Reports of the Academy of Sciences of the USSR

A. F. BELYAEV, S. A. TSYGANOV

1964

SovietRxiv

Abstract

Full Text

Reports of the Academy of Sciences of the USSR

1964. Volume 157, No. 2

PHYSICAL CHEMISTRY

A. F. BELYAEV, S. A. TSYGANOV

ON THE MECHANISM OF COMBUSTION OF SMOKELESS POWDER AT ELEVATED PRESSURES

(Presented by Academician Ya. B. Zel' dovich on 3 March 1964)

It was shown (1) that in volatile nitroesters the combustion reactions proceed in the gas phase. Pokhil (2) established that in smokeless powders (the basis of which is a nonvolatile nitroester—cellulose nitrate) an overall exothermic reaction arises in the condensed phase, ending in dispersion of the substance at a temperature of 300-400° C; further heating occurs in the smoke-gas mixture near the surface of the substance.

Thus, in powder an overall exothermic reaction proceeds in the condensed phase; in the gas phase the finest particles are suspended. These particles are capable of an overall exothermic transformation.

The indicated differences in the mechanism lead to a difference in $V(P)$—the dependence of the burning rate V on the pressure P, the simplest form of which is $V = bP^{\nu}$. For a second-order reaction in volatile nitroesters, in accordance with Zel' dovich' s theory (1,3), $\nu \simeq 1$; for smokeless powders at pressures up to 100 atm $\nu \leqslant 0.7$. We carried out experiments to determine $V(P)$ for smokeless powder N, for the volatile nitroester TEN, and for TEN with which 5% of intensively ground charcoal had been thoroughly mixed. The experiments were conducted in a constant-pressure bomb in compressed nitrogen (pressure interval 10-100 atm) with specimens 8 mm in diameter (TEN and TEN with carbon were pressed). The results obtained are given in the graph of Fig. 1. Straight line 1 is powder N; straight line 2 is TEN; straight line 3 is TEN with carbon. All points lie on straight lines (the adopted simplest law $V(P)$ is satisfied), whose slopes differ, and therefore

$$\nu = \frac{d \lg V}{d \lg P}.$$

For powder N, $\nu \simeq 0.7$. For volatile TEN, with the leading reaction in the gas phase, $\nu = 0.95$; the dependence $V(P)$ is close to a simple linear one. Finally, for TEN with charcoal the slope of the straight line is the smallest, and $\nu = 0.6$–0.65. Thus, in the pressure interval 10-100 ata, volatile nitroester with 5% charcoal has a "powder-like" dependence $V(P)$, even more sharply expressed than that of powder N, and, in particular, can burn stably at elevated pressure in a semi-closed volume. TEN has an excess of fuel; the addition to it of carbon, which, as we see, increases the burning rate, increases the deficiency of oxygen.

It is natural to suppose that, in the presence of charcoal particles, heterogeneous reactions arise on their surface and inside the pores, accelerating, especially at low pressures, the transformation of gaseous intermediate products. Microphotography has established that, during the combustion of TEN with carbon, near the surface at a distance of ~ 0.1 mm a narrow luminous layer of incandescent particles arises. Near the surface the particles move more slowly than the vaporized substance, and their concentration is increased. By accelerating the reactions of the gaseous intermediate products, the incandescent carbon itself reacts with them and is gasified.

From what has been set forth above, certain conclusions may be drawn concerning the mechanism of combustion of smokeless powder. Pokhil (^{2}) noted in his time that, as the dispersed particles of powder decompose, the carbon content in them increases; in the final stage of existence of the "smoke," "sooty" particles (^{4}) and "threads" are formed, apparently close in composition

and structure to charcoal. Heller and Gordon (5) noted that "threads" of "dark carbonaceous material" are found on the surface of extinguished powder. During combustion these "threads" become incandescent and form a characteristic "spark zone" near the surface of the powder, undoubtedly existing at moderate pressures.

Pokhil pointed to the important role of heterogeneous reactions in the smoke-gas mixture, without tying them to any particular stage in the transformation of the "smoke."

From the results of our experiments presented above one may conclude that, in the pressure interval 10-100 ata, the effective action of dispersed powder particles on the combustion process of the powder itself arises at the final stage of existence of the "smoke" and consists in accelerating reactions of gaseous intermediate products on the surface of carbon-enriched particles and "threads." Apparently, these reactions occur near the temperature 1300-1500° K, for which Pokhil et al. (4) established the maximum value of the rate of volumetric heat release in the gas phase near the powder surface*.

Fig. 1. Dependence of burning rate on pressure (on a logarithmic scale)

The carbonaceous particles and "threads" are then incandescent and glow, forming the spark zone—the zone of the leading combustion reaction of the powder at moderate pressures.

Fig. 1. Dependence of burning rate on pressure (on a logarithmic scale)

Figure 1: Fig. 1. Dependence of burning rate on pressure (on a logarithmic scale)

Our assumption that, in the combustion of smokeless powder and TNT with carbon, the mechanism of the leading stage of the reaction is similar applies only to elevated pressures. With a substantial change in pressure, the character of combustion, its mechanism, the mechanism of the leading reactions, and the basic combustion laws may change radically. In vacuum, heated powder can burn flamelessly (2) (with a relatively low rate and a large temperature coefficient (6)); volatile TNT in vacuum (without carbon or with carbon) can only sublime. A substantial difference in the character of combustion is also observed at atmospheric pressure. Even at 6-7 ata, TNT with carbon gives a reduced value of the burning rate, not fitting the dependence established for this system in the interval 10-100 ata. If, at elevated pressures, the processes in the reaction layer of the powder and of the dispersed particles noticeably affected the character of combustion and the dependence $V(P)$, then the powder would differ in this respect from volatile TNT with carbon. Since no such difference was found under the conditions of our experiments, we believe that, in the pressure interval 10-100 ata, of the three factors characteristic of powder and indicated at the beginning of the article, only the second is essential—the presence of particles, specifically particles enriched with carbon, representing the final stage in the transformation of the smoke. The observed rate of gasification and dispersion of the powder, as well as the further gasification of the particles formed, is governed primarily by the heat flux from the spark zone.

Exploratory experiments were carried out on the combustion of several other substances with an admixture of charcoal. For Trotyl (a nitro compound), 6% admixture—an admixture of charcoal also increases V and lowers ν from ~ 0.75 to ~ 0.45 (!). In hexogen (nitroamine), a 3% admixture of charcoal does not increase, but decreases the burning rate and slightly decreases ν (from ~ 0.9 to ~ 0.8). It is possible that in hexogen other intermediate products arise (than in nitroesters and nitro compounds), for which charcoal is essentially an inert admixture. In a mixture of 20% TNT and 80% ammonium nitrate, with an admixture of charcoal, ν decreases from ~ 0.9–1.0 to ~ 0.65 (the burning rate increases).

Let us consider some general problems. It is obvious that if the leading stage

---

* The existence of condensed particles should not be credited with the appearance of a "step" (plateau) on the curve $T(x)$—the temperature profile along the height of the flame: under certain conditions it also arises in the combustion of volatile evaporating systems (6) and is associated with chemical stadiality. However, in the presence of particles the temperature gradient near the surface increases, and the formation of the "step" appears more distinctly and sharply.

of combustion is associated with the spark zone, then when using Zel' dovich's theory—the foundation of the theory of combustion of powders and explosives —it is necessary to take into account that the reactions of gaseous intermediate products proceed only partly as homogeneous reactions, and partly as heterogeneous reactions on the surface of carbonaceous incandescent particles. Here we shall merely note that the rate of a homogeneous gas reaction of second order is $w \sim P^2$, where P is pressure, and since the burning rate $V \sim \sqrt{w}$, then $V \sim P$. For a heterogeneous reaction at moderate pressures $w \sim PS^*$, where S^* is the total surface area of particles per unit volume, which in a powder must also depend on P. If one assumes $S^* = \text{const}$ (which is incorrect), then $w \sim P$ and $V \sim P^{0.5}$. If the concentration at the particle surface changes, then allowing for diffusion may give $\nu < 0.5$. Thus, the presence of a homogeneous-heterogeneous process substantially complicates the problem; one can only assert that in this case $\nu < 1$. Similar problems of the dependence $V(P)$ were considered for black powder by O. I. Leipunsky[7] on the basis of a mechanism assuming a reaction of the oxygen of saltpeter on the surface of charcoal particles.

At very high pressures the role of heterogeneous reactions becomes negligible and homogeneous gas reactions dominate. In accordance with this, for smokeless powders, beginning from ~ 500 to the highest of the applied[8] pressures $\sim 10{,}000$ atm, the law $V(P)$ is close to linear ($\nu \simeq 1$) and is analogous to $V(P)$ for volatile explosives, provided that the regime of layer-by-layer combustion is maintained.

The experiments described above lead to the conclusion that at pressures of 10–100 atm the reactions in the smoke-gas stage are reactions of gaseous intermediate products, substantially accelerated by a heterogeneous process on the surface of incandescent, relatively inert carbonaceous particles. Only at low (several atmospheres and below) pressures does the circumstance become significant that the condensed phase of the powder and the dispersed particles at the beginning of their formation are capable of a total exothermic transformation.

The facts and considerations set forth above may prove to be significant because carbon-rich sooty particles, which accelerate the transformation of gaseous intermediate products, may be formed during the combustion of a number of systems, including mixed systems.

Institute of Chemical Physics
Academy of Sciences of the USSR

Received
19 II 1964

REFERENCES CITED

[1] A. F. Belyaev, ZhFKh, **14**, 1009 (1940).
[2] P. F. Pokhil, *Physics of Explosion*, Coll. 2, Publishing House of the Academy of Sciences of the USSR, 1953.
[3] Ya. B. Zel' dovich, ZhETF, **12**, 498 (1942).

[4] P. F. Pokhil, V. M. Mal' tsev, G. V. Lukashen' ya, DAN, **135**, 913 (1960).
[5] C. A. Heller, A. S. Gordon, J. Phys. Chem., **59**, 773 (1955).
[6] A. F. Belyaev, G. V. Lukashen' ya, Zhurn. prikl. mekh. i tekhn. fiz., No. 5, 117 (1963).
[7] O. I. Leipunsky, ZhFKh, **34**, No. 1, 177 (1960).
[8] J. Basset, J. Basset, C. R., **231**, 649 (1950).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.