Journal of Thermal Analysis, Vol. 33 (1988) 87–95

INFLUENCE OF THE SAMPLE MASS AND THE PRESENCE OF THE REACTION PRODUCTS ON THE THERMOANALYTICAL RESULTS

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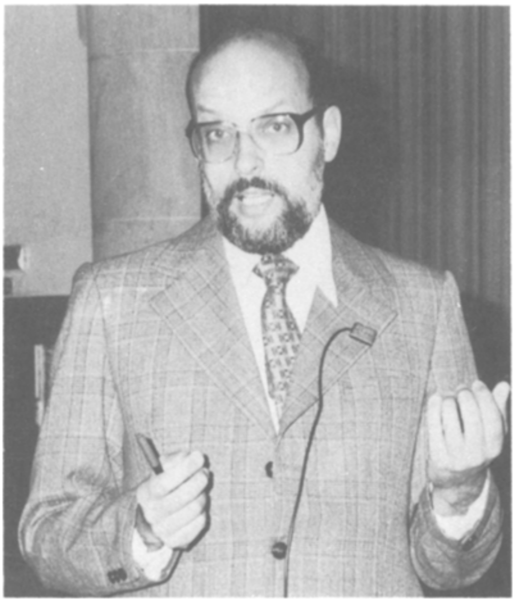

It has been known from the very beginning of the thermal analysis that the transport processes can significantly influence the thermoanalytical results. In this paper, three characteristic examples are given to show that this problem is more complex and arises more frequently than it is generally believed. The studied reactions are the carbon monoxide evolution from calcium oxalate, the thermal degradation of polytetrafluoroethylene, and the thermal decomposition of azodicarbonamide. TG and DSC experiments were carried out with sample masses varying between 0.05 and 8 mg. The necessity of the development of new kinetic models is concluded.

50 years ago Saito studied the thermal decomposition of calcium carbonate by thermogravimetry and reported the effect of the sample mass, sample reactivity and the presence of a CO_2 atmosphere on the thermogravimetric curves [1]. Since then many excellent works have been published

John Wiley & Sons, Limited, Chichester
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dealing with this type of effects. Nevertheless, the present day thermoanalytical literature still shows that

i) the mass transfer is believed to affect only a few special reactions (dehydration, carbonate decomposition, etc.)
ii) mass transfer problems are supposed to be present only at high sample masses or heating rates
iii) oversimplified reaction kinetic equations are applied without any experimental check on the real simplicity of the studied reactions.

According to our experience, the reality is more complex. In this paper, three characteristic examples are selected to illustrate the variety of effects produced by Nature in this field. The examples belong to three different type of reactions: a simple oxalate decomposition, a polymer degradation and the decomposition of a common industrial blowing agent.

Experimental

Instrumental

Perkin Elmer TGS–2 and DSC–2 were used with computerized data acquisition and data processing. (A PDP 11/34 computer was applied to reduce the random noise of the experimental curves and to obtain reliable DTG curves and base line corrections.) The measurements were carried out at low heating rates and sample masses. Part of the measurements were repeated at high heating rates, up to 60 deg/min. The TG and DSC measurements were carried out in 140 ml/min argon and 40 ml/min nitrogen flow, respectively.

Materials

Calcium oxalate monohydrate: analytically pure reagent Polytetrafluoroethylene: BDH laboratory reagent Azodicarbonamide ($H_2NCONNCONH_2$): Genitron AC2 from Fisons Ltd.

Results and discussion

Calcium oxalate monohydrate

The first and last decomposition steps of this substance (dehydration and carbonate decomposition) are well known examples for the influence of the volatile decomposition products on the course of simple chemically reversible reactions. It may be well worth mentioning that the chemically irreversible second reaction is also influenced by the presence of the evolved carbon monoxide [2]. This effect is so significant, that the usual dependence of the peak temperature on the heating rate can fully be compensated by a proper change of the initial sample mass. In Fig. 1, DSC curves of two different heating rates (10 and 20 deg/min) are shown. In this case the doubling of the heating rate could be counterbalanced by halving of the initial sample mass. The fit between the two curves indicates a strong mass transfer control in the given range of experimental parameters.

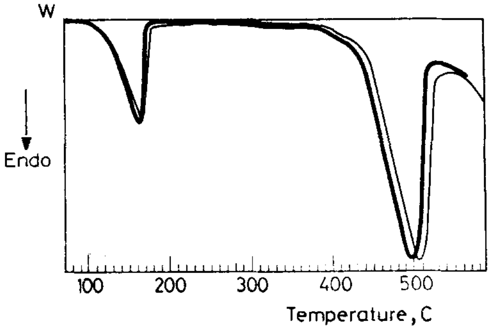

Fig. 1 Correspondence between the DSC curves of calciumoxalate monohydrate at 10 deg/min and 1.82 mg (——) and 20 deg/min and 0.91 mg (——).

Another irregularity in the DSC curves of $CaC_2O_4 \cdot H_2O$ was connected with the peculiar dependence of the magnitude of the measured heat consumption on the sample mass. Carrying out the experiments with low sample masses, the measured specific heat consumption was considerably higher than in the case of higher sample masses. At a low heating rate, 2.5 deg/min, the increase of the sample mass from 1 mg to 3 mg changed the measured specific reaction heat from −266 to −212 kJ/mol. At a higher heating rate, 40 deg/min, sample masses of 0.24, 0.45 and 1.8 mg led to specific reaction heats of −282,

−239 and −134 kJ/mol, respectively. (See Fig. 2). The comparison of the experiments of different heating rates showed that the observed specific reaction heat depends primarily on the evolution rate of the carbon monoxide. When the increase of the reaction rate arising from a higher heating rate was compensated by an appropriate decrease of the sample mass, the apparent specific reaction heat did not change. Thus experiments carried out at 10, 20 and 40 deg/min with sample masses of 1.8, 0.9 and 0.45 mg, respectively, yielded approximately the same reaction heats: −241, −238 and −239 kJ/mol. Thermogravimetric measurements under similar experimental conditions did not evidence any considerable alteration from the theoretical mass loss value of the reaction $CaC_2O_4 = CaCO_3 + CO$. Hence the observed irregularity is probably caused by a secondary reaction taking place outside of the sample. (Note, that a carefully tested power compensation DSC was used, the reaction is endothermic, and the observed differences were very much higher than the experimental uncertainty.) A possible explanation may be due to the highly exothermic disproportion reaction $2\,CO = C + CO_2$. which can easily occur on the hot platinum surfaces of the measuring cell. Since the rate of this reaction increases with the CO concentration, the relative error caused by its heat effect increases with the sample mass. It is possible that the formed carbon is oxidized by the oxygen traces being in the inert gas. A direct oxidation of the carbon monoxide by the oxygen traces, however, can hardly result in the observed dependence of the apparent specific reaction heat on the sample mass.

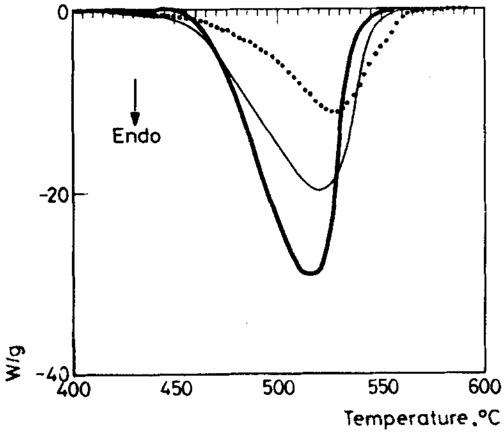

Fig. 2 DSC peak of the CO evolution from calciumoxalate monohydrate at 40 deg/min with sample masses of 1.8 mg (••), 0.45 mg (——), and 0.24 mg (——). (The peaks were normalized with the sample masses.)

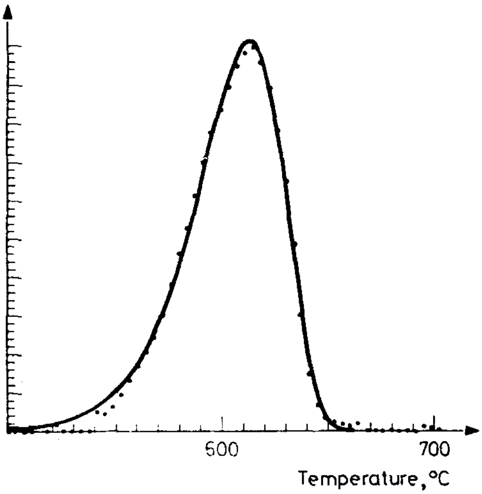

Fig. 3 Least squares kinetic evaluation of the DTG curve (··) of 0.08 mg polytetrafluoroethylene at 60 deg/min. The best fitting kinetic curve (——) belongs to parameters n = 0.96, E = 308 kJ/mol and $A = 10^{-17}$ s^{-1}.

Polytetrafluoroethylene

Polytetrafluoroethylene decomposes through a thermal depolymerization leading almost entirely to monomers. Its kinetics was extensively studied between 1953–1965 and there was no agreement whether it is a first order or a zero order reaction [3]. We have studied the reaction kinetic by evaluating DTG curves by the method of least squares. (A true least squares method was applied: the kinetic parameters were systematically varied until the best fit was achieved between the observed DTG curve and the corresponding theoretical curve. An example is shown in Fig. 3.) According to our experience, the decomposition is a nearly zero order process in an inert atmosphere when usual sample masses and heating rates are used, e.g. 6 mg and 4 deg/min. However, a nearly first order kinetics was obtained at low initial sample masses. If the sample mass was sufficiently low, first order kinetics could be obtained even at heating rates as high as 60 deg/min. Thus a sample mass of 0.08 mg yielded a reaction order of 0.96, activation energy of 308 kJ/mol, and preexponential factor of 10^{17} s^{-1} at 60 deg/min. (See Fig. 3.) The obtained kinetic parameters are in accordance with the results of several earlier investigators [3] and can be interpreted in such a way that the breaking of the C–C bonds in the polymeric chains are followed by the complete depolymerization of the formed radicals. It may be well worth considering how can quite usual thermoanalytical conditions (6 mg sample at 4 deg/min) transform this simple mechanism into a virtually zero order process. It is reasonable to suppose that the monomers, having a higher concentration in the deeper parts of the sample during the degradation, slow down the depolymerization by polymerizing back to the radicals. The radicals, escaping the immediate "unzipping" there, have more chance to participate in second order recombination reactions. In this way a C–C bond scission leads to considerable less monomer formation in the deeper parts of the sample and the decomposition of the whole sample appears to be a surface reaction.

Azodicarbonamide

Azodicarbonamide ($H_2NCONNCONH_2$) is a blowing agent commonly used for foaming of plastics as well as for bread making. It decomposes to about 32% (m/m) light gases (N_2, CO, CO_2), 27% condensable volatiles and 41% solid residue [4]. The reaction is exothermic with a reaction heat of about 131 kJ/mol and its isothermal kinetics can be describe by the Prout-Tompkins equation [5]. In the present study, isothermal and non-isothermal TG and DSC measurements were carried out. We found that the use of covered sample holders in isothermal TG experiments with 1 mg sample mass considerably speeded up the reaction. These experiments alone can not reveal the real cause of the speedup: it may be due to a chemical interaction between the sample and the decomposition products as well as to a local overheating or to the small amount of oxygen remaining in the covered sample holders. To exclude the later two cases, we checked the possible influence of the oxygen and the effect of smaller sample sizes (up to 0.05 mg) in separate experiments. The TG curves with 1 mg sample mass did not change when 30% oxygen was added to the carrier gas. The domain of the lower sample masses was studied by DSC. It may be interesting to note that no significant heat production was observed when a sample of 0.1 mg was placed in an open sample holder and heated with a heating rate of 10 deg/min. However, the application of hermetically sealed sample holders resulted in sharp, well defined and reproducible peaks. (See Fig. 4.) Applying smaller samples in the same type of sample holders shifted the decomposition to a higher temperature. (See Fig. 5.) The heat transfer problems can surely be excluded in this range of sample masses. In this way, the thermal decomposition of the azodicarbonamide clearly shows that the presence of the volatile products can speed up a thermal decomposition reaction.

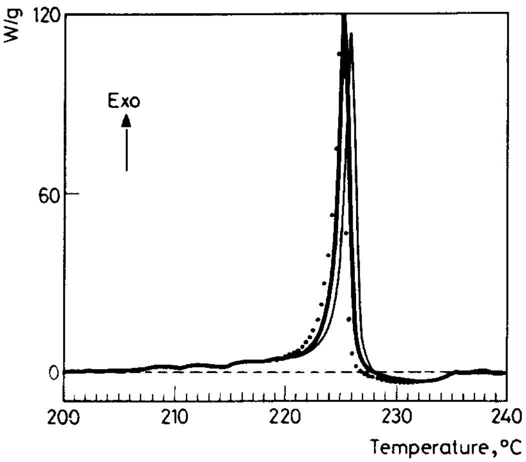

Fig. 4 Reproducibility of the DSC curves azodicarbonamide at 10 deg/min with sample masses of 0.1 mg in sealed sample holders. (3 parallel experiments.)

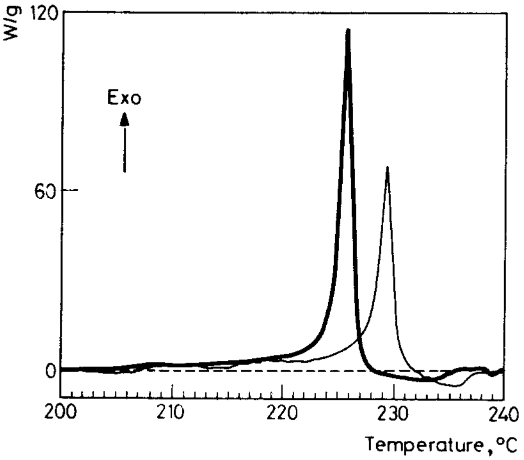

Fig. 5 DSC peaks of azodicarbonamide at sample masses of 0.1 mg (——) and 0.05 mg (——) in sealed sample holders at 10 deg/min.

Conclusions

During an experience of 20 years in thermal analysis, we observed more frequently the effect of the sample mass on the studied reactions than the lack of such effects. In this paper, three characteristic examples were shown. It may be interesting to consider here briefly the relationship of the sample mass problems and the kinetic evaluation of the data. We do not doubt the necessity of some sort of physically meaningful mathematical description of the thermal decomposition processes. (Without a proper mathematical model, the information content of the experimental results can not be fully exploited.) The effect of the decomposition products on the decomposing sample is probably well worth including in the models. The situation here is different from the case of the heat transfer problems. The heat transfer is a physical phenomenon which should be avoided experimentally in thermal decomposition studies. On the other hand, the effect of the decomposition products on the decomposition is an integral part of the chemistry of the process. The real understanding of the decomposition processes hardly seems possible without the careful study of the possible interactions between the sample and the reaction products. The survey of the literature dealing with this topic is the subject of a detailed review to be appear soon [6]. However, the available models seem to be restricted only to the simple chemically reversible processes. Since the decomposition reactions studied by thermal analysis exhibit a wide variety of chemical mechanisms, it is highly probably that a wide variety of individual models should be elaborated in the future. Obviously, the mathematical models may exclude the secondary reactions taking place outside of the decomposing samples. As it was illustrated by DSC study of calcium oxalate monohydrate, disturbing secondary reactions may arise even if the reaction products are common compounds having relatively high chemical stability under ordinary circumstances. This type of secondary reactions should carefully be eliminated by proper experimental conditions.

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Zusammenfassung — Seit den Anfängen der Thermoanalyse ist bekannt, dass Transportprozesse die thermoanalytischen Ergebnisse weitgehend beeinflussen können. Es werden hier drei Beispiele beschrieben, die zeigen, dass dieses Problem weitauf komplizierter ist und häufiger auftritt als allgemein angenommen wird. Die untersuchten Reaktionen sind die Kohlenmonoxidabspaltung aus Calziumoxalat, die thermische Zersetzung von Polytetrafluoräthylen und der thermische Zerfall von Azodicarbonamid. Die TG- und DSC- Untersuchungen wurden mit Probenmassen zwischen 0.05 und 8 mg durchgeführt. Es wird auf die Notwendigkeit der Entwicklung neuer kinetischer Modelle geschlossen.

РЕЗЮМЕ — С самого начала термического анализа было известно, что процессы переноса могут значительно затрагивать термоаналитические результаты. Представлены три характерных примера, показывающих что эта проблема более сложная и более часто встречающаяся, чем предполагалось ранее. Такими примерами служат реакция выделения окиси углерода при термическом разложении оксалата кальция, реакции термического разложения политетрафторэтилена и азодикарбамида. ТГ и ДСК измерения были проведены с образцами, вес которых изменялся в интервале 0,05 и 8 мг. Сделано заключение о необходимости разработки новых кинетических моделей.