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SPECTROSCOPIC STUDIES OF COMBUSTION
ZONES IN FLAME OF CONDENSED SYSTEMS

V. M. Maltsev, et al

Foreign Technology Division
Wright-Patterson Air Force Base, Ohio

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U. S. BOARD ON GEOGRAPHIC NAMES TRANSLITERATION SYSTEM

Block	Italic	Transliteration	Block	Italic	Transliteration
А а	<i>А а</i>	A, a	Р р	<i>Р р</i>	R, r
Б б	<i>Б б</i>	B, b	С с	<i>С с</i>	S, s
В в	<i>В в</i>	V, v	Т т	<i>Т т</i>	T, t
Г г	<i>Г г</i>	G, g	У у	<i>У у</i>	U, u
Д д	<i>Д д</i>	D, d	Ф ф	<i>Ф ф</i>	F, f
Е е	<i>Е е</i>	Ye, ye; E, e*	Х х	<i>Х х</i>	Kh, kh
Ж ж	<i>Ж ж</i>	Zh, zh	Ц ц	<i>Ц ц</i>	Ts, ts
З з	<i>З з</i>	Z, z	Ч ч	<i>Ч ч</i>	Ch, ch
И и	<i>И и</i>	I, i	Ш ш	<i>Ш ш</i>	Sh, sh
Й й	<i>Й й</i>	Y, y	Щ щ	<i>Щ щ</i>	Shch, shch
К к	<i>К к</i>	K, k	Ъ ъ	<i>Ъ ъ</i>	"
Л л	<i>Л л</i>	L, l	Ы ы	<i>Ы ы</i>	Y, y
М м	<i>М м</i>	M, m	Ь ь	<i>Ь ь</i>	'
Н н	<i>Н н</i>	N, n	Э э	<i>Э э</i>	E, e
О о	<i>О о</i>	O, o	Ю ю	<i>Ю ю</i>	Yu, yu
П п	<i>П п</i>	P, p	Я я	<i>Я я</i>	Ya, ya

* ye initially, after vowels, and after ъ, ь; e elsewhere. When written as ѣ in Russian, transliterate as yě or ě. The use of diacritical marks is preferred, but such marks may be omitted when expediency dictates.

FOLLOWING ARE THE CORRESPONDING RUSSIAN AND ENGLISH
 DESIGNATIONS OF THE TRIGONOMETRIC FUNCTIONS

Russian	English
sin	sin
cos	cos
tg	tan
ctg	cot
sec	sec
cosec	csc
sh	sinh
ch	cosh
th	tanh
cth	coth
sch	sech
csch	csch
arc sin	sin ⁻¹
arc cos	cos ⁻¹
arc tg	tan ⁻¹
arc ctg	cot ⁻¹
arc sec	sec ⁻¹
arc cosec	csc ⁻¹
arc sh	sinh ⁻¹
arc ch	cosh ⁻¹
arc th	tanh ⁻¹
arc cth	coth ⁻¹
arc sch	sech ⁻¹
arc csch	csch ⁻¹
—	
rot	curl
lg	log

GREEK ALPHABET

Alpha	A	α	•	Nu	N	ν
Beta	B	β		Xi	Ξ	ξ
Gamma	Γ	γ		Omicron	Ο	ο
Delta	Δ	δ		Pi	Π	π
Epsilon	Ε	ε	•	Rho	Ρ	ρ
Zeta	Ζ	ζ		Sigma	Σ	σ
Eta	Η	η		Tau	Τ	τ
Theta	Θ	θ	•	Upsilon	Υ	υ
Iota	Ι	ι		Phi	Φ	φ
Kappa	Κ	κ	•	Chi	Χ	χ
Lambda	Λ	λ		Psi	Ψ	ψ
Mu	Μ	μ		Omega	Ω	ω

SPECTROSCOPIC STUDIES OF COMBUSTION ZONES IN FLAME OF CONDENSED SYSTEMS

V. M. Mal'tsev, A. G. Stasenko, B. A. Seleznev,
P. F. Pokhil
(Moscow)

Spectroscopic studies on identifying and qualitatively estimating the intermediate products in the combustion process have had a substantial influence on the development of the theory of chain reactions and chemical kinetics [1-3]. At the present time spectroscopic studies are interesting from the standpoint of studying the reaction mechanisms in a flame when condensed systems are burned.

In the present study we pose the problem of identifying the flame radiation spectrum of condensed systems, establishing the distribution of revealed products with respect to the height of the flame, and, if possible, establishing their degree of participation in the combustion process.

We studied the flame radiation spectrum of hexogen, a model mixed composition based on ammonium perchlorate and polymethylmethacrylate, and nitrocellulose. Specimens of the studied composition were burned in a constant pressure bomb in a range of from 1 to 40 atm in a medium of nitrogen and argon.

The burning specimen was photographed in order to estimate the nature of combustion (dimensions of combustion zones, flame structure). The flame which formed during combustion was studied by two spectral methods - photographic and photoelectric [4]. The photographic method is more useful in obtaining a general pattern of the spectrum in measuring wavelengths and in identifying the spectra. The photoelectric method was used primarily for quantitative measurements of spectrum intensity.

Two spectrographs were used in the study: the ISP-51 [ИСП-51] (working range 3600-10,000 Å) and the ISP-28 (wavelength range 2000-6000 Å). The radiation spectrum obtained at the spectrograph output could be recorded on film or on a drum attachment, set in motion through the reduction gear of the motor.

Another goal of the present work, in addition to identifying radiation spectrums, was to establish the distribution of revealed products along the flame. The photographic method used for this consisted of illuminating the burning fuel specimen from behind by a mercury light source through an interference filter, which cut out a narrow spectral range near the 4358 Å line. The fuel specimen and the image of the mercury source were focused on the spectrograph slit. The flame spectrum of the fuel and the mercury line were simultaneously registered through the spectrograph slit at a certain exposure time. The unburned part of the specimen overlapped the light of the mercury lamp, and this was used to determine the position of the fuel surface on the photographic film. By comparing the place by which the flame components began to radiate with the initial radiation point of the mercury line it was possible to obtain a spatial type boundary between the component and the fuel surface.

Combustion of Condensed Systems

A characteristic of the combustion of condensed systems is the multistage nature of the conversion of the original substance

into the final products.

Figure 1 shows the temperature distribution without nitrocellulose with respect to flame height, obtained by the infrared pyrometry method of [5]. The rapid rise in temperature near the charge surface of the nitrocellulose is caused by the completion of the decomposition reaction of the dispersed mass of the condensed phase.[6], and this agrees with the results obtained from measuring the transparency of the flame in [7]. In the second flame zone we observe an insignificant increase in temperature ("dark zone") above which (already in the third zone) there is a significant increase in temperature, which is caused by exothermal reactions at a high rate of heat liberation. In the third zone temperature reaches its maximal value. Characteristic is the presence on the temperature curves of a plateau, which as pressure rises degenerates into a barely noticeable hump, and at higher pressures disappears altogether. Here the maximal temperature zone approaches the specimen-fuel surface.

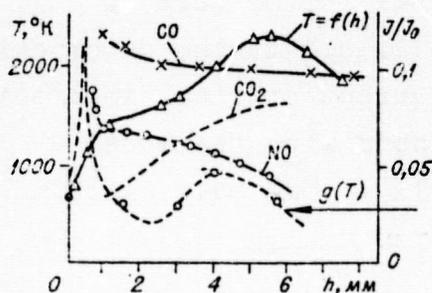


Figure 1. Temperature distribution, functions of $g(T)$ and relative intensity of CO , CO_2 , and NO with respect to flame height of nitrocellulose, $p=30$ atm.

Processing the temperature profiles obtained by the thermocouple method of [8] in the condensed fuel phase and by the infrared pyrometry method of [5] in the smoke-gas and gas zones of the flame [4] made it possible to calculate heat liberation resulting from chemical reactions in each of the flame zones and heat conduction from the smoke-gas zone into the condensed phase as a function of pressure. If we study the $g(T)$ curve in Fig. 1, we see that the rate of heat liberation reaches its first

maximum in the reaction layer of the condensed fuel phase. The second maximum in the rate of heat liberation lies at a certain distance from the charge surface and is caused by the intensive decomposition of the dispersed fuel mass. Thereafter the value of this function decreases, then rises again, reaching its third maximum in the maximal temperature zone of the flame.

Nitrocellulose. Studies on the decomposition kinetics of nitrocellulose [9] have revealed that the first possible act of decomposition is the separation of NO_2 from the nitrocellulose molecule, as a result of which the nitrogen dioxide and atomic oxygen, obtained from the breaking of the O-NO_2 chain, enter into a reaction with the powder residue and produce other decomposition products - NO_2 , CO_2 , CO , H_2O , N_2 . The composition and quantitative yield of the decomposition products of nitrocellulose were studied in [10]. Spectroscopically determined in [9] was the concentration of NO_2 in the decomposition products of nitrocellulose at inert gas flows at a temperature of 135°C . It was shown that 40-50% of the nitrogen exists in the form of NO_2 . It should be mentioned that since nitrocellulose at the decomposition temperature is in a solid state, a current-chemical decomposition can occur within it, which is associated with the local formation and development of its nuclei [11]. The main emitting agents of the flame have been established:

CO_2 , CO , NO , NO_2 , N_2H_2 , O_2 , OH , CN , C_2 .

Essential in studying the problem of flame radiation is the particular place marking the beginning of luminescence in certain components in the products with respect to the surface of the specimen. Figures 1 and 2 show the distribution of the main components with respect to flame height for nitrocellulose at a pressure of 30 atm (I/I_0 is the ratio of the intensity of the studied spectral line to the intensity of the mercury source line $\lambda=4358 \text{ \AA}$). With respect to flame height at a distance

of 0.5-0.7 mm from the combustion surface the radical OH becomes luminous. In the "dark zone" at a height of 1.5-2 mm the radical CN is intensely luminous. This is apparently related to the increased concentration of bound nitrogen in the decomposition products of the nitrocellulose. The C_2 radical appears near the maximal temperature zone. In addition to the indicated radicals, the decline in CO and NO and the increase in the concentration of CO_2 , H_2 and N_2 with respect to flame height are recorded.

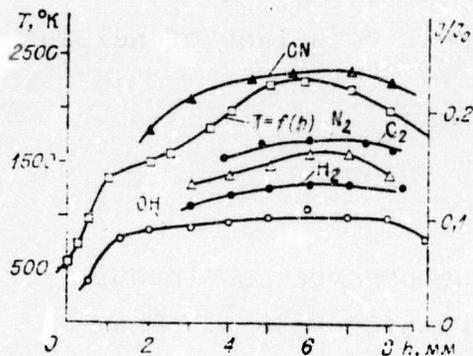


Figure 2. Distribution of temperature and relative intensity of CN, N_2 , H_2 , and OH with respect to the flame height of nitrocellulose, $p=30$ atm.

The radiation spectrum of the nitrocellulose flame differs greatly from the spectrum of the studied composition by its significant increase in the intensity of the continuum, corresponding to reactions $NO-O \rightarrow NO_2 + hv$ and $CO-O \rightarrow CO_2 + hv$. This can be explained by the presence of a considerable amount of nitrogen oxides, as well as CO and CO_2 , in the decomposition products of the nitrocellulose.

Hexogen. Data for the thermal decomposition of hexogen [12] indicate that in a pressure range of up to 1 atm at temperatures from 213 to 299°C the main decomposition products are H_2 , NO, CO_2 , N_2O , N_2 , CO. The distribution of temperature and detected combustion products with respect to flame height in hexogen at a pressure of 38 atm is shown in Fig. 3. On the immediate combustion surface of the hexogen specimen we observe an intense radiation on the part of radical OH. At a distance of 0.1 mm

radiation intensity reaches its maximal value, and changes only slightly farther up the flame. The luminescence of radicals C_2 , CN, CN [sic] appears at a distance of 0.1-0.2 mm from the combustion surface and increases noticeably in the direction of the maximal temperature zone of the flame.

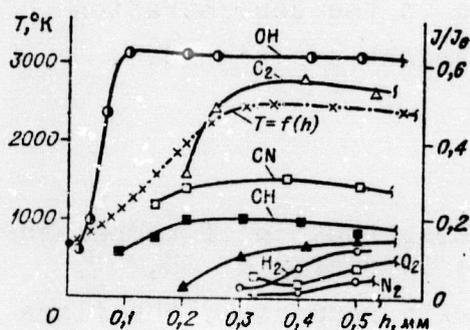


Figure 3. Distribution of temperature and relative intensity of OH, C_2 , CN, CH, H_2 , O_2 , N_2 with respect to height of hexogen flame, $p=30$ atm.

In addition to the indicated bands we observe continuous spectrums in the ranges of $5200-6000 \text{ \AA}$ and $3400-4500 \text{ \AA}$. The first spectrum may also belong to the reaction $NO+O \rightarrow NO_2+h\nu$, while the second belongs to $CO+O \rightarrow CO_2+h\nu$.

Ammonium perchlorate+polymethylmethacrylate. A great number of experimental studies [13, 14] have been dedicated to the thermal decomposition of ammonium perchlorate. We can assume that Cl_2 , O_2 , H_2O , NO, HCl, HClO represent the main decomposition products. Figure 4 shows the distribution of temperature and the main detected combustion products with respect to flame height. It should be mentioned that near the charge surface we observe intensive luminescence on the part of radical OH, which exceeds the luminescence of radicals C_2 and CN. The considerable intensity of the OH band can be explained by the intensive formation of O and H as the active intermediate products of the decomposition of the mixture. In the radiation spectrum, just as in the case of nitrocellulose and hexogen, two intensive continuums are revealed in the ranges of $3400-4500 \text{ \AA}$ and $4000-6000 \text{ \AA}$.

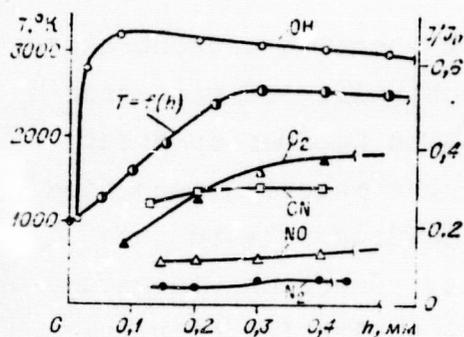


Figure 4. Distribution of temperature and relative intensity of OH, C_2 , CN, NO, and N_2 with respect to flame height for ammonium perchlorate-polymethylmethacrylate composition.

Discussion of Results

In the decomposition of the condensed phase of the studied compositions a fuel mixture is formed, and the oxidation-reduction reactions which occur among the components with significant heat liberation initiate the flame, creating an extended combustion zone with a certain temperature distribution. Now let us turn to the mechanism of reactions in the gas phase.

V. N. Kondrat'yev [1] proposes two different oxidation mechanisms for the hydrocarbons in the combustion range and the slow oxidation range. Since OH, CH, C_2 , and CO bands, which indicate the presence of atomic oxygen in the combustion zone, are characteristic of the usual hot-hydrocarbon flames, atoms and radicals are the greatest contributors to the development of reactions in the gas phase of hydrocarbon flames.

This stage mechanism was also spectroscopically established by the presence in the flame of both complete oxidation products and intermediate products. In the opinion of V. N. Kondrat'yev this stage characteristic is of a probability nature, in that under conditions of slow oxidation of a hydrocarbon we observe processes which occur with the least expenditure of energy, particularly the direct connection process (the processes of free radical and atom formation are suppressed in this case). However, under hot flame conditions processes occur in which

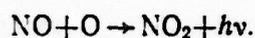
free radicals and atoms participate, since when the concentration of active centers is high the relative probability of processes occurring with atom and radical participation becomes so great that there occurs a qualitative change in the reaction mechanism. From this standpoint we must ascribe the leading role in the combustion mechanism to atoms and radicals. Reactions in which they participate are associated with small activation energies, which, according to the quantum mechanics idea of an elementary chemical act, are necessary for the conversion of the activated complex from one quantum state to another. The mechanism of converting the chemical energy which is liberated in the elementary chemical act into electron excitation energy has not yet been fully explained.

Studied in [2] are the two mechanisms of conversion of chemical energy into electron excitation energy. The condition which determines any of the indicated excitation mechanisms is that of a thermal effect in the reaction sufficient for exciting the appropriate radiation. This is essential in the case of the exchange mechanism, where the excitation process is related to the breaking of the chemical bonds, i.e., to a loss of energy. Thus, this mechanism should be assumed only in those cases where chemical unstable molecules participate in it.

The experimental results on identifying the flame radiation spectrum of condensed systems (nitrocellulose, hexogen, ammonium perchlorate+polymethylmethacrylate) presented in this study indicate the existence in the flame of radicals OH, CH, CN, C₂, NH and the final products characteristic of the radiation of hydrocarbon flames.

Now let us look at the general spectral regularities observed in the combustion products of hexogen, nitrocellulose, and ammonium perchlorate+polymethylmethacrylate.

In the spectrums of the radiated flames we observe an unbroken radiation continuum from 4000 to 6000 Å, as well as a continuum from 3400 to 4500 Å. In [3] it was demonstrated that the radiation of the 4000-6000 Å continuum is related to the reaction between the nitric oxide and the free oxygen atoms



The energy liberated in this reaction constitutes 72 Cal/mole. The reaction is of even broader interest in that the appearance of the continuum in the radiation spectrum is an indicator for the presence of atomic oxygen in the flame.

The luminescence of the second continuum in the combustion products should belong to the reaction $\text{CO} + \text{O} \rightarrow \text{CO}_2 + h\nu$, which also enables us to determine the presence of free atomic oxygen in the flame.

Now let us dwell on the problem of free oxygen appearing in the flame. Some authors [1] believe that for atomic oxygen to develop any random process is sufficient. In the case of condensed combustion one of the main products of the decomposition of the solid phase is nitrous oxide. The decomposition of N_2O molecules occurs according to the following mechanism: $\text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O} - 53$ Cal/mole. Due to the fact that under flame conditions the N_2O molecule can acquire such energy within a certain flame zone, i.e., within a certain temperature interval, we should consider the decomposition reaction of N_2O one possible source of oxygen atoms. The continuation of the second state of the reaction under flame conditions can apparently be rather diverse, for example, $\text{O} + \text{O} + \text{M} \rightarrow \text{O}_2 + \text{M} + 117$ Cal/mole, It is possible that the third participant in the collision is one of the molecules which has a greater probability of reaction with O than does O with O. Other double collisions are possible, for example, $\text{O} + \text{NO}_2$ and $\text{O} + \text{H}_2 \rightarrow \text{OH} + \text{H}$.

As already mentioned, the radical OH has relatively intense radiation in the combustion products near the specimen surface. Farther up the flame the radiation of CH, CN and C₂ exceeds the value one might expect in establishing thermodynamic and chemical equilibrium. Apparently the very intense radiation of these radicals can be caused by chemiluminescence (chemical reaction in the flame which results in the formation of the radicals found in excited electron states).

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