Thermochimica Acta, 134 (1988) 237–241
Elsevier Science Publishers B.V., Amsterdam

THE INFLUENCE OF TRIOCTYL METHYL AMMONIUM SALTS ON THE DECOMPOSITION OF INITIATORS STUDIED BY DSC

A.PERDIH[1], T.MALAVAŠIČ[2] AND I.VIZOVIŠEK[1]
[2]Department of Chemistry and Chemical Technology, University "E.Kardelj" of Ljubljana (Yugoslavia)
[2]"Boris Kidrič" Institute of Chemistry, Ljubljana (Yugoslavia)

ABSTRACT

The influence of 15 different trioctyl methyl ammonium salts on thermal decomposition of dibenzoyl peroxide and the influence of trioctyl methyl ammonium chloride on 4 other types of initiators was studied by differential scanning calorimetry. The studied salts decreased the decomposition temperature and the enthalpy of decomposition. The degree of the influence of these salts depended on the sterical hindrance of the initiators, on their ability to form anions and on the properties of the anion of the trioctyl methyl ammonium salts.

INTRODUCTION

Besides in two-phase systems, quaternary ammonium salts had a definite influence on the polymerization of vinyl monomers in one-phase systems as well. Such an influence was observed in solution /1/ as well as in bulk systems /2-5/ with methylmetacrylate monomer and dibenzoyl peroxide (DBPO) as the initiator. These polymerization studies /1-5/ were performed around 50°C only.

Since the kinetic parameters of the thermal decomposition of some polymerization initiators were already determined by differential scanning calorimetry (DSC) /6/, this method was used in this work as well in the opinion to clarify the influence of some quaternary ammonium salts on the thermal decomposition of some polymerization iniciators.

EXPERIMENTAL

Dibenzoyl peroxide (DBPO), dilauroyl peroxide (L_2O_2), and 2,2´, azoisobutyronitrile (AIBN) were recrystallized from ethanol. t-Butyl perbenzoate (tBPB), and dicumyl peroxide (diCUP) were used as received. Trioctyl methyl ammonium chloride (TOMACl) was purified, while other trioctyl methyl ammonium salts (TOMAX; X indicating the corresponding anion) were prepared as described elswhere /7/.

Thermal Analysis Proc. 9th ICTA Congress, Jerusalem, Israel, 21–25 Aug. 1988
0040-6031/88/$03.50

The solutions of the initiators and TOMAX in dimethyl phthalate in the molar ratio 1:1, in some experiments with TOMACl also 1:2, were heated in a differential scanning calorimeter DSC 7, Perkin Elmer, in the temperature interval of 30 to 200°C with the rate of 10 K/min. From DSC curves, the starting temperatures, the temperatures of maximum decomposition rates, the temperatures of the end of reaction as well as the decomposition enthalpies were calculated.

RESULTS AND DISCUSSION

In Tab. 1 the starting temperatures, the temperatures of maximum decomposition rates (peak temperatures), the temperatures of the end of decomposition as well as the decomposition enthalpies as calculated from DSC curves, for some DBPO-TOMAX combinations in comparison to DBPO alone are given. The salts are arranged in order of decreasing peak temperatures.

Table 1: Characteristic decomposition temperatures of DBPO in the presence of different TOMAX. Molar ratio DBPO:TOMAX = 1:1

Anion (X^-)	Start (°C)	Peak (°C)	End (°C)	ΔH (J/g)
	67	136	168	- 1682
Tetrachlorozincate	67	133	155	- 1585
4-toluenesulfonate	83	132	150	- 1215
Methanesulfonate	79	129	152	- 1361
Trifluoroacetate	77	125	150	- 1428
Dichromate	71	124	144	- 1345
Benzoate	60	120	144	- 1430
Perchlorate	75	116	136	- 1377
2,4-dichlorobenzoate	74	115	143	- 1382
Acetate	64	116	140	- 657
Fluoride	82	113	138	- 622
Trifluoromethanesulfonate	65	110	118	- 1251
2-metoxybenzoate	64	108	141	- 1276
Bromide	37	105	167	- 1745
Chloride	37	70	108	- 893
2-methylbenzoate	37	69	93	- 120

All the tested quaternary ammonium salts decreased the peak temperature of DBPO decomposition.

The efficiency of different TOMAX was as follows. Tetrachlorozincate, 4-toluene-sulfonate and methanesulfonate did not decrease much the peak temperature compared to DBPO alone. More efficient were trifluoroacetate, benzoate and acetate. The latter is characterised also by a low ΔH. Among substituted benzoates, 2,4-dichlorobenzoate was slightly more efficient than benzoate, whereas 2-metoxybenzoate and especially 2-methylbenzoate decreased the peak temperature considerable. The efficiency of halogen was in the order: Cl > Br > F. Chloride and fluoride gave rise to low ΔH.

In all systems the decomposition of the initiators proceeded in a broad temperature interval. Above approx. 150°C the TOMA cations started to decompose and therefore the end of the decomposition reaction of initiators was hardly to define exactly. The only exception was the decomposition of DBPO in the presence of TOMA trifluoromethanesulfonate which decomposed in a well defined interval of 53°C with a sharp ending transition.

The influence of TOMACl on other initiators was different. The temperatures of decomposition of diCUP and AIBN were only slightly affected by TOMACl. Greater influence was found in the case of tBPB, cf. Tab. 2. Especially interesting was the influence of TOMACl on the decomposition of L_2O_2, Fig. 1.

Table 2: The influence of TOMACl on characteristic decomposition temperatures of different initiators

Initiator:TOMACl		Start (°C)	Peak (°C)	End (°C)	ΔH J/g
AIBN	1 : 0	70	123	141	- 1232
	1 : 1	83	121	142	- 1121
diCUP	1 : 0	140	175	187	- 716
	1 : 1	97	170	188	- 891
tBPB	1 : 0	117	172	200	- 1701
	1 : 1	97	146	163	- 1165
L_2O_2	1 : 0	61	116	159	- 882
	1 : 1	63	78;102	127	- 587
	1 : 2	57	70;102	119	- 495
DBPO	1 : 0	70	137	165	- 1682
	1 : 1	37	70	108	- 893
	1 : 2	37	71	102	- 469

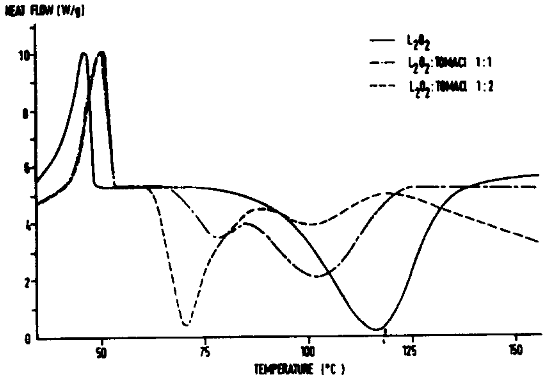

Fig.1.: Courses of polymerization of MMA in different solvents

L_2O_2 alone exhibits a melting peak at 46°C and a decomposition peak at 116°C. In the presence of TOMACl two decomposition peaks can be seen. At the molar ratio of 1:1 the initiator decomposed with a smaller peak with a maximum at 78°C and a higher one at 102°C. Changing the molar ratio of L_2O_2 : TOMACl to 1:2 the intensity of the two decomposition peaks reversed and the peak temperatures were 70 and 102°C, respectively. ΔH decreased with the increasing TOMACl amount. In the presence of TOMACl the melting peak of L_2O_2 increased for 5°C. The increase of the melting peak temperature was much more expressed in the case of AIBN.

The influence of quaternary ammonium salts on the decomposition of the initiators seems to be governed by the ability of the initiator molecules to solvate the salt and by the ability to form anions. For this reason the sterically hindered initiators like diCUP and AIBN can not be influenced in their decomposition temperature. Appreciable influence could be observed in the case of tBPB which is less hindered and is able to give at least one anion. Diacyl peroxides are strongly influenced, especially DBPO. L_2O_2 on the other hand is less influenced than DBPO and depending on molar ratio between L_2O_2 and TOMACl a stepwise effect was found.

CONCLUSIONS

Quaternary ammonium salts decrease the temperture as well as the enthalpy of decomposition of polymerization initiators in the case that they are not sterically hindered and that are able to form anions. The degree of influence depends on the relative affinity of the anions for the quaternary ammonium cation as well.

REFERENCES

1. P.Ghosh and S.N.Maity, Eur. Polymer J. 14 (1978) 855.
2. F.Jagodic and A.Perdih, IUPAC Macro ´88, Section I Polymer Chemistry, Abstracts, Bucharest 1983, p. 341
3. F.Jagodic and A.Perdih, VIII. jugoslovanski simpozij za kemijo in tehnologijo makromolekul, Izvlečki, Bled 1984, p. 36.
4. F.Jagodic and A.Perdih, 30 th IUPAC International Symposium on Macromolecules, Abstracts, The Hague 1985, p. 177.
5. F.Jagodic and A.Perdih, 31 st IUPAC Macromolecular Symposium, Microsymposium I, Abstracts, Merseburg 1987, p. 141.
6. A.Može, T.Malavašič, I.Vizovišek and S.Lapanje, Angew. Makromol. Chem. 46 (1975) 89.
7. A.Perdih, in preparation.