

Kinetics of Solid State Thermal Monomerization of 9-Cyanoanthracene Photodimer (9CNAD) and Photodimerization of 9-Cyanoanthracene (9CNA)

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The kinetics of the thermal monomerization of 9-cyanoanthracene dimer (9CNAD) has been followed both dynamically and isothermally by differential scanning calorimetry (DSC) and isothermally by spectrophotometry. The reaction is found to be similar to many other solid state decomposition reactions and exhibits an induction period corresponding to surface nucleation, an acceleratory region reflecting the formation of the product at the surface of nuclei and a deceleratory region where the reaction centres interact. These DSC experiments yield activation parameters which are different from previously published data. The more reliable isothermal study by spectrophotometry confirms that the reaction occurs in three stages; an induction period, a zero order process with an activation enthalpy of 98 kJ mol^{-1} followed by a first-order process with an activation enthalpy of 68 kJ mol^{-1} . The involvement of an intermediate radical is postulated.

By following the build up of luminescence which develops as a result of the photodimerization of 9-cyanoanthracene single crystals with time and temperature it has been possible to obtain an activation enthalpy for this reaction. The value of 22 kJ mol^{-1} is identified with the energy required to bring a pair of 9-cyanoanthracene molecules into a favoured "incipient dimer" orientation to form a chemically bonded species and relates to a diffusion controlled process.

In the field of organic solid state topochemistry^{1, 2} several photochemical studies have been performed;^{3, 4} reversible reactions such as those relating to anthracene and di-*para*-anthracene are well understood.⁵ Thermal reactions, however, have been studied less but it is apparent from the work of Donati *et al.*⁶ and Paul and Curtin⁷ that there are severe limitations to the development of a thorough understanding of the kinetics and mechanisms of crystalline reactivity. An attempt to remedy this situation by considering the thermal reactivity of the same system (the reversible thermal reaction of the photoisomer of 6,7,14,15-tetrahydro-15,16[1',2']-8,13[1',2']-dibenzodibenzo[*a,g*]cyclododecene(bi-[anthracene-9,10-dimethylene]) under homogeneous and heterogeneous reaction conditions has been made by Mau.⁸ However, this system is idealized and bears little relationship to the "real" situation normally encountered in the reactivity of organic single crystals, even though it does provide reliable experimental parameters. Recently, considerable success has been achieved in the application of both dynamic and isothermal differential scanning calorimetry to the thermal polymerization reaction involving 2,4-hexadiyne-1,6 diol bis (*p*-toluenesulphonate).⁹⁻¹¹

Upon irradiation ($\lambda_{\text{exc}} \approx 360 \text{ nm}$) crystalline 9-cyanoanthracene (9CNA) yields a centrosymmetric photodimer;¹² given a mirror-symmetric arrangement of molecules in the room-temperature crystalline modification¹³ this reaction does not conform to the topochemical theory of Cohen and Schmidt.¹³ It has been postulated that

the reaction occurs at structural defects where the excitation energy may be localized. Luminescence studies¹⁴⁻¹⁶ indicate the presence of intermediates in the reacting crystals which may be identified with different excimeric species resulting from unusual relative orientations of molecules in pairs at such defects.

Dynamic, thermal studies of the monomerization of crystalline photodimers have been performed but the results are complicated by crystal growth of the monomer species and the inherent experimental difficulties of differential calorimetric studies.⁶ In addition the methods of analysing such experimental data have been criticized.¹⁷

Here we report the results of (a) both dynamic and isothermal studies of the kinetics for the thermal monomerization of crystalline 9CNAD and (b) a luminescence study of the photodimerization of crystalline 9CNA that allows us to propose mechanisms for these processes.

EXPERIMENTAL

9CNA was prepared by recrystallization from EtOH, giving an absorption spectrum in solution comprising a single sharp maximum at 256.5 nm. The dimer was prepared by irradiation under inert conditions (N₂ flow) of an ethanolic solution of 9CNA with u.v. radiation ($\lambda = 350\text{--}370$ nm) from a 100 W high pressure mercury lamp. Purification of the dimer was carried out by dissolving in the least amount of chloroform followed by addition of ethanol. The dimer u.v. absorption spectrum with a maximum at ≈ 220 nm shows negligible absorption at the wavelength of maximum absorption of the monomer.

Differential scanning calorimetry was conducted on the dimer using a commercial instrument (Perkin-Elmer Model DSC 1B). Because of the sublimation of 9CNAD, special pans for sublimable materials were used. Both programmed temperature and isothermal differential calorimetry techniques were employed and were executed according to published procedures [see *e.g.*, ref. (10)].

The kinetics of photodimerization of 9CNA was evaluated by following the fluorescence on a microscope (Reichert Zetopan with fluorescence attachment) equipped with a hot stage. Excitation was performed with 365 nm light from a mercury arc and the fluorescence was recorded in incident light. The kinetics of photodimerization at different temperatures in the range of 299–335.5 K were studied by monitoring the increase in fluorescence intensity of the 440 nm maximum[†] with time at increasing temperatures.¹⁶ Times involved in following the intensity of fluorescence at different temperatures lie within the linear portion of the fluorescence against time dependence and the emission recorded corresponds to that of monomeric 9CNA trapped within a cage of photodimers.¹⁸

The kinetics of isothermal decomposition of the dimer was also investigated in the temperature range of 388 to 400 K for polycrystalline films by a spectroscopic technique. The method consisted of the preparation of controlled amounts of the dimer (7.35×10^{-8} mol) as thin films on the internal walls of tubes by vacuum evaporation of solutions of the dimer of known molarities followed by sealing under one atmosphere pressure of air and total immersion of the tubes in a bath of controlled temperature. The use of the sealed tubes and the complete immersion in the bath was necessary because it was found that 9CNAD undergoes partial sublimation and condensation on the colder parts without decomposition when open tubes were used. Analysis for the monomer was performed by dissolution in known amounts of ethanol and measurement of absorbance at 256.5 nm.

RESULTS

DIFFERENTIAL SCANNING CALORIMETRY (DSC)

Fig. 1 illustrates typical differential scanning calorigrams at different heating rates. The decomposition is exothermic and is followed by sharp melting of the dimer at 480 K in agreement with previous findings.⁶

[†] At this wavelength the contribution from the excimeric emission is minimal (<10 %).

Upon heating the dimer crystals become opaque and monomer crystal growth can be observed. Using the fluorescence microscope, the green fluorescence, typical of 9CNA, increases in intensity from the blue emitting specimen. It is thus expected that the exothermic portion of the calorigram would involve heats of monomerization and crystallization and thus using it in evaluation of activation energies of monomerization, as has been done previously,⁶ is not acceptable.

The rate (D) of the second stage of the thermal decomposition of 9CNAD may be obtained from the dynamic differential calorimetric profiles by means of the expression $D = 1/A \cdot dH/dt$ with $dH/dt = X$ the height of the profile above the base line at a given temperature T and A the total area of the peak. Plots of X/A against $1/T$ yield the energy of activation for interfacial decomposition. This has a value of 268 kJ mol^{-1} and compares with two values of 360 and $\approx 175 \text{ kJ mol}^{-1}$ obtained by Donati *et al.*⁶ Our results are consistent with a zero-order reaction.

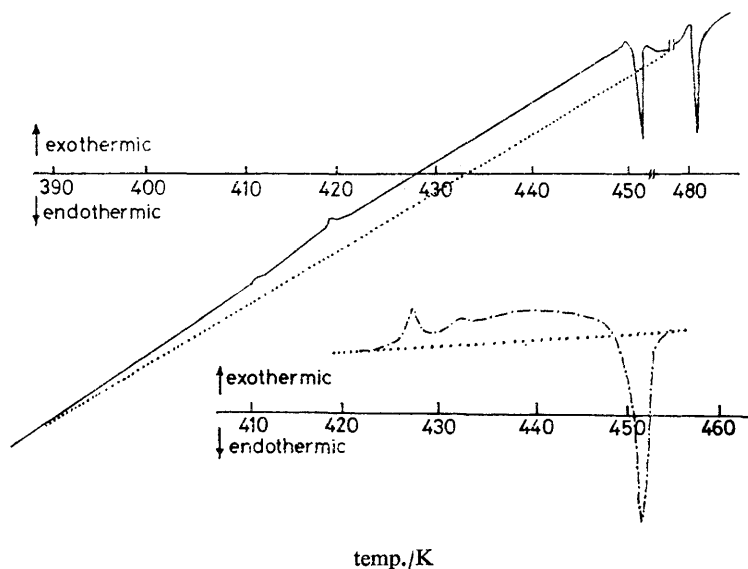


FIG. 1.—Typical differential scanning calorigrams at different scanning rates (—) 2 K min^{-1} and (· · · · ·) 8 K min^{-1} .

Fig. 2(a) shows a series of differential calorimetric profiles following isothermal scanning at various temperatures. These consist of an initial horizontal portion which is identified with the induction period, a rise to a maximum where the reaction proceeds at the fastest rate and then a decay back to the horizontal. The induction times (t_0) for the monomerization are short (*cf. e.g.*, the case of a typical polymerization);⁹⁻¹¹ a plot according to the Eyring equation yields an activation enthalpy of 141 kJ mol^{-1} [fig. 2(b)] and values for the activation entropy (table 1). Analysis for the second stage of the reaction under isothermal conditions take the form of (α, t) dependences [see fig. 2(c)] with α obtained from the relationship $\alpha = x/a$ where x is the area swept up to a time t and a the total area under the curve. This confirms the second stage to be zero-order but since the reaction is fast at these higher temperatures ($\approx 420 \text{ K}$) large errors are inherent in any evaluated activation parameter.

TABLE 1.—ACTIVATION PARAMETERS FOR 9CNAD DECOMPOSITION AND 9CNA DIMERIZATION

technique	reference	details	E_a /kJ mol ⁻¹	ΔH^* /kJ mol ⁻¹	ΔS^* /J mol ⁻¹ K ⁻¹
9CNAD decomposition					
DSC (dynamic)	6	curved activation energy plot implying two stages. high temperature (first order). low temperature (first order).	360 163-175	— —	— —
DSC (dynamic)	this work	single value for the activation energy of a zero order process.	268.0 (±12.0)	264.0 (±12.0)	+328.0 (±14.7)
DSC (isothermal)	this work	three stages : induction period (zero order) second stage (zero order) third stage (first order)	143.0 (±2.4) — —	141.0 (±2.4) — —	+78.57 (±1.3) — —
spectrophotometric study (isothermal)	this work	three stages : induction period (zero order) second stage (zero order) third stage (first order)	112.736 (±9.0) 105.454 (±4.2) 69.581 (±0.35)	113.943 (±9.1) 102.18 (±4.1) 66.303 (±0.45)	+13.103 (±1.0) -37.046 (±3.00) -131.913 (±2.8)
9CNA dimerization					
luminescence	this work	following increase of luminescence at 440 nm	22.077 (±0.4)	18.231 (±0.4)	-193.825 (±11.2)

ΔS^* is obtained from the intercept of the equation

$$\ln(k'/T) = \ln(k/h) - \Delta H^*/RT + \Delta S^*/R$$

where k and h are Boltzmann and Planck's constants, respectively. Values of activation parameters in the text are quoted to nearest integral values.

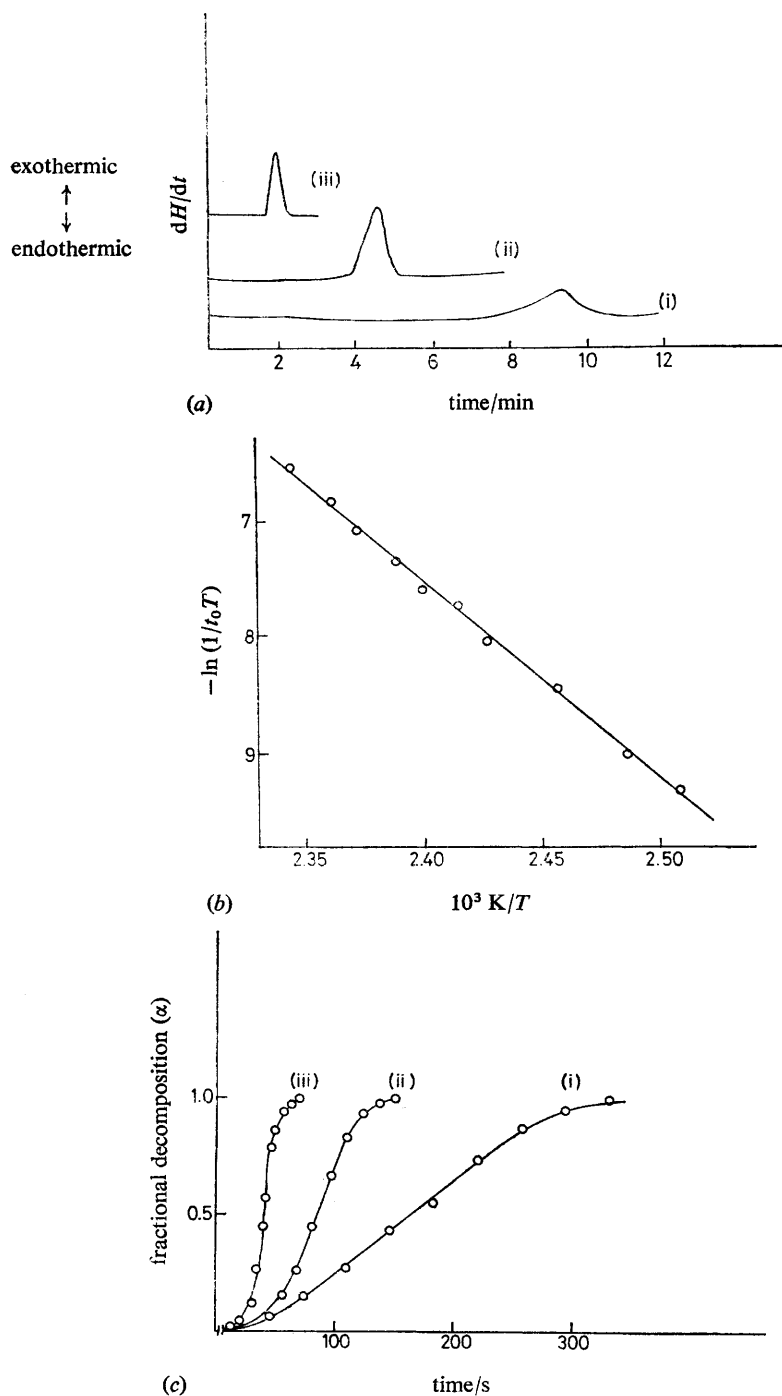


FIG. 2.—(a) Isothermal calorimetric profiles for the decomposition of 9CNAD at (i) 412, (ii) 418.5 and (iii) 426.5 K. (b) Dependence of $\ln(1/t_0T)$ on $10^3 K/T$ for the induction stage of the thermal decomposition of 9CNAD. (c) Typical (α, t) plots for the second and third stages of the decomposition obtained from isothermal calorimetry at (i) 407, (ii) 412 and (iii) 421.5 K.

KINETICS OF ISOTHERMAL DECOMPOSITION OF DIMER FILMS (SPECTROPHOTOMETRIC STUDY)

Fig. 3(a) shows that the fractional decomposition against time plot for the dimer exhibits three stages of decomposition. The second stage is linear and typical of a zero order process, whereas the third stage obeys a first order law. The values of the rate constants obtained from the slopes of the lines of the second stage of the process were used to evaluate the activation parameters by application of the Eyring equation.¹⁹ The first order plots for the third stage are shown in fig. 3(b). Values of the activation parameters are listed in table 1.

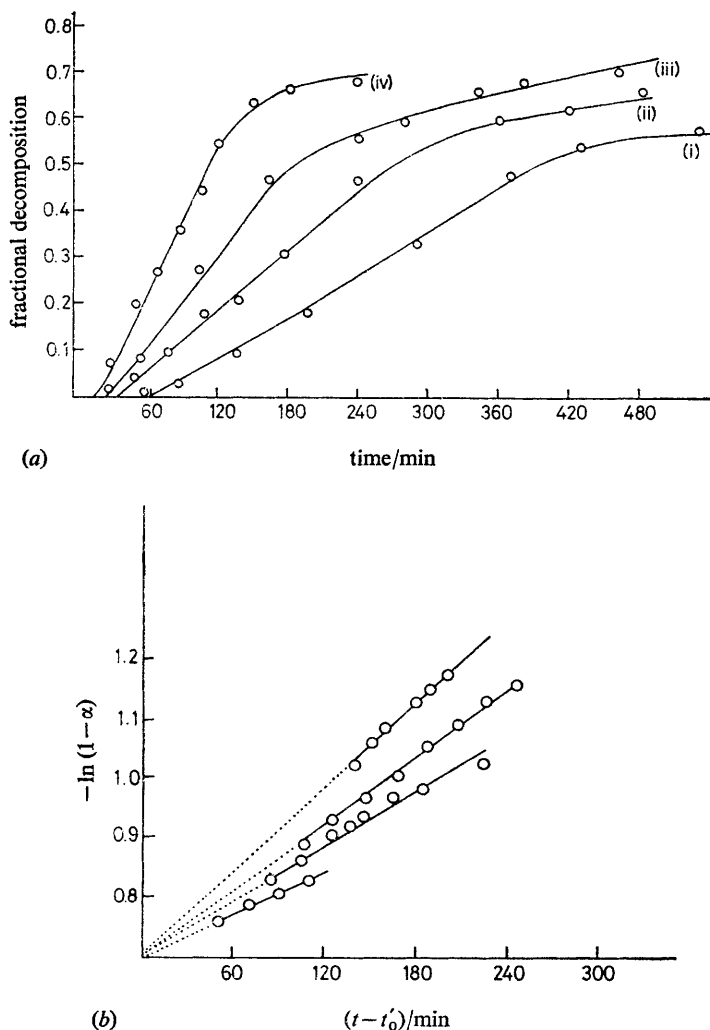


FIG. 3.—(a) Fractional decomposition against time plots for isothermal decomposition of 9CNAD at (i) 388, (ii) 392, (iii) 396 and (iv) 400 K. (b) Unimolecular decay law for the third stage of decomposition; t'_0 represents the time before commencement of the third stage; (· · ·) are extensions of the first order plots.

KINETICS OF PHOTODIMERIZATION OF 9CNA SINGLE CRYSTALS (FLUORESCENCE STUDY)

9CNA crystals exhibit a green excimer emission with a maximum emission in the region of 495 nm but, upon irradiation with 365 nm light, peaks at 440 and 460 nm develop which may be attributed to monomeric species trapped within dimeric regions. Plots of the peak intensity against time demonstrate that the intensity of the 440 nm peak increases linearly with time for considerable time intervals. This dependence

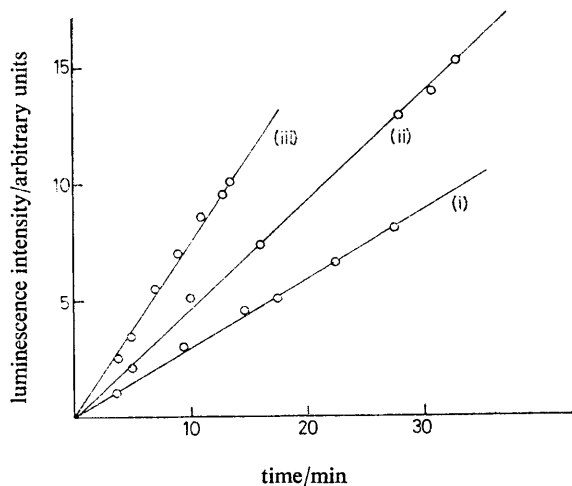


FIG. 4.—Build up of fluorescence intensity at 440 nm with time at different temperatures for the same crystal. From the slopes of the lines the values of the rate constants are obtained. (i) 298, (ii) 321.5 and (iii) 335.5 K.

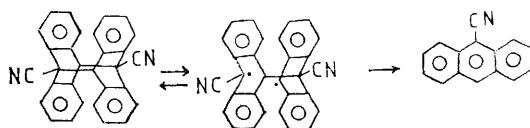
may be used for kinetic studies. The increase of fluorescence intensity at 440 nm of a crystal was followed at different temperatures for a total irradiation time which falls within the linear portion of the fluorescence against time curve; a typical representation of the data is shown in fig. 4. The linearity of the plots indicates that the process is zero order; from the rate constants the activation enthalpies are obtained. These activation parameters are given in table 1.

DISCUSSION

THERMAL MONOMERIZATION OF 9CNAD

The evaluation of kinetic parameters from dynamic DSC experiments is always open to criticism as pointed out by Clarke and Thomas¹⁷ and extreme care must be exercised in the definition and use of the terms "kinetic order" and "activation energy" for solid state reactions studied thermoanalytically. Clarke and Thomas clearly demonstrated that for (α, t) dependences exhibiting linear portions the use of an expression of the form $D = 1/A \cdot dH/dt$ (see earlier) for the evaluation of rate constants is justified, and that the activation parameters derived represent the true activation parameters for interfacial reaction. Our isothermal studies performed calorimetrically and by spectrophotometry clearly identify three stages to the reaction in the temperature range 388 to 440 K. The induction stage with an activation energy as determined by spectrophotometry of 112 kJ mol⁻¹ corresponds to the formation of nuclei of the monomer phase within the photodimer matrix. Following this we

have a second acceleratory stage corresponding to a linear portion of the (α, t) dependence in the region of $\alpha =$ up to 0.5. We ascribe zero-order kinetics (constant reaction rate) to this stage of the reaction with an activation energy of 105 kJ mol^{-1} . Since the activation energies for both the first and second stages are similar, the second stage may be identified with both the propagation of nuclei (growth) and the nucleation of further reaction centres with equal probability. In the later stages of the reaction (the third stage or "decay period") the kinetics obey a unimolecular law as is the case for many other solid-state decompositions.¹⁹ The activation energy of 69 kJ mol^{-1} is identified with the decomposition of dimer dispersed within the product monomer matrix and, as such, the reaction simulates behaviour in solution.⁸ During the second stage reaction occurs at the interface between monomer nuclei and a rigid, crystalline, dimer "cage", whereas in the third stage the reaction proceeds at the interface between the decomposing dimer sites and a relatively weak solution-like (non-crystalline) monomer "cage". The reaction must include a reversible step to explain the molecular response to the "cage" effect and since at all stages the decomposition involves the breaking of two C—C bonds linking two anthracenic moieties an intermediate state must be postulated. A possible sequence is outlined in scheme 1;



SCHEME 1

we note that an electronic structure that correlates with that of the benzyl radical has been proposed by Ferguson and Puza²⁰ as an intermediate in the photodissociation of dianthracene. During the decomposition of 9CNAD when thermal phonons participate in the reaction, bond breaking takes place to form the intermediate represented in scheme 1. Due to lattice constraints on the dimer, however, the radicals tend to recombine, when they have to surmount an additional barrier characteristic of "lattice cage" constraints in order to yield two 9CNA molecules. The extent of this additional barrier is higher in the second stage of the reaction. The values of the entropies of activation (see table 1) confirm such an interpretation since, for the third stage, the value is lower—implying the involvement of a more symmetric activation state within a less random process. A situation that relates to the third stage of the decomposition of 9CNAD has been described by Mau⁸ where the reaction rates but not the activation energies for thermal isomerization of the photoisomer of 6,7,14,15-tetrahydro-15,16[1',2']8,13[1'',2'']-dibenzenodibenzo [*a,g*] cyclododecene (bi[anthracene-9,10-dimethylene] in solid solution are affected by the environment.

PHOTODIMERIZATION OF 9CNA

From the study of the photodimerization of 9CNA crystals, by following the increase in intensity of the monomeric emission with a maximum at 440 nm, the activation energy is found to be small. This is expected of a photochemical reaction; in this case the activation energy must refer to the rearrangement of the excimer to form a chemically bonded dimer. Although we cannot specify the precise mechanism we can make some observations. Our experiments record the rate of change of fluorescence intensity as a function of time of irradiation at different temperatures and thus monitors the increase in concentration of monomer molecules trapped

within the dimer layer as its thickness increases. There is a linear increase in the fluorescence intensity as a function of time of irradiation (up to 4 h) at each separate temperature, implying no change in the rate of photodimerization. Thus we have zero-order kinetics over the early part of the reaction. Ludmer²¹ in a recent study reports no change in the quantum yield of photodimerization at 293 K up to 3 % conversion but at further conversion observes an autocatalytic process.

Current work is directed at obtaining the energetics for recombination of different incipient dimer pairs of 9CNA generated within a dimer host crystal so that the role of diffusion in solid state reactivity may be elucidated.

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