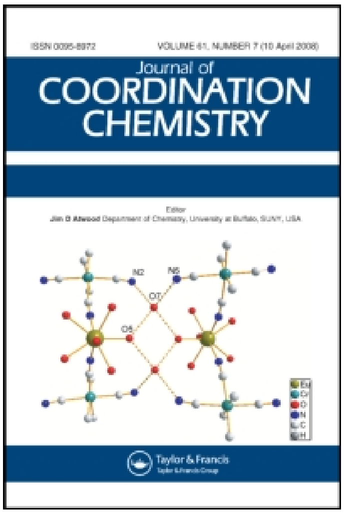

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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First published on: 22 July 2010

To cite this Article Jones, John G. , Mcknight, John and Twigg, Martyn V.(2010) 'Replacement of imidazoles by azide at an iron(III) porphyrin center: part 1 replacement of *N*-methylimidazole in *bis*-(*N*-methylimidazole)tetraphenylporphyrinato iron(III)', Journal of Coordination Chemistry, 63: 14, 2766 — 2778, First published on: 22 July 2010 (iFirst)

To link to this Article: DOI: 10.1080/00958972.2010.503274

URL: http://dx.doi.org/10.1080/00958972.2010.503274

Journal of Coordination Chemistry
Vol. 63, Nos. 14–16, 20 July–20 August 2010, 2766–2778

Replacement of imidazoles by azide at an iron(III) porphyrin center: part 1 replacement of *N*-methylimidazole in *bis*-(*N*-methylimidazole)tetraphenylporphyrinato iron(III)

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(*Received 30 March 2010; in final form 27 April 2010*)

Addition of tetra-*n*-butylammonium azide to acetone solutions of the tetraphenylporphyrinato iron(III) complex $[Fe(TPP)(MeIm)_2]^+N_3^-$ formed *in situ* from the reaction of *N*-methylimidazole and $[Fe(TPP)N_3]$ afforded equilibrium amounts of $[Fe(TPP)(MeIm)_2]^+$ and $[Fe(TPP)(MeIm)N_3]$. Equilibrium experiments made using a range of known concentrations of added tetra-*n*-butylammonium azide and *N*-methylimidazole using stopped-flow apparatus gave an estimate of about 50 for the equilibrium constant for the formation of $[Fe(TPP)(MeIm)N_3]$ from the addition of azide to $[Fe(TPP)(MeIm)_2]^+$. Kinetic studies indicated that the substitution of azide ion by *N*-methylimidazole is a dissociative process, and the results were interpreted using a stationary state approach in which $[Fe(TPP)(MeIm)]^+$ was the transient intermediate that discriminated in favor of the reaction with azide as opposed to the reaction with *N*-methylimidazole by about a factor of two. Loss of *N*-methylimidazole from $[Fe(TPP)(MeIm)_2]^+$ is at least 50 times faster than that from the product $[Fe(TPP)(MeIm)N_3]$. Using calculated values of free azide concentrations from experimentally determined ion-pair formation constants led to success in rationalizing results obtained under different conditions.

Keywords: Azide; *N*-methylimidazole; Tetraphenylporphyriniron(III); $[Fe(TPP)(MeIm)_2]^+$; $[Fe(TPP)(MeIm)N_3]$; Ion-pair formation; Stopped-flow

1. Introduction

Previously, we reported [1] the results of a study on the kinetics and equilibria involved in the two-step formation of $[Fe(TPP)(MeIm)_2)]^+N_3^-$ from $[Fe(TPP)N_3]$ and MeIm*, equations (1) and (2). This differed from the earlier studies [2–11] using [Fe(TPP)X] $(X = F, Cl)$ in that the intermediate in this study, $[Fe(TPP)(MeIm)N_3]$, is stable at room temperature and can be prepared as a crystalline solid [12]. It contains iron in the low-spin Fe(III) state, whereas intermediates in the earlier studies, [Fe(TPP)(N-base)Cl]

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2010 Taylor & Francis
DOI: 10.1080/00958972.2010.503274

and [Fe(TPP)(N-base)F], are only transiently stable at −40°C and have optical spectra characteristic of high-spin Fe(III) compounds [2–11, 13–16]. In our previous work [1], we found that the second stage reaction, equation (2), was rate determining, and kinetic and thermodynamic parameters were determined for this reaction.

$$[\mathrm{Fe(TPP)N_3}] + \mathrm{MeIm} = [\mathrm{Fe(TPP)(MeIm)N_3}] \tag{1}$$

$$[\mathrm{Fe(TPP)(MeIm)N_3}] + \mathrm{MeIm} = [\mathrm{Fe(TPP)(MeIm)_2}]^+ + \mathrm{N_3^-} \tag{2}$$

Equilibrium parameters were also determined for the fast interconversion of $[\mathrm{Fe(TPP)N_3}]$ and $[\mathrm{Fe(TPP)(MeIm)N_3}]$ in the presence of excess MeIm. A free-energy profile was constructed for the two-stage formation of $[\mathrm{Fe(TPP)(MeIm)_2}]^+\mathrm{N_3^-}$ from $[\mathrm{Fe(TPP)N_3}]$ and the results compared with those for related Fe(III) porphyrin systems.

We have now found that the second stage reaction, equation (2), can be reversed in the presence of MeIm by the addition of an excess of tetra-*n*-butylammonium azide ($\mathrm{N}(n\text{-}\mathrm{C_4H_9})_4\mathrm{N_3}$) using the same solvent that was used previously, dry acetone. The product is $[\mathrm{Fe(TPP)(MeIm)N_3}]$ and under the conditions of this study, which were essentially the same as those used previously [1]. But with added azide present, there was no evidence for the transformation of $[\mathrm{Fe(TPP)(MeIm)N_3}]$ to $[\mathrm{Fe(TPP)N_3}]$. However, now both the concentration of MeIm and $\mathrm{N_3^-}$ were in excess and effectively constant and well defined throughout the course of the reactions because each was substantially more than the total concentration of the porphyrin complexes present. In our earlier study, $\mathrm{N_3^-}$ in solution was only derived from the dissociation of $[\mathrm{Fe(TPP)N_3}]$ and so its concentration varied during the reactions from around zero at the beginning to about $2 \times 10^{-5}\,\mathrm{mol\,L^{-1}}$ at the end of the reaction.

Our finding that reaction (2) is reversible enabled a thorough investigation of this reaction, particularly of the thermodynamic equilibrium, by varying the concentration of both $\mathrm{N_3^-}$ and MeIm. Using higher concentrations of $\mathrm{N_3^-}$ meant that the possibility of ion pairing might have been important, and $\mathrm{N_3^-}$ in acetone (dielectric constant 20.7) is likely to be partitioned between free $\mathrm{N_3^-}$ and ion-paired $\mathrm{N_3^-}$, thereby reducing the effective concentration of $\mathrm{N_3^-}$. These effects are considered in this article, along with the results obtained by keeping the total concentration of electrolyte constant using tetra-*n*-butylammonium perchlorate ($\mathrm{N}(n\text{-}\mathrm{C_4H_9})_4\mathrm{ClO_4}$). Full details of the conductance studies that established the ion-pairing constants used in this article will be described in a subsequent publication.

2. Experimental

2.1. *Liquids*

Dimethylformamide (DMF, reagent grade BDH) was distilled from calcium hydride under a reduced pressure of nitrogen and used immediately. Acetone (AnalaR) was dried over molecular sieves (Linde 4A, activated at 200°C for 4 h at 10 mm Hg). The dry acetone was filtered through an oven-dried sintered-glass filter and kept in a sealed flask in a dry box. *N*-methylimidazole (Aldrich) was dried over crushed KOH and distilled from calcium hydride and kept under dry nitrogen over activated molecular sieves (Linde 4A).

2.2. *Solids*

Iron(III) tetraphenylporphyrin azide, [Fe(TPP)N_3], was prepared from spectroscopically pure tetraphenylporphyrin *via* iron insertion to give [Fe(TPP)Cl], followed by alkali treatment to form $[(Fe(TPP))_2O]$, and final conversion to the azide using a dilute aqueous solution of hydrazoic acid as detailed below.

2.2.1. Preparation of [Fe(TPP)Cl]. Spectroscopically pure tetraphenylporphyrin (2.94 g), obtained from the Rothenmund reaction [17, 18], that had been treated with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) [19] to remove traces of chlorin, was dissolved in dry DMF (550 mL). The solution was brought to reflux and anhydrous $FeCl_2$ (2.0 g) dissolved in the minimum amount of dry DMF was added, and refluxing continued for 0.5 h. After allowing the solution to cool, it was filtered through sintered glass and the retained crystals extracted with dichloromethane. The remaining filtrate was poured into an equal volume of distilled water and the product extracted with dichloromethane. The combined dichloromethane extracts were evaporated in the presence of a small amount of added methanol and crystallization ensued. The product obtained by filtration was washed with pentane and dried at 60°C for 2 h. If the visible spectrum of the product showed the characteristic narrow bands of unconverted $(TPP)H_2$, the purification treatment was repeated to give complete conversion. The yield of spectroscopically pure [Fe(TPP)Cl] was typically 80%.

2.2.2. Preparation of $[(Fe(TPP))_2O]$ (μ-oxo-dimer). Dichloromethane (500 mL, AnalaR) was deacidified by shaking with aqueous NaOH 100 mL ($2\,mol\,L^{-1}$) in a separating funnel, and the lower layer dried with two successive treatments of anhydrous $CaCl_2$. In a typical preparation, [Fe(TPP)Cl] (800 mg) in dry dichloromethane (50 mL) was shaken with three successive portions of aqueous NaOH (100 ml, $2\,mol\,L^{-1}$). The dark brown lower layer was separated and dried over anhydrous Na_2CO_3. The spectrum of the μ-oxo-dimer had distinguishing peaks in the visible spectrum at 408, 570, and 610 nm, and its final purification was by column chromatography. The dried dichloromethane extracts were transferred to a chromatography column (60 mL) containing alkaline alumina (30 mL) and eluted with dry de-acidified dichloromethane. The main band near the top of the column was preceded by a pale green band. The brown eluate solution had the spectrum of $[Fe(TPP)_2O]$, and its volume was reduced by 75% on a rotary evaporator and the product precipitated by the addition of methanol; the crystals were collected by filtration and dried at 80°C for 2 h. The yield was typically greater than 90%.

2.2.3. Preparation of [Fe(TPP)N_3]. The method employed was a modification of that of Summerville and Cohen [20]. Hydrazoic acid solution was prepared by passing a saturated aqueous NaN_3 solution (150 mL) through an acid cation ion-exchange column (50W-X8, 125 mL). The resulting solution was then shaken with $[Fe(TPP)_2O]$ (400 mg) in freshly distilled benzene (300 mL) and the mixture allowed to stand for 0.5 h. The aqueous layer was then discarded and the benzene layer washed three times with an equal volume of distilled water, dried over anhydrous $MgSO_4$, and filtered. After reducing the volume of the filtrate to one-third on a rotary evaporator (with exclusion of moisture), pentane was added to give crystals of the product, which were separated by filtration and dried (4 h at 60°C). The yield was 92%. The product was discarded if its visible spectrum in dry acetone had bands characteristic of $[Fe(TPP)_2O]$ (570 and 610 nm), resulting from incomplete conversion of the reactant or hydrolysis of $[Fe(TPP)N_3]$. None of the $[Fe(TPP)N_3]$ used in the present stopped-flow experiments contained $[(Fe(TPP))_2O]$, and elemental analyses were similar to or better than those reported previously.

2.2.4. Tetra-*n*-butylammonium perchlorate. $N(n\text{-}C_4H_9)_4ClO_4$ was prepared by adding a concentrated aqueous solution of $N(n\text{-}C_4H_9)_4OH$ (Aldrich) to a saturated solution of $NaClO_4$. The resulting white precipitate was harvested by filtration, washed, and recrystallized from aqueous methanol, and then dried over phosphorus pentoxide in a vacuum desiccator.

2.2.5. Tetra-*n*-butylammonium azide. $N(n\text{-}C_4H_9)_4N_3$ was prepared from a concentrated aqueous solution of $N(n\text{-}C_4H_9)_4OH$ and saturated NaN_3 according to the procedure outlined by Brandstrom *et al.* [21]. In a typical preparation, $N(n\text{-}C_4H_9)_4OH$ solution (Aldrich) (10 mL 40%) was diluted with an equal volume of distilled water and extracted three times with deacidified chloroform (shaken with sodium hydroxide solution) to remove traces of $N(n\text{-}C_4H_9)_4Br$ that was often present in the commercial $N(n\text{-}C_4H_9)_4OH$ solutions. The purified aqueous $N(n\text{-}C_4H_9)_4OH$ solution was mixed with a saturated solution of NaN_3 (2.0 g). A white precipitate formed that re-dissolved, and the desired product was isolated by the extraction with chloroform, evaporation of the solution to dryness, and removal of remaining traces of chloroform in vacuo over phosphorus pentoxide. The pure product was obtained by recrytallization from dry benzene or toluene. Analyses were typically $C = 67.2\%$, $H = 13.0\%$, and $N = 20.1\%$; $C_{16}H_{36}N_4$ requires: $C = 67.53\%$, $H = 12.78\%$, and $N = 19.69\%$. It was confirmed that no bromide was present in the product and it was observed by the oxidation of azide with acidic $NaNO_2$ in a procedure based on that of Vogel [22, 23] followed by titration with mercuric nitrate at pH 3 to estimate bromide. Total azide was estimated using Arnold's method with ammonium ceric sulfate [24].

2.3. *Kinetic and equilibrium measurements*

Kinetic and equilibrium measurements were made using stopped-flow equipment and procedures described previously [1].

3. Results and discussion

3.1. *Conductance studies*

Ion-pair formation constants for $\left[Fe(TPP)(MeIm)_2\right]^+N_3^-$, $N(n\text{-}C_4H_9)_4^+ClO_4^-$, and $N(n\text{-}C_4H_9)_4^+N_3^-$ in dry acetone (with rigorous exclusion of moisture) were determined from conductance measurements. All of the compounds behaved as weak electrolytes, and the values of the determined ion-pair formation constants collected in table 1 were

Table 1. Ion-pair formation constants (K_{IP}) for selected salts in dry acetone at 25.0°C.

Salt	K_{IP}	Source
$N(n\text{-}C_4H_9)_4^+ClO_4^-$	104	[32]
$N(n\text{-}C_4H_9)_4^+N_3^-$	335	[33]
$[Fe(TPP)(MeIm)_2]^+N_3^-$	335 est.	[33][a]

[a] Measurements made in the presence of 5 mol L^{-1} MeIm to ensure the complete formation of $[Fe(TPP)(MeIm)_2]^+$.

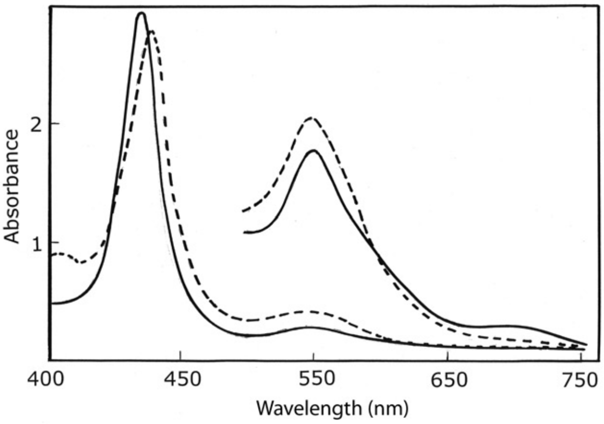

Figure 1. Visible spectrum of $[Fe(TPP)(MeIm)_2]^+$ in dry acetone at 25°C (————) and in the presence of excess added $N(n\text{-}C_4H_9)_4N_3$ (– – – –). The inset has the absorbance scale increased by a factor of five.

used to calculate the proportion of N_3^- present as free ionic and ion-paired species in the reactant solutions used in this study.

3.2. *Equilibrium measurements*

Stopped-flow equipment was used to monitor the progress of the reaction when an acetone solution of $[Fe(TPP)N_3]$ was mixed with a solution of MeIm. The disparity in the fast formation of $[Fe(TPP)(MeIm)N_3]$ and the much slower reaction to give the final product $[Fe(TPP)(MeIm)_2]N_3$ enabled the equilibrium constant for the first reaction, equation (1), to be estimated. Thus addition of a solution of $N(n\text{-}C_4H_9)_4N_3$ to one of $[Fe(TPP)(MeIm)_2]N_3$ generated *in situ* from $[Fe(TPP)N_3]$ and MeIm gave a distinct change in the optical spectrum, as shown in figure 1. The absorbance changes were greatest at 445 and 550 nm.

Addition of a solution of $[Fe(TPP)N_3]$ containing different amounts of $N(n\text{-}C_4H_9)_4N_3$ at 25°C to one of MeIm so that the final concentration of MeIm was 0.01 mol L^{-1} resulted in the absorbance changes listed in table 2, where A_S is the absorbance of the intermediate $[Fe(TPP)(MeIm)N_3]$ immediately after the first reaction, A_E the absorbance when the reaction reached equilibrium, and A_F the absorbance if the

Table 2. Absorbance changes following mixing equal volumes of dry acetone solutions of $[Fe(TPP)N_3]$ containing different amounts of $N(n\text{-}C_4H_9)_4N_3$ to one of MeIm ($0.02\,mol\,L^{-1}$) so that the final concentration of MeIm was $0.01\,mol\,L^{-1}$ at 25.0°C.

$[N_3^-]$	A_S	A_E	A_F	ΔA_1	ΔA_2
0			0.19		
0.00125	0.645	0.578	0.19	0.067	0.388
0.0025	0.592	0.575	0.19	0.017	0.385
0.0045	0.641	0.623	0.19	0.018	0.433
0.005	0.650	0.641	0.19	0.009	0.451
0.01	0.664	0.655	0.19	0.009	0.465

See text for definitions of the absorbance symbols.

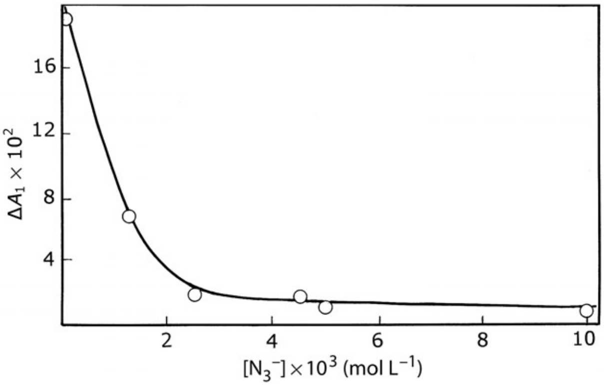

Figure 2. Absorbance changes at 445 nm when $N(n\text{-}C_4H_9)_4N_3$ was added to an acetone solution of $[Fe(TPP)(MeIm)_2]^+$ containing $0.01\,mol\,L^{-1}$ MeIm at 25°C with the total porphyrin concentration of about $5\times10^{-5}\,mol\,L^{-1}$.

reaction had gone to completely transform $[Fe(TPP)N_3]$ into $[Fe(TPP)(MeIm)_2]N_3$. The term A_F was measured by mixing the porphyrin solution containing no added $N(n\text{-}C_4H_9)_4N_3$ to the MeIm solution. It can be shown that $\Delta A_1 = (A_S - A_E)$ is proportional to the amount of $[Fe(TPP)(MeIm)_2]N_3$ present at equilibrium, and that $\Delta A_2 = (A_E - A_F)$ is proportional to the amount of $[Fe(TPP)(MeIm)N_3]$ at equilibrium. Then the equilibrium constant for the reaction in equation (1) is given by equation (3), provided $[MeIm] \gg [Fe(TPP)N_3]$, and $[N(n\text{-}C_4H_9)_4N_3] \gg [Fe(TPP)N_3]$.

$$K = \Delta A_1[N(n\text{-}C_4H_9)_4N_3]/\Delta A_2[MeIm] \tag{3}$$

This treatment depends heavily on the actual values of A_S and A_F and can be subject to considerable error; similarly ΔA_1 values become small as $[N(n\text{-}C_4H_9)_4N_3]$ increases relative to [MeIm], and all of these effects contribute to the total error associated with K. Averaging the five values of K calculated from the data in table 2 gave $K = 67 \pm 23$ for reaction (4).

$$[Fe(TPP)(MeIm)_2)]^+ + N_3^- \rightleftarrows [Fe(TPP)(MeIm)N_3] + MeIm \tag{4}$$

Figure 2 shows these results graphically in the form of a plot of ΔA_1 against increasing $[N(n\text{-}C_4H_9)_4N_3]$ indicating the extent to which the amount of

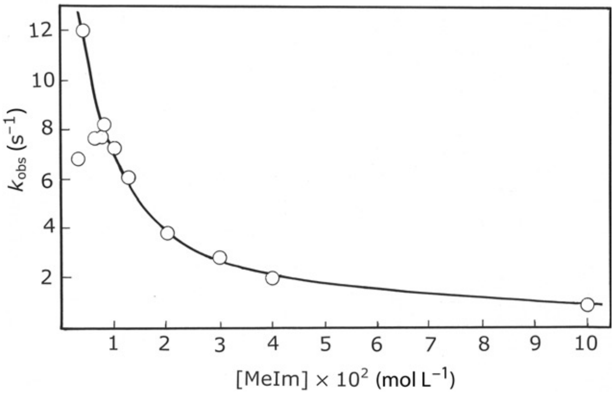

Figure 3. Variation of the observed first-order rate constant (k_{obs}) for the conversion of $[Fe(TPP)(MeIm)_2]^+$ to $[Fe(TPP)(MeIm)N_3]$ in the presence of $N(n\text{-}C_4H_9)_4N_3$ (2.75×10^{-3} mol L^{-1}) and varying concentrations of MeIm in dry acetone.

$[Fe(TPP)(MeIm)_2]^+$ decreased as the reaction proceeded, entirely in line with the equilibrium nature of the reaction.

3.3. *Kinetic studies*

Adding azide, as $N(n\text{-}C_4H_9)_4N_3$, to a solution of $[Fe(TPP)(MeIm)_2]^+$ gave the neutral product $[Fe(TPP)(MeIm)N_3]$ and this reaction could be studied by the stopped-flow method. In these experiments, an acetone solution of $[Fe(TTP)N_3]$ that had been converted to $[Fe(TPP)(MeIm)_2]^+$ by addition of a known excess of MeIm was mixed with a solution containing a known amount of $N(n\text{-}C_4H_9)_4N_3$. The resulting absorbance increases at 445 nm were analyzed as accurate first-order processes to give observed first-order rate constants. In figure 3, results are presented which show the effect of adding the same amount of azide (2.75×10^{-3} mol L^{-1} in the mixed solution) to solutions containing varying amounts of MeIm. The observed first-order rate constants decreased as the concentration of MeIm increased, and in figure 4, it is shown that their values were inversely proportional to the concentration of MeIm present. This behavior is characteristic of a dissociative ligand-replacement reaction involving a transient intermediate [25], and previously high pressure techniques, refined and extensively used by van Eldik and his coworkers [26–28], demonstrated the dissociative nature of other axial ligand exchange reactions at iron porphyrin centers [29]. Equation (5) characterizes this process in terms of the stationary state intermediate $[Fe(TPP)(MeIm)]^+$, formed by the fission of one Fe–N bond in the *bis*-MeIm complex. Since the concentration of added azide is over 100-fold greater than that from $[Fe(TPP)N_3]$, only the amount added is considered in deriving equation (6) for the observed rate constant based on the mechanism in equation (5).

$$[Fe(TPP)(MeIm)_2]^+ \underset{k_2[MeIm]}{\overset{k_1}{\rightleftarrows}} [Fe(TPP)(MeIm)]^+ + MeIm \underset{k_4}{\overset{k_3[N_3^-]}{\rightleftarrows}} [Fe(TPP)(MeIm)N_3] \tag{5}$$

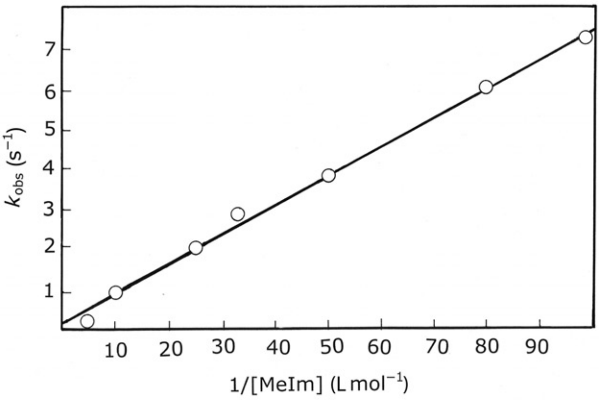

Figure 4. Plot of the observed rate constant (k_{obs}/s^{-1}) against 1/[MeIm] for the addition of azide (N(n-C_4H_9)$_4N_3$, 2.75×10^{-3} mol L^{-1}) to $[Fe(TPP)(MeIm)_2]^+$ in the presence of varying concentrations of MeIm in dry acetone.

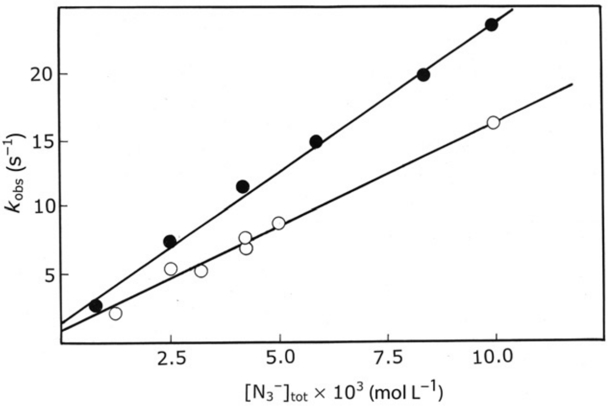

Figure 5. Plots of k_{obs} (s^{-1}) for the addition of azide (N(n-C_4H_9)$_4N_3$) to $[Fe(TPP)(MeIm)_2]^+$ in the presence of a constant concentration MeIm (open points 0.02 mol L^{-1}, solid points 0.01 mol L^{-1}) at 25°C with total ionic strength 0.01 mol L^{-1} in dry acetone.

$$k_{obs} = (k_1k_3[N_3^-] + k_2k_4[MeIm])/(k_2[MeIm] + k_3[N_3^-]) \quad (6)$$

$$k_{obs} = k_1k_3[N_3^-]/k_2[MeIm] + k_4 \quad (7)$$

Only by assuming that $k_2[MeIm] \gg k_3[N_3^-]$ is a simplified expression of the correct form, equation (7), obtained which explains the dependence of observed rate constant on added MeIm in the presence of constant added azide. Equation (7) also explains the linear dependence of observed rate constant on added azide in the presence of a constant concentration of MeIm as described below.

In experiments where the concentration of MeIm was kept constant but the concentration of azide was varied, the observed rate constants changed in an almost linear fashion with total added azide concentration, as shown in figure 5 for [MeIm] = 0.01 and 0.02 mol L^{-1}, respectively. The linearity was better when

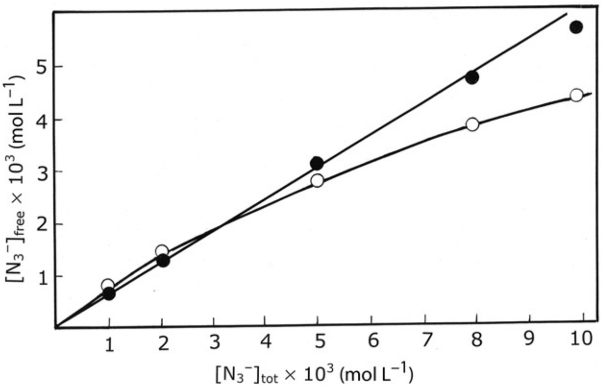

Figure 6. Plots of calculated $[N_3^-]_{free}$ against total added $[N(n\text{-}C_4H_9)_4N_3]$ for azide/perchlorate mixtures (constant ionic strength, solid points) and $[N(n\text{-}C_4H_9)_4N_3]$ alone (open points) in dry acetone at 25°C.

0.02 mol L^{-1} MeIm was present. The total ionic strength was kept constant for the results shown in figure 5 at 0.01 mol L^{-1} with $N(n\text{-}C_4H_9)_4ClO_4$, and there were also experiments performed without added $N(n\text{-}C_4H_9)_4ClO_4$.

In figure 4, the slope 0.066 represents $k_1k_3[N_3^-]/k_2$ with $[N_3^-] = 0.00275$ mol L^{-1}, giving $k_1k_3/k_2 = 24$ with a relative standard error of 5.5%. However, the intercept k_4, 0.314 s^{-1}, was ill defined having a relative standard error of 72%. Thus, the equilibrium constant ($K = k_1k_3/k_2k_4$) was also defined poorly as 76 ± 55 s^{-1}. The series of experiments represented by figure 5 provided slightly better estimates of the kinetic and thermodynamic parameters. With [MeIm] = 0.02 mol L^{-1}, the slope $k_1k_3/(k_2[\text{MeIm}])$ was 1525 s^{-1} with a relative standard error of 6.4%, and the intercept, k_4, was 0.969 s^{-1} with a relative standard error of 51% giving $K = 30 \pm 16$. With [MeIm] = 0.01 mol L^{-1}, the slope $k_1k_3/(k_2[\text{MeIm}])$ was 2215 s^{-1} with a relative standard error of 3.3%, and an intercept, k_4, of 1.579 s^{-1} with a relative standard error of 28% gave a better value for $K = 14.0 \pm 4.0$.

In this study, the absorbance changes monitored were small, and in different experiments the media were different with different concentrations of MeIm or N_3^-. So it is not surprising that the numerical agreement was not perfect. Thus, comparing the results in figure 5, the slopes should be inversely proportional to the concentration of MeIm but they are only very approximately so. However, it is instructive to compare the two sets of results where the concentration of MeIm was the same, namely 0.02 mol L^{-1} MeIm. In figure 4 the interpolated value of k_{obs} at [MeIm] = 0.02 mol L^{-1} is 3.61 s^{-1}, whereas in figure 5 the corresponding value for k_{obs} is 5.16 s^{-1}. This difference reflects a higher ionic strength in the latter case (0.01 compared with 0.00275 mol L^{-1}) that facilitates the ionic reaction by raising the dielectric of the medium. It therefore seemed appropriate, instead of using the formula concentration of azide in solution, to calculate the amount of "free" ionic azide present using the measured ion-pair association constants. Such an approach worked well previously when ion pairs were involved in substitution and oxidation reactions of iron complexes [30, 31].

Figure 6 shows that when an ionic strength of 0.01 mol L^{-1} is maintained with azide/perchlorate mixtures (solid points), the concentration of "free" azide is diminished

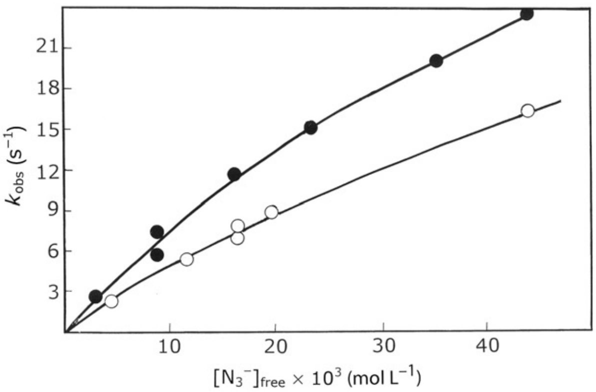

Figure 7. Variation of observed rate constant (k_{obs}) with $[N_3^-]_{free}$ in the presence of excess MeIm (solid points 0.01 mol L^{-1}, open points 0.02 mol L^{-1}) in dry acetone at 25°C with a total constant ionic strength 0.01 mol L^{-1}.

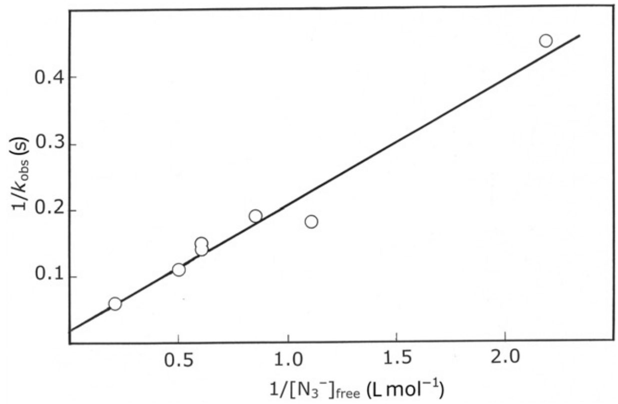

Figure 8. Plot of $1/k_{obs}$ (s^{-1}) against $1/[N_3^-]_{free}$ for the reaction of $N(n\text{-}C_4H_9)_4N_3$ with $[Fe(TPP)(MeIm)_2]^+$ in the presence of excess MeIm (0.02 mol L^{-1}) with constant total ionic strength (0.01 mol L^{-1}) in dry acetone at 25°C.

because of ion-pair formation, but the concentration of free azide ion in the concentration range considered is a linear function of the concentration of total azide. In contrast, the relationship is more complex when azide is the sole electrolyte and the ionic strength varies (open points). The calculated free azide concentrations were used in the plot of k_{obs} against the "free" azide concentration shown in figure 7, and also in the plot of $1/k_{obs}$ against $1/[N_3^-]_{free}$ shown in figure 8. In figure 7 excess MeIm concentrations were used (solid points 0.01 mol L^{-1}, open points 0.02 mol L^{-1}) that gave two different curved lines, but there was good linearity in the "double reciprocal" plot in figure 8.

There is a theoretical basis for this observed behavior. The curvature in figure 7 can be accounted for if the k_2[MeIm] term is not much greater than the value of $k_3[N_3^-]$ as the concentration of N_{3free}^- is increased while that of MeIm is constant.

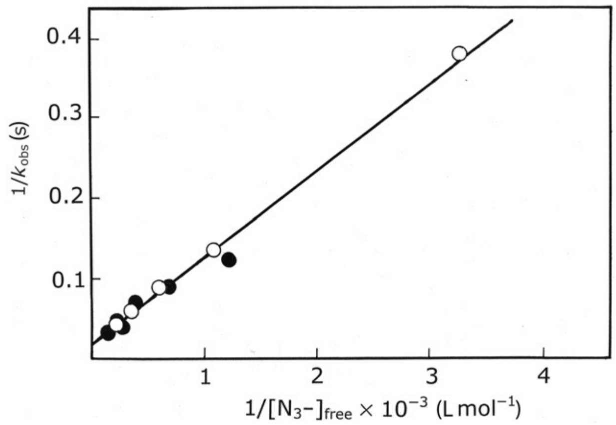

Figure 9. Plot of $1/k_{obs}$ (s^{-1}) against $1/[N_3^-]_{free}$ for the reaction of $N(n\text{-}C_4H_9)_4N_3$ with $[Fe(TPP)(MeIm)_2]^+$ in the presence of excess MeIm (0.01 mol L^{-1}) in dry acetone at 25°C. Open points with constant azide/perchlorate ionic strength = 0.01 mol L^{-1}, solid points with ionic strength varying with $[N_3^-]_{total}$.

Taking reciprocals of both sides of equation (5) gives equation (8). Then, with increasing $[N^-_{3free}]$ if $k_1k_3[N_3^-] \gg k_2k_4[\text{MeIm}]$, equation (9) results.

$$1/k_{obs} = (k_2[\text{MeIm}] + k_3[N_3^-])/(k_1k_3[N_3^-] + k_2k_4[\text{MeIm}]) \qquad (8)$$

$$1/k_{obs} = (k_2[\text{MeIm}]/k_1k_3[N_3^-]) + 1/k_1 \qquad (9)$$

Equation (9) is of the right form to give the linear plot of $1/k_{obs}$ against $1/[N^-_{3free}]$ shown in figure 8, with a constant MeIm concentration of 0.02 mol L^{-1}. The slope ($k_2[\text{MeIm}]/k_1k_3$) had a value of 1.86×10^{-4} with a relative standard error of 9.7%, and an intercept ($1/k_1$) was 0.0140 ± 0.0194. These values gave an estimate of the discrimination ratio (k_2/k_3) of 0.645 with a large associated error, but this lends some support that rate constant for the reaction of azide with the steady state intermediate $[Fe(TPP)(MeIm)]^+$ is probably greater than that for its reaction with MeIm, and that $[Fe(TPP)(MeIm)]^+$ only slightly discriminates between the two incoming ligands, azide, and MeIm.

The situation was convincing when 0.01 mol L^{-1} MeIm was used as shown in figure 9, that is a graph of $1/k_{obs}$ against $1/[N^-_{3free}]$ combining both reactions with azide alone (filled points) and with azide/perchlorate mixtures maintaining a constant ionic strength of 0.01 mol L^{-1} (open points). The points comprise a common data set showing the concentration of free azide along with that of MeIm are the important factors determining the observed rate constants at 25°C. A regression analysis gave a slope of $106 \pm 4 \times 10^{-6}$ (relative standard error of 3.6%) and a significant intercept of 1.95 ± 0.45 (relative standard error of 23%) that when combined gave a discrimination ratio of 0.543 for k_2/k_3, confirming that the intermediate $[Fe(TPP)(MeIm)]^+$ is almost twice as reactive toward free azide than toward MeIm. Comparing the value of k_1 (51.3) with that of k_4 (between 0.36 and 0.97), determined from the earlier experiments, suggested the fission of MeIm from $[Fe(TPP)(MeIm)_2]^+$ to give the intermediate $[Fe(TPP)(MeIm)]^+$ is much easier than the fission of azide from the non-electrolyte $[Fe(TPP)(MeIm)N_3]$. A simple explanation for this is that the latter reaction involves charge separation in a low dielectric solvent, whereas the former involves no charge separation, though each case involves the breaking of a Fe–N bond.

Comparing the results of this study with those from our earlier study [1] in which the reaction proceeded in the opposite direction and the concentration of ionic species was very low, not constant, and entirely from the starting material [Fe(TPP)N_3], the derived value of k_4 was $0.017\,s^{-1}$, more than an order of magnitude less than that determined in this study. This difference can be attributed to the more polar environment provided by the relatively high ionic concentration that promotes the ionization of coordinated azide from [Fe(TPP)(MeIm)N_3].

4. Conclusions

Addition of azide in the form of $N(n\text{-}C_4H_9)_4N_3$ to $[Fe(TPP)(MeIm)_2]^+$ in dry acetone led to displacement of MeIm to form equilibrium amounts of the starting material along with the nonelectrolyte product [Fe(TPP)(MeIm)N_3]. Both equilibrium and kinetic measurements were made using stopped-flow apparatus involving varying known concentrations of azide and *N*-methylimidazole. The kinetic results were accounted for by the loss of *N*-methylimidazole from $[Fe(TPP)(MeIm)_2]^+$ being a dissociative process described by a stationary state approach involving the transient intermediate $[Fe(TPP)(MeIm)]^+$. The results enabled an estimate to be made for the equilibrium constant for the formation of [Fe(TPP)(MeIm)N_3] by the addition of azide to $[Fe(TPP)(MeIm)_2]^+$ and to establish the intermediate $[Fe(TPP)(MeIm)]^+$ discriminated in favor of the reaction with azide over reaction with MeIm by nearly a factor of two, and that fission of MeIm from the starting material is at least 50 times easier than from [Fe(TPP)(MeIm)N_3]. The approach of using calculated values of free azide in solution using experimentally determined ion-pairing formation constants put results obtained under different conditions on a common basis.

Acknowledgments

JGJ gratefully acknowledges the support from the University of Ulster, and a joint NATO grant with Professor Dwight A. Sweigart, Department of Chemistry, Brown University, Providence, Rhode Island, USA, and also many fruitful discussions. JMcK acknowledges the receipt of a quota award from the Department of Education for Northern Ireland and a grant to visit Professor Sweigart's laboratory.

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