Journal of Thermal Analysis, Vol. 12 (1977) 391–396

SIMULTANEOUS TG AND TGT INVESTIGATIONS OF THE DECOMPOSITION OF 1-OXY-2-DIAZONAPHTHALENE-5-SULPHOCHLORIDE UNDER QUASI-ISOTHERMAL CONDITIONS

J. PAULIK, F. PAULIK, M. ARNOLD and K. A. WEHLMANN*

Institute for General and Analytical Chemistry, Technical University, Budapest, Hungary
**Hoechst AG., Premises Kalle, Frankfurt am Main, G. F. R.*

(Received March 16, 1977)

A derivatographic examination was made of the exothermic decomposition of 1-oxy-2-diazonaphthalene-5-sulphochloride. It was found that the DTA, DTG and TG curves traced under the conventional conditions could not be interpreted, since their course changed from case to case according to the experimental conditions. As a result of the combined application of the multiplate sample holder and the quasi-isothermal heating technique the course of the decomposition became unambiguous. The diazo group split off at 116°, while the sulphochloride group departed between 200 and 400°. This latter process could also be traced separately by the continuous measurement of the liberated sulphur dioxide and chlorine thermo-gas-titrimetrically.

In an earlier paper [1] we demonstrated on the example of nitrocellulose the pernicious effect of the slow heat transport between the sample and its surroundings upon the course of exothermic reactions under the conditions of conventional thermoanalytical examinations. This is generally manifested in the fact that the sample is not able to conduct away the liberated heat instantaneously. The temperature of the sample increases spontaneously above the furnace temperature, which leads to the acceleration of the reactions. This often causes transformations to take place in an explosion-like way.

It was also proved experimentally that in such cases the quasi-isothermal heating technique [2] can be applied advantageously. In this case the heating programmer of the derivatograph controls the furnace temperature so that this is somewhat lower than that of the sample during the whole transformation process, this temperature difference being such that the decomposition reaction takes place at a constant preselected minute rate (0.3 – 0.5 mg/min). In this way the overheating of the sample can be eliminated, the transformation does not accelerate and its rate can be controlled. From the point of view of a better knowledge of the kinetics and mechanisms of decomposition reactions, the significance of this technique can be judged from the following example.

It is well known that diazo group-containing compounds are rather unstable. They decompose at a relatively low temperature accompanied by liberation of an appreciable amount of heat. Accordingly, their large-scale storage and transport in industry involve problems. Consequently, a better knowledge of the course of their decomposition is of importance from theoretical and practical aspects.

However, as Fig. 1 proves, the classical thermoanalytical methods do not offer much information in this respect.

Figure 1 demonstrates the results of the simultaneous DTA, DTG and TG examination of 1-oxy-2-diazonaphthalene-5-sulphochloride. The examination was carried out by using the crucible of the derivatograph, in a nitrogen atmosphere and at a heating rate of 3°/min. In the tracing of the three curves, the experimental conditions differed from one another only in so far as the sample amount was 100 mg in the first case (curves 1, 6 and 9), 50 mg in the second case (curves 2, 5 and 8) and 20 mg in the third case (curves 3, 4 and 7).

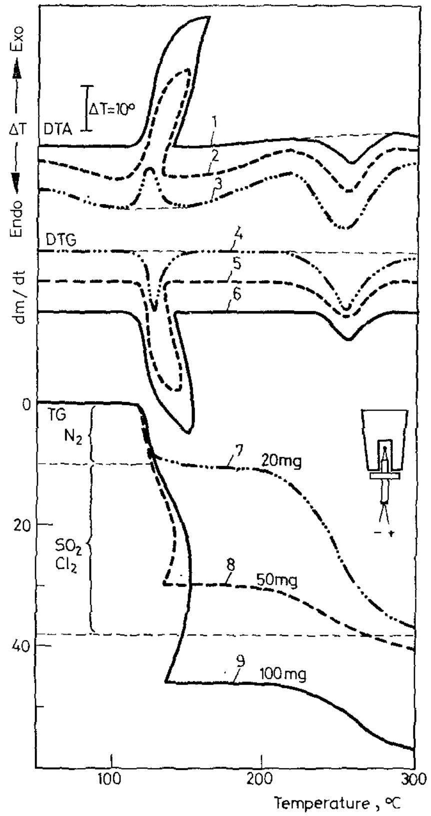

Fig. 1. Simultaneous DTA, DTG and TG examinations under conventional conditions. Sample amount: 100 mg (curves 1, 6 and 9), 50 mg (curves 2, 5 and 8), 20 mg (curves 3, 4 and 7). Sample holder: crucible. Heating rate: 3°/min. Atmosphere: nitrogen

It was surprising that the first step of the TG curves at about 120° was the bigger, the larger the sample amount investigated. However, the extent of the weight losses occurring up to 300° also changed with the weight of the sample.

For several reasons, it seemed justified to suppose that in the course of the decomposition first the diazo group splits off with the formation of nitrogen, whereupon the sulphochloride group departs with the formation of sulphur dioxide and chlorine, and the decomposition of the residual organic material only thereafter begins. The theoretical amounts of nitrogen, sulphur dioxide and chlorine corresponding to the composition of the sample are indicated in the Figure.

However, the above-mentioned supposition seemed to be supported only by the course of the TG curve traced on use of the smallest sample amount (curve 7), while the two other TG curves were in contradiction with the above suggestion.

The special form of the curves traced against temperature and the big exothermic peaks of the DTA curves (curves 1 and 2) proved the strong overheating of the sample in the two latter cases. Accordingly, the decomposition took place at a higher temperature, and due to this the mechanism of the decomposition process presumably changed too.

According to the DTA curve, the "sample temperature" increased by about 30° over the furnace temperature. If we want to be quite precise, then we have to speak about the temperature of the crucible instead of that of the sample, since the thermocouple situated in the recess of the bottom of the crucible actually measures the temperature of the crucible. With respect to the poor thermal conductivity of the sample, it can be supposed that in the centre of the sample and especially in the centre of the individual grains, the temperature difference was much higher than 30°.

The above experiment was repeated with the difference that the sample was spread in a thin layer over the large surface (10 cm^2) of the multiplate sample holder. It was hoped that thereby the sample holder, in contact with the sample over a large surface, would be able to conduct away and transfer to the surroundings the heat liberated. As curves 1–4 of Fig. 2 show, certain results could be attained in this way, but in the case of larger layer thicknesses the sample again became overheated and the mechanism of the reaction changed.

Similarly, only partial results could be attained when the sample was placed in the crucible but the quasi-isothermal heating rate of 0.3 mg/min was applied. The results of this experiment are also shown in Fig. 2 (curves 5–8).

However, the final solution of the problem could be attained by the combined application of the quasi-isothermal heating technique and the multiplate sample holder. As curves 2–4 in Fig. 3 show, on change of the sample amount between 20 and 500 mg and its layer thickness between 2 and 50 mg/cm^2, the course of the decomposition remained unchanged.

According to these curves, the decomposition started at 120°. Soon, the sample temperature spontaneously fell back to 116° and remained unchanged until the end of the first decomposition process. The interim weight loss of about 10% corresponded to the nitrogen amount escaping in the course of the splitting-off of the diazo group. Thereafter the sample weight remained constant up to 200° showing that the composition of the sample did not change. At 200° a slow weight loss process began which attained its maximum rate at 260°. Up to 500° the sample lost a further 38% of its weight. This weight loss was larger than that corresponding to the amount of sulphur dioxide and chlorine liberated. Accordingly, besides the splitting-off of the sulphochloride group it was also necessary to reckon with the occurrence of other pyrolytic processes. In order to be able to define separately the process of the splitting-off of the sulphochloride group, the examination was repeated with the simultaneous quasi-isothermal thermogravimetric and thermo-gas-titrimetric (TGT) method [3]. With this method, besides the measurement of the weight of the sample, the departing sulphur dioxide and chlorine (quantitatively absorbed in peroxide-containing water) are transformed into sulphuric acid and hydrochloric acid, respectively, which can continuously be titrated with sodium hydroxide solution. In order to avoid the possible interfering effects of other gaseous decomposition products (e.g. carbon

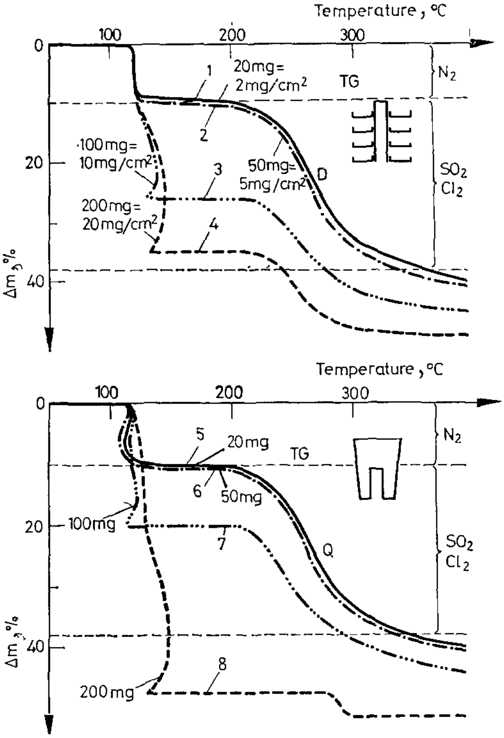

Fig. 2. Change in the courses of the TG curves with the experimental conditions. *Curves* 1—4: Heating rate 3°/min, N_2 atm. Multiplate sample holder of 10 cm² surface area. Sample amount: 20 mg (curve 1), 50 mg (curve 2), 100 mg (curve 3), 200 mg (curve 4). *Curves* 5—8: Quasi-isothermal heating, rate of weight change: 0.3 mg/min. N_2 atm. Crucible. Sample amount: 20 mg (curve 5), 50 mg (curve 6), 100 mg (curve 7), 200 mg (curve 8)

dioxide) the titration was carried out at pH 4. The titration curve shown in Fig. 3 (curve 1) represents the computed equivalent amounts of sulphur dioxide and chlorine. As a control, after the measurement the sulphate and chloride ion contents of the absorption liquid were also determined separately gravimetrically.

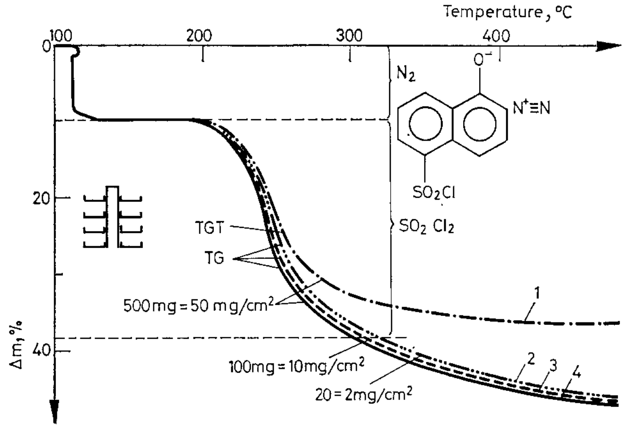

Fig. 3. Simultaneous TG and TGT examinations under quasi-isothermal conditions. Rate of weight change: 0.3 mg/min. N_2 atm. Multiplate sample holder of 10 cm^2 surface area. Sample amount: 20 mg (curve 2), 100 mg (curve 4) 500 mg (curves 1 and 4)

The results of the titration and the gravimetric determination were in good agreement. Accordingly, we may accept the suggestion that curve 1 demonstrates the partial process of the splitting-off of the sulphochloride group and the difference between the courses of the TG and TGT curves can be attribted to the complicated decomposition process of the solid organic residue and the departure of the volatile decomposition products.

*

The authors wish to thank prof. E. Pungor for valuable discussions.

References

1. F. Paulik, J. Paulik and M. Arnold, J. Thermal Anal. 12 (1977)
2. F. Paulik and J. Paulik, J. Thermal Anal., 5 (1973) 253.
3. F. Paulik and J. Paulik, Anal. Chim. Acta 67 (1973) 437.

Résumé — Les auteurs ont étudié à l'aide d'un *Derivatograph* la décomposition exothermique de l'1-oxy-2-diazo naphtalène 5-sulfochlorure. Ils ont trouvé que les courbes ATD, TG et TGD obtenues suivant les conditions habituelles ne pouvaient pas être interprétées, étant donné que leur allure changeait d'un cas à l'autre, selon les conditions d'expérience. Au contraire, sous l'effet conjugué de l'utilisation d'un support échantillon multiplaques et de l'emploi de la technique de chauffage quasi-isotherme, la décomposition s'effectue de manière univoque. On a établi ainsi que le groupe diazo se sépare à 116° et le groupe sulfochlorure à 200—400°. Les auteurs ont pu également enregistrer ce dernier processus par la mesure, en continu, de l'anhydride sulfureux et du chlore dégagés, par analyse titrimétrique des gaz émis.

Zusammenfassung — Die Autoren prüften mittels des Derivatographen die exotherme Zersetzung von 1-Oxy-2-Diazo-Naphtalin-5-Sulfochlorid. Sie stellten fest, daß die unter herkömmlichen Bedingungen aufgenommenen DTA, DTG und TG Kurven nicht interpretiert werden konnten, da ihr Verlauf je nach den Versuchsbedingungen von Fall zu Fall verschieden war. Als Ergebnis des gewöhnlichen Einsatzes des Vielplatten-Probenbehälters und der quasi isothermen Aufheizungstechnik wurde der Zersetzungsverlauf eindeutig. Es wurde festgestellt, daß die Diazo-Gruppe bei 116° abgespalten wurde, während sich die Sulfochlorid-Gruppe bei 200—400° abtrennte. Die Autoren konnten diesen letzten Vorgang auch gesondert verfolgen, und zwar durch kontinuierliches Messen des freigesetzten Schwefeldioxids und Chlors mittels Thermo-Gas-Titrimetrie.

Резюме — Авторы исследовали экзотермическое разложение 1-окси-2-диазо-нафталин-5--сульфохлорида с помощью дериватографа. Установлено, что кривые ДТА, ДТГ и ТГ, снятые при обычных условиях, не могут быть интерпретированы, поскольку их поведение изменяется от случая к случаю согласно экспериментальных условий. В результате общего применения многопластинчатого держателя образцов и техники квази-изотермического нагрева, ход разложения становится однозначным. Отмечено, что при 116° отщепляется диазогруппа, в то время как сульфохлоридная группа отделяется в интервале 200—400°. Авторы смогли также отдельно проследить этот последний процесс путем непрерывного измерения выделяющихся двуокиси серы и хлора с помощью термо-газо-титриметрической техники.