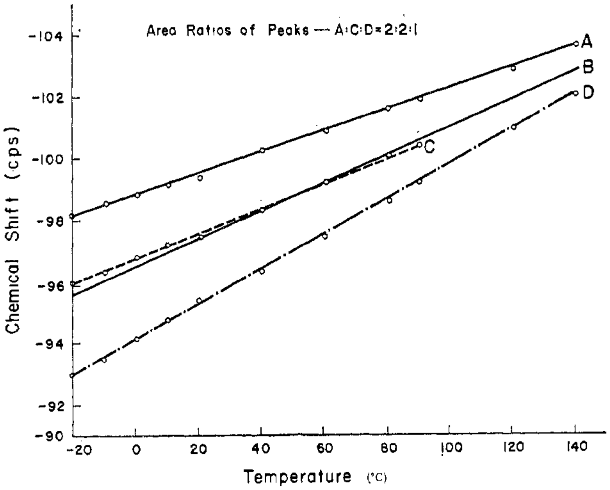

Figure 1.—Temperature dependence of chemical shifts of methyl groups in $(CH_3As)_5$–C_6D_6 solution: A, most downfield methyl; B, midpoint; C, middle methyl; D, most upfield methyl.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
TRINITY UNIVERSITY, SAN ANTONIO, TEXAS 78212

Rates of Reaction of Bis(8-mercaptoquinoline)nickel(II) with Alkyl and Aryl Halides

BY JOHN A. BURKE, JR., AND EDWARD C. BRINK, JR.

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The reactions occurring at metal-coordinated sulfur atoms have been well demonstrated.[1–4] It seems that these reactions with alkyl halide take place without the rupture of the metal-to-sulfur bond. The rates of reaction of some dimeric and trimeric nickel(II) complexes of β-mercaptoethylamine with alkyl and aryl halides have been measured. The Arrhenius parameters have low values compared with the data for reactions that conform to SN2 kinetic mechanisms.[2] These reactions have been shown to occur only at sulfur atoms bonded to one nickel ion; *i.e.*, the bridging sulfur atoms are inert to the organic halides.[5]

Recently it has been shown that chelated thioethers undergo S-demethylation under mild conditions.[3,6] The demethylations of 8-methylthioquinoline and dimethyl-*o*-methylthiophenylarsine complexes have been studied more thoroughly. In the case of the latter ligand, the palladium and platinum complexes of a 2:1 ligand to metal ratio were also observed to undergo reaction with alkyl and aryl halides in chloroform solution to yield the thioether complexes. Again bridging sulfur atoms are unreactive.

It has been possible in the work reported here to methylate the nickel(II) complex of 8-mercaptoquinoline under room-temperature conditions in chloroform. The stoichiometry of the reaction is given in eq 1. The rates of reaction of this complex with

$$Ni(C_9H_6NS)_2 + 2CH_3I \longrightarrow Ni(C_9H_6NSCH_3)_2I_2 \qquad (1)$$

methyl iodide, benzyl chloride, benzyl bromide, and α,α′-dibromo-*o*-xylene have been determined spectrophotometrically as a function of temperature.

Experimental Section

Bis(8-mercaptoquinoline)nickel(II) was prepared by stirring nickel chloride hexahydrate with 8-mercaptoquinoline hydrochloride, supplied by K & K Laboratories, in a 3:1 ethanol–hypophosphorous acid solution. The acid served to prevent oxidation of the ligand to the disulfide and did not appreciably hamper the formation of the complex. A 2:1 mole ratio of metal ion to ligand was refluxed for 1 hr. The insoluble dark red precipitate was filtered on a sintered-glass funnel and washed successively with water, ethanol, and chloroform. Recrystallization from chloroform followed by air drying yielded bis(8-mercaptoquinoline)nickel(II) monohydrate. The analyses were performed by Galbraith Laboratories, Inc. *Anal.* Calcd for $Ni(C_9H_6NS)_2 \cdot H_2O$: C, 54.58; H, 3.56; N, 7.25. Found: C, 54.55; H, 3.58; N, 6.80.

Bis(S-methyl-8-mercaptoquinoline)nickel(II) iodide was prepared in a manner analogous to that reported by Busch, *et al.*[2] Bis(8-mercaptoquinoline)nickel(II) was treated with an excess of methyl iodide in 250 ml of chloroform at room temperature overnight. The reaction of the dark red complex yielded a bright yellow solution when the reaction was complete. Reduction in solution volume under reduced pressure to 20 ml followed by addition of cold ethanol induced the precipitation of the yellow product. The precipitate was suction filtered, washed with chloroform, and air dried. *Anal.* Calcd for $Ni(C_9H_6NSCH_3)_2I_2 \cdot H_2O$: C, 35.27; H, 2.96; N, 4.11. Found: C, 34.81; H, 2.92; N, 4.02.

Kinetic measurements were made on the reactions of bis(8-mercaptoquinoline)nickel(II) monohydrate with benzyl bromide, benzyl chloride, methyl iodide, and α,α′-dibromo-*o*-xylene in chloroform. Baker Analyzed reagent benzyl bromide and benzyl chloride were used. The benzyl chloride was redistilled and the fraction boiling from 178 to 180° was collected. Methyl iodide and α,α′-dibromo-*o*-xylene supplied by Eastman Organic Chemicals, as well as the benzyl bromide above, were used without further purification. Baker Analyzed reagent chloroform was used as the solvent.

The concentration of bis(8-mercaptoquinoline)nickel(II) was followed with a Beckman DU spectrophotometer. The visible absorption spectrum of the bis(8-mercaptoquinoline)nickel(II) shows bands at 539 mμ and at 390 mμ. The optical cells were thermostated to ±0.1° with Beckman dual thermospacers by circulating water from a regulated bath. All solutions were brought to temperature before mixing the complex stock solution with the appropriate organic halide solution. A 10–1000-fold

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[1] R. G. V. Ewens and C. S. Gibson, *J. Chem. Soc.*, 431 (1949).

[2] D. H. Busch, J. A. Burke, 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] L. F. Lindoy, S. E. Livingstone, and T. N. Lockyer, *Inorg. Chem.*, **6**, 652 (1967).

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

[6] L. F. Lindoy, S. E. Livingstone, and T. N. Lockyer, *Nature*, **211**, 519 (1966).

excess of organic halide was always present in the reaction mixture. After mixing, the sample was placed in a silica cuvette and the reaction was followed at the 539-mμ absorption of bis(8-mercaptoquinoline)nickel(II) (a = 4000). The absorbance at this wavelength was observed to approach zero on long standing. The final visible spectra of the reaction mixtures of the methyl iodide rate determinations are identical with the spectrum of the isolated bis(S-methyl-8-mercaptoquinoline)nickel(II) iodide in chloroform solution with a single visible band at 410 mμ.

The pseudo-first-order rate constants were evaluated from the slope of log (A_0/A) *vs.* time plots where A_0 is the initial absorbance and A is the absorbance observed at a given time. These plots were normally observed to be linear for at least 3 half-lives in each set of determinations. Determinations at several concentrations of organic halide demonstrated the first-order dependence of this reactant.

Results and Discussion

The results of the kinetic measurements at three temperatures for each organic halide are given in Table I. The values of the rate constants are the averages of several determinations at more than one concentration of organic halide. These rate constants are precise to ±6%. The rates relative to that of benzyl chloride are 1.0, 159, 8.3, and 68.0 for benzyl chloride, benzyl bromide, methyl iodide, and α,α′-dibromo-*o*-xylene, respectively.

The isolation of the product of the reaction of bis-(8-mercaptoquinoline)nickel(II) and methyl iodide shows that both of the sulfur atoms in the complex are vulnerable to attack by alkyl and aryl halides. This observation, coupled with the fact that sulfur atoms that bridge two nickel ions are inert to such attacks as in the case of bis[N-methylbis(β-mercaptoethylamine)]dinickel(II),[2] supports the hypothesis that bis(8-mercaptoquinoline)nickel(II) exists essentially as monomeric species in chloroform solutions. Weakly bridged mercaptide polymers which are labile cannot be excluded, however. Although it would be desirable to obtain the molecular weight of the starting material, limited solubility prevented this determination. The previously reported diamagnetism[7] of this complex supports a square-planar molecular structure. The relative simplicity of the molecular structure, the solubility of the complex in a noncoordinating solvent, and the intense color of the complex have made it an ideal substance to use in studying the reactions of the coordinated sulfur atoms.

TABLE I

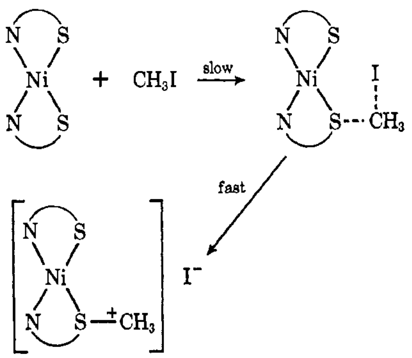
KINETIC PARAMETERS FOR THE REACTIONS OF BIS(8-MERCAPTOQUINOLINE)NICKEL(II) WITH METHYL IODIDE, BENZYL CHLORIDE, BENZYL BROMIDE, AND α,α′-DIBROMO-*o*-XYLENE

Organic halide	Temp, °C	[RX],[a] M	k, M^{-1} sec^{-1}	No. of determinations
$C_6H_5CH_2Br$	15.0	0.160–0.420	1.41×10^{-3}	3
	30.0	0.00370–0.0740	4.05×10^{-3}	4
	40.0	0.0384–0.154	5.95×10^{-3}	4
($A = 6.2 \times 10^5\ M^{-1}$ sec^{-1}, E_a = 11 kcal/mol)				
CH_3I	15.0	1.60–3.21	7.07×10^{-5}	2
	20.6	0.642–3.41	10.0×10^{-5}	3
	30.0	0.796–3.21	21.2×10^{-5}	5
($A = 3.5 \times 10^5\ M^{-1}$ sec^{-1}, E_a = 13 kcal/mol)				
$C_6H_5CH_2Cl$	21.0	0.521–0.699	1.35×10^{-5}	2
	30.0	0.348–0.871	2.55×10^{-5}	3
	40.0	0.871–1.04	4.27×10^{-5}	2
($A = 4.5 \times 10^3\ M^{-1}$ sec^{-1}, E_a = 11 kcal/mol)				
$C_6H_4(CH_2Br)_2$	18.0	0.142–0.709	8.29×10^{-4}	2
	30.0	0.959–1.92	17.4×10^{-4}	2
	40.0	0.959–2.88	30.2×10^{-4}	2
($A = 7.0 \times 10^4\ M^{-1}$ sec^{-1}, E_a = 11 kcal/mol)				

[a] The range of molar concentrations used for alkyl or aryl halide in the reactions with a nickel complex concentration of approximately 2×10^{-4} M.

The kinetic data for the reactions of alkyl halides with bis(8-mercaptoquinoline)nickel(II) and bis[N-methylbis(β-mercaptoethylamine)]dinickel(II) are indeed quite similar. The energies of activation for the latter complex range from 7 to 13 kcal/mol and the rates relative to benzyl chloride are 1, 125, and 21 for benzyl chloride, benzyl bromide, and methyl iodide, respectively.[2] This similarity in kinetic parameters certainly suggests that the same mechanism is operating for the two systems. The first-order dependence of the reaction rate on the complex and the alkyl or aryl halide and the absence of consecutive rates in both cases indicate that the reaction leading to the dialkylated products proceeds at a rate much faster than the initial alkylation.

The mechanism that was proposed for bis[N-methylbis(β-mercaptoethylamine)]dinickel(II)[2] as applied to the present work is illustrated in eq 2, where $\overset{\frown}{\mathrm{N\ S}}$



(2)

is used to represent 8-mercaptoquinoline. If the results of this study are examined in the light of this mechanism, it would seem appropriate that the aromatic structure of 8-mercaptoquinoline should render the sulfur atoms less nucleophilic than the sulfur atoms of the β-mercaptoethylamine complex. This hypothesis leads to the prediction that the reaction should proceed at a slower rate for the aromatic system as it has been observed, *i.e.*, alkyl and aryl halides studied react approximately one-tenth as fast with bis(8-mercaptoquinoline)nickel(II) as with bis[N-methylbis(β-mercaptoethylamine)]dinickel(II) in chloroform at room temperature.

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(7) W. Hieber and R. Brück, *Z. Anorg. Allgem. Chem.*, **269**, 28 (1952).