Catalytic Decomposition of Organic Peroxides by 4,4'-Diamino-*trans*-Stilbene (DTS)/Montmorillonite Complex: II. *p*-Nitro and *p*-Methyl Dibenzoyl Peroxide

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Abstract. The kinetics of the induced decomposition of p-NO_2- and p-CH_3-dibenzoyl peroxide in the presence of 4,4'-diamino-*trans*-stilbene (DTS) were studied in ethanol under both homogeneous and heterogeneous conditions. The heterogeneous reaction was carried out in the presence of the DTS/montmorillonite complex. The decomposition reaction was found to be second order and three-halves order for the peroxide concentration in homogeneous and heterogeneous systems, respectively. The reaction was first order for the amine concentration in the homogeneous system. The activation energies for the decomposition reaction were obtained as 54.7 ± 2 and 59.5 ± 3 kJ mol^{-1} for p-NO_2- and p-CH_3-dibenzoyl peroxides, respectively, in the homogeneous systems and are higher than the corresponding values of 41 ± 1.5 and 47.6 ± 1 kJ mol^{-1} for the p-NO_2 and p-CH_3 derivatives in heterogeneous media.

Key words. Organic peroxide reactions, montmorillonite/4,4'-diaminostilbene intercalate.

1. Introduction

The influences of diphenylamine and benzidine on the rate of the decomposition of dibenzoyl peroxide (DBP) and p-NO_2-DBP have been reported previously [1, 2]. The kinetics of the unimolecular spontaneous and the bimolecular amine induced decomposition of DBP in partially restricted polymer media have also been investigated [3, 4]. The kinetics of the decomposition of DBP, p-NO_2-DBP, p-CH_3-DBP and halogenated dibenzoyl peroxide has been studied in ethanol medium in the presence of the benzidine/montmorillonite intercalate [5, 6]. Recently, the decomposition of DBP was studied in the presence of 4,4'-diamino-*trans*-stilbene (DTS) in a homogeneous system as well as in the presence of the DTS/montmorillonite complex under heterogeneous conditions [7].

The present investigation aims at the comparison between the homogeneous and heterogeneous decomposition reactions of p-NO_2-DBP and p-CH_3-DBP with DTS. The heterogeneous reaction was carried out in the presence of the DTS/montmorillonite complex.

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2. Experimental

2.1. PREPARATION OF SODIUM-EXCHANGED CLAY

A fraction finer than 0.69 μm equivalent spherical diameter of the sodium-exchanged clay was prepared as mentioned previously [8]. Fully-hydrated montmorillonite has a d (001) of 15.1 ± 0.1 Å and loses 14.5% of its weight on heating to 300 °C for 3 hours as detected by thermogravimetric analysis [9].

2.2. PREPARATION OF THE DTS/MONTMORILLONITE COMPLEX

The DTS/montmorillonite complex was prepared as mentioned elsewhere [7]. The complex has a green colouration which turned brown very quickly on standing. The brown complex is the doubly charged diprotonated species [7] H_3^+ N—Ph—CH= CH—Ph—NH_3^+. It is very stable and may persist for several months. This renders its catalytic activity more reliable.

2.3. THE PEROXIDE SOLUTION

The peroxide derivatives were prepared from the reaction of the corresponding benzoyl chlorides and sodium peroxide and were purified by the appropriate crystallization methods [10]. Solutions of p-NO$_2$-DBP and p-CH$_3$-DBP in ethanol were prepared with a concentration of 1×10^{-3} M.

2.4. KINETIC MEASUREMENTS

The decomposition in the homogeneous and heterogeneous systems in the presence of the DTS/montmorillonite complex was followed iodometrically as mentioned elsewhere [7].

3. Results

3.1. HOMOGENEOUS DECOMPOSITION OF p-NO$_2$-DBP AND p-CH$_3$-DBP IN THE PRESENCE OF DTS IN ETHANOL

The decomposition reaction of p-NO$_2$-DBP was studied in the presence of DTS in ethanol. The reaction was carried out at constant peroxide concentration (1×10^{-3} M) and with two different initial concentrations of DTS (2×10^{-4} M and 3×10^{-4} M). The order of the reaction n was determined by Ostwald's method of isolation [11]. The reaction was found to follow second order kinetics with respect to the peroxide concentration as shown in Figure 1 and first order kinetics with respect to the DTS concentration.

The rate of the reaction can be written as follows:

$$\frac{dx}{dt} = k_3[\text{peroxide}]^2[\text{DTS}] \tag{1}$$

where k_3 (L^2 mol^{-2} min^{-1}) is the third order reaction rate constant. The second order integrated rate equation with respect to the peroxide concentration can be written as follows:
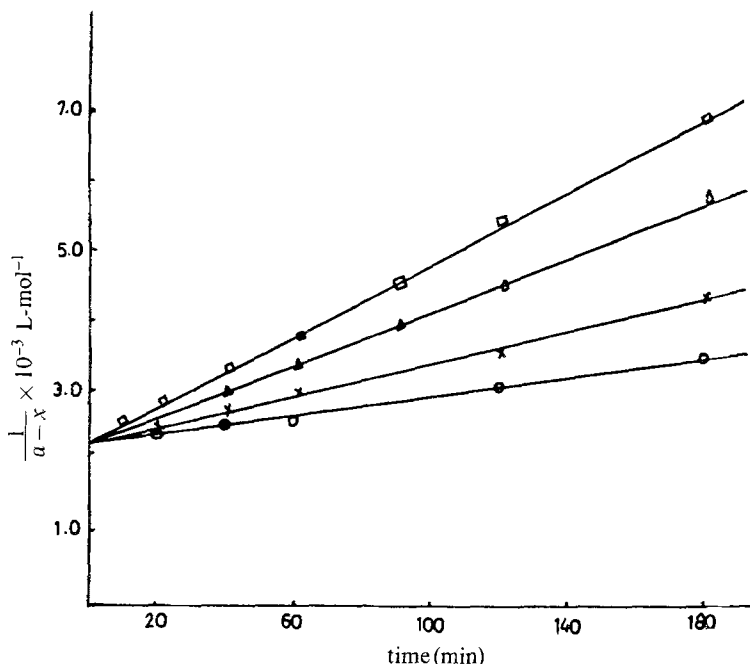
Fig. 1. Illustration of the integrated rate equation of a second-order system of p-NO_2-DBP/DTS with constant initial concentrations of the peroxide and the DTS equal to 1×10^{-3} M and 2×10^{-4} M respectively at four different temperatures: $\bigcirc$: 30 °C, $\times$: 35 °C, $\triangle$: 40 °C and $\square$: 45 °C.

$$\frac{1}{a-x} = \frac{1}{a} + k_{obs} \cdot t \qquad (2)$$

where a is the initial peroxide concentration, and x is the amount decomposed at time t.

Thus,

$$k_{obs} = k_3[DTS] \qquad (3)$$

This means that the third order reaction rate constant, k_3 can be determined from Equation (3). The values of the observed rate constant, k_{obs} as well as of k_3 are listed in Tables I and II. The values of k_3, which are only temperature dependent, were introduced into an Arrhenius plot and the activation energies together with other activation parameters are summarized in Tables I and II.

The activation parameters were also deduced. The change of the free energy of activation, ΔG^*, was deduced from Eyring's equation [12]. The change of the enthalpy of activation, ΔH^* was always smaller than the value of E by the amount RT. The change of the entropy of activation, ΔS^* was evaluated from the relationship:

$$\Delta G^* = \Delta H^* - T\Delta S^* \qquad (4)$$

3.2. HETEROGENEOUS DECOMPOSITION OF p-NO_2-DBP AND p-CH_3-DBP IN THE PRESENCE OF THE DTS/MONTMORILLONITE COMPLEX IN ETHANOL

The decomposition reactions of p-NO_2-DBP and p-CH_3-DBP were studied in the

Table I. Rate constants and activation parameters for the decomposition of p-NO$_2$-DBP (1×10^{-3} M) with DTS in both homogeneous and heterogeneous systems

System	Conc. of DTS (M)	Temp. (°C)	k_{obs}	k	E_a (kJ/mol)	ΔH^* (kJ/mol)	ΔG^* (kJ/mol)	ΔS^* (J mol^{-1} deg^{-1})
Homo-geneous	2×10^{-4}	30	5.00	2.50×10^4				
		35	9.14	4.57×10^4				
		40	13.40	6.70×10^4				
		45	17.60	8.80×10^4				
					54.7 ± 2	52.1	78.7	-64
Homo-geneous	3×10^{-4}	30	7.62	2.54×10^4				
		35	13.77	4.54×10^4				
		40	20.10	6.70×10^4				
		45	27.00	9.00×10^4				
Hetero-geneous (0.0513 g dry clay)		30	0.189	3.68				
		35	0.248	4.83				
		40	0.319	6.33				
		45	0.412	8.03				
					41 ± 1.5	38.4	82.3	-141.4
Hetero-geneous (0.077 g dry clay)		30	0.284	3.69				
		35	0.372	4.83				
		40	0.476	6.18				
		45	0.623	8.09				

For homogeneous reaction: $k_{obs} = $ L mol^{-1}; $k = k_3 = $ L^2 mol^{-2} min^{-1}.
For heterogeneous reaction: $k_{obs} = $ L$^{1/2}$ mol$^{-1/2}$ min^{-1}; $k = k_{1.5} = $ L$^{1/2}$ mol$^{-1/2}$ min^{-1} (per g dry clay).

Table II. Rate constants and activation parameters for the decomposition of p-CH$_3$-DBP (1×10^{-3} M) with DTS in both homogeneous and heterogeneous systems

System	Conc. of amine (M)	Temp. (°C)	k_{obs}	k	E_a (kJ/mol)	ΔH^* (kJ/mol)	ΔG^* (kJ/mol)	ΔS^* (J deg^{-1} mol^{-1})
Homo-geneous	2×10^{-4}	30	6.25	3.12×10^4				
		35	11.50	5.75×10^4				
		40	15.25	7.63×10^4				
		45	21.0	10.5×10^4	59.56 ± 3	56.96	78.69	-69.42
Homo-geneous	3×10^{-4}	30	9.14	3.08×10^4				
		35	15.96	5.30×10^4				
		40	22.70	7.56×10^4				
		45	29.76	9.92×10^4				
Hetero-geneous (0.077 g dry clay)		30	0.2	2.59				
		35	0.27	3.51				
		40	0.33	4.29				
		45	0.40	5.19	47.56 ± 1	44.96	87.28	-136.26

For homogeneous reaction $k_{obs} = $ L mol^{-1} min^{-1}, $k = k_3 = $ L^2 mol^{-2} min^{-1}.
For heterogeneous reaction k_{obs}: L$^{1/2}$ mol$^{-1/2}$ min^{-1}, $k = k_{1.5} = $ L$^{1/2}$ mol$^{-1/2}$ min^{-1}.
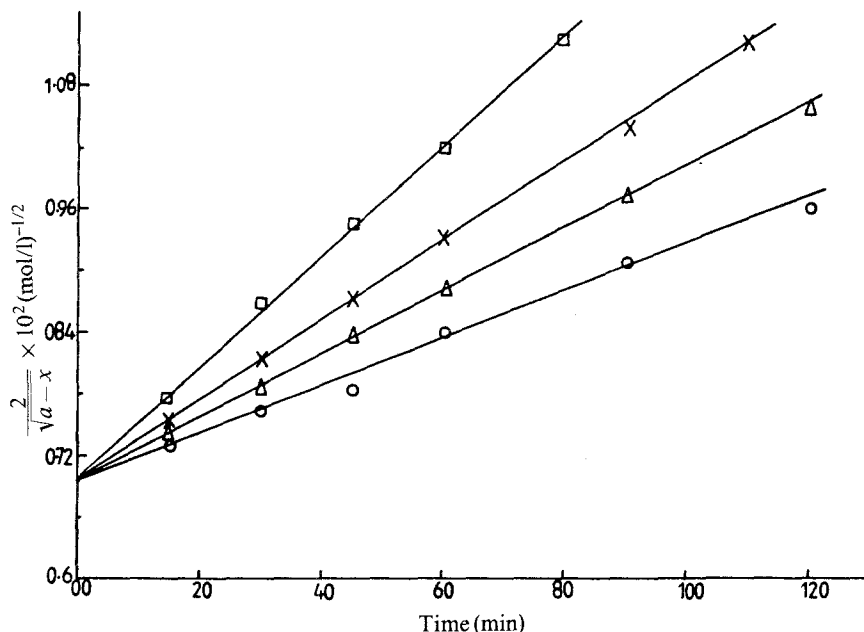
Fig. 2.   Illustration of the integrated rate equation representing a three-halves order for the heterogeneous decomposition of p-NO_2-DBP in the presence of 0.9 g of the DTS/montmorillonite complex at four different temperatures: $\bigcirc$: 30 °C, $\triangle$: 35 °C, $\times$: 40 °C and $\square$: 45 °C.

presence of the DTS/montmorillonite complex in ethanol. The reaction was carried out at constant peroxide concentration (1×10^{-3} M) and with two different weights of the clay complex (0.06 g and 0.09 g). These weights correspond to 0.0513 g and 0.077 g dry clay after the removal of *ca.* 14.5% water of hydration. These dry weights correspond to 1.796×10^{-4} and 2.693×10^{-4} moles of DTS, respectively, as calculated from the cation exchange capacity (c.e.c.) measurements. Each of these concentrations is considered to be constant because the DTS in the clay complex acts as a catalyst. The order of the decomposition reaction with respect to the peroxide was found to be 1.5 and the rate of the reaction can be written as follows:

$$\frac{2}{\sqrt{a - x}} = \frac{2}{\sqrt{a}} + k_{obs} \cdot t \tag{5}$$

Thus,
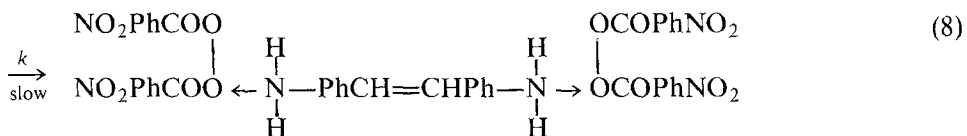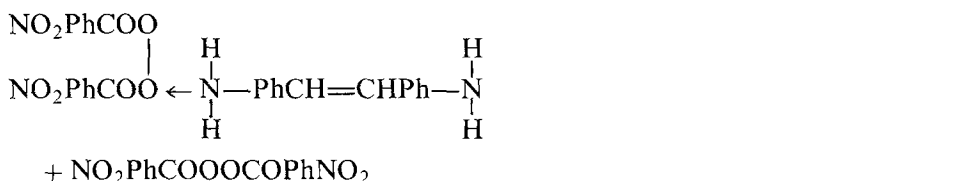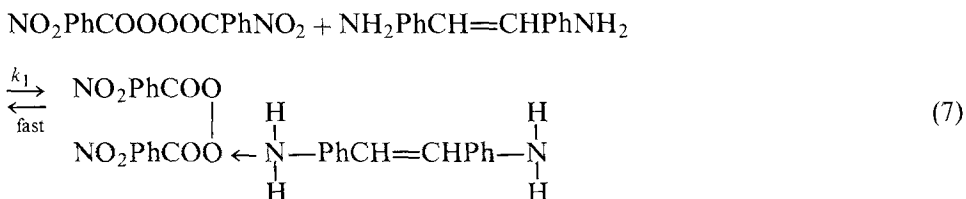
$$k_{obs} = k_{1.5} \cdot w \tag{6}$$

where w is the amount of intercalated DTS in a certain weight of clay. $k_{1.5}$ can be determined from Equation (6). The values of the observed rate constant, k_{obs} and those of $k_{1.5}$ are listed in Tables I and II. The values of $k_{1.5}$, which are only temperature dependent, were introduced into an Arrhenius plot and yielded activation energy values which are summarized together with other activation parameters in Tables I and II.

4. Discussion

4.1. THE MECHANISM OF THE HOMOGENEOUS REACTION

Aromatic amines induce peroxide decomposition via the formation of the intermediate charge transfer state [1]. An overall order of 3 for the homogeneous decomposition reaction may lead to the suggestion of the following mechanism for p-NO$_2$-DBP which is also the case with p-CH$_3$-DBP:

$$NO_2PhCOOOOCPhNO_2 + NH_2PhCH{=}CHPhNH_2$$

$$\underset{\text{fast}}{\overset{k_1}{\rightleftharpoons}} \quad \begin{array}{c} NO_2PhCOO \\ | \qquad\quad H \qquad\qquad\qquad\qquad H \\ NO_2PhCOO \leftarrow N{-}PhCH{=}CHPh{-}N \\ \qquad\qquad H \qquad\qquad\qquad\qquad H \end{array} \tag{7}$$

$$\begin{array}{c} NO_2PhCOO \\ | \qquad\quad H \qquad\qquad\qquad\qquad H \\ NO_2PhCOO \leftarrow N{-}PhCH{=}CHPh{-}N \\ \qquad\qquad H \qquad\qquad\qquad\qquad H \end{array}$$

$$+ \; NO_2PhCOOOCOPhNO_2$$

$$\underset{\text{slow}}{\overset{k}{\longrightarrow}} \quad \begin{array}{c} NO_2PhCOO \qquad\qquad\qquad\qquad\qquad OCOPhNO_2 \\ | \qquad\quad H \qquad\qquad\qquad H \quad | \\ NO_2PhCOO \leftarrow N{-}PhCH{=}CHPh{-}N \rightarrow OCOPhNO_2 \\ \qquad\qquad H \qquad\qquad\qquad H \end{array} \tag{8}$$

$$\overset{\text{fast}}{\longrightarrow} \quad \text{Products} \tag{9}$$

The rate equation can be written as follows:

$$\frac{dx}{dt} = \frac{-d[\text{peroxide}]}{dt} = k[\overset{NO_2PhCOO}{\underset{|}{NO_2PhCOO}} \leftarrow NH_2PhCH{=}CHPhNH_2]$$

$$[NO_2PhCOOOOCPhNO_2] \tag{10}$$

From Equation (7) we have:

$$[\overset{NO_2PhCOO}{\underset{|}{NO_2PhCOO}} \leftarrow NH_2PhCH{=}CHPhNH_2]$$

$$= k_1[NO_2PhCOOOOCPhNO_2][NH_2PhCH{=}CHPhNH_2]$$

Thus Equation (10) becomes:

$$\frac{dx}{dt} = \frac{-d[\text{peroxide}]}{dt} = k\,k_1[NO_2PhCOOOOCPhNO_2]^2$$

$$[NH_2PhCH{=}CHPhNH_2] \tag{11}$$

This means that k_3 (in Equation 1) is equal to $k \cdot k_1$ (in Equation 11).

4.2. THE MECHANISM OF THE HETEROGENEOUS REACTION

There are three possibilities for the mechanism of the reaction

i – The DTS goes into solution where it encounters the peroxide molecules and the decomposition occurs in a homogeneous system.

ii – The DTS/peroxide reaction occurs in a layer at the surface of the clays.

iii – The reaction occurs in the reaction zone between the silicate layers of the clay. The first possibility must be disregarded since it was found that the reaction was three-halves order in the heterogeneous system while it was second order in the homogeneous system with respect to the peroxide.

If mechanism (ii) were correct then one would expect that intraparticle diffusion would be much slower than the chemical reaction. Intraparticle diffusion can affect the rate of the reaction but it can never be the sole rate-determining step. Accordingly the reaction has to occur only in a thin layer at the surface of the clay because the reactant molecules would react before they have time to penetrate into the interior of the clay catalyst. In this mechanism the rate of the reaction may be controlled either by film diffusion or chemical reaction at the clay surface, whichever of these two processes is the slower one. Complete film diffusion control is a rare phenomenon with a low activation energy (8.4 to 20.9 kJ/mol^{-1}) [13]. On the other hand, if the reaction occurred on the surface of the clay, one would expect that the decomposition would occur at a measurable rate when the peroxide was dissolved in different solvents. But it was found that if the peroxide was dissolved in benzene or carbon tetrachloride no decomposition is catalysed by the intercalated clay. The reaction only occurs when the peroxide is dissolved in ethanol. It is known that montmorillonite has an affinity for polar organic compounds and has no affinity for nonpolar organic compounds [14, 15]. Thus one also disregards the idea of reaction occurring on the clay surface.

The most probable mechanism is thus the occurrence of the reaction in the reaction zone between the silicate layers of the post-intercalated DTS/montmorillonite complex. This agrees with the experimental findings of the occurrence of the reaction in ethanol since montmorillonite has an affinity to it.

4.3. THE ACTIVATION PARAMETERS

The activation energies in the heterogeneous systems are lower than those in the homogeneous system. This is in good agreement with the fact that the activation energies of reactions decrease in the presence of catalysts owing to the changes in the reaction mechanisms.

The enthaply of activation, ΔH^* (Tables I and II) is a measure of the height of the energy barrier, particularly of bond strengths within and between the reactants, which must be overcome to attain the transition state. This means that in the heterogeneous reaction the transition state is attained more easily than that in the homogeneous system.

The value of ΔG^* in the homogeneous reaction was smaller than that in the heterogeneous system (Tables I and II). This means that the tendency of the equilibrium between the reactants and the activated state to shift itself in the direction of the latter was greater in the homogeneous system than with the heterogeneous system.

The decrease in entropy in the homogeneous system is less than the corresponding decrease in the heterogeneous system (Tables I and II). This is consistent with the fact that the activated complex is more ordered in the heterogeneous system.

The p-nitro or p-methyl-substituted benxoyl peroxides have more catalytic reactivity in the decomposition reaction than the unsubstituted peroxide molecule [7]. The reactivity decreases in the order p-NO$_2$-DBP $> p$-CH$_3$-DBP $>$ DBP.

This can be explained on the basis that, dibenzoyl peroxide molecules have both electrophilic and nucleophilic characters (i.e. the electron-repelling or electron-attracting substituents in the peroxide molecules enhance the rate of the induced decomposition).

This is in agreement with the present and the earlier results [16]. The ability of the nitro-group to induce a decomposition reaction is higher than that of the methyl group. This may be correlated with the difference in Hammett σ values.

References

1. S. E. Morsi, A. B. Zaki, T. M. El-Shamy, and A. Habib: *Eur. Polymer. J.* **12**, 417 (1976).
2. S. E. Morsi, A. B. Zaki, and A. Habib: *Z. Phys. Chem. Leipzig* **262**, 196 (1981).
3. S. E. Morsi, A. B. Zaki, and M. A. El-Khyami: *Eur. Polymer J.* **13**, 851 (1977).
4. A. B. Zaki, T. M. El-Shamy, M. A. El-Khyami, and S. E. Morsi: *Indian J. Chem.* **19**, 163 (1980).
5. S. E. Morsi, A. B. Zaki, G. B. El-Hefnawy, and A. Habib: *Z. Phys. Chem. Leipzig* **263**, 1249 (1982).
6. A. B. Zaki, G. B. El-Hefnawy, A. Habib, and S. E. Morsi: *Z. Phys. Chem. Leipzig* **263**, 161 (1982).
7. A. M. Habib, S. H. Kandil, M. Y. El-Sheikh, and A. A. Saafan: *J. Incl. Phenom.* **3**, 379 (1985).
8. D. T. B. Tennakoon, J. M. Thomas, M. J. Tricker, and T. O. Williams: *J. Chem. Soc., Dalton Trans.* 2207 (1974).
9. A. M. Habib, M. F. Abd-El-Magid, A. Saafan, and R. M. Issa: *J. Incl. Phenom.* **4**, 185 (1986).
10. A. I. Vogel: *A Textbook of Practical Organic Chemistry.* London: Longman, Green p. 808 (1948).
11. G. Pannetier and P. Souchay: *Chemical Kinetics*, New York, Elsevier p. 155 (1967).
12. S. Glasstone, K. J. Laidler, and H. Eyring: *Chemical Kinetics*, New York, McGraw-Hill, p. 197 (1941).
13. F. Helfferich: *Ion Exchange.* New York: McGraw-Hill, p. 129, 525 (1962).
14. R. M. Barrer and J. S. S. Reay: *Trans. Faraday Soc.* **53**, 1253 (1957).
15. V. C. Farmer: *Soil Sci.* **112**, 62 (1971).
16. A. M. Habib, M. Y. El-Sheikh, A. B. Zaki, and S. E. Morsi: *J. Incl. Phenom.* **4**, 169 (1986).