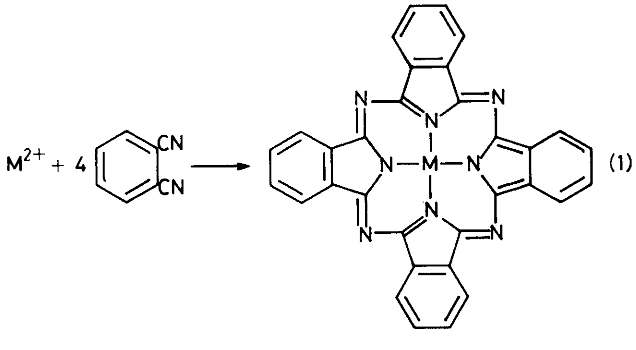
High-pressure Conditions for Improved Synthesis of Phthalocyanines *

Stephen J. Edmondson, Jon S. Hill, Neil S. Isaacs, and Philip C. H. Mitchell
Department of Chemistry, The University, Whiteknights, Reading RG6 2AD

Improved rates of formation and yields of phthalocyanines are observed when the reaction between phthalonitrile and a metal salt is carried out at pressures around 10 kbar. The reaction also benefits from the presence of a superbase, 1,5-diazabicyclo[4.3.0]non-5-ene or 1,8-diazabicyclo[5.4.0]-undec-7-ene, and a reducing agent, hydroquinone. In addition to providing superior yields of metallophthalocyanines from a variety of metal salts, these improvements permit the synthesis of phthalocyanines otherwise difficult to obtain. High pressure combined with a reducing agent is particularly advantageous. In the absence of a metal salt, good yields of metal-free phthalocyanine were obtained.

Preparation of metallophthalocyanines from the reaction between metal salts, particularly CuCl, and phthalonitrile is carried out on a large scale industrially, the copper derivative being an important blue pigment. Typically, temperatures around 200 °C are needed and reaction times of hours. The reaction, although sometimes described by equation (1), is, in reality, complex; the equation gives no clue to the source of the two electrons evidently needed.[1] It is assumed that reducing equivalents can be provided by oxidation of excess of metal atoms or low-valent ions (when the metal is supplied in this form, as with copper) or by oxidation of the organic reactant when the metal is provided as a bi- or higher-valent salt. Such syntheses are, therefore, often low yield, giving a mixture of products from which the pure phthalocyanines may be difficult to obtain.

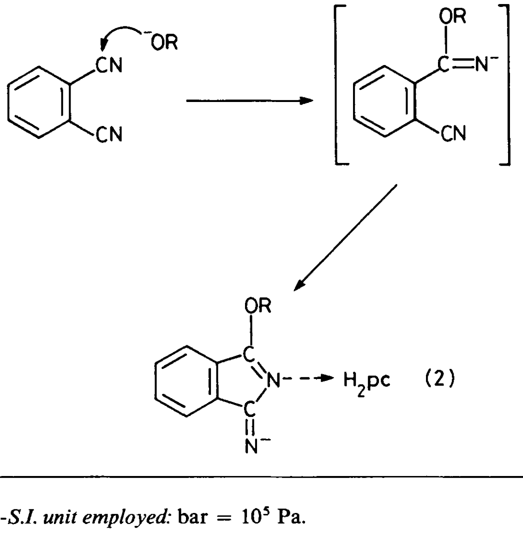


(1)

Our interest in preparing a range of metallophthalocyanines prompted us to devise improved syntheses. We were especially interested in the possibility that yields could be improved by application of high pressures. As far as we are aware no previous work has been reported on the pressure-induced synthesis of inorganic macrocycles, of which the phthalocyanines are an important example.

In general, reactions which have a large negative volume of activation, *i.e.* the volume of the system decreases from the initial to the transition state, are accelerated by pressure. The two most important factors leading to a negative volume of activation are bond formation and ion formation, for which the associated volume change is solvent dependent. As we see from equation (1), the reaction of four phthalonitrile molecules with a metal ion to give a metallophthalocyanine involves the formation of eight C–N bonds and four M–N bonds. Although the detailed mechanism of the reaction is not known, it seems reasonable to expect some considerable degree of bond formation in the transition state formed by association of the reacting species and that, therefore, the rates of formation of the metallophthalocyanines, and perhaps yields also, would be increased by running reactions at high pressure. We describe here our study of the synthesis of phthalocyanines at pressures of 9—12 kbar and temperatures of 60—100 °C. Some representative experiments were carried out in order to evaluate the feasibility of the high-pressure route. The possibility of preparing superphthalocyanines and sandwich-type diphthalocyanines by the application of pressure was also studied.

In addition to studying the effect of high pressure alone, we carried out some experiments with an organic superbase added as a catalyst and with a reducing agent (here, hydroquinone) to supply the equivalents needed according to equation (1). It has been shown previously[2,3] that organic superbases and alcohols generate metal alkoxides which act as the true catalysts; it may be supposed that their function is the activation of one cyano group which, in turn, initiates a chain of anionic additions leading ultimately to the cyclic product [equation (2)].



(2)

---

* *Non-S.I. unit employed:* bar = 10^5 Pa.

We found that high pressure and a reducing agent (here, hydroquinone following earlier work[4]) also very much improved yields in phthalocyanine syntheses and provided a route to some phthalocyanines otherwise difficult to obtain.

Experimental

High-pressure reactions (to 12 kbar) were carried out in our piston and cylinder apparatus.[5] The reagents were placed in a poly(tetrafluoroethylene) (ptfe) cylinder enclosed by a sliding stopper sealed by neoprene O-rings. The fluid high-pressure medium was dioctyl adipate. Pressure was applied by a hydraulic ram and calibrated using a strain gauge. The temperature of the whole apparatus could be controlled to ±5 °C and pressures to ±100 bar. In general alcohols, usually methanol or ethanol, were chosen as the reaction solvent since phthalonitrile and metal salts are sufficiently soluble at the temperatures used. Quantities were: metal salt, 0.9 mmol; phthalodinitrile, 3.6 mmol; alcohol, 3 cm^3. The products were extracted with methanol and acetone to remove soluble, low-molar-mass impurities and sublimed *in vacuo*. The phthalocyanines were identified and determined from their characteristic visible spectra in solution in, usually, dichloromethane. Yields (see below) refer to the pure sublimed phthalocyanine.

Table 1. Effect of pressure on phthalocyanine yields in the absence of added base or reducing agent

Conditions				
P/kbar	*T*/°C	*t*/h	Solvent	Yield/%
(*a*) [Co(pc)] from cobalt(II) nitrate				
0.001	80	6	EtOH	0
0.001	200	2	Octanol	7
9	65	1	MeOH	8
9	65	1	EtOH	8
9	65	2	$\mathrm{Pr^iOH}$	0
(*b*) [Cu(pc)] from $\mathrm{CuCl_2}$				
0.001	90	70	MeOH	0
9	30	1	MeOH	0
9	90	70	MeOH	51

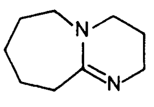
Results and Discussion

Our results are presented in Tables 1—3 which show the effect of pressure, added base, and reducing agent on yields of the various phthalocyanines.

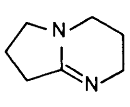
Effect of Increased Pressure in the Absence of Added Base or Reducing Agent.—Data are in Table 1. The effect of reaction time and temperature in addition to pressure on the synthesis of cobalt and copper phthalocyanines is reported. Clearly high pressure increases the yield of the metal phthalocyanine especially at longer reaction times as for copper. With high pressure it is possible to obtain a good yield of a phthalocyanine at moderate temperatures (60—90 compared with 200 °C at atmospheric pressure). However, whether pressure has an effect depends on the metal; in reactions at 9—12 kbar and 60—90 °C for less than 24 h yields of metal phthalocyanine were insignificant when starting with molybdenum complexes, oxovanadium(IV) sulphate, and manganese, nickel, aluminium, and silver nitrates or sulphates.

Effect of a Superbase Catalyst.—Organic superbases catalyse the formation of phthalocyanines (see Introduction). We used the compounds 1,8-diazabicyclo[5.4.0]undec-7-ene (dbu) and 1,5-diazabicyclo[4.3.0]non-5-ene (dbn). A summary of the results of high-pressure experiments carried out with these catalysts is given in Table 2.

The data for copper show that the effect of the catalyst in increasing yields is greatest at short reaction times and that the yield increases with the amount of catalyst. The bases also facilitated the formation of molybdenum and lanthanum phthalocyanines but not cobalt and nickel phthalocyanines. The combined effect of high pressure and added base on the synthesis of the phthalocyanines depends, of course, on how the base is bound in the transition state. We would expect pressure



dbu



dbn

Table 2. Effect of superbase catalysts on phthalocyanine yields

Conditions*					
P/kbar	*T*/°C	*t*/h	Solvent	Catalyst/ mole equivalent	Yield/%
(*a*) [Cu(pc)] from $\mathrm{CuCl_2}$					
0.001	90	5	EtOH	1.0 dbu	0.8
9	90	70	MeOH	None	51
9	65	0.1	MeOH	0.044 dbu	0.4
9	65	0.1	MeOH	0.22 dbu	3
9	65	0.2	MeOH	0.78 dbu	12
9	65	0.2	MeOH	1.55 dbu	14
(*b*) [MoO(pc)] from $[\mathrm{MoO_2(acac)_2}]$					
9	65	18	MeOH	0.12 dbn	13
9	65	18	MeOH	0.79 dbn	15
(*c*) $[\mathrm{La(pc)_2}]^-$ from $\mathrm{La(NO_3)_3{\cdot}6H_2O}$					
9	90	22	MeOH	1.0 dbn	10

* acac = Acetylacetonate.

Table 3. Effect of hydroquinone on phthalocyanine yields

Conditions					
P/kbar	T/°C	t/h	Solvent	Hydroquinone/ mole equivalent	Yield/%
(*a*) H_2pc from phthalodinitrile					
0.001	200	70	Octanol	0.23	0
12	90	24	EtOH	0.23	45
10	90	70	MeOH	1.32	55
(*b*) [Mn(pc)] from manganese(II) sulphate					
9	65	18	MeOH	None	2
11	90	16	MeOH	0.25	33
11	90	16	MeOH	0.40	50
11.5	100	1.75	MeOH	0.25	36
(*c*) [Fe(pc)] from ferrocene					
11.5	90	1.75	MeOH	0.23	16
12	90	3.5	MeOH	0.5	25
12	90	3.5	MeOH	0.9	17
(*d*) [Co(pc)] from cobalt(II) nitrate					
0.001	200	3	Octanol	0.25	36
10	80	0.5	MeOH	0.12	3
10	80	0.5	MeOH	0.25	9
11	90	1	MeOH	0.25	33
11	90	1	MeOH	0.50	25
11	90	1	MeOH	0.92	16
(*e*) [Ni(pc)] from nickel(II) nitrate					
9	65	24	MeOH	None	1
11.5	100	1.75	MeOH	0.25	46
(*f*) [Cu(pc)] from $CuCl_2$					
12	90	21	MeOH	0.25	0
(*g*) [Zn(pc)] from zinc(II) nitrate					
9	90	16	MeOH	0.51	28
12	90	24	MeOH	1.0	13
(*h*) [Cd(pc)] from cadmium(II) nitrate					
12	90	16	MeOH	0.23	10
(*i*) [MoO(pc)] from $[MoO_2(acac)_2]$					
12	90	24	MeOH	0.23	0
(*j*) $[La(pc)_2]^-$ from $La(NO_3)_3 \cdot 6H_2O$					
12	90	20	MeOH	0.23	90
(*k*) H_2pc from lead(II) nitrate					
12	90	20	MeOH	0.25	41
(*l*) Dioxouranium superphthalocyanine* from UO_2Cl_2					
9	90	22	MeOH	0.23	27

* Superphthalocyanine refers to an expanded five-subunit macrocycle *cf.* the four-subunit macrocycle phthalocyanine.

to increase the association between the base and phthalonitrile which should enhance the pressure coefficient of the reaction rate. The effect of the base was to increase yields in the high-pressure experiments except with cobalt.

Effect of Increased Pressure and a Reducing Agent.—We decided to use hydroquinone as a reducing agent following the earlier work of Marullo and Snow.[4] Hydroquinone is a two-electron reducing agent and provides the two electrons needed to form the phthalocyanine ring from four phthalonitrile molecules [*cf.* equation (1)]. Inclusion of hydroquinone in the reaction mixture greatly increased phthalocyanine yields. Data are in Table 3.

For the metal-free phthalocyanine from phthalonitrile, the combined effect of pressure and the reducing agent was dramatic, the yield increasing from 0 at 1 atm (101 325 Pa) to more than 50% depending on the amount of hydroquinone. Similarly in the synthesis of manganese phthalocyanine at high pressure the addition of hydroquinone increased the yield from 2 to more than 30% and for nickel from 1 to 46%. Note that there appears to be an optimum amount of hydroquinone. This is most clearly shown in the yields of [Co(pc)] and is also evident in the results for iron and zinc. Increasing the mole ratio of hydroquinone from 0.5 to *ca.* 1.0:1 causes the yields to decrease.

We conclude that the use of high pressure combined with a reducing agent such as hydroquinone can greatly increase yields of metal-free and metallophthalocyanines in conventional preparations starting from 1,2-dicyanobenzene and a metal salt. We are currently extending this approach to substituted phthalocyanines and other macrocycles.

Acknowledgements

We thank the S.E.R.C. for the provision of a research studentship (to S. J. E.) and for DSM (Geleen, Netherlands) (to J. S. H.).

References

1 F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' Wiley, 4th edn., 1980, p. 134.
2 F. Baumann, B. Bienert, G. Rosch, H. Vollman, and W. Wolf, *Angew. Chem.*, 1956, **68**, 133.
3 H. Tomoda, S. Saito, and S. Shiraishi, *Chem. Lett.*, 1983, 313; V. F. Borodkin, *Zh. Prikl. Khim.* (*Leningrad*), 1958, **31**, 813.
4 N. P. Marullo and A. W. Snow, *ACS Symp. Ser.*, 1982, **195**, 325.
5 M. G. B. Drew, A. V. George, N. S. Isaacs, and T. H. Rzepa, *J. Chem. Soc., Perkin Trans. 1*, 1985, 1277.

Received 8*th May* 1989; *Paper* 9/01908A