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MECHANISM OF THE COMBUSTION OF AMMONIUM AND HYDRAZINIUM SALTS

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Foreign Technology Division
Wright-Patterson Air Force Base, Ohio

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

* ye initially, after vowels, and after ъ, ь; e elsewhere. When written as ё in Russian, transliterate as yё or ё. 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}

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rot	curl
lg	log

MECHANISM OF THE COMBUSTION OF AMMONIUM AND HYDRAZINIUM* SALTS

G. B. Manelis and V. A. Strunin
(Chernogolovka)

Many ammonium and hydrazinium salts (for example, perchlorates, nitrates) are capable of self-sustaining combustion. A characteristic feature of these compounds is the rather high decomposition rate in the condensed phase and a vaporization capability.

The kinetics of the reactions are basically explained by the following scheme [1, 2]:

the initial stage is the reversible proton transfer

$$RH^{+}X^{-}_{\text{к}} \rightleftharpoons R_{\text{к}} + HX_{\text{к}}.$$

The dissociation products vaporize (endothermal process) or decompose (exothermal process).

The decomposition rate which limits the process can be

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*Translator's Note. In the original Russian article and in this translation, hydrazine salts are referenced as hydrazinium salts because of the pertinency of the hydrazino radical ($N_2H_5^+$).

functions of, in the general case, the concentration of R (hydrazine) and the concentration of HX (acid):

$$w_{\text{уд}} = K[R]_{\text{к}}^{m}[HX]_{\text{к}}^{n}. \qquad (1)$$

The solubilities of R and HX in the initial substance are different, and are determined by the equilibrium constant $K_1 = [R]_{\text{к}}[HX]_{\text{к}}$ and the equation of the conservation of matter as the substance dissolves and vaporizes:

$$([R]_{\text{к}} + [RH^{+}]_{\text{к}})V_{\text{к}} + [R]_{\text{г}}V_{\text{г}} = ([HX]_{\text{к}} + [X^{-}]_{\text{к}})V_{\text{к}} + [HX]_{\text{г}}V_{\text{г}}, \qquad (2)$$

where V - volume; subscripts к and г designate the condensed and gaseous phases.

The concentrations of the components in the condensed phase are proportional to the concentrations in the gaseous phase (the Henry law)

$$[R]_{\text{к}} = K_{R}RT[R]_{\text{г}}; \quad [HX]_{\text{к}} = K_{HX}RT[HX]_{\text{г}}, \qquad (3)$$

where K_r and K_{HX} - solubility constants.

From equation (2) it follows that if $[HX]_{\text{к}}$ exceeds $[R]_{\text{к}}$ because of the high solubility of this product, in order to conserve the balance $[HX]_{\text{г}}$ should be less than $[R]_{\text{г}}$. Since the amount of vapor carried away by the end products of the decomposition depends on their volume and, consequently, on pressure, $[R]_{\text{к}}$, $[HX]_{\text{к}}$, and the reaction rate will also change with pressure.

Let us examine one of the simple cases, when

$$w_{\text{уд}} = K[HX]_{\text{к}}^{n}. \qquad (4)$$

Considering that

$$V_{\text{г}}/V_{\text{к}} = [m_c\eta_c + m_p(1-\eta_c)]\,\rho RT/p; \qquad (5)$$

$$p=\left[1+\frac{m_p(1-\eta_c)}{m_c\eta_c}\right]p_c; \qquad (6)$$

$$[\mathrm{RH}^+]_{\text{к}}=[\mathrm{X}^-]_{\text{к}}, \qquad (7)$$

from equation (2) we obtain

$$[\mathrm{HX}]_{\text{к}}^2=\frac{K_1K_{\mathrm{XH}}}{K_{\mathrm{R}}}\cdot\frac{1+K_{\mathrm{R}}\rho^{-1}\,[m_p^{-1}p+(m_c^{-1}-m_p^{-1})p_c]}{1+K_{\mathrm{HX}}\rho^{-1}\,[m_p^{-1}p+(m_c^{-1}-m_p^{-1})p_c]}, \qquad (8)$$

where η - percentage of the vaporized substance; m_p and m_c - number of moles formed during the decomposition and vaporization of one mole of substance; ρ - density of the condensed phase; p - pressure; $p_c=B\exp(-L/RT)$ - saturated vapor pressure.

The combustion rate, under the assumption that the foremost process is the exothermal decomposition of a substance in the condensed phase while the gaseous phase processes play secondary role, is expressed by the following formula for the simplest case of a zero-order reaction [3, 4, 5] with consideration of (4) and (8):

$$u^2=\frac{2\lambda RT_{\text{п}}^2K_0\exp(-E/RT_{\text{п}})}{(1-\eta_c)^2\rho QE}\cdot\frac{K_1K_{\mathrm{HX}}}{K_{\mathrm{R}}}\cdot\frac{1+aK_{\mathrm{R}}\rho}{1+aK_{\mathrm{HX}}\rho}; \qquad (9)$$

$$T_{\text{п}}=T_0+\frac{(1-\eta_c)Q}{c}-\frac{\eta_cQ_c}{c}=T_m-\frac{\eta_c(Q+Q_c)}{c}, \qquad (10)$$

where λ - thermal conductivity; c - heat capacity; Q - decomposition heat; Q_c - vaporization heat; K_0 - preexponent; E - activation energy; $T_{\text{п}}$ - temperature of the combustion surface; T_0 - initial temperature; T_m - maximum temperature, $a=1/\rho\,m_p$ (considering $p_c \ll p$).

The equations of matter (6) and heat (10) balances define the $T_{\text{п}}$-p function.

The pressure coefficient equals (it is assumed here that K_1, K_R, and K_{HX} depend only slightly on temperature; $Q_c=0$; $m_p=m_c$)

$$\nu = \frac{p\partial u}{u\partial p} = \frac{(T_m - T_n)E}{2RT_n^2}\left[1 + \frac{(T_m - T_n)L}{RT_n^2}\right]^{-1} - \frac{a(K_{HX} - K_R)p}{2(1+aK_R p)(1+aK_{HX} p)}. \qquad (11)$$

The temperature coefficient

$$\beta = \frac{\partial u}{u\partial T_0} = \left(\frac{E}{2RT_n^2} + \frac{T_m - T_n}{T_n - T_0} \cdot \frac{L}{RT_n^2}\right) \cdot \frac{\partial T_n}{\partial T_0}, \qquad (12)$$

where

$$\frac{\partial T_n}{\partial T_0} = \left[1 + \frac{(T_m - T_n)L}{RT_n^2}\right]^{-1}. \qquad (13)$$

Combustion rate vs pressure is determined by two factors: the increase in the temperature of the combustion surface and the change in concentration of the product, which accelerates the reaction, with an increase in pressure. If the solubilities of the dissociation products in the condensed phase are the same ($K_R=K_{HX}$), the u-p function is determined only by the first factor. If $K_R>K_{HX}$, it becomes stronger in a certain region of pressures; if $K_R<K_{HX}$, it becomes weaker and can have the opposite sign ($\nu<0$).

Figure 1 shows, in dimensionless form, the combustion rate vs pressure with different ratios between K_R and K_{HX}, calculated from the formulas

$$\omega^2 = e^{-\varepsilon/\Theta_n} \cdot \frac{K_{HX}}{K_R} \cdot \frac{1+aK_R\pi}{1+aK_{HX}\pi}; \qquad \pi = \frac{1-\Theta_0}{1-\Theta_n}\, e^{-\varkappa/\Theta_n},$$

where

$$\Theta_n = T_n/T_m;$$
$$\pi = p/B;$$
$$\varepsilon = E/RT_m = 10;$$
$$\varkappa = L/RT_m = 10;$$

$$\Theta_0 = T_0/T_m = 0.2;$$

$$a K_{HX} = 10^7.$$

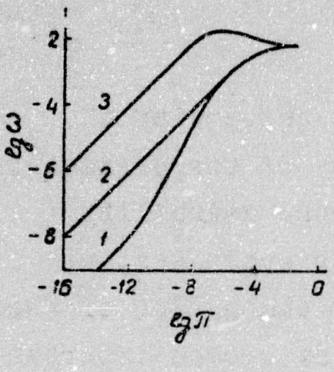

Figure 1. Combustion rate vs pressure in dimensionless form: 1 - $K_{HX}/K_R = 10^{-4}$; 2 - $K_{HX}/K_R = 1$; 3 - $K_{HX}/K_R = 10^4$.

If products capable of shifting the equilibrium of the initial reaction of proton transfer are formed during the thermal decomposition of a substance, they can influence the combustion rate and its pressure relationship by changing the concentration of the product-reaction accelerator. Let product F (for example, H_2O) decrease the concentration of HX as follows:

$$F + HX \overset{K_2}{\rightleftarrows} FH^+ + X^-.$$

It is evident that

$$[F]_k = K_F RT[F]_{\text{г}} \sim p.$$

Instead of equation (7), we should write

$$[RH^+]_k + [FH^+]_k = [X^-]_k.$$

Using these relationships it is possible to obtain expressions for the concentration (HX) and combustion rate [6]. In this case the case in combustion rate and the value of ν with pressure becomes greater.

If one of the decomposition products can combine with R, the concentration of HX increases, which leads to a corresponding increase in the combustion rate and an increase in ν.

Similarly, we analyzed cases when decomposition is accelerated by product R, i.e., when

$$w_{y1} = K[R]_{k}^{m}.$$

Turning to a comparison of the data given above with the experimental data, it should be noted that many of the parameters appearing in the obtained formulas (primarily the solubility constants) are unknown at the present time. Nevertheless, a qualitative explanation of the features of the combustion of these compounds on the basis of the examined mechanism seemed important to us.

It is well known that the decomposition of ammonium perchlorate [1], hydrazinium perchlorate and diperchlorate [7], and ammonium nitrate [1] is determined by the kinetics of the decomposition of the acid, and is accelerated by additives of other acids, whereas hydrazinium nitrate decomposes [2] basically through the decomposition of hydrazine. The first group of substances corresponds to the scheme examined above.

The rules of ammonium perchlorate combustion have been studied most thoroughly. Proceeding from data on the greater vapor pressure of ammonia compared to that of perchloric acid, it is to be expected that during combustion the solubility of perchloric acid in the condensed phase will be higher, i.e., $K_{HX} > K_{R}$. Then, according to (9) and (11), with an increase in pressure there should be a decrease in the combustion rate of ammonium perchlorate, similar to that of curve 3, Fig. 1. Experimental data [8, 9] agree with this conclusion. In the pressure region 150-400 atm (tech) a decrease in the rate is observed.

It is interesting to note that the ignition of ammonium perchlorate in combustible shells [8, 9] moderates this reduction which, in some cases, is replaced by a plateau. As the calculations in [6] show, this effect can be explained in our model. An increase in the effective heat of the reaction leads to the fact that the temperature of the combustion surface changes to a greater extent with an increase in pressure and, as a result of this, the effect of the first factor in formula (11) becomes greater.

During the combustion of perchlorates of organic amines [11, 12], on the u(p) curves we observed regions of a drop in the rate or a discontinuation of combustion with subsequent restoration of the combustion capability. The mechanism of these phenomena is also apparently associated with the examined effect of kinetic deceleration.

Another feature of the process of the combustion of these substances consists of the fact that in the region of a drop in the rate, the combustion acquires an unstable pulsed nature. A number of criteria on the stability of the stationary combustion of condensed systems exists in the literature. The most common of these is the Novozhilov criterion [13], obtained from an examination of the connection between the combustion rate and the surface temperature and the temperature gradient of the combustion surface, both functions of pressure. The combustion regime is stable if

$$\delta = \frac{(k-1)^2}{r(k+1)} < 1, \tag{14}$$

where $k = (T_n - T_0)\,\frac{\partial u}{u\,\partial T_0}$;

$$r = \frac{\partial T_n}{\partial T_0} \quad \text{when } p = \text{const}.$$

Using (12) and (13) together with (14) leads to the following type of stability criterion:

$$\delta = \frac{\left[\frac{(T_п - T_0)E}{2RT_п^2} - 1\right]^2}{1 + \frac{(T_п - T_0)E}{2RT_п^2} - \left(T_0 + \frac{Q}{c} - T_п\right)\frac{2L}{RT_п^2}}. \qquad (15)$$

Combustion stability increases with a decrease in activation energy E and an increase in vaporization heat L, i.e., with a decrease $\nu \approx E/2L$, and also with an increase in the thermal effect of the reaction Q and the initial temperature T_0.

Equation $\delta(T_п)=1$ which determines the stability limit is cubic in $T_п$ and has three roots which, with definite parameter ratios, can be real [14] and can fall in the region of real values of $T_п$.

Figure 2 shows δ vs dimensionless temperature $\Theta_п$ for different values of parameter $\varepsilon=E/RT_m$. Depending on the value of this parameter, the combustion process can be stable throughout the region of a change in $T_п$ and, accordingly, p (curve 1, δ is less than 1 everywhere), stable at low and high pressures and unstable in the intermediate region (curve 2, twice intersecting $\delta=1$) and stable at low pressures (curve 3, once intersecting $\delta=1$). A decrease in the parameter $\varkappa=L/RT$ causes changes in the nature of the curves. Thus, the relationships resulting from the examined mechanism, which determine combustion stability, are in qualitative agreement with the experimental data.

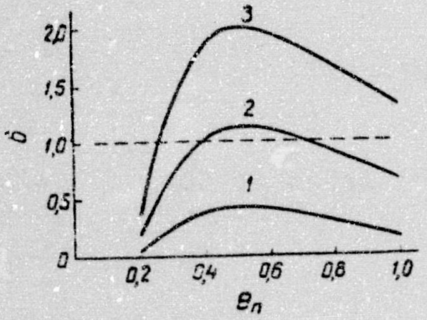

Figure 2. Stability criterion vs temperature of the combustion surface in dimensionless form. ($\varkappa=1$; $\Theta_0=0.15$): 1 - $\varepsilon=4$; 2 - $\varepsilon=6$; 3 - $\varepsilon=8$.

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