

DIFFERENTIAL SCANNING CALORIMETRY STUDY OF THE THERMAL DECOMPOSITION OF PEROXIDES IN THE ABSENCE OF A SOLVENT

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The thermal decompositions of benzoyl peroxide (Bz_2O_2), dicumyl peroxide (DICUP) and α, α' -bis (t-butylperoxy)m/p-diisopropylbenzene (Peroximon F) in the absence of solvents have been studied by means of DSC alone.

The DSC curves allowed calculation of the half-lifetime ($t_{1/2}$) and the time (t_1) required to decompose the whole of the peroxides. The t_1 and $t_{1/2}$ values found for the pure peroxides are lower than those in the literature for decomposition in solution.

The heat of decomposition and the activation energy for each peroxide are reported.

Organic peroxides are widely used in the polymer industry, principally as initiators in free radical polymerization or as cross-linking or curing agents for thermoplastics, elastomers, polyester resins, etc. They are also employed to initiate many other radical reactions, such as halogenation, oxidation, or addition to double bonds [1]. Their use as initiators or cross-linking agents is due to the fact that they decompose thermally, the peroxide linkage cleaving to yield free radicals. The rate of decomposition is generally estimated by consideration of the half-lifetime, which is the time required to reduce the active oxygen content of a low-concentration peroxide solution by 50% at a given temperature. The half-lifetime ($t_{1/2}$) data at different temperatures for various peroxides are given in many technical publications [2]. Less information is available about the thermal decompositions of pure peroxides. The study of such reactions may be complicated by explosions or by a very high reaction rate, possibly due to a large amount of induced decomposition.

The aim of this work is to study, by means of DSC only, the thermal decompositions of three peroxides: benzoyl peroxide, dicumyl peroxide and α, α' -bis (t-butylperoxy)-m/p-diisopropylbenzene.

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Experimental

The following reactants were used:

Benzoyl peroxide (Bz_2O_2). Purification was carried out by crystallization of a Carlo Erba product: % peroxide > 98. Dicumyl peroxide (DICUP) from AKZO Chemie: % peroxide = 95. α , α' -bis (t-butylperoxy)-m/p-diisopropylbenzene (Peroximon F) containing 35% para and 65% meta isomer from Montefluos S.p.A.: % peroxide = 95.

DICUP and Peroximon F were used without further purification.

DSC curves were obtained on a DSC-2 Perkin-Elmer instrument. Samples of 3-6 mg peroxide powder 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 preset at 308 K and the sample was either heated to 493-503 K at 5 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. The activation energy from scanning experiments was obtained by using the Kinetic Program of the Perkin-Elmer Thermal Analysis Data Station.

Results and discussion

The obtained data were analysed by assuming that the evolved heat is proportional to the extent of reaction.

The thermal reaction of decomposition was investigated only in DSC dynamic and isothermal experiments.

figures 1a, 1b and 1c show three typical DSC curves obtained in isothermal experiments using the studied materials. The enthalpy values measured at different temperatures or obtained in dynamic experiments are listed in Table 1. The last two columns show for comparison literature activation energy data and the values obtained in dynamic DSC experiments.

The data indicate that the heat of decomposition increases with temperature in isothermal experiments. It is possible that the decomposition path of a pure peroxide changes with temperature [3], in accordance with what has been observed in the case of DICUP and Peroximon [4] dissolved in undecane. The energy of activation for each peroxide as calculated from dynamic experiments is lower than that found in the literature. The heat evolved in the decomposition of pure benzoyl peroxide is higher than that measured by Barrett [5] in solution. The differences

Table 1 Enthalpy and activation energy values determined for peroxides decomposition in comparison with literature data obtained in solution

Peroxide	ΔH , kJ/mole		ΔH , kJ/mole				E_a , kJ/mole dynamic experiments	E_a , kJ/mole literature
	dynamic experiments 5 deg/min	dynamic experiments	isothermal experiments					
	373 K	378 K	423 K	428 K	433 K	438 K		
BZ ₂ O ₂		195.1	225.0				76.2	~125 ⁽⁵⁾
DICUP	399.3		125.7	126.1	133.8	143.2	105.9	155 ± 4 ⁽⁴⁾
Peroximon F	218.3			170.0	221.8	326.2	113.7	161 ± 6 ⁽⁴⁾
	318.0							

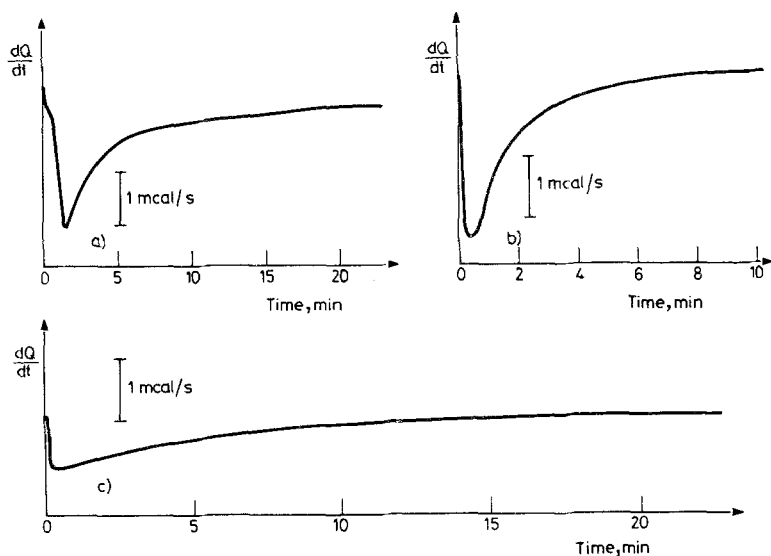


Fig. 1 Typical DSC curves obtained in isothermal experiments: a) Bz_2O_2 , 378 K b) DICUP, 433 K c) Peroximon F, 428 K

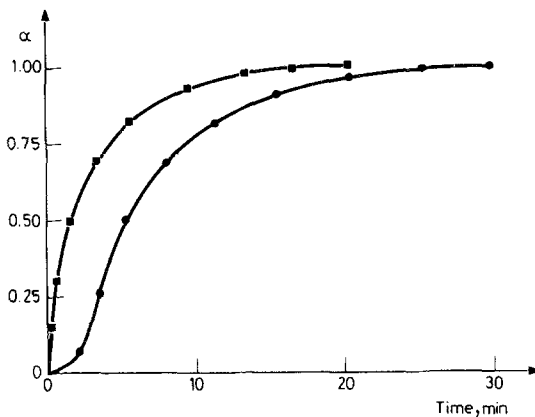


Fig. 2 Fraction (α) of Bz_2O_2 decomposed vs. time: ■ 378 K ● 373 K

may be attributed to the different reaction conditions. In fact, the values found in the literature were generally determined in experiments using solutions of peroxide, the most important reactions being the thermal breaking of the peroxidic bond and radical transfer to the solvent. Besides the rupture of the oxygen–oxygen bond, the decomposition of a pure peroxide involves a series of other possible reactions [6].

Figures 2, 3 and 4 show the decomposition of peroxides vs. heating time. The curves allow the calculation of $t_{1/2}$ and t_1 , i.e. the times required to decompose half

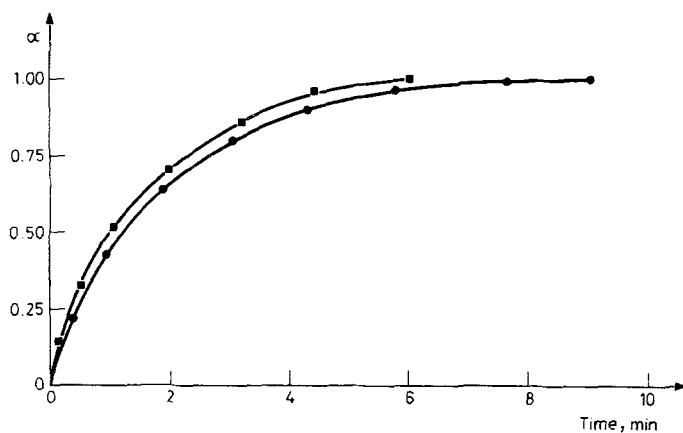


Fig. 3 Fraction (α) of DICUP decomposed vs. time: ■ 438 K ● 433 K

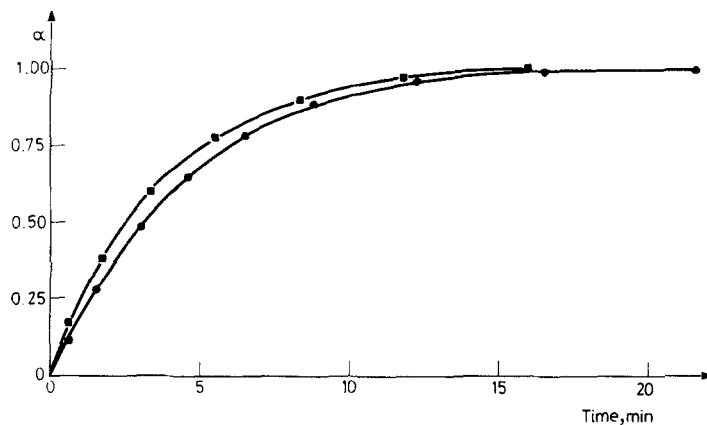


Fig. 4 Fraction (α) of Peroximon F decomposed vs. time: ■ 438 K ● 428 K

Table 2 Values of $t_{1/2}$ and t_1 for isothermal decomposition of pure peroxides in comparison with literature data obtained in solution

Peroxide	Temperature, K	$t_{1/2}$, min	t_1 , min	$t_{1/2}$, literature ⁽²⁾ min
Bz ₂ O ₂	378	1.6	20.2	13.0
DICUP	423	2.9	24.1	14.5
DICUP	428	2.4	15.3	8.5
DICUP	433	1.2	9.5	5.5
DICUP	438	1.0	6.0	3.2
Peroximon F	428	3.2	21.5	16.2
Peroximon F	433	2.6	20.6	10.2
Peroximon F	438	2.5	15.9	7.2

or the whole of the peroxide. The fraction reacted α was calculated as the fraction of the total measured enthalpy.

Table 2 contains $t_{1/2}$ and t_1 values found at different temperatures using pure peroxides. For comparison, literature $t_{1/2}$ values for the thermal decomposition of

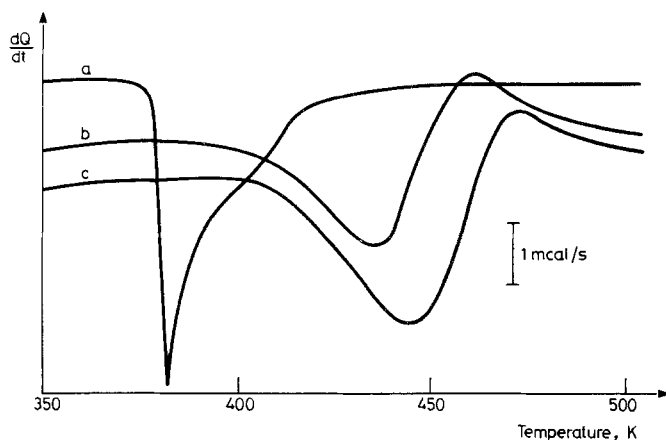


Fig. 5 Typical DSC curves obtained in dynamic experiments: a) Bz_2O_2 , 5 deg/min
b) DICUP, 5 deg/min c) Peroximon F 5 deg/min

peroxides in aromatic or paraffinic hydrocarbons [2]. The data indicate that a pure peroxide decomposes at a reaction rate higher than that observed in solution.

Figure 5 shows typical DSC curves obtained in dynamic experiments, the samples being heated at 5 deg/min. Analysis of the DSC dynamic curves allows evaluation of the starting temperatures for the exothermal decomposition reactions: 372.5 K (Bz_2O_2), 395 K (DICUP) and 403 K (Peroximon F).

Conclusions

The results obtained merely from DSC measurements of the thermal decomposition of Bz_2O_2 , DICUP and Peroximon F indicate that in isothermal experiments the heat of decomposition increases with the temperature and is generally lower than the value obtained in dynamic measurements.

The $t_{1/2}$ for pure peroxides are about $1/3$ of the corresponding values determined in hydrocarbon solution.

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Zusammenfassung — Die thermische Zersetzung von Benzoylperoxid (Bz_2O_2), Dicumylperoxid (DICUP) und α , Bis (t-butylperoxy)m/p-diisopropylbenzol (Peroximon F) wurde in Abwesenheit von Lösungsmitteln allein mittels DSC untersucht. Aus den DSC-Kurven konnten die Halbwertszeit ($t_{1/2}$) und die für die Zersetzung des ganzen Peroxids erforderliche Zeit (t_1) berechnet werden. Die für die reinen Peroxide ermittelten t_1 - und $t_{1/2}$ -Werte sind niedriger als die in der Literatur für die Zersetzung in Lösung angegebenen Werte. Zersetzungswärme und Aktivierungsenergie sind für alle untersuchten Peroxide angegeben.

Резюме — Методом ДСК изучено термическое разложение растворов перекиси бензоила, перекиси дикумола и α -бис-/трет-бутилпероксид(м)п-диизопрпилбензола. ДСК-кривые позволили вычислить время полураспада ($t_{1/2}$) и время (t_1) полного распада перекисей. Найденные значения t_1 и $t_{1/2}$ для чистых перекисей являются более низкими по сравнению с литературными данными для их растворов. Для каждого перекисного соединения приведены теплота разложения и энергия активации.