for 1:1 complex formation between alkyl halides and high-spin hemes in *N*-methylpyrrolidone–acetic acid has been obtained,[2] though no direct observation of such species has been reported. In the present system, an excess of sodium dithionite (presumably by rapidly rereducing the iron(III) porphyrin) allows observation of the halide complex formation preceding oxidation of the heme by CCl_4.

The dotted line in Figure 1 has generally been taken as characteristic of iron–alkyls in solution.[10-12] The present work suggests structures assigned on this basis may be incorrect. The exact geometry of the alkyl halide–heme binding in these complexes awaits further investigation. We tentatively formulate them as loosely affiliating with iron.[13]

Complex formation with halides appears to be a general reaction of hemes, and it is not limited to the specific system examined here. For example, iron(III) octaethylporphyrin can be reduced to the heme by group 1 and 2[17] organometals[14] in toluene. Addition of methyl iodide to these solutions produces a visible spectrum nearly identical with that of the complex shown in Figure 1. The NMR spectrum corresponds exactly to $S = 1$ octaethylheme.

Experimental Section

Materials. Chloroiron(III) deuteroporphyrin IX was obtained as previously described.[1] Methyl iodide (Aldrich, reagent grade), methyl bromide (Matheson, 99.5%), (^{14}C)methyl iodide (New England Nuclear), deuterium oxide (99.8% D), perdeuterio-iso-propanol and perdeuteriomethyl iodide, Aldrich, 99+% D, Gold Label) were used without purification. The specific activity of the (^{14}C)methyl iodide was 1.86×10^6 dpm/μL or 10 mc/millimole. Mallinckrodt AR grade isopropyl alcohol, carbon tetrachloride, and methylene chloride were freshly distilled. Sodium dithionite (Fisher Scientific) solutions were made up fresh and used within 15 min.

Solutions of deuterohemin (1.2–12.0 mg) in 1.5 mL of 0.1 M NaOH were diluted with water and phosphate buffer (10^{-2} M, pH 7.2) as described by Brault et al.[5] Forty milliliters of this solution was added to 50 mL of isopropyl alcohol and made up to 100 mL with buffer. The final concentration in these stock solutions was 2.0×10^{-5}–2.00×10^{-4} M. The visible spectrum (Figure 1) resembled that of a μ-oxo dimer.

Stock solutions of higher concentrations were also prepared in 1:1 0.1 M sodium hydroxide–isopropyl alcohol. The visible spectra were identical with those prepared in the buffer solution. Magnetic measurements by the Evans method in the manner recently described[15] indicate a μ_{ef} of 5.79 μ_B or a high-spin iron(III) complex.

NMR Analyses. Solutions of the complex for NMR analysis were prepared by adding 10 μL of 0.22 M sodium dithionite and 1 μL of perdeuteriomethyl iodide, under argon, to 550 μL of an argon-purged solution of 3.6×10^{-3} M hemin in 1:1 perdeuterioisopropyl alcohol–D_2O (0.1 M in NaOH). The solutions were prepared in a long (9-in.) NMR tube that was fitted with a 14/20 ST glass joint. To this was attached a joint that contained an in-line serum-capped stopcock and a similarly equipped splayed side arm. The argon inlet was No 22 gauge hypodermic tubing inserted through the center stopcock to the bottom of the tube. The splayed outlet stopcock was also used for reagent addition. Before it was sealed, the bottom half of the tube was cooled in an *i*-PrOH–CO_2 bath and the argon inlet tube was pulled up into the upper fitting. Properly sealed tubes exhibited the same visible spectrum (dotted line, Figure 1) for months. Visible spectra of the optically dense NMR solutions were taken of the film on the sides of the tube above the solution. An appropriately equipped Cary 118C spectrophotometer was employed for this purpose, and careful alignment was essential. NMR spectra were recorded in a 300-MHz Nicolet machine. For routine spectra of non-paramagnetic porphyrin samples a Varian EM-390 spectrometer was employed.

^{14}C Counting. A Packard Tricarb Model 3255 liquid scintillation counter was employed. The counting matrix was Packard "Instagel". Usually 0.25–100 μL of sample was counted and corrected as previously described.[16]

Reactions. In a typical reaction a four-neck flask was equipped with argon inlet and outlet stopcocks, a serum-capped stopcock, a manometer, a bottom stopcock port for a solution transfer, and a magnetic stirring bar. The flask was charged with 150 mL of 2.00×10^{-4} M hemin in buffer–*i*-PrOH. The free space was 46 mL. The solution was briefly evacuated and thoroughly purged with argon. Under slight argon pressure and purge 330 μL of 0.1 M sodium dithionite was added with stirring. The brown solution immediately became red (dashed line, Figure 1). Methyl iodide, 180 μL (3.0×10^{-3} mol), was added and the solution was stirred for 10 min. The visible spectrum corresponded to the dotted line in Figure 1. At this time the argon stopcocks were closed and 3 mL of concentrated HCl was added. The solution developed the purple color of the porphyrin dication. No pressure change was observed, and no methane could be detected in either the liquid or gas phase by gas chromatography (four-ft. Porapak Q column, detectability <0.5%). The whole was opened to air and concentrated to near-dryness on a rotary evaporator at 60 °C. The porphyrin residue was taken up entirely in methanol containing 5% HCl and allowed to stand 3 days. The solutions was stripped to dryness. The cation dimethyl ester was taken up in methylene chloride washed with sodium acetate–water, dried over sodium sulfate, filtered, and stripped to dryness. The porphyrin ester was dissolved in 0.5 mL of $CDCl_3$. The NMR spectrum of this solution was identical with that of deuteroporphyrin IX dimethyl ester.

In similar fashion 25 mL of 2.0×10^{-4} M hemin was reacted with 13 μL of 0.425 M sodium dithionite and 3 μL of $^{14}CH_3I$ (4.8×10^{-5} mol, 5.6×10^6 dpm). After 1.5 h, the red complex solution was made slightly acidic with 12 μL of concentrated HCl and opened to air. The brown hemin solution was distilled in vacuo at 25 °C and reduced to a volume of 5 mL. The distillate receiver was cooled in an *i*-PrOH–CO_2 bath. The hemin precipitated from the concentrate and was centrifuged, washed with water, and centrifuged three times. The entire hemin was dissolved in 1 mL of methanol and counted for radioactivity. No counts above background were detected (±0.5%). The combined disillate and water washes contained 99 ± 1% of the original counts. In addition to CH_3I gas chromatography of the disillate showed the presence of traces of CH_3OH.

Reactions could also be conducted in appropriately equipped spectrophotometric cells.[15] The spectra reported in Figure 1 were obtained in this way. Gassing solutions of the complex with carbon monoxide produced the spectrum of the carbonyl adduct of deuteroheme. Addition of *N*-methylimidazole produced the iron(II) bis(*N*-methylimidazole) adduct. The spectra were identical with those obtained by corresponding treatment of the iron (II) porphyrin in the absence of methyl iodide.

The rate of complex formation with methyl iodide was assessed from repeated scans of the visible spectrum over the 600–450-nm regions.

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Registry No. Chloroiron(III) deuteroporphyrin IX, 21007-21-6; iron(II) porphyrin IX, 18922-88-8.

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[17] In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

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A Reconsideration of the Kinetics of the Arbuzov Reaction Involving $[CpCo(dppe)X]^+$ (X^- = Cl^-, Br^-, I^-) and $P(OR)_3$ (R = Me, Et)

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Several conclusions about the kinetics of the Arbuzov reaction involving $[CpCo(dppe)X]^+$ (X^- = Cl^-, Br^-, I^-) and $P(OMe)_3$[1]

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Table I. Rate Constant Data for Reactions 1 and 2 (Acetone-d_6)[a]

X^-	T, °C 0	10	20	30	40
			a. k_{obsd}, L mol^{-1} s^{-1}		
Cl^-			$1.1\ (0.1) \times 10^{-2}$	$3.5\ (0.15) \times 10^{-2}$	$5.7\ (0.5) \times 10^{-2}$
Br^-		$1.6\ (0.05) \times 10^{-1}$	$2.4\ (0.3) \times 10^{-1}$	1.6 (0.1)	
I^-	$7.2\ (0.6) \times 10^{-2}$	$6.3\ (0.3) \times 10^{-1}$	$7.6\ (0.3) \times 10^{-1}$		
			b. k_2, L mol^{-1} s^{-1}		
Cl^-			9.2 (0.9)	$3.2\ (0.3) \times 10$	$1.8\ (0.2) \times 10^2$
Br^-		1.9 (0.2)	8.7 (1)	$3.0\ (0.4) \times 10$	
I^-	$9.9\ (1) \times 10^{-1}$	1.75 (0.15)	5.9 (0.5)		

[a] Parenthetical numbers are errors estimated from the standard deviation.

Table II. Activation State Parameters for k_2[a]

X^-	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
Cl^-	27 (4)	36 (8)
Br^-	24 (4)	26 (7)
I^-	14 (4)	-8 (4)

[a] Parenthetical numbers are estimated errors.

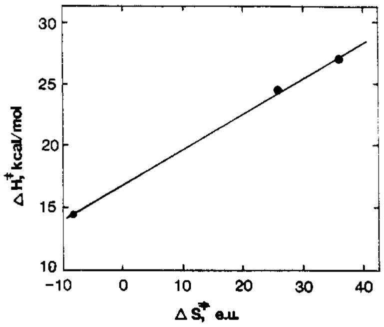

Figure 1. Correlation of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the dealkylation step of the Arbuzov reaction, k_2.

require reconsideration in light of computational errors that were present in the rate constant and Arrhenius calculations. The mechanistic sequence described by reactions 1 and 2 is not affected.

$$[CpCo(dppe)X]^+ + P(OR)_3 \xrightarrow{K_{eq}} [CpCo(dppe)P(OR)_3]^{2+} + X^- \quad (1)$$

$$[CpCo(dppe)P(OR)_3]^{2+} + X^- \xrightarrow{k_2} [CpCo(dppe)P(O)(OR)_2]^+ + RX \quad (2)$$

However, the relative roles of $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ in the dealkylation step, k_2, need further comment.

Table I contains the revised data for the rate constants K_{obsd} ($=K_{eq}k_2$) and k_2 in which three of the original values were found to be incorrect. The error estimates for K_{eq}[1] should be approximately doubled, owing to the practical difficutly of measuring small differences in the integrated intensities of the associated species. Table II contains the revised values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ calculated for the dealkylation step, k_2.

It is apparent that the nucleophilicity of X^-, which contributes to the value of $\Delta H^{\ddagger}$, plays a greater role in the rate of the reaction than previously suggested. This result is in line with the established trend[2] in the nucleophilic strength of Cl^-, Br^-, and I^-. $\Delta S^{\ddagger}$ is also quite sensitive to X^-, suggesting that the concert of bond breaking, bond formation, and charge redistribution occurring in the transition state of the k_2 step is sharply influenced by the choice of the nucleophile. As before,[1] a direct correlation between $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ exists (Figure 1), suggesting that, despite the differences in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for this series, the mechanism of the dealkylation step among these compounds is the same.

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Registry No. [CpCo(dppe)Cl], 97391-44-1; [CpCo(dppe)Br], 97391-45-2; [CpCo(dppe)I], 97391-46-3; $P(OMe)_3$, 121-45-9.

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Simplified Procedure for the Preparation of Metal Diselenolenes[†]

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While metal dithiolenes are relatively easy to prepare, particularly the mnt (maleonitriledithiolato) complexes, the selenium analogues are rarer because the precursor diselenolato ligands are unknown and the diselete ("1,2-diselenetene", precursor for the neutral diselenolene complexes) requires extreme conditions for its preparation;[2] in fact, only the bis(trifluoromethyl)diselete is known so that only the trifluoromethyl derivatives of metal diselenolenes ("*cis*-1,2-bis(trifluoromethyl)ethene-1,2-diselenolato-metal" complexes) are known to date.

In this publication we present a new, simplified method for the preparation of metal diselenolenes containing both methyl and trifluoromethyl groups as substituents. While the procedure appears to be general, in this report we deal only with the nickel complexes.

Results and Discussion

Bis[1,2-bis(trifluoromethyl)ethenediselenolato]nickel (**1**) is usually prepared according to Scheme I.[2]

The main difficulty with this procedure rests with the preparation of the heterocycle **2**. The latter is prepared by the reaction of hexafluorobut-2-yne with refluxing selenium (bp 688)! The crude product is formed as an impure (purified by distillation) red oil containing foul-smelling organoselenium contaminants. Furthermore, it would appear that this procedure is limited to the preparation of analogues of **2** that contain electron-withdrawing functional groups and a functionality that can survive the drastic conditions involved.

Our approach to a more general preparation of nickel diselenolenes is shown in Schemes II and III.

The conditions for the preparation of heterocycle **4** are essentially those developed by Cava[3] for the preparation of the carboxymethyl analogue of **4**. Compound **4** is an easily purifiable amber solid, soluble in most organic solvents. In the reaction

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[†] Work mostly performed at Bell Laboratories.