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Note

Determination of condensed-phase kinetics constants

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A discussion of the differential scanning calorimetric determination of kinetics constants for decompositions in the vapor phase has been presented[1]. It was shown that the rate curve of the condensed-phase reaction, obtained from an isothermal DSC run, was superimposed on a constant-vapor-pressure decomposition (Fig. 1). The dashed line in the figure shows the vapor-phase contribution to the overall rate.

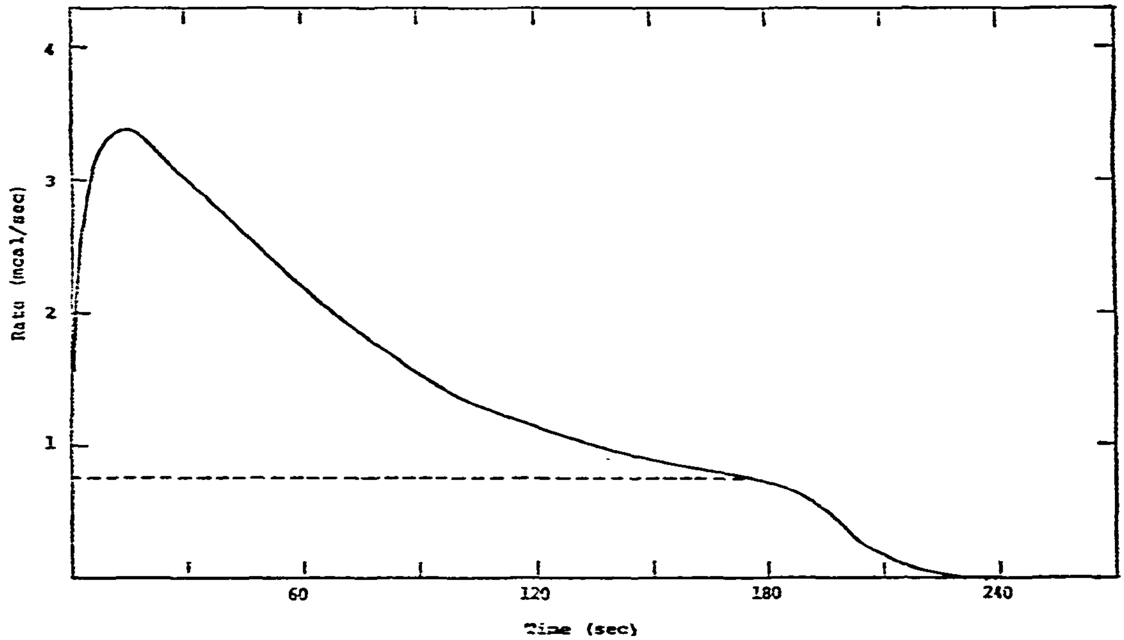

Fig. 1. DSC curve obtained from 0.909 mg Wabash RDX at 515 K in a sealed cell of 0.022-ml internal volume perforated one time (0.1-mm diam.).

In such a system, the rate expression should be

$$dx/dt = k_1[1-x-f(p)]+k_2f(p) \tag{1}$$

where k_1 is the rate constant in the condensed phase and k_2 is the rate constant in the vapor phase. The DSC recorder deflection at any time (b) is proportional to the rate, and f(p), the mass of reactant in the vapor phase, is constant at constant temperature and pressure until all of the condensed phase has decomposed. Therefore,

$$b = \frac{k_1}{\alpha}(1-x)+c \tag{2}$$

where α is a proportionality constant. Then,

$$\ln(b-c) = C+\ln(1-x) \tag{3}$$

But $-\ln(1-x) = k_1 t + c'$ for a first-order reaction; therefore,

$$\ln(b-c) = C-k_1 t \tag{4}$$

where c is the constant contribution to the recorder deflection caused by the reaction in the vapor phase.

The rate constant for the reaction is determined from the slope of a plot of ln ($b-c$) versus time[2]. That is, measurements are made of the net deflection between the dashed line (vapor-phase contribution) and the overall rate curve, and a first-order plot is made of these measurements.

It is obvious from eqn (4) that the vapor-phase contribution must be subtracted from the overall deflection before the first-order plot for the decomposition in the condensed phase is made; however, it was not immediately obvious to me how important the establishment of an accurate baseline was for the condensed-phase reaction at all temperatures. A large number of measurements on RDX (hexahydro-1,3,5-trinitro-s-triazine) have been made at different temperatures over a number of years, and values for its activation energy, E, and pre-exponential, Z, have been reported[1]: $E = 43.1$ kcal mol^{-1} and $Z = 2.44 \times 10^{16}$ sec^{-1}. Although the agreement between these values and literature values was quite good, they were obtained ignoring the small vapor-phase contribution at temperatures below 505 K. The process has now been re-evaluated with carefully established vapor-phase baselines at all temperatures, and the kinetics constants are found to be $E = 47.1$ kcal mol^{-1} and $Z = 2.02 \times 10^{18}$ sec^{-1}. These results are in almost perfect agreement with Robertson's constants[3]: $E = 47.5$ kcal mol^{-1} and $Z = 2.17 \times 10^{18}$ sec^{-1}.

Some of the vapor-phase contributions are very small at lower temperatures. For example, the vapor-phase deflection at 480 K is only ~2 mm on a 25-cm recorder for RDX in a 0.022-ml DSC cell; consequently, the vapor-phase deflection is quite difficult to establish.

The higher signal-to-noise ratio of the Perkin-Elmer DSC-2, compared with the DSC-1B, makes it possible more easily to measure vapor-phase contributions at lower temperatures. A very long "tail" is run at the end of the rate curve, marking the true baseline. The small shoulder caused by the vapor-phase reaction can usually be detected above the true baseline with some confidence, and the inflection marking the shoulder can be extrapolated back to zero time to provide the baseline for the condensed-phase measurements. A convenient method for the accurate establishment of the inflection point is the "method of concentric arcs"[4].

I believe that this modification to the DSC method for the determination of kinetics constants provides a more accurate procedure, and I hope that other workers in the field will not fall into the same trap I did.

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