Short Communication

ERRORS IN THE EVALUATION OF THE THERMAL (KINETIC) STABILITY OF COMPOUNDS BY MEANS OF THE START TEMPERATURE OF THERMAL DECOMPOSITION IN THE PRESENCE OF ISOKINETIC POINTS

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The evaluation of the relative kinetic stability of a sequence of compounds in thermal decomposition processes based solely on the start temperature of thermolysis may be incorrect, if the temperature range of the thermal decomposition includes an isokinetic point.

It was observed earlier that in the case of constant sensitivities of the sensor in the thermoanalytical instrument, one and the same rate of reaction value will be found at the start temperatures of thermal decomposition processes. If one single topochemical mechanism is valid for the whole series of compounds studied, this will result in identical rate constants of thermal decomposition at the temperatures at which decomposition starts. In this case (if certain special requirements to experimental conditions are satisfied) the temperature sequence may coincide with the traditional sequence of kinetic stability (relative to the rate constants at a standard temperature) [1].

However, the possibility that isokinetic points exist cause difficulties in the analysis of kinetic stability.

Let us consider, by way of example, the thermal decomposition of urea (*U*) inclusion compounds with *n*-alkanes. The thermal decomposition kinetics of the compounds were investigated under non-isothermal conditions, using a continuous-flow reactor (sample mass 5 . . . 10 mg, rate of temperature increase 4 . . . 6°/min, flow rate of helium 140 cm^3/min) [2]. For the compounds $C_9H_{20} \cdot 7.45\ U$ and $C_{10}H_{22} \cdot 8.06\ U$, the temperatures at which the thermal decomposition starts are $30 \pm 3°$ and $31 \pm 3°$, resp. For the compounds $C_{11}H_{24} \cdot 8.80\ U$ and $C_{12}H_{26} \cdot 9.42\ U$, the corresponding temperatures are $50 \pm 3°$ and $53 \pm 3°$, resp. It would, however, be incorrect to consider the compounds in each pair equally stable, based solely on the closeness of the start temperatures of their thermal decompositions, since this closeness may by related to the presence of isokinetic points in these temperature ranges. In fact, the analysis of the relationship $\lg k$ *vs.* $1/T$ does indicate the existence of isokinetic points: 33° for the first pair of compounds, and 68° for the second pair.

At temperatures above 33° $C_{10}H_{22} \cdot 8.06\ U$ is more stable than $C_9H_{20} \cdot 7.45\ U$, and at temperatures above 68° $C_{12}H_{26} \cdot 9.42\ U$ is more stable than $C_{11}H_{24} \cdot 8.80\ U$ (Fig. 1).

This example demonstrates that an evaluation of the kinetic stability in thermal decomposition processes of a series of compounds, based solely on the start temperature of the thermal decomposition, may be insufficient and unreliable if an isokinetic point exists in the temperature range of thermal decomposition. Only a full kinetic analysis of the process will safeguard against errors in establishing sequences of kinetic stability.

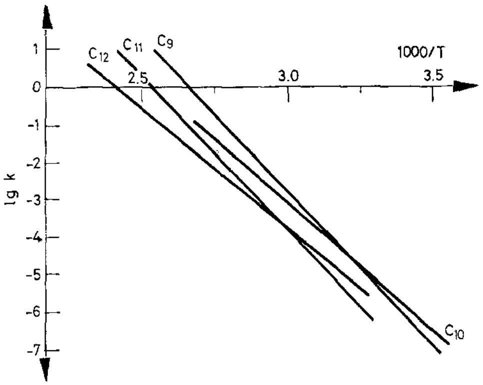

Fig. 1. Thermolysis of urea inclusion compounds with *n*-alkanes. Relationship between the rate constant of thermolysis and temperature. C_9— $C_9H_{20} \cdot 7.45$ urea; C_{10}— $C_{10}H_{22} \cdot 8.06$ urea; C_{11}— $C_{11}H_{24} \cdot 8.80$ urea; C_{12}— $C_{12}H_{26} \cdot 9.42$ urea

Analogous difficulties will arise in the interpretation of the thermodynamic stability at the thermal decomposition (quasi-equilibrum mode of operation of the Q-derivatograph) in the existence range of isoequilibrium points.

References

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2. V. A. Logvinenko, O. V. Gegola, G. N. Chekhova and Yu. A. Dyadin, Conference on the kinetics and mechanism of chemical reactions in solids. Novosibirsk, 1977. Thesises of the papers (in Russian). Part 1. p. 150.