Polish J. Chem., **75**, 949–955 (2001)

Methyl Transfer from Methylcobalt(III) Phthalocyanine to Bromide and Iodide Ions in Sulfolane

by W. Gałęzowski

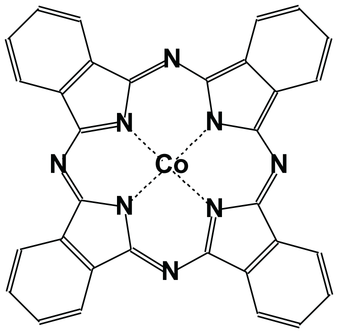
Faculty of Chemistry, A. Mickiewicz University, Grunwaldzka 6, 60-780, Poznań, Poland
e-mail:wlodgal@main.amu.edu.pl

(Received December 28th, 2000; revised manuscript February 12th, 2001)

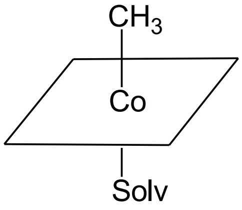
Rates of methyl transfer from methylcobalt(III) phthalocyanine ($MeCo^{III}Pc$) to bromide and iodide nucleophiles in sulfolane were measured in the temperature range 20–40°C. In contrast to iodide, bromide ion forms an unreactive complex $MeCo^{III}PcBr^-$, formation constant for which was determined. Rates of reaction between $Co^{I}Pc^-$ and methyl iodide were also measured. Identity rate constant for methyl transfer between two $Co^{I}Pc^-$ nucleophiles of 51 M^{-1} s^{-1} at 25°C was obtained using the Marcus equation. This identity rate is the largest out of many determined in this solvent.

Key words: cobalt nucleophiles, cobalt phthalocyanine, identity rate constants

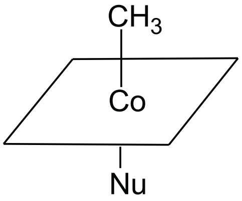
Previously, the rates and equilibria for the title reactions were measured in dimethylacetamide (DMA) solvent [1] and a large identity rate of methyl transfer between cobalt nucleophiles was found. However, this identity rate cannot be directly compared to values for a broad range of nucleophiles. Relatively basic solvents, such as DMA, could not be used for studies of methyl transfers involving reactive cationic methyl donors. For this reason, sulfolane solvent that is a relatively weak nucleophile was chosen by Lewis. Identity methyl transfer rate constants are available for a number of nucleophiles in this solvent [2]. Since these rates are subject to substantial solvent effects [2], it seems interesting to learn if the kinetics of the methyl transfer reactions, involving cobalt nucleophiles, will be affected by switching from dimethylacetamide to sulfolane solvent. There is some compelling evidence that complexation on the sixth axial coordination site in $MeCo^{III}Pc$ substantially diminishes the rates of its demethylation. One candidate for a ligand is the nucleophile itself. For instance, in dimethylacetamide cyanide ion forms reversibly a complex that does not react with another cyanide ion to give MeCN [1]. In DMA, with iodide such a complexation was absent but $\Delta S^{\ddagger}$ for this reaction was positive [1], which is rather unusual for an S_N2 reaction. Similarly, positive activation entropy values were found for the reaction of bromide with $MeCo^{III}Pc$, although complications from some weak ligation of $MeCo^{III}Pc$ by Br^- could not be completely ruled out. Such atypical activation parameters could be explained if solvent ligand dissociation had to precede the methyl transfer step. Sulfolane is a worse ligand than dimethylacetamide, and in the former $\Delta S^{\ddagger}$ might come out negative, as expected for a bimolecular reaction.



$Co^{II}Pc$



$MeCo^{III}Pc$



$MeCo^{III}PcNu^-$

EXPERIMENTAL

Materials. Sulfolane 99% (GC) from Aldrich was fractionally distilled under reduced pressure at about 130°C from calcium hydride. The fraction of absorbance at 300 nm smaller than 0.15 was collected. A eutectic mixture of sulfolane and dimethylsulfone (5.25 mol %) was used in this work to facilitate handling of the solvent and solutions [3]. Dimethylsulfone 98% from Aldrich was recrystallized from water and dried in vacuo to constant weight. Methylcobalt(III) phthalocyanine was prepared as described elsewhere [1]. Cobalt(II) phthalocyanine was a commercial reagent from Aldrich. Tetrabutylammonium bromide and sodium iodide were dried *in vacuo* to a constant weight. Methyl iodide from Aldrich was freshly distilled from calcium hydride. This reagent must be free of traces of iodine. The working solutions of Co^IPc^- were made by appropriate dilutions of *ca*. 0.0004 M stock solution. Stock solutions of Co^IPc^- were prepared by treating a suspension of $Co^{II}Pc$ in sulfolane with $NaBH_4$, followed by filtration of the resulting green solution under a nitrogen atmosphere.

All experiments were performed at very reduced light levels. Photolysis of $MeCo^{III}Pc$ solutions in fluorescent or sun light is completed in a few minutes. With respect to solubility, sulfolane is an inconvenient solvent for studying the chemistry of cobalt phthalocyanines. The concentration of a saturated solution of $MeCo^{III}Pc$ in sulfolane at room temperature is about 3×10^{-5} M. This reflects the difference between sulfolane and coordinating solvents such as dimethylacetamide. Solubility of $Co^{II}Pc$ in sulfolane is extremely poor.

Kinetic and equilibrium measurements. The rates of reaction of $MeCo^{III}Pc$ with bromide and iodide were measured under aerobic conditions in a Hewlett Packard 8452A diode array spectrophotometer, fitted with a thermostatable cell holder, by following the increase in absorbance at 336 nm and the decrease at 670 nm. Concentrations of the cobalt complex were about 5×10^{-6} M and the nucleophile was always in large excess to assure pseudo-first-order conditions. The rates of reaction of Co^IPc^- with methyl iodide were measured using an Applied Photophysics stopped flow instrument. Methyl iodide was in large excess over Co^IPc^-.

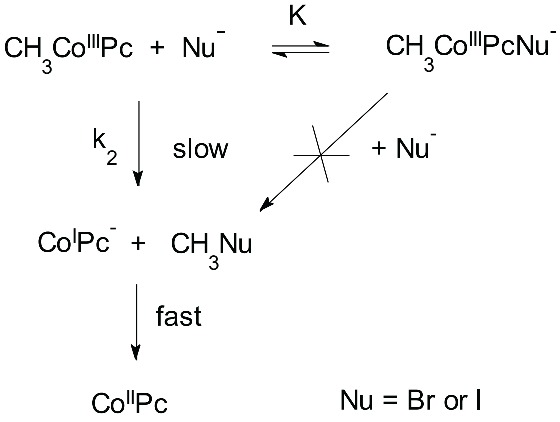
RESULTS AND DISCUSSION

Ultraviolet and visible absorption spectra of cobalt phthalocyanine complexes in sulfolane are virtually identical with those measured in dimethylacetamide [4,1]. Spectra of methylcobalt(III) phthalocyanines have a 318 nm band in the Soret region. This band is little affected by complexation of $MeCo^{III}Pc$ with bromide. Upon thermal demethylation by halide nucleophiles or photolysis the 318 nm band shifts to 326 nm. This is accompanied by a substantial loss in intensity of the α band at 666 nm. The spectra of photolysis product of $MeCo^{III}Pc$ in sulfolane and the product of thermal reactions with bromide show slight differences. The latter has some absorption around 400 nm and the 666 nm band is slightly shifted to longer wavelengths. These differences disappear when bromide is added to the photolysis product. This indicates that there is some ligation of $Co^{II}Pc$ by bromide in sulfolane or even oxidation to a Co^{III} complex [1]. Upon addition of Br^- to $MeCo^{III}Pc$ a new, weak absorption band is rapidly formed (λ_{max} 466 nm, $\varepsilon_{466} = 12400$, isosbestic points at 382 and 516 nm). This band, assigned to $MeCo^{III}PcBr^-$, slowly disappears, while absorption between 384 and 438 nm increases at the rate of methyl transfer. A similar, very low intensity band at about 470 nm was also observed in DMA [1], but those spectral changes were hardly detectable, probably due to a smaller formation constant in the better coordinating DMA solvent.

$$MeCo^{III}Pc + Br^- \rightleftarrows MeCo^{III}PcBr^- \qquad (1)$$

An attempt to measure the rate of reaction (1) by stopped flow was unsuccessful. The reaction for $[Br^-] = 0.01$ M at 25°C was too fast. Spectrophotometric equilibrium constants for reaction (1) were measured at 20 and 25°C using the Benesi-Hildebrand [5] method and their values are 26 ± 2 and 28 ± 2, respectively; $\varepsilon_{466} = 12400 \pm 700$. They are not significantly different from less accurate values obtained from kinetics (Table 1). No clear indication of ligation of $MeCo^{III}Pc$ or $Co^{II}Pc$ by iodide in the ultraviolet and visible spectra was found.

Scheme 1



The initial product of methyl transfer reaction, Co^{I}Pc$^-$, is rapidly oxidized to Co^{II}Pc and under anaerobic conditions it is not observed (Scheme 1). However, Co^{I}Pc$^-$ was formed in large quantities when MeCo^{III}Pc and iodide, or bromide, were combined in dimethylacetamide under argon [1]. These equilibrium measurements require that concentration of the cobalt complex is relatively high. Such concentration levels could not be achieved in sulfolane; therefore, the equilibrium measurements were not performed in this solvent.

Table 1. Rate constants for methyl transfer from CH$_3$Co^{III}Pc to Br$^-$ in sulfolane.

Temp., °C	10^3 [Bu$_4$NBr], M	10^3 k$_{obs}$, s$^{-1\ a)}$	k$_2$, M^{-1} s$^{-1\ b)}$	K, M$^{-1\ b)}$
20	1.99–19.05	0.080–0.42	0.043 ± 0.001	37 ± 8
25	1.99–19.05	0.12–0.73	0.064 ± 0.002	31 ± 6
35	1.99–19.05	0.48–2.78	0.255 ± 0.004	39 ± 4
40	1.99–19.05	0.84–4.59	0.46 ± 0.02	32 ± 8

$\Delta H^{\ddagger} = 88 \pm 2$ kJ/mol, $\Delta S^{\ddagger} = 29 \pm 8$ J K^{-1} mol^{-1}.

[a)] non-linear changes with [Br$^-$].

[b)] found from the double reciprocal plot, eq. (2).

Table 2. Rate constants for methyl transfer from CH$_3$Co^{III}Pc to I$^-$ in sulfolane.

Temp., °C	10^3 [NaI], M	10^3 k$_{obs}$, s^{-1}	k$_2$, M^{-1} s^{-1}
20	0.995–9.52	0.153–2.09	0.19 ± 0.02
25	0.995–9.52	0.36–3.57	0.37 ± 0.02
35	0.995–4.88	1.27–4.61	0.86 ± 0.06
40	0.995–2.95	1.53–4.62	1.57 ± 0.02

$\Delta H^{\ddagger} = 75 \pm 4$ kJ/mol, $\Delta S^{\ddagger} = -4 \pm 16$ J K^{-1} mol^{-1}.

Rate constants for methyl transfer from MeCo^{III}Pc to Br$^-$ and I$^-$ are presented in Tables 1 and 2; k$_{obs}$ were measured spectrophotometrically with Br$^-$ or I$^-$ in large excess over the cobalt complex. Plots of k$_{obs}$ *vs* [I$^-$] are linear, while with bromide there is a downward curvature (Fig. 1a). The curvature of the plot of k$_{obs}$ *vs* [Br$^-$] can be explained by the inertness of anionic MeCo^{III}PcBr$^-$ in methyl transfer reaction, which is in line with a general scheme of nucleophilic attack at carbon and cobalt. In accord with this mechanism, the rates of demethylation of MeCo^{III}Pc by cyanide [1] or thiophenoxide [6] in DMA show a weak dependence on concentration of the nucleophile.

An obvious alternative is ion pairing of the bromide ion. Although ion pairing in polar sulfolane is very limited [7] and was further minimized by using tetrabutylammonium salt, it cannot be completely ruled out and it can contribute to those curvatures. The plots of 1/k$_{obs}$ *vs* 1/[Br$^-$] give straight lines (Fig. 1b). The second-order rate constant for methyl transfer reaction and formation constant of the unreactive complex can be found from the slope and the intercept, according to

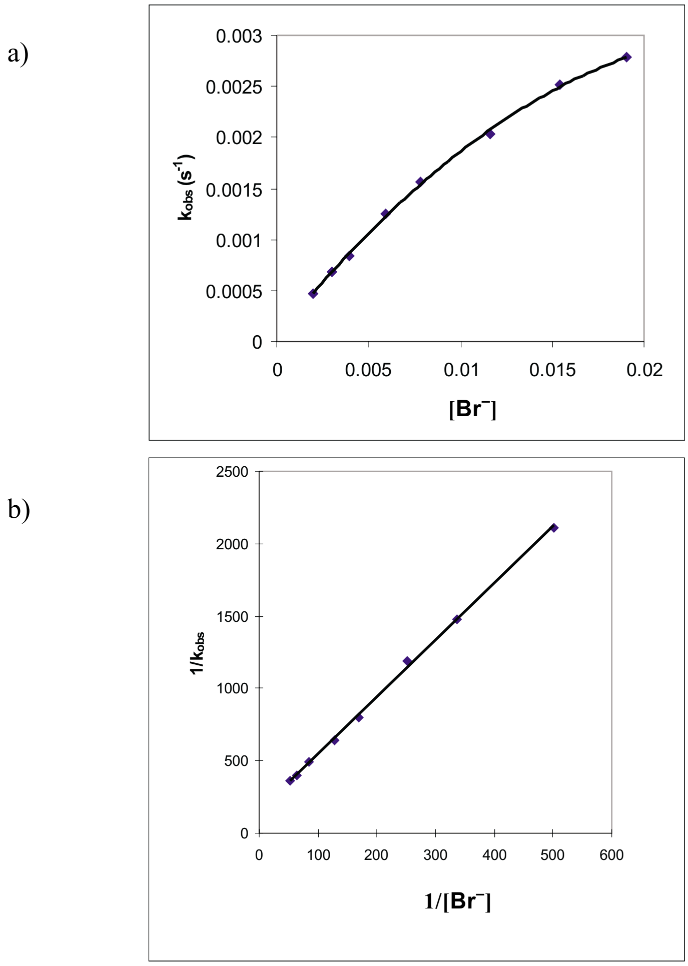


Figure 1. Plot of k_{obs} *vs* [Br^-] (a) and $1/k_{obs}$ *vs* 1/[Br^-] (b) for methyl transfer from $MeCo^{III}Pc$ to Br^- at 35°C in sulfolane.

$$\frac{1}{k_{obs}} = \frac{1}{k_2[Nu^-]} + \frac{K}{k_2} \tag{2}$$

where k_2 is the second-order rate constant and K is the formation constant for $MeCo^{III}PcBr^-$. The values of K, found in this way, are not very accurate, due to low values of the equilibrium constants. The second-order rate constants for methyl transfer from cobalt to bromide or iodide in sulfolane are surprisingly close to those obtained in DMA. Both sulfolane and DMA are polar solvents, but they are of quite different nucleophilicity. Inspection of activation parameters leads to a tentative conclusion that both $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values are lower in sulfolane than in DMA [1]. However, activation entropy values are still close to 0, which is too high for a typical S_N2 reaction and would rather suggest a single electron transfer (SET) mechanism [8]. On the other hand, low k_I/k_{Br} ratio of about 5 is consistent with the S_N2 mechanism. There is accumulating evidence that although some alkyl transfers to or from cobalt complexes are homolytic processes [9,10], primary alkyl groups are transferred by S_N2 mechanism [11]. It is noteworthy that $\Delta H^‡$ and $\Delta S^‡$ for the reaction of Co^IPc^- with methyl iodide are just what a S_N2 reaction demands (Table 3).

Rate constants for the reaction of Co^IPc^- with methyl iodide are given in Table 3. The plots of k_{obs} *vs* $[CH_3I]$ are straight lines. The k_2 value at 25°C is less than twice as large in sulfolane, than in DMA.

Table 3 Rate constants for methyl transfer from CH_3I to Co^IPc^- in sulfolane.

Temp., °C	$10^3\,[CH_3I]$, M	k_{obs}, s^{-1}	k_2, $M^{-1}\,s^{-1}$
15	3.2–16.1	0.323–1.56	96 ± 2
20	3.2–16.1	0.376–2.11	133 ± 2
25	3.2–16.1	0.568–2.88	177 ± 6
30	3.2–16.1	0.789–3.89	243 ± 8

$\Delta H^‡ = 42.2 \pm 0.8$ kJ/mol, $\Delta S^‡ = -60 \pm 2\ J\ K^{-1}\ mol^{-1}$.

The equilibrium constant for reaction (3) can be calculated from kinetic data as a ratio of two second-order rate constants.

$$MeCo^{III}Pc + I^- \rightleftarrows Co^IPc^- + CH_3I \qquad (3)$$

In DMA, such calculations gave results consistent with equilibrium measurements; thus, there is a reason to believe that a reliable result can be obtained in sulfolane as well. The equilibrium constant in sulfolane at 25°C is 0.0021, which is not much different from the value of 0.0035 in DMA [1].

$$Co^IPc^- + MeCo^{III}Pc \longrightarrow MeCo^{III}Pc + Co^IPc^- \qquad (4)$$

Using known values for identity rates of methyl transfer between two iodide ions in sulfolane [12] an identity rate constant, k_{CoCo}, for reaction (4) can be estimated from the Marcus equation (5).

$$k_{CoI} = (k_{CoCo}k_{II}K_{CoI})^{1/2} \qquad (5)$$

where k_{CoI} is the second-order rate constant of reaction (3), K_{CoI} is the equilibrium constant for reaction (3) and k_{II} is iodide identity rate constant. The calculated values of k_{CoCo} in sulfolane are 51 and 106 $M^{-1}\ s^{-1}$ at 25 and 35°C, respectively. They are much larger than any of fifteen identity rate constants determined so far in this solvent [2], the second best nucleophile being iodide with identity rate constant of 2.62 at 35°C.

Acknowledgment

Financial support from the Polish State Committee for Scientific Research (Grant 3 T09A 06914) is gratefully acknowledged.

REFERENCES

1. Gałęzowski W., Ibrahim P.N. and Lewis E.S., *J. Am. Chem. Soc*., **115**, 8660 (1993).
2. Lewis E.S., Douglas T.A. and McLaughlin M.L., *Isr. J. Chem*., **26**, 331 (1985).`
3. Lewis E.S., Kukes S. and Slater C.D., *J. Am. Chem. Soc*., **102**, 303 (1980).
4. Day P., Hill H.A. and Price M.G., *J. Chem. Soc. A*, 90 (1968).
5. Benesi H.A. and Hildebrand J.H., *J. Am. Chem. Soc*., **71**, 2703 (1949).
6. Gałęzowski W. and Lewis E.S., *J. Org. Phys. Chem*., **7**, 90 (1994).
7. Popowych O., *Nonaqueous Solution Chemistry*, J. Wiley and Sons. NY, 1981; p 284.
8. Lewis E.S., *J. Am. Chem. Soc*., **111**, 7576 (1989).
9. Okabe M. and Tada M., *Bull. Chem. Soc. Jpn*., **55**, 1498 (1982).
10. Martin B.D. and Finke R., *J. Am. Chem. Soc*., **114**, 585 (1992).
11. Zhou D-L., Walder P., Scheffold R. and Walder L., *Helv. Chim. Acta*, **75**, 995 (1992).
12. Lewis E.S., McLaughlin M.L. and Douglas T.A., *J. Am. Chem. Soc*., **107**, 6668 (1985).