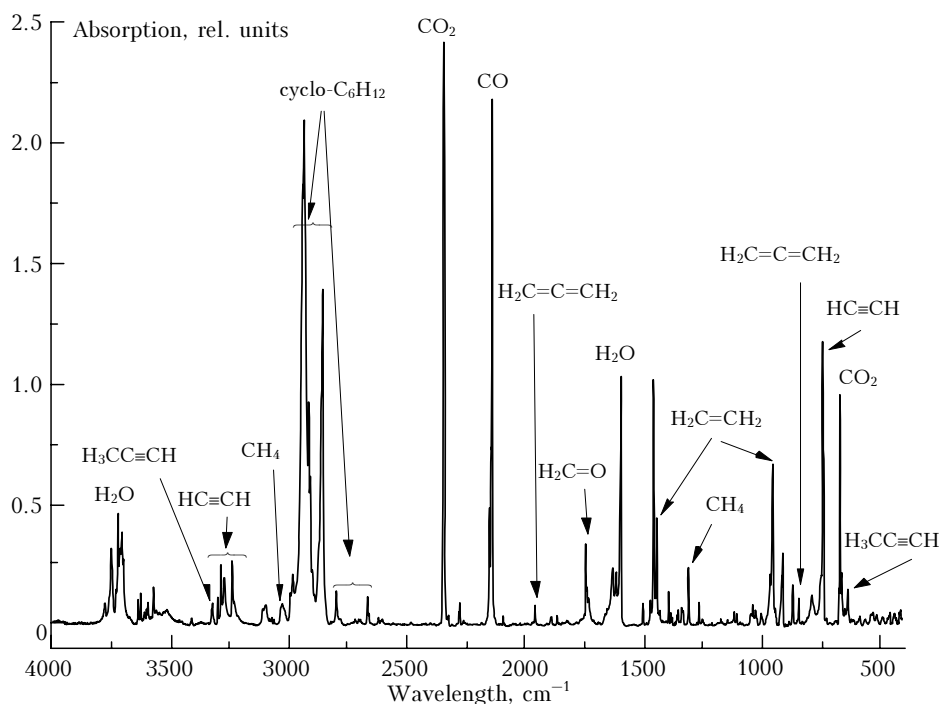
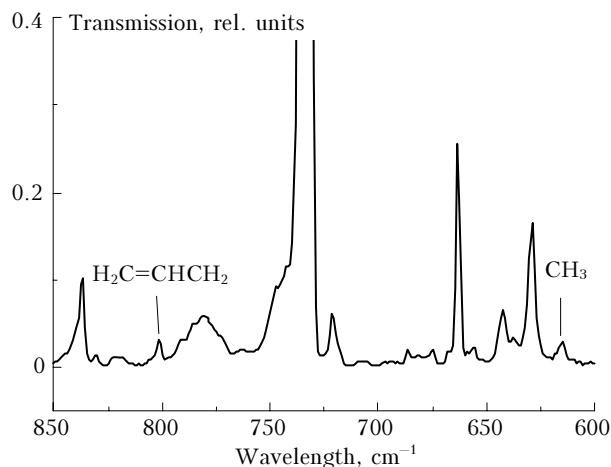


Fig. 2. The matrix IR spectrum of discharge products (10 kV, 1 kHz) in the Ar-*c*- C_6H_{12} (0.4%)– O_2 (2%) mixtures; *c*- C_6H_{12} (0.05 mmole) and O_2 (0.27 mmole) are sputtered.

Table 2. Experimentally recorded IR bands identical for the Ar-c-C₆H₁₂ and Ar-c-C₆H₁₂ O₂ mixtures

Wavelength, cm ⁻¹	Assignment	Wavelength, cm ⁻¹	Assignment	Wavelength, cm ⁻¹	Assignment
3777	H ₂ O	2666	c-C ₆ H ₁₂	1306	CH ₄
3757	H ₂ O	2660	c-C ₆ H ₁₂	1268	c-C ₆ H ₁₂
3731	—	2619	c-C ₆ H ₁₂	1260	c-C ₆ H ₁₂
3724	—	2345	CO ₂	1247	—
3712	H ₂ O	2339	CO ₂	1112	c-C ₆ H ₁₂
3707	—	2328	CO ¹⁸ O	1101	HOO
3700	—	2322	CO ¹⁸ O	1041	c-C ₆ H ₁₂
3638	—	2279	¹³ CO ₂	1023	c-C ₆ H ₁₂
3628	—	2274	¹³ CO ₂	998	—
3574	H ₂ O	2259	—	960	C ₂ H ₄
3323	CH ₃ C≡CH	2149	CO	948	C ₂ H ₄
3303	C ₂ H ₂	2143	CO	937	C ₂ H ₄
3289	C ₂ H ₂	2138	CO	913	diallyl
3276	C ₂ H ₂	1956	H ₂ C=C=CH ₂	906	c-C ₆ H ₁₂
3240	C ₂ H ₂	1863	HCO	864	c-C ₆ H ₁₂
3033	CH ₄	1742	H ₂ CO	862	c-C ₆ H ₁₂
2941	c-C ₆ H ₁₂	1624	H ₂ O	837	H ₂ C=C=CH ₂
2936	c-C ₆ H ₁₂	1608	H ₂ O	801	H ₂ C=CHCH ₂ •
2929	c-C ₆ H ₁₂	1593	H ₂ O	781	—
2916	c-C ₆ H ₁₂	1590	H ₂ O	737	C ₂ H ₂
2908	c-C ₆ H ₁₂	1467	c-C ₆ H ₁₂	731	C ₂ H ₂
2901	c-C ₆ H ₁₂	1454	c-C ₆ H ₁₂	721	HCN
2898	c-C ₆ H ₁₂	1450	c-C ₆ H ₁₂	663	CO ₂
2874	c-C ₆ H ₁₂	1440	C ₂ H ₄	642	—
2863	c-C ₆ H ₁₂	1389	HOO	629	CH ₃ C≡CH
2856	c-C ₆ H ₁₂	1380	C ₄ H ₁₀ ?	617	CH ₃
2798	c-C ₆ H ₁₂	1335	C ₂ H ₂	522	c-C ₆ H ₁₂

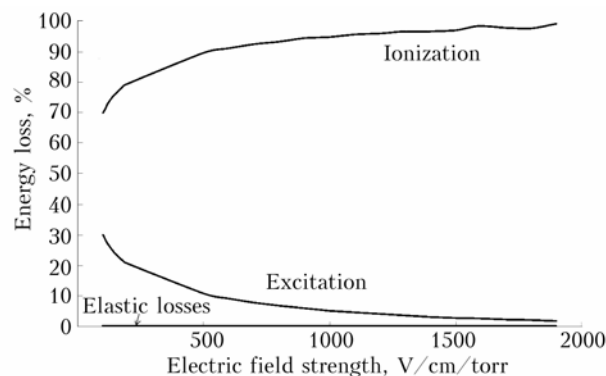
**Fig. 3.** The fragment of matrix IR spectrum of discharge products (10 kV, 1 kHz) in the Ar-c-C₆H₁₂ (0.4%)–O₂ (2%) mixtures.

Addition of oxygen (up to 2%) in the reaction mixture does not influence the formation of the above-listed ethylenes and alkynes. Along with this, bands of methyl and allyl radicals and hydrogen cyanide disappeared from the spectrum, while the yield of oxygen-containing products increased noticeably. Weak influence of oxygen additives on the yield of unsaturated organic compounds evidences mainly nonradical ways of their formation. In particular, in contrast to the discharge in methane

mixtures (see above), the dimerization of CH and CH₂ could be the main way of acetylene and ethylene formation.

At the same time, similarly to the methane case, HCN formation without oxygen and its disappearance in the presence of oxygen in cyclohexane experiments assume the presence of CH radicals in the reaction mixture, yielding hydrogen cyanide in the interaction with excited nitrogen molecules.³

Thus, the used conditions turned out to be too rigid for direct recording of primary discharge intermediates formed from cyclohexane. This is confirmed by the theoretically calculated electron energy loss spectrum in a glow discharge (Fig. 4).

**Fig. 4.** Electron energy losses in a glow discharge for the mixture of Ar (99%) with CH₄ (1%) at 0.1 torr.

Mathematical simulation with the use of BOLSIG software complex²⁴ has shown an electron energy of about 80 eV to be attained in the used conditions. The concentration of reactive charged particles in the reaction zone at the high electron energy is extremely high and, as is expected, plasma chemical reactions are controlled by reactions of not radical but charged particles.²⁵ Nevertheless, the used approach for the first time allowed the direct spectroscopic recording of a number of radical particles, formed from cyclohexane (CH₃ and, hypothetically, allyl radicals) or while interacting cyclohexane decay products with oxygen (HOO, HCO). Indirect data (NCH formation) have been also obtained, which evidence the CH radicals formation while decaying cyclohexane in glow discharge conditions.

Acknowledgements

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