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Letter to the Editor

Comments on the "Letter to the editor" by M.-L. You and C.-M. Shu (Journal of Thermal Analysis and Calorimetry, 2010;100:367–369) as response to the "Letter to the editor" by M. Malow and K.-D. Wehrstedt (Journal of Thermal Analysis and Calorimetry, 2009;98:885–886)

K. D. Wehrstedt · M. Malow

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Sir,

We read the comments by You and Shu [1] as a response to our comments [2] to their previous published paper [3] with interest. The authors give some statements and conclusions concerning the thermal behaviours of organic peroxides which should not be unremarked to avoid misunderstandings and to reflect the current state of scientific and technical knowledge.

- The oxygen balance stands for the quantity of oxygen required for the complete conversion of the elements present in a compound to their corresponding combustion products. In addition, the active or available oxygen content of organic peroxides is directly associated with the ability of a substance to decompose more or less rapidly [4]. An oxidising substance, generally by yielding oxygen, cause or contribute to the combustion of other substances [5]. This is not the case for all commercially used organic peroxides except peroxy acetic acids.
- It is correct that there are some differences concerning TMR between small-scale (DSC) and large-scale tests (e.g. with 20 kg in the UN H.1 test) but simulated or calculated values should not be far away from experimental data. A TMR of 11.6 min at 37 °C for a cylinder of 0.79 m^3 filled with dilauroyl peroxide (LPO) (technically pure) has nothing to do with real scenarios. Our simulation on basis of DSC measurements shows that LPO is stable at least at 42 °C under the same conditions for more than 80 h. But obviously also here the kinetic simulation does not reflect the reality well enough. This illustrates the quality dependence of a simulation on the available experimentally determined data as well as on the quality even of the simulation software particularly if melting and decomposition happen nearly at the same temperature (overlapping of thermodynamic and kinetic impacts).
- The statement that the SADT of LPO is 28.6 °C according to IOSH is at least questionable because it is not stated under which conditions this value was determined. "The SADT is defined as the lowest temperature at which self-accelerating decomposition may occur with a substance in the packaging as used in transport. The SADT is a measure of the combined effect of the ambient temperature, decomposition kinetics, package size and the heat transfer properties of the substance and its packaging. [6]" The Table 1 as used by the authors is copied from Bosch et al. [7] without the remark that these values were calculated and not experimentally determined in contrast to the SADT values listed in the UN Recommendations [6, 7]. A critical discussion of the partially wide differences between the calculated and the experimentally determined data does not take place. Some calculated SADT values listed in Table 1 are really wrong and are contradictory to all the experiences concerning storage and transport of such substances.
- Finally, it is always interesting to discuss some phenomena of organic peroxides with colleagues but our recommendation is to carry out good experiments to obtain reliable data as a basis for simulations. Software or simulation programs should be validated by experiments.

K. D. Wehrstedt (✉) · M. Malow
Division II.2 "Reactive Substances and Systems", BAM Federal Institute for Materials Research and Testing, Unter den Eichen 87, 12205 Berlin, Germany
e-mail: klaus-dieter.wehrstedt@bam.de

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