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COMBUSTION OF NITRIC AND NITROUS ACID ESTERS

B. N. Kondrikov, et al

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B. N. Kondrikov, T. T. Sidorova

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П п	*П п*	P, p	Я я	*Я я*	Ya, ya

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COMBUSTION OF NITRIC AND NITROUS ACID ESTERS

B. N. Kondrikov and T. T. Sidorova

Moscow

The combustion of nitric acid esters is of particular technical interest and, moreover, is a source of information about the operational mechanism in mixtures, containing nitrogen peroxide as an oxidizing agent. Useful information can also be obtained during the combustion of nitrous acid esters, for which, in view of the relative inertness of NO, the pattern is often simpler.

The esters were obtained by the methods described in literature [1, 2], and were usually vacuum distilled, by removing the middle fraction (approximately half of the total amount). The nitrites were stored in the condenser and were used for carrying out experiments, as a rule, within a period of 2-3 days after they were produced. The experiments were carried out in a nitrogen atmosphere in a constant-pressure bomb having up to 400 at. The liquid explosives were poured into small quartz glass beakers 8-10 mm in diameter and 40-50 mm in height with glass walls 1-2 mm thick and were ignited with a wire heated by an electric current. The solid substances were pressed to a high density in small plexiglas tubes 4 or 7 mm in diameter. The combustion rate was determined employing a photographic recorder.

1. The results of the experiments on the combustion of nitrites were recently published [3]. They show, that combustion takes place in two main stages, in the first of which the nitrite is decomposed, in the second - the decomposition products react with the liberation of heat. This conclusion is confirmed by the following data. The decomposition products of a mixture of EGDN[1] and 2,3-BGDN and pure 1,2-PGDN are identical (Table 1). The combustion rates of EGDN and 1,2-PGDN differ considerably, and 2,3-BGDN in its pure form generally does not burn. At the same time the combustion rates of a mixture of EGDN with 2,3-BGDN and pure 1,2-PGDN in the entire investigated pressure range (50-300 at) are completely identical. There are also data in literature. It was demonstrated in work [4], that the combustion of methyl nitrite near the mouth of a burner yields only NO, CH_2O, and CH_3OH - the usual products of thermal decomposition [5]. In the subsequent stages they disappear, converting into the final combustion products (H_2, H_2O, CO, N_2, and others).

The most probable decomposition products of the investigated nitrites in accordance with kinetic works [2, 4-6] are cited in Table 1. It is possible to note, that formaldehyde occupies a special position among the decomposition products. Actually, among the investigated nitrites, only those in the decomposition products of which CH_2O is present are capable of combustion. The 1,3- and 2,3-butylene glycol dinitrites, which upon decomposition do not yield formaldehyde, but acetaldehyde, are not capable of independent combustion, whereas 1,4-BGDN, the probable decomposition products of which by analogy with 1,4-BGDNa are formaldehyde and ethylene [7], burns stably. Ethyl nitrite, which with respect to the oxygen balance is close to 1,3- and 2,3-BGDN, is also capable of combustion,

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[1] Arbitrary designations: EGDN - ethylene glycol dinitrite, 1,2- and 1,3-PGDN - 1,2- and 1,3-propylene glycol dinitrites, BGDN - butylene glycol dinitrite; GDN - glycol dinitrate, NGC - nitroglycerin; GCDN - glycerin dinitrate, DEGDN - diethylene glycol dinitrate, 1,2- and 1,3-PGDNa - 1,2- and 1,3-propylene glycol dinitrates, BGDNa - butylene glycol dinitrate; ETN - erythritol tetranitrate, MHN - manitol hexanitrate, GAN - glycolic acid nitrate.

but in contrast to them is capable of decomposition with the formation of formaldehyde. A mixture of EGDN with 10% hexane, in whose decomposition products there is more formaldehyde, burns more rapidly than 1,3- and even more so than 2,3-PGDN.

Table 1

(1) Нитриты	α	(2) u (при 200 ат), см/сек	(3) Продукты термораспада [2, 4—6]
(4) Метилнитрит	0,57	(1,7)*	CH_3OH, $H\cdot$, CH_2O
(5) ЭГДН	0,66	(1,18)*	CH_2O
(6) ЭГДН+10% гексана	0.45	0,43	$2CH_2O+1/6\ C_6H_{14}$
(7) 1,3-ПГДН	0,44	0,38	$CH_2O+C_2H_4+NO_2$
(8) Этилнитрит	0,31	0,35	CH_2O+CH_3
(9) 1,2-ПГДН	0,44	0,30	$CH_3CHO+CH_2O$
(10) 2,3-БГДН+ЭГДН	0,44	0,30	$CH_3CHO+CH_2O$
(11) 1,4-БГДН	0,33	0,25	$2CH_2O+C_2H_4$**
(12) ЭГДН+19% гексана	0,33	0,19	$2CH_2O+1/3C_6H_{14}$
(13) 1,3-БГДН	0,33	Не горит	$CH_3CHO+C_2H_4+NO_2$
(14) 2,3-БГДН	0,33	Не горит	CH_3CHO

Note. The value with the asterisk is an extrapolation; the two asterisks are another type of decomposition: $ONOCH_2CH_2CH_2CH_2ONO = OCHCH_2CH_2CH_2OH + NO + NO_2$ [2]. Upon the decomposition of all nitrites the formation of NO is assumed.

KEY: (1) Nitrites; (2) u (at 200 at), cm/s; (3) Thermodecomposition products [2, 4-6]; (4) Methyl nitrite; (5) EGDN; (6) EGDN + 10% hexane; (7) 1,3-PGDN; (8) Ethyl nitrite; (9) 1,2-PGDN; (10) 2,3-BGDN + EGDN; (11) 1,4-BGDN; (12) EGDN + 19% hexane; (13) 1,3-BGDN; (14) 2,3-BGDN; (15) Does not burn.

Apparently the reactions of the atoms and the radicals play an essential role in the combustion of the decomposition products. Ethyl nitrite, when p is greater than 100 at, burns only in the presence of NO_2, or substances (1-1.5%), which yield NO_2 upon decomposition - ethyl nitrate or methyl nitrate. In accordance with the data of [4] in the presence of 2% NO_2 an equimolecular mixture of CH_2O with NO becomes capable of combustion.

It is possible to assume, that the main particle responsible for flame propagation in the combustion of organic nitrites, is atomic hydrogen. The possible reactions with its participation are [4, 8]:

$$R\cdot + CH_2O \rightarrow RH + CO + H\cdot$$
$$H\cdot + CH_2O \rightarrow H_2 + CO + H\cdot$$
$$H\cdot + NO \rightarrow HNO$$
$$HNO + NO \rightarrow N_2 + HO;$$

In the first of these formaldehyde yields an atom of hydrogen. In the second, regeneration of the latter occurs. Finally, the third and fourth reactions lead to the reduction of NO to N_2. It is easy to see that the other decomposition products, enumerated in Table 1 (acetaldehyde, ethylene), do not yield and do not regenerate atomic hydrogen and, accordingly, burn more poorly than formaldehyde.[1]

2. Let us examine the combustion of nitroesters. The dependence of the combustion rate of almost all the liquid nitrates on pressure is close to directly proportional. ETN reveals an analogous dependence. An exception is DEGDN and, at 30-80 at, ethyl nitrate, for which the dependence of combustion rate on pressure is weaker.

The combustion rates of nitrates at 30 at are presented in Table 2. In general, approximately the same regularities are observed as for nitrites. An equimolecular mixture of GDN and 2,3-BGDHa, yielding upon decomposition the same products, as 1,2-PGDNa, burns at a rate close to that for the latter. It is possible to assume, that in the case of nitroesters decomposition with the

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[1] In view of the high reactivity of nitrites, during their combustion other reactions are also possible: interaction with aldehydes, formed upon decomposition, or added to the nitrite (benzaldehyde is especially effective), reactions of NO with C-nitroso-compounds, and perhaps also with nitrite itself with the formation of N_2 and NO_2. This can also be possibly explained by the drop in combustion rate with pressure, observed for the majority of nitrites in the 80-150 at pressure range [3].

formation of NO_2 and organic products is the first stage of combustion. Subsequently, however, the interaction of NO_2 not only with these products is possible, but also with the nitrate itself [7].

Table 2

(1) Нитраты	α	(2) $u_м$ (при 30 ат), г/см²·сек	(3) Продукты термораспада [7, 14]
(4) НГЛ	1,0	(1)*	CH_2O
(5) ДНПГ-1,3	0,67	0,41	$(CH_2)_2O^{**}+CH_2O$
(6) 2,3-ДНБГ+НГЛ	0,67	0,37	$CH_3CHO+CH_2O$
(7) ДНПГ-1,2	0,67	0,36	$CH_3CHO+CH_2O$
(8) ДНГЦ	0,78	0,36	$CH_2OHCHO^{**}+CH_2O$
(9) ДНБГ-1,4	0,50	0,30	$2CH_2O+C_2H_4$
(10) Этилнитрат	0,46	0,27	CH_2O+CH_3
(11) Оксиэтилнитрат	0,62	0,27	CH_2O+CH_2OH
(12) ДНБГ-1,3	0,50	0,20	$(CH_2)_2O^{**}+CH_3CHO$
(13) ДНБГ-2,3	0,50	0,17	CH_3CHO

Note. The value with the asterisk is an extrapolation; the two asterisks mean not experimentally confirmed. In all cases NO_2 also forms upon decomposition.

KEY: (1) Nitrates; (2) u_m(at 30 at), g/cm²·s; (3) Thermodecomposition products [7, 14]; (4) GDN; (5) 1,3-PGDNa; (6) 2,3-BGDNa + GDN; (7) 1,2-PGDNa; (8) GCDN; (9) 1,4-BGDNa; (10) Ethyl nitrate; (11) Oxyethyl nitrate; (12) 1,3-BGDNa; (13) 2,3-BGDNa.

The role of formaldehyde is also great. The combustion rate of 1,4-BGDN is one and a half times higher than 1,3-BGDNa and 2,3-BGDNa. In the combustion products of the former [7] there is much CH_2O, in the decomposition products of the latter there is none. The combustion rate of ethyl nitrate, which also yields formaldehyde, is one and a half times higher than 1,3-BGDNa and 2,3-BGDNa, although it is also somewhat less than 1,4-BGDNa. Oxyethyl nitrate burns at the same rate as ethyl nitrate. The decomposition products of these substances contain one and the same quantity of CH_2O and NO_2, only instead of methyl upon the decomposition of oxyethyl nitrate, probably, the radical CH_2OH is formed (at 100 at, carboxymethyl nitrate is also close to them). GCDN burns at the same rate as

1,2-PGDNa. Their decomposition products contain the same quantity of CH_2O and NO_2, the difference consists only in the fact, that 1,2-PGDNa yields acetaldehyde, and GCDN, apparently, - glycol aldehyde.

It is interesting to compare the combustion rates of nitrates of the nitroglycerin series with each other. At moderate (up to 100-150 at) pressure, NGC has the highest combustion rate, then follow methyl nitrate, MHN, ETN, and GDN. For the extreme members of the series the rates differ by 3-4 times. MHN is close to NGC, and ETN - to GDN.

MHN and ETN revealed a characteristic, not observed earlier for explosive substances. At 150-200 at, a sharp increase in the dependence of their combustion rate on pressure occurred. The exponent ν in the formula $u = Bp^{\nu}$ increased from 1.0 up to 1.5-1.7. The rapid increase in rate continued over a range of ~50 at, after which ν again decreased. The combustion rates of both nitrates after this became almost identical and exceeded the combustion rate of NGC.

The solid nitrates - ETN, MHN, and GAN - revealed another curious characteristic: in spite of the high heat of explosion they did not burn at atmospheric and at moderately increased pressure. Stable combustion began for ETN at 120, and for MHN and GAN - at 70 at. Glow pulsation was observed at the stability boundary during combustion. Combustion was obtained in a vacuum for MHN: at a residual pressure of 140-170 mm Hg in three experiments out of four a column of MHN 5-7 mm in height burnt at a rate of 0.1 $g/cm^2 \cdot s$. Above and below this narrow pressure range combustion died out. Analogous behavior was detected earlier for two other nitroesters - NGC and ETN - by K. K. Andreyev [9]. It was also obtained in the case of aromatic nitro-compounds - styphnic acid and trinitrophloroglucinol [10].[1]

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[1] Zones of instability and damping of combustion, sometimes of considerable extent, were also observed for ammonium perchlorate and a number of organic perchlorates [11].

Combustion damping at elevated pressure is common in many of the enumerated cases. This phenomenon was theoretically predicted by Ya. B. Zel'dovich within the framework of the theory of thermal instability of combustion [12], in accordance with which the combustion of substances with a driving reaction in the gas phase is damped, if the dimensionless number $Z = \beta(T_{к} - T_0)$ becomes greater than unity. Here β is the temperature coefficient of combustion rate; $T_{к}$ - the boiling point of the explosive substances; T_0 - the initial temperature. The existing tentative data confirm this point of view. Thus, for all the nitroesters investigated in this regard at atmospheric pressure $\beta = (5-8) \cdot 10^{-3}$ deg^{-1} [13]. The boiling point of the solid nitrates in question, probably, is higher than that of NGC (250°). For ETN it is 270°. It is easy to see, that in this case $Z > 1$. Deviations from the theory, observed for a number of nitroesters, and especially for powders, can be explained, if we consider the additional sources and sinks of heat (radiation, exothermic reaction in the k-phase, heat exchange with the surrounding medium, heat of fusion, and others), affecting the thermal balance of the k-phase, and the temperature gradient near the surface. In the first approximation these thermal effects can be taken into account, having recorded the initial temperature in the form $T_0' = T_0 + \Sigma(Q_i/c_{к})$ where $c_{к}$ - the specific heat of the k-phase, and Q_i - the thermal effect taken with the appropriate sign. In this way it is possible to explain the appearance of stable combustion with increased pressure in the case of those explosive substances, for which at atmospheric or moderately elevated pressure damping is observed.

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