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Note

Decomposition of benzoyl peroxide in the presence of copper(II) bis-(−)ephedrinate investigated by differential scanning calorimetry

P. AMBROVIČ AND V. HORANSKÁ
Polymer Institute of the Slovak Academy of Sciences, Bratislava (Czechoslovakia)
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This is a sequel of the study of the catalytic effect of copper(II) bis-(−)-ephedrinate (Cueph) on the decomposition of organic peroxides in non-polar solvents[1–3]. Since differential calorimetry provides possibilities of studying the course of the thermal decomposition of crystalline benzoyl peroxide[4–6], we used this method for investigating its catalyzed decomposition in the presence of Cueph.

Besides the DSC curves of the mixtures consisting of benzoyl peroxide and Cueph, Fig. 1 presents the curves of pure components of the investigated system also. As is seen, the difference between the melting points of pure components exceeds 60°C.

The decomposition of benzoyl peroxide in the presence of Cueph begins at temperatures which are even 50°C below the temperature of the thermal decomposition of pure benzoyl peroxide. At certain concentrations of Cueph, two exothermic peaks (Fig. 1, curve 3 and 4) are observed on the curves. Further increase in the Cueph content of the mixture results in making the catalytic decomposition of benzoyl peroxide more distinct. The fact that at certain concentrations of Cueph the decomposition of benzoyl peroxide proceeds in two different ways (catalyzed and thermal) can be explained by the microheterogenity of the reaction system. Thus it is possible that the non-catalyzed thermal decomposition of benzoyl peroxide may occur in the places with zero concentration of Cueph.

The calculation of rate constants and activation energies from the DSC curves is affected by the fact that the decomposition of Cueph takes place simultaneously with the catalyzed decomposition of benzoyl peroxide. The decomposition heat of pure Cueph (2.6 kcal mole^{-1}) is relatively small in comparison with the decomposition heat of pure benzoyl peroxide (72 kcal mole^{-1}). But owing to the difference between the mechanism of catalyzed and thermal decomposition of pure benzoyl peroxide the proportion of the contributions to the total reaction heat might be different. At low concentrations it is possible to neglect the contribution of the reaction heat of Cueph. In the case of a mixture containing 0.55 mol % of Cueph (Fig. 1, curve 2) the activation energy calculated for the decomposition of benzoyl peroxide equals 14.3 kcal mole^{-1} while it is equal to 21.4 kcal mole^{-1} (ref. 5) for the decomposition of pure benzoyl peroxide.

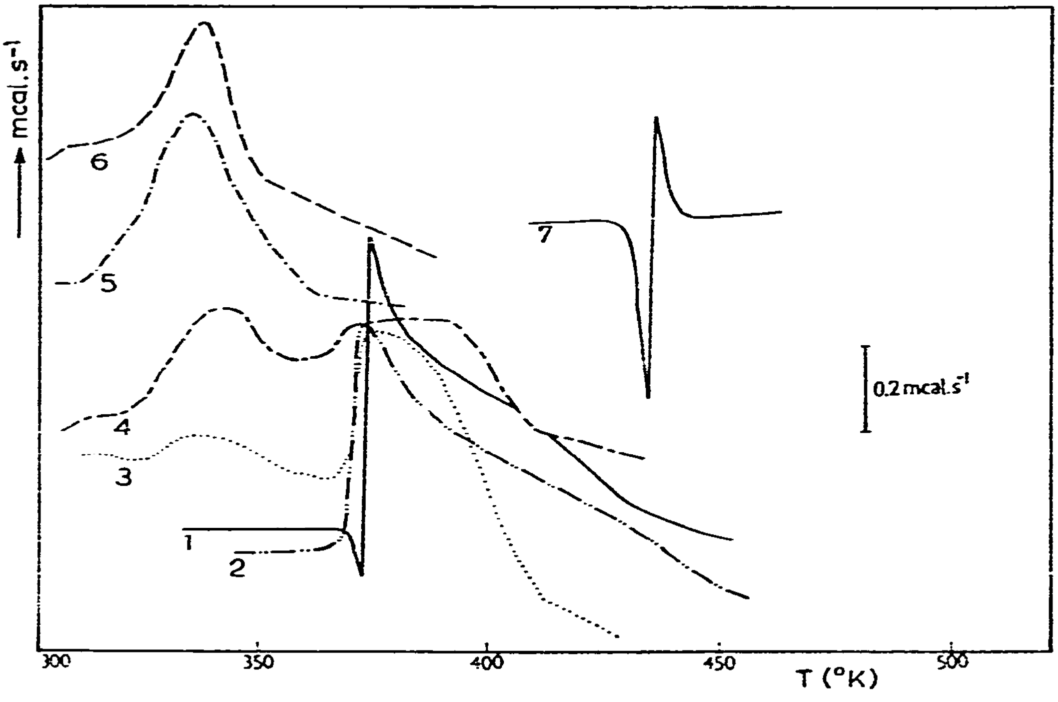

Fig. 1. Differential scanning calorimeter curves of benzoyl peroxide decomposition in the presence of Cueph. Weight of sample 1 mg, rate of heating 4°/min. Curve 1, pure benzoyl peroxide; curve 2, benzoyl peroxide with an admixture of 0.55 mol % of Cueph; curve 3, benzoyl peroxide with an admixture of 5.75 mol % of Cueph; curve 4, benzoyl peroxide with an admixture of 12 mol % of Cueph; curve 5, benzoyl peroxide with an admixture of 26.6 mol % of Cueph; curve 6, benzoyl peroxide with an admixture of 45 mol % of Cueph; curve 7, pure Cueph (this curve has been recorded at a four times smaller sensitivity than curves 1–6).

The catalytic effect of Cueph on the decomposition of benzoyl peroxide may be explained as follows. In crystalline benzoyl peroxide a small decomposition takes place even at room temperature. Thus some liquefied "disorder centres" are formed in certain places of crystalline sample. These centres bring about the microheterogenity of system and contain peroxidic radicals. Similarly as in benzene solution[1] these radicals can enter the transfer reactions with the nitrogen of the amino-group of ligand. In such transfer reaction a radical with unpaired-electron is formed. This electron is localized on the nitrogen of ligand. In a reaction system some radical can also arise because of the interaction of benzoyl peroxide with amino-groups of ligand while in addition to benzoic acid some peroxidic radicals localized on the nitrogen of amino-group are formed according to the known mechanism[8]. In such reaction system the further probable reaction is a homolytic cleavage of the bond between the central metal atom in Cueph, i.e. bivalent copper and the donor atoms of ligand. In this manner the formal valency of copper is reduced and a biradical is formed which can be further stabilized by isomerisation under formation of ketone. The compounds of univalent copper are known to be able to catalyze[9] the decomposition of benzoyl peroxide under formation of radicals. In the presence of Cueph in crystalline phase the effect of amino-group of ligand on the decomposition of benzoyl peroxide may be more distinct as compared with its decomposition in benzene solution[1] because the abstraction of CO_2 group from benzoyl peroxy-radical is not probable. This reaction is especially typical for benzene medium and the alkyl radical thus formed may also reduce bivalent copper and thus enhance the catalytic function of copper. Thus it may be assumed that the catalytic decomposition of benzoyl peroxide in melt in the presence of Cueph represents a complex of several reactions the final result of which is a decrease in the activation energy of benzoyl peroxide decomposition.

REFERENCES

1 J. Bartoň, J. Tiňo and V. Horanská, *Makromol. Chem.*, 164 (1973) 215.
2 J. Bartoň and V. Horanská, *Makromol. Chem.*, 157 (1972) 87.
3 V. Horanská and J. Bartoň, *Plaste Kautschuk*, in press.
4 P. Ambrovič and M. Lazár, *Eur. Polym. J., Suppl.*, (1969) 316..
5 M. Lazár and P. Ambrovič, *Chem. Z.*, 23 (1969) 881.
6 J. Mikovič and M. Lazár, *Thermochim. Acta*, 2 (1971) 321.
7 K. E. J. Barett, *J. Appl. Polym. Sci.*, 11 (1967) 1617.
8 S. Hasegava, S. Kashino and Y. Mukahi, *Bull. Chem. Soc. Jap.*, 44 (1971) 69.
9 J. K. Kochi, *Tetrahedron*, 18 (1962) 48; J. K. Kochi, *J. Amer. Chem. Soc.*, 85 (1963) 1958; J. K. Kochi and A. Bemis, *Tetrahedron*, 24 (1968) 5099.