

# THE THERMAL DECOMPOSITION OF RDX AT TEMPERATURES BELOW THE MELTING POINT

## IV.\* CATALYSIS OF THE DECOMPOSITION BY FORMALDEHYDE

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### Abstract

The kinetics of the decomposition of RDX have been investigated in the presence of formaldehyde over the temperature range 170–197° with the RDX sample spread. This indicated a marked increase in the positive-catalytic effect of the formaldehyde with decreasing reaction temperature; however, the kinetics were not altered by the added formaldehyde.

The activation energy was about 44 kcal mol<sup>-1</sup>. It is suggested that the previously obtained activation energy of about this figure, for the decomposition of heaped samples of RDX in the absence of added formaldehyde, was due to catalysis of the reaction by the decomposition product formaldehyde.

### INTRODUCTION

Previous work<sup>1,2</sup> has indicated that the activation energy of the decomposition of RDX at temperatures below the melting point is, with the RDX sample spread, approximately equivalent to the energy of the weakest bond in RDX (66 kcal mol<sup>-1</sup>). However, with the sample initially heaped, the activation energies of the induction and acceleration rates are about 46 kcal mol<sup>-1</sup>. This lowering of the activation energy was attributed<sup>1-3</sup> to the formation of gaseous decomposition products with positive-catalytic properties. It was envisaged that the catalysis took place as the gaseous products permeated through the heaped sample.

Additional work<sup>1</sup> indicated that the gaseous decomposition product formaldehyde had positive-catalytic properties. As a consequence it was postulated that one of the reactions taking place in the decomposition was



The extent of this reaction in the decomposition would depend on the geometry of the sample.

\* Part III, *Aust. J. Chem.*, 1971, **24**, 945.

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<sup>1</sup> Batten, J. J., *Aust. J. Chem.*, 1971, **24**, 945.

<sup>2</sup> Batten, J. J., and Murdie, D. C., *Aust. J. Chem.*, 1970, **23**, 749.

<sup>3</sup> Batten, J. J., and Murdie, D. C., *Aust. J. Chem.*, 1970, **23**, 737.

Combining these two observations now leads to the suggestion that the above observed lowering of the activation energy is due to catalysis of the decomposition by the gaseous product formaldehyde, i.e. to reaction (5).

The aim of this paper is to offer additional evidence for the catalysis by formaldehyde and to support the suggestion made above, namely that the lowering of the activation energy is due to the influence of the product formaldehyde on the reaction.

To this latter end the hypothesis is advanced that, if this catalysis does exist, then the activation energy of the decomposition *with the sample spread* in the presence of added formaldehyde should be less than that obtained previously<sup>1,2</sup> for a spread sample in the presence of an inert gas, i.e. nitrogen. Further, if sufficient contact is achieved between the RDX sample and the added formaldehyde, then the activation energy so obtained should approximate that obtained previously *for heaped samples*. Thus, to test this hypothesis, the activation energy was determined with the sample spread in the presence of added formaldehyde.

## EXPERIMENTAL

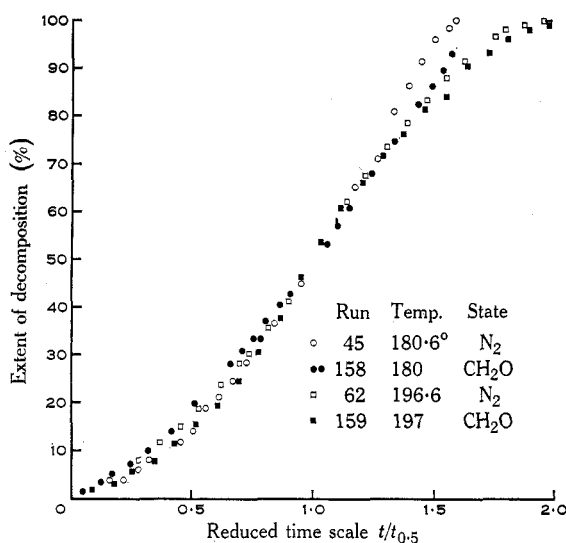
The experimental procedure has been described previously.<sup>1</sup> In each experiment the weight of dry paraformaldehyde was adjusted so that the pressure of formaldehyde at the reaction temperature was approximately constant at about 130 mmHg.

## RESULTS

### (i) Influence of Formaldehyde on Kinetics

Sigmoidal-shaped curves of extent of decomposition plotted against reaction time were obtained for the reaction in the presence of formaldehyde throughout the temperature range studied (170–197°).

Fig. 1.—Reduced time scale plot of the kinetic data for the decompositions of 0.2-g samples of RDX in the spread condition in the presence of nitrogen and of formaldehyde.



In order to show if the above kinetic data are similar to or different from those obtained for the decomposition in the presence of nitrogen, it is necessary to plot

the data on a common time basis.<sup>2,3</sup> Thus in Figure 1 are given reduced time scale plots ( $t/t_{0.5}$ ) of the decomposition-time curves for the reactions at two reaction temperatures. At constant temperature all the points fall close to the one line; thus it is inferred that the kinetics of the reactions are similar.

Notwithstanding this similarity of the kinetics, visual observation of the sample during the decomposition indicated that, at constant temperature, the sample in the presence of formaldehyde underwent the liquefaction process at a lower percentage decomposed than was observed for the decomposition in the presence of nitrogen (see Table 1).

TABLE 1

BEHAVIOUR OF THE RDX SAMPLE AT DIFFERENT TEMPERATURES IN THE PRESENCE OF NITROGEN OR FORMALDEHYDE

	Sample at 196.5°		Sample at 180°	
	Nitrogen <sup>a</sup>	Formaldehyde	Nitrogen <sup>a</sup>	Formaldehyde
Extent of decomposition (%)				
first appearance of bubbles	36	—	72	53
vigorous frothing	43	20	79	68
complete liquefaction	60	31	88	86

<sup>a</sup> From ref. 3.

### (ii) Influence of Formaldehyde on Rates

From Figure 2 it will be seen that the reaction is substantially accelerated in the presence of formaldehyde, that the extent of the acceleration increases steadily

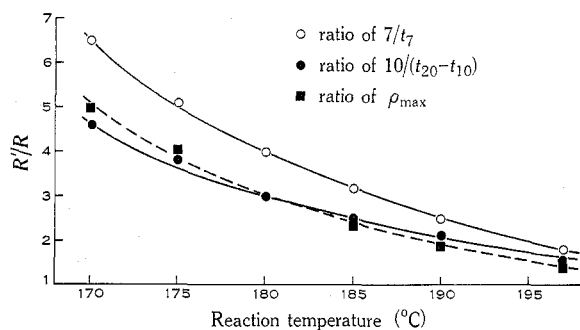


Fig. 2.—Ratio of the rate ( $R'$ ) in the presence of formaldehyde to the rate ( $R$ ) in the presence of nitrogen at various reaction temperatures with the sample spread.

with decreasing reaction temperature, and that at the lowest temperature studied there is about a sixfold increase in the rate.

### (iii) Influence of Formaldehyde on Activation Energy

The variation of the kinetic parameters with temperature is shown in Figure 3. This indicates that in each case a reasonable straight line can be fitted to the data, by the method of least squares, over the whole temperature range (170–197°).

Table 2 indicates that the activation energy with the sample spread in the presence of the added formaldehyde is approximately  $44 \text{ kcal mol}^{-1}$  ( $184 \text{ kJ mol}^{-1}$ ) at all stages of the decomposition up to the end of the maximum rate.

Fig. 3.—Arrhenius plots for the thermal decomposition of 0.2-g samples of RDX in the spread condition in the presence of formaldehyde (full lines). Broken lines are for the decomposition with the sample spread in the presence of nitrogen, and are included for comparison (from ref. 2).

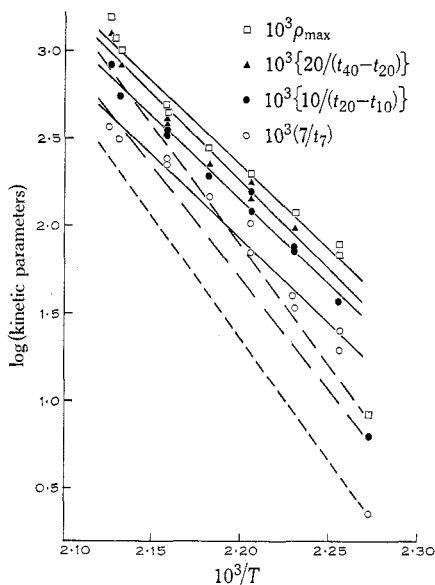


TABLE 2

ACTIVATION ENERGIES FOR THE DECOMPOSITION OF RDX AT TEMPERATURES BELOW ITS MELTING POINT

Rate	Kinetic Parameter	Activation Energy ( $\text{kcal mol}^{-1}$ )		
		Formaldehyde Present Sample Spread <sup>a</sup>	Nitrogen Present Sample Spread <sup>b</sup>	Nitrogen Present Sample Heaped <sup>b</sup>
Induction	$7/t_7$	44.3	64.3	49.4
Acceleration	$10/(t_{20}-t_{10})$	43.8	59.7	43.1
	$20/(t_{40}-t_{20})$	45.9	—	42.2
Maximum	$\rho_{\max}$	43.8	63.6	62.2

<sup>a</sup> The slopes of the Arrhenius plots, together with their respective variances, from which these activation energies were calculated were  $(-9.687; 0.301)$ ,  $(-9.588; 0.167)$ ,  $(-10.008; 0.569)$ , and  $(-9.589; 0.235)$  respectively.

<sup>b</sup> From ref. 2.

## DISCUSSION

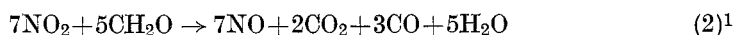
Since it is probable that the added formaldehyde may react with some of the decomposition products of RDX,<sup>1</sup> the study of the effect of formaldehyde on the decomposition of RDX is best evaluated from rate measurements of the initial stages of the reaction. Thus, to avoid the above complication, in this work the main emphasis will be placed on results for the rates  $7/t_7$  and  $10/(t_{20}-t_{10})$ .

Because of the very marked increase in the accelerating effect of formaldehyde observed as the reaction temperatures decrease, it may be stated categorically that formaldehyde does catalyse the decomposition of RDX. This increase in the accelerating effect of a gaseous positive-catalyst with decreasing reaction temperature is analogous to its effect<sup>4-6</sup> in the gas-phase oxidation of methanol catalysed either by nitrogen dioxide or hydrogen bromide.

The results indicate (see Table 2) that not only is it possible to lower the activation energy for RDX decomposition by carrying out the reaction in the presence of the gaseous positive-catalyst formaldehyde with the sample spread, but also by so doing it is possible to reproduce approximately those activation energies for the uncatalysed reaction when the sample was initially heaped. It is pertinent to mention that although these activation energies for the induction and acceleration rates are approximately equal (i.e. the reactions "catalysed, spread" and "uncatalysed, heaped"), the rates for the former reaction are approximately ten times those of the latter throughout the whole of the temperature range.

This work supports the suggestion proposed in the Introduction that the reason for the previous<sup>2</sup> values of the activation energy being less than the energy of the weakest bond in RDX was due to catalysis of the reaction by the decomposition product formaldehyde. These lower values were obtained with heaped sample beds where the contact time of the gaseous decomposition products with the undecomposed RDX is longer than with spread samples. The work therefore supports the possibility of the existence of the autocatalytic reaction (5).

An additional role of the added formaldehyde is suggested by the observations of its effect on the liquefaction of the sample (Table 1). As this liquefaction is undoubtedly associated with the presence of the non-volatile residue<sup>1</sup> (NVR), then the enhanced liquefaction can be interpreted in the following manner. Because the reaction



would remove nitrogen dioxide from the system, then part of the role of the added formaldehyde could be to suppress the interaction of nitrogen dioxide with the non-volatile residue:<sup>1</sup>



Thus, when compared with the uncatalysed reaction, in the presence of the formaldehyde more of the non-volatile residue will be available for the liquefaction of the RDX and, therefore, this liquefaction would occur at a lower percentage decomposed. The activation energy<sup>7</sup> of reaction (2) is  $15.1 \text{ kcal mol}^{-1}$ .

<sup>4</sup> Batten, J. J., *Aust. J. Chem.*, 1964, **17**, 551.

<sup>5</sup> Batten, J. J., *Aust. J. Chem.*, 1964, **17**, 539.

<sup>6</sup> Batten, J. J., *Aust. J. Chem.*, 1964, **17**, 172.

<sup>7</sup> Pollard, F. H., and Wyatt, R. M. H., *Trans. Faraday Soc.*, 1949, **45**, 760.