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DIFFERENTIAL SCANNING CALORIMETRY STUDY OF THERMAL DECOMPOSITION OF BENZOYL PEROXIDE AND 2,2'-AZOBISISOBUTYRONITRILE MIXTURES

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The thermal decompositions of benzoyl peroxide (Bz_2O_2), 2,2'-azobisisobutyronitrile (AIBN) and their mixtures in the absence of a solvent have been studied with DSC alone.

At 373 K (Bz_2O_2 m.p. = 376.5 K, AIBN m.p. = 374 K) mixtures of the two compounds show a higher decomposition ΔH than expected from ΔH isothermal measurements on the pure compounds; the same decomposition ΔH values can be calculated as the sum of values obtained from DSC dynamic experiments. At 353 K and 363 K, isothermally measured enthalpy variations show a possible induced decomposition effect in Bz_2O_2 caused by radicals generated by AIBN decomposition.

Benzoyl peroxide (Bz_2O_2) and 2,2'-azobisisobutyronitrile (AIBN) decompose at low temperatures and are two of the more common radical polymerization initiators. Their thermal decomposition in solution has been subject of many papers [1, 2].

Some of the results indicate that AIBN decomposes at low temperatures, and generates radicals stabilized by resonance [3] that are scarcely reactive.

Bz_2O_2 decomposes at higher temperatures, undergoes induced decomposition phenomena [4] and gives highly reactive radicals which are able, for example, to extract hydrogen atoms from a hydrocarbon substrate [5].

Few papers [6, 7] deal with the thermal decomposition of AIBN and Bz_2O_2 in the absence of solvents.

The present study considers the thermal decomposition of AIBN and Bz_2O_2 mixtures in the absence of solvent at temperatures lower than the melting point of the compounds or very close them.

The reactions have been investigated only in DSC experiments.

Experimental

Benzoyl peroxide was purified by precipitation in methanol from chloroform solution, while 2,2'-azobisisobutyronitrile (Fluka, 98% purity) was used without additional purification.

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DSC curves were obtained on a Perkin–Elmer DSC-2 instrument. Samples of 3–6 mg of the compounds or their mixtures were weighed in aluminium pans closed by covers in which a small hole had been made to allow gas generated by reagent decomposition to escape.

The instrument was present at 323 K and the sample was either heated to 493–573 K at 10 deg/min (dynamic test) or rapidly heated (160 deg/min) to a pre-determined temperature (isothermal test). Indium was used as the standard for calibrating the temperature axis and the enthalpy output. All experiments were carried out in nitrogen atmosphere.

Results

The thermal decomposition of AIBN was studied at 353, 363 and 370 K. The results are shown in Table 1. Dynamic experiments in the temperature range 323–523 K with a heating rate of 10 deg/min gave $\Delta H = 805.6$ J/g.

Table 1 AIBN thermal decomposition at temperatures lower than the melting point

Temperature, K	No. of peaks in the curve	ΔH, J/g total	ΔH, J/g 1st peak	ΔH kJ/mole
353	1	113.8	–	18.7
363	1	123.9	–	20.3
370	2	428.4	61.3	70.2

No enthalpy variation was observed at 348 K after heating for 32 minutes.

The decomposition process is significant at 353 K (see Table 1).

The thermal decomposition of Bz_2O_2 was studied at 368, 373 and 378 K. Table 2 shows the results obtained. DSC curves from dynamic experiments within the temperature range 323–553 K with a heating rate of 10 deg/min gave $\Delta H = 1602.0$ J/g or 387.6 kJ/mol.

No enthalpy variation was observed at 363 K even after heating for 46 minutes, and decomposition occurred perceptibly at 368 K.

The thermal decompositions of mixtures having the AIBN/Bz_2O_2 weight compositions 90:10, 70:30, 50:50 and 30:70 were studied at 353, 363 and 378 K. The mixtures decomposed without induction times and the DSC curves showed only one peak.

Table 2 Thermal decomposition of Bz_2O_2

Temperature, K	ΔH, J/g	ΔH, kJ/mole
368	674.9	163.3
373	806.0	195.1
378	801.1	193.9

Table 3 gives the results obtained in the isothermal experiments.

Figure 1 shows both the enthalpy variations measured for the various mixtures at 378 K and the corresponding values obtained in the DSC dynamic experiments within the temperature range 323–573 K with a heating rate of 10 deg/min. The results are easily comparable and the two curves display similar progress.

Table 3 Thermal decomposition of AIBN/Bz_2O_2 mixtures

Temperature, K			353	
AIBN:Bz_2O_2 %, (w:w)	90:10	70:30	50:50	30:70
$\Delta H_{observed}$, J/g	98.9	69.3	59.2	50.1
$\Delta H_{calculated}$, J/g	102.4	79.7	56.9	34.1
Temperature, K			363	
AIBN:Bz_2O_2 %, (w:w)	90:10	70:30	50:50	30:70
$\Delta H_{observed}$, J/g	56.6	466.6	755.5	230.1
$\Delta H_{calculated}$, J/g	111.5	86.7	61.9	37.2
Temperature, K			378	
AIBN:Bz_2O_2 %, (w:w)	90:10	70:30	50:50	30:70
$\Delta H_{observed}$, J/g	1077.7	1020.2	1132.3	1274.7
$\Delta H_{calculated}$, J/g	885.2	1044.5	1203.1	1363.1

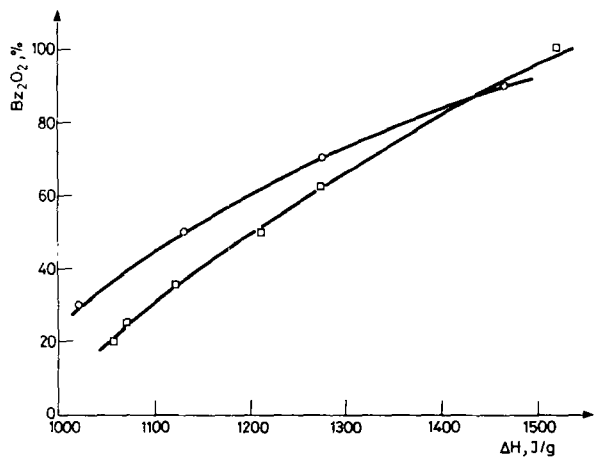

Fig. 1 Enthalpy variations for various AIBN/Bz_2O_2 mixtures: ○ isothermal tests at 378 K, □ dynamic experiments within the temperature range 323–573 with a heating rate of 10 deg/min

Discussion

Bz_2O_2 decomposition is significant from 368 K on, and at 389 K $\Delta H =$ = 193.9 kJ/mol. This value agrees with the 192.7 kJ/mol found by other authors [6] from dynamic experiments with a heating rate of 1 deg/min, but it is lower than the 387.6 kJ/mol we measured with a heating rate of 10 deg/min.

Figure 2a shows a typical Bz_2O_2 enthalpic pattern at 378 K. The DSC curves of AIBN at 353 and 363 K have only one peak, whereas two peaks (see Fig. 2b) are observed in the curve registered at 370 K.

At this temperature the total measured ΔH is 70.2 kJ/mol, which is lower than the 132.0 kJ/mol obtained from dynamic DSC measurements with a heating rate of 10 deg/min.

Figure 2c shows the typical DSC decomposition curve at 378 K of the 70:30 AIBN/Bz_2O_2 mixture.

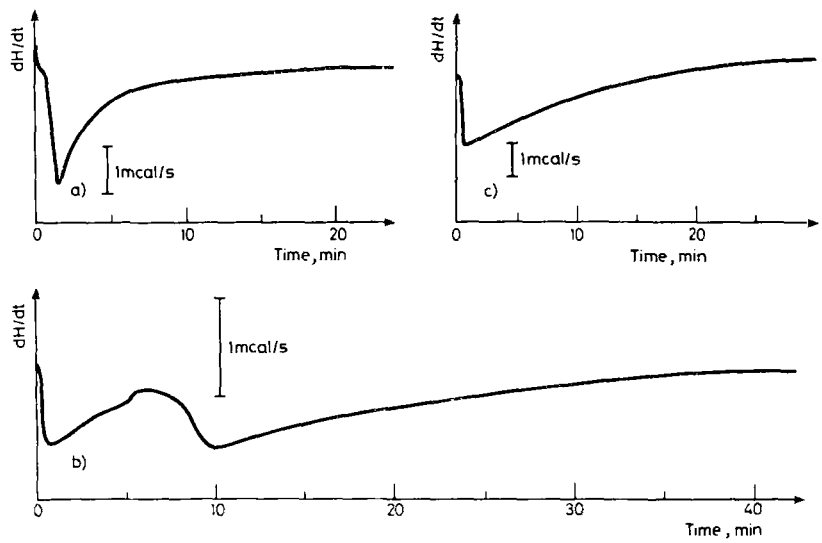

Fig. 2 Typical DSC curves: a) Bz_2O_2 at 378 K; b) AIBN at 370 K; c) 70:30 AIBN/Bz_2O_2 mixture at 378 K

At 378 K, just above the melting points of Bz_2O_2 and AIBN (see Table 3), mixtures decompose with ΔH values similar to those calculated merely with additive criteria, using as basis $\Delta H = 805.6$ J/g for AIBN and $\Delta H = 1602.0$ J/g for Bz_2O_2, obtained from dynamic experiments with a heating rate of 10 deg/min.

We could not perform such calculations using as basis the decomposition ΔH values of pure Bz_2O_2 or AIBN measured at 378 K, for decomposition of AIBN begins when the sample is heated at the desired temperature, and the $\Delta H = 801.1$ J/g found for Bz_2O_2 is clearly lower than the value measured in dynamic experiments and cannot be used for additive reckoning.

The low ΔH value observed for Bz_2O_2 at 378 K, a temperature close to the melting point, could be explained by supposing a "cage effect", which should help the recombination of primary radicals.

In contrast, the higher ΔH values observed in dynamic measurements could be related to a "cage effect" weakening, due to the fact that the temperature achieved during the dynamic tests is progressively higher than the melting point and promotes the rapid migration of the initial radicals and the peroxide decomposition reaction.

The high ΔH values measured for mixtures at 378 K are probably related both to possible cross reactions between the radicals arising from the decomposition of the two compounds and to possible peroxide-induced decomposition.

On the basis of the previous experimental data, Bz_2O_2 decomposition at 353 and 363 K is negligible and the enthalpy variations in mixtures at these temperatures should be computed as due only to AIBN. The ΔH observed for AIBN decomposition at 353 and 363 K were 113.8 J/g and 123.9 J/g.

In contrast, the results obtained in experiments lasting less than 45 minutes (Table 3) show that the heat developing at 353 K for the 30:70 mixture and at 363 K for the 70:30, 50:50 and 30:70 mixtures is greater than that calculated on the basis of the above assumption.

This result is probably related to Bz_2O_2 undergoing decomposition induced by radicals generated by AIBN decomposition.

Conclusions

The results obtained merely from DSC measurements of enthalpy variations indicate that mixtures of Bz_2O_2 and AIBN decompose to a much greater extent than was foreseen on the basis of isothermal experiments. Moreover, in the case of mixtures at 353 and 363 K we can suppose that Bz_2O_2 decomposition is induced by radicals generated from AIBN.

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Zusammenfassung — Die thermische Zersetzung von Benzoylperoxid (Bz_2O_2) und 2,2'-Azobisisobutyronitril (AIBN) und von Gemischen dieser Verbindungen wurde in Abwesenheit von Lösungsmitteln mittels DSC untersucht. Bei einer Temperatur von 378 K (Fp. von Bz_2O_2 = 376.5 K, Fp. von AIBN = 374 K) zeigen Gemische beider Komponenten eine höhere Zersetzungsenthalpie als nach aus isothermen Messungen für die reinen Substanzen erhaltenen Enthalpien zu erwarten wäre. Die gleichen Werte für die Zersetzungsenthalpien können auch als Summe von durch dynamische DSC-Experimente erhaltenen Werten berechnet werden. Bei isothermer Arbeitsweise bei 353 und 363 K auftretende Enthalpieänderungen deuten auf einen möglicherweise induzierten Zersetzungsprozeß hin, der durch bei der Zersetzung von AIBN entstandene Radikale verursacht wird.

Резюме — Методом ДСК изучено термическое разложение в присутствии растворителя перекиси бензоила (Bz_2O_2), 2,2-азобис-изобутиронитрила (АИБН) и их смесей. При температуре 378 K (Т. пл. Bz_2O_2 = 376,5 K, Т. пл. АИБН = 374 K) смеси обоих соединений показывает более высокое значение ΔH реакции разложения по сравнению с значениями, ожидаемыми на основе изотермических измерений ΔH для чистых соединений. Изотермические измерения изменения энтальпии при 353 и 363 K показали эффект возможного индуцированного разложения перекиси бензоила радикалами, образующимися при разложении АИБН.