

## **A Kinetic Study of the Decomposition of Benzoyl Peroxide Assisted by Lewis Acids**

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### Summary

The rates of decomposition of benzoyl peroxide have been studied in solvent alone and in presence of three Lewis acids, viz., boron trifluoride etherate, aluminum chloride and antimony pentachloride at the temperature range of 10-90°C. The rates have also been studied in presence of acetonitrile (to mimic the action of a complexing monomer) and an efficient radical trap such as *m*-dinitrobenzene. Benzoyl peroxide undergo rapid decompositions at room temperatures or below in presence of Lewis acids such as aluminum chloride and antimony pentachloride via a polar mechanism to yield >96% phenylbenzoate and one mole of carbon dioxide. Kinetics do not indicate the presence of trappable free radicals. The implication of these results to the initiation of alternating copolymerizations of donor with acceptor monomers is discussed.

### Introduction

The reaction of donor with acceptor monomers under the influence of suitable complexing agents and in presence of free radical initiators produces alternating copolymers (GAYLORD, TAKAHASHI 1969, HIRAI 1976). Examples are alternating  $\alpha$ -olefin-acrylic ester copolymers using boron trifluoride-AIBN initiators (LOGOTETHIS, MCKENNA 1974, 1975, 1977), alternating copolymerization of isobutylene, butadiene or ethylene with acrylonitrile using metal halides-peroxide initiators (KAWASAKI et.al. 1971a, 1971b, 1971c) and polymerizations using organoaluminum halide-peroxide or AIBN initiator systems (GAYLORD, MAITI 1971, MILOVSKYA et.al. 1972). Two general observations on the nature of these copolymerizations have been made. One, that these polymerizations proceed at rates substantially higher than the corresponding free radical copolymerizations conducted without complexing agents (GAYLORD, TAKAHASHI 1969) and two, that AIBN

initiated reaction proceed at high rates at temperature at which the spontaneous thermal rate of AIBN decomposition is extremely small (GAYLORD, MATYSKA 1970, HIRANO et.al. 1967).

With organoaluminum compounds and AIBN, a lowering in the activation energy of AIBN decomposition and an enhanced rate of radical formation was observed (HIRANO et.al. 1967). However, with zinc chloride the rate of AIBN decomposition was found unaffected (FUNT et.al. 1975). The difference was attributed to the differing sites of complexation of  $Zn^{+2}$  and Al with AIBN. Logotethis and Mckenna (1977) also observed an enhancement in the rate of free radical decomposition of AIBN with two equivalents of  $BF_3$  corresponding to a  $20^\circ C$  decrease in the temperature of decomposition of the initiator.

On the contrary literature suggests that organic peroxides in presence of metal halide Lewis acids decompose predominantly by a non-radical pathway (carboxyl inversion route) to yield phenylbenzoate and carbon dioxide (HUISGEN, EDL 1962, EDWARD et.al. 1962, DENNY, DENNY 1962, DENNY et.al. 1964). In view of our interest in the study of complex copolymerization of  $\alpha$ -olefins with acrylic monomers, we undertook a kinetic examination of the decomposition of benzoyl peroxide assisted by Lewis acids. We hoped that such a study may help clarify whether trappable free radicals are indeed formed during such assisted decomposition which could initiate complex copolymerizations.

### Experimental

Benzoyl peroxide was recrystallized from chloroform-methanol mixture. Boron trifluoride etherate and antimony pentachloride were freshly distilled under  $N_2$  prior to use. Aluminum chloride was purified by repeated vacuum sublimation. Solvents were dried and distilled under  $N_2$ . All reagents were stored in serum capped bottles under a positive pressure of  $N_2$ . All transfers of solvents and air sensitive compounds were effected either through a hypodermic syringe under a positive pressure of  $N_2$  or in an inert atmosphere box under a continuous flow of  $N_2$ . The rates of decomposition were determined from the volume of evolved carbon dioxide gas measured with a gas burette (SMID et.al. 1956, REMBAUM, SZWARC 1964). A typical procedure is illustrated below:

A two neck flask equipped with a magnetic stirrer and fitted with reflux condenser and rubber septum was connected to a gas burette and an exit bubbler through a 3-way stop cock. The flask was thoroughly flushed

with  $N_2$  and immersed in a constant temperature bath. Water, at  $10^\circ C$  was circulated in the condenser. A solution of benzoyl peroxide and Lewis acid were mixed, the volumes having been appropriately adjusted so that the solution was 0.05 M in each component. When half the volume of the solution had been injected, the timer was set to zero. Subsequently the evolved gas was measured at periodic intervals. The volume was corrected for normal temperature and pressure as well as for the vapour pressure of the solvent at the reaction temperature. In those cases where the rate was high even at room temperature, the Lewis acid solution was added to a thermostated benzoyl peroxide solution, the zero time marked when half the volume of Lewis acid had been discharged.

### Results and discussion

The rates of decomposition of benzoyl peroxide were compared in solvent alone and in presence of boron trifluoride etherate, aluminum chloride and antimony pentachloride. The rates were also compared in presence of equimolar amounts of acetonitrile (to mimic the action of an acceptor monomer such as acrylonitrile) and in presence of an efficient radical trap such as *m*-dinitrobenzene (BARTLETT, NOZAKI 1946). Typical plots of carbon dioxide evolved as a function of time are given in figures 1-3. The rates were evaluated at three temperatures and activation energies computed. The results are summarized in Tables 1 and 2. In all cases benzoyl peroxide concentration was 0.05 M, thereby avoiding higher order terms arising out of radical-induced decomposition (SWERN 1971). In view of the ability of antimony pentachloride to chlorinate benzene, carbon tetrachloride was used as solvent with this Lewis acid.

Gas evolution measurements indicated that decomposition of benzoyl peroxide assisted by Lewis acids evolve only one mole of carbon dioxide in contrast to thermal decomposition of peroxide. The rate of benzoyl peroxide decomposition assisted by Lewis acids decreased in the order  $SbCl_5 > AlCl_3 > BF_3 \cdot Et_2O$ . The rate of Lewis acid assisted peroxide decomposition was practically unaffected by addition of acetonitrile as a complexing solvent (Table 2). Evidently nitrile complexes of Lewis acids are equally effective in promoting decomposition of benzoyl peroxide by a carboxy inversion mechanism. Whereas the rate of simple thermal decomposition of benzoyl peroxide is substantially retarded by the presence of *m*-dinitrobenzene, those of Lewis acid assisted decomposition either remain unaffected or enhanced in presence of *m*-dinitrobenzene (Table 2). This indicates that no

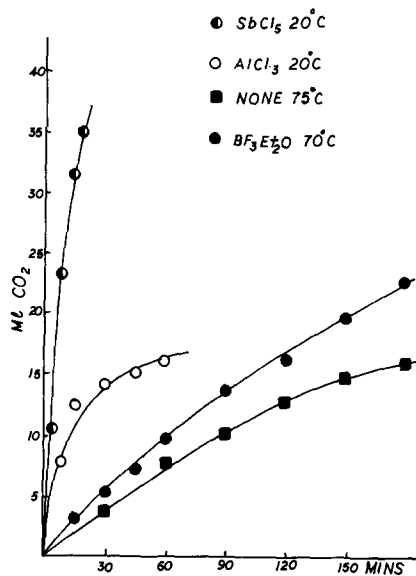
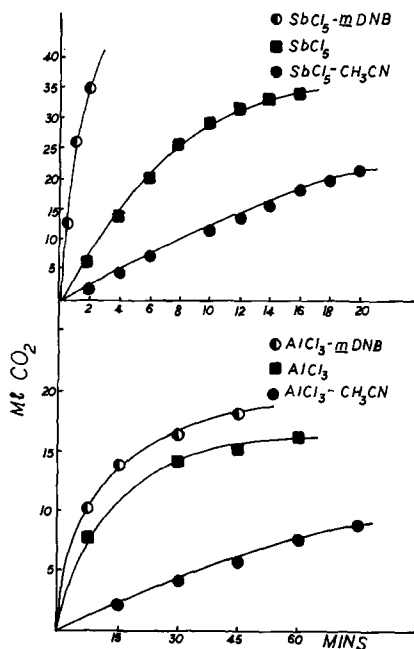


Fig. 1. Rates of decomposition of benzoyl peroxide in presence and absence of Lewis Acids



Figs 2 and 3. Effect of additives on  $SbCl_5$  and  $AlCl_3$  assisted decomposition of Benzoyl Peroxide, 20°C

TABLE 1  
Rates of Decomposition of Benzoyl Peroxide in Presence of Lewis Acids<sup>a</sup>

Lewis Acid	Rate, k (min <sup>-1</sup> ) x 10 <sup>2</sup> , Temp. °C			E <sub>a</sub> KJ mole <sup>-1</sup>
	10	15	20	
none				
BF <sub>3</sub> :Et <sub>2</sub> O			1.2 <sup>c</sup>	
AlCl <sub>3</sub>		3.0	3.9	5.6
SbCl <sub>5</sub> <sup>e</sup>	3.6	5.2	8.5	
			0.16	0.26
			0.39	0.67 <sup>d</sup>
			0.39 <sup>b</sup>	105
			0.39	52
			0.67 <sup>d</sup>	43
			0.39	61

<sup>a</sup> (Bz<sub>2</sub>O<sub>2</sub>) = (Lewis Acid) = 0.05 M in benzene

<sup>b</sup> Lit. rate at 85°C = 0.33 x 10<sup>-2</sup> min<sup>-1</sup>, E<sub>a</sub> = 28.3 Kcal mole<sup>-1</sup> (A. Conix and G. Smets, J. Polym. Sci., 10 52(1953))

<sup>c</sup> Extrapolated from higher temperatures

<sup>d</sup> 90°C

<sup>e</sup> Solvent; CCl<sub>4</sub>

TABLE 2  
 Rates of Decomposition of Benzoyl Peroxide in presence of Lewis Acid:  
 Effect of Acetonitrile and *m*-Dinitrobenzene on Rate<sup>a</sup>

Lewis Acid	Additive	Rate, $k$ ( $\text{min}^{-1}$ ) $\times 10^2$ , Temp °C		
		20	70	75
none	<i>m</i> -DNB			0.09
BF <sub>3</sub> ·Et <sub>2</sub> O	CH <sub>3</sub> CN		0.22	
	<i>m</i> -DNB		0.33	
AlCl <sub>3</sub>	CH <sub>3</sub> CN	2.9		
	<i>m</i> -DNB	7.0		
SbCl <sub>5</sub>	CH <sub>3</sub> CN	8.6		
	<i>m</i> -DNB	40		

<sup>a</sup> (Bz<sub>2</sub>O<sub>2</sub>) = (Lewis Acid) = (Additive) = 0.05 M in benzene. In all cases acid solution was added to a solution of benzoyl peroxide and *m*-DNB or CH<sub>3</sub>CN.

trappable free radicals are formed during the Lewis acid assisted decomposition of benzoyl peroxide and that the product phenyl benzoate is formed via a polar mechanism. The rate enhancements conferred by *m*-DNE is quite surprising and may be attributed to its preferential solvating power for Lewis acids. The products of decomposition was shown to be phenylbenzoate (>96%) by gas chromatography analysis.

The alternating copolymerization of donor with acceptor monomers in presence of complexing Lewis acids has been postulated to occur via (i) a ternary molecular complex mechanism (ii) cross propagation mechanism and (iii) complexed radical mechanism (HIRAI 1976). No one mechanism is considered to be fully satisfactory in explaining all the features of complex copolymerizations. Initiation of such copolymerizations can occur spontaneously as in the case of alkyl aluminum catalyzed alternating copolymerization of acrylonitrile and propylene (KURAN et.al. 1974) or zinc chloride catalysed copolymerization of acrylonitrile with butadiene (KURAN 1972), or by addition of a free radical initiator to the Lewis acid-acceptor-donor ternary complex. In the latter case the initiator residues are found attached to the final copolymer. This is the case where copolymerizations occur at room temperatures or below with initiators such as EASQ-AIBN (GAYLORD, MATYSKA 1970),  $\text{BF}_3$ -AIBN (LOGOTETHIS, MCKENNA 1977) and  $\text{AlEt}_3$ -AIBN (HIRANO et.al. 1967). With  $\text{ZnCl}_2$ -AIBN, initiation of copolymerization occur at  $70^\circ\text{C}$  where radicals are generated by simple thermal decomposition and the effect of  $\text{ZnCl}_2$  is only to enhance the reactivity of the acceptor monomer in the propagation step.

In view of our experimental results, none of the above mechanisms of initiation can hold for alternating copolymerizations with Lewis acid-benzoyl peroxide system. Initiation may occur by hydrogen abstraction of an excited ternary complex from solvent or monomer or by intercomplex hydrogen transfer (GAYLORD et.al. 1975a). The rapid decomposition of benzoyl peroxide in presence of Lewis acid may result in the generation of excitation energy which is transferred to the ternary molecular complex in the ground state (GAYLORD 1975b).

### Conclusions

Lewis acids catalyze a rapid decomposition of benzoyl peroxide at temperatures far below the thermal decomposition temperature of benzoyl peroxide. However, the Lewis assisted decomposition proceed by an ionic carboxy inversion mechanism to yield >96% phenylbenzoate and one mole of carbon dioxide. No

trappable free radicals could be detected. It is tentatively proposed that complex copolymerization initiated by Lewis acid -peroxide systems proceed by hydrogen abstraction by an excited ternary molecular complex from solvent or monomer.

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