Catalytic Decomposition of Organic Peroxides by 4,4′-Diamino-*trans*-stilbene (DTS)/Montmorillonite Complex. I. Dibenzoyl Peroxide (DBP)

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Abstract. The decomposition of DBP was studied in the presence of DTS in an ethanolic homogeneous solution and with DTS intercalated in montmorillonite clay mineral as a heterogeneous reaction. The kinetic parameters obtained from the two systems were monitored and indicated that the homogeneous system follows second order reaction kinetics for DBP, whereas the heterogeneous one follows a three-halves order. The heterogeneous system was found to possess higher catalytic efficiency and the reaction was shown to take place within the internal surfaces of the clay mineral. This was attributed to the great surface area of the catalyst, Lewis and Brönsted acid sites and its great ability to sorb the polar organic species.

Key words: Montmorillonite, intercalation, heterogeneous catalysis, dibenzoyl peroxide, 4,4′-diamino-*trans*-stilbene.

1. Introduction

Previous studies of the rate of decomposition of DBP have indicated first, second, or third-order kinetics [1] depending on the solvent medium. It was found that the orders of reaction are complex, that the rapid decomposition could be inhibited by air (oxygen), by hydroquinone or quinone and that the decomposition was retarded by aromatic compounds. These observations are taken to indicate the existence of a chain reaction in which radicals derived from the solvent attack undissociated DBP molecules.

The decomposition of DBP in the presence of benzidine [2] in benzene solvent revealed that the reaction follows first order kinetics with respect to DBP and benzidine (benz) according to the following equation:

$$dx/dt = K_2[P][A] \tag{1}$$

in which $[P]$ represents the peroxide concentration and $[A]$ is the benzidine concentration. The intermediate complex has a 1 : 1 ratio (DBP : benz) and the benzidine molecules could have either planar or twisted configurations according to the type of acceptor [2]. During our experiments on the benz/DBP system, a blue colouration was obtained at high concentrations

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[3,4] which is due to benzidine blue [5]. The benzidine blue has been found in other redox systems of layered silicate intercalates of montmorillonite [5].

In the present study we have investigated the catalytic activities of amine/montmorillonite intercalates in the decomposition of DBP using 4,4'-diamino-*trans*-stilbene dihydrochloride (DTS) to investigate the nature of the intercalate complex and to evaluate the kinetic parameters of the decomposition process. The study has also been performed in a homogeneous medium for comparison.

2. Experimental

2.1. PREPARATION OF THE AMINE/MONTMORILLONITE COMPLEX

The crude Wyoming montmorillonite (Colorado, U.S.A.) was purified as mentioned elsewhere [6]. The intercalate of DTS was easily formed by addition of an excess of aqueous DTS to definite amounts of colliodal suspensions of purified sodium exchanged Wyoming clay. The clay took on a green colouration that turned brown on standing. The intercalated amount of DTS/g clay was 35 m mole/100 g of airdried clay. The brown colour is due to the doubly charged diprotonated species [5] [$^+H_3N-Ph-CH=CH-Ph-NH_3{}^+$].

2.2. PREPARATION OF DIBENZOYL PEROXIDE (DBP) SOLUTIONS AND THE KINETIC MEASUREMENTS

A 10^{-3} M ethanolic solution of DBP (BDH grade) was used and the kinetic measurements were followed iodometrically. Definite weights of the DTS/montmorillonite complex were placed in conical flasks contained in a shaker thermostat with a temperature accuracy of $\pm 0.1\,^\circ$C. To each conical flask 10 ml of a 0.001 M ethanolic solution of DBP were added at the zero reaction time. At different intervals a conical flask was removed from the thermostat, quickly quenched by adding about 3 g of dry ice, 10 ml of glacial acetic acid and 2 ml of a freshly-prepared saturated solution of potassium iodide.

The flasks were left in the dark for 20 min [7]. The decomposed amount of DBP in each conical flask was determined by titration against standard sodium thiosulphate solution. The weight of the clay varied from 0.06–0.09 g while the peroxide concentration was kept constant at 1×10^{-3} M. The same titration method was also applied to the homogeneous reactions. The DTS concentrations were varied from 2 to 8×10^{-4} M, while the DBP concentration was kept constant at 1×10^{-3} M.

3. Results

3.1. HOMOGENEOUS DECOMPOSITION OF DBP BY DTS IN ALCOHOLIC SOLVENT

The decomposition of DBP was carried out at four different temperatures: 30, 35, 40 and 45°C.

The initial peroxide concentration was kept constant at 1×10^{-3} M while different concentrations of the amine were taken, namely 2, 4, 6 and 8×10^{-4} M. The percentage decomposition-time curve of DBP at 35°C is shown in Figure 1. The kinetics of dibenzoyl peroxide decomposition at different amine concentrations was investigated. Figure 2 shows the decomposition of DBP at 35°C. The reactions follows second-order kinetics with respect to DBP. It was observed that the rate of the reaction increased as the concentration of amine increased.
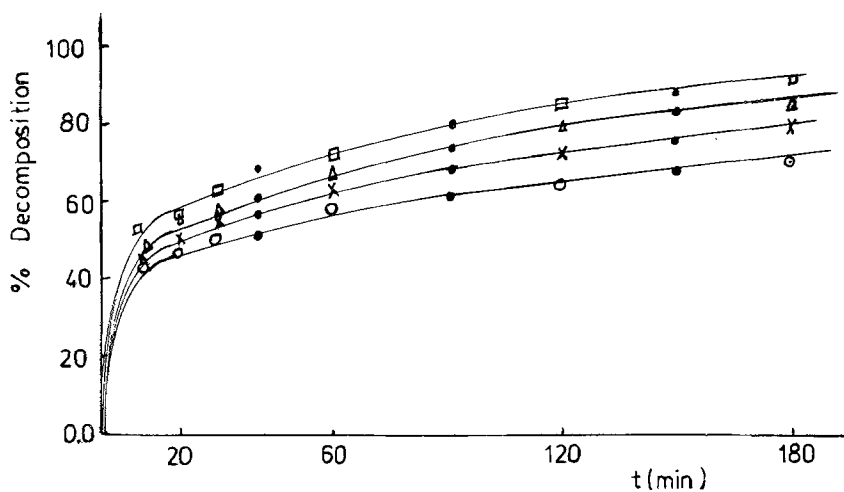
Fig. 1.   The percentage decomposition of DBP in the presence of different concentrations of DTS ○: 2×10^{-4} M, ✕ : 4×10^{-4} M, △: 6×10^{-4} M and □: 8×10^{-4} M at 35°C, ●: Theoretical points derived from the kinetic analysis.
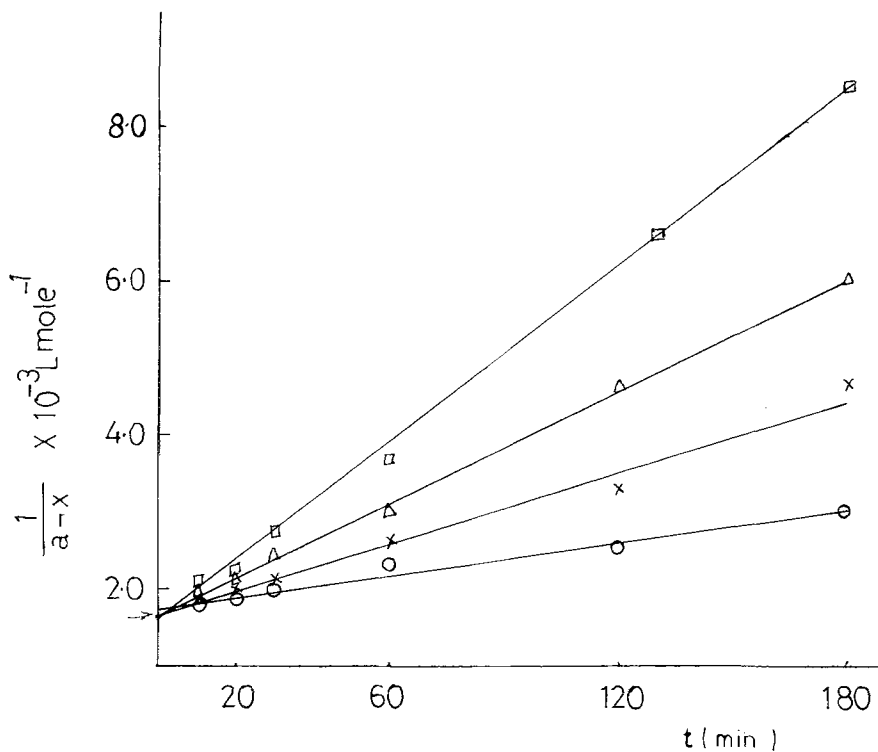

Fig. 2.   The homogeneous intergrated second-order rate equation at a constant DBP concentration of 1×10^{-4} M and different concentrations of DTS ○: 2×10^{-4}, ✕ : 4×10^{-4}, △: 6×10^{-4} and □: 8×10^{-4} M at 35°C.
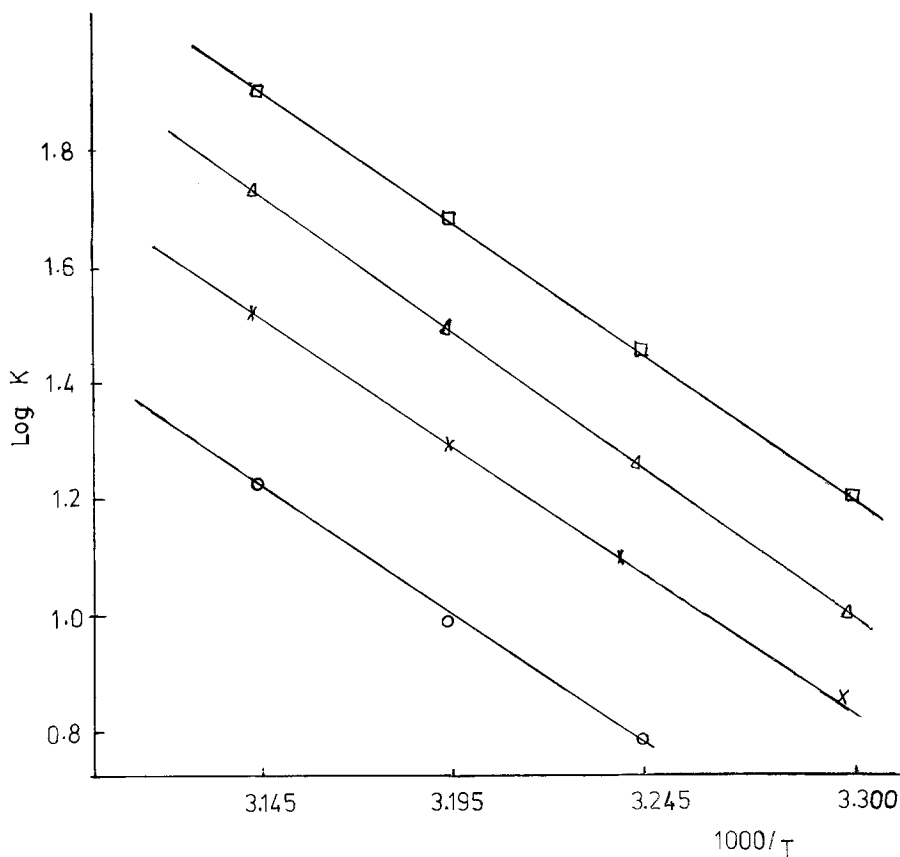
Fig. 3.   An Arrhenius plot representing the activation energy for the homogeneous decomposition of DBP at DTS concentrations of $\bigcirc: 2 \times 10^{-4}$, $\times: 4 \times 10^{-4}$, $\triangle: 6 \times 10^{-4}$ and $\square: 8 \times 10^{-4}$ M at a DBP concentration of 10^{-3} M.

The values of the rate constant k obtained for each amine concentration were introduced in Arrhenius plots and yielded an average activation energy of 64.8 ± 1 KJ mol^{-1} (see Figure 3).

3.2. HETEROGENEOUS DECOMPOSITION STUDIES OF DBP BY DTS/MONTMORILLONITE COMPLEX

The decomposition of DBP in the presence of DTS intercalated between silicate sheets of montmorillonite was carried out at 30, 35, 40 and 45°C. The initial peroxide concentration was kept constant at 1×10^{-3} M while the weight of the clay was varied between 0.06 and 0.09 g. This corresponded to amine concentrations of 2.1, 2.45, 2.8 and 3.15×10^{-4} M, respectively.

No decomposition was detected when the peroxide solution was mixed with the clay in the absence of DTS under identical experimental conditions. As seen in Figure 4, the reaction followed a three-halves order kinetics. The values of the observed rate constant k_{obs} increased as the weight of clay increased. Each value of k_{obs} at different temperatures of the amine/clay complex was introduced into Arrhenius plots and yielded an average activation energy of 52.2 ± 2 KJ/mol^{-1} (Figure 5).
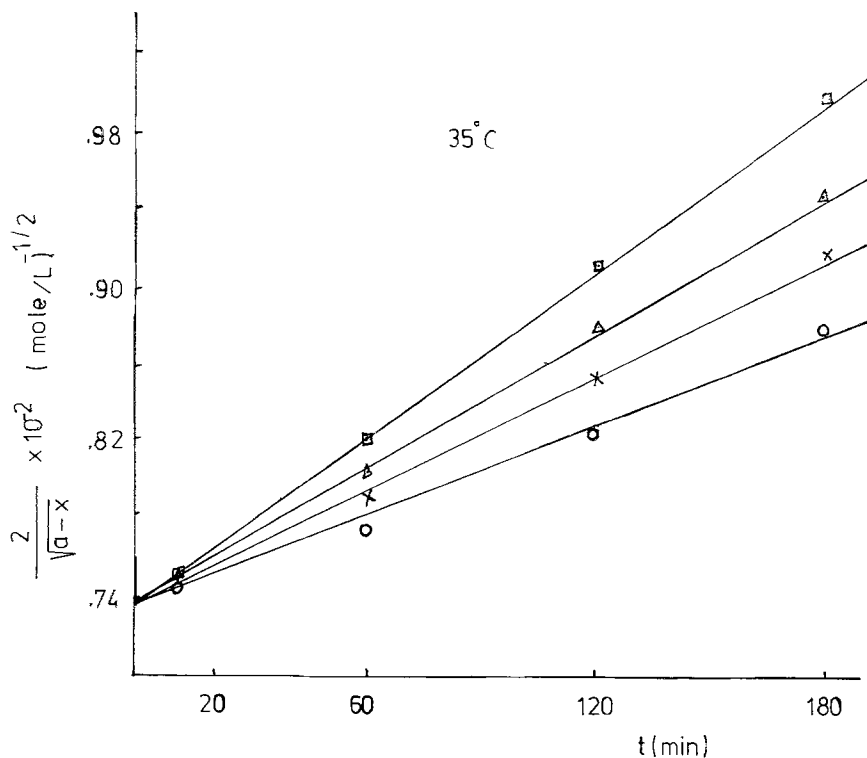
Fig. 4.   The integrated rate equation representing the overall kinetic order of 1.5 in the case of a constant peroxide concentration (1×10^{-4} M) and different weights of the amine/montmorillonite intercalate $\bigcirc$: 0.06 g, $\times$: 0.07 g, $\triangle$: 0.08 g and $\square$: 0.09 g at 35°C.

Table I.   Homogeneous and heterogeneous kinetic parameters of the induced decomposition of DBP by DTS

Condition of reaction	Concentration of amine (M)	Rate cons. k^+	ΔG^* KJ mol^{-1}	E_a KJ mol^{-1}	ΔH^* KJ mol^{-1}	ΔS^* J mol deg^{-1}
Homogeneous	2×10^{-4}	7.78				
	4×10^{-4}	15.6				
	6×10^{-4}	24.4	80.35	64.8	62.6	− 57.6
	8×10^{-4}	34.3				
Heterogeneous	0.06 g	0.075				
	0.07 g	0.097				
	0.08 g	0.117	90.5	52.2	49.2	− 131.8
	0.09 g	0.144				

[a] The values of k are reported at 35°C and dimensions are mol^{-1} min^{-1} for homogeneous reactions and mol$^{-1/2}$ min^{-1} for heterogeneous reactions.
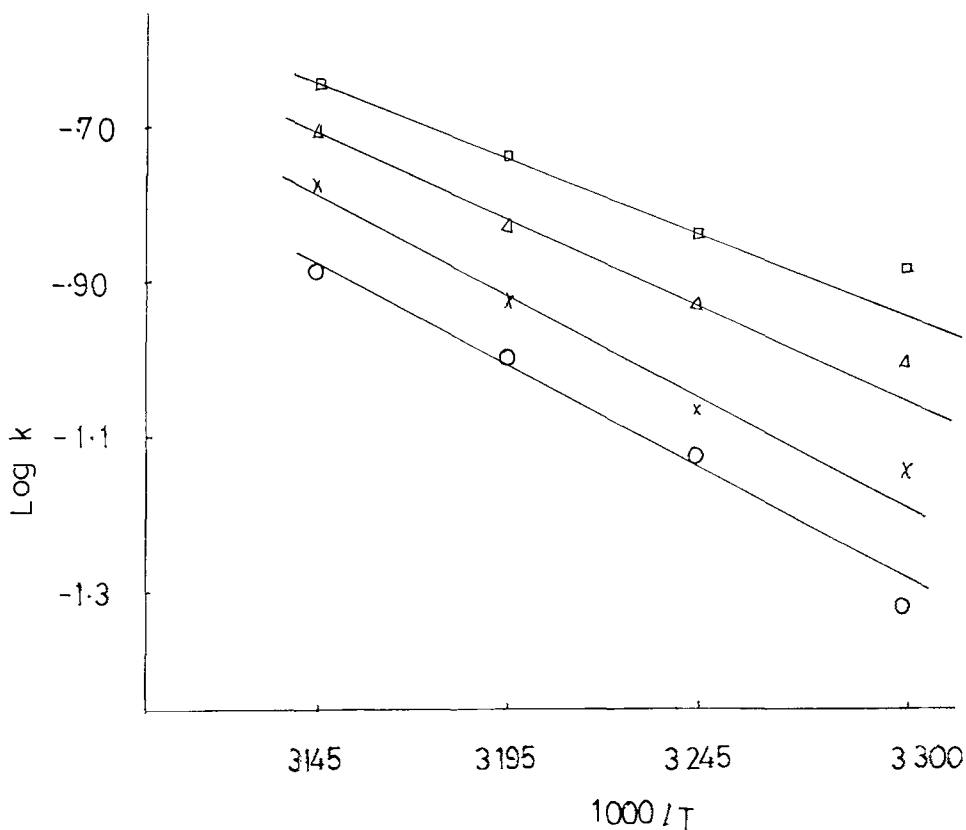
Fig. 5. An Arrhenius plot representing the activation energy for the heterogeneous decomposition of DBP at different weights of DTS/montmorillonite intercalate $\bigcirc$: 0.06 g, $\times$: 0.07 g, $\triangle$: 0.08 g and $\square$: 0.09 g at 35 °C.

4. Discussion

4.1. HOMOGENEOUS STUDIES

Published data on the kinetics of amine induced decomposition of dibenzoyl peroxide (DBP) have revealed that the rate of decomposition depends on the solvent [1]. In the present work, the best fitting kinetic equations were found to follow second-order kinetics for DBP. Also, at constant DBP concentration, the rate constant doubled as the amine concentration was doubled (see Table I). This leads us to suggest that the rate of reaction follows the equation

$$\mathrm{d}x/\mathrm{d}t = k_3[\mathrm{P}]^2[\mathrm{A}] \tag{2}$$

Where [P] is the peroxide concentration and [A] is the amine concentration. The over-all order is third-order kinetics. Thus the mechanism in scheme (1) was suggested.

The activation energy for the homolytic bond cleavage of (—O—O—) in DBP has a value of 130 kJ mol^{-1} whereas the radical induced decomposition of DBP in solution has an activation energy of 96 kJ mol^{-1} [8]. In the present work, the activation energy obtained has a value of 64.8 $\pm$ 1 KJ mol^{-1}. This means that DTS acts as a catalyst in the decomposition reaction of DBP. The peroxide molecules act as acceptors and the decomposition of DBP

2 PhCOOOOCPh + NH$_2$—Ph—CH=CH—Ph—NH$_2$

Scheme (1)   PRODUCTS
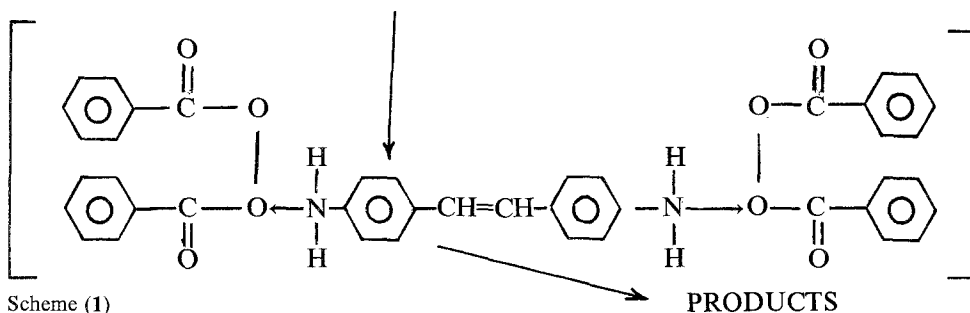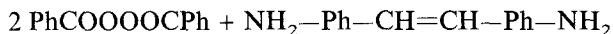
takes place as a result of charge transfer from the amine donor to the peroxide acceptor [9]. The formation of the intermediate complex leads to the formation of a highly distorted benzoyl peroxide molecule. Thus the peroxide molecules acquire a high potential energy, and become metastable and decompose. The lower energy of activation for the induced decomposition of DBP using DTS is lower than that when using benzidine indicating that the catalytic efficiency of DTS is higher than benzidine. This can be explained on the basis that DTS molecules have longer chains and are more flexible than benzidine molecules. This facilitates the formation of the intermediate complex leading to decomposition.

4.2. HETEROGENEOUS STUDIES

4.2.1. Kinetic Studies of DBP

The kinetic order of the heterogeneous catalyzed decomposition of DBP in the presence of DTS/montmorillonite was found to be three halves in DBP. This can be attributed to the fact that the kinetic order of peroxide decomposition depends on the type of chain termination which is solvent-dependent [2,3]. Table I summarizes the results obtained at constant peroxide concentration of 1×10^{-3} M at 35°C for both heterogeneous and homogeneous reactions. The free energy, enthalpy and entropy of activation were calculated from Eyring's equation [3]. The rate determining step in the decomposition of DBP in the presence of the amine/montmorillonite intercalate may be one of the following three possibilities:

(a) The peroxide molecules diffuse from the bulk of solution to the external surfaces of the clay where the reaction with the amine/clay complex takes place.
(b) The peroxide molecules at the external surfaces of the clay are adsorbed to the internal surfaces by intercalation and interact with the amine-clay complex.
(c) The amine species leave the clay surface to the bulk solution and react with DBP molecules.

The results obtained in Table I indicate that values of the rate constants for homogeneous reaction are much larger than for heterogeneous reactions at approximately the same conditions. It has also been seen that the decomposition of DBP in such a reaction does not occur in a nonpolar solvent such as benzene. Again the concentration measurements of amine in the bulk solution was beyond detectable limits. This means that possibilities (a) and (c) are unlikely to occur. The best explanation of these results is (b). The peroxide molecules are sorbed inside the clay surfaces by intercalation and react with the perpendicularly oriented

amine–clay complex which is in the form of its diprotonated species. If we compare the activation energy values for the homogeneous and heterogeneous systems, it is clear that the latter system has a greater catalytic efficiency (see Table I). This may be attributed to the greater surface area of the clay supported catalyst as well as the presence of Lewis and Brönsted acid sites that oxidise the amine molecules (DTS) to the deprotonated species. The clay acts as a cage for the reaction. The nature of the intercalated DTS/montmorillonite complex is still unclear and needs further studies.

4.2.2. Orientation of Organic Molecules in Montmorillonite

The orientation of the organic molecules in montmorillonite is based on data given by Pauling [10] for molecular shapes and sizes. The lowest observed spacing with aromatic molecules, 12.5 Å, probably represents a coplanar arrangement of such atoms which may be parallel to the silicate sheet [11].

The deduced thickness of an aromatic ring is 3 Å which is shorter than the normal Van der Waals thickness observed in crystals of aromatic hydrocarbons (3.7 Å) [12]. It is interesting that this thickness is hardly affected by the introduction of methyl groups although their normal Van der Waals diameter of 4 Å is greater than the ring thickness. It can be concluded that these substituents are coplanar with the ring and that their normal Van der Waals radii are reduced.
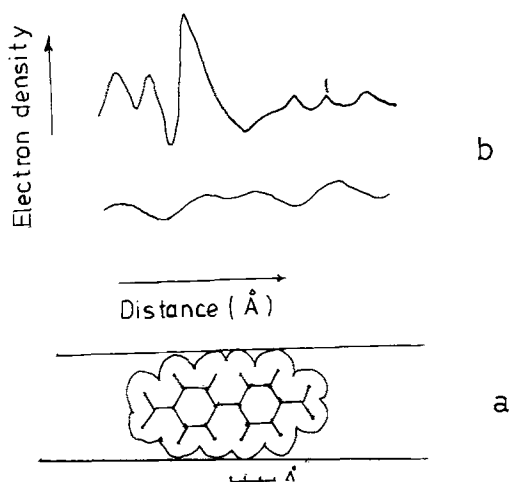

Fig. 6. A one-dimensional Fourier synthesis of a benzidine complex ($d001 = 15.2$ Å). (a) The perpendicular orientation of benzidine molecules between the silicate sheet structure of montmorillonite clay minerals as proposed by R. Green-Kelly [11]. (b) The electron density variations perpendicular to the silicate sheet as measured by R. Green-Kelly [11].

The Fourier synthesis of the benzidine complex has already been defined by Green-Kelly [11] and it was concluded that the observed intensities could not be explained by a two layer arrangement. In Figure 6b, the triple peaks in the electron density sketch of the interlamellar space suggest that the molecule is oriented so that its plane is perpendicular to the plane of the silicate sheets (Figure 6a). By analogy, we suggest that DTS has a perpendicular orientation to the silicate sheet of montmorillonite.

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