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Rate of Reaction of TNT in Detonation by Direct Pressure Measurements*

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A description of an experimental method of obtaining pressure-time data for the decomposition of coarse TNT following partial detonation is given. This method consisted of photographing (with a streak camera) the displacement of a slug shot from a smooth bore cannon. The velocity and acceleration of the slug were obtained by numerical differentiation of the displacement-time data derived from the photograph. Pressure-time curves were obtained which exhibited pressure maxima at times that were dependent upon the particle size of the TNT detonated in the cannon. Peak pressures for TNT of 4–6 standard mesh particle size occurred between 140–200 μsec, peak pressures for 8–10 mesh occurred between 115–140 μsec, and pressure maxima for "fine" TNT occurred between 50–70 μsec. The pressure-time curves were analyzed, and reaction times of the coarse TNT were calculated by two different methods. One method yielded a value of the reaction time for each pressure-time coordinate and the other a reaction time in terms of the time at which maximum pressure occurred. The results obtained by these two methods were not the same. However, when corrections were made for gas leakage from the cannon, rather good agreement resulted. The most probable value computed (after leakage corrections were made) for the 4–6 TNT was found to be about 300 μsec and for the 8–10 TNT about 200 μsec. On the basis of these reaction times the grain erosion velocity for the TNT in the cannon was evidently much greater than linear burning rates at the same pressure obtained experimentally for explosive deflagration.

APPLICATION of the nozzle[1] and curved front[2] theories to the experimental velocity-diameter curves for various particle sizes of spherically-grained low-density TNT gave the following effective reaction times (in seconds) for detonation (T_2) conditions:

$$\tau = 2.3\times10^{-5}\bar{R}_g \quad \text{(nozzle theory)}$$
$$\tau = 1.07\times10^{-5}\bar{R}_g \quad \text{(curved front theory)}$$

where $\bar{R}_g$ is the average grain radius. Thus the effective reaction time for 4–6 mesh TNT, for example, was 4.6 microseconds and 2.1 microseconds, respectively, according to the nozzle and curved front theories.

Evidence has been found that the total reaction times in detonation may be much longer than the effective times indicated by the "nozzle" and "curved front" theories. This evidence, based on extrapolations of isothermal decomposition data,[3] involves some uncertainties and is far from crucial. However, if it is true, it should be possible to demonstrate this by direct rate-of pressure-development measurements, at least for the most slowly reacting explosives such as 4–6 mesh TNT. To test this possibility the "cannon" method described in this article was designed. The method was not intended to be an accurate one for the measurement of reaction rate, but rather a direct method to determine approximately the total reaction times. While the method may appear somewhat cumbersome, it actually was the only type found suitable for this purpose; the initial pressures and shock intensity were too large for the use of piezoelectric gauge techniques. The procedure consisted of finding the pressure-time curve for an explosive by means of measurements of the acceleration of a slug propelled from the cannon by the explosion following detonation.

Consider a cannon with a cylindrical firing chamber two inches in diameter and two inches long about half-filled with TNT (see Fig. 1). The detonation wave would require roughly 10 μsec to traverse the TNT. (From direct probe measurements in the cannon it was found that about 20 μsec were required for the ionization wave to reach the base of the slug.) If the total reaction zone length were comparable to the predictions of the "curved front" theory or the "nozzle" theory, by the time the detonation wave has traversed the explosive, that explosive in the region A would have completely reacted, and that in the region B would have largely reacted. For such a fast reaction, by the time the shock wave reached the slug the reaction would have reached completion. If, on the other hand, the reaction zone length were large in comparison to the dimensions of the chamber, by the time the detonation wave has

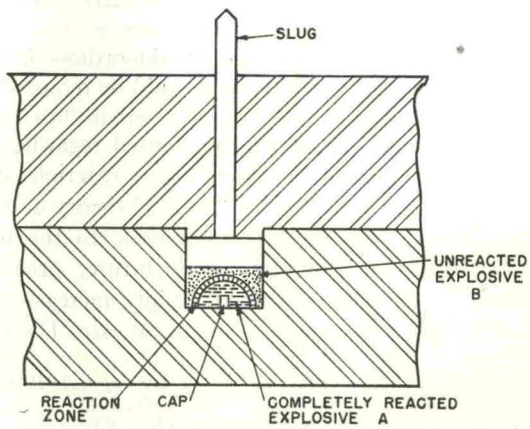

FIG. 1. Cross section of "cannon."

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[1] H. Jones, Proc. Roy. Soc. (London) **A189**, 415 (1947).
[2] Eyring, Powell, Duffey, and Parlin, Chem. Revs. **45**, 16 (1949).
[3] Cook, Horsley, Partridge, and Ursenbach, J. Chem. Phys. **24**, 60 (1956).

traversed the explosive only a small fraction of the explosive would have reacted, and no part of it would have reacted completely in any particular region of the cannon chamber. The detonation wave, however, would have effectively initiated the reaction, and since the explosive would very quickly become distributed throughout the firing chamber, most of the explosive decomposition would therefore take place under temperature and pressure conditions corresponding to uniform filling of the firing chamber.

According to the Eyring absolute reaction rate theory the specific rate constant is given by the equation[4]

$$k_r=\frac{kT}{h}\exp(\Delta S^{\neq}/R)\exp(-\Delta H^{\neq}/RT). \qquad (1)$$

Since the total reaction time is inversely proportional to the rate constant, using Eq. (1) the ratio of the reaction time of a given explosive under "explosion" conditions to the reaction time under "detonation" conditions should be

$$\frac{\tau_3}{\tau_2}=\frac{T_2}{T_3}\exp\left[\frac{\Delta H^{\neq}}{R}(1/T_3-1/T_2)\right] \qquad (2)$$

where T_2 is the detonation temperature, and T_3 is the temperature corresponding to the actual conditions in the chamber. Assuming the Cook $\alpha=\alpha(v)$ equation of state, the detonation temperature of TNT at a density of 1.05 g/cm^3 was calculated to be 3700°K. (For the low densities considered all equations of state which have been applied in detonation theory should give practically the same result.[5] Hence the arguments presented here do not depend significantly on which equation of state one employs. Therefore a relatively simple and convenient one was used.) For detonation of the same product in the cannon at an average loading density of about 0.39 g/cm^3, the temperature T_3 was calculated by the same equation of state to be 2500°K neglecting the initial temperature transient associated with the initial large density change from 1.05 to 0.39 g/cm^3. Using Eq. (2) and the value of $\Delta H=34$ kcal/mole given by Robertson,[6] one calculates $\tau_3/\tau_2=13.6$.

From simple kinetic theory considerations it was concluded that about 40–50 μsec should be required for pressure gradients to reach essentially zero in the cannon firing chamber for the arrangement used regardless of the reaction time. Thus if the effective reaction times in detonation predicted by the "nozzle" theory and the "curved front" theory were comparable to the total reaction times for the same temperature, pressures measured in the cannon should rapidly increase with time and reach a maximum at about 50 μsec. The time of appearance of this peak pressure, moreover, should be quite insensitive to the particle size and the reaction rate of the explosive detonated, because the pressure time curve would not be related at all to the chemical reaction rate but rather to the attainment of pressure equilibrium in the chamber. Experimental verification of these conclusions is given in Fig. 2 which presents a pressure-time curve obtained by detonation of 25 g of fine PETN in the cannon. The peak pressure was measured to be 3300 atmospheres and appeared at 50 μsec, and PETN is known to possess a total reaction time much less than 50 μsec.

On the other hand, if the total reaction time were much longer and the explosive detonated in the cannon were reacting relatively slowly, a pressure-time curve should be measured for which the peak pressure would appear later than 50 μsec. In this case the pressures measured should be associated with the chemical reaction rate, and consequently the time of appearance of the maximum pressure should be dependent upon the particle size of the explosive detonated in the cannon. The maximum pressure should then appear at the time at which the rate of pressure increase due to chemical reaction equaled the rate of pressure decrease due to adiabatic expansion and gas leakage from the firing chamber. Moreover, an analysis of the section of the pressure-time curves for times greater than the time required for the pressure gradient to reach zero should provide a means for studying reaction rates.

It was felt that the "cannon" test would be a desirable one even if the total reaction times were much shorter than one can measure by the cannon method. Although the "cannon" method would then necessarily fail, the negative result would allow one to eliminate models of long reaction time. One would, of course, still be faced with the possibility that an entirely different mecha-

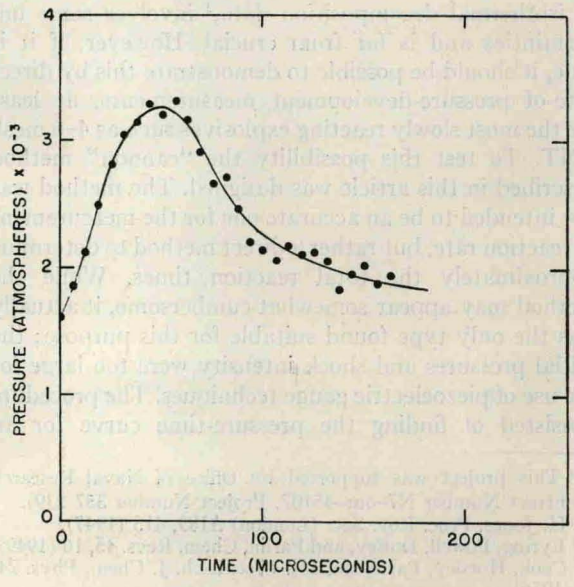

FIG. 2. Pressure-time curve for fine PETN.

[4] Glasstone, Laidler, and Eyring, *The Theory of Rate Processes* (McGraw-Hill Book Company Inc., New York, 1941).

[5] Cook, Keyes, Horsley, and Filler, J. Phys. Chem. **58**, 1114 (1954).

[6] A. J. B. Robertson, Trans. Faraday Soc. **44**, 1677 (1948).