TECHNICAL NOTE

Guenter Hellmiss,[1] *Dr. rer. nat. and*
Wolfgang Schwanebeck,[1] *Dr. Ing.*

Aspects of the Investigation of the Chemical Processes of Self-Heating as a Fire Cause by Means of Quantitative Thermal Analysis

ABSTRACT: A procedure for the investigation of chemical self-heating processes as possible fire causes is presented. The temperature rise for adiabatic conditions is calculated from reaction enthalpy and specific heat and compared with the relevant ignition temperature of the system. The thermodynamic data can be provided by means of differential scanning calorimetry. Additional information can be obtained from thermogravimetric measurements.

KEYWORDS: forensic science, fires, thermal analysis, fire investigation, self-heating (spontaneous ignition), measuring method, differential scanning calorimetry, thermogravimetry

When investigating fires, especially in industrial and agricultural areas, the question of self-heating as a fire cause often arises. Forensic scientists in West Germany and in some other European countries are often confronted with this problem. Unfortunately, however, in the field of forensic science relatively few efforts have so far been made to develop meaningful methods of investigating such processes. Among methods that have been used in the past more or less frequently are thermal instability tests, for example, the so-called Mackey Test, which was introduced in 1896 in the textile industry. Such methods allow relatively rough statements only [1,2], and some of them are limited to certain classes of substances.

In English literature self-heating often is called "spontaneous ignition" or "spontaneous combustion." This is somewhat misleading. According to discussions in Ref 3, one should use the term self-heating for the chemical process, which, depending upon particular conditions, may cause either self-ignition or ignition of neighboring materials.

Considered here are exothermic chemical reactions that result in the heating of the substance or substances concerned and normally of the surroundings, too; biological processes, such as those responsible for the self-heating of hay, are not considered here.

Procedure for Calculating the Adiabatic Temperature Rise

As a first step for characterizing such processes the adiabatic rise of temperature can be determined, that is, the temperature rise when no heat is dissipated to the surroundings. According to Eq 1 in Table 1 the adiabatic temperature rise can be calculated from the appropriate mean values of the reaction enthalpy per mass unit ΔH and of the specific heat c_p for reactions run at constant pressure. The temperature T_E then has to be compared with the relevant ignition temperature T_I.

For the quantitative determination of ΔH and c_p the method of differential scanning calorimetry (DSC) is especially suitable, as has been demonstrated elsewhere [4]. The principle of this method is illustrated in Fig. 1, a schematic plot of the heat released per unit time $\dot{Q}_s$ against the sample temperature T for an exothermic reaction. The baseline $\dot{Q}_0$ represents a DSC curve obtained with empty sample and reference holders. The displacement of the curve $\dot{Q}_s$ with respect to the baseline $\dot{Q}_0$ at temperature T_1 is proportional to the heat capacity of the sample. The hatched area reflects the reaction enthalpy (see Eqs 2 and 3 in Table 1).

Figure 2 shows a DSC curve of a two-component adhesive (an epoxy resin with a hardener), the self-heating of which, according to the opinion of the investigating criminal police service, caused a fire. The DSC curve (of which the baseline is not shown here) shows an exothermic peak, the evaluation of which gives ΔH values varying with the ratio of hardener to epoxy component. A maximum value of $\Delta H = -310 \text{ J/g}$ is measured for a mixture ratio of about 1 : 1. At temperatures of up to 330 K the specific heat is $c_p = 2.4 \text{ J/g} \cdot \text{K}$. From these results $\Delta T_{ad} \approx$ 130 K is calculated. If, for instance, $T_0 = 20°\text{C}$, then $T_E \approx 150°\text{C}$ (see Table 2). According to the DSC and TG curves in Fig. 2 and to the literature (for example, Ref 5), ignition of cured epoxy resins takes place at temperatures above 500 K, so that self-ignition can be ruled out in this case by this simple thermodynamic procedure. Details of reaction kinetics and of heat dissipation need not be considered.

TABLE 1—*Formulas used.*

$$\Delta T_{ad} = T_E - T_0 = \frac{-\overline{\Delta H}}{c_p} \tag{1}$$

ΔH = reaction enthalpy per mass unit
c_p = specific heat at constant pressure
T_0, T_E = temperatures at beginning and end of reaction, respectively

T_E to be compared with T_I

T_I = relevant ignition temperature

$$c_p = \frac{\dot{Q}_s(T_1) - \dot{Q}_0(T_1)}{\alpha \cdot m} \tag{2}$$

m = total mass of substance
α = $\frac{dT}{dt}$ = rate of heating
(see Fig. 1)

$$\overline{\Delta H} = \frac{\int_{T_1}^{T_1}(\Delta \dot{Q} - m \cdot c_p \cdot \alpha)\, dT}{\alpha \cdot m} = \frac{F}{\alpha \cdot m} \tag{3}$$
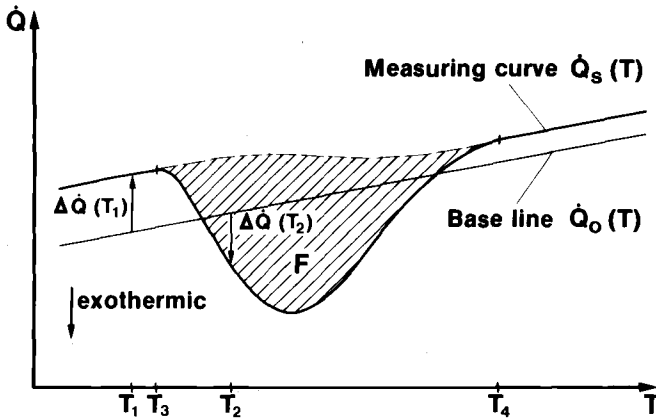
F = hatched area

(see Fig. 1)

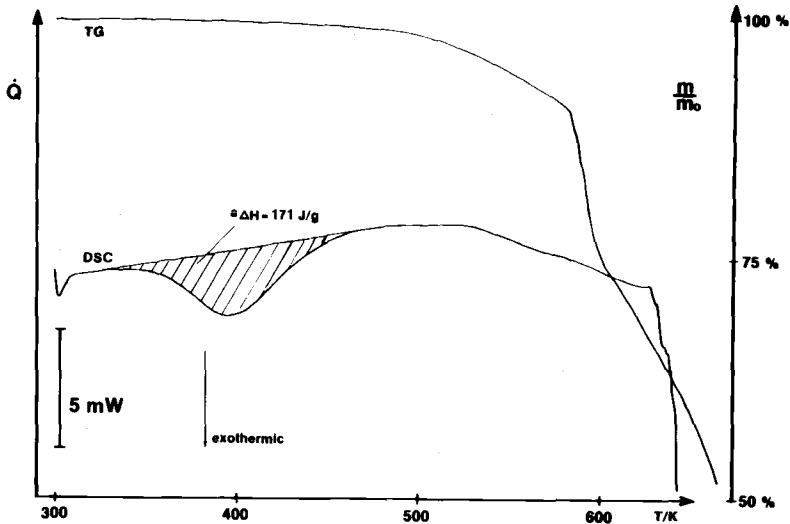FIG. 1—*Schematic differential scanning calorimetry (DSC) curve.*

FIG. 2—*Differential scanning calorimetry (DSC) and thermogravimetry (TG) curves of an epoxy resin.*

Such cases in which adiabacity is a sufficient approximation are not exceptional (for example, Ref 6). On the other hand, if heat dissipation (and therefore reaction kinetics, too) have to be taken into account, exact statements are of course no longer possible using only thermodynamic arguments and then the determination of the adiabatic temperature rise is only a first step.

The following case, in which different species of soot had to be investigated, may be regarded as an example for this. Since the background of this case has been described in detail in Ref 4, only the results are given here. Figure 3 shows the DSC curves of soots from acetylene and crude oil and of ground coal (where again the baselines have not been drawn). No reaction for acetylene soot and only the normal combustion reaction at nearly 550 K and an endothermic peak at low temperature for the soot from crude oil are to be seen. With ground coal, on the other hand, one finds an exothermic reaction starting at about 470 K with $\Delta H \simeq -2300$ J/g.

TABLE 2—*Calculation of adiabatic temperature rise.*

first example: *epoxy resin*

$\overline{\Delta H}$ = – 310 Jg^{-1}

$\overline{c_p}$ = 2,4 Jg^{-1} K^{-1}

ΔT_{ad} ≈ 130 K

T_0 = 293 K ⟶ T_E ≈ 423 K

second example: *ground coal*

$\overline{\Delta H}$ ≈ – 2300 Jg^{-1}

c_{p_0} = 1,7 Jg^{-1} K^{-1} for graphite
at 800 K

ΔT_{ad} > 1300 K

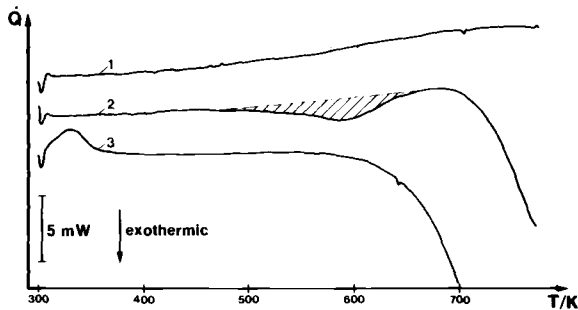

FIG. 3—*DSC curves of three carbonaceous materials:* (1) *acetylene soot,* (2) *ground coal, and* (3) *crude oil soot.*

Using c_p = 1.7 J/g · K (specific heat of graphite at T = 800 K), an adiabatic temperature rise of at least 1300 K is derived (Table 2). With an ignition temperature for coal dusts of 700 K or less (compare DSC curve 2 in Fig. 3 and data given in the literature, for example, Ref 7) the conclusion is that self-ignition of ground coal is readily possible under adiabatic conditions. But as it is known that self-ignition of coal dusts normally takes place only after long induction times if reaction starts near room temperature, adiabacity in this case is only a poor approximation. Nevertheless the procedure gives a valuable result, namely, in this case that the calculated (hypothetical) adiabatic temperature rise is so enormous that one may conclude that self-ignition is likely to occur under conditions of sufficiently slow heat dissipation.

Differential Scanning Calorimetry and Thermogravimetry

In such cases further details both of the DSC and TG curves may help in assessing the possibility of ignition. For example, one can roughly estimate the onset of significant heat release of
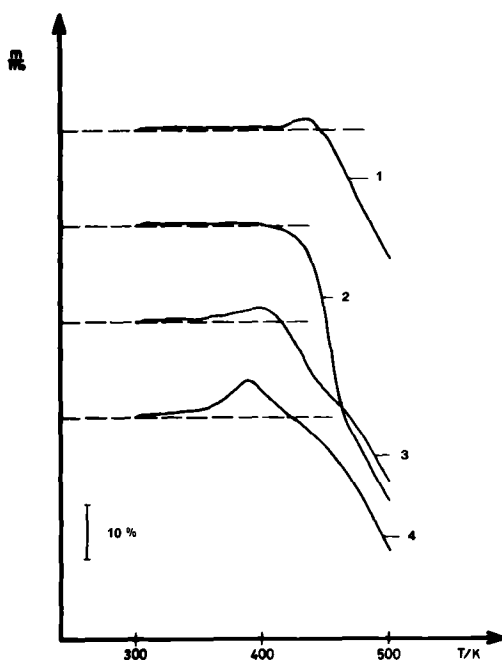
FIG. 4—*TG curves of linseed oil and three constituent unsaturated fatty acids:* (1) *linseed oil,* (2) *oleic acid,* (3) *linoleic acid, and* (4) *linolenic acid. Dashed lines:* m/mo = *100%.*

the exothermic reaction (see second case), state whether it runs in one or more steps or whether the surrounding gas atmosphere influences the reaction.

In some cases the method of thermogravimetry, by which the change of weight with temperature is measured, can supply additional information. In Fig. 2 no substantial weight change occurs at temperatures of the first DSC peak. So the assumption is confirmed that this peak reflects the thermal effect of the hardening (polymerization) reaction.

Under an atmosphere of oxygen one finds, for instance, with ground coal or with linseed oil and some of its components a slight increase in weight at the beginning as may be seen in Fig. 4. For ground coal, this probably indicates the chemisorptive addition of oxygen to the reactive coal surface. In the case of linseed oil the weight increase may be regarded as a consequence of the addition of molecular oxygen to carbon-carbon double bonds.

Therefore, also in cases where adiabacity is only a poor approximation, the determination of the adiabatic temperature rise and details of the DSC and TG curves are a valuable means for assessing the possibility of an ignition. In those cases, however, further improvements are necessary.

Conclusion

The procedure presented here for the investigation of possible self-heating cases contains the following essential steps:

From reaction enthalpy and specific heat, determined by means of differential scanning calorimetry, the adiabatic temperature rise ΔT_{ad} is evaluated. $T_E = T_0 + \Delta T_{ad}$ then is compared with the relevant ignition temperature T_I of the system. If $T_E < T_I$, self-ignition must be ruled out. If $T_E \geq T_I$, self-ignition is possible in principle.

According to the authors' experience many cases can be solved in this way both for $T_E < T_I$ and $T_E \geq T_I$. In cases where a simple thermodynamic procedure is not sufficient, the calculated adiabatic temperature rise as well as details derived from DSC and TG curves can help in assessing the possibility of an ignition, though here further improvements are necessary.

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Address requests for reprints or additional information to
Dr. Guenter Hellmiss
Bundeskriminalamt
11 Thaerstr., Postfach 1820
Wiesbaden, W. Germany 6200