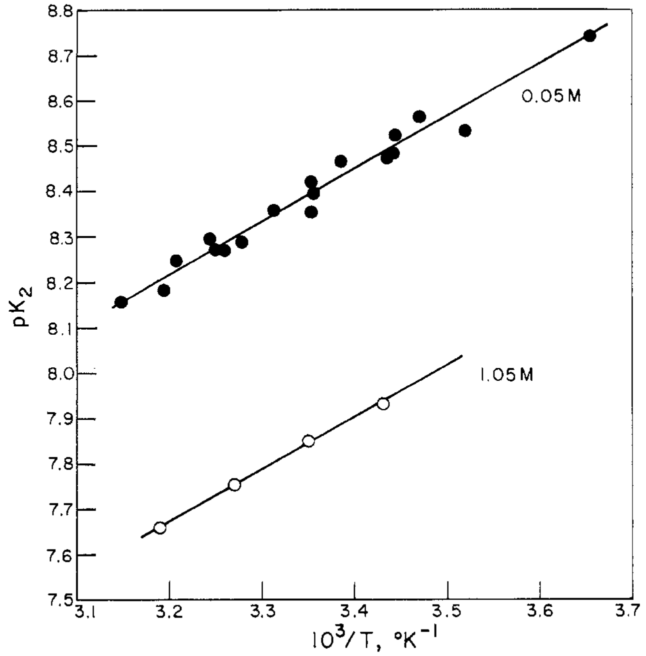


Figure 2.—The variation of apparent ionization constant at ionic strengths 0.05 and 1.05 M with temperature. The data are plotted in accordance with the equation $pK_2 = (\Delta H/2.3RT)$ + constant.

and hydrolyzed in strong sodium hydroxide by a modification of the procedure described by Klement[11] to yield disodium phosphoramidate hexahydrate. O,O′-Diphenylphosphoramidate (6.25 g, 0.025 mole) was boiled for 12 min in 4 g of NaOH dissolved in 15 ml of water. Addition of 5 ml of water and slow cooling to 0° yielded a fine, needlelike precipitate which was filtered and washed several times with 95% ethanol; yield 4.5 g (72%); mp 64–66°. Disodium phosphoramidate hexahydrate was recrystallized from a small volume of water containing one pellet of NaOH; addition of ethanol precipitated the product (mp 64–66°). Titration with standard 0.05 M HCl gave a molecular weight of 249 (calcd 249). This compound was prepared as needed a few days before use. It was protected from the light and stored in a desiccator in a freezer.

Ionization Constant of Phosphoramidic Acid and Its Anion as a Function of Ionic Strength at 25°.—Disodium phosphoramidate hexahydrate (25–200 mg) was dissolved in 20 ml of CO_2-free water in a water-jacketed beaker containing a thermometer and connected to a constant-temperature bath maintained at 25 ± 0.01°. One or two equivalents of standard 1 N HCl, dispensed from a 1-ml Gilmont micropipet in small increments, was added and the solution was rapidly stirred. The pH was measured after each addition of acid on a Corning pH meter, Model 12. The pH meter was previously standardized with two standard buffers. The pH 7.00 ± 0.01 standard buffer was purchased from Coleman. The pH 4.00 ± 0.01 standard buffer was 0.050 M potassium acid *o*-phthalate. The meter was checked at pH 10.00 ± 0.01 with a standard buffer purchased from Coleman. The pH meter can be read to ±0.002 unit or better on expanded scale, but repeat measurements on the same solution were reproducible to only ±0.003.

Concentrations are in moles per liter.

The second equivalent of acid was added rapidly in fewer increments so that no correction for hydrolysis of the sample was necessary. Corrections were applied below pH 4 for the amount of acid required to titrate the water.

The acid was standardized by potentiometric titration against 1 ml of standardized 1 M NaOH. The sodium hydroxide was standardized by potentiometric titration against dry reagent grade potassium acid *o*-phthalate.

The pK was defined as the pH of the solution at $^1/_2$ and $^3/_2$ neutralization. The ionic strength was varied by taking different weights of disodium phosphoramidate and the molar ionic strength was calculated from the concentration of all ionic species at $^1/_2$ and $^3/_2$ neutralization. The experimental end points agreed within 1% with the calculated end points.

Ionization Constant of Phosphoramidic Acid and Its Anion as a Function of Temperature.—A solution of the disodium salt in CO_2-free water, or 1 M NaCl in CO_2-free water, was titrated with 1 or 2 equiv of standard 1 N HCl and the pH was measured as before. The temperature of the solution was maintained constant to ±0.02° by means of a loosely covered water-jacketed beaker connected to a constant-temperature bath. The pH meter was previously standardized with two standard buffers at each temperature as described above. The ionic strength of the solution was 0.05 and 1.05 M for the addition of 0.5 equiv of acid and 0.04 M for the addition of 1.5 equiv of acid. The pK was defined as the pH of the solution at $^1/_2$ and $^3/_2$ neutralization. The experimental end points agreed within 1% with the calculated end points.

At higher ionic strength (1 M NaCl) only four temperatures were used and only the second ionization constant was studied. Three titrations were done at each temperature and the pK_a values were reproducible to ±0.02.

The first ionization constant was measured at only four temperatures, three titrations at each temperature and only at the lower ionic strength. Reproducibility was 0.01.

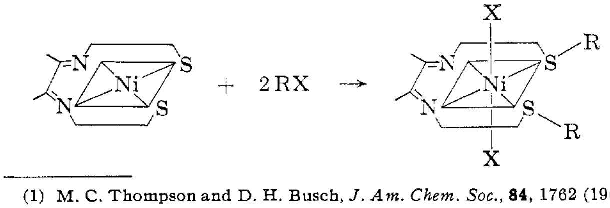
CONTRIBUTION FROM THE EVANS AND
MCPHERSON CHEMICAL LABORATORIES,
THE OHIO STATE UNIVERSITY, COLUMBUS, OHIO 43210

Reactions of Coordinated Ligands. XV. Demonstration of the Kinetic Coordination Template Effect

BY ELLIOTT L. BLINN AND DARYLE H. BUSCH

Received June 26, 1967

2,3-Pentanedionebis(mercaptoethylimino)nickel(II) (Ni(PE)) is a planar diamagnetic complex which contains two terminal *cis*-mercaptide groups.[1,2] The integrity of this *cis* configuration is assured by the presence of three fused five-membered rings, and the crystal structure[3] reported for the related 2,3-butanedione derivative confirms these conclusions. When this complex reacts with any monofunctional alkylating agent, both mercapto groups are alkylated and the resulting product contains coordinated thioether[4]



(1)

---

[11] R. Klement, *Inorg. Syn.*, **6**, 100 (1960).

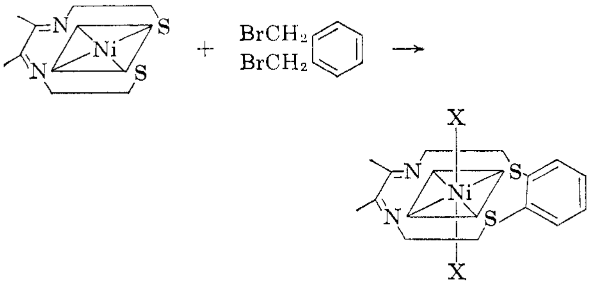
(1) M. C. Thompson and D. H. Busch, *J. Am. Chem. Soc.*, **84**, 1762 (1962).

(2) M. C. Thompson and D. H. Busch, *ibid.*, **86**, 213 (1964).

(3) Q. Fernando and P. Wheatley, *Inorg. Chem.*, **4**, 1726 (1965).

(4) D. H. Busch, D. C. Jicha, M. C. Thompson, J. W. Wrathall, and E. Blinn, *J. Am. Chem. Soc.*, **86**, 3642 (1964).

If the bifunctional reagent α,α'-dibromo-o-xylene is employed, a new chelate ring is formed and the product of reaction is a macrocyclic complex[5]



(2)

The probability of ring closure to form this macrocyclic ligand is greatly enhanced by the presence of the metal atom which holds the mercapto groups in *cis* positions. This directive influence has been called the *kinetic coordination template effect.* The effect has previously been demonstrated by synthetic means. Products that are best rationalized by use of this concept have been isolated in high yields. The purpose of this note is to report a second way of illustrating the kinetic coordination template effect.

Results and Discussion

A simple demonstration of the kinetic nature of this template effect can be seen in spectrophotometric scans taken over the visible spectral region as a function of time while a reaction was in process. Figures 1 and 2 reproduce these spectral scans for the reactions of 2,3-pentanedionebis(mercaptoethylimino)nickel(II) with α,α'-dibromo-o-xylene and benzyl bromide, respectively, both in 1,2-dichloroethane. The most obvious difference in these two figures is the simplicity of the sequence of scans for the reaction with α,α'-dibromo-o-xylene (Figure 1) as compared with those for the reaction with benzyl bromide (Figure 2). In the latter case, the optical density increases for the first 3.5 min within the wavelength ranges between 6000 and 6400 Å and between 3800 and 4900 Å; it then slowly decays. Obviously, an intermediate is formed in great enough concentration to dominate the spectrum. The intermediate has an absorption peak at 4700 Å and a shoulder at 4300 Å. In the spectrum of the final product, the peaks of both the intermediate and the starting material have disappeared. An isosbestic point between the starting material and the intermediate occurs at 5900 Å. This is more clearly shown in Figure 3.

In the reaction of 2,3-pentanedionebis(mercaptoethylimino)nickel(II) with α,α'-dibromo-o-xylene in 1,2-dichoroethane a single isosbestic point is observed (Figure 1). It is significant that this isosbestic point is congruent for every spectrum in the series of scans. Further, the optical density changes are all unidirectional. Thus, there is no evidence for an intermediate and this indicates that a single rate-determining step dominates the reaction.

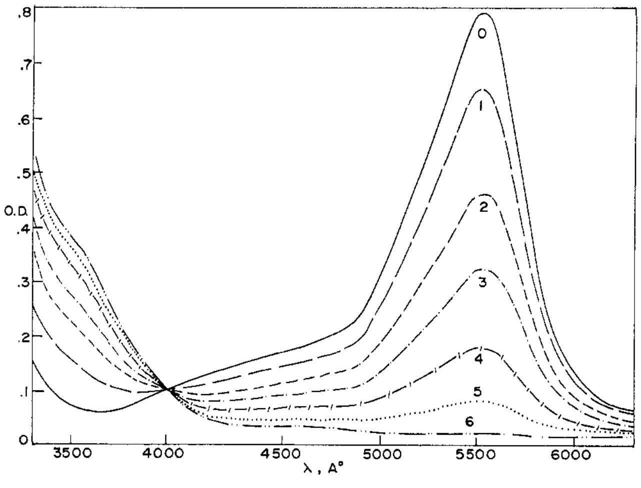


Figure 1.—Visible spectra obtained during the reaction of Ni(PE) with α,α'-dibromo-o-xylene in 1,2-dichloroethane at 25°. [Ni(PE)] = 2.12×10^{-4} M, [$C_8H_8Br_2$] = 3.61×10^{-3} M, chart speed = 25 Å/sec. Spectrum: 0, t = 0; 1, t = 1.5 min; 2, t = 5 min; 3, t = 9 min; 4, t = 17 min; 5, t = 28 min; 6, t = 50 min. All data were obtained at 6300 Å.

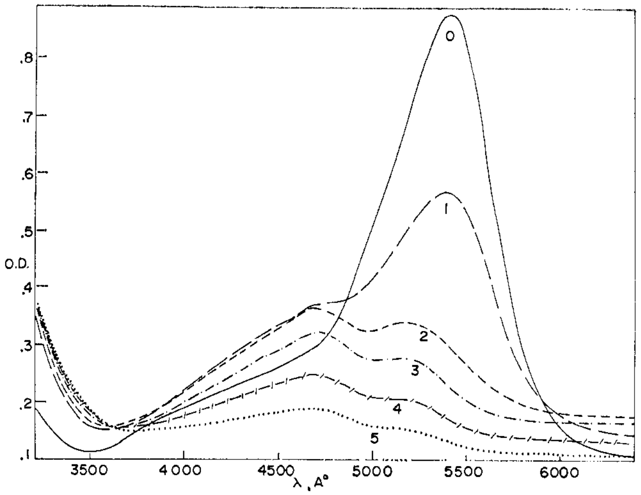


Figure 2.—Visible spectra obtained during the reaction of Ni(PE) with benzyl bromide in 1,2-dichloroethane at 25°. [Ni(PE)] = 2.2×10^{-1} M, [$C_6H_4CH_2Br$] = 4.48×10^{-2} M, chart speed = 25 Å/sec. Spectrum: 0, t = 0; 1, t = 30 sec; 2, t = 3.5 min; 3, t = 7 min; 4, t = 14 min; 5, t = 27 min. All data were obtained at 6500 Å.

Examination of additional systems adds support to the suggestion that the differences noted in the spectral scans are due to the kinetic template effect. First, it has been demonstrated that a large variety of alkylating agents give similar spectral scans to those reported in Figure 2 for benzyl bromide and 2,3-pentanedionebis(mercaptoethylimino)nickel(II). The alkylating agents tested include methyl iodide, propyl bromide, p-methylbenzyl bromide, p-nitrobenzyl bromide, and p-bromobenzyl bromide. Just as in the case of benzyl bromide, scans for these alkylating agents indicate that consecutive reactions occur at comparable rates so that appreciable concentrations of an intermediate build up. These are all in contrast with the reaction of α,α'-dibromo-o-xylene which results in simpler kinetics. At this point it has not been ascertained whether the simplicity of the reaction with

---

(5) M. C. Thompson and D. H. Busch, *J. Am. Chem. Soc.*, **86**, 3651 (1964).

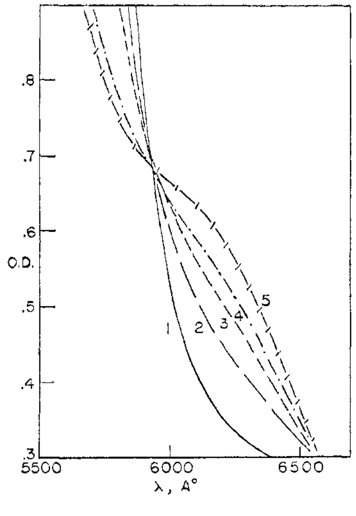


Figure 3.—Isosbestic point between starting material and intermediate in the reaction of Ni(PE) with benzyl bromide in 1,2-dichloroethane at 25°. All data were obtained at 7000 Å; chart speed = 25 Å/sec.

α,α'-dibromo-o-xylene is due to the number of halides present in the reagent or to the fact that this reaction creates a new chelate ring.

The answer to this question can be found in the figure summarizing spectral scans for the reaction of α,α'-dibromo-p-xylene with 2,3-pentanedionebis(mercaptoethylimino)nickel(II) in 1,2-dichloroethane (Figure 4). Like its isomer, α,α'-dibromo-o-xylene, the reagent contains two halides, but, because these halides are in *para* positions, they cannot create a new chelate ring. The sequence of scans for this reaction proceeds in a way almost identical with that observed for the reaction of benzyl bromide with 2,3-pentanedionebis(mercaptoethylimino)nickel(II) (compare Figures 2 and 4). This proves without question that the difference between successive scans for the monofunctional alkylating and benzylating agents and those for α,α'-dibromo-o-xylene arises because the latter reagent creates a new chelate ring *in situ* and not as a result of the number of halides available for reaction.

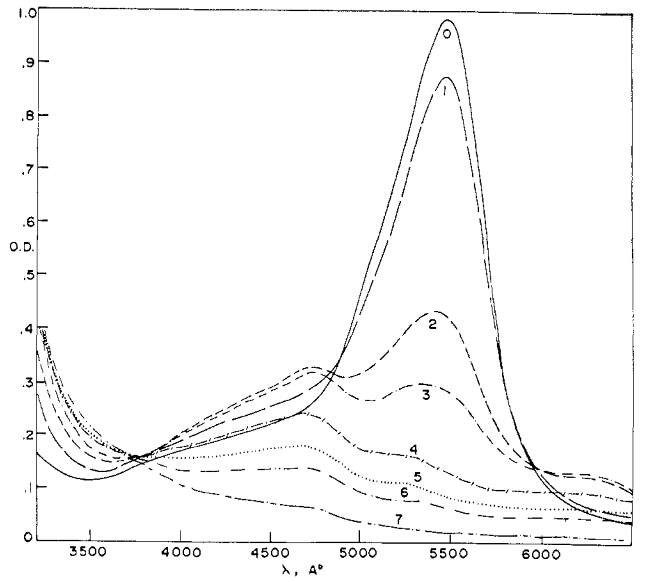
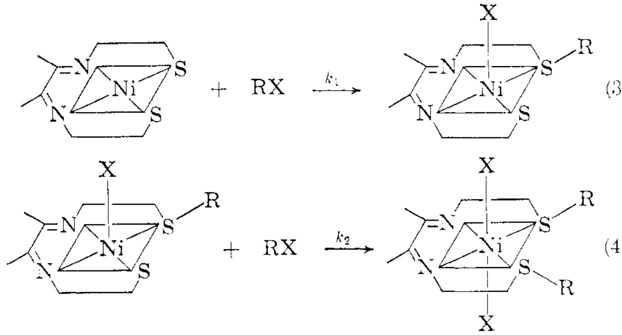


Figure 4.—Visible spectra obtained during the reaction of Ni(PE) with α,α'-dibromo-p-xylene in 1,2-dichloroethane at 25°. [Ni(PE)] = 1.52×10^{-4} M, [$C_8H_8Br_2$] = 6.64×10^{-3} M, chart speed = 25 Å/sec. Spectrum: 0, t = 0; 1, t = 25 sec; 2, t = 6.5 min; 3, t = 11 min and 15 sec; 4, t = 27 min and 15 sec; 5, t = 48 min; 6, t = 57 min; 7, t = 2 hr and 18 min. All data were obtained at 6500 Å.

The most obvious interpretation of the data shown in Figures 1–4 assumes that 2,3-pentanedionebis(mercaptoethylimino)nickel(II) reacts with monofunctional alkyl and benzyl halides in two consecutive, measurably slow steps



(3)

(4)

Judicious choice of wavelengths for rate measurements has made it possible to determine second-order rate constants for each of the successive steps for the reaction with benzyl bromide (Table I). The first constant could be estimated from measurements at 4500 Å (near the absorption maximum for the intermediate) while the second constant was obtained from data taken at 5880 Å, the position of the isosbestos point between starting material and intermediate. The concentration of benzyl bromide ranged from 1.15×10^{-2} to 2.12×10^{-1} M, while the concentration of complex varied over the interval 6.6–74 $\times 10^{-4}$ M. The ratio of benzyl bromide concentration to that of complex varied from 12 to 260. Thus, assuming second-order kinetics, measurements were made under pseudo-first-order conditions. For both steps the order with respect to benzyl bromide is unity. At 25° in dichloroethane $k_1 = 0.353 \pm 0.026$ M^{-1} sec^{-1} and $k_2 = 9.85$ $(\pm 0.15) \times 10^{-3}$ M^{-1} sec^{-1}. The first step exceeds the second in velocity by a factor of approximately 36. This may be due, in part, to the steric hindrance imposed on the remaining unreacted mercapto group by the benzyl group of the newly formed thioether and also to the fact that the number of terminal mercapto groups has been reduced by half.

The reaction of α,α'-dibromo-o-xylene with 2,3-pentanedionebis(mercaptoethylimino)nickel(II) in 1,2-dichloroethane conforms to the integrated first-order rate expression. The ratio of the concentration of α,α'-dibromo-o-xylene to that of the complex has been varied from 18:1 to 209:1. Within this range of excess α,α'-dibromo-o-xylene, the ratio of the observed first-order rate constant to the concentration of α,α'-dibromo-o-xylene is approximately constant (Table II). This ratio, the second-order rate constant,

TABLE I

RATE CONSTANTS FOR THE REACTION OF Ni(PE) WITH BENZYL BROMIDE IN 1,2-DICHLOROETHANE AT 25° AND λ 4500 Å (EXCEPT AS NOTED)

10^2 [C_6H_5-CH_2Br], M	10^4 [Ni-(PE)], M	10^3 k_1, sec^{-1}	k_2, M^{-1} sec^{-1}	10^2 [C_6H_5-CH_2Br], M	10^4 [Ni-(PE)], M	10^3 k_1, sec^{-1}	k_2, M^{-1} sec^{-1}
3.21	6.62	12.9	0.402	1.15	10.3	3.87	0.336
8.02	7.63	25.9	0.323	12.8	74.0	1.28[a]	0.010[a]
2.87	10.3	10.0	0.348	21.2	49.5	2.05[a]	0.0097[a]

[a] These rate constants are for the second consecutive reaction; λ = 5880 Å.

TABLE II

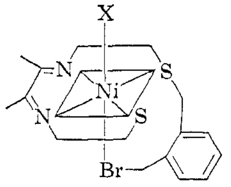
RATE CONSTANTS FOR THE REACTION OF Ni(PE) WITH α,α'-DIBROMO-o-XYLENE IN 1,2-DICHLOROETHANE AT 25° AND λ = 5400 Å (EXCEPT AS NOTED)

10^2 [Xy], M	10^4 [Ni-(PE)], M	10^3k_1, sec^{-1}	k_2, M^{-1} sec^{-1}	10^2 [Xy], M	10^4 [Ni-(PE)], M	10^3k_1, sec^{-1}	k_2, M^{-1} sec^{-1}
0.858	4.74	6.18	0.720	1.65	1.19	8.65	0.524
1.32	1.54	6.75	0.511	1.52	1.19	8.23	0.541
3.22	1.54	1.90	0.590	1.52	1.56	9.65	0.635[a]
8.05	7.93	4.50	0.559	1.43	1.56	9.04	0.632[b]
3.13	1.19	18.85	0.602	3.12	1.56	20.9	0.670[a]

[a] λ = 3500 Å. [b] λ = 3300 Å.

has a value of $0.57_8 \pm 0.05_0$ M^{-1} sec^{-1} (measured at 5400 Å) at a temperature of 25°. This rate is only about 1.6 times that for the corresponding reaction with benzyl bromide. Whereas the rate of the second step in the benzyl bromide case is about $^1/_{36}$ that of the first step, the second step is too fast to observe in the case of α,α'-dibromo-o-xylene. It seems plausible to assume that detectable amounts of intermediate would build up if the second rate exceeded the first by less than a factor of 10. This suggests that the relative rates of the first and second consecutive steps change by a factor of at least 350 in going from the process involving benzyl bromide to that using α,α'-dibromo-o-xylene.

In the case of the reaction of 2,3-pentanedionebis(mercaptoethylimino)nickel(II) with α,α'-dibromo-o-xylene a sterically directed mechanism is imposed by the *cis* configuration of the sulfurs. Apparently, the first step is slow and the second step is very rapid. After the combining of the first mercapto group with the reagent, the remaining sulfur and the halide are oriented in position for the cyclization reaction



This explains the conclusion that measurable concentrations of the intermediate are not formed and is the essence of the kinetic coordination template effect.

The kinetic template effect is not unique to the complex 2,3-pentanedionebis(mercaptoethylimino)nickel(II). Other 2,3-diketobis(mercaptoethylimine)-nickel(II) complexes react in the same fashion and give comparable second-order rate constants. The kinetic template effect is also not unique to the solvent 1,2-dichloroethane. Spectral scans for the reaction of 2,3-pentanedionebis(mercaptoethylimino)nickel(II) with α,α'-dibromo-o-xylene and benzyl bromide in benzene, chloroform, and methanol appear very much like the scans reported for 1,2-dichloroethane. Also, under the proper conditions a template effect can be observed for 1,4-dibromobutane. At very high concentrations of 1,4-dibromobutane (100-fold excess) the spectral scans for reaction of this alkylating agent with 2,3-pentanedionebis(mercaptoethylimino)nickel(II) look very similar to those for any of the monofunctional alkylating agents. However, at lower concentrations of 1,4-dibromobutane (stoichiometric ratios) the spectral scans for this reaction resemble that of α,α'-dibromo-o-xylene. It therefore appears that at high concentrations of alkylating agent, 2 moles of the reagent reacts with the sulfurs thereby preventing cyclization. At lower concentration of alkylating agent there is sufficient time to close the ring before a second molecule of alkyl halide attacks the emaining mercaptide. This is in keeping with the respective second-order and first-order rate laws for the competing paths.

The entropies and heats of activation for these reactions are comparable in magnitude to those found for N-substituted mercaptoethylamine–nickel(II) complexes (Tables III and IV).[6,7]

TABLE III

TEMPERATURE DEPENDENCE OF RATE CONSTANTS FOR REACTION OF Ni(PE) WITH ALKYLATING AGENTS IN 1,2-DICHLOROETHANE

$C_6H_5CH_2Br$		o-$C_6H_4(CH_2Br)_2$	
Temp, °C	k_2, M^{-1} sec^{-1}	Temp, °C	k_2, M^{-1} sec^{-1}
25	0.35_3	25	0.57_8
35	0.70_5	35	0.90_0
45	1.0_3	45	1.8_5
55	1.76	55	2.4_0

TABLE IV

ENTROPIES AND HEATS OF ACTIVATION[a] FOR THE REACTION OF 2,3-PENTANEDIONEBIS(MERCAPTOETHYLIMINO)NICKEL(II) WITH A VARIETY OF ALKYLATING AGENTS

Reagent	ΔH_a, kcal	ΔS_a, eu
Benzyl bromide	10	−26
α,α'-Dibromo-o-xylene	9.6	−27
1,3-Dibromopropane	12	−35
1,4-Dibromobutane	10	−38

[a] On the basis of the errors in the rate constants, these values are estimated to be accurate to within a maximum uncertainty of 30% of their values.

Experimental Section

Materials.—2,3-Pentanedionebis(mercaptoethylimine)nickel(II) was prepared by a modification of the method of Thompson and Busch.[2] Benzyl bromide was distilled under reduced pressure and checked for purity by vapor phase chromatography. The remaining alkylating agents are all solid compounds and were used as obtained from Matheson Coleman and Bell. These materials were stored in the dark. 1,2-Dichloroethane was dis-

---

(6) D. H. Busch, J. A. Burke, Jr., D. C. Jicha, M. C. Thompson, and M. L. Morris, Advances in Chemistry Series, No. 37, American Chemical Society, Washington, D. C., 1963, p 125.

(7) E. L. Blinn, Thesis, The Ohio State University, 1967.

tilled over phosphorus(V) oxide, methanol was distilled from magnesium, and thiophene-free benzene was distilled from calcium hydride.

Apparatus.—The temperatures of samples and reagents were maintained constant with a Sargent S-8405 bath rated at ±0.01°. Lower temperatures required the use of a cooling coil through which Freon was passed. A Haak thermostat and pump (Model F) were used to circulate thermostated water through jacketed cells in the Cary 14 spectrophotometer. While most measurements were made in solutions prepared by routine mixing and delivery to the cell, the more rapid rates were measured by use of a spring syringe of the type described by Gordon.[8] The kind assistance of Dr. Gordon in duplicating the syringe is greatly appreciated. Spectral scans and rate measurements were recorded on the Cary 14 spectrophotometer.

Procedures for Rate Measurements.—All solutions and cells were equilibrated at reaction temperature prior to initiation of reactions. Manual mixing techniques permitted first measurements to be made some 10–20 sec after mixing. Time was recorded on a Kodak timer and chart speed of 5 in./min (Cary 14) was used. The use of the spring syringe permitted measurements to be made during the first few seconds of reaction as well. Our techniques are detailed elsewhere.[7,9]

Acknowledgment.—This investigation was supported by U. S. Public Health Service Grant GM-10040 from the National Institute of General Medical Sciences. This sponsorship is deeply appreciated.

[8] G. Gordon, *J. Sci. Instr.*, **41**, 480 (1964).

[9] E. L. Blinn and D. H. Busch, *J. Am. Chem. Soc.*, in press.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
STATE UNIVERSITY OF NEW YORK AT BINGHAMTON,
BINGHAMTON, NEW YORK 13901

Substitution Reactions of Metallic Complexes of β,β',β''-Triaminotriethylamine. III. Kinetics of Solvolysis of *cis*-Dibromo(triaminotriethylamine)cobalt(III) Cation in Nonaqueous Solvents

BY STANLEY K. MADAN AND JOSEPH PEONE, JR.

Received October 18, 1967

In a recent article we described the kinetics of aquation of the *cis*-dibromo(triaminotriethylamine)cobalt(III) cation.[1] This report describes the solvolysis of this cation in dimethyl sulfoxide (DMSO), N,N-dimethylformamide (DMF), N-methylformamide (NMF), and formamide, and presents a comparison of these solvents and water as solvolytic reagents. Furthermore, the paucity of kinetic data on reactions of transition metal complexes in nonaqueous solvents prompted us to undertake this investigation.[2,3] Recently, Asperger, *et al.*,[4] Langford,[5,6] and others[7,8] have studied the solvolytic reaction of the *trans*- and *cis*-$[Co(en)_2Cl_2]^+$ cations in nonaqueous solvents. A correlation of the dielectric strengths of the solvents with "k" values has been made by Asperger and coworkers.[4]

For the four solvents mentioned above, forward reaction 1 is considerably faster than forward reaction 2, so that no serious interference is caused by reaction 2 in the study of reaction 1. Under the conditions of the experiment reported here, equilibrium was not observed for the four solvents in reaction 1 and for N-methylformamide and formamide in reaction 2.

$$\mathit{cis}\text{-}[\mathrm{Co(tren)Br_2}]^+ + \mathrm{solv} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathit{cis}\text{-}[\mathrm{Co(tren)Br(solv)}]^{2+} + \mathrm{Br}^- \qquad (1)$$

$$\mathit{cis}\text{-}[\mathrm{Co(tren)Br(solv)}]^{2+} + \mathrm{solv} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \mathit{cis}\text{-}[\mathrm{Co(tren)(solv)_2}]^{3+} + \mathrm{Br}^- \qquad (2)$$

Experimental Section

Reagents. (a) **Complex *cis*-$[Co(tren)Br_2]Br$.**—The synthesis of this compound has been reported previously.[1]

(b) **Salts.**—The salts $Mg(ClO_4)_2$ and NaCl were anhydrous reagent grade quality.

(c) **Solvents.**—The solvents were Fisher Certified reagents and no attempt was made at further purification. Langford and Langford[5] reported equivalent kinetic results with Fisher Certified reagent DMF and specially purified DMF refluxed over BaO and distilled at reduced pressure. No attempts were made to isolate solvent-substituted products of *cis*-$[Co(tren)Br_2]^+$.

Electronic Absorption Spectra.—The spectra in the visible and near-visible region of the various species were obtained with a Cary Model 14 recording spectrophotometer. Approximately millimolar solutions in the appropriate solvent were scanned in matched cells of 1-cm light path.

Kinetic Measurements. (a) **Spectrophotometric Procedure.**—The change in absorbance was followed with time, and the wavelength chosen for the study of the reaction was one at which a substantial absorption difference occurs between reactant and product. For instance, this difference between the dibromo complex and the monosolvated bromo complex occurs at 420 mμ. This wavelength was therefore the one used in the study of reaction 1. Reaction 1 was also followed at 670 mμ to confirm the assumption that no other unexpected side reactions were complicating the reaction. Measurements were made on the same Cary Model 14 described above. The temperature was controlled to within ±0.05° by circulating thermostated water through the compartment surrounding the cells. The concentration of complex in these runs was 0.6–3 m*M*. Experimental infinity absorptions were obtained after 10 half-lives. As reported in an earlier work,[1] the concentration of the complex can be obtained from A_∞ values of the monosolvated species after t_∞ for reaction 1 (again $k_1 \gg k_2$). Once a Beer's law plot is made on known concentrations at 420 mμ, the concentration of each kinetic run can be measured spectrophotometrically. Results comparable to within 1% were obtained from kinetic runs on solutions whose concentrations were determined by direct weighing of the complex into a known solution volume and with solutions whose concentrations were determined from A_∞.

(b) **Conductometric Procedure.**—The reaction was followed conductometrically. For these measurements an RC-18 Industrial Instruments conductance bridge equipped with a 1000- and 3000-c signal and a cathode ray oscillograph as the null detector

---

[1] Part II: S. K. Madan and J. Peone, Jr., *Inorg. Chem.*, **6**, 463 (1967).

[2] F. Basolo and R. G. Pearson, *Advan. Inorg. Chem. Radiochem.*, **3**, 1 (1961).

[3] D. R. Stranks in "Modern Coordination Chemistry," J. Lewis and R. C. Wilkins, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, p 125.

[4] S. Asperger, M. Orhanovic, M. Pribanic, and V. Reic, *J. Chem. Soc.*, 589 (1966).

[5] C. H. Langford and P. Langford, *Inorg. Chem.*, **2**, 300 (1963).

[6] C. H. Langford, *ibid.*, **3**, 228 (1964).

[7] M. L. Tobe and D. W. Watts, *J. Chem. Soc.*, 2991 (1964).

[8] M. L. Tobe and D. W. Watts, *ibid.*, 4614 (1964).