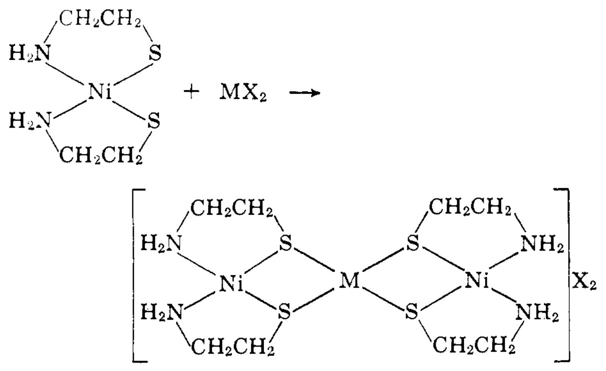
Reactions of Coordinated Ligands. XIX. The Mechanisms of Reaction of Benzyl Bromide with a Variety of Mercaptoaminenickel(II) Complexes

Elliott L. Blinn and Daryle H. Busch

Contribution from the Evans and McPherson Chemical Laboratories, The Ohio State University, Columbus, Ohio. *Received January 18, 1968*

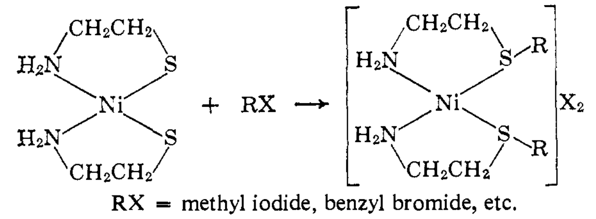
Abstract: Rate determinations have been conducted on the reactions of benzyl bromide with a series of nickel(II) complexes of the composition NiL_2, where L = N,N-dimethyl-β-mercaptoethylamine (Me_2L), N-*n*-propyl-β-mercaptoethylamine (*n*-PrL), N-*n*-octyl-β-mercaptoethylamine (OctL), or N-*n*-decyl-β-mercaptoethylamine (DecL). Over limited concentration ranges, the complexes obey second-order rate laws with the derivatives of secondary amines reacting approximately three times as fast as the complex of Me_2L. At high concentrations of benzyl bromide, the reaction rates for $Ni(PrL)_2$ and $Ni(DecL)_2$ increase less rapidly than predicted by the second-order rate law. The more extensive data for $Ni(PrL)_2$ are in quantitative agreement with the stepwise mechanism $NiL_2 + RX \rightleftharpoons NiL_2 \cdot RX$ (K) and $NiL_2 \cdot RX \longrightarrow NiL(RL)X$ (k), where the rate law gives a pseudo-first-order rate constant of the form $k_{obsd} = kK[RX]/(1 + K[RX])$. This is consistent with preequilibrium coordination of the halide to the central nickel(II) ion, followed by rate-determining nucleophilic substitution by the coordinated sulfur. Coordination by the metal ion is presumed to promote the breaking of the C–Br bond. $Ni(Me_2L)_2$ does not show such strong metal ion effects because the axial methyl groups at least partially block the metal ion.

The mercaptide ion is one of the most reactive nucleophiles in organic chemistry.[1] Although coordinating the mercaptide ion to a metal ion should limit its nucleophilic character, the mercaptide ion nevertheless remains a strong nucleophile when bound to nickel(II).[2] This is evidenced by the reactions of bis(β-mercaptoethylamine)nickel(II) with a variety of metal halides to form bridged complexes (eq 1)[3] and by the conversion of a coordinated mercaptide[4] to a coordinated thioether (eq 2). This nucleophilic efficacy of the mercaptide ion, whether coordinated or uncoordinated, makes it possible to study the influence of a metal ion on a nucleophilic displacement mechanism. The alkylation or benzylation of the coordinated mercaptide group is one of the most convenient reactions to study because the products have been isolated and characterized in both organic and inorganic systems. Also the kinetics of the alkylation reactions of organic mercaptides have been studied. Burke[5] studied the kinetics of the alkylation and benzylation of $Ni_2\{CH_3N(CH_2CH_2S)_2\}_2$ and $Ni_3(NH_2CH_2CH_2S)_4Cl_2$ and obtained some rudimentary information on the nature of these reactions. Because of the limited types of mercaptide complexes then available, Burke could not reach definitive conclusions on the influence of the metal ion on these reaction mechanisms. The major limitation of that study was that the only available compounds did not make it possible to distinguish among the different variables that might contribute to the reactions. Since both the nickel ions and the mercaptide were equally available for interaction with the alkylating agent, it was impossible to draw conclusions on the initial position of interaction. A more extensive investigation on the influence of the metal ion is now possible because there is a variety of monomeric mercaptoamine complexes that differ sufficiently in structure to permit the isolation of a number of variables. The key compounds were synthesized during the researches of Root[6] and Kothari.[7]



(1)

M = Ni(II), Pd(II), Pt(II), Cd(II), Cu(II), Co(II), Hg(II)



(2)

RX = methyl iodide, benzyl bromide, etc.

The complexes used to the greatest advantage in this investigation are the nitrogen-substituted mercaptoethylaminenickel(II) complexes. Because of the steric limitations imposed on the nickel complex by substituting different alkyl groups on the nitrogen atoms, it is possible to selectively alter the accessibility of the nickel ion and/or the mercaptide ion to incoming groups and thus partially inhibit the alkylation reaction. Consequently, it is possible to study the reactions of

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[1] F. E. Ray, "Organic Chemistry," J. B. Lippincott, Philadelphia, Pa., 1947; E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart & Winston, Inc., New York, N. Y., 1962.

[2] 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.

[3] D. C. Jicha and D. H. Busch, *Inorg. Chem.*, 1, 878 (1962).

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

[5] J. A. Burke, M.S. Thesis, The Ohio State University, 1961.

[6] C. Root, Ph.D. Dissertation, The Ohio State University, 1966; C. A. Root and D. H. Busch, *Inorg. Chem.*, 7, 789 (1968).

[7] V. Kothari, Ph.D. Dissertation, The Ohio State University, 1966.

alkyl halides and benzyl halides with complexes that vary in the availability of sites in the coordination sphere. In this manner, information has been gained relevant in detail to the manner of interaction between the reactants. The point of initial interaction between the complex and the organic molecule is a matter of primary concern.

The nitrogen-substituted mercaptoethylamine-nickel(II) complexes used in the investigation include $Ni(Me_2NCH_2CH_2S)_2$, $Ni(C_8H_{17}NHCH_2CH_2S)_2$, $Ni(C_3H_7NHCH_2CH_2S)_2$, and $Ni(C_{10}H_{21}NHCH_2CH_2S)_2$. These complexes vary in their structures, particularly in the accessibility of the different reactive sites in the complexes. Also, these complexes exhibit good solubilities and therefore can be studied over a range of conditions. This has made possible study on the nature of the interactions between mercaptoamine-nickel(II) complexes and alkyl or benzyl halides.

Experimental Section

Reagents and Complexes. All N-substituted mercaptoethylaminenickel(II) complexes were prepared and purified by the established procedures of Root.[6] Benzyl bromide was purified by distilling under reduced pressure and 1,2-dichloroethane was distilled over phosphorus pentoxide.

Kinetic Measurements. The change in absorbance with time was followed with the Cary 14 spectrophotometer. The wavelength was chosen such that the greatest optical density difference occurred between the starting material and the initial product. For N-substituted mercaptoethylamine complexes, kinetics were measured at 4150 and 4950 Å, while bis(N,N-dimethyl-β-mercaptoethylamine)nickel(II) was studied at 5940 and 4250 Å. The temperature was controlled with a Haake thermostat by circulating thermostated water through a jacketed spectral cell.

Solutions of the proper concentrations were prepared from benzyl bromide and metal complexes, and these solutions were preequilibrated in a constant-temperature bath. No more than two or three runs were obtained from a given stock solution.

All the experiments were run in dilute solutions in the presence of 5- to 200-fold excess of benzyl bromide. Two methods were employed in studying the kinetics of these reactions. In one of the methods, aliquots of complex and benzylating agent solutions were pipetted into an erlenmeyer flask, mixed, and finally poured into the constant-temperature cell. The other method makes use of the spring syringe. In this method the mixing is effected directly in the cell. One milliliter of the solution of the complex is placed in the constant-temperature cell and 0.5 ml of benzylating agent solution is shot directly into the cell. Gordon[8] was able to mix two solutions with a spring syringe in a 20-mm spectrophotometric cell in less than 30 msec. Since the response of the Cary spectrophotometer is limited by the chart drive, measurements could only be observed after about 3 sec. Based on Gordon's results and for present purposes, mixing can be considered almost instantaneous. Regardless of the method employed, the rate constants obtained were all reproducible within acceptable experimental error.

Results

In all the experiments the optical density increases with time, asymptotically approaching a plateau. The plateau is identified as the optical density at infinite time. The function log $(D_\infty - D)$ is plotted against time in order to obtain pseudo-first-order rate constants. Rate constants obtained using the time infinity method and the Guggenheim method are usually in good agreement. The Guggenheim method was not used to calculate most of the pseudo-first-order rate constants because the optical densities at large times do not vary to any great degree. A plot of the pseudo-first-order rate constant *vs.* the concentration of alkylating agent produces a straight line whose slope is equal to the second-order rate constant.

The entropies and enthalpies of activation were calculated from the equation

$$\ln (k_r h/Tk) = (\Delta S_a/R) - (\Delta H_a/RT) \qquad (3)$$

by plotting log $k_r h/Tk$ *vs.* $1/T$, where k_r is the rate constant, T is the absolute temperature, and k is the Boltzmann constant.

The credibility of the data was checked by varying the different sources of error. Since there are no obvious isosbestic points at which to study these reactions and since they are multistep processes, it is necessary to check whether the rate constants obtained are independent of the wavelength for which they are calculated. The change in optical density was measured at two wavelengths and the derived rate constants were compared. They agreed well in all cases tested. The rate constants are not affected by using different synthetic batches of metal complex or by using stored *vs.* freshly distilled akylating agent.

Before discussing the data, there is a distinct point of difficulty for all these systems which must be considered. For all the bis(N-monosubstituted β-mercaptoethylamine)nickel(II) complexes, there are *background* reactions in all solvents. The optical density increases with time in a similar manner to that observed when these complexes react with an alkylating agent. These background reactions are considerably slower than the reactions with an alkylating agent. For example, there is an observed rate constant of $k_1 = 1.6 \times 10^{-5}$ sec^{-1} for bis(N-propyl-β-mercaptoethylamine)nickel(II) in 1,2-dichloroethane, whereas the rates of reaction of the same complex with substituted benzyl bromides fall in the range from 3.2 to 4.5 $\times 10^{-3}$ sec^{-1}. Therefore, these background reactions do not prevent study of most of the alkylation reactions.

A background reaction also occurs for the bis(N,N-dimethyl-β-mercaptoethylamine)nickel(II) complex in solution, but this reaction is far slower than that of the nitrogen-monosubstituted β-mercaptoethylamine complexes. No noticeable change in optical density can be observed for about 3 hr.

Since only the first step in these reactions will give the desired information, assurance must be obtained that we are measuring only that first slow step. The spectra of these reactions, taken as a function of time, provide the best indication of the occurrence of the first step in these reactions. In all the cases studied, such scans reveal an increase in optical density followed by a slow decrease in optical density. All rate measurements are taken on the first step observed in the scans. Also, in most cases, the kinetic data conform to a simple pseudo-first-order rate law with a parametric dependence on the alkyl halide concentration. Finally, experiments using the spring syringe gave no indication that a prior reaction occurs at relatively short elapsed times.

The visible spectra pertaining to the reaction of bis(N-substituted β-mercaptoethylamine)nickel(II) with benzyl bromide as a function of time are illustrated in Figure 1. From this figure it is evident that the optical density increases rapidly for some 11 min and then decreases very slowly (40 hr). The starting material has a peak at 4800 Å and one at 3300 Å, while the

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

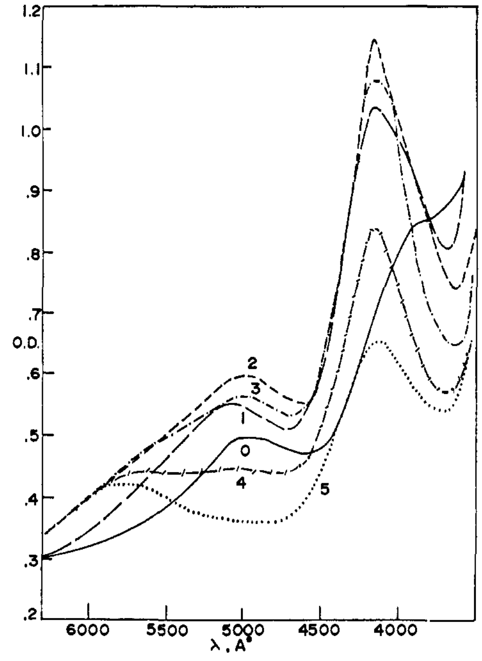


Figure 1. Visible spectra obtained during the reaction of bis(N-decyl-β-mercaptoethylamine)nickel(II) with benzyl bromide in 1,2-dichloroethane at 20° ([$Ni(C_{10}H_{21}NHCH_2CH_2S)_2$] = 3.3 × 10^{-4} *M*, [$C_6H_5CH_2Br$] = 1.435 × 10^{-2} *M*, chart speed = 25 Å/sec): (0) *t* = 0, (1) *t* = 35 sec, (2) *t* = 3 min and 45 sec, (3) *t* = 20 min, (4) *t* = 2 hr (all initiated at 6300 Å).

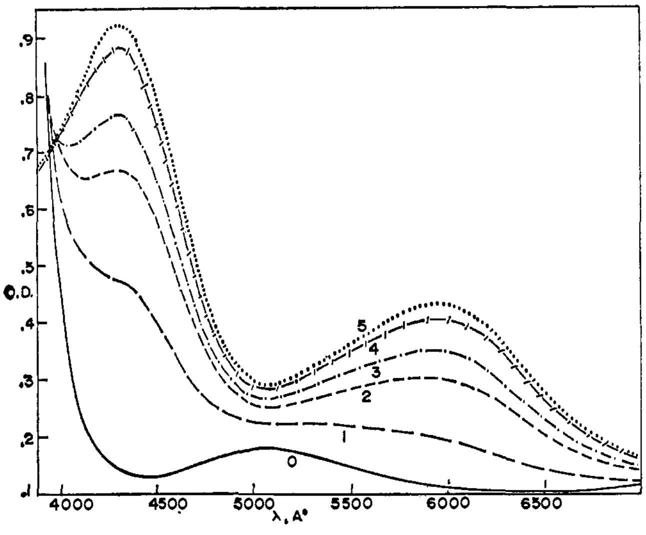


Figure 2. Visible spectra obtained during the reaction of bis(N,N dimethyl-β-mercaptoethylamine)nickel(II) with benzyl bromide in 1,2-dichloroethane at 25° ([$Ni(Me_2NCH_2CH_2S)_2$] = 3.40 × 10^{-4} *M*, [$C_6H_5CH_2Br$] = 1.04 × 10^{-2} *M*, chart speed = 25 Å/sec): (0) *t* = 35 sec, (2) *t* = 4 min, (3) *t* = 7 min; (4) *t* = 15 min, (5) *t* = 2 hr and 2 min (all reactions initiated at 7000 Å).

intermediate has peaks at 4900, 4250, and 3100 Å. At any wavelength between 5000 and 4000 Å, the extinction coefficient of the intermediate is much larger than that of the starting material. The greatest optical density change is seen at 4250 Å, and thus most of the kinetics were measured at that wavelength. The optical density of the intermediate then decreases in intensity with time until bands develop at 5800, 4200, and 3100 Å. The lowest energy band of the starting material and intermediate has no counterpart in the spectrum of the final product. Similar sequences of scans are found for the reactions of all bis(N-substituted β-mercaptoethylamine)nickel(II) with benzyl bromide.

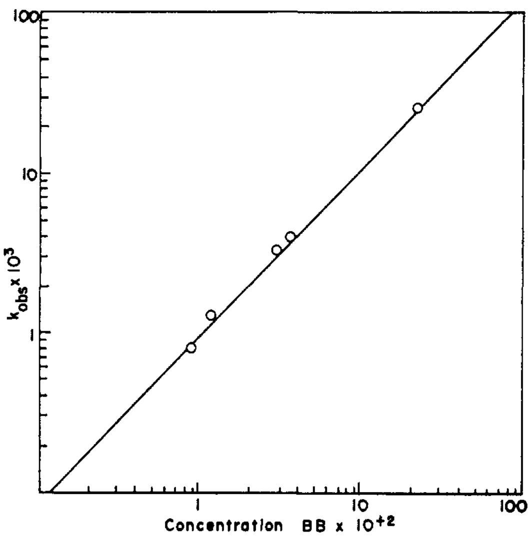


Figure 3. Log-log plot of k_{obsd} *vs.* [$C_6H_5CH_2Br$] for the reaction with $Ni(Me_2NCH_2CH_2S)_2$ in 1,2-dichloroethane at 25° (Table I).

The series of scans for the reaction of bis(N,N-dimethyl-β-mercaptoethylamine)nickel(II) with benzyl bromide in 1,2-dichloroethane (Figure 2) do not follow the same spectral sequence as observed for the N-monosubstituted mercaptoethylamine complexes. The optical density increases with time, but there is little evidence for any subsequent decrease in optical density. The starting material has a peak at 5000 Å, while the instantaneous product has peaks at 4250 and 5900 Å. The low-energy band shifts by 900 Å, while the corresponding shift for the N-monosubstituted complexes is 150 Å or less. It should be noted that only some 20 Å separate the different spectra peaks at about 3700 Å, and it is conceivable that an isosbestic point would exist in this region if there were no interference from a background reaction.

Kinetic data (Table I) for the reaction of bis(N,N-dimethyl-β-mercaptoethylamine)nickel(II) in excess benzyl bromide follow a first-order rate law with respect to metal complex, when the excess of benzyl bromide to nickel complex is within the range from 6- to 35-fold excess. The plot of log k_1 *vs.* log [$C_6H_5CH_2Br$] has a slope of 1.04 (Figure 3). Thus, the reaction is first order with respect to benzyl bromide. The arithmetic mean for the second-order rate constant between the concentration range of 0.79 and 22.2 *M* benzyl bromide is 0.105 M^{-1} sec^{-1} and the standard deviation is ±0.0074 M^{-1} sec^{-1}. In order to test whether the expression $k_{obsd} = k_2[C_6H_5CH_2Br]$ accounts for all the data, k_1 was plotted against the concentration of benzyl bromide. The intercept of this plot is quite small, having a magnitude comparable to its uncertainty and, therefore, no other term is required in the rate law.

The reaction of bis(N-propyl-β-mercaptoethylamine)nickel(II) (Table II) with benzyl bromide is first order in complex and first order in benzyl bromide. This relationship is valid only under the condition in which the benzyl bromide represents between 17- and 133-fold excess of the $Ni(C_3H_7NHCH_2CH_2S)_2$. Within this

Table I. Rate Constants for the Reaction of Bis(N,N-dimethyl-β-mercaptoethylamine)nickel(II) with Benzyl Bromide in 1,2-Dichloroethane at 25°

[NiL$_2$] × 10^3 M	λ, Å	[C$_6$H$_5$CH$_2$-Br] × 10^2 M	k_1 × 10^3 sec^{-1}	k_2, M^{-1} sec^{-1}
1.64	5940	2.38	2.20	0.096
1.64	5490	1.17	1.27	0.108
1.36	5940	0.79	0.79	0.110
1.36	4280	2.30	2.17	0.094
1.32	4150	2.96	3.24	0.100
1.68	4950	2.37	2.54	0.107
1.19	4150	22.2	25.00	0.112
1.12	4150	3.63	3.86	0.106

range of excess benzyl bromide this system follows a first-order rate law. A plot of k_1 *vs.* concentration results in a straight line with an intercept approximately equal to zero, and the plot of the log k *vs.* log concentration, within this range of excess of benzyl bromide, results in a slope of 1.12 (Figure 4). Within the concentration range of benzyl bromide from 1.18 × 10^{-2} to 5.97 × 10^{-2} M, the average second-order rate constant is 0.27_8 M^{-1} sec^{-1} and the standard deviation is $\pm 0.01_8$ M^{-1} sec^{-1}.

Table II. Rate Constants for the Reaction of Bis(N-propyl-β-mercaptoethylamine)nickel(II) with Benzyl Bromide in 1,2-Dichloroethane at 25°

[NiL$_2$] × 10^4 M	λ, Å	[C$_6$H$_5$CH$_2$Br] × 10^2 M	k_1 × 10^3 sec^{-1}	k_2, M^{-1} sec^{-1}
6.72	5140	2.96	8.34	0.282
6.72	4150	1.18	3.22	0.273
6.35	4150	3.82	10.00	0.262
9.32	4950	2.96	9.00	0.304
4.80	4150	1.49	4.13	0.277
5.15	4150	14.9	32.00	0.215
1.35	4150	4.10	12.2	0.297
4.42	4150	28.3	35.0	0.123
4.50	4150	14.2	20.9	0.147
6.15	4150	22.4	39.7	0.177
4.80	4150	5.97	14.7	0.246

At very high concentrations of benzyl bromide, the system does not follow this simple kinetic pattern. At benzyl bromide concentrations of 4.5 × 10^{-2} M and greater, the second-order rate constant calculated from $k_2 = k_{\text{obsd}}[\text{RX}]$ decreases with increasing concentration of benzylating agent.

Table III. Rate Constant for the Reaction of Bis(N-octyl-β-mercaptoethylamine)nickel(II) with Benzyl Bromide in 1,2-Dichloroethane at 25°

[NiL$_2$] × 10^4 M	λ, Å	[C$_6$H$_5$CH$_2$Br] × 10^2 M	k_1 × 10^3 sec^{-1}	k_2, M^{-1} sec^{-1}
6.17	4150	2.96	8.00	0.270
5.53	4150	2.37	6.67	0.281
5.15	4950	2.37	7.38	0.311
5.15	4150	2.37	5.12	0.216

The reactions of bis(N-octyl-β-mercaptoethylamine)nickel(II) (Table III) and bis(N-decyl-β-mercaptoethylamine)nickel(II) (Table IV) with benzyl bromide in 1,2-dichloroethane proceed kinetically in a very similar manner to that observed for bis(N-propyl-β-mercaptoethylamine)nickel(II). Excellent pseudo-first-order graphs have been obtained for both compounds at *compromise concentrations* of benzyl bromide (1.18 × 10^{-2}–2.96 × 10^{-2} M), and the order with respect to benzyl bromide is also unity. At very high concentrations of benzyl bromide a more complicated behavior is observed as was reported above for bis(N-propyl-β-mercaptoethylamine)nickel(II).

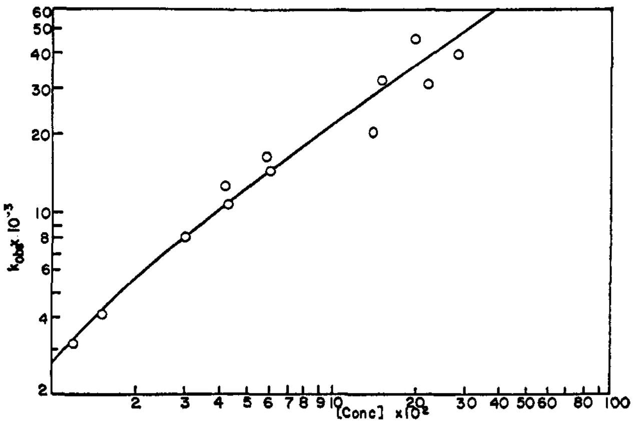


Figure 4. Log–log plot of the dependence of k_{obsd} on [C$_6$H$_5$CH$_2$Br] for the reaction with Ni(C$_3$H$_7$NHCH$_2$CH$_2$S)$_2$ in 1,2-dichloroethane at 25° (Table II).

Table IV. Rate Constants for the Reaction of Bis(N-decyl-β-mercaptoethylamine)nickel(II) with Benzyl Bromide in 1,2-Dichloroethane at 25°

[NiL$_2$] × 10^4 M	λ, Å	[C$_6$H$_5$CH$_2$Br] × 10^2 M	k_1 × 10^3 sec^{-1}	k_2, M^{-1} sec^{-1}
7.95	4950	2.37	7.86	0.332
7.95	4950	1.18	4.17	0.353
5.18	4150	2.37	6.83	0.288
4.82	4150	2.96	8.18	0.276
3.68	4150	22.40	26.8	0.120

The average second-order rate constant for the reaction of bis(N-decyl-β-mercaptoethylamine)nickel(II) with benzyl bromide is 0.31_2 M^{-1} sec^{-1}. The standard deviation is ±0.037 M^{-1} sec^{-1}. This deviation is sufficiently large to place the second-order rate constants for this reaction within the range of values found for the analogous reaction with bis(N-propyl-β-mercaptoethylamine)nickel(II). The second-order rate constant for the reaction of bis(N-octyl-β-mercaptoethylamine)nickel(II) with benzyl bromide is 0.270 M^{-1} sec^{-1} with an average deviation of ±0.035 M^{-1} sec^{-1}.

Discussion

The reactions of the N-substituted β-mercaptoethylaminenickel(II) complexes with benzyl bromide have a few common characteristics. For example, all these reactions exhibit a first-order dependence on the metal complex, and all the reaction rates are dependent on the concentration of benzyl bromide. Within a benzyl bromide concentration range of 1.0 × 10^{-2} to 6.0 × 10^{-2} M, the parametric dependence on benzyl bromide concentration approximates the first order for all the nitrogen-substituted β-mercaptoethylamine nickel(II) complexes. The very fact that the rate is dependent on both the complex and the benzylating agent suggests that an irreversible heterolytic cleavage of a sulfur–metal bond is not simultaneously the rate-determining step and the first reaction in the mechanism in all these reactions. Also, all these reactions have low energies of activation, 8.8–10.7 kcal (Table V), and this militates against heterolytic cleavage of the nickel–sulfur bond in the rate-determining step.[5] The large negative entropy (Table V) is consistent with an association process in a solvent of low polarity rather than with a dissociation process.

Table V. Enthalpies and Entropies of Activation for the Reactions of Nickel(II) Complexes of Substituted Mercaptoethylamines with Benzyl Bromide

Complex[a]	RX	$\Delta S_a^{\ddagger}$	$\Delta H_a^{\ddagger}$
$Ni(Me_2L)_2$	Benzyl bromide	−35.0	8.8
$Ni(PrL)_2$	Benzyl bromide	−29.2	9.4
$Ni(DecL)_2$	Benzyl bromide	−25.2	10.7

[a] Me_2L = N,N-dimethyl-β-mercaptoethylamine, PrL = N-*n*-propyl-β-mercaptoethylamine, and DecL = N-*n*-decyl-β-mercaptoethylamine.

The reactions of the nitrogen-substituted mercaptoethylaminenickel(II) complexes with benzyl bromide can be subdivided into two categories, those involving complexes of the type $Ni(RNHCH_2CH_2S)_2$ and that with bis(N,N-dimethyl-β-mercaptoethylamine)nickel(II). There are a number of criteria that justify this classfication. Although all these reactions conform to a pseudo-first-order rate law, there is no single form for the dependence on benzyl bromide concentration which is common to all the reactions. There appears to be a first-order dependence on $[C_6H_5CH_2Br]$ in the reaction of bis(N,N-dimethyl-β-mercaptoethylamine)nickel(II) over a wide range of concentrations of benzyl bromide (0.79×10^{-2}–22.2×10^{-2} *M*). In the analogous reaction with bis(N-substituted β-mercaptoethylamine)nickel(II) this simple behavior is restricted to a more limited concentration range. The order with respect to benzyl bromide decreases from unity as the concentration of benzyl bromide increases. This subject is discussed in a more quantitative manner later, but the concept that must now be stressed is that the empirical rate law appears to be different for the two classes of compounds.

The distinction is also justified on the basis of the spectral scans obtained for the benzyl bromide reactions. The scans for all the complexes of the type $Ni(RNHCH_2CH_2S)_2$ are very similar to each other (Figure 1), but they are different from that for the analogous reaction with bis(N,N-dimethyl-β-mercaptoethylamine)nickel(II) (Figure 2).

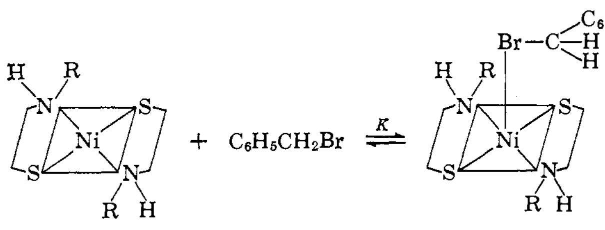
Finally, the second-order rate constants for the reactions of bis(N-substituted β-mercaptoethylamine)nickel(II) are similar in magnitude to each other (Table VI), but they are approximately three times larger than the corresponding rate constants with bis(N,N-dimethyl-β-mercaptoethylamine)nickel(II). For all data on N-monosubstituted derivatives, assuming them to have the same mean value, $k = 0.285 \pm 0.023$ M^{-1} sec^{-1}.

Table VI. Second-Order Rate Constants for the Reactions of Nitrogen-Substituted β-Mercaptoethylaminenickel(II) Complexes with Benzyl Bromide in 1,2-Dichloroethane at 25°

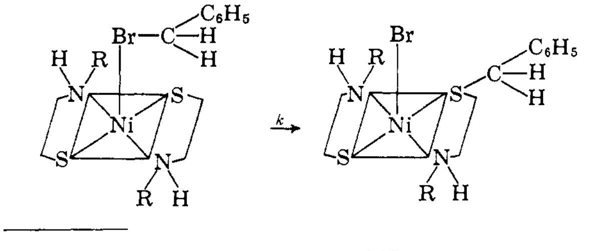
Complex	Concn range of $C_6H_5CH_2Nr$, *M*	k_2, M^{-1} sec^{-1}
$Ni(Me_2L)_2$	0.79×10^{-2}–22.2×10^{-2}	0.105 ± 0.007
$Ni(PrL)_2$	1.1×10^{-2}–5.97×10^{-2}	0.278 ± 0.018
$Ni(OctL)_2$	2.37×10^{-2}–2.96×10^{-2}	0.270 ± 0.035
$Ni(DecL)_2$	1.18×10^{-2}–2.96×10^{-2}	0.312 ± 0.037

The structures of the N-substituted β-mercaptoethylaminenickel(II) complexes can be used to explain most of the differences discussed above. In the solid state, bis(N,N-dimethyl-β-mercaptoethylamine)nickel(II) has a *trans* structure and contains two axial methyl groups, one above and one below the plane of the nickel ion.[9] Its nucleophilic sulfur atoms are located, with the remaining equatorial methyl groups, in the plane of the nickel ion. Assuming the same structure in solution, with the metal complex in such a configuration, the two sulfur atoms, as well as the nickel ion, are partially shielded from external reagents. If the axial methyl groups in bis(N,N-dimethyl-β-mercaptoethylamine)nickel(II) are replaced with hydrogen atoms, the nickel ion becomes more available for reaction regardless of the length of the linear alkyl groups. If the equatorial positions contain the hydrogens and the axial positions contain the various alkyl groups, the coordinated mercapto group is more susceptible to attack by benzyl bromide than in the case of bis(N,N-dimethyl-β-mercaptoethylamine)nickel(II). On steric grounds it would be predicted that bis(N-substituted β-mercaptoethylamine)nickel(II) complexes should react faster at any given temperature than bis(N,N-dimethyl-β-mercaptoethylamine)nickel(II). At this point, the data that have been discussed give no hint as to whether or not the nickel ion is assisting in these nucleophilic displacement reactions, as suggested by Burke,[5] but the data do indicate that the rate constants are sensitive to the steric requirements of different nitrogen-substituted β-mercaptoethylaminenickel(II) complexes.

Nickel-ion promotion of this nucleophilic displacement reaction is most easily explained using a mechanism involving a preequilibrium. The most obvious and reasonable preequilibrium involves coordination of the benzyl bromide to the metal atom of bis(substituted β-mercaptoethylamine)nickel(II) (eq 4). The subsequent step would be rate determining (eq 5),



(4)



(5)

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[9] E. Amma, *Inorg. Chem.*, **6**, 2009 (1967).

and this probably would involve the displacement of the halide by the mercaptide ion. If the nickel ion does not play a role in this reaction, there is no need to assume a preequilibrium. Such a mechanism suggests that extrapolation of the optical density data to zero time would result in an extinction coefficient for the metal complex which fails to coincide with the value obtained using only starting complex and the same solvent. The extrapolated extinction coefficients for the systems $Ni(RNHCH_2CH_2S)_2$–benzyl bromide should correspond to the preequilibrium mixture of reactant and product, $Ni(RNHCH_2CH_2S)_2 \cdot RX$, and not to pure starting material. Of course, if the extinction coefficient of the preequilibrium product coincides with that of the starting material, or if only minute amounts of the preequilibrium product are formed, no distinction can be made between the two alternate mechanisms by such comparisons. Coincidental spectra are not expected over a wide range of wavelengths, and therefore this experiment could be used as a diagnostic tool to help differentiate between the two most obvious possible mechanisms. A further limitation is found in the possibility that charge-transfer spectral effects might occur without being directly related to mechanism.

Table VII. Comparison of Experimental and Expected[a] Optical Densities at Zero Time for the Reaction of Bis(N-propyl-β-mercaptoethylamine)nickel(II) with Benzyl Bromide in 1,2-Dichloroethane at 25°

Expt	$[Ni(PrL)_2]$ × 10^4 M	[RX] × 10^2 M	λ, Å	OD Expected	OD Found
109	8.27	2.77	4000	0.200	0.150
110	8.27	1.11	4000	0.235	0.185
111	5.47	2.77	4500	0.110	0.090
112	4.76	2.76	4000	0.175	0.115
113	5.47	2.77	4250	0.130	0.120

[a] The OD for pure complex solutions is time dependent so that all "expected" values are by direct measurement.

The data of Table VII clearly indicate no correspondence between the experimental and expected optical densities at zero time. Therefore, it is quite possible that a preequilibrium does precede the rate-determining step.

The rate expression for a mechanism involving a preequilibrium followed by an irreversible displacement reaction is in eq 6, where $[A]_0$ is the concentration of

$$dx/dt = kK[A]_0[RX]/(1 + K[RX]) \tag{6}$$

complex. Under pseudo-first-order conditions, the ratio of the observed rate constant to the concentration of benzyl bromide is given by eq 7. If the K[RX]

$$\frac{k_{obsd}}{[RX]} = \frac{kK}{(1 + K[RX])} \tag{7}$$

term is considerably less than 1 (*i.e.*, at moderate concentrations of benzyl bromide), the parameter $k_{obsd}/[C_6H_5CH_2Br]$ would appear to be independent of the concentration of benzyl bromide. At higher concentration of benzyl bromide the denominator of eq 7 would differ substantially from unity and the parameter $k_{obsd}/[C_6H_5CH_2Br]$ would decrease with increasing concentration of benzyl bromide. The data given in Tables II–IV indicate that this is the case for the reaction of bis(N-substituted β-mercaptoethylamine)nickel(II) with benzyl bromide. Between an excess of benzyl bromide over complex of 17- to 133-fold, the ratio of $k_{obsd}/[C_6H_5CH_2Br]$ remains constant at a value of 0.278 M^{-1} sec^{-1}. At excesses greater than this, the parameter $k_{obsd}/[C_6H_5CH_2Br]$ decreases as the concentration of benzyl bromide increases. Equation 8 predicts that a plot of $1/k_{obsd}$ against $1/[C_6H_5CH_2Br]$

$$\frac{1}{k_{obsd}} = \frac{1}{kK[RX]} + \frac{1}{k} \tag{8}$$

should result in a linear relationship. The intercept of this plot is $1/k$ and the slope is equal to $1/kK$. Figure 5 shows that the rate data yield a straight line as required by the preequilibrium model. The value for k is 0.11 sec^{-1}, and the equilibrium constant is equal to 2.63 l./mole at 25° in dichloroethane. This rate law is consistent with all the other experiments on this system. All this offers strong support for the preequilibrium mechanism wherein the metal ion polarizes the C–Br bond and accelerates the reaction. The data presented above are consistent with the structures assumed for the bis(N-substituted β-mercaptoethylamine)nickel(II) complexes. The most favorable condition for preequilibrium coordination to the nickel ion requires the alkyl groups on the nitrogen to occupy equatorial positions. This argues against a *cis* orientation of the nitrogens, since it is unlikely that both alkyl groups are then in equatorial positions due to the steric hindrance.

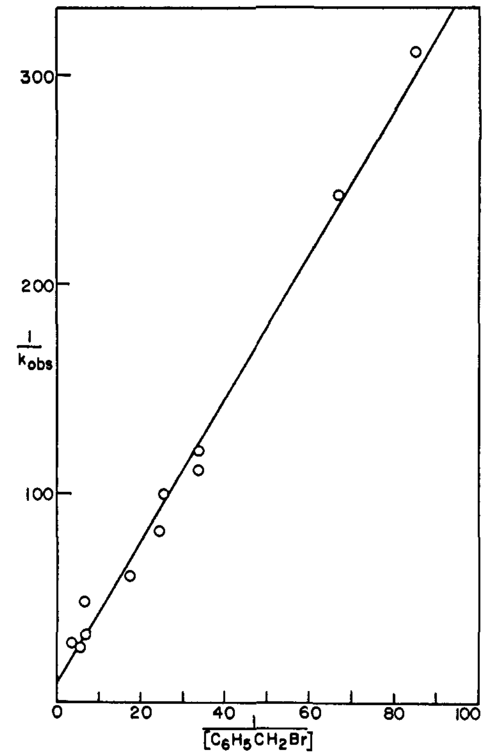

Figure 5. Plot of $1/k_{obsd}$ *vs.* $1/[C_6H_5CH_2Br]$ for the reaction with bis(N-propyl-β-mercaptoethylamine)nickel(II) in 1,2-dichloroethane (4250 Å, 25°).

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