The Thermal Decomposition of 1,3,5-Trinitrohexahydro-1,3,5-triazine (RDX)

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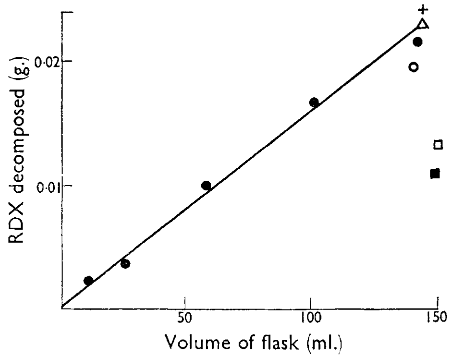
THE pressure–time curve obtained for the thermal decomposition of RDX below its melting point (204°) has been interpreted[1] as a slow solid-state reaction leading to a product which liquifies the reactant at the temperature of the experiment and accelerates its decomposition. The ratio of the rates of decomposition in the liquid and solid phases is said to be approximately 10 : 1. We have studied the decomposition and conclude that the initial reaction occurs in the gas phase and not in the solid state.



FIGURE

Initial conditions: + 0·200 g. RDX, evacuated; ● 0·100 g. RDX, evacuated; △ 0·072 g. RDX, evacuated; ○ 0·020 g. RDX, evacuated; □ 0·200 g. RDX, 58 mm. nitrogen; ■ 0·200 g. RDX, 119 mm. nitrogen.

Reaction flasks[2] of volumes between 11 and 150 ml. containing 0·02—0·2 g. RDX were either evacuated or filled to a known pressure with nitrogen and sealed. They were completely immersed in a bath at 195° for 1 hr., cooled to room temperature, opened under vacuum to determine the pressure of gaseous products, and the residual RDX estimated by nonaqueous titration.[3] The results, illustrated in the Figure, show that the rate of decomposition is (a) directly proportional to the volume of the reaction vessel; (b) for a constant volume, independent of the amount of RDX present; and (c) retarded by the presence of inert gases *e.g.* nitrogen.

It is clear from (a) and (b) that RDX does not decompose in the solid state to any significant extent at this temperature. In the early stages of the decomposition, RDX exerts its equilibrium vapour pressure[4] and the gas then decomposes into several products including a liquid, hydroxymethylformamide which dissolves some of the RDX and results in an accelerating reaction. The rate of reaction in the gas phase is at least equal to that in the liquid phase, but since the overall rate is controlled by the vapour pressure of RDX, and its value is not known with any degree of accuracy at present, an absolute value for the rate constant for the gas-phase reaction cannot be calculated.

(*Received, January 1st*, 1968; *Com.* 006.)

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