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METHYL TRANSFER FROM MeCo(III)Pc TO THIOPHENOXIDE

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Transfer of the cobalt-bound methyl in MeCo(III)Pc to thiophenoxide ion was studied (H_2Pc is the planar macrocyclic phthalocyanine; the cobalt is held in the center in this plane). In dimethylacetamide solution, the reaction is rapid, requiring stopped flow for the kinetics, and yielding MeSPh and Co(I)Pc$^-$ in good yield. The kinetics are not simple second order, but instead approach a constant rate at high [PhS$^-$], attributed to the reversible formation of an inert complex with PhS$^-$ occupying the vacant octahedral site in MeCo(III)Pc, on the other side of the phthalocyanine plane from the methyl group. The kinetics allow the estimation of the equilibrium constant, K, and the S_N2 rate constant, k, which at 25 °C have values of *ca.* $9{\cdot}4 \times 10^3$ l mol^{-1} and $1{\cdot}8 \times 10^4$ l mol^{-1}, respectively. Although these values are rough, the ratio k/K is firm at $1{\cdot}91 \pm 0{\cdot}02$ s^{-1}; this is the limit of the rate at high [PhS$^-$]. An alternative mechanism, which is entirely consistent with the kinetics, involves a rate-determining homolysis of the Co—S bond of the same complex. The mechanism is not favored because the product yields are high for a radical combination process and alternative chain processes are kinetically unacceptable. Further, the rate constant is about what would be expected from the reactivity of other nucleophiles in S_N2 reactions. Further arguments in favor of the S_N2 mechanism are presented. This transfer of the methyl group from Co to S is part of the possible analogy to the vitamin B_{12}-promoted methionine synthesis in nature. The other step in the biological, enzymatic process is the transfer of methyl from the nitrogen of *N*-methyltetrahydrofolate to cobalt. An attempt to model this with the very reactive *N*-methyl-2,6-dichloropyridinium ion was unsuccessful; the reaction took an entirely different course, presumably initiated by electron transfer, but leading to substantial loss of Cl$^-$ from the pyridine. No more than 0.5% methyl transfer took place. This system does mimic well the complete natural enzymatic process.

INTRODUCTION

In an earlier study[1] it was shown that Co(I)Pc$^-$ (**1**$^-$) was a good leaving group from MeCo(III)Pc (**3**) [the notation is that in Ref. 1 in which the number corresponds to the formal oxidation state: **1**$^-$ = Co(I)Pc$^-$, **2** = Co(II)Pc, **3** = **MeCo(III)Pc**] in the solvent dimethylacetamide (DMA) with the nucleophiles I$^-$, Br$^-$ and CN$^-$. Cobalt complexes both as Co(I) and Co(II) are leaving groups in cases in which the nucleophile is also a cobalt complex,[2,3] and reactions with thiolate nucleophiles have often been studied with alkyl cobalt complexes with dimethylglyoxime and related complexing agents and also vitamin B_{12}.[4–6] In the study on **3** the susceptibility of **1**$^-$ to undergo oxidation to Co(II)Pc, **2**, made it difficult to demonstrate that **1**$^-$ was indeed the product in the most dilute solutions. In this work the nucleophile PhS$^-$ was studied. In the presence of excess thiophenoxide, **1**$^-$ is indefinitely stable. This nucleophile is powerful, with a Pearson *et al.*[7] n_{MeI} value of 9·9, predicting a very high rate constant. In the case of CN$^-$ a complex with **3** was formed rapidly and reversibly, making the equilibrium concentration of uncomplexed **3** very low. Hence the rate of the overall reaction was low. It was of interest to see if this competition between attack at methyl and attack at cobalt might be general.

In the vitamin B_{12}-mediated enzymatic synthesis of methionine there is a transfer of the methyl group of *N*-methyltetrahydrofolic acid to the B_{12s} cobalt, followed by the transfer to the sulfur of homocysteine.[8] Since methionine (as its *S*-adenosylated derivative) is the prime source of methylating ability in all living cells, many successful attempts have been made to model the second step, methyl transfer from cobalt to sulfur. Modeling the first step using various Co(I) complex nucleophiles and methylated amines or ammonium ions has not been successful. We therefore studied the possible methylation of **1**$^-$ by *N*-methyl-2,6-dichloropyridinium ion, which by extension of the work of Arnett and Reich[9] should be a more powerful methylating agent than any described by them or studied as methyl donors to cobalt.

EXPERIMENTAL

Materials. Methylcobalt(III)phthalocyanine (**3**) and solutions of sodium cobalt(I)phthalocyanine (**1**$^-$) in DMA were prepared as described earlier.[1] Dimethylace-

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tamide (DMA) was of chromatographic grade from Aldrich, treated with CaH_2 and vacuum distilled in an atmosphere of argon; this extra purification was probably only relevant to the studies starting with $\mathbf{1}^-$.

Sodium thiophenoxide was prepared by treatment of commercial thiophenol with the calculated amount of carbonate-free NaOH, evaporating the solvent and drying in a Fischer pistol, during which time a small amount of material, apparently diphenyl disulfide, sublimed from the sample.

N-Methyl-2,6-dichloropyridinium trifluoromethanesulfonate was prepared by heating commercial 2,6-dichloropyridine (37 g, 0·25 mol) with methyl trifluoromethanesulfonate (23 ml, 0·20 mol) for about 10 min at about 90 °C. The resulting crystalline mass was crushed and washed with diethyl ether, then recrystallized from water, again washed with diethyl ether and dried, giving the desired salt (46 g, 75%), m.p. 224–225 °C. ^{1}H NMR (250 mHz in acetone-d_6), δ 4·67 (s, 3H), 8·41 (2H, d, $J = 8·27$ Hz), 8·70 (1H, t, $J = 8·29$ Hz). The mother liquor from the recrystallization was acidic and contained chloride ion, but an aqueous solution of the crystals gave no perceptible precipitate with silver nitrate. On briefly heating it, this aqueous solution did give Cl^-, produced even faster in ethanol. The salt could also be recrystallized from acetone.

For the reaction of **3** with PhS^-, sodiumthiophenoxide [25 ml of a solution of 0·333 g (2·5 mmol) in DMA] was mixed with **3**·0·2THF (11 mg, $1·83 \times 10^{-2}$ mmol) and stirred for 18 h. A 1 ml sample of the now green solution was withdrawn through a septum and placed in a 0·095 mm argon-filled cell. The absorbance at 698 nm was 0·47, indicating a concentration of $6·95 \times 10^{-4}$ M [the molar absorptivity (ε) of $\mathbf{1}^-$ is[1] $7·1 \times 10^4$ l mol^{-1} cm^{-1}] and a yield of 95%. The reminder of the green solution was combined with diethyl ether (50 ml) containing 10 μl of a 10% diethyl ether solution of methyl *p*-toly sulfide as an internal standard in a separating funnel. It was then shaken successively with 25 ml of water, twice with 25 ml portions of 1 M NaOH solution and three times with 10 ml portions of water. Oxidation during this process gave solid **2**, so the ether solution was filtered and analysed by gas chromatography (GC). The yield of methyl phenyl sulfide was 89%; a second run gave a yield of 87%. The multiple extractions could have concentrated the internal standard relative to the reaction product, so a quantitative yield cannot be excluded.

Kinetics were measured using a Durrum stopped-flow instrument at 698 nm (following the formation of $\mathbf{1}^-$) connected to a computer using an OLIS interface and software to establish the pseudo-first-order rate constants for the reactions in which the concentration of thiophenoxide in one of the drive syringes was much greater than the concentration (about 10^{-5} M) of **3** in the other. Several rate constant determinations were made at each concentration of the thiophenoxide solution, and allowance was made for the factor of two dilution on mixing. Precautions were taken to minimize the exposure of the PhS′ solutions to air and the **3** solutions to light; the photolysis of **3** during the stopped-flow measurements is negligible in the times involved, especially since the 698 nm light is not strongly absorbed by **3**. Preliminary attempts to measure the reaction in a Hewlett-Packard diode-array spectrophotometer were not successful as the reaction is too fast.

Evidence for an intermediate in the $\mathbf{3} + PhS^-$ *reaction.* When the spectra of **3** and the product of its reaction with PhS^- are superimposed, the isosbestic point occurs at 678 nm, but stoped-flow runs only at 686 nm showed no change in absorbance throughout the run. Hence there is a species present throughout the kinetic run with a longer wavelength maximum than **3**, which is converted by the observed kinetics into $\mathbf{1}^-$. The reaction is too fast to obtain a complete spectrum of this intermediate.

Reaction of $\mathbf{1}^-$ with *N*-methyl-2,6-dichloropyridinium triflate in DMA was attempted even though neither reagent is stable in this solution for very long. A very rapid reaction took place, with oxidation of the $\mathbf{1}^-$ to **2**, which precipitated in part, preventing a spectrophotometric yield determination. There was also a precipitate of NaCl, and the yield of Cl^- by silver nitrate titration in several runs corresponded to about 1·2 mol per mole of the pyridinium salt. The solution was worked up by dilution with diethyl ether, washing with water and then concentrating to look for 2,6-dichloropyridine by GC with 4-bromochlorobenzene as an internal standard. The yields in three experiments were 1%, a trace and 0.38% . The possibility that this was derived from unmethylated amine in the starting material was explored, and the largest was attributable to this source, but the two lower values using carefully recrystallized methylpyridinium salt might not be in error.

RESULTS

The following reaction was observed in the presence of excess PhS^-:

$$\mathbf{3} + PhS^- \rightarrow \mathbf{1}^- + MeSPh \qquad (1)$$

The yield of $\mathbf{1}^-$ was essentially quantitative and that of the thioanisole was at least 89%. There was no evidence of other products. However, if **2** had been a direct product, it would not have been observed, since it is reduced by excess thiophenoxide under the conditions of the experiment. The only other reasonable product from the thiophenoxide is diphenyl disulfide in not more than 0.1% yield based on total thiophenoxide, an amount undetectable in the presence of that from air

Table 1. Pseudo-first-order rate constants, k_{app}, for the reaction of **3** with excess PhS^- [a]

	Temperature (°C)					
$[PhS^-]$(M)	20	25	25[b]	30	35	40
0·001		1·73 ± 0·02	1·72			5·48 ± 0·18
0·002		1·78 ± 0·01	1·81			6·80 ± 0·25
0·003		1·82 ± 0·01	1·83			6·68 ± 0·05
0·004		1·84 ± 0·01	1·85			6·69 ± 0·05
0·005	1·24 ± 0·002	1·86 ± 0·01	1·86	2·64 ± 0·04	4·17 ± 0·06	6·66 ± 0·01
0·050		1·92 ± 0·01	1·90			7·49 ± 0·08

[a] Rate constant units are s^{-1}. Errors are estimated from at least three runs.
[b] The values in this column were calculated using equation (3) with $k = 1{\cdot}79 \times 10^4$ l mol^{-1} s^{-1} and $K = 9{\cdot}4 \times 10^3$ l mol^{-1}.

oxidation. No effort was made to find methane in a yield of at most 11% from **3**. The kinetic runs showed no deviation from pseudo-first-order behavior for the appearance of $\mathbf{1}^-$, making any important side-reaction unlikely. It is therefore reasonable to assume that the reaction is totally represented by equation (1).

The kinetics, although accurately pseudo-first order, were not those of a typical S_N2 reaction; instead, the apparent first-order rate constants approached a constant high value as the $[PhS^-]$ increased, as shown Table 1, which gives the apparent first-order rate constants at several thiophenoxide concentrations and temperatures. Only at 25 and 40 °C were data taken over a range of thiophenoxide concentrations, and the data at 25 °C are the more reliable. The data at $[PhS^-] = 0{\cdot}005$ M fit the Eyring equation well, yielding $\Delta H^{\ddagger} = 14{\cdot}6$ kcal mol^{-1} and $\Delta S^{\ddagger} = -8{\cdot}4$ al mol^{-1} K^{-1} (1 cal = 4·184 J). As will be seen in the Discussion section, these rates are combinations of equilibrium and kinetic processes and therefore this temperature dependence is not meaningful. There is a spectral shift of the presumed **3** in solutions containing PhS^-, as shown by a shift in the isosbestic point of the reacting mixture relative to separate solutions of the initial and final species, hence a transient extra species is indicated.

Most quaternary ammonium salts are unreactive toward $\mathbf{1}^-$; the reaction of $\mathbf{1}^-$ with *N*-methyl-2,6-dichloropyridinium triflate in DMA is an exception. A very fast color change gives **2**, and Cl^- is detected in quantity when the reaction is worked up. There is a new reaction of complicated but incompletely established nature. There is little, if any, evidence for nitrogen to cobalt methyl transfer.

DISCUSSION

The products of this reaction are just what the simple S_N2 reaction, equation (1), demands. The kinetics are not those expected. However, a simple modification, the rapid and reversible formation of an unreactive complex, $\mathbf{3}{\cdot}SPh^-$, in which the SPh anion occupies the vacant octahedral site **3**, suffices to bring the mechanism and kinetics together. The significant extent of reaction (2) leads directly to the equation (3), which takes into consideration the fraction of **3** made unreactive by the complexation. Here the apparent first-order rate constant, k_{app}, for the conversion of the initial absorbing species to $\mathbf{1}^-$ is expressed in terms of the rate constant k for reaction (1) and the equilibrium constant K for reaction (2).

$$\mathbf{3} + SPh^- \rightleftharpoons \mathbf{3}{\cdot}SPh^- \qquad (2)$$

$$k_{app} = k[SPh^-]/(1 + K[SPh^-]) \qquad (3)$$

The extensive formation of the complex is supported by the evidence of a new isosbestic point. When the monochromator was set at 686 nm, there was no change in absorbance during a run; separate solutions of **3** and $\mathbf{1}^-$ (with thiophenoxide to suppress oxidation) had equal molar absorptivities at 678 nm. The shift to longer wavelengths is analogous to that seen when **3** is in the presence of CN^-; the complex shows a shift of the maximum of 11 nm to longer wavelengths.[1]

The two constants in equation (3) can be evaluated easily from the slope and intercept of a double reciprocal plot of $1/k_{app}$ vs $1/[SPh^-]$, as as shown in equation (4) and in Figure 1, which shows the 25 °C data in Table 1.

$$1/k_{app} = 1/k[SPh^-] + K/k \qquad (4)$$

The least-squares fit of this plot gives the results $k = 1{\cdot}79 \times 10^4$ l mol^{-1} s^{-1} and $K = 9{\cdot}4 \times 10^3$ l mol^{-1}, and the column headed 25[b] shows that equation (3) fits the data fairly well. Nevertheless, these values are not well determined. As an example, the values $k = 1{\cdot}5 \times 10^4$ and $K = 7{\cdot}7 \times 10^3$ fit nearly as well. The ratio $k/K = 1{\cdot}91 \pm 0{\cdot}02$ s^{-1} is firm. The data at 40 °C fit less well to the double reciprocal plot, as is obvious from the fact that the values of k_{app} do not increase monotonically down the table. Much rougher values of $k = 2{\cdot}3 \times 10^4$ and $K = 3 \times 10^4$ can be estimated; again,

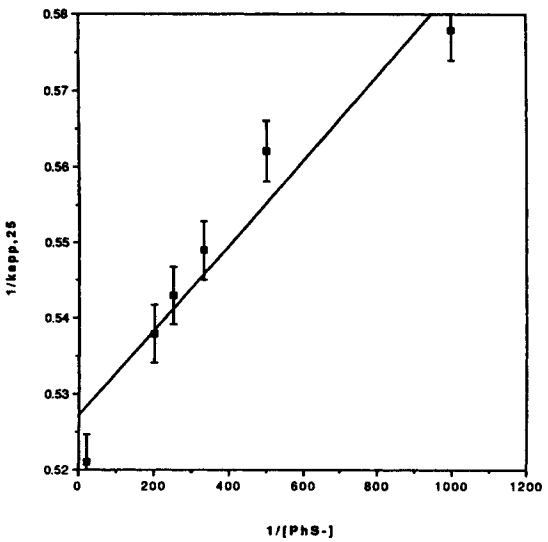

Figure 1. Plot of $1/k_{app}$ vs $1/[PhS^-]$ at 25 °C for the reaction of **3** with PhS^- in DMA to give $\mathbf{1}^-$ and MeSPh. The slope is $1/k$ and the intercept is K/k. Error bars correspond to a 0·7% error in k

k/K is better determined with a value of 7.4 s^{-1}; it is not worthwhile to be quantitative about the temperature dependence of k or K; the plausible conclusion that k increases with increase in temperature and K falls with increase in temperature is barely justified. For this reason, there is little justification to put much emphasis on the temperature dependence at $[PhS^-] = 0{\cdot}005$ M, even though the fit of five points to the Eyring plot is fairly good.

Reactions of MeB_{12} or methylcobaloximes with thiolate ion have been studied before, but in no case have rate constants for both methyl attack and equilibrium constants for cobalt attack been observed. Thus, in water, ionized mercaptoethanol slowly attacks MeB_{12} with good second-order kinetics,[10] but there is no evidence of any displacement of the dimethylbenzimidazole ligand by mercaptide. In this reaction B_{12s} is not stable in the presence of excess RS^-, the observed product is B_{12r}, analogous to the failure to observe $\mathbf{1}^-$ in the reactions of dilute solutions of **3** with iodide, bromide or cyanide.[1]

Several thiolates attack methylcobaloxime giving less than quantitative yields of the methyl transfer product at somewhat elevated temperatures.[6a] The other observed product is the complex with a cobalt–sulfur bond. These results were interpreted in terms of competitive attack at methyl and at cobalt; the latter product was inert, A complex analogous to the parent methylated dimethylglyoxime complex except that the two hydrogen bonding protons are replaced by BF_2 groups is more reactive; the yields of the methyl transfer product are high.

At room temperature the parent cobaloxime in ethanol is reported[11] to give with various RS^- only the product of attack on cobalt. This is compatible with Ref. 6a only if the activation energy for cobalt attack is much less than that for methyl transfer, a likely situation.

Equations (1) and (2) are exactly analogous to those written[1] for the reaction of CN^- with **3**. The establishment of the rate and equilibrium constants is different. In the cyanide case of the equilibrium constant was measured directly; in the present case, the reaction is too fast. In the cyanide case the kinetics gave only the limiting rate k/K; in the present case the non-linearity of k_{app} with $[PhS^-]$ gave both the rate and equilibrium constants.

The comparison of rates of different nucleophiles with **3** in DMA is illuminating. With the nucleophiles CN^-, I^- and pHS^-, the rates are 0·0980,[1] 0·492[1] and $1{\cdot}8 \times 10^4$. The Pearson *et al.* n_{MeI} values[7] are 6·7, 7·4 and 9·9 (in methanol). Clearly the thiophenoxide rate is over 100 times the rate predicted by the n values (with $s = 1$). On the other hand, in the solvent sulfolane, the rate constant for the reaction of iodide ion with MeI[12] is $1{\cdot}4\ s^{-1}$ and the rate constant for the reaction of PhS^- with MeI[13] is $5{\cdot}7 \times 10^4$, hence the relative reactivities of thiophenoxide to iodide with MeI in sulfolane are $4{\cdot}1 \times 10^4$ to 1, compared with the rate constant ratio of **3** with thiophenoxide and iodide of $3{\cdot}7 \times 10^4$ in DMA. Therefore, when the rates in the more nearly comparable dipolar aprotic solvents are used, it is clear that there is no particular anomaly; the rate of attack of PhS^- on **3** compared with iodide on **3** is about what would be expected for a normal S_N2 reaction.

There is further evidence for S_N2 attack on **3**. Evidence based on the effect of RX on the rate of reaction with $\mathbf{1}^-$ lead to the conclusion that this was a normal nucleophilic displacement.[1] Since the reaction of **3** with I^- is the reverse of the methylation of $\mathbf{1}^-$ by MeI, we can conclude that the reaction of **3** with I^- is also normal and mechanistically uncomplicated. Is there reason to believe that there is a change of mechanism with RS^-? Reaction of alkyl-B_{12} with thiols also follows the familiar order of alkyd groups[14] and is therefore also S_N2 in nature. The extension to the reaction of **3** with PhS^- is therefore entirely justified. Nevertheless, a radical mechanism was proposed[15,16] for the MeB_{12}–RS^- reaction on the basis that an oxidizing agent seemed necessary. The existence of later contradictory evidence,[10] together with an explanation of the earlier results, makes the free radical mechanism much less plausible. The comparison of rates of methyl transfer from cobalt is interesting. Ignoring differences in temperature, solvent and the structure of RS^-, the parent cobaloxime is the slowest, the BF_2-modified cobaloxime is faster and **3** is the fastest. The rates of

methylation of Co(I) anions is in the opposite order, with 1^- the slowest and the parent Co(I) dimethylglyoxime the fastest. This suggests that the larger part of the rate differences is due to the thermodynamic term in the Marcus equation. An extremely high barrier for thiolate methyl transfer identity reaction[16] makes small differences in cobalt nucleophile identity methyl transfer reactions less influential.

A different mechanism is entirely consistent with the observed kinetics, that is, a rate-determining homolysis of $3{\cdot}SPh^-$, $MeCo(III)PcSPh^-$, equation (5) or (6), which have exactly the same transition state composition as the rate-determining reaction (1).

$$3{\cdot}SPh^- \rightarrow MeCo(II)Pc^- + PhS^{\cdot} \quad (5)$$

$$3{\cdot}SPh^- \rightarrow Co(II)PcPhS^- + Me^{\cdot} \quad (6)$$

Neither $MeCo(II)Pc^-$ nor $Co(II)PcPhS^-$ is expected to be particularly stable; the first is analogous to methyl-B_{12r}, which is reported[17] to be very short-lived if it exists at all, and the second should fall apart at least as easily to 1^- and $PhS^{\cdot}$ or to **2** and PhS^- Two possible routes to the products can be considered. The first is the combination of methyl and thiyl radicals, which certainly would give the observed sulfide. Such a combination can hardly be that of free radicals in solution, for there are too many other fates of the radicals available; A cage process would help, but since the two radicals are formed on opposite sides of the large planar phthalocyanine, high yield cage recombination seems unlikely. A second process can be written, for example $Me^{\cdot} + 3 \cdot SPh^- \rightarrow MeSPh + 1^- + Me^{\cdot}$, or the less attractive $PhS^{\cdot} + 3 \cdot SPh^- \rightarrow MeSPh + 1^- + PhS^{\cdot}$. While such a chain reaction is a better way to obtain a product in good yield, either one resulting in 3/2-order kinetics in **3**. The nucleophilic substitution (1) proceeding at a rate close to that predicted is thus the preferred mechanism.

The question of why the equilibrium constant for complex formation with PhS^- is so much less than it is with CN^-, even though PhS^- is a better nucleophile toward carbon, is not quantitatively explained. However, Pearson *et al.*'s table,[7] which gives PhS^- a much greater nucleophilic character toward carbon, gives CN^- and PhS^- almost equal nucleophilic character towards platinum, an imperfect model for bonding to cobalt but surely better than the carbon nucleophilicity.

The fast transfer of methyl from cobalt to sulfur is an adequate analogy to the second part of the B_{12}-promoted natural methionine synthesis.[8] The first step of the natural enzymatic process is the transfer of methyl from *N*-methyltetrahydrofolate to B_{12s} and it is of interest to see if methyl can be transferred to the cobalt of 1^- from any methylamine derivative. The work of Arnett and Reich[9] on rates and equilibria of Menschutkin reactions shows that some quaternary ammonium salts can react at reasonable rates with iodide ion, and one of the most reactive is *N*-methyl-2-chloropyridinium ion. The simplified Marcus equation cannot be used for these electrostatically unsymmetrical reactions, nor can Hammett constants deal with the 2- or 6-substitution. A crude estimate of the reaction with **3** leads to the conclusion that the equilibrium should not be very unfavorable, but the rate would be small. This suggested the use of *N*-methyl-2,6-dichloropyridinium ion, which by extrapolation from the Arnett and Reich data should be a many times more powerful methylating agent than that with a single chlorine. Further, the extra steric effect of the 2- and 6-substituents should promote the reactivity,[18] and perhaps be a better mimic of methyltetrahydrofolate, in which substituents near the *N*-methyl group may have a similar effect. A search for the reaction (7) was therefore made.

$$2,6\text{-}Cl_2PyMe^+ + 1^- \rightarrow 2,6\text{-}Cl_2Py + 3 \quad (7)$$

The expected electronic and steric effects of the two chlorines were manifested in the relatively slow reaction of the free pyridine with methyl triflate compared, for example, with the 3,5-dichloropyridine isomer, which reacted rapidly on mixing at room temperature. The result of mixing *N*-methyl-2,6-dichloropyridinium triflate with 1^- was an immediate color change corresponding to oxidation of 1^- to **2**, possibly by an electron transfer reaction to the pyridinium ion. Other processes releasing substantial chloride ion were also present; the nature of the overall reaction was not established. An effort to detect slight methyl transfer accompanying the major reaction by finding the unmethylated pyridine gave equivocal results. The yield of unmethylated pyridine was certainly less than 1%, and may have been zero; efforts to eliminate contamination of the methylated salt by the protonated salt seemed adequate, but a level of much less than 1% contaminant would have vitiated the result. If there was a methyl transfer its rate would have to be less than 1% of that for the fast competing reaction.

The absence of a convincingly detectable reaction (7) can be attributed to one or all of three factors. First, the natural reaction is enzymatic, and there may be fairly specific roles of the enzyme, not modeled by simple cobalt complexes. Second, reaction (7) is an anion–cation reaction. It can be expected to be much faster in a much less polar medium than DMA. Thus the reaction of octyldimethylsulfonium ion with iodide is about 100 times faster in chloroform than it is in acetonitrile.[19] Third, 1^- is not as powerful a nucleophile as B_{12s}, as shown by the *n* values quoted by Eckert and Ugi,[20] 10·8 and 14·8 respectively, and it is probably unable to demethylate nitrogen even in the absence of other reactions.

CONCLUSIONS

The reaction of **3** with SPh^- by reaction (1) is fairly

fast; the mechanism is an S_N2 attack by sulfur on the methyl group. There is an accompanying complexation giving $3 \cdot SPh^-$ but, unlike in earlier reports, this complexation is reversible and MeSPh is produced in good yield. The rate constant of reaction (1) and the equilibrium constant for the complex formation are both established. This arises because 1^- is a much better leaving group than previously studied Co(I) complexes. Correspondingly, 1^- is not a strong enough nucleophile to demethylate an amine or ammonium salt.

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