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Phthalocyanine Ring Systems from Phthalodinitrile via Radical–Anionic Cyclisation

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SUMMARY

A study has been made of the lithium-surface initiated conversion of phthalodinitrile to metal-free phthalocyanine Attention has been given to the kinetics of phthalocyanine formation and to partial characterisation Infra-red, X-ray and differential scanning calorimetric analyses have provided supporting evidence of phthalocyanine formation. The level of conversion was found to maximise at $\simeq 30\%$*, irrespective of the initial phthalodinitrile concentration, indicating the presence of a surface catalysed reaction Attempts have been made to determine characteristic features of the initial stages of cyclisation.*

1. INTRODUCTION

Phthalocyanine and metal phthalocyanines, containing central metal atoms from every group in the periodic table, have been prepared. While there is no one method which may be used to prepare all phthalocyanine compounds, some methods can be used to form several metal complexes.[1] Examples include (i) the reaction of phthalonitrile with a metal or metal

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salt at elevated temperatures, (ii) the reaction of phthalic anhydride, phthalic acid or phthalimide with urea, metal salts and a catalyst, (iii) the reaction of σ-cyanobenzamide with a metal and (iv) the reaction of phthalocyanine or of a replaceable metal phthalocyanine with a metal, forming a more stable phthalocyanine

Two general methods have been proposed for preparing metal-free phthalocyanine systems:[2] (i) directly from phthalonitrile and (ii) indirectly from an acid and a metal phthalocyanine containing a replaceable metal

Some methods for forming metal-free phthalocyanine directly include: heating phthalonitrile to 350–360°C for 7 h in a sealed tube; heating phthalonitrile in dimethylaniline or in quinoline solution while passing ammonia through the solution,[3] heating phthalonitrile in triethanolamine to 170–180°C for 4 h,[4] heating phthalonitrile with acetamide and/or formamide to the boil for 8 h;[5] heating phthalonitrile with a dihydroxybenzene, glycol or glycerine,[6] and heating phthalonitrile in an inert solvent in the presence of cyclohexylamine or piperidine.[7]

Methods of forming a metal phthalocyanine with a replaceable metal, which is subsequently removed with an acid, are heating phthalonitrile with a sodium alcoholate;[8,9] with sodium cyanamide,[10] with sodium cyanamide and a solvent,[11] with calcium metal in an alcohol, with calcium or barium oxides,[12] with calcium oxide and methylglucamine;[13] with an alcohol and sodium hydride,[14] or with magnesium and a solvent under pressure [15]

Other methods for making labile metal phthalocyanines include Linstead's and Thorpe's early patent[16] using cyanobenzamide or phthalimide as the phthalocyanine-forming intermediate, and magnesium metal Methods of removing the metal from labile metal phthalocyanines include dissolution of tin phthalocyanine in concentrated H_2SO_4, followed by drowning in water,[17] and boiling alkaline earth metal phthalocyanines with HCl or stirring an alkali metal phthalocyanine with cold methyl alcohol, diluting with warm water and filtering [18] Heating an alkali metal with the ammonium salt of a strong acid in a crystallising solvent converts it to β-phthalocyanine [19]

Much of the synthetic work associated with the formation of phthalocyanine ring systems is very well established More recent studies concern product evaluation and improvement. The route chosen for the production of phthalocyanine ring systems reported here is in various ways different from the established methods Here we are concerned with the use of relatively inert solvents, anhydrous systems, low temperatures and addition methods of product formation. These are conditions often favoured in polymerisation processes based on anionic or radical–anionic intermediates

Typical catalysts for anionic initiation include alkali metals, alkali metal amides, alkyls, aryls, hydroxides and cyanides. These catalysts can be used to convert mononitriles to cyclic trimers, but apparently the reaction does not continue to linear polymers [20] Triazine, pyrimidine and pyridine ring compounds can all be produced from mononitriles in the presence of a base. Dinitriles, however, are capable of anionic polymerisation. A polymeric triazine-based structure is suggested, but not proved, for the polymerisation product of fumaronitrile in the presence of sodium methanolate and heat [21]

Less interest has been shown in the radical reactions for nitriles than in their ionic reactions Certain examples are relevant. For benzyl cyanide, hydrogen abstraction from the α-methylene group is seen as a dominant feature of radically initiated polymerisation. This is followed by reaction of alternate pendent nitrile groups to give a polymer carrying a six-membered ring repeat structure.[23,24] Phthalonitrile gives the tetramer phthalocyanine under nitrogen when initiated using di-*tert*-butyl peroxide and *tert*-butyl hydroperoxide as initiators [25] Copolymerisation of phthalonitrile with diphenylmaleonitrile and diphenylsuccinonitrile gave tetrazaporphin and its derivatives.[25] The topic of phthalocyanine systems has received recent attention, for example, in studies of polymeric phthalocyanines [26–28] It would seem a reasonable proposition that phthalocyanine ring formation might occur via a radical–anionic type of mechanism to produce either monomeric or polymeric phthalocyanines, or both Phthalodinitrile possesses the desired characteristics for this type of study

2. EXPERIMENTAL

2.1. Reagents

Phthalodinitrile (analytical grade, from BDH Ltd) was recrystallised from petroleum ether (boiling range 60–80 °C)/toluene (20/80 v/v) and dried in a vacuum oven at 323 K Tetrahydrofuran (reagent grade, from BDH Ltd, containing 0·1 % quinol as stabiliser) was initially stored over sodium wire for one week; 200 cm^3 aliquots were then refluxed over 5 g of lithium aluminium hydride for 4 h. The refluxed tetrahydrofuran was distilled over fresh lithium aluminium hydride in a dry, deoxygenated, nitrogen atmosphere, and 30 cm^3 aliquots of this freshly distilled solvent were transferred to glass ampoules and degassed via a succession of freeze/thaw cycles at $1 \times 10^{-3}\,N\,m^{-2}$. The ampoules were sealed at $1 \times 10^{-3}\,N\,m^{-2}$ and left at 273 K in a refrigerator until required. The methanol for cleaning lithium metal (used in the initiation reaction in tetrahydrofuran) was of analytical grade, as supplied by BDH Ltd It was stored over, and distilled from, calcium oxide immediately prior to use in the glove box assembly

2.2. Cyclisation reactions

These were carried out under a dry, deoxygenated nitrogen atmosphere in a glove box fitted with all relevant ancillary equipment Care was taken to ensure that the glove box assembly was continuously purged with dry nitrogen under positive pressure The experimental procedure described below was carried out in this environment.

Purified tetrahydrofuran, methanol and phthalodinitrile were placed in the glove box which was then flooded with dry nitrogen for a minimum of 15 min before any experimental procedure was undertaken Solutions of phthalodinitrile, in tetrahydrofuran, in the range 0 08–0·48 g were assembled using 8 cm^3 of solvent in each case. These solutions were contained in sealable glass vessels (capacity 10 cm^3), the seal being maintained via a polyethylene cap. Approximately uniform pieces of lithium were carefully flattened and cut to the required dimensions and mass (0 047–0 048 g) inside the glove box. Each of these was then cleaned by immersion for a few seconds in the dry methanol and then washed in two 20-cm^3 aliquots of dry tetrahydrofuran before being added to one of the assembled solutions of phthalonitrile in tetrahydrofuran For each nitrile concentration, several glass vessels were available, so that a range of reaction times might be covered Each nitrile solution/lithium combination was thoroughly flushed by introducing a bleed of dry, deoxygenated nitrogen gas. The nitrogen flow was discontinued and the vessel sealed The vessels were undisturbed during the reaction time which varied from 15 min to one week All the reactions were carried out at room temperature.

After the required time, the lithium was removed from the solution and washed with water-free acetone to ensure removal of all product and reactant from the surface The vessels were then carefully removed from the glove box In each instance, tetrahydrofuran and acetone were removed by rotary evaporation. The dry solid residue was dissolved in concentrated sulphuric acid (10 cm^3) with stirring for 10–15 min and left for 1 h. The solution in sulphuric acid was poured slowly into ice–water while stirring took place, then left overnight. The dark blue product which precipitated from the solution initially as a suspension was repeatedly washed until neutral Final separation was achieved by centrifugation. The product was dried at 353 K, under vacuum, to constant weight.

Partial characterisation was carried out through elemental analysis (by courtesy of the Department of Organic Chemistry, University of Leeds, Great Britain), infra-red spectroscopy, X-ray diffraction studies and scanning electron microscopy (by courtesy of the Wolfson Organic Powders Unit, University of Leeds, Great Britain). Comparisons between the product of the radical–anionic modification of phthalonitrile and a purified sample of Monastral Fast Blue G (a commercially available, metal-free phthalocyanine) were made in each instance.

3. RESULTS

The radical–anionically induced cyclisation of phthalonitrile is very water sensitive. Water is believed to destroy the initiating species. Without precautions already described, reproducibility of yield and product quality was found to be impossible to achieve

The effect of varying the concentration of phthalonitrile on the rate of reaction was examined in the range 0.0781–0·469 mol of phthalonitrile per litre of solution in tetrahydrofuran. The 'cyclisation' reaction was allowed to proceed over a period of 144 h for each nitrile concentration. Figure 1 represents the conversion of phthalodinitrile to phthalocyanine product in terms of the percentage by weight based on the original mass of phthalodinitrile. From such information it is possible to calculate the rate of cyclisation at a particular time (R_t). Extrapolation of R_t versus reaction time back to zero time provides an indication of the initial reaction rate, R_0. Simple manipulation of these data gives the value of x in $R_0 = k_0[\mathrm{Ph(CN)_2}]^x$, $x = 1{\cdot}48 \simeq 1{\cdot}50$. Table 1 provides data concerning

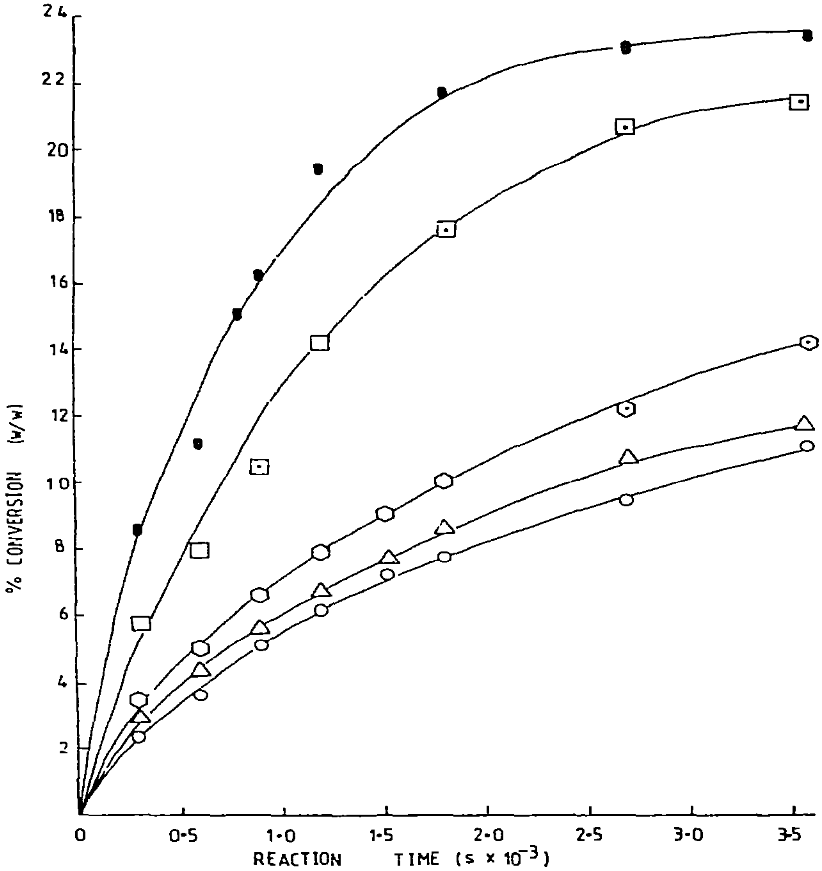

Fig. 1. Variation of phthalodinitrile conversion to phthalocyanine ring product with reaction time Conversion is expressed as the percentage by weight of phthalodinitrile converted based on the mass of phthalodinitrile present Phthalodinitrile concentrations (mol litre^{-1}) are ○, 0 0781, △, 0 234, ⊙, 0 273, ⊡, 0 313, ●, 0 469

the initial reaction rate, R_0, the phthalodinitrile concentration dependence and the initial rate constant obtained from studies involving a range of phthalodinitrile concentrations. Also included in Table 1 are values of the percentage conversion achieved after 144 h for each nitrile concentration

Elemental analysis showed the cyclisation reaction product after treatment with concentrated sulphuric acid to be metal-free phthalocyanine Monastral Fast Blue G (C.I Pigment Blue 16), in purified form, was used for comparison purposes Infra-red spectroscopic analysis,

TABLE 1

Kinetic Data from Phthalodinitrile Cyclisation in Lithium/Tetrahydrofuran/Phthalodinitrile Mixtures

$[Ph(CN)_2]$ *(mol litre*$^{-1}$*)*	$10^5 \times R_0$ *(mol litre*$^{-1}$ s^{-1}*)*	$10^4 \times k_0$ *(mol litre*$^{-1/2}$ s^{-1}*)*	*Percentage conversion after 144 h*
0.0781	0.590	2.66	18.6
0.234	3.20	2.83	19.6
0.273	3.85	2.59	22.1
0.313	4.90	2.79	28.0
0.469	7.95	2.49	32.6

$\bar{k}_0 = 2.67 \times 10^{-4}$ mol$^{-1/2}$ litre$^{-1/2}$ s^{-1}
$x = 1.48$ in $R_0 = k[\mathrm{Ph(CN)_2}]^x$

differential scanning calorimetry and X-ray diffraction studies were also used in characterisation of the reaction products. The results support the finding that the insoluble products of the radical–anionic cyclisation of phthalodinitrile, under the conditions described, were metal-free β-phthalocyanine. No lithium was found in the products Thus, the counter-ion to the anionic cyclisation intermediate is not present in the final product. This provides an insight into the cyclisation mechanism.

During the synthesis of the proposed phthalocyanine, by-products soluble in tetrahydrofuran were formed. These were invariably reddish brown in colour. Analysis, though made difficult by the presence of lithium in the composition, showed the soluble product to be predominantly dilithium phthalocyanine. This formed the major component of all the side-reaction products in each instance Aspects associated with the formation and further characterisation of the dilithium phthalocyanine were not considered any further, though they might warrant subsequent study

4. DISCUSSION

The evidence presented is strongly in favour of cyclisation to metal-free phthalocyanine being a significant feature of the lithium-induced reactions of phthalodinitrile. The relative ease of cyclisation in this way is of interest. The conventional routes to phthalocyanines are relatively unsophisticated and involve multistep processes at elevated temperatures. The route outlined here operates at low temperatures, with efficiency in the initial stages of reaction. Several alternative routes, however, provide phthalocyanines with good ultimate yields. As we have seen, even at an initial phthalodinitrile concentration of 0·469 mol litre^{-1} of tetrahydrofuran, the conversion levels out at approximately 25 % after 72 h. As intimated earlier, one problem concerns the fact that the reaction appears to be surface-catalysed and that the surface area of the lithium will be relatively small. A possible solution to this dilemma concerns the use of lithium in finely divided form so as to increase the surface area available per unit mass of lithium. Such a proposition is worthy of further attention.

With regard to the cyclisation process, both the kinetic aspects and the mechanistic features offer considerable complexity. The flat disc of lithium metal in the inert solvent tetrahydrofuran provides a suitable medium for a radical–anionic reaction to take place. In simple terms, such an ionic reaction can be thought of as an electron exchange from the metal to a receptor of high electron affinity.[29] In this study we are dealing with phthalodinitrile, which provides the necessary electron acceptance capacity. Thus,

$$e^{-} + \mathrm{P} \rightarrow \mathrm{P}^{\dot{-}}$$

where e^{-} denotes the electron donated by the lithium, P the phthalodinitrile and $\mathrm{P}^{\dot{-}}$, the phthalodinitrile radical–anion. Another possible route to electron exchange initiation includes electrochemical polymerisation[30] where monomer radical–anion formation can be made to occur at the cathode, and monomer radical–cation formation can be made to occur at the anode. A variety of mono- and di-nitriles have tendencies to undergo polymerisation and cyclisation reactions. Indeed, phthalodinitrile has been shown to produce the cyclic tetramer, phthalocyanine, under nitrogen with conventional initiators, though this reaction, thought to be radical in character, occurs at elevated temperatures and provides low yields.

In practice, radical anions are most frequently generated in aprotic solvents, using alkali or alkaline earth metals as reducing agents. The efficiency of the reduction process is dependent on the electron affinity of the acceptor, the solvation requirements of the cation, the ionisation potential of the metal and its heat of sublimation.

In the phthalodinitrile/tetrahydrofuran/lithium situation, three major physical possibilities can be visualised.

(i) Electron exchange at the surface, not involving rupture of the surface, to the phthalodinitrile from the lithium. The newly formed radical–anion may then dimerise at the surface to produce the dianion. The dianion may then migrate from the surface, together with the associated counter-ions, to undergo tetramerisation in the bulk solution The viability of the dianion in solution will be dependent on the solvent. In the search for stability, cyclisation of the tetramer must compete with further propagation to produce a linear polymer. The product formed, as described, indicates that the predominating event is that of cyclisation, though the formation of low molecular mass linear polymeric fragments cannot be entirely ruled out.

(ii) As (i) with regard to the formation of the primary radical–anion, but with the difference that the newly formed radical–anion moves away from the surface with its associated counter-ion, Li^+ This would suggest that the initiator (Li metal) surface would be continually eroded although lithium would not necessarily be present in the product. Whether it was, would depend on the strength of the association between the cation and anion centres, and any competitive features In this instance, tetramer formation would result from the nitrile radical–anion. No dimerisation on the surface would take place This would occur in the bulk solution, to be followed by tetramerisation and possible release of the lithium. Events following migration from the surface will be considerably influenced by the ability of the solvent to provide stability for the dianion before termination occurs, requiring consideration of three aspects of the overall reaction, namely initiation, propagation and termination of the reactive species.

(iii) The third possibility is that the entire process occurs at the surface, which affects the events through steric hindrance, thus forcing the growing macro-radical–anion to cyclise. One can envisage the various anion centres and attendant lithium counter-ions being held at the surface via electrostatic attraction between the anion (resulting from electron exchange, supported by the solvent) and the lithium cation held in the surface. Geometric arrangement at the surface could provide a means whereby cyclisation becomes

> feasible. The cyano group has high electron affinity and could compete with the surface for interaction with the electron density of the newly formed nitrilium anion. Ring closure would rapidly follow to leave an electronically neutral molecule with no basis for close affinity with the surface. At this point the near-neutral phthalocyanine ring system could be removed from the surface by continuous shaking. If this mechanism is valid, then the whole cyclisation process is surface catalysed. The ring system would leave the surface with two negatively charged centres which could achieve stability by proton abstraction from the solvent (tetrahydrofuran).

From the experimental data, we are able to obtain an approximate value for the rate constant for the initial stages of the cyclisation reaction. Such a derivation requires the calculation of the dependence of the initial rate on the phthalodinitrile concentration. This has been shown to be approximately 1.5. Use of the expression $R_0 \propto [\mathrm{Ph(CN)_2}]^x$ provides a route to the rate constant in the usual way, i.e.

$$\log R_0 = \log k_0 + x \log [\mathrm{Ph(CN)_2}] \tag{1}$$

where R_0, $[\mathrm{Ph(CN)_2}]$ and x are known. Log $\bar{k}_0$ can be calculated for each group of experimental data. An average value for the rate constant, k_0, can thus be obtained, it is 2.67×10^{-4} litre$^{1/2}$ mol$^{-1/2}$ s^{-1}.

The magnitude of the initial reaction rates is not unusual for radical-anion reactions. The information provides an insight into the mechanism of the initial reaction. A dependency of 1.5 for the relationship between the initial rate of phthalocyanine product formation and the phthalodinitrile concentration may be explained by consideration of conventional free radical reactions in which the initiator efficiency is itself dependent on the concentration of monomer or primary reagent (in this case, phthalodinitrile).

Thus, on the basis of conventional radical reaction conditions in which the rapid establishment of a steady-state situation is assumed, the following approach may be applied to the phthalodinitrile cyclisation process involving lithium

$$R_i = k_i f [\mathrm{I}] \tag{2}$$

where R_i denotes the rate of initiation of active centres, k_i denotes the rate constant for initiation of active centres, f denotes the efficiency of use of the initiation species and [I] denotes the initiator concentration, lithium centres. In termination of chain growth,

$$R_t = 2k_t[\mathrm{P}^{\dot{-}}]^2 \tag{3}$$

where R_t denotes the rate of termination of active centres, in this case through tetramerisation, k_t is the rate constant for termination and $[\mathrm{P}^{\dot{-}}]$ is the concentration of phthalodinitrile radical–anion centres In termination, two of these centres will be mutually destroyed. Hence, termination is second order with respect to the $[\mathrm{P}^{\dot{-}}]$ concentration

In the steady state, the rate of initiation is balanced by the rate of termination, i.e

$$R_i = R_t \tag{4}$$

$$R_i = 2k_t[\mathrm{P}^{\dot{-}}]^2 \tag{5}$$

$$[\mathrm{P}^{\dot{-}}] = (R_i/2k_t)^{1/2} \tag{6}$$

Considering the cyclisation reaction,

$$R_c = k_c[\mathrm{P}][\mathrm{P}^{\dot{-}}] \tag{7}$$

where R_c is the rate constant of cyclisation, $[\mathrm{P}^{\dot{-}}]$ is the radical–anion concentration and [P] is the phthalodinitrile concentration. Replacing $[\mathrm{P}^{\dot{-}}]$, from eqns (6) and (2),

$$R_c = k_c[\mathrm{P}][R_i/2k_t]^{1/2} \tag{8}$$

$$R_c = k_c[\mathrm{P}]\left[\frac{k_i f[\mathrm{I}]}{2k_t}\right]^{1/2} \tag{9}$$

In this instance, the phthalodinitrile will be directly involved in initiation so that the efficiency factor, f, itself is proportional to the nitrile concentration, and R_c becomes proportional to $[\mathrm{P}]^{3/2}$

The experimental data show that the initial rate of cyclisation, R_0, is proportional to the $\frac{3}{2}$ power of the nitrile concentration and it is tempting, therefore, to suggest that the cyclisation process follows conventional radical kinetics through the setting up of a steady-state situation Equally, it can be postulated that the nitrile is directly involved in initiation. This interpretation of the results beyond the treatment given here must be regarded with caution, in the absence of supporting information. This is especially so when consideration is given to the fact that an investigation of the initiator dependence was not feasible owing to difficulties associated with presenting the initiator to the reaction medium in a uniform manner.

It remains to be seen whether or not the extent of conversion beyond *ca.* 30 % can be improved by modifying the physical nature of the lithium as it is presented to the reaction system. An obvious change is the use of finely divided lithium, which enables a much higher surface area to be made available, so that the cyclisation is given greater opportunity of success.

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