CHEMISTRY LETTERS, pp. 1177-1180, 1972. Published by the Chemical Society of Japan

DECOMPOSITION OF BENZOYL PEROXIDE IN THE PRESENCE OF POLY-p-N,N-DIMETHYLAMINOSTYRENE

Norio KUNIEDA, Hideaki MOCHIZUKI, and Masayoshi KINOSHITA

Department of Applied Chemistry, Fuculty of Engineering,
Osaka City University, Sugimoto-cho, Sumiyoshi-ku, Osaka

Benzoyl peroxide(BPO) decomposes readily in the presence of poly-p-N,N-dimethylaminostyrene(poly-DMAS), and the initial rate of the decomposition of BPO in the presence of poly-DMAS is about 23 times faster than that in the presence of N,N-dimethylaniline. The fact of the enhancement of the rate attributed to polymeric effect of poly-DMAS and the data of kinetics were discussed.

N,N-Dimethylaniline(DMA) has been known to have a high reactivity towards benzoyl peroxide(BPO).1) Actually, the addition of an equimolar amount of DMA was found to accelerate the rate of the decomposition of BPO by over 50 times(in benzene, at 30°C, see Table 1). Now, we have found that BPO also decomposes readily in the presence of poly-p-N,N-dimethylaminostyrene(poly-DMAS) and the initial rate of the decomposition of BPO in the presence of poly-DMAS is faster than that in the presence of DMA in benzene. This communication will describe a preliminary investigation of the reaction of decomposition of BPO in the presence of poly-DMAS.

The rate equation of $v_o = -d[BPO]/dt = k_2[BPO][DMA]$ has been established for the reaction of BPO and DMA.2) We have found that the experimental rate equation for the reaction of BPO with poly-DMAS also accords with an equation of $v_o = -d[BPO]/dt = k_2[BPO][DMAS]$ ([DMAS]; mole concentration of p-N,N-dimethylaminostyrene unit in poly-DMAS). The reaction was carried out in benzene, and the initial rate, v_o , of the decomposition of BPO was measured according to the NaI-$Na_2S_2O_3$ titration method in isopropyl alcohol.3)

When poly-DMAS(0.222g, 0.0015 mole unit of p-N,N-dimethylaminostyrene) and BPO (0.363g, 0.0015 mol) was dissolved in 50 ml of benzene and the solution was kept for 3 hrs at 30°C under an atmosphere of nitrogen, benzoic acid(0.182g, 0.00149 mol) was obtained together with 0.270g of polymer from the solution. The IR spectrum of the polymer obtained showed absorptions at 3350 and 1650 cm^{-1}, which are attributed to secondary amino group and carbonyl group, respectively. The incorporation of ^{18}O into the products was examined using ^{18}O-labeled BPO. When ^{18}O-labeled BPO(1.43 atom%-^{18}O-excess, on carbonyl oxygen)(0.182g) was treated with poly-DMAS(0.111g) in 25 ml benzene by the same procedure mentioned above, the values of atom%-^{18}O-excess of benzoic acid and polymer obtained were 0.698 and 0.313, respectively. This means that the ^{18}O-content on carbonyl oxygen of BPO started is included almost completely in benzoic acid obtained. Inspection of these results that the feature of the reaction of BPO with poly-DMAS is similar to that of the reaction of BPO with DMA which is well studied.[5)] At the initial stage, the reaction seems to proceed through the rate-limitting formation of a quarternary ammonium salt, $[\sim\!\sim\!\sim C_6H_4N^+(CH_3)_2\text{-O-CO-}C_6H_5][C_6H_5COO^-]$.

However, one finds in Table 1 that poly-DMAS accelerates the rate by about 23 times in comparison with DMA and by about 5 times in comparison with N,N-dimethyl-p-toluidine(DMT; used as a unit model of poly-DMAS)(see runs 2, 4 and 7 in Table 1).

In order to observe the influences of the molecular weight of poly-DMAS and the viscosity of the reaction system on the rate, 1) two samples of polymers of different molecular weight ($[\eta]$ = 0.18 and 0.46, in benzene) were used as the substrate, 2) poly-styrene was added in the BPO-DMA reaction system. But no changes of the rate were observed in both the experiments (see runs 3, 5 and 6 in Table 1).

Moreover, the rates in the presence of copolymers which have different compositions between N,N-dimethylaminostyrene(DMAS) and styrene(St) were measured. As Fig. 1 shows, the rates are increased with the increase of the ratio of DMAS units in the copolymer, and then the rate increases steeply at the point of [DMAS]/([DMAS]+[St]) = 0.5. From this result, it is obvious that two or more N,N-dimethylaminophenyl groups in poly-DMAS which lie in adjoining positions affect the rate of the reaction of BPO with poly-DMAS.

Table 1. Rate of decomposition of BPO and LPO (at 30°C, in benzene)

No.	Substrate	Peroxide	$[S] \times 10^2$ a) (mol/l)	$[P] \times 10^2$ c) (mol/l)	$v_0 \times 10^5$ (mol/l·min)
1	None	BPO		1.25	0.40
2	DMA	BPO	1.25	1.25	2.20
3	DMA + poly-St[d)]	BPO	1.25	1.25	2.30
4	DMT[e)]	BPO	0.50	0.50	1.50
5	Poly-DMAS $[\eta]$ = 0.18	BPO	1.25[b)]	1.25	50.0
6	Poly-DMAS $[\eta]$ = 0.46	BPO	1.25[b)]	1.25	48.0
7	Poly-DMAS $[\eta]$ = 0.46	BPO	0.50[b)]	0.50	7.50
8	p-Methoxystyrene-DMAS copolymer[f)]	BPO	0.50[b)]	0.50	1.20
9	Tetra Base[g)]	BPO	0.25	0.50	1.30
10	DMT	LPO	5.00	5.00	39.8[h)]
11	Poly-DMAS	LPO	5.00[b)]	5.00	41.4[h)]

a) Initial concentration of substrate added. b) Mole concentration of p-N,N-dimethylaminostyrene unit in polymer. c) Initial concentration of peroxide. d) Poly-styrene(1.25×10^{-1} mol/l based on styrene unit) was added to BPO-DMA system. e) N,N-Dimethyl-p-toluidine. f) [p-Methoxystyrene]/[DMAS] = 1.16; [DMAS] = 5×10^{-3} mol/l. g) $CH_2[C_6H_4N(CH_3)_2\text{-p}]_2$. h) at 60°C.

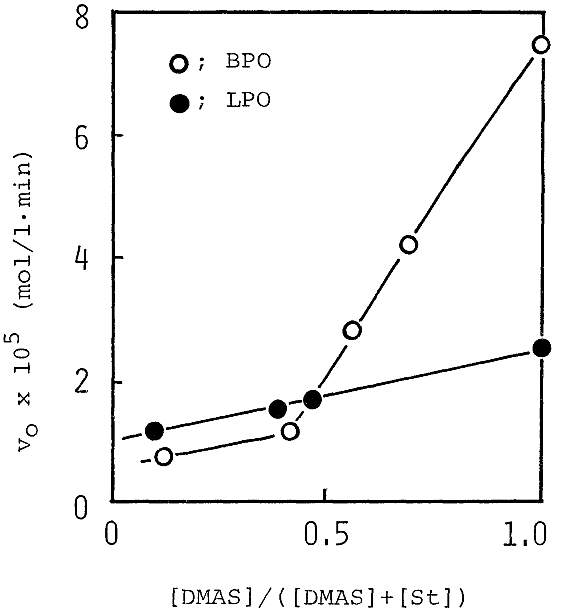

Fig. 1
Rate in the presence of copolymer of DMAS and Styrene of various compositions; v_0 plotted against mole ratio of DMAS in copolymer.

$[BPO]_0 = 0.5 \times 10^{-2}$ mol/l
$[DMAS]_0 = 0.5 \times 10^{-2}$ mol/l ($[DMAS]_0$; initial mole concentration of p-N,N-dimethylaminostyrene unit in the copolymer), 30°C, in benzene

$[LPO]_0 = 1.0 \times 10^{-2}$ mol/l
$[DMAS]_0 = 2.0 \times 10^{-2}$ mol/l
at 45°C, in benzene

Table 1 also lists the decomposition rates of BPO in the presence of Tetra Base (for a model which has two N,N-dimethylaminophenyl groups in the neighbouring positions) and p-methoxystyrene-DMAS copolymer. But the rate enhancements attributed to the presence of these substrates were not found.

The rate of decomposition of lauroyl peroxide(LPO) was measured in the presence of poly-DMAS. The experimental rate equation for the reaction of LPO with poly-DMAS was also found to accord with an equation of $v_0 = -d[LPO]/dt = k_2[LPO][DMAS]$, in the same fashion as BPO- poly-DMAS system.

Table 2. Activation parameters for various systems in benzene

No.		Ea(kcal/mol)	$\Delta S^{\ddagger}$ (e.u.)
1	BPO[a)]	33.6	13.8
2	BPO-DMT	15.6	-18.8
3	BPO-poly-DMAS	15.4	-15.5
4	BPO-(p-Methoxystyrene -DMAS) copolymer	17.9	-11.3
5	BPO-Tetra Base	13.3	-24.7
6	LPO-DMT	18.1	-16.5
7	LPO-poly-DMAS	17.4	-17.9

a) For the thermal decomposition in benzene, Ref.4.

However, the rate of decomposition of LPO in the presence of poly-DMAS was found to be equal to that in the presence of DMT, as shown in Table 1 (see runs 10 and 11). For the reaction in the presence of DMAS-Styrene copolymer, the effect of the composition of the copolymer on the rate of the decomposition of LPO was not large, as shown in Fig. 1.

The energies and entropies of activation of the various systems are summarized in Table 2. The remarkable differences of the parameters between peroxide-DMT system and peroxide-poly-DMAS system, however, were not observed, though $\Delta S^{\ddagger}$ value of BPO-poly-DMAS system is slightly larger than that of BPO-DMT system.

The more detailed investigations now in progress in our laboratory will shed further light on the study of mechanism of the title reaction.

REFERENCES

1) a) K. Nozaki and P. D. Bartlett, J. Amer. Chem. Soc., 68, 1689 (1946).
   b) L. Horner and E. Schwenk, Angew. Chem., 61, 411 (1949) and the subsequent papers.
   c) M. Imoto and S. Choe, J. Polymer Sci., 15, 485 (1955) and the subsequent papers.
2) K. F. O'Driscoll and E. N. Richezza, J. Polymer Sci., 46, 211 (1960); M. Imoto and K. Takemoto, ibid., 18, 377 (1955); Ref. 1c.
3) V. R. Kokatnur and M. Jelling, J. Amer. Chem. Soc., 63, 1432 (1941).
4) P. D. Bartlett and R. R. Hiatt, ibid., 80, 1398 (1958).
5) M. Imoto and K. Takemoto, Kobunshi Kagaku, 13, 331 (1956); M. Imoto, T. Otsu, and T. Ohta, Makromol. Chem., 16, 10 (1955); Ref. 1c and 4.

(Received September 14, 1972)