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A Kinetic Study of the System Phthalocyanine–Copper(II) Chloride–Sulfuric Acid

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Abstract

In solutions of phthalocyanine, H_2Pc, ($c = 1-3 \times 10^{-5}$ mol dm^{-3}) and copper(II) chloride ($c \approx 10^{-3}$ mol dm^{-3}) in sulfuric acid ($c = 16-18$ mol dm^{-3}), two pseudo first-order reactions take place: (1) decomposition of H_2Pc; (2) conversion of H_2Pc into copper(II) phthalocyanine, CuPc. Reaction (1) is H_2O concentration dependent and its rate constant increases from 0.088 to 1.88 h^{-1} as the H_2SO_4 concentration changes from 18 to 16 mol dm^{-3}. The rate constant of (2) does not vary significantly with H_2SO_4 concentration and lies around the 0.05 h^{-1} mark. The CuPc formed in reaction (2) does not decompose under the above conditions.

Introduction

Phthalocyanine and its metal complexes are well known for their poor solubility in most common solvents. At the same time, they exhibit a surprisingly good solubility in concentrated sulfuric acid [1]. The latter property is sometimes used in the purification and separation of metallophthalocyanines. The nature of the H_2SO_4 solutions and the reactions taking place in them have not been extensively investigated and are rather poorly understood [2–4]. The few published papers deal mostly with the dissociation of some metallophthalocyanines in concentrated H_2SO_4 to yield H_2Pc and M^{2+} ions [5]. However, the opposite process – the possibility of converting H_2Pc into metallophthalocyanines in concentrated H_2SO_4 – has not been examined.

In a previous and still unpublished work we studied the conversion of H_2Pc into MPc (M = Cu, Ni, Co) under 'dry' conditions and found that on heating an intimate mixture of solid H_2Pc and MCl_2 at ≈550 °C and 10^{-3} Torr the metallophthalocyanine sublimes and is obtained in 20–50% yield. In this paper the solution system H_2Pc–$CuCl_2$–H_2SO_4 has been selected and a quantitative study of the reactions taking place in it has been undertaken. The aim was to establish if an analogous conversion of H_2Pc into CuPc occurs at all in H_2SO_4 solution.

Experimental

Reagents

Phthalocyanine was prepared from sublimed lead(II) phthalocyanine by a literature procedure [6] in which PbPc is demetallized by treatment with 1:1 aqueous hydrochloric acid. Copper(II) chloride dihydrate and concentrated sulfuric acid were of pro analysi purity.

Instrumentation

Spectrophotometric measurements were conducted at 20 °C by a Varian Superscan 3 UV–Vis spectrophotometer using quartz cuvettes of 1 cm path.

Kinetics Study

The reaction kinetics was studied at 20 °C in H_2SO_4 as the solvent, and four different concentrations of the acid were chosen for the study: 16, 16.5, 17 and 18 mol dm^{-3}. As the H_2Pc decomposition rate decreases with the increase of the H_2SO_4 concentration (*vide infra*), each reaction solution was prepared as follows. A few drops of the saturated H_2Pc solution in concentrated H_2SO_4 ($c = 18$ mol dm^{-3}) were added into 4 cm^3 of the saturated $CuCl_2$ solution in H_2SO_4 of appropriate concentration. The resulting system was $\approx 10^{-3}$ mol dm^{-3} in $CuCl_2$ and $1-3 \times 10^{-5}$ mol dm^{-3} in H_2Pc. The reactions taking place in this solution were monitored spectrophotometrically at 745 nm [$\epsilon(H_2Pc) = 0.57 \times 10^5$ dm^3 mol^{-1} cm^{-1}; $\epsilon(CuPc) = 0.29 \times 10^5$], 774 nm [$\epsilon(H_2Pc) = 0.72 \times 10^5$; $\epsilon(CuPc) = 1.06 \times 10^5$] and 791 nm [$\epsilon(H_2Pc) = 0.35 \times 10^5$; $\epsilon(CuPc) = 2.43 \times 10^5$]. The H_2Pc and CuPc concentrations obtained from the measured absorbances are listed versus time in Table 1, two runs having been done for each H_2SO_4 concentration.

Results and Discussion

In the system consisting of H_2Pc and $CuCl_2$ dissolved in H_2SO_4 ($c = 16-18$ mol dm^{-3}) the following reactions take place simultaneously at 20 °C

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TABLE 1. Concentration change of H_2Pc and CuPc with time at 20 °C in H_2SO_4 solution of H_2Pc and $CuCl_2$

τ (h)	$C(H_2Pc)$ (10^{-6} mol dm^{-3})		C(CuPc) (10^{-6} mol dm^{-3})	
	Run I	Run II	Run I	Run II
16 mol dm^{-3} H_2SO_4				
0.00	11.9	11.6	0.872	0.882
0.08	10.3	9.80	0.935	0.928
0.17	9.07	8.44	0.989	0.972
0.25	7.64	7.54	1.02	1.01
0.33	6.53	6.91	1.06	1.05
0.42	5.45	5.53	1.08	1.10
0.50	4.62	4.70	1.13	1.10
0.58	3.90	3.98	1.14	1.11
0.67	3.45	3.35	1.17	1.15
0.75	2.89	2.72	1.13	1.14
0.83	2.42	2.34	1.18	1.15
0.92	1.97		1.14	
1.00	1.69		1.20	
16.5 mol dm^{-3} H_2SO_4				
0.00	15.4	12.7	0.819	0.787
0.17	13.2	11.1	0.962	0.892
0.33	12.1	9.49	1.06	0.973
0.50	10.3	8.11	1.11	1.02
0.67	9.18	6.78	1.18	1.07
0.83	7.80	5.87	1.22	1.15
1.00	6.62	4.97	1.32	1.17
1.17	5.54	3.89	1.33	1.19
1.33	4.72	3.16	1.35	1.23
1.50	3.64	2.53	1.42	1.22
1.67	3.08	1.98	1.42	1.24
1.83	2.53		1.44	
17 mol dm^{-3} H_2SO_4				
0.0	29.0	19.7	0.740	0.791
0.5	24.3	17.2	1.33	1.27
1.0	20.3	13.9	1.81	1.69
1.5	16.9	12.7	2.27	2.07
2.0	13.5	9.80	2.58	2.36
2.5	11.2	8.97	2.80	2.68
3.0	8.99	7.50	3.05	2.88
3.5	7.25	6.43	3.27	3.03
4.0	6.67	5.42	3.36	3.17
5.0	4.32	4.02	3.65	3.44
6.0	3.02	2.80	3.77	3.61
7.0	2.00	2.10	3.87	3.77
18 mol dm^{-3} H_2SO_4				
0	18.6	23.5	0.701	0.725
2	14.1	18.4	2.19	2.75
4	10.9	11.9	3.28	4.18
6		9.50		5.30
8	7.00	7.12	4.89	6.16
10	4.90	5.15	5.42	6.75
12	4.24	3.98	5.71	7.01

$$H_2Pc \xrightarrow{k_1} \text{decomposition products} \tag{1}$$

$$H_2Pc + CuCl_2 \xrightarrow{k_2'} CuPc + 2HCl \tag{2}$$

The reaction conditions were so chosen that $CuCl_2$ was present in large excess relative to H_2Pc (see 'Experimental'). Thus the reaction (2) was a pseudo first-order one with the rate constant: $k_2 = k_2' \times C(CuCl_2)$. From the concentration versus time data in Table 1 it can be seen that significant amounts of CuPc are found in the reaction solution even at the very beginning of concentration measurements. A likely reason for this lies in the fact that the preparation of each reaction solution involved the addition (of a few drops) of a concentrated H_2Pc solution into a $CuCl_2$ solution. As the two solutions come into contact, the local H_2Pc concentration is temporarily much higher than it is immediately afterwards when complete mixing has been achieved. This would for a short time considerably speed up reaction (2), giving rise to the observed 'initial' CuPc concentration.

The data in Table 1 were first qualitatively analyzed by a Monte Carlo treatment [7] which showed that the reaction system is best described by eqns. (1) and (2). After that, the overall disappearance rate constant for H_2Pc, expressed by the sum $k_{12} = k_1 + k_2$, was determined by linear regression analysis of the $\ln[C_o(H_2Pc)/C(H_2Pc)]$ versus time data, and the results are given in Table 2. The individual constants k_1 and k_2 were determined as follows. The rate expressions corresponding to eqns. (1) and (2) when combined and integrated yield the expression (3)

TABLE 2. Decomposition rate constants for H_2Pc in the H_2SO_4 solution of H_2Pc and $CuCl_2$

$C(H_2SO_4)$ (mol dm^{-3})	Run no.	k_{12} h^{-1}	SE [a]	(R^2) [b]
16	1	1.96	0.02	0.996
16	2	1.92	0.05	0.987
16	av.	1.94		
16.5	1	0.98	0.03	0.990
16.5	2	1.11	0.03	0.990
16.5	av.	1.045		
17	1	0.38	0.004	0.999
17	2	0.32	0.004	0.998
17	av.	0.35		
18	1	0.12	0.004	0.995
18	2	0.15	0.004	0.996
18	av.	0.135		

[a] SE = Standard deviation of k_{12}. [b] R = Correlation coefficient of the fit.

TABLE 3. Rate constants for the conversion of H_2Pc into CuPc and for the decomposition of H_2Pc

$C(H_2SO_4)$ (mol dm^{-3})	Run no.	SDF [a] ($\times 10^{-8}$)	AE [b] (%)	k_2 (h^{-1})	$SE(k_2)$	k_1 (h^{-1})
16	1	2.0	1.3	0.062	0.001	1.90
16	2	1.1	0.7	0.058	0.001	1.86
16	av.			0.060		1.88
16.5	1	1.9	1.2	0.048	0.0006	0.93
16.5	2	1.4	1.0	0.049	0.0006	1.06
16.5	av.			0.048		1.00
17	1	2.8	0.8	0.044	0.0002	0.34
17	2	2.3	0.6	0.054	0.0002	0.27
17	av.			0.049		0.30
18	1	6.2	1.2	0.043	0.0003	0.077
18	2	6.5	0.8	0.049	0.0003	0.10
18	av.			0.046		0.088

[a] Standard deviation of the fit. [b] Average error of the fit.

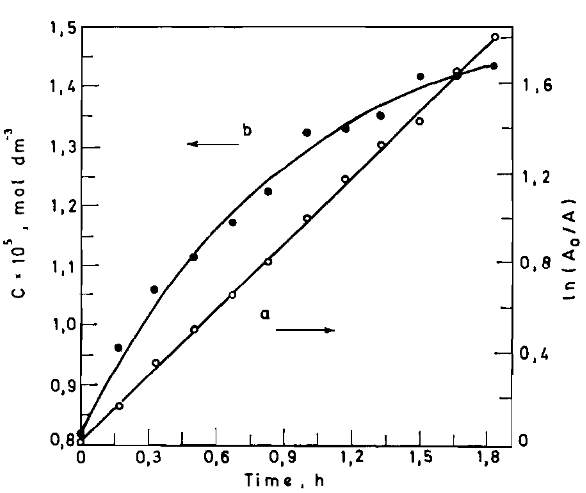
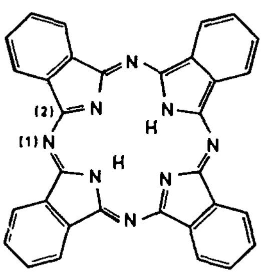


Fig. 1. Graphical representation of the reaction run no. 1 in 16.5 mol dm^{-3} H_2SO_4. (a) The linear regression line for the H_2Pc data (open circles); A_0 and A are the initial and actual H_2Pc concentration, respectively (the right-hand ordinate). (b) The non-linear regression curve for the CuPc data (filled circles); C is the CuPc concentration (the left-hand ordinate).

$$C = C_0 + \frac{k_{12}A_0}{k_{12}}(1 - \exp(-k_{12}\tau)) \qquad (3)$$

where $C = C(\mathrm{CuPc})$; $C_0 = C_0(\mathrm{CuPc})$; $A_0 = C_0(H_2Pc)$. Equation (3) was fitted to the data in Table 1 by a non-linear regression treatment [8] with one parameter (k_2). The results obtained are presented in Table 3, in which the k_1 values were calculated from $k_1 = k_{12} - k_2$; as an illustration, Fig. 1 shows graphically experimental data and the resulting fits for a typical reaction run. The k_1 values agree well with those reported for the H_2Pc–H_2SO_4 system in the absence of metal cations [2].



Scheme 1.

The data in Table 3 show that the reaction (1) rate increases as the H_2SO_4 concentration decreases, which indicates that the rate is proportional to the H_2O concentration. Since the H_2O concentration is about 4 mol dm^{-3} even in the most concentrated of the H_2SO_4 solutions studied (18 mol dm^{-3}), it means that reaction (1) can also be regarded as a pseudo first-order reaction. If the rates of the two reactions are compared it is seen that at high H_2SO_4 concentrations the rate constants k_1 and k_2 do not markedly differ, whereas in 16 mol dm^{-3} H_2SO_4 reaction (1) proceeds about 30 times faster than reaction (2).

Regarding a possible mechanism of the reaction (1) it should be kept in mind that in these highly acidic solutions H_2Pc mostly exists in protonated form, with the bridging aza nitrogens (1 on Scheme 1) serving as proton acceptors. Secondly, the H_2O/H_2SO_4 molar ratio increases from 0.22 to 0.80 as the H_2SO_4 concentration is changed from 18 to 16 mol dm^{-3}. The increase in the availability of the H_2O molecules (as the H_2SO_4 concentration is lowered from 18 to 16 mol dm^{-3}) is actually even more sharp, since at very high H_2SO_4 concentrations the water content is mostly in the form of H_3O^+ ions rather than H_2O molecules. In view of these facts a likely mechanism for the decomposition of phthalocyanine could involve a nucleophilic attack of the H_2O molecule onto the pyrrole carbon atom (2 on Scheme 1), the latter being susceptible to such an attack due to the protonation of the neighbouring aza nitrogen (1). This could be followed by the hydrolytic break of the N(1)–C(2) bond which amounts to the Pc ring opening and the formation of a species containing the COH and NH_2^+ groups at its ends. The species could then react further in steps similar to the above ones which would eventually lead to its fragmentation.

The second reaction occurring in the H_2Pc–$CuCl_2$–H_2SO_4 system is the conversion of H_2Pc into CuPc (reaction (2)). The k_2 values in Table 3 show that in contrast to reaction (1) the actual conversion of H_2Pc into CuPc is essentially independent of the H_2SO_4 concentration. This suggests that reaction (2) does not proceed through a conceivable temporary opening of the Pc ring since such process would be expected – on the basis of the preceding discussion – to be dependent on the H_2O concentration. Instead, the conversion of H_2Pc into CuPc probably occurs by a S_N2 mechanism in which the Cu^{2+} ion axially approaches the center of the Pc plane while two H^+ ions leave the plane from the opposite side.

It is worth noticing that in contrast to H_2Pc, copper(II) phthalocyanine produced by reaction (2) does not decompose at a significant rate under the conditions of this study. In fact, it was earlier found that CuPc decomposes in H_2SO_4 at a measurable rate only at higher temperatures (e.g. at 100 °C, $k = 0.1\ h^{-1}$ and $k = 0.01\ h^{-1}$ in 16.2 and 18.2 mol dm^{-3} H_2SO_4, respectively [9]). The greater stability of CuPc relative to H_2Pc is obviously a reflection of strong coordinative Cu–N bonds in CuPc. The strong bonds can be expected to impede the Pc ring opening, the latter step being necessary if decomposition is to occur.

Acknowledgement

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