

Heterogeneous Decomposition of *p*-Methoxy- and *p*-Methyl-Dibenzoyl Peroxides by a Montmorillonite Amine Intercalate

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Abstract. A kinetic study of the heterogeneous thermal decomposition of *p*-MeO-DBP and *p*-Me-DBP catalysed by the montmorillonite benzidine intercalate has been made. The kinetics of decomposition were observed to follow a three-halves order reaction with respect to the peroxides. The activation parameters in heterogeneous media have lower values compared with the corresponding values in homogeneous ones. The relationships between ΔH^* and ΔS^* were plotted and show two converging straight lines which indicate that both electron donating and withdrawing substituents on the peroxide enhance the rate of decomposition under these conditions.

Key words: Montmorillonite, decomposition of organic peroxides, heterogeneous catalysis and benzidine reaction.

1. Introduction

There is a growing interest in using montmorillonite clay loaded with organic amines in the decomposition of organic peroxides. Such studies are important from the technological point of view, since montmorillonite has wide applications.

Benzidine reacts with montmorillonite in aqueous media producing a blue colouration which reversibly changes to a yellow or yellowish-green material on dehydration. Matsunaga *et al.* [1] concluded that the blue colouration of the clay is attributed to the formation of the unipositively-charged benzidine radical cation (Bzn^+). The yellow colour, which is formed during dehydration of the clay, is due to the presence of dipositive radical cations of benzidine (Bzn^{2+}). These are thought to be formed by a disproportionation reaction caused by the production of protons at the clay surface when the clay is dehydrated. Protonated benzidine species (HBzn^+) are also thought to be produced during dehydration according to the following equation:



The surface of dehydrated montmorillonite is known to be acidic due to the presence of protons arising from the ionisation of residual water molecules [2].

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The homogeneous decomposition of substituted benzoyl peroxides in solutions and in solids has been thoroughly investigated [3–7]. In previous communications [8, 9], we reported the heterogeneous decomposition of dibenzoyl peroxide, its halogenated substituents and *p*-nitrodibenzoyl peroxide on the benzidine-montmorillonite intercalate.

In this study we report the kinetics of decomposition of *p*-methoxy- and *p*-methyl-dibenzoyl peroxide (*p*-MeO-DBP and *p*-Me-DBP) catalysed by the benzidine/montmorillonite intercalate and come to a general conclusion regarding the effects of both electron-withdrawing and electron-donating substituents in the peroxide on the rate of heterogeneous decomposition.

2. Experimental

2.1. PREPARATION OF MATERIALS

Wyoming montmorillonite (Colorado, U.S.A.) was purified to get rid of all dense components by suspending in deionised water and allowing it to sediment. The supernatant solution which contained fine particles was removed. This operation was repeated several times and the pure fine clay particles ($< 0.69 \mu\text{m}$ equivalent spherical diameter) were obtained through ultracentrifugation followed by drying in a desiccator over calcium chloride [10].

The Na-montmorillonite was obtained by the suspension of the purified clay in 1M NaCl solution in deionised water, shaking for 24 h, centrifugation and washing with deionised water until all chloride ions were removed (tested with AgNO_3 solution) and dried under vacuum in a desiccator [10].

The benzidine-montmorillonite complex was prepared by equilibrating a known weight of Na-montmorillonite with a given volume of aqueous benzidine of 1×10^{-3} M. The mixture which results in a blue colour was shaken for 24 h, separated by centrifugation and dried. The amount of benzidine uptake by a known weight of montmorillonite was determined by the construction of a calibration curve for the absorbance of benzidine at $\lambda_{\text{max}} = 280$ nm before and after intercalation.

The peroxides were prepared according to the method of Price and Krobs [6]. Ethanolic solutions of peroxides were prepared at a concentration of 3×10^{-4} M.

2.2. KINETIC MEASUREMENTS

Known weights of the montmorillonite-benzidine complex were placed in flasks immersed in a shaker thermostat. Appropriate volumes of peroxide solutions of known concentrations were added to each flask. The time of addition was noted [7]. At specific intervals, a conical flask was removed from the thermostat and the reaction quenched by the addition of about 2 g dry-ice followed by 10 ml glacial acetic acid and 2 ml freshly saturated solution of potassium iodide. The reaction mixture was left in the dark for about 20 min. The undecomposed amounts of peroxide were determined titrimetrically [7]. The least-squares method was used to obtain the best fits of straight lines representing the appropriate rate equation.

3. Results and Discussion

We found that the montmorillonite clay alone, without any intercalated benzidine has no significant catalytic effect on the decomposition of organic peroxides.

The heterogeneous catalytic decompositions of *p*-MeO-DBP and *p*-Me-DBP by the

montmorillonite-benzidine complex were carried out in the temperature range 35 to 55°. The concentration of peroxides was kept constant (3×10^{-4} M), while the weight of the clay complex was varied in the range 0.06–0.12 g, corresponding to benzidine concentrations of 4.74×10^{-4} – 9.48×10^{-4} M. The heterogeneous decomposition was found to be three-halves order for *p*-MeO-DBP (Figure 1) and also for *p*-Me-DBP according to the equation

$$\frac{2}{\sqrt{a-x}} - \frac{2}{\sqrt{a}} = k_{\text{tru}}[\text{benz}]t = k_{\text{obs}}t \quad (2)$$

where k_{obs} is the observed rate constant, k_{tru} is the true specific rate constant, and t is the time in minutes.

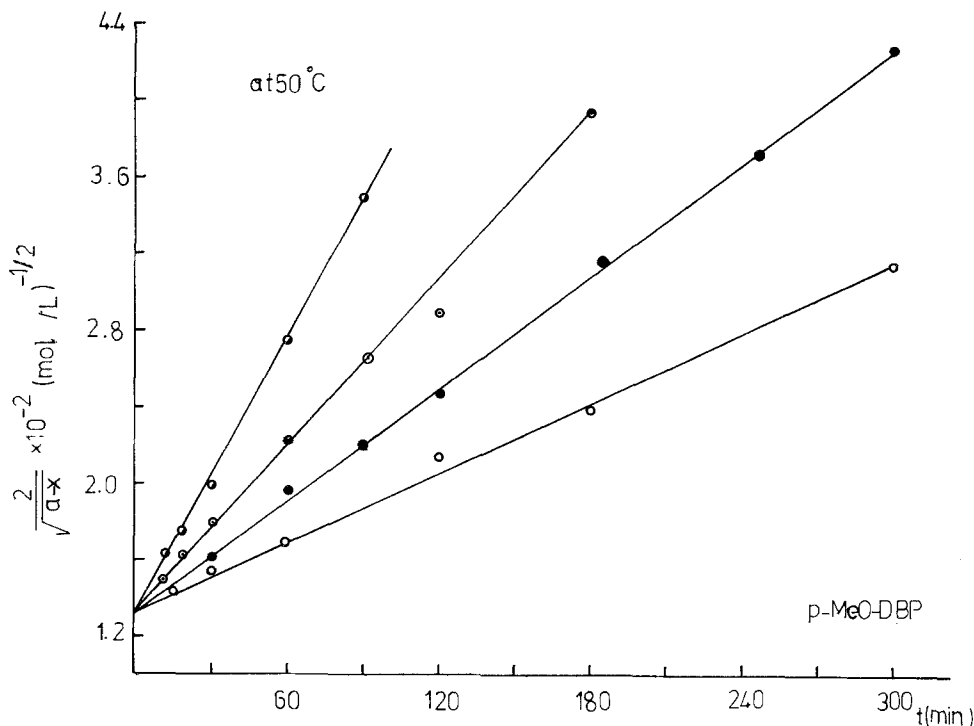


Fig. 1. The heterogeneous three-halves order rate equation at a constant *p*-MeO-DBP concentration of 3×10^{-4} M, and different concentrations of benzidine ○: 4.74, ●: 6.32, ○: 7.90 and ●: 9.48×10^{-4} M at 50°C.

It is shown that the observed rate constant increases with increasing weight of the montmorillonite-benzidine complex. When the values of k_{obs} were introduced into Arrhenius plots, an average activation energy was obtained (Table I). The activation parameters were deduced from Eyring's equation [11].

$$k_{\text{obs}} = \frac{kt}{h} e^{-\Delta G^*/RT}, \quad (3)$$

where k_{obs} is the rate constant, k is the Boltzman constant, and h is the Planck's constant

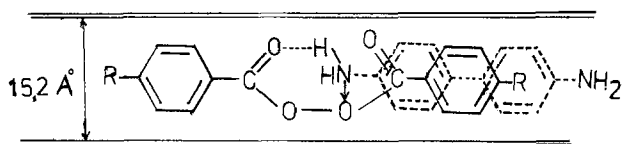
Table I. Activation parameters for different substituted DBP in heterogeneous reactions

Peroxides	E_a KJ mol ⁻¹	ΔH^* KJ mol ⁻¹	ΔG^* KJ mol ⁻¹	ΔS^* J deg ⁻¹ mol ⁻¹
DBP	70.7 ± 0.312	68.2	86.96	- 58.16
<i>p</i> -NO ₂ -DBP	32.22 ± 0.221	29.7	81.17	- 168.2
<i>p</i> -Cl-DBP	57.74 ± 0.321	55.23	84.22	- 92.9
<i>o</i> -Cl-DBP	27.61 ± 0.23	25.1	86.19	- 196.65
<i>p</i> -Br-DBP	61.5 ± 0.113	59.0	84.52	- 80.8
<i>o</i> -Br-DBP	40.58 ± 0.21	38.1	98.6	- 154.14
<i>p</i> -CH ₃ O-DBP	53.5 ± 0.12	50.87	102.4	- 151.12
<i>p</i> -CH ₃ -DBP	61.81 ± 0.034	58.81		- 137.94

^a Ref. [8], ^b Ref. [9].

3.1. THE KINETIC AND ACTIVATION PARAMETERS

In the previous investigations [12–14] it was found that the homogeneously-induced decomposition of peroxide showed a first-order dependence with respect to peroxide. In the present work, the heterogeneously-induced decomposition of the peroxides was found to be of three-halves order with respect to the peroxide. In this case, the benzidine was confined to the small volume of intercalate and the local concentration would be expected to be higher than when the amine is dispersed in a homogeneous medium. It is thus expected that the chain termination step may be different. The results obtained in Table I show that both electron-withdrawing and electron-donating substituents on benzoyl peroxide enhance the rate of heterogeneous-induced decomposition of peroxide by the montmorillonite-benzidine complex. This may suggest that the reaction between peroxides and the oriented benzidine within the silicate sheets of montmorillonite proceeds via both the proton and electron transfer processes, as suggested in Scheme (1). The reactivity of the withdrawing substituents in DBP may be due to a change in the dipole direction [14–16]. The electron-withdrawing substituents would decrease the electron density on the peroxy oxygen atoms and facilitate the nucleophilic attack of nitrogen atom of the benzidine on the peroxy oxygen which will result in a lowering of the value of the activation energy. On the other hand, the electron donating substituents on the aroyl peroxide would increase the electron density on the carbonyl oxygen atoms of the aroyl peroxide, thus facilitating its interaction with the hydrogen of the benzidine and also result in a lowering of the activation energy [13]. So this would confirm that there is a multicentre mechanism (Scheme (1)).



Scheme 1

It is seen from Table II that the values of the activation parameters of the catalytic decomposition of the organic peroxides in homogeneous benzidine solutions are higher than the corresponding values in the benzidine/montmorillonite intercalate. This is because the

Table II. Activation parameters for *p*-CH₃-O and *p*-CH₃-DBP in homogeneous reactions^a

Peroxides	E_a KJ mol ⁻¹	ΔH^* KJ mol ⁻¹	ΔG^* KJ mol ⁻¹	ΔS^* J deg ⁻¹ mol ⁻¹
<i>p</i> -CH ₃ O-DBP	63.6 ± 0.48	61.06	74.3	-78.4
<i>p</i> -CH ₃ -DBP	67.07 ± 0.88	64.5	72.1	-61.5

^a Taken from reference [21].

benzidine species in the latter case have ordered orientation and the positively charged benzidine species facilitate the interaction with the peroxide molecules.

A plot of ΔH^* versus ΔS^* (Figure 2) shows two straight lines, one correlating to the electron-withdrawing substituents and the other correlating to the electron-donating ones.

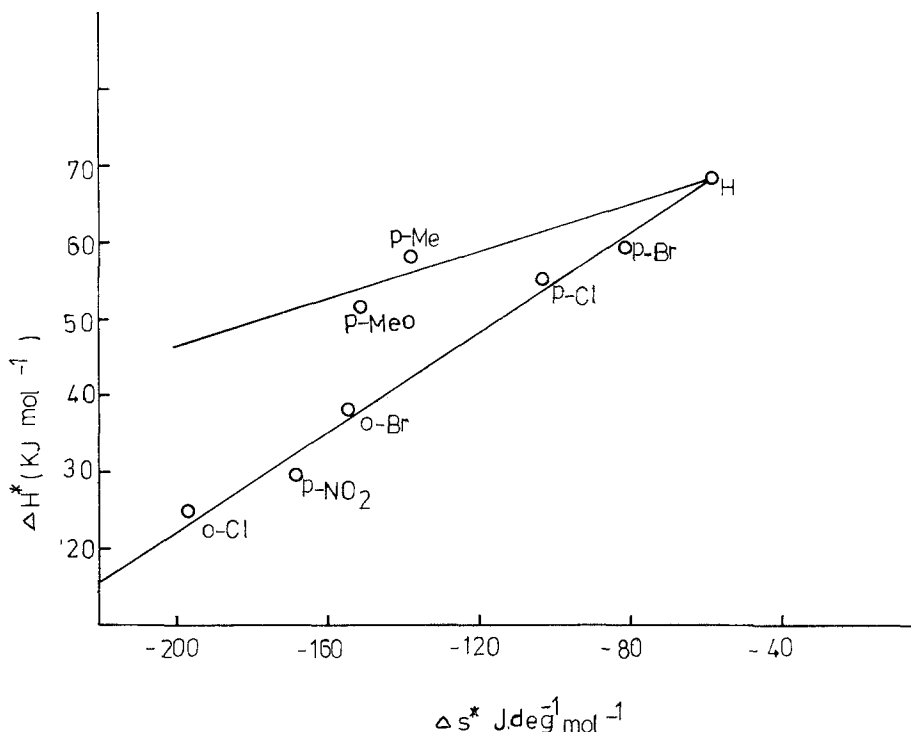
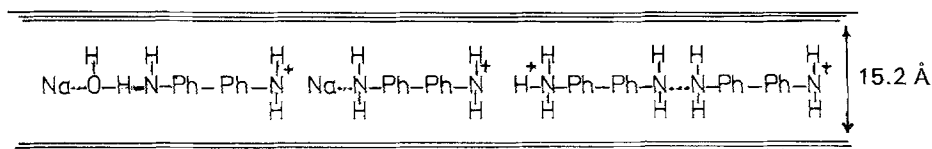


Fig. 2. A plot illustrating the relation between enthalpy and entropy of activation for different peroxide molecules.

3.2. THE NATURE OF THE INTERCALATED CLAY AND THE MECHANISM

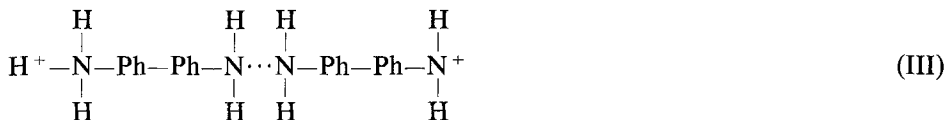
The infrared spectrum of post-intercalated benzidine montmorillonite complex has been reported before and some bands were not assigned [17]. We can assign the unassigned band at 3410 cm⁻¹ as being due to -NH₂ asymmetric stretching of type II (i.e., NH₂ linked to central Na⁺ through a water bridge). The band at 3220 cm⁻¹ is due to NH₂ linked directly to central Na⁺ (Type I). The band at 3355 cm⁻¹ is due to both Types I and II NH₂ vibrations. Thus,

benzidine is present as both Types I and II on dehydration. Since the clay is not completely anhydrous but contains Type I water, one thus has to assume that the benzidine is present in the same manner as aniline [18], with the formation of the benzdinium-benzidine hemisalt and the structures present within the clay surface can be represented by Scheme (2).



Scheme 2

The following species might therefore be present between the silicate sheets.



Species (III) is apparent only on dehydration due to the ionisation of the water which yields the protons necessary for protonation processes.

Regarding the orientation of benzidine between the silicate sheets, it was concluded from earlier studies [19,20] that the plane of the benzene ring of benzidine is perpendicular to the silicate sheets, since the one-dimensional Fourier analysis for the uptake of benzidine by montmorillonite gives a d 001 spacing of 15.2 Å [19,20]. Thus, one has to imagine the pictorial representation is according to Scheme (2), which conforms to our previous communications [8,9,20] which indicate that decomposition takes place within the montmorillonite sheets.

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