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## Abstract

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# EXPLOSIVE DECOMPOSITION OF NITROUS OXIDE

*(Presented by Academician Ya. B. Zel' dovich on 18 February 1960)*

In studying the critical ignition conditions of mixtures of cyclohexane and nitrous oxide, we noted an unusually low limiting fuel content in lean mixtures: 0.33% $C_6H_{12}$. The heat of combustion of cyclohexane in such a mixture is sufficient for adiabatic heating by no more than 400°. Since combustion under such conditions is impossible, it is evident that the exothermic decomposition of nitrous oxide raised the combustion temperature $T_b$. In this connection we assumed that a stationary flame of nitrous oxide decomposition might be possible. Let us recall the phenomenon of self-ignition of $N_2O$, predicted by D. A. Frank-Kamenetskii ([1]) and discovered experimentally by Ya. B. Zel' dovich and V. I. Yakovlev ([2]). Later, ignition of $N_2O$ upon its compression in a shock tube ([3]) was observed ($T \approx 1400^\circ K$).

The possibility of flame propagation through cold nitrous oxide when it is ignited by a point impulse was considered by us from the standpoint of the theory of the flame-propagation limit ([4]). Heat losses from the layers of combustion products adjacent to the reaction zone may lead to progressive conductive cooling of the reaction zone itself, to slowing of the latter, and to extinction of the flame. In tubes of sufficiently large diameter $d > d_{cr}$ (usually $d_{cr} \approx 5$ cm at 1 atm), heat transfer to the walls is insignificant and heat losses occur by radiation.

The relative role of heat losses increases with decreasing normal flame velocity $u_n$. At some minimum $u_n = u_{cr}$, a critical regime is reached, determining the concentration limits of flame propagation. For air mixtures of carbon monoxide, Ya. B. Zel'dovich calculated $u_{cr} = 2$-$3$ cm/sec; subsequent precise measurements ([5]) gave, for a number of air mixtures of hydrocarbons and CO, $u_{cr} = 3.1 \div 4.2$ cm/sec. These considerations make it possible to give a principled answer to the question of the possibility of igniting $N_2O$.

It may be assumed that, in the combustion of $N_2O$, the product of the intensity by the width of the absorption zone in the unburned gas is small in comparison with the total radiated energy. In this case, heat transfer by radiation from a unit mass of combustion products does not depend on pressure. Therefore, at variable pressure the flame-propagation limit is determined not by the value $u_{cr}$, but by the mass burning velocity $u\rho$ ($\rho$ is the density), whose magnitude determines the rate of heat transfer. Since $u\rho \sim \sqrt{\bar{\Phi}}$ ([6]), where $\Phi$ is the reaction

rate in the flame, for any exothermic process with order greater than zero, heat losses from the reaction zone decrease with increasing pressure $p$; at $p > p_{cr}$, a stationary combustion regime becomes possible.

The value $p_{cr}$ can be very roughly estimated by assuming that for any combustible mixture at $p = 1$ atm, $u_{cr} = 3$ cm/sec. Applied to the decomposition of $N_2O$, this assumption should overestimate the calculated $p_{cr}$, since the radiation of $O_2$ and $N_2$ is considerably weaker than that of $CO_2$ and $H_2O$, and for mixtures of hydrocarbons one should expect larger $u_{cr}$ than for $N_2O$. Apparently, even small amounts of NO present in the combustion products of $N_2O$ have a substantial effect on the radiation intensity. It should also be noted that the value $u_{cr}$ depends not only on the radiation intensity—in analogous conditions it is larger at higher values of the activation energy.

It is known that nitrous oxide decomposes monomolecularly; at sufficiently high pressures, according to first order, the asymptotic (at $p = \infty$) value of the reaction-rate constant is $k_\infty = 4.2 \cdot 10^9 \cdot e^{-53000/RT}$ sec$^{-1}$ ([7]). A thermodynamic calculation gives $T_b = 1860°$K; in this case the equilibrium content of NO in the reaction products is 0.61%, and $T_b$ does not depend on pressure. The thermal conductivity of the reaction products $\lambda$ at $T = T_b$ was calculated by us by the method of Hirschfelder ([8]), on the basis of the collision constants he gives, $\lambda = 2.90 \cdot 10^{-4}$ cal/cm $\cdot$ sec $\cdot$ deg. The theory of normal combustion ([6]) gives

$$u_n = \sqrt{2\lambda(T_b)\theta^2(T_b)k_\infty(T_b)RT_0^2/pQ(T_b - T_0)T_b},$$

where $\theta = RT^2/A$, $A$ is the activation energy, $T_0 = 290°$K is the temperature of the gas being ignited, and $Q = 1.95 \cdot 10^4$ cal/mole is the heat effect of the reaction. In the absence of heat losses, $u_n = 1.7$ and 0.54 cm/sec at 1 and 10 atm, respectively. Taking $u_{cr}p_{cr} = 3$ cm $\cdot$ atm/sec, we find $p_{cr} = 3.1$ atm. Interpolation of later data ([9]) gives, for the conditions of our experiments, $k = 1.2 \cdot 10^{11} \cdot e^{-60900/RT}$, whence it follows that $p_{cr} = 1.2$ atm.

The experimental determination of the critical ignition conditions was carried out by us in a cylindrical stainless-steel bomb 61 mm in diameter and 545 mm high. For visual observation along the generatrix of the bomb there were 5 windows at equal distances. Ignition was produced by burning through, with short-circuit current from a $220 \times 12$ transformer, a copper wire 0.2–0.3 mm in diameter, attached to the ends of the spark-plug electrodes at one end of the bomb.

The experiments showed that cold $N_2O$ can indeed be ignited. On ignition at the lower end of the vertically positioned bomb, $p_{cr} = 1.60 \pm 0.08$ atm. This value is well reproducible. In a number of experiments with ignition by current from a transformer having 10 times greater power, $p_{cr}$ did not change. Nor does $p_{cr}$ change under isobaric combustion; for this purpose, before ignition the bomb was connected to a 40-liter buffer filled with nitrogen at the same pressure.

To determine the influence of $T_b$ on the critical ignition pressure, we added elemental nitrogen to the nitrous oxide. Experiments carried out with ignition at the lower end of the bomb showed that $p_{cr}$ rises strongly even with small additions of inert gas: $N_2$ (%) 4.5, 10.0; $\Delta T_b^\circ$ 61, 137; $p_{cr}$ (atm) 2.15, 4.5.

Such an effect is equivalent to the known phenomenon of the widening of concentration ignition limits with increasing pressure. These results are of interest to compare with the statement of Spalding ([10]), evidently erroneous, according to which the concentration ignition limits widen with increasing pressure only in the case where the order of the reaction in the flame is higher than first (in reality, higher than zero).

On ignition at the upper end of the tube, $p_{cr}$ increases to 10 atm. It is known that the ratio of the critical concentrations of the deficient component $\pi_{cr}$ at the ignition limit from above and from below, when the diffusion coefficient and thermal diffusivity are equal, reaches 1.20 ([11]). It is evident that the corresponding change in $\Phi$ in our experiments, at constant $\pi$ and $T_b$, is achieved by changing the pressure. In view of the low order of the reaction, the influence of the pressure change here is comparatively weak. An increase of $p_{cr}$ by a factor of 6.25 on ignition from above and from below is equivalent to the corresponding change in the initial concentration in experiments with nitrogen dilution. Extrapolating the dependence described, we find that $p_{cr} = 10$ atm approximately at 13-19% $N_2$ ($\Delta T_b = 179$-$264^\circ$), i.e., the equivalent $\Delta\pi_{cr}$ has a reasonable value.

The calculated value of the critical ignition pressure given above should be compared with that observed for ignition from above, since we considered flame propagation without the participation of such

an external stimulator such as convection. At the same time it remains unclear why the calculated $p_{cr}$ is too low, and not the reverse, as should have been expected, although it is of the correct order of magnitude.

From the results obtained, practical conclusions should be drawn. Nitrous oxide is formed in many industrial operations; it is obtained in pure form for medical purposes, compressed and liquefied without special precautions. In principle one cannot exclude the possibility of its ignition, for example by discharges of static electricity, during heating by adiabatic compression and in a shock wave.

It should be noted that in preliminary experiments on the ignition of $N_2O$ in an apparatus ([12]) with an explosion-chamber volume of 70 $cm^3$, at $p = 50$ ata, explosions of great force were observed. Combustion in the harmful volume—the connecting tubes of stainless steel (Kh18N9T) with an internal diameter of 4 mm and a wall thickness of 1.2 mm—led in one of the experiments to their rupture along the generatrix and to the destruction of a 600-ata manometer. It follows from this that the maximum pressure reached from 1000 to 4000 ata.

**Fig. 1**

The products of the explosive decomposition of $N_2O$ contain appreciable

Fig. 1

Figure 1: Fig. 1

amounts of $NO_2$, evidently formed from the primary combustion product NO. To determine the yield of NO, a certain amount of the reaction products, determined by the volume of the bomb and the decrease in pressure, was slowly passed through a bubbler with a titrated alkali solution. The excess alkali was back-titrated potentiometrically with a glass electrode (without oxidation of nitrite). Control spectrophotometric determinations of $NO_2$ confirmed our results. Figure 1 shows the dependence of the $NO_2$ content on the initial pressure. The amount of NO formed increases as the pressure is lowered, which at first glance seems unusual. At the ignition limit the yield of NO is 2.7%; at high pressures the yield of NO asymptotically approaches the equilibrium value.

It is known that, in the combustion of mixtures containing $N_2 + O_2$, NO is always formed. Its concentration does not depend on the characteristics of the fuel or on the process of its combustion and is always less than the equilibrium concentration at $T = T_b$ ([13]). In our experiments the concentration of NO is greater than the equilibrium one. An analogous effect was observed in the slow decomposition of $N_2O$.

An explanation for the formation of superequilibrium amounts of NO requires further investigation.

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