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TG AND TGT INVESTIGATIONS OF THE DECOMPOSITION OF NITROCELLULOSE UNDER QUASI-ISOTHERMAL CONDITIONS

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A derivatographic study was made of the influence of the slow heat transport between the sample and its surroundings upon the courses of exothermic transformations. It was found that if the sample was placed in a thin film layer on the multiplate sample holder and the quasi-isothermal heating technique was applied, then the rate of the decomposition could already be regulated at will, up to a certain limit. Under the conventional thermoanalytical conditions the same sample decomposed in an explosion-like way. The examinations were supplemented with thermo-gas-titrimetric (TGT) measurements.

In thermal analysis many difficulties are caused by mass and heat transport processes which exert pernicious effects upon the chemical and physical transformations and hence upon the course of thermoanalytical curves.

It is known that the courses of reactions of inorganic compounds leading to equilibrium can be significantly influenced by the uncontrollable changes taking place in the partial pressure of the gaseous decomposition products in contact with the solid sample and indirectly by the experimental conditions controlling the transport of the gaseous products [1, 2].

The slow heat transport similarly disadvantageously influences the courses of endothermic transformation processes, for a sample with poor thermal conductivity is not able to absorb instantaneously the heat amount corresponding to the transformation heat. Due to this, the transformations usually take place in a protracted manner and in a broad temperature interval, with the consequence that at times the processes, i.e. the thermal curves, become distorted [1].

Thermoanalysts have attempted to reduce these pernicious effects of mass and heat transport in different ways. Noteworthy results were attained in this respect by applying a lower or higher pressure than the atmospheric one, by purposeful variation of the shape of the sample holders, by drastic reduction of the sample amount, by introduction of a "selfgenerated" atmosphere, and so on [3, 4]. The same intentions led to the development of quasi-isothermal and quasi-isobaric thermogravimetry too [1].

The problem can be studied in the most reliable way on the example of the thermal decomposition of inorganic compounds leading to equilibrium. Figure 1 demonstrates the decomposition of calcium carbonate under different conditions.

Curve 1 was traced in the conventional way (dynamic heating programme, atmospheric pressure, open crucible), while curve 2 was obtained under quasi-isothermal and quasi-isobaric (labyrinth crucible) conditions.

On application of the quasi-isothermal heating technique, the transformations took place two orders of magnitude more slowly than with the dynamic heating programme. Thus, the time was sufficient for the sample to absorb the heat of transformation. At the same time, with the application of the labyrinth crucible the stability of the partial pressure of the gaseous decomposition products could be ensured in the vicinity of the sample, in contrast with the open crucible in the inside of which the partial pressure of the gaseous products continuously changed in an uncontrollable way during the whole transformation. By elimination of the earlier-mentioned two error sources, the course of curve 2 became quite unambiguous and nearly ideal. By taking curve 2 as the basis of comparison, it can be stated that the great difference between curves 1 and 2 can be attributed solely to the pernicious effects of heat and gas transport processes which are always present in examinations carried out under dynamic heating conditions.

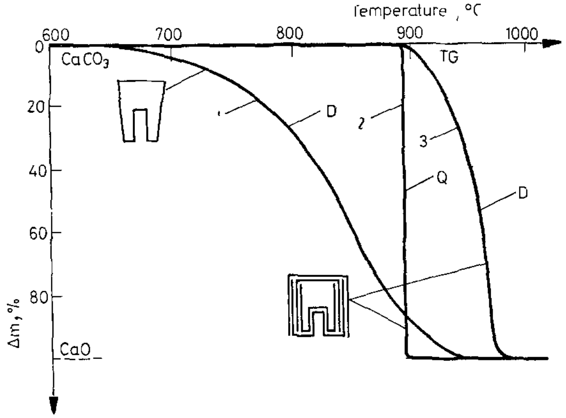

Fig. 1. Decomposition of calcium carbonate. Heating: dynamic (10°/min) (curves 1, 3) and quasi-isothermal (0.3 mg/min) (curve 2). Sample holder: crucible (curve 1) and labyrinth crucible (curves 2, 3)

Of course, besides these two processes, other partial processes (nucleus formation, nucleus growth, self-diffusion, gas-diffusion across the new phase, etc.) can also play a role in the courses of thermal transformations. However, since in general the above two processes are the slowest ones, in the case of transformations leading to equilibrium, within the frame defined by the relationship existing between decomposition pressure and temperature, mainly these two processes determine the courses of dynamic thermoanalytical curves.

Curves 2 and 3 in Fig. 1 were obtained under quasi-isothermal and dynamic heating conditions, but in both cases the labyrinth crucible was used. Accordingly, both cases the partial pressure of the gaseous decomposition products remained at 1 atm during the decomposition. Consequently, the great difference between the courses of the two curves can be explained solely by the unfavourable effect of the slow heat transport being the result of the dynamic heating.

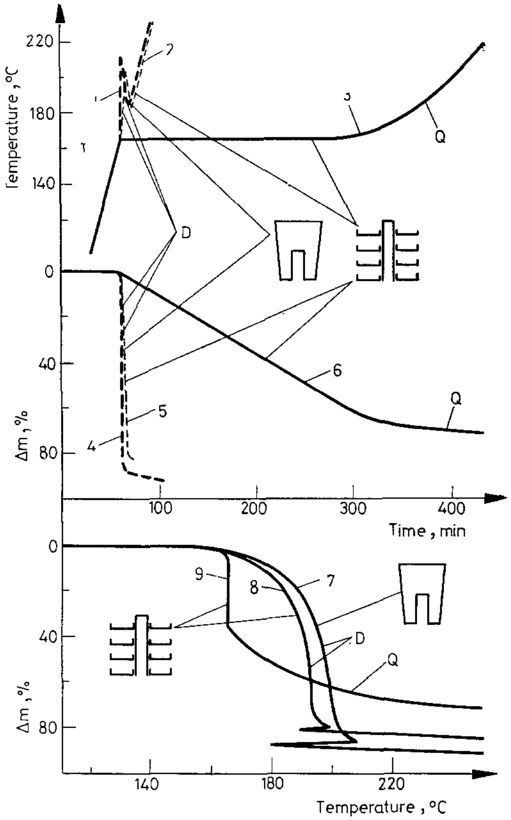

Fig. 2. Influence of the heating rate upon the decomposition of nitrocellulose. TG and T curves vs. time (curves 1—6) and temperature (curves 7—9). Heating: dynamic (3°/min) (curves 1, 2, 4, 5, 7, 8) and quasi-isothermal (0.3 mg/min) (curves 3, 6, 9). Nitrogen atmosphere. Fibrous material in crucible (curves 1, 4, 7) and a film (layer thickness: 10 mg/cm^2) on the multiplate sample holder (curves 2, 3, 5, 6, 8, 9)

One has to reckon with an error of this type in every case when a reaction of either an inorganic or an organic compound which does not lead to equilibrium is examined. Though the cause is the same, the character of the occurring error will be different, depending on whether the reaction is endothermic or exothermic: sample ~~with~~ poor thermal conductivity is not able either to conduct away immediately the heat liberated, or to absorb with sufficient speed the heat amount necessary for the transformation. However, while this condition causes endothermic transformations to take place in a protracted manner and in a broad temperature interval, in the case of exothermic reactions just the reverse occurs: the initially liberated heat raises the sample temperature somewhat above the temperature of the surroundings, causing the acceleration of the reaction. As a consequence, more heat is liberated, the sample temperature increases even more and the decomposition becomes quicker. Hence, depending on the experimental conditions, the transformation may even become an explosion-like decomposition process.

For the study of this question, nitrocellulose proved to be an ideal model substance. Curves 1, 4 and 7 of Fig. 2 represent the thermal decomposition of nitrocellulose as functions of time and temperature. The 100 mg fibrous sample, with a viscosity of 350 c. Poise and a nitro group content, of 28% was examined with the derivatograph in a crucible at a heating rate of 3°/min in a nitrogen atmosphere.

These curves show that under the given conditions the decomposition started at 165°, whereupon the weight (curve 4) and temperature (curve 1) of the sample began to change more and more quickly. The decomposition ended with a high rate at 210°. Thereafter, the temperature of the crucible, containing a small residue, suddenly fell back by 25°, proving that the liberated heat had increased the temperature of the crucible above the furnace temperature.

To reduce the decomposition rate, the multiplate sample holder of the derivatograph was earlier applied with success in many cases [2]. In the present case (curves 2, 5 and 8 of Fig. 2) the nitrocellulose was transferred in a dissolved state to the surface of the plates. After drying of the solution, the sample was again 100 mg in weight and formed a quite thin layer (10 mg/cm^2) upon the plates.

As curve 2 proves, the platinum plates, with their high heat capacity and conductivity and in contact with the sample over a large surface, were able to conduct away part of the liberated heat. In this way the decomposition took place somewhat more slowly (curve 5) and at a somewhat lower temperature (curve 8) during the whole process, but the overheating of the material could not be totally eliminated even in this case.

Finally, as curves 3, 6 and 9 in Fig. 2 indicate, this problem could be successfully solved by application of the quasi-isothermal heating technique [1].

In this case too the sample was placed on the multiplate sample holder, in the same way as described above. Now, however, the heating programmer controlled the temperature of the sample and sample holder so that the decomposition should take place at a strictly constant rate of 0.3 mg/min. This could be achieved by the heating programmer of the derivatograph maintaining a certain difference between the furnace and sample temperatures during the whole process, thereby controlling the heat transport between the sample and its surroundings so that the sample temperature should always be at a value ensuring decomposition at a preselected, low constant rate. The working principle of the quasi-isothermal heating programmer differs in the case of endothermic and exothermic reactions only in so far as the furnace temperature is kept at a somewhat higher value than that of the sample in the former case, and — at somewhat lower value in the latter case.

The differences between the courses of the curves traced by applying the two different kinds of heating techniques (Fig. 2) is marked. On application of the quasi-isothermal heating technique no overheating of the sample occurred (curve 3) and the decomposition took place at a predetermined, very low, constant rate (0.3 mg/min) (curve 6).

However, the different conditions changed not only the kinetics of the decomposition, but also its mechanism, as can be concluded from the course of the TG curve, recorded against temperature (curve 9).

It is well known that the mechanisms of decompositions of organic compounds are generally exceedingly complicated. In spite of this, the temperature *vs.* weight change pairs in the TG curve sometimes offer a possibility for very cautious, rather general conclusions. The value of the decomposition temperature and the further course of the temperature give information about the heat stability not only of the compound investigated, but also of the transitionally formed solid decomposition products, while the magnitude of the weight change is characteristic of the quantitative conditions.

On this basis, two periods of the decomposition can be distinguished in curve 9. First, without any temperature change the sample lost 40% of its original weight at 165°, while in the temperature interval 165–250° a further weight loss of 30% took place.

It could not be doubted that mainly the splitting-off of the nitro groups is characteristic for the first period of decomposition. However, from the course of the curves it could not be decided whether under the given conditions the nitro groups exerted only a small oxidizing effect upon the cellulose molecule, their greater part escaping as NO_2 which immediately decomposed into N_2O_3 and O_2, or whether the decomposition of the sample could be characterized by the strong oxidizing effect of the nitro groups and their reduction to nitrogen.

In order to settle this question, our examinations were repeated under quasi-isothermal conditions by applying the combined thermogravimetric (TG) and thermo-gas-titrimetric (TGT) method [5]. With this method, besides measurement of the weight changes of the sample, the escaping N_2O_3 gases could also be measured via their quantitative absorption in H_2O_2-containing water, when they are transformed to HNO_3, which can be continuously titrated with NaOH. The correctness of this procedure was proved by control examinations performed by determining the N_2O_3 evolved in the course of the decomposition of $AgNO_3$. To eliminate the interfering effects of other gaseous decomposition products (e.g. CO_2), the titration was carried out at pH 4.

The result of these examinations was a negative one. Only the departure of some tenths of one percent of N_2O_3 could be observed. A similar result was also obtained by applying the dynamic heating programme.

It was found earlier that, by applying the quasi-isothermal heating programme, not only inorganic, but also organic compounds decompose at a constant temperature only if it is a simple reaction and not a complex one, composed of several partial processes.

Accordingly, from the spontaneous stabilization of the temperature (curve 9) the conclusion can be drawn that the decomposition mechanism in the first period of the decomposition was a relatively simple one.

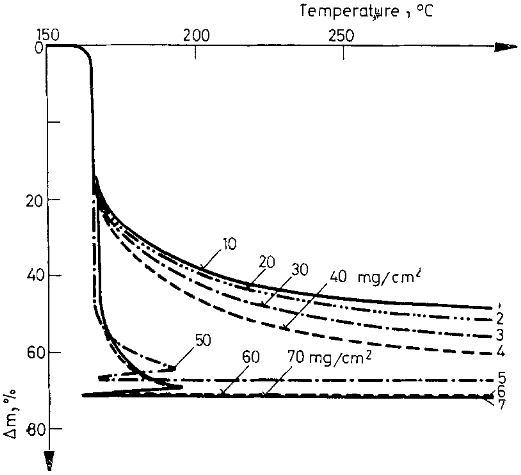

Fig. 3. Influence of the layer thickness upon the decomposition of nitrocellulose. Heating: quasi-isothermal (0.3 mg/min). N_2 atmosphere. Multiplate sample holder. Layer thickness: 10, 20, 30, 40, 50, 60 and 70 mg/cm^2 (curves 1–7)

Starting from the same idea, it can also be assumed that the second period of the decomposition was composed of numerous subsequent partial reactions. According to our present knowledge regarding the pyrolysis of organic compounds, this complicated process could be characterized in general with the concept that compounds of increasing thermal stability are being formed in the solid phase, though only transitionally, because at higher temperatures these compounds too would decompose to give place to compounds of even higher thermal stability. The solid residue can be regarded as elemental carbon only above 1000°. The compositions of the departing gases and of the solid phases become poorer in oxygen and richer in hydrogen as the temperature rises.

The curves prove that the decomposition of nitrocellulose took place in different ways depending on the applied heating programme (see curves 7 and 8, in contrast to curve 9). The decomposition path must have taken another direction just because of the overheating of the sample. The change in the mechanism of the decomposition is proved by the circumstance that the amount of the solid residue remaining after the dynamic heating at 250° was about half (curve 8) or one-third (curve 7) of that observed in the case of the quasi-isothermal heating technique (curve 9).

Figure 3 well demonstrates the influence of those experimental conditions which, due to the slow heat transport, are responsible for the overheating of the sample. These curves were traced by using the multiplate sample holder and the quasi-isothermal heating technique and they differ from one another only in so far as the sample on the plates was of different layer thicknesses. From the courses of these curves the following conclusions can be drawn: under the given conditions, up to a layer thickness of 40 mg/cm^2 the heat transport takes place without hindrance towards the surroundings, but for a layer thickness of 40–50 mg/cm^2 a sudden change occurs in the heat transport conditions, the sample becomes overheated and the decomposition mechanism changes (curves 5, 6 and 7).

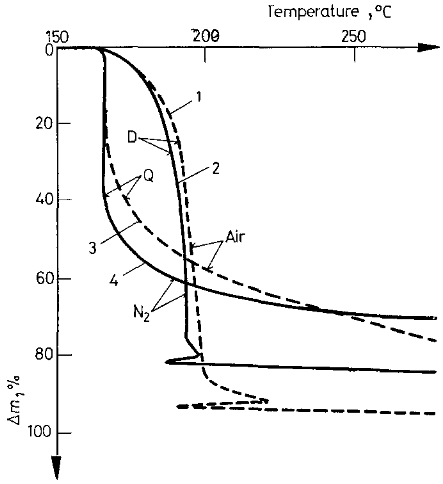

Fig. 4. Influence of the atmosphere upon the decomposition of nitrocellulose. Heating: dynamic (3°/min) (curves 1, 2), and quasi-isothermal (0.3 mg/min) (curves 3, 4). Multiplate sample holder. Layer thickness of the film: 10 mg/cm^2. Atmosphere: air (curves 1, 3) and nitrogen (curves 2, 4)

Experiments were also carried out to determine to what extent the presence of oxygen influences the decomposition of nitrocellulose. As Fig. 4 shows, for both the dynamic heating (curve 1) and the quasi-isothermal conditions (curve 3) the presence of oxygen has a far lower influence upon the decomposition of nitrocellulose than the other experimental conditions determining the rate of heat transport.

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RÉSUMÉ — Les auteurs ont étudié à l'aide d'un *Derivatograph* l'influence du transfert de chaleur lent entre l'échantillon et son environnement, sur l'allure des transformations exothermiques. Les résultats montrent que si l'échantillon est placé sous forme de films minces sur le support multiplaques et s'il est chauffé en régime quasi-isotherme, la vitesse de la décomposition peut-être contrôlée, jusqu'à une certaine limite, à volonté. Si l'on applique les conditions habituelles de l'analyse thermique, le même échantillon se décompose de manière explosive. Les auteurs ont complété leurs études en effectuant également l'analyse titrimétrique des gaz émis.

ZUSAMMENFASSUNG — Die Autoren untersuchten mit dem Derivatographen die Wirkung der langsamen Wärmeübertragung zwischen Probe und Umgebung auf den Verlauf exothermer Umwandlungen. Es wurde festgestellt, daß bei Auftragung der Probe in einer dünnen Filmschicht auf den Mehrplatten-Probenbehälter und bei Anwendung einer quasi-isothermen Aufheiztechnik die Zersetzungsgeschwindigkeit bis zu einer gewissen Grenze bereits nach Belieben gesteuert werden kann. Dieselbe Probe wird unter den üblichen thermoanalytischen Bedingungen explosionsartig zersetzt. Die Autoren ergänzten ihre Prüfungen auch mit thermogas-titrimetrischen (TGT) Messungen.

Резюме — С помощью дериватографа авторы изучили влияние медленного теплового транспорта между образцом и его окружением, влияющим на ход экзотермических превращений. Они нашли, что если образец был помещен в виде тонко-пленочного слоя на многопластинчатый держатель образцов с применением техники квази-изотермического нагрева, тогда скорость разложения могла быть регулирована по желанию до определенного предела. Тот же самый образец при обычных термоаналитических условиях разлагался со взрывом. Авторы дополнили свои исследования термо-газо-титриметрическими измерениями (ТГТ).