J. Chem. Soc., Faraday Trans. 1, 1982, **78**, 1923-1935

Kinetics of Complex Formation between Zinc *meso*-Tetraphenylporphyrin and some Nitrogen Bases in Aprotic Solvents, Studied by an Improved Microwave Temperature-jump Method

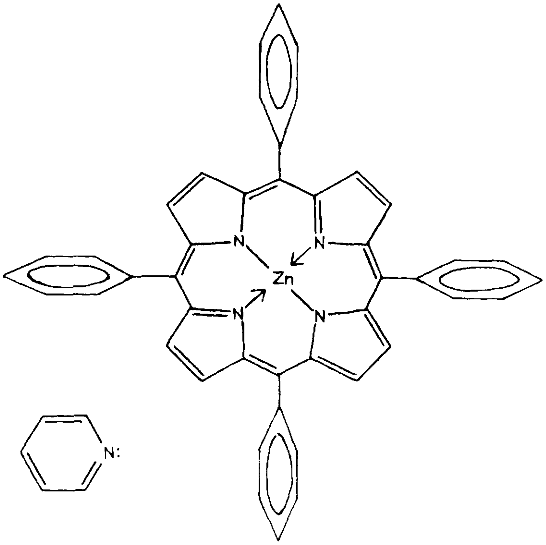
By Edward F. Caldin* and John P. Field

University Chemical Laboratory, University of Kent, Canterbury, Kent CT2 7NH

Received 12*th August*, 1981

Rate and equilibrium constants have been determined over a range of temperature for the reactions of zinc *meso*-tetraphenylporphyrin with pyridine (in chlorobenzene, 1-chlorobutane and toluene), with 2-methylpyridine (in 1-chlorobutane), and with imidazole (in 1-chlorobutane). Rates were measured by means of an improved microwave temperature-jump apparatus incorporating signal-averaging, and at low temperatures by the stopped-flow method, with spectrophotometric detection. The forward rate constants are lower by about an order of magnitude than the values calculated for diffusion control from the simple Smoluchowski model. A two-step mechanism appears likely. Solvent and steric effects on the rate are discussed.

Metalloporphyrins form addition complexes with a variety of electron-donor substances in solution. These reactions have been much studied in recent years,[1] partly because of their biological importance; those of haem are the most obvious instances, while chlorophylls and vitamin B_{12} have related structures. Zinc *meso*-tetraphenylporphyrin, Zn(TPP) (**I**), is particularly suitable for physical investigation; it forms stable 1:1 complexes with pyridines in solution, according to eqn (1)



(I)

$$\mathrm{Zn(TPP)} + \mathrm{py} \rightleftharpoons \mathrm{Zn(TPP)py} \qquad (1)$$

and these have been well studied from the spectroscopic and thermodynamic points of view.[2-7] These complexes provide simpler systems than those of haem, since Zn(TPP) accepts one and only one axial ligand, the metal is always in the 2+ oxidation state, and there are no empty *d*-orbitals.[4] The complexes are easy to detect, being deeply coloured, and the equilibrium constants are high. The crystal structure of the analogous Zn(TpyP)py shows that the pyridine molecule is attached axially to the zinc atom, the Zn—N distance being 2.143 Å; the bond appears to be long and comparatively weak.[8] The complex formation is very fast; the p.m.r. spectrum of Zn(TPP)py in benzene indicates rapid exchange of ligand, with no sign of line-broadening even at −60 °C.[3]

From the point of view of chemical kinetics, these systems permit a study of the approach of a relatively small molecule to the centre of a large disc-like molecule, when each molecule has a restricted site and the geometry of the complex is well-defined. The geometrical and electronic properties of both molecules can be varied by substituents. The long bond should reduce the contribution of repulsion to the activation barrier. Comparisons with theories of diffusion control should be illuminating.

Kinetic studies of very fast reactions in non-conducting solutions can in principle be made by various special techniques, such as electric-field-jump, ultrasonic-absorption, laser temperature-jump or microwave temperature-jump. (The standard type of temperature-jump apparatus, based on Joule heating, cannot be used, since it requires a conducting solution.) We have used the microwave temperature-jump technique at temperatures down to −55 °C. This technique has recently been greatly improved, as regards sensitivity, by the adoption of signal-averaging, to which it is ideally suited. Pulses are applied up to 20 times a second, to a flowing solution, so that it is easy to average 2000 traces as a standard procedure taking < 2 min. The gain in sensitivity (signal/noise) is *ca.* 50-fold. The effect is to overcome the limitation due to the small temperature-rise in an individual pulse (*ca.* 0.1 °C), and so make the technique comparable with other relaxation techniques as regards sensitivity (see later, fig. 3). Low-temperature thermostats have also been brought into use. Another improvement in technique is the development of low-temperature stopped-flow machines; in some favourable cases, rates at −100 °C were low enough to measure by this method.

EXPERIMENTAL

MATERIALS

meso-Tetraphenylporphyrin (H_2TPP) was prepared and freed from chlorin by methods given in the literature.[1, 9-12] Zinc *meso*-tetraphenylporphyrin Zn(TPP) was prepared[1] by adding a saturated solution of zinc acetate in methanol to a boiling solution of H_2TPP in ethanol-free chloroform. Pyridine and 2-methylpyridine were purified by distillation from KOH pellets and stored over KOH and molecular sieve (3A). Imidazole was recrystallised twice from ethanol, air-dried and kept over P_2O_5.

Chlorobenzene (A.R.) was washed with concentrated H_2SO_4, washed with aqueous $NaHCO_3$ and water and dried with $CaSO_4$ followed by molecular sieve (3A); if kept > 1 week, it was again washed and dried. Chlorobutane (Fisons, H.P.L.C.) was washed with aqueous $NaHCO_3$ and water, dried over $CaSO_4$, filtered, distilled [b.p. 78 °C; lit. (Beilstein) 78.4 °C] and kept over molecular sieve (3A). Toluene (A.R.) was refluxed with sodium wire, distilled off and stored over molecular sieve.

DETERMINATION OF EQUILIBRIUM CONSTANTS

Equilibrium constants K (see table 1) were determined from measured absorbances at 602 nm, by the method given by Kirksey *et al.*[3] (The method of Vogel and Searly[13] gives practically

TABLE 1.— EQUILIBRIUM CONSTANTS *etc.* FOR REACTIONS OF ZnTPP WITH BASES[a]

base	solvent	λ_{max}/nm	temp. /°C	$a/10^{-5}$ mol dm^{-3}	$b/10^{-5}$ mol dm^{-3}	$K/10^3$ dm^3 mol^{-1}	$K/10^3$ dm^3 mol^{-1} 25 °C	$-\Delta H^\ominus$ /kcal mol^{-1}	$-\Delta S^\ominus$ /cal K^{-1} mol^{-1}
pyridine	BuCl	602, 562, 544	11	3.6	2-10	$40._8\pm4$	16.8 ± 2	9.4 ± 0.6	12 ± 2
			18.3	3.6	2-10	$23._5\pm4$			
			25.9	3.6	2-10	$15._7\pm0.8$			
			39.3	3.6	2-10	$8._4\pm0.7$			
	PhCl	605, 564, 551	10.3	4.7	2-13	$1.3_8\pm0.5$	5.6 ± 0.3	10.4 ± 0.2	17 ± 1
			21.0	4.7	4-25	$7.1_8\pm0.15$			
			29.5	4.7	4-85	$4.4_6\pm0.35$			
			37.6	4.7	4-85	$2.7_2\pm0.13$			
	$PhCh_3$[b]	605, 564, 551	20.3	2.9	12-125	$6.2_2\pm0.6$	4.8 ± 0.5	9.3 ± 0.1	14 ± 1
			29.9	2.9	12-125	$3.7_2\pm0.3$			
			39.8	2.9	12-125	$2.3_2\pm0.13$			
2-Me-py	BuCl	602, 562, 544	7.5	5.6	46-280	$1.2_9\pm0.2$	0.56 ± 0.03	7.7 ± 0.2	13.4 ± 1
			15.4	5.6	46-280	$0.8_4\pm0.05$			
			23.0	5.6	46-280	$0.6_2\pm0.04$			
			30.8	5.6	46-280	$0.4_5\pm0.03$			
			39.3	5.6	46-280	0.30 ± 0.02			
	PhCl	505, 564, 551	10.8	4.7	130-780	$0.54\pm0.01_5$	0.28 ± 0.01	8.0 ± 0.05	16.0 ± 0.2
			20.0	4.7	130-780	$0.35\pm0.01_5$			
			29.5	4.7	130-780	0.22 ± 0.01			
			38.6	4.7	260-1560	0.15 ± 0.01			
imidazole	BuCl	602, 562, 544	12.0	5.7	1.4-7	235 ± 170	83 ± 10	9.7 ± 1.5	10.1 ± 5
			17.8	5.7	1.4-11	144 ± 26			
			26.8	5.7	1.4-11	74 ± 5			
			34.9	5.7	1.4-11	$51._5\pm3$			
	PhCl	602, 564, 550	10.5	4.5	1-6	139 ± 7	49 ± 2	12.1 ± 0.2	19.1 ± 1
			20.2	4.5	1-6	68 ± 4			
			29.6	4.5	1-6	37 ± 4			
			38.0	4.5	1-8	$20._5\pm1.5$			

[a] a = formal conc. of ZnTPP; [b] b = formal conc. of base, 1 cal ≡ 4.184 J; [c] values of K at 25 °C assumed same as for benzene [ref. (2)].

the same results with such large values of K.) Absorbance measurements were made on a Cary 219 or Pye-Unicam SP8000 spectrophotometer, the former being considerably more precise. Values of $\Delta H^{\ominus}$ (and hence $\Delta S^{\ominus}$) were calculated from a plot of log K against $1/T$ by a weighted-least-squares computer program, the weight given to each value of K being proportional to $1/\sigma^2$ where σ is the standard deviation. For the complex of Zn(TPP) with pyridine in toluene, the values of K and $\Delta H^{\ominus}$ are assumed to be the same as in benzene; the justification for this is that for this complex the spectroscopic data[4] (and thermodynamic data where available[7]) are very similar for benzene, toluene and chlorobenzene. Errors quoted are standard deviations from the 'best' values.

DETERMINATION OF RATE CONSTANTS

MICROWAVE TEMPERATURE-JUMP APPARATUS WITH SIGNAL-AVERAGING AND LOW-TEMPERATURE THERMOSTAT

Rate constants from 3×10^8 to 4×10^9 dm^3 mol^{-1} s^{-1} were determined with the aid of a microwave temperature-jump apparatus (fig 1). The pulsed-magnetron system is essentially the same as in the original description,[14] but in other respects the apparatus has been much modified and its performance greatly improved.[15]

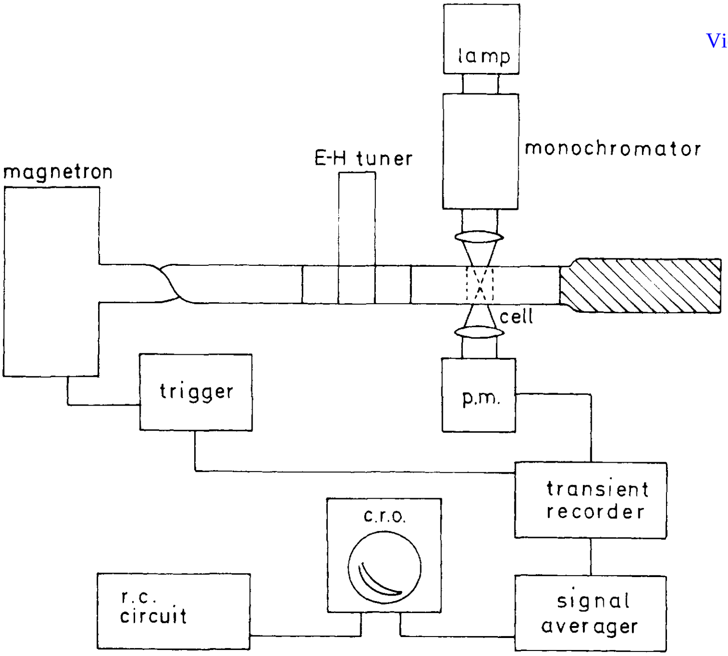


FIG. 1.—Microwave temperature-jump apparatus, block diagram.

(*a*) The cell (fig. 2) is made of Teflon and has a conical quartz window at each end, wrapped with Teflon tape to prevent leakage.

(*b*) The tuning of the cavity is now quickly effected by an EH tuner.

(*c*) The wavelength of the monitoring light-beam is now controlled by a Bausch and Lomb monochromator, in place of filters.

(*d*) Signal-averaging has been added to the detection system. The weakest point of the apparatus had been that a single microwave pulse effects a temperature jump of only a few tenths of a degree. A dramatic improvement is effected by signal-averaging (as first done by Brumm and Rüppel):[16, 17] the method is ideally suited to this, since the magnetron can be pulsed

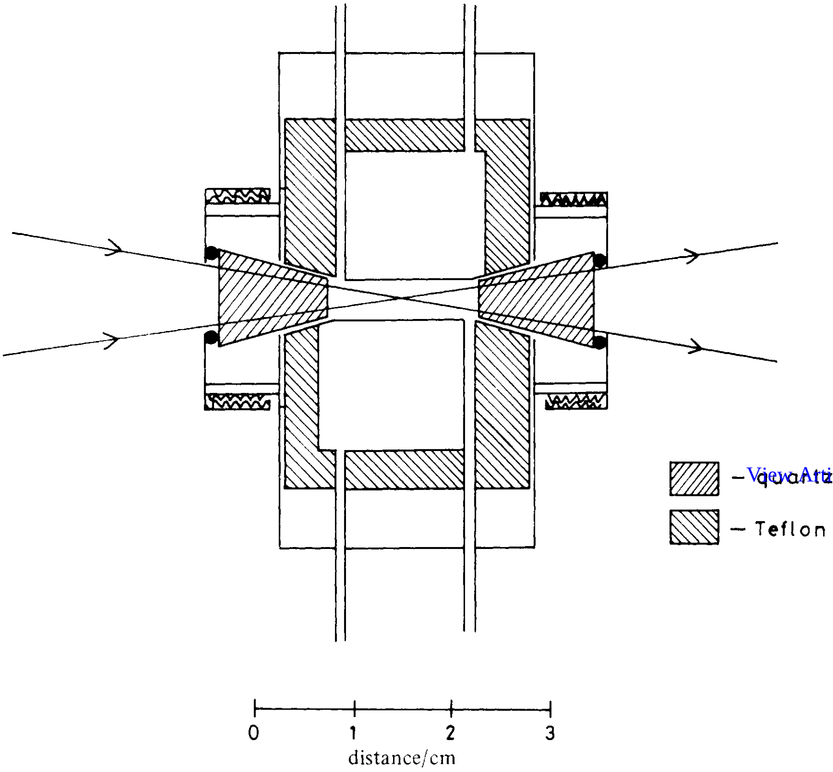


FIG. 2.—Reaction cell of microwave temperature-jump apparatus.

20 times a second. The signal from the photomultiplier is taken to a transient-recorder (Datalab, DL 905) coupled to a signal-averager (Datalab, DL 403B). It is normal to accumulate 2000 traces, for which only 100 s is required. The effect of averaging should theoretically be to increase the signal-to-noise ratio by a factor of $(2000)^{\frac{1}{2}}$ or *ca.* 45. The increased sensitivity, illustrated in fig. 3, permits quantitative studies which would otherwise be impossible. The effect is the same as if the temperature-jump were increased to several degrees. The performance of our apparatus is similar to that of the one described by Aubard *et al.*[18]

(*e*) The relaxation time is determined by displaying the signal-averaged trace on the screen of a double-beam oscilloscope and matching it with a synthetic exponential generated by an *RC* circuit.[19] In this work, the signal-to-noise ratio was in the region of 10 to 50, and each determination of a relaxation time was replicated three times. Relaxation times could be determined with an accuracy of *ca.* ±5%.

(*f*) The geometry of the optical system has been studied, with a view to eliminating artifacts. The chief artifact is an increase of absorbance which may last up to 50 μs, apparently due mainly to change in the refractive index of the solvent upon rapid heating. It is minimised by the use of the arrangements shown in fig. 1 and 2, with a lens between the monochromator and the cell, the positions being adjusted so that the light-beam comes to a focus inside the cell and internal reflection is minimised. With careful adjustment the artifact is over within the response time of the detector. Adjustments can be made either with pure solvent in the cell, until the averaged trace is a horizontal line, or by using a solution of a system such as ZnTPP and pyridine, where the temperature-jump leads to an increase of the absorbance due to Zn(TPP) (at 551 nm, in chlorobenzene) and a decrease in the absorbance due to the complex (at 564 nm); the artifact absorbance change is added to the former but subtracted from the latter, and has

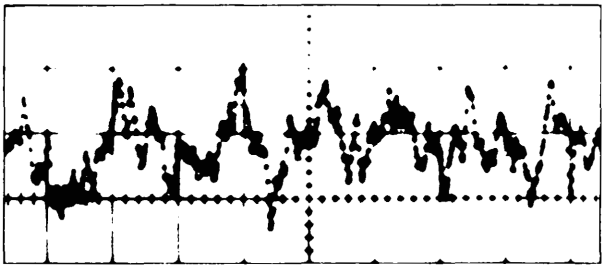
TABLE 2.—RATE CONSTANTS *etc.* FOR REACTION OF ZnTPP WITH BASES IN VARIOUS SOLVENTS[a]

base	solvent	temp. /°C	$\log_{10}$ (K/dm^2 mol^{-1})	no. of solutions	$a/10^{-5}$ mol dm^{-3}	$b/10^{-5}$ mol dm^{-3}	$(\bar{a}+\bar{b})/10^{-6}$ mol dm^{-3}	$\log_{10}(k_\mathrm{f}$ /dm^3 mol^{-1} s^{-1})	$\log_{10}(k_\mathrm{D}$ /s^{-1})	$\log[(k_\mathrm{f}/k_\mathrm{D})$ /dm^3 mol^{-1}]	$-\log$ $(k_\mathrm{f}/k_\mathrm{D})^c$
pyridine	BuCl	12.0	4.565	4	1-7	3-6.5	3-6	9.398 ± 0.005	—	—	0.90
		1.25	4.848	4	3.5-11	5-20	4-12	9.324 ± 0.03	—	—	0.90
		−5.0	5.021	4	3.5-11	5-20	3-11	9.230 ± 0.03	—	—	0.95
		−10.5	5.182	4	3.5-11	5-20	3-10	9.140 ± 0.05	—	—	1.00
		−15.5	5.334	4	2-10	3-20	2-11	9.033 ± 0.02	—	—	1.07
		−21.25	5.532	4	2-10	3-20	2-10	8.863 ± 0.04	—	—	1.19
		−83.0^b	—	5	0.03	0.04-0.35	0.04-0.3	7.695 ± 0.03	—	—	1.68
		−92.3^b	—	5	0.03	0.04-0.5	0.04-0.5	7.515 ± 0.03	—	—	1.72
		−98.0^b	—	7	0.03	0.1-1.5	0.1-1.5	7.362 ± 0.02	—	—	1.77
		−101.5^b	—	7	0.03	0.04-1.0	0.04-1	7.146 ± 0.01	—	—	1.93
	PhCl	9.8	4.155	5	4.7	4-27	6-25	8.918 ± 0.02	4.71 ± 0.06	4.21 ± 0.03	1.09
		3.6	4.336	5	4.7	4-27	5-24	8.837 ± 0.02	4.53 ± 0.05	4.31 ± 0.03	1.12
		−4.4	4.579	5	2.3, 4.7	2-15	3-12	8.818 ± 0.05	—	—	1.07
		−5.3	4.608	5	2.7, 4	2.5-13	4-10	8.755 ± 0.02	4.12 ± 0.03	4.64 ± 0.03	1.12
		−11.4	4.804	5	2.7, 4	2.5-13	3-10	8.733 ± 0.03	3.90 ± 0.13	4.83 ± 0.04	1.09
		−16.6	4.980	5	2.7, 4	2.5-13	2-10	8.668 ± 0.03	3.89 ± 0.11	4.88 ± 0.04	1.11
		−23.2	5.212	5	2.7, 4	2.5-13	2-9	8.606 ± 0.03	3.78 ± 0.12	4.83 ± 0.04	1.11
		−28.3	5.401	5	2.7, 4	2.5-13	2-9	8.521 ± 0.11	—	—	1.14

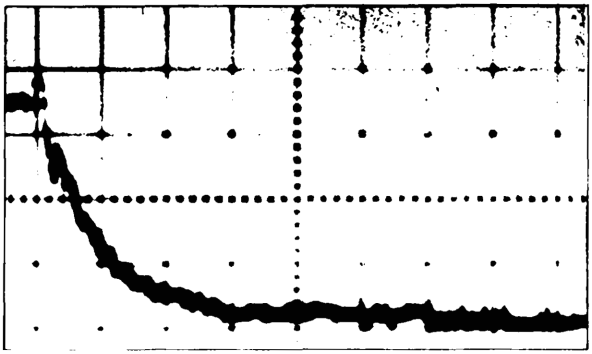
	PhCH$_3$	-71.6^b	6.920	5	0.14	0.15-0.3	0.7-1.9	7.968 ± 0.03	—	—	1.39
		-75.6^b	7.185	7	0.14	0.15-0.3	0.8-1.9	7.821 ± 0.01	—	—	1.48
		-80.2^b	7.366	7	0.14	0.1-0.45	0.4-3	7.696 ± 0.03	—	—	1.54
		-82.5^b	7.491	8	0.03	0.1-0.55	0.6-5	7.655 ± 0.02	—	—	1.55
		-84.6^b	7.608	6	0.14	0.1-0.25	0.3-1.3	7.589 ± 0.06	—	—	1.58
		-87.1^b	7.752	6	0.03	0.1-0.5	0.4-4.5	7.324 ± 0.03	—	—	1.81
		-88.8^b	7.852	7	1.4	0.1-0.5	0.3-3	7.173 ± 0.07	—	—	1.93
		-91.5^b	8.013	7	0.03	0.1-0.65	0.8-6	7.104 ± 0.04	—	—	1.96
							$10^5(\bar{a}+\bar{b})$				
2-Me-py	BuCl	-32.2	4.092	3	2-4	9-10	9-10	8.841 ± 0.07	4.40 ± 0.04	4.44 ± 0.11	1.10
		-40.6	4.346	3	3-5	3-14	4-12	8.763 ± 0.02	4.30 ± 0.03	4.46 ± 0.05	1.12
		-48.0	4.586	3	3-5	3-14	4-11	8.681 ± 0.01	3.86 ± 0.5	4.82 ± 0.5	1.13
		-55.0	4.827	3	3-5	3-14	3-11	8.688 ± 0.06	4.48 ± 0.2	4.21 ± 0.3	1.04
imidazole	BuCl	21.5	5.000	4	2-8	1.7-5	2-5	9.543 ± 0.04	—	—	0.85
		16.4	5.130	6	2-12	1.7-7	2-7	9.543 ± 0.02	—	—	0.80
		10.8	5.276	6	2-14	1.5-7	1.5-8	9.201 ± 0.01	—	—	1.10
		5.2	5.428	6	1-10	0.8-5	1-5	9.086 ± 0.02	—	—	1.16
		5.1	5.430	4	2-9	1.5-5	1-5	9.004 ± 0.08	—	—	1.25
		0.7	5.553	6	1-10	0.8-5	1-5	9.072 ± 0.02	—	—	1.14
		-100.6^b	—	5		0.7-7		5.25 ± 0.05	—	—	4.05

---

[a] A = ZnTPP, B = base. a, b = formal concentrations; $\bar{a}$, $\bar{b}$ = concentrations at equilibrium; [b] rates from stopped-flow measurements; otherwise from temperature-jump.
[c] k_D = diffusion-controlled rate constant calculated from the Smoluchowski equation.



(a)



(b)

FIG. 3.—Effect of signal-averaging on traces from Zn(TPP)+pyridine in chlorobenzene. (*a*) Trace from single microwave pulse, (*b*) signal-averaged trace from *ca.* 2000 pulses (in 200 s). Time-base, 20 μs per division.

different effects on the relaxation times observed at the two wavelengths, so adjustment is successful when the two relaxation times are equal. Slight adjustments may have to be made when the solvent is changed.

(*g*) Temperature-control to *ca.* ±0.1 °C is effected by circulating the reaction solution, by means of a peristaltic pump, through a coil immersed in a thermostat bath and thence into the microwave cell. (The use of a repetitive pulse requires a flowing solution in any case.) For temperatures down to −60 °C, the thermostat bath liquid is methanol; its temperature is controlled by cooling with a 'cold finger' containing cardice–acetone and heating intermittently by means of a commercial sealed heater unit, controlled by a thermistor. Alternatively a cryostat bath similar to that of Scott and Brickwedde,[20, 21] with freon as bath liquid, may be used; the temperature of the bath may be controlled to ±0.01 °C down to −100 °C.

(*h*) Spectrophotometric monitoring is facilitated by the large change of molar absorbance: Zn(TPP) shows an absorbance maximum at 544 nm in BuCl or 551 nm in PhCl with $\varepsilon \approx 25000$ dm^3 mol^{-1} cm^{-1}; the complexes have maxima at 562 nm ($\varepsilon \approx 25000$ dm^3 mol^{-1} cm^{-1}) and 602 ($\varepsilon \approx 9500$ cm^3 mol^{-1} cm^{-1}). The wavelength chosen for the monitoring light-beam was chosen according to the concentrations and the value of K, as either 540-550, 562-570 or 602 nm. (The Soret band could not be used, because of its very high molar absorbance; the value of K is such that the optimum concentration of the complex is of the order of 10^{-5} mol dm^{-3}, and the absorbance due to the Soret band at this concentration would be 5, which is much too large for the detection system.)

STOPPED-FLOW MEASUREMENTS

Measurements were also made with a low-temperature, stopped-flow apparatus, the half-life of the reaction being increased by taking advantage of the very high molar absorbance of the Soret band (*ca.* 5×10^5 dm^3 mol^{-1} cm^{-1} at $\lambda_{\text{max}} = 417$ nm) in ZnTPP and the shifted Soret band of the complex ($\lambda_{\text{max}} = 426$ nm), which allowed the use of concentrations below 10^{-6} mol dm^{-3}. These stopped-flow measurements considerably extended the temperature range for some of the systems, and for reactions in toluene they are the only ones available, since the microwave temperature-jump method is applicable only to fairly polar solvents. The apparatus used was of the Canterbury type[22] (Nortech Instruments), with cooling by liquid nitrogen. The temperature of the bath was controlled by a thermistor and measured with a quartz-crystal thermometer.

RESULTS

KINETIC RESULTS

The observed first-order rate constant k(obs) or τ^{-1} corresponding to the reaction scheme (1) is related to the forward and backward rate constants (k_f, k_b) and the equilibrium concentrations ($\bar{a}$, $\bar{b}$) by

$$k(\text{obs}) = k_f(\bar{a}+\bar{b})+k_b = k_b[K(\bar{a}+\bar{b})+1]. \qquad (2)$$

A plot of k(obs) against $(\bar{a}+\bar{b})$ should therefore be a straight line with a slope of k_f and an intercept of k_b. Straight lines were fitted to the data by a weighted-least-squares computer program. The results are shown in table 2. A plot of k(obs) against $[K(\bar{a}+\bar{b}+1)]$ should be a straight line through the origin; these plots are satisfactory. The stopped-flow experiments, with base in excess, give linear plots of k(obs) against b, whose slopes give k_f (table 2). Activation enthalpies for the forward reaction, $\Delta H_f^{\neq}$, and the corresponding activation entropies, $\Delta S_f^{\neq}$, were determined from plots of log k_f against $1/T$, by a weighted-least-squares computer program. These were also possible for the reverse reaction in some systems, but in others the values of k_b were too small. The results are summarised in table 3. For pyridine in chlorobenzene and 2-methylpyridine in chlorobutane, the plots are satisfactory; for pyridine in chlorobutane, the temperature-range is exceptionally long (−100 to +20 °C) and the agreement between temperature-jump and stopped-flow measurements at widely different temperatures is satisfactory. For pyridine in toluene and for imidazole in chlorobutane, the points are rather scattered and the error is relatively large.

TABLE 3.—KINETIC PARAMETERS FOR REACTIONS OF Zn(TPP) WITH BASES

base	solvent	max. temp./K	$\log_{10}k_f$[a] at 298 K	$\Delta H_f^{\neq}$	$\Delta H_b^{\neq}$	$\Delta H_b^{\neq} - \Delta H_f^{\neq}$	$-\Delta H^{\ominus}$[b]	$\Delta S_f^{\neq}$
pyridine	BuCl	285	9.55	3.9±0.05	—	—	9.4±0.6	−2.1±0.2
	PhCl	283	9.00	2.35±0.04	10.5±1.6	8.2±1.7	10.4±0.2	−9.8±0.2
	$PhCH_3$	201	[c]9.5±0.2	6.7±0.6	—	—	9.5±0.2	+8.2±3.0
2-Me-py	BuCl	241	[c]9.2±0.8	1.8±0.4	—	—	7.7±0.2	+10.5±2
imidazole	BuCl	294	9.5±0.5	7.5±0.2	—	—	9.7±1.5	+9.9±1

[a] k_f = forward rate constant/dm^3 mol^{-1} s^{-1}, at 298 K: [b] from table 1; [c] long extrapolation; ΔH in kcal mol^{-1}, ΔS in cal K^{-1} mol^{-1} (1 cal ≡ 4.184 J). All values by weighted-least-squares computation.

It is of interest to compare the temperature dependence of k_f with that of the

TABLE 4.—COMPARISON OF KINETIC PARAMETERS WITH DIFFUSION-CONTROLLED VALUES

base	solvent	temp. range/K	k_f/k_D 25 °C	k_f/k_D −30 °C	k_f/k_D −80 °C	$\Delta H_D^{\neq}$ /kcal mol^{-1}	$\Delta H_f^{\neq} - \Delta H_D^{\neq}$ [a] /kcal mol^{-1}
pyridine	BuCl	172-255	0.15	0.07	0.02	1.8	2.1 ± 0.05
	PhCl	245-283	0.08	0.08	[b]0.08	2.25	0.1 ± 0.04
	$PhCH_3$	182-207		0.3	0.03	2.0	4.7 ± 0.6
2-Me-py	BuCl	218-241	[b]0.07	0.08	[b]0.08	1.8	0.0 ± 0.4
imidazole	BuCl	172 ± 294	0.1	0.02	—	1.8	5.7 ± 0.5

[a] Values of $\Delta H_f^{\neq}$ from table 3; [b] long extrapolation. For the two-step mechanism, with the first step viscosity-controlled, the values of $(\Delta H_f^{\neq} - \Delta H_D^{\neq})$ in the last column represent $(\Delta H_2^{\neq} - \Delta H_1^{\neq})$; with the second step viscosity-controlled, they represent $\Delta H_1^{\ominus}$.[15] (1 cal ≡ 4.184 J.)

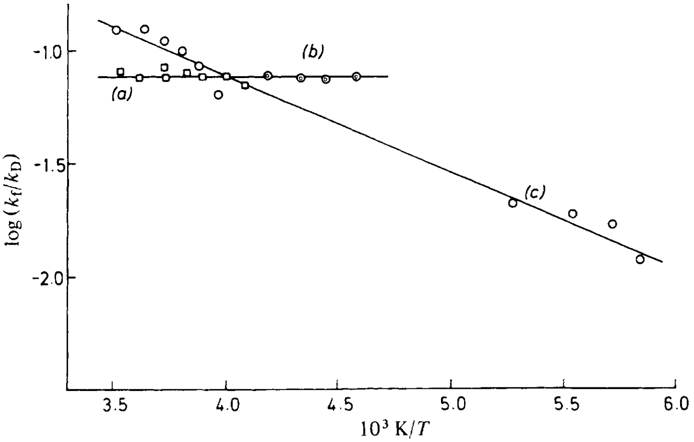


FIG. 4.—Arrhenius-type plots of $\log(k_f/k_D)$ against $1/T$ (where $k_D = 4\,RT/\eta$) for reactions of Zn(TPP) with ligand bases (*a*) pyridine in chlorobenzene, (*b*) 2-methylpyridine in 1-chlorobutane, (*c*) pyridine in 1-chlorobutane.

viscosity (η) of the solvent. This is conveniently done by comparing k_f at each temperature with the corresponding value of the diffusion-controlled rate constant k_D, taken as $4RT/\eta$. Values of $\log.(k_f/k_D)$ are given in table 2, and some of them are plotted against $1/T$ in fig. 4. Such plots facilitate the comparison of viscosity-controlled rates in different solvents. The slope gives the value of $(\Delta H_f^{\neq} - \Delta H_D^{\neq})$, *i.e.* the difference between the experimental value of $\Delta H_f^{\neq}$ and the value calculated for diffusion control from the temperature coefficient of viscosity. The numerical data are collected in table 4.

ENTHALPIES OF SOLUTION

A few experiments were done to determine rough maximum values for enthalpies of solution of the reagents. For the bases, simple calorimetry was used; the enthalpy of solution was found to be < 0.3 kcal mol^{-1} for pyridine in chlorobutane, chlorobenzene and toluene, and for 2-methylpyridine in chlorobutane. For Zn(TPP) in chlorobutane, the method was inconvenient because the solubility is low; the enthalpy was calculated from the solubility determined at -30 and -60 °C, and was found to be < 0.1 kcal $\mathrm{mol^{-1}}$.

DISCUSSION

EQUILIBRIUM CONSTANTS

The equilibrium constants at 25 °C (table 1) are in the range 10^2–10^5 $\mathrm{dm^3\ mol^{-1}}$. For a given solvent (chlorobutane or chlorobenzene), the variations from base to base are due to the variations in $\Delta H^{\ominus}$, while $\Delta S^{\ominus}$ is approximately constant. The reactions are all markedly exothermic. The standard entropy changes are all negative, *ca.* -12 cal $\mathrm{K^{-1}\ mol^{-1}}$ (50 J $\mathrm{K^{-1}\ mol^{-1}}$) for reactions in chlorobutane and *ca.* -17 cal $\mathrm{K^{-1}\ mol^{-1}}$ (70 J $\mathrm{K^{-1}\ mol^{-1}}$) for reactions in chlorobenzene. The fact that the values both of $\Delta H^{\ominus}$ and of $\Delta S^{\ominus}$ are uniformly more negative in chlorobenzene than in chlorobutane may indicate that there is weaker solvation of the bases in chlorobenzene. If we compare the various bases, the relative values of K and of $\Delta H^{\ominus}$ should be related to their electron-donating power;[5] the observed values then indicate the order of donor strength as imidazole > pyridine > 2-methylpyridine.

RATE AND ACTIVATION PARAMETERS

The forward rate constants k_f at 25 °C (table 3) are all in the range 10^9-10^{10} $\mathrm{dm^3\ mol^{-1}\ s^{-1}}$, and are not far from the value of k_D $(= 4\boldsymbol{R}T/\eta)$, while the activation enthalpy $\Delta H_\mathrm{f}^{\neq}$ varies from a value nearly equal to $\Delta H_\mathrm{D}^{\neq}$ to one 5.7 kcal $\mathrm{mol^{-1}}$ (24 kJ $\mathrm{mol^{-1}}$) higher. Here k_D and $\Delta H_\mathrm{D}^{\neq}$ are the values calculated for spherical molecules without steric requirements, moving in a homogeneous fluid and reacting at every encounter. If this model applied to our reactions, we should expect $k_\mathrm{f} = k_\mathrm{D}$ and $\Delta H_\mathrm{f}^{\neq} - \Delta H_\mathrm{D}^{\neq}$ $(\equiv \Delta\Delta H^{\neq}) = 0$, at all temperatures. None of the systems in table 4 obeys the first relation, although two out of five obey the second. This simple one-step model, without activation or geometrical constraints, is evidently inadequate. A model which takes into account the effects of geometrical factors, *i.e.* the sizes of the molecules and of their reactive sites, as well as diffusion, has been considered by Schmitz and Schurr,[23, 24] who envisaged a single-step reaction involving translational and rotational diffusion of two mobile orientable spheres, of comparable radii, the small sphere having a limited reaction site. The result can account for $k_\mathrm{f} < k_\mathrm{D}$, but not for values of $\Delta H_\mathrm{f}^{\neq}$ which are markedly different from those of $\Delta H_\mathrm{D}^{\neq}$, as observed.

Comparisons of the changes in activation enthalpy $(\Delta H_\mathrm{f}^{\neq})$ and activation entropy $(\Delta S_\mathrm{f}^{\neq})$ are of interest. The effects on the rate of the changes in $\Delta H_\mathrm{f}^{\neq}$ and $\Delta S_\mathrm{f}^{\neq}$ are largely compensatory. The entropies of activation for the three bases in chlorobutane are linearly related to the enthalpies, with a correlation coefficient of 0.998; and similarly the values of $\Delta S_\mathrm{f}^{\neq}$ and $\Delta H_\mathrm{f}^{\neq}$ for pyridine in the three solvents (chlorobutane, chlorobenzene and toluene) are linearly related, with a correlation coefficient of 0.99998. Such correlations are often found in a series of similar reactions, and may be interpreted as indicating that solvation or bonding changes vary along the series. Geometrical restrictions do not appear to be capable of explaining such a correlation.

An activation requirement for effective encounter, as well as correct geometrical orientation, is embodied in Noyes' treatment[25] of a one-step model [eqn (5) of ref. (15)]. Two-step models with similar assumptions have also been developed.[15] In all these treatments, a value of $\Delta H_\mathrm{f}^{\neq}$ in excess of $\Delta H_\mathrm{D}^{\neq}$, *i.e.* a positive value of $\Delta\Delta H^{\neq}$, may be interpreted in terms of solvation or bonding changes contributing to the activation energy.

For a comparison of bases in the same solvent, we have the series 2-methylpyridine, pyridine and imidazole, in chlorobutane. The rate constant at 25 °C is the same within experimental error for all three bases, but $\Delta\Delta H^{\neq}$ increases markedly in the series (0, 2.1 and 5.7 kcal mol^{-1}), in the same order as K and $-\Delta H^{\ominus}$, *i.e.* with increasing electron-donor strength of the base.[5-7] This is the reverse of the order that would be expected if the step requiring activation energy were the reaction between ZnTPP and unsolvated base, and suggests that the activation energy is required to desolvate the base. The relatively large value of $\Delta\Delta H^{\neq}$ for imidazole is attributable to the strong solute–solvent interaction which will result from its large dipole moment (*ca.* 4 D) and its ability to donate hydrogen bonds (which chlorobutane can accept[26,27]).

We can also compare the behaviour of pyridine in the series of solvents chlorobenzene, chlorobutane and toluene. The rate constants at 25 °C are again much the same, but $\Delta\Delta H^{\neq}$ increases considerably in the series (0, 2.1 and 4.7 kcal mol^{-1}). The increase from chlorobenzene to chlorobutane can be attributed to the more polar character of the latter, which will solvate pyridine more strongly; but the further increase with toluene cannot be understood in this way (the dipole moments of the solvent molecules are, respectively, 1.56, 2.0 and 0.38 Debye). Toluene is known to solvate ZnTPP, however,[28] by π–π interaction between the aromatic rings,[29] with a solvation energy in the region of 1-2 kcal mol^{-1}, and it seems likely that desolvation of the ZnTPP molecule rather than the base is here the major requirement.

In summary, it appears that in these reactions diffusion and activation are both involved, in varying degrees, and that the activation energy is due mainly to the need for desolvation, either of base or of ZnTPP, depending on the system.

We acknowledge S.R.C. support, including a postdoctoral post for J.P.F.; also preliminary work on signal-averaging by Dr B. H. Robinson and Dr R. Day, and helpful discussions with them and with Dr F. Ann Walker and Dr R. S. Drago.

[1] *Porphyrins and Metalloporphyrins*, ed. K. E. Smith (Elsevier, Amsterdam, 1975).
[2] J. R. Miller and G. B. Dorough, *J. Am. Chem. Soc.*, 1952, **74**, 3977.
[3] C. H. Kirksey, P. Hambright and C. B. Storm, *Inorg. Chem.*, 1969, **8**, 2141.
[4] M. Nappa and J. S. Valentine, *J. Am. Chem. Soc.*, 1978, **100**, 5075.
[5] D. Gust and D. N. Neal, *J. Chem. Soc., Chem. Commun.*, 1978, 681.
[6] G. C. Vogel and J. R. Stahlbusch, *Inorg. Chem.*, 1977, **16**, 950.
[7] G. C. Vogel and B. A. Beckmann, *Inorg. Chem.*, 1976, **15**, 483.
[8] D. M. Collins and J. L. Hoard, *J. Am. Chem. Soc.*, 1970, **92**, 3761.
[9] A. D. Adler, F. R. Longo, J. D. Finarelli, J. Goldmacher, J. Assar and L. Korsakoff, *J. Org. Chem.*, 1967, **32**, 476.
[10] G. M. Badger, R. A. Jones and P. L. Laslett, *Austr. J. Chem.*, 1964, **17**, 1028.
[11] G. H. Barnett, M. F. Hudson and K. M. Smith, *J. Chem. Soc., Perkin Trans. 1*, 1975, 1401.
[12] G. H. Barnett, M. F. Hudson and K. M. Smith, *Tetrahedron Lett.*, 1973, 2887.
[13] G. C. Vogel and L. A. Searby, *Inorg. Chem.*, 1973, **12**, 936.
[14] E. F. Caldin and J. E. Crooks, *J. Sci. Instrum.*, 1967, **44**, 449.
[15] G. D. Burfoot and E. F. Caldin, *J. Chem. Soc., Faraday Trans. 1*, 1976, **72**, 963.
[16] H. E. Buchwald and H. Rüppel, *J. Phys. E*, 1971, **4**, 105.
[17] H. Rüppel and H. J. Witt, in *Methods in Enzymology*, vol. XVI, *Fast Reactions*, ed. K. Kustin (Academic Press, New York, 1969), p. 337.
[18] J. Aubard, J. M. Nozeran, P. Levoir, J. J. Meyer and J. E. Dubois, *Rev. Sci. Instrum.*, 1979, **50**, 52.
[19] C. J. Wilson, in preparation; E. F. Caldin, C. J. Wilson and O. Rogne, *J. Chem. Soc., Faraday Trans. 1*, 1978, **74**, 1796.
[20] R. B. Scott and F. G. Brickwedde, *J. Res. Natl. Bur. Stand.*, 1931, **6**, 401.
[21] C. R. Allen, A. J. W. Brook and E. F. Caldin, *Trans. Faraday Soc.*, 1960, **56**, 788.
[22] E. F. Caldin, J. E. Crooks and A. Queen, *J. Phys. E*, 1973, **6**, 930.
[23] K. S. Schmitz and J. M. Schurr, *J. Phys. Chem.*, 1972, **76**, 534.
[24] J. M. Schurr and K. S. Schmitz, *J. Phys. Chem.*, 1976, **80**, 1934.
[25] R. M. Noyes, *Prog. React. Kinet.*, 1961, **1**, 129.

[26] E. M. Arnett, L. Joris, E. Mitchell, T. S. S. R. Murty, T. M. Garrie and P. v. R. Schleyer, *J. Am. Chem. Soc.*, 1970, **92**, 2365.

[27] R. L. Benoit and C. Louis, in *The Chemistry of Non-aqueous Solvents*, ed. J. J. Lagowski (Academic Press, London, 1978), vol. VA, chap. 2, p. 914.

[28] W. R. Scheidt, M. E. Kastner and K. Hatano, *Inorg. Chem.*, 1978, **17**, 706.

[29] F. Ann Walker and M. Benson, *J. Am. Chem. Soc.*, 1980, **102**, 5530, and earlier papers.

(PAPER 1/1298)