Molecular Interactions in Non-aqueous Solvents. Part 3.† Kinetics and Energetics of Dimerization of a Tetrasubstituted Copper(II) Phthalocyanine Dye

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The kinetics and energetics of the dimerization of 4,4′,4″,4‴-tetrakisoctadecylsulphonamidocopper(II) phthalocyanine (CuPC) dye in benzene is reported. A negative activation energy of −62.27 kJ mol^{-1} for the generalized dimerization process (i) indicates a multi-step reaction mechanism. Results are interpreted in the light of previously

$$\mathrm{CuPC} + \mathrm{CuPC} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} (\mathrm{CuPC})_2 \qquad \text{(i)}$$

reported calorimetric data and as a multi-step reaction. Additionally, the kinetics of dimerization of the CuPC dye in carbon tetrachloride at 25 °C are reported with the apparent forward rate constant (k_f) being 3.6 (±0.4) × 10^7 l mol^{-1} s^{-1} and the reverse rate constant (k_r) being 30 (±3) s^{-1}.

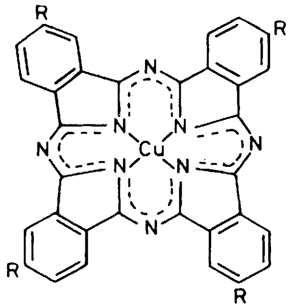
INVESTIGATORS have long recognized that selected properties of dyes do not always follow classical interpretations. For example, as early as 1944 Sheppard and Geddes [1] concluded that the deviation from Beer's Law of a solution of metal phthalocyanine dyes resulted from the formation of aggregates of dye molecules in the solution. Since that time, interest in the aggregation of dye molecules has been aroused since dramatic colour changes are known to occur [2,3] and also this aggregation leads to enhanced photosensitizing properties of the molecules.[4,5] This property of aggregation has been noted for a variety of dyes including cyanine,[3,6] metal phthalocyanine,[1] arylazonaphthol,[7,8] and thia-aza-anthracene.[9]

Much of the work on the dimerization process of dye aggregation has been centred on the determination of the equilibrium constant for the dimerization.[10,11] Others have reported thermodynamic quantities (ΔH, ΔS, K, and ΔC_p) obtained by thermometric titration.[12,13] Other studies [14-16] which have focused on determining the kinetics of similar dimer systems have been in aqueous media where hydrophobic interaction may have played a large part in the results obtained. Little has been done in solvents where the impetus towards dimer formation is the dye–dye interaction rather than the possible hydrophobic exclusion of the dye by solvents such as water. Neither has much kinetics work been accomplished in solvents where solvation may play a significant role. The primary equilibrium work has been on metal(II) phthalocyanines in benzene and carbon tetrachloride.[10-13] The present study was undertaken to study a system where solvation may have played an important role in the dimerization; indeed the results indicate that the solvent has a large part to play in the mechanism.

We herein report the investigation of the kinetics and energetics of the dimerization reaction of a copper(II) phthalocyanine dye in benzene and also the kinetics of the dimerization of the dye in carbon tetrachloride at 25 °C.

EXPERIMENTAL

4,4′,4″,4‴-Tetrakisoctadecyclsulphonamidocopper(II) phthalocyanine (I)(CuPC) was prepared in a manner similar to that described by Zickendraht [17] and Monahan.[10] The resultant dye (CuPC) was further precipitated four times from a 5% chloroform solution by addition of twice the volume of methanol.



(I) R = $\mathrm{SO_2NH(CH_2)_{17}CH_3}$

All solvents used were twice distilled, reagent-grade solvents. The distillation was performed on an 8-ft glass, silvered column filled with glass circles. The first and last 15% of the distillation were discarded. Solvents were stored over type 3A Linde molecular sieves. Karl Fischer titrations of the solvents indicated that the water content was less than the detection limit (0.07 mg H_2O per ml solvent).

Solutions of the dye were prepared by serial dilution of a stock solution of CuPC to the desired concentration. Concentrations were checked by measuring the absorbance of the dye at the isosbestic point (660 nm) using a Beckman DB spectrophotometer.

Kinetic measurements were made by placing a solution of CuPC in benzene or carbon tetrachloride in one syringe of a model D-110 Durrum–Gibson stopped flow spectrophotometer and pure solvent in the other syringe. For CuPC in benzene at all temperatures, the dilution ratio was 1 : 1; for CuPC in carbon tetrachloride the dilution ratio was 10 : 1

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† Parts 1 and 2, see refs. 12 and 13.

A summary of rate constants for reaction (1). $K_{\text{kin}} = k_f/k_r$, K'_{kin} is calculated using equation (4), and K_{calc} is the equilibrium constant calculated using calorimetric data

Temperature (°C)	Solvent	k_f/l mol^{-1} s^{-1}	k_r/s^{-1}	K_{kin}	K'_{kin}	K_{calc}
20	Benzene	1.4 ($\pm$0.1) $\times$ 10^4	0.10 ($\pm$0.01)	1.40 ($\pm$0.20) $\times$ 10^5	1.48 $\times$ 10^5	1.79 $\times$ 10^4
25	Benzene	8.7 ($\pm$0.7) $\times$ 10^3	0.12 ($\pm$0.01)	7.25 ($\pm$0.15) $\times$ 10^4	3.75 $\times$ 10^4	1.34 $\times$ 10^4
30	Benzene	5.4 ($\pm$0.4) $\times$ 10^3	0.13 ($\pm$0.01)	4.10 ($\pm$0.50) $\times$ 10^4	2.50 $\times$ 10^4	1.00 $\times$ 10^4
35	Benzene	3.5 ($\pm$0.2) $\times$ 10^3	0.18 ($\pm$0.02)	1.94 ($\pm$0.37) $\times$ 10^4	3.50 $\times$ 10)^4	9.00 $\times$ 10^3
	Carbon tetrachloride	3.6 ($\pm$0.4) $\times$ 10^7	30.0 ($\pm$3.00)	1.20 ($\pm$0.10) $\times$ 10^6	Not calculated	3.00 $\times$ 10^6

(solvent–dye solution) using the variable-ratio syringes supplied by the Durrum Company. The two solutions were rapidly mixed using a gas-driven ram plunger.

The time-dependent absorbance was monitored at 678 nm ($\lambda_{\text{max.}}$ for monomer) and at 625 nm ($\lambda_{\text{max.}}$ for dimer) for the CuPC in benzene and at 625 nm ($\lambda_{\text{max.}}$ for dimer) and at 692 nm ($\lambda_{\text{max.}}$ for monomer) for CuPC in carbon tetrachloride. The amplitude of the relaxation at each wavelength was comparable but, however, opposite in direction. No relaxations were observed at 820 nm, a wavelength at which the absorbance of the dimer and the monomer is negligible, in either benzene or carbon tetrachloride. Temperature was controlled to ± 0.1 °C. Relaxation data were taken at 5 ° intervals at 20—35 °C. Data could not be taken above 35 °C for CuPC in benzene owing to bubble formation in the cuvettes and syringes. Neither could data be taken above 25 °C for CuPC in carbon tetrachloride for the same reason. Below 25 °C for CuPC in carbon tetrachloride and below 20 °C for CuPC in benzene, data could not be taken because the magnitude of the equilibrium constant was such that the magnitude of the perturbation was so small that neither accurate nor reliable data could be obtained.

RESULTS

Spectrophotometric [10,11] and calorimetric [12,13] results from previous work on this system have led us to conclude that the monomer–dimer model is the most appropriate to use. To calculate the rate constants for a simple monomer-dimer model such as in equation (1) where CuPC denotes the

$$\text{CuPC} + \text{CuPC} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} (\text{CuPC})_2 \qquad (1)$$

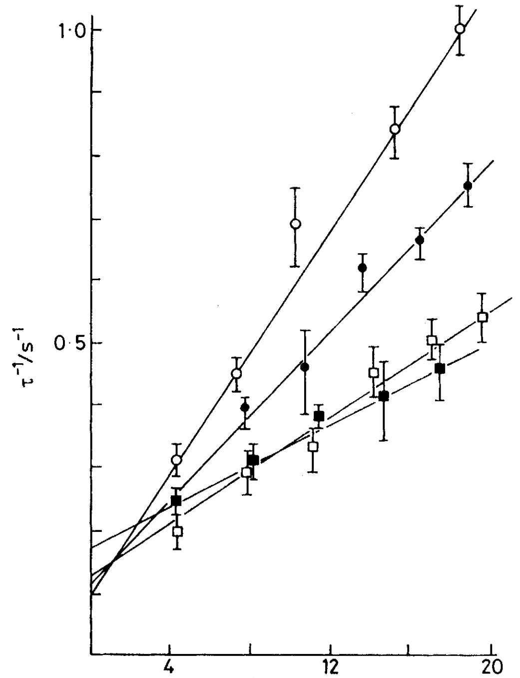

FIGURE 1 Relaxation plots for the dimerization of CuPC in benzene: ○, 20 °C; ●, 25 °C; □, 30 °C; ■ 35 °C

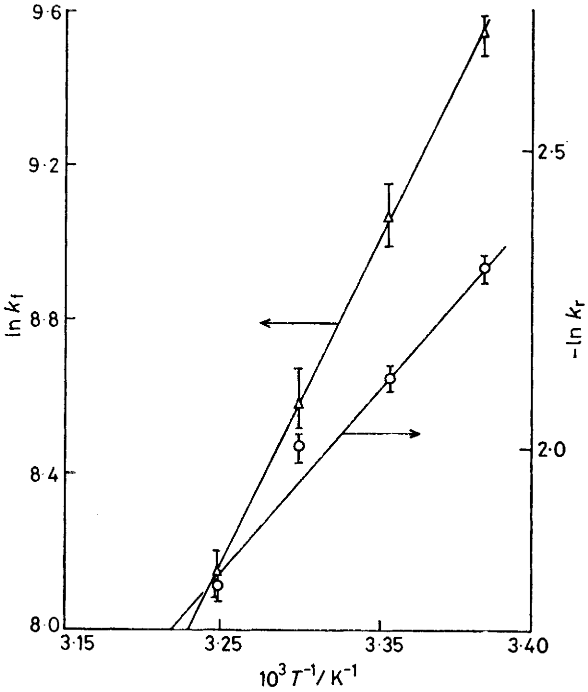

FIGURE 2 Arrhenius plots for the dimerization of CuPC in benzene

monomer and $(\text{CuPC})_2$ the dimer, the relaxation expression (using methods proposed by Eigen,[18] Castellan,[19] or Hague [20]) equation (2) is obtained where $[\text{CuPC}]_\infty$ denotes the

$$(1/\tau) = 4k_f[\text{CuPC}]_\infty + k_r \qquad (2)$$

concentration of CuPC monomer at infinite time after dilution (*i.e.* the concentration at a new equilibrium position). An alternative expression which tends to eliminate any possible contribution by higher aggregates such as trimers, *etc.*, is obtained by substituting equation (3)

$$[\text{CuPC}]_\infty = (-1 \pm \sqrt{1 + 8\,K_D C_T})/4K_D \qquad (3)$$

into equation (2) and squaring both sides. The result is given by equation (4). This equation offers a means of

$$(1/\tau)^2 = \frac{8k_f^2}{K_D}\,C_T + \frac{k_f^2}{K_D^2} \qquad (4)$$

obtaining the equilibrium constant directly other than by division of two rate constants.

Four to eight relaxation times at each concentration of dye were averaged to obtain the requisite kinetic data. The Table gives a summary of kinetic data for CuPC in benzene and carbon tetrachloride. The table entries refer to the rate constants (k_f and k_r) in equation (1), K_{kin} is the ratio k_f/k_r where k_f and k_r are obtained from equation (2), K'_{kin} is the equilibrium constant calculated using equation (4), and K_{calc} is the equilibrium constant calculated using previously reported calorimetric data.[12,13] Figure 1 portrays the dependence of the relaxation time upon temperature and concentration of monomer for the dimerization of CuPC in benzene. Figure 2 portrays the dependence of the apparent rate constant upon temperature. Calculation of apparent activation energies for the forward and reverse reactions from the Arrhenius equation are −62.27 and +27.7 kJ mol^{-1} for k_f and k_r, respectively. Included in the Table are the apparent rate constants for the dimerization of CuPC in carbon tetrachloride at 25 °C obtained from the relaxation plot of Figure 3.

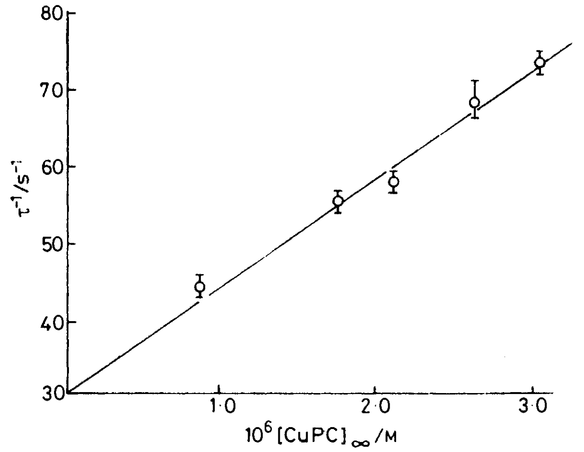

FIGURE 3 Relaxation plot for the dimerization of CuPC in carbon tetrachloride at 25 °C

DISCUSSION

(A) *Role of Temperature.*—The observation of an apparent negative activation energy is not an unusual circumstance since others[9,14,15,21] have also reported negative activation energies. Two primary explanations have been given to account for this observation. Glasstone *et al.*[22] have proposed that a dielectric constant which changes rapidly with temperature may account for such an apparent negative activation energy. However, this explanation must be discarded for this system for several reasons including (1) that the temperature range is probably insufficient to cause the needed variation in dielectric constant, (2) that this explanation holds primarily if not exclusively for ionic reactions, and (3) the direction of the dielectric constant change with temperature is opposite to that needed to produce a negative activation energy.

The other most often encountered explanation is that a multi-step reaction occurs rather than a single step reaction from which the apparent rate constants were calculated. For reactions of this type, the classical explanation is that a rapid pre-equilibrium occurs before the rate-determining step such as described by Winstein[23] for solvolysis reactions, by Hogen-Esch and Smid[24] for the reaction of lithium with fluorene, by Eigen[25] for inorganic ligand substitution reactions, and by Spencer and Sutter[9] for the dimerization of Methylene Blue. The reaction mechanism is depicted as two successive equilibria (5) and (6), the first reaching equilibrium on a faster time scale than the second.

$$\mathrm{CuPC} + \mathrm{CuPC} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{CuPC||CuPC} \quad \text{(Fast)} \quad (5)$$

$$\mathrm{CuPC||CuPC} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} (\mathrm{CuPC})_2 \quad \text{(Slow)} \quad (6)$$

In equilibria (5) and (6) CuPC||CuPC has several possible interpretations including that two monomers are in the same solvent cage but not fully associated in the dimer, or that a reorientation occurs to give a product of lower energy, or that the loss of a solvent molecule occurs from the intermediate product. These possibilities are kinetically indistinguishable.

Whatever the nature of the intermediate, this mechanism would be expected to yield two relaxation times upon experimentation. The relaxation times would be exhibited in three different modes depending upon the relative times in which each equilibrium is established. If equilibrium (5) or (6) was established much faster than the other, one would then expect two widely separated relaxation times, whereas if the equilibria were established on a similar time scale, interaction would occur in a coupled manner analogous to the normal modes of vibration of a molecule. The mechanism will now be examined to formulate relaxation expressions for each case.

Assume first that equilibrium (5) is established more rapidly. This is equivalent to saying that a steady-state concentration of the intermediate exists and that the concentration of the intermediate is governed or controlled by the pre-equilibrium (5). Since two separate equilibria are involved in this mechanism, one would expect to have two separate relaxation times, but the two would be widely separated in time. Since the first equilibrium is established on a much faster time scale, its relaxation time can be expected to be essentially independent of the other relaxation time. This is generally true in any mechanism where one or more equilibria are established on widely differing time scales. The first of the two relaxation expressions obtained by invoking this assumption is given by equation (7).

$$(1/\tau_1) = 4k_1[\mathrm{CuPC}]_\infty + k_{-1} \qquad (7)$$

The relaxation expression for the second expression is not so easily obtained. Using again the procedures suggested by others[18-20] the second relaxation expression (8)* is obtained.

$$(1/\tau_2) = \frac{4k_1k_2}{k_1 + k_{-1}}\Big/[\mathrm{CuPC}]_\infty + k_{-2} \qquad (8)$$

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* A detailed derivation of the relaxation expressions may be obtained upon request.

A second set of relaxation expressions is obtained by rearranging the mechanism to (9) and (10). As with the first mechanism, a steady-state concentration of the

$$(\mathrm{CuPC})_2 \xrightleftharpoons[k_2]{k_{-2}} \mathrm{CuPC||CuPC} \qquad \text{(Fast)} \quad (9)$$

$$\mathrm{CuPC||CuPC} \xrightleftharpoons[k_1]{k_{-1}} \mathrm{CuPC} + \mathrm{CuPC} \qquad \text{(Slow)} \quad (10)$$

intermediate is assumed, but the controlling factor in the concentration of the intermediate is the first-order dissociation of the dimer. The first relaxation expression (11) obtained for this mechanism is independent of any concentration. The second relaxation expression is (12).

$$(1/\tau_1) = k_2 + k_{-2} \qquad (11)$$

$$(1/\tau_2) = 2k_1[\mathrm{CuPC}]_\infty + \frac{k_{-1}\,k_{-2}}{2(k_2 + k_{-2})} \qquad (12)$$

The third and last situation is one where there is significant interaction between the two equilibria (5) and (6) and the rates of the two reactions are comparable. This last case requires that two approximately equal relaxation times be present. No evidence of two relaxation times was observed in any of the experiments performed. Thus this case will be examined no further.

The results in the Table indicate a tendency of the rate constant, k_f, to decrease with increasing temperature, whereas, the rate constant, k_r, increases with increasing temperature. The relatively poor agreement of the ratio of the rate constants with the calculated equilibrium constant indicates that something other than the simplistic model of equation (1) is in effect. Additionally, the poor agreement of the equilibrium constant calculated using equation (4) with the thermodynamic equilibrium constant indicates that something other than a simple monomer–dimer reaction occurs.

The validity of the two models can be further examined by first plotting $1/\tau$ *versus* $[\mathrm{CuPC}]_\infty$ to determine the slope and intercept of the relaxation expression (12) and thus determine the rate constant, k_1 (= slope/2) and the complex ratio of rate constants (= the intercept). The Table gives these results of slope and intercept (where k_f = slope/4 and k_r = intercept). The slope obtained from this treatment is proportional to k_1 and is seen to decrease with increasing temperature. Thus it is unlikely that this model compared with the single step model is valid, either. If one were to assume that the expression to be evaluated here was (11), no variation of relaxation time should have been noted for a change in concentration. Thus this mechanism must be ruled out.

On the other hand, if the mechanism proposed in equations (5) and (6) [where equilibrium (5) is established on a much more rapid time scale] is valid, then upon examination of the relaxation expression (8), one sees qualitatively that the constant term (k_{-2}) should increase with increasing temperature. Since one would expect two relaxation times to be observable, a lower limit on the faster relaxation time may be set as 1 ms (the approximate mixing time of the stopped flow) since only one relaxation was observed which was slower than 1 ms.

One can deduce several possible consequences of applying simplifying assumptions to equation (8). For example, if one makes the assumption that $k_1 \approx k_{-1}$ then the equation (8) can be simplified to (13) since the

$$1/\tau_2 = \frac{4k_1k_2}{k_{-1}}[\mathrm{CuPC}]_\infty + k_{-2} \qquad (13)$$

ratio $k_{-1}/[\mathrm{CuPC}]_\infty$ would be much larger than k_1. Qualitatively this implies that as the difference between k_1 and $k_{-1}/[\mathrm{CuPC}]_\infty$ becomes greater, the agreement between the ratio of slope to intercept and K_{kin} will become better. This difference would become greater if either of two situations were to occur. The first of these is that the energy of activation of the intermediate is much smaller than the energy of activation of the association. The second is that since the enthalpy of the pre-equilibrium is likely to be exothermic, the ratio k_1/k_{-1} (the equilibrium constant of the pre-equilibrium) would become smaller with increasing temperature. Upon examination of the results in the Table, one sees that as the temperature is increased, the ratio k_f/k_r agrees more closely with the equilibrium constant calculated using calorimetric and spectrophotometric data.

(B) *Role of the Solvent.*—The apparent rates of reaction for the dimerization of CuPC in benzene and in carbon tetrachloride are seen to be quite dissimilar (Table). The dielectric constants of the two solvents are nearly the same (*D* 2.228 at 25 °C for carbon tetrachloride and 2.274 at 25 °C for benzene[26]). Thus this small difference in dielectric constant would hardly account for the factor of *ca.* 4 000 increase in the rate constant by changing the solvent from benzene to carbon tetrachloride.

A reasonable explanation for the large difference in rates can be obtained by examination of the molecular structures of the solvent and the dye (I). Carbon tetrachloride is a tetrahedral molecule whereas benzene is a planar molecule with six π electrons. CuPC (I) is a highly conjugated molecule and has a large abundance of π electrons. Thus benzene could solvate the monomer and dimer to a greater extent than would carbon tetrachloride, primarily owing to the greater ease with which two flat molecules each having π character can interact. If the monomer of CuPC is much more highly solvated in benzene than in carbon tetrachloride, the monomer in benzene would tend to be stabilized to a greater extent. This stabilization would cause a shift in the equilibrium to the monomer. Concomitant with this equilibrium shift would come a lowering in the rate of the association reaction since the activation energy would effectively be higher. A similar argument holds for the stabilization of dimer in benzene relative to carbon tetrachloride. As a result the apparent rate of dimer formation is slower in benzene as was observed experimentally.

A fuller comparison of solvation effects is not possible since activation parameters could not be obtained for CuPC in carbon tetrachloride. Since activation parameters cannot be compared, nothing can be inferred about the similarity or dissimilarity of reaction mechanisms in carbon tetrachloride and benzene.

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