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ANALYSIS OF COMPLEX THERMOANALYTICAL CURVES: THE THERMODYNAMIC AND KINETIC PARAMETERS OF ISOPROPYLAMMONIUM NITRATE

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A method is presented to determine thermodynamic and kinetic parameters from complex thermoanalytical curves. Such curves are obtained when thermoanalytical events like phase transition and chemical decomposition overlap.

Isopropylammonium nitrate was taken as an example to demonstrate how these parameters were determined from non-isothermal TG and DSC curves by constructing DSC-DTG sum curves.

The thermodynamic and kinetic analysis of non-isothermal DSC and TG curves is difficult if the reaction intervals of the key thermoanalytical events overlap. The key events are phase transition (transitions in the solid, sublimation, liquefaction or evaporization) and chemical reaction. Hence, procedures are of interest which discriminate between these events to simplify the analysis.

As shown earlier (ref. 1) DSC can be treated as the derivative of the TG. In case that the thermoanalytical curve is not too complex, phase transition and chemical decomposition can be separated by forming the sum of the (digitalized and normalized) DSC and DTG curves thereby eliminating one of the interfering events. The sign of DTG determines which of the two will be eliminated : As viewed by DTG, both, phase transition and decomposition have negative signs (if accompanied by weight loss on heating) as opposed to DSC where phase transition is negative but decomposition positive. Hence, forming the sum of DSC and DTG eliminates decomposition whereas that of DSC and inverted DTG eliminates phase transition.

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By constructing DSC-DTG sum curves phase transition and decomposition appear separately and can be analyzed in the usual fashion. In the following DSC-DTG sum curves were used to calculate thermodynamic and kinetic parameters from the (overlapping) evaporization and decomposition intervals of isopropylammonium nitrate (IPAN).

METHODS

Construction of the DSC-DTG sum curves

The basis for this procedure is the relation:

$$DSC(T) = P\ DTG(T), \tag{1}$$

where P denotes a proportional factor. The relevant sum curves are:

$$Se(T) = DSC(T) + P\ DTG(T) \quad \text{and} \tag{2}$$
$$Sd(T) = DSC(T) + \text{inverted } P\ DTG(T). \tag{3}$$

Se(T) describes the evaporation interval and Sd(T) that of decomposition. To get Se(T) and Sd(T) the experimental DSC and TG curves were digitized (580 data points per 100 C intervals), the derivative taken and the data normalized with respect to weight, heating rate and instrumental sensitivity. DTG was corrected for offset drift. DTG was noisy and had to be smoothed.

The proportional factor P was determined by dividing DSC and DTG at the maximum according to equ. (1). However, corrections had to be made on P the criterion thereby being the difference sum of DSC and P DTG to equal zero (ref. 2).

The evaporization enthalpy was calculated by taking half of the integral of the DSC-DTG sum curve and normalizing on the converted mass. This mass was found from the TG curve at that temperature where the sum curve was minimal. This tem-

perature marks the transition from evaporization to decomposition.

The reaction enthalpy was obtained in a similar fashion from the DSC-inverted DTG sum curve. DTG was inverted by reflecting at DTG(T) = 0.

The kinetic parameters were determined by fitting the theoretical DTG to the DSC-inverted DTG sum curve by a non-linear least-squares program (ref. 3). The theoretical DTG of a nth order reaction ($n \neq 1$) is

$$dm/dT = -z/\beta \exp(-E/RT)\,(1 + z/\beta(n-1)\,S(T))^{n/(1-n)} \qquad (4)$$

where m=mass of the reactand, T=temperature, z=frequency factor, ß=linear heating rate, E=activation energy, R=gas constant, n=order of reaction, S(T)=integral of the Arrhenius function. The fit parameters are n, E and z.

Experimental

A Mettler TG and DSC (TA 3000) was used. Care was taken (and this was crucial) to correlate the DSC and TG temperatures by calibration with standards. The correlaion obtained was +/- 1 ^{o}C. The heating rate employed was 5 C/min.

Small sample weights (2 mg) were used. The covers of the flat aluminum pans were pierced to allow easy escape of the gaseous products. The chamber was purged by a stream of Ar.

IPAN was synthezised by dropwise addition of a cooled 50% mixture of isopropyl ammonia and water to 30% HNO_3, the proportions being stoichiometric. The purity of the product was checked by IR and elementary analysis.

RESULTS AND DISCUSSION

IPAN melts at 72 C and susceptible evaporation is noted at 150 C overlapped by decomposition at 200 C. The overlapping

intervals of evaporization and decomposition are evident from an inspection of Figs.1 and 2 which display the DSC and TG curves as obtained by the experiment.

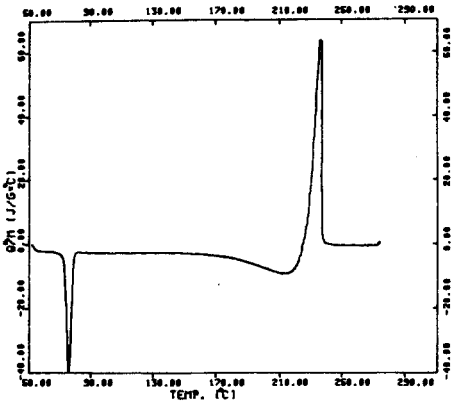

Fig. 1 DSC of IPAN in Ar, heating rate 5 C/min.

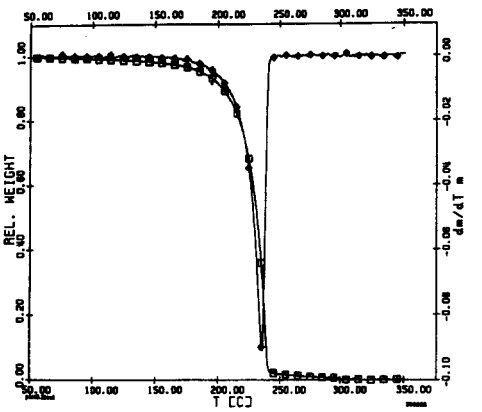

Fig. 2 TG of IPAN in Ar, heating rate 5 C/min.

The enthalpy of evaporization was calculated by integrating the addition sum curve Se(T) = DSC(T) + P DTG(T). The enthalpy is 864 J/g which is one half of the Se(T) integral. Because of the direction of the signs in Se(T) the portion of evaporarization is doubled whereas that of decomposition is eliminated. In Fig. 3 DSC(T) and DTG(T) are compared to SE(T)= 1/2 Se(T) the cross-hatching thereby marking the complete evaporization interval.

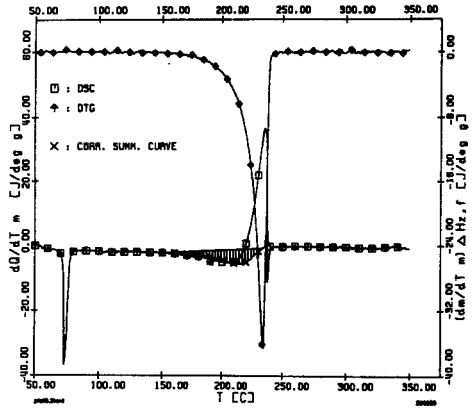

Fig. 3 Comparison of SE(T), DSC and DTG

Conversely, in Sd(T) = DSC(T) + inverted DTG(T) the portion of decomposition is doubled wheras that of evaporization is eliminated. In Fig. 4 the function SD(T) = 1/2 Sd(T) is compared to DSC and inverted DTG and the crosshatching in in turn denotes the complete decomposition interval. The enthalpy of decomposition is 497 J/g.

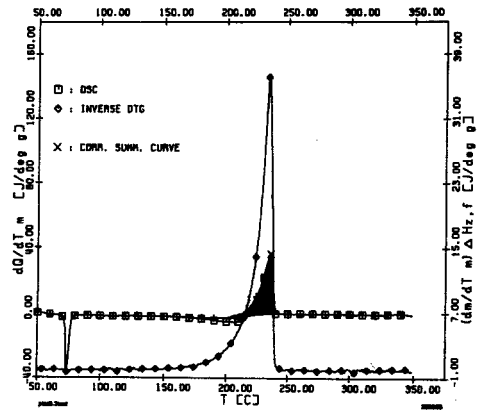

Fig. 4 Comparison of SD(T), DSC and inverted DTG

In a subsequent step the kinetic parameters were determined by fitting equ. (4) to SD(T). The result is displayed in Fig. 5 where SD(T) is represented by the points used in the

calculation whereas the fit curve is depicted by the drawn line. The standard deviation of the best fit was 10.4 % and the kinetic parameters obtained were n = 0.3, log z = 31.2 and E = 325 kJ/mole.

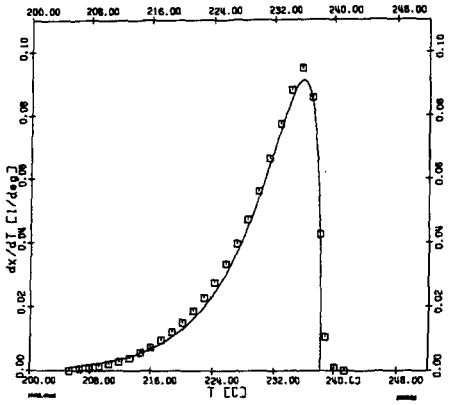

Fig. 5 Fit of the theoretical DSC to SD(T)

We assessed the quality of this method by comparing the standard deviations of fits to the original DSC and DTG curves by selecting those parts which showed less overlapping by the phase transition. Such a fit is depicted in Fig.6 for the DSC interval 210 to 240 C. The graph reveals the flatness of the fit curve when compared to the experimental cur-

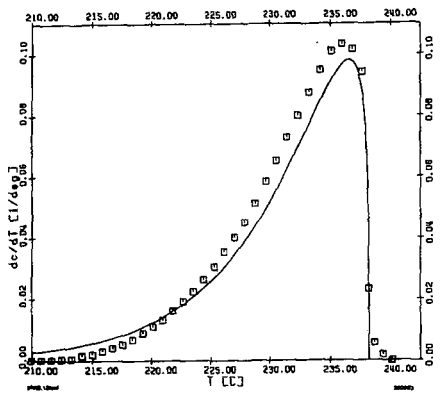

Fig. 6 Fit of the theoretical DSC to the original DSC

ve. The standard deviation of this fit was 16.8%. Even worse that for the DTG curve which amounted to 27 %.

On inspecting the kinetic parameters one should observe that the parameters represent a formal description of the IPAN overall decomposition process. In general, the alkylammonium nitrates exhibit a complex decomposition pattern involving a variety of pathways (ref. 4). The overall kinetics, however, is not understood.

Furthermore, the results display a linear compensation effect (ref. 5) and sets of differing values were obtained for log z and E the span ranging from 13.8 to 31.2 and 158 to 325 kJ/mole, respectively. The presence of this effect is documented by the linear relationship of log z against E. However, the linear relationship in turn reflects the common origin of the parameters and, hence, their reproducibility.

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Zusammenfassung - Es wird ein Verfahren zur Bestimmung thermodynamischer und kinetischer Parameter von komplexen thermoanalytischen Kurven beschrieben. Kurven dieser Art entstehen bei der Überlappung thermoanalytischer Ereignisse wie z.B. Phasenumwandlungen und chemiche Zersetzungen.

Am Beispiel von Isopropylammoniumnitrat wird demonstriert, wie die einzelnen Parameter der nicht-isothermen TG und DSC Kurven durch Konstruktion von DSC-DTG-Summenkurven ermittelt werden.

Резюме – Представлен метод для определения термодинамических и кинетических параметров из сложных термоаналитических кривых. Такие кривые получаются в том случае, если фазовый переход и химическое разложение перекрываются. Изопропиламмоний нитрат был взят в качестве примера для показа того, как эти параметры были определены из неизотермических кривых ТГ и ДСК путем построения суммарных кривых ДСК-ДТГ.