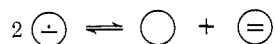


Figure 11.

lent hydrogens. One of the two equivalent sets of hydrogens has a hyperfine coupling constant too low to resolve under the conditions used: $\Delta H_P = 4.5$ G, $\Delta H_H = 1.5$ G (Figure 11). Unfortunately, as with the other bridged bimetallic species, which exist in an equilibrium (except systems 21 and 22), the value of the equilibrium constant precludes infrared studies on the



radical anion alone; the system could only be investigated as the dianion, produced by exhaustive electrolysis. Addition of halogen to $[\text{LFe}(\text{CO})_3]_2$ systems is known to lead to a structure with a dihedral angle of 180° , *via trans* addition and rupture of the metal-metal bond. It is not known what electrochemical reduction to the dianion accomplishes. Mössbauer spectroscopy and broad-line nmr techniques are currently being applied to this and similar systems to further investigate geometry. Only then can an analysis of the system be made.

Conclusions

Based upon the results of this study, it is concluded that the transmission of charge in these systems in which all other factors can be assumed constant occurs primarily by a σ effect. From the fact that both force constants decrease upon electrochemical reduction it is concluded that there is an isotropic inductive effect. There is also a directional σ effect which is quite pronounced, being in all cases examined stronger than the π effect, as is evidenced by the larger change observed in k_1 relative to k_2 . Two possible explanations of these directional qualities are: (1) the polarization theory proposed by Grinberg⁴² or (2) a consideration of the σ molecular orbitals which, owing to the symmetry involved, place the carbonyl group *trans* to a ligand in a different molecular orbital from the molecular orbital involving the carbonyl groups *cis* to the ligand.

Although the theories of Cotton and Graham suffice to explain the changes resulting in metal carbonyls due to a change in the π and σ donor-acceptor properties of a ligand, they proved inadequate to explain the transmission of charge density in a molecule with a fixed (assumed) π and σ framework. The theories of Brown have proven adequate to handle both. Since the former theories were not designed to explain the latter phenomenon and are not based on experiments in which this phenomenon is a major factor, there seems to be no reason *a priori* to expect them to be applicable. It should be realized, however, that these factors are present, and they should be taken into consideration.

Acknowledgments. The authors wish to thank the Army Research Office (Durham) for its support on Grant 31-124-G845 and the National Science Foundation for its support on Grant GP7410, and to gratefully acknowledge the help of Mr. Gerald Dulaney in the programming aspects of the work.

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Kinetics and Mechanism of the Iodide Ion Reduction of S,S-Dimethylsulfiminium Perchlorate

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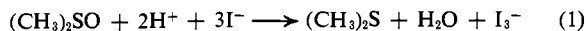
Abstract: The kinetics of the reaction $(\text{CH}_3)_2\text{SNH}_2^+ + 3\text{I}^- + 2\text{H}^+ \rightarrow (\text{CH}_3)_2\text{S} + \text{I}_3^- + \text{NH}_4^+$ have been measured spectrophotometrically in water and in DMSO-water solvents over the range $X_{\text{DMSO}} = 0-1.00$. The observed rate law is $d[\text{I}_3^-]/dt = k_1[(\text{CH}_3)_2\text{SNH}_2^+][\text{H}^+][\text{I}^-]$. In aqueous solution at 25° and 0.120 M ionic strength, $k_1 = 0.56 \pm 0.02$ $\text{M}^{-2} \text{sec}^{-1}$, $\Delta H^\ddagger = 12.2 \pm 0.4$ kcal/mole, and $\Delta S^\ddagger = -19 \pm 1$ eu. The deuterium solvent isotope effect observed is $k_{\text{H}_2\text{O}}/k_{\text{D}_2\text{O}} = 0.27$. The reaction is catalyzed by added thiourea, but not by bromide or chloride ions. The mechanism proposed involves nucleophilic displacement at the sulfur center by a soft base nucleophile, iodide ion or thiourea.

The effect of solvent on nucleophilic reactivity has been widely recognized.¹ We have been interested in nucleophilic displacement reactions at sulfur

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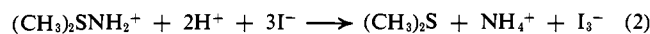
centers and the role played by the solvent in modifying the order of nucleophilic reactivity toward these centers. Recent reports have contributed greatly to the over-all understanding of those factors which influence

reactivity toward a variety of sulfur centers.² In an earlier study we reported a nucleophilic order, $\text{Cl}^- > \text{Br}^- > \text{I}^-$, in the reaction



occurring in dimethyl sulfoxide (DMSO)-water solvents.³ This represents an inversion in order from that observed in water^{2g,h} brought about by the dipolar aprotic DMSO.

When the synthesis of $[(\text{CH}_3)_2\text{SNH}]_2\text{SO}_4$ was reported by Appel and Büchner,⁴ it was apparent that $(\text{CH}_3)_2\text{SNH}_2^+$ would provide the basis for a closely related system in which to further examine reaction at sulfur centers. The reaction



was selected for study. It was thought that reaction 2 might proceed *via* nucleophilic displacement by iodide ion on sulfur. Kinetic data have been obtained to examine the mechanism in detail.

Experimental Section

Reagents. Crown-Zellerbach dimethyl sulfoxide (Spectrograde) was used as received. DMSO-water solvent mixtures were prepared on a weight basis by dropwise addition of redistilled water to DMSO at a mixing temperature of approximately 10°. For use in the aqueous kinetic experiments, redistilled water was boiled and cooled while being swept with prepurified N_2 . Stohler Isotope D_2O , 99.8% purity, also was deoxygenated before use.

All potassium salts were reagent grade and were dried at 110° before use. Acid solutions were prepared from 72% reagent grade perchloric acid. Eastman White Label thiourea, methyl sulfide, and ethyl sulfide were used as received. Hydroxylamine sulfate, Matheson Coleman and Bell 99+%, was dried at 110° before use.

Preparation of Sulfiminium Compounds. S,S-Dimethylsulfiminium sulfate, $[(\text{CH}_3)_2\text{SNH}]_2\text{SO}_4$, and S,S-diethylsulfiminium sulfate, $[(\text{C}_2\text{H}_5)_2\text{SNH}]_2\text{SO}_4$, were prepared by the method of Appel and Büchner.⁴ An equivalent amount of sodium methoxide was used in place of sodium metal. The hydroxylamine-O-sulfonic acid required was prepared from hydroxylammonium sulfate and 30% SO_3 in H_2SO_4 .⁵ The sulfate salts were recrystallized once from dry methanol-ether and stored over P_2O_{10} . $[(\text{CH}_3)_2\text{SNH}]_2\text{SO}_4$ was converted to the perchlorate by addition of 1.00 g of NaClO_4 in 5.0 ml of dry methanol to a solution of 1.03 g of $[(\text{CH}_3)_2\text{SNH}]_2\text{SO}_4$ in 22 ml of dry methanol at 0°. The mixture was stirred for 10 min at 0° followed by vacuum filtration to remove the Na_2SO_4 formed. The filtrate was poured into 100 ml of dry ether at 0°. After washing the $(\text{CH}_3)_2\text{SNH}_2\text{ClO}_4$ with dry ether, the solid was placed in a vacuum desiccator over P_2O_{10} . Although no difficulty was experienced, this perchlorate is a potentially hazardous compound. It should be prepared only in small quantities and handled with care.

The sulfiminium salts were analyzed iodometrically. A weighed sample and a large excess of KI were added to 1 M H_2SO_4 which had been deoxygenated. The iodine produced was titrated with standard thiosulfate. During some of the analyses, small quantities of water-insoluble $(\text{CH}_3)_2\text{SI}_2$ were formed. After titration of the aqueous iodine, the bulk of the aqueous solution was separated from the dense $(\text{CH}_3)_2\text{SI}_2$ droplets. Added DMSO quickly dissolves the $(\text{CH}_3)_2\text{SI}_2$ and, after addition of more H_2SO_4 , the titration can be completed. The purity of the sulfiminium salts ranged

from 95 to 98%. When, after several weeks, the purity level fell below 95%, fresh samples were prepared for use in the kinetic experiments. Varian A-60 nmr spectra were obtained in aqueous solution, using sodium 3-trimethylsilyl-1-propanesulfonate as an internal standard: $(\text{CH}_3)_2\text{SNH}_2\text{ClO}_4$, CH_3 (-182 cps); $[(\text{C}_2\text{H}_5)_2\text{SNH}]_2\text{SO}_4$, CH_3 (-86 cps) and CH_2 (-197 cps). *Anal.* Calcd for $\text{C}_8\text{H}_{18}\text{ClNO}_4\text{S}$: C, 13.5; H, 4.5. Found: C, 13.4; H, 4.4. Calcd for $\text{C}_8\text{H}_{24}\text{N}_2\text{O}_4\text{S}_2$: C, 31.1; H, 7.8. Found: C, 30.4; H, 7.4.

Stoichiometry. The stoichiometry of reaction 2 was verified by analysis of iodine produced and hydrogen ion consumed. $(\text{CH}_3)_2\text{SNH}_2\text{ClO}_4$ was added to a solution containing a known excess amount of perchloric acid and potassium iodide. Prepurified nitrogen was used to minimize air oxidation. After the reaction was complete (3-4 hr), the iodine produced was titrated with thio-sulfate and subsequently the remaining acid titrated to the methyl red end point with sodium hydroxide. The results for a solution containing initially 0.527 mmole of $(\text{CH}_3)_2\text{SNH}_2\text{ClO}_4$, 2.45 mmoles of HClO_4 , and 5.6 mmoles of KI (solution volume 45 ml) are (moles of H^+ consumed)/(moles of I_2 produced) = 2.12. The stoichiometry was also verified in 0.150 mole fraction of DMSO where (moles of H^+ consumed)/(moles I_2 produced) = 2.00.

Kinetic Measurements. The reaction was followed by measuring the absorbance of I_3^- (the only significantly absorbing species) at 365 $\text{m}\mu$ in DMSO- H_2O solvents ($\epsilon_{13} = 25,800 \text{ M}^{-1} \text{ cm}^{-1}$)⁶ and at 353 $\text{m}\mu$ in water ($\epsilon_{13} = 26,400 \text{ M}^{-1} \text{ cm}^{-1}$).⁶ In DMSO-water mixtures, iodine is essentially completely converted to triiodide ion when $[\text{I}^-]_0 = 0.05\text{--}0.10 \text{ M}$.⁷ For example, in 0.200 mole fraction of DMSO, $K_D(\text{I}_3^-) = 1.8 \times 10^{-4}$ (23°), so that $[\text{I}_3^-] = 0.9972\text{I}_2$ at $[\text{I}^-] = 0.060 \text{ M}$. In water, theoretical values of $A_{\infty}(\text{I}_3^-)$ are based on $K_D(\text{I}_3^-) = 1.39 \times 10^{-3}$ (25°).⁸ For aqueous kinetic runs, initial concentrations of H^+ and I^- were in 50-1000-fold stoichiometric excess over the initial concentration of the sulfiminium salt. Since $A_{\infty}(\text{I}_3^-)$ values varied because of air oxidation, kinetic runs in aqueous solution were carried out under nitrogen, following removal of oxygen from the solvent. Initial rates were measured in DMSO-water solvents, usually with $[(\text{CH}_3)_2\text{SNH}_2\text{ClO}_4]_0$ in the range $(0.4\text{--}1.5) \times 10^{-3} \text{ M}$. The resulting rate constants have been corrected for the slight decrease in $[(\text{CH}_3)_2\text{SNH}_2\text{ClO}_4]$ during the run.

After dissolution of the sulfiminium salt, an aliquot of the stock solution was added rapidly to the other reactant solutions to minimize any hydrolysis which might occur. The previously thermostated reactant solutions were mixed thoroughly and quickly placed in 1-cm glass-stoppered silica cells. Absorbances were measured using a Beckman Model DU spectrophotometer with a cell compartment thermostated to $\pm 0.05^\circ$. Ionic strength was maintained at 0.120 M in all runs using potassium perchlorate.

Reaction of $(\text{CH}_3)_2\text{SNH}_2\text{ClO}_4$ with Thiourea in Water. This reaction was followed by measuring the decrease in absorbance at 235 $\text{m}\mu$ where thiourea, but not $(\text{CH}_3)_2\text{SNH}_2^+$, has an appreciable absorbance. Infinite time absorbances were in good agreement with those expected for $(\text{H}_2\text{N})_2\text{CSSC}(\text{NH}_2)_2^{2+}$.⁹ An attempt was made to detect cationic products other than $(\text{H}_2\text{N})_2\text{CSSC}(\text{NH}_2)_2^{2+}$ by allowing thiourea to react with a very large excess of $(\text{CH}_3)_2\text{SNH}_2^+$. A mixture containing $[(\text{H}_2\text{N})_2\text{CS}] = 8.9 \times 10^{-5} \text{ M}$, $[(\text{CH}_3)_2\text{SNH}_2\text{ClO}_4] = 1.94 \times 10^{-2} \text{ M}$, and $[\text{H}^+] = 0.010 \text{ M}$ was allowed to react for 25 min at 25° and then was placed on a Dowex 50W X-4, 50-100 mesh ion-exchange column in the Na^+ form. The column was eluted with 0.20 M NaClO_4 -0.010 M HClO_4 . The spectra (245-300 $\text{m}\mu$) of the various fractions contained no features other than those expected for the reactants and $(\text{H}_2\text{N})_2\text{CSSC}(\text{NH}_2)_2^{2+}$.

Results

Reduction of S,S-Dimethylsulfiminium Perchlorate in DMSO-Water Solvent Mixtures. Initial rates of appearance of triiodide ion, $(d[\text{I}_3^-]/dt)_0$, M sec^{-1} , were measured for the first 1-3% of reaction. Plots of absorbance, A , vs. time were linear for solvents containing 0.500-1.00 mole fraction of DMSO (X_{DMSO}). The

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(8) R. W. Ramette and R. W. Sanford, Jr., *J. Am. Chem. Soc.*, **87**, 5001 (1965).

(9) Under the reaction conditions, ϵ is 1940 $\text{M}^{-1} \text{ cm}^{-1}$ for $(\text{H}_2\text{N})_2\text{CSSC}(\text{NH}_2)_2^{2+}$. $[(\text{H}_2\text{N})_2\text{CS}]_2\text{Cl}_2$ was prepared by the method of P. W. Preisler and L. Berger, *J. Am. Chem. Soc.*, **69**, 322 (1947).

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(5) H. J. Matsuguma and L. F. Audrieth, *Inorg. Syn.*, **5**, 122 (1957).

slopes of these plots were taken as the initial rates, with an uncertainty of $\pm 2\%$. The addition of the reaction product, dimethyl sulfide, had no effect on the rate, nor did the addition of oxygen gas to the reactant solutions. In several cases the reaction was followed for times corresponding to 10% conversion of $(\text{CH}_3)_2\text{SNH}_2\text{ClO}_4$ to products. The decrease in rate was very small, eliminating the possibility that the triiodide was being produced by small amounts of hydroxylamine-O-sulfonic acid, initially present as an impurity in $(\text{CH}_3)_2\text{SNH}_2\text{ClO}_4$.

Initial rates were measured as a function of initial concentrations of hydrogen ion, iodide ion, and S,S-dimethylsulfiminium ion. The kinetic results obtained in $X_{\text{DMSO}} = 0.500$ to establish the rate law conform quite accurately to the expression

$$d[\text{I}_3^-]/dt = k_I[(\text{CH}_3)_2\text{SNH}_2^+][\text{H}^+][\text{I}^-] \quad (3)$$

Concentration data and values of the calculated third-order rate constant, k_I , are presented in Table I.

Table I. Kinetic Data for the Reduction of S,S-Dimethylsulfiminium Perchlorate in 0.500 Mole Fraction of DMSO at 25.17° and 0.120 M Ionic Strength

$10^4[(\text{CH}_3)_2\text{SNH}_2\text{ClO}_4]_0, M$	$10^2[\text{I}^-]_0, M$	$10^3[\text{H}^+]_0, M$	$10^2k_I, M^{-2} \text{sec}^{-1}$
3.39-20.5	6.00	4.96	2.48 ± 0.05^a
10.3	6.00	1.68-8.43	2.44 ± 0.07^a
10.2	8.95	1.21-6.06	2.57 ± 0.05^b
10.1	2.28-11.4	4.93	2.50 ± 0.08^a
10.4	0.20-1.20	28.7	2.2 ± 0.1^b

^a Value of k_I based on the average of five runs in the concentration range indicated. ^b Average of three runs.

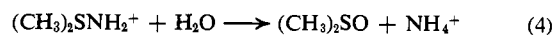
Values of k_I were obtained by dividing the observed initial rate by the initial concentrations of $(\text{CH}_3)_2\text{SNH}_2^+$, H^+ , and I^- . Since I^- and ClO_4^- were the only anions present, it was assumed that no significant ion-pairing occurs.¹⁰ The average value of $k_I = (2.5 \pm 0.1) \times 10^{-2} M^{-2} \text{sec}^{-1}$ in $X_{\text{DMSO}} = 0.500$ is based on runs for which $[\text{I}^-]_0 > 2 \times 10^{-2} M$. At lower iodide concentrations, the value of k_I was systematically smaller, similar to the behavior discussed below for $X_{\text{DMSO}} = 0.300$.

For a series of runs in which $[\text{I}^-]_0 = 4.55 \times 10^{-2} M$, $[\text{H}^+]_0 = 6.36 \times 10^{-3} M$, and $[(\text{CH}_3)_2\text{SNH}_2\text{ClO}_4]_0 = 1.25 \times 10^{-3} M$, values of $10^2k_I, M^{-2} \text{sec}^{-1}$ (ionic strength in parentheses), are 2.66 (0.0532 M), 2.52 (0.0880 M), 2.50 (0.120 M), and 2.47 (0.192 M). Although there is a trend toward lower rates with increasing ionic strength, the differences are within the level of experimental error.

The results for $X_{\text{DMSO}} = 1.00-0.150$ also obey eq 3 from which the values of k_I in Table II have been computed. When $X_{\text{DMSO}} = 0.300$, the plots of A vs. t are distinctly curved, the slopes decreasing with time. Values of k_I for $X_{\text{DMSO}} = 0.300$ in Table II are based on initial rate data collected during the first 1000 sec corresponding to $< 1\%$ reaction. At lower iodide concentrations, k_I values decrease and the extent of curvature increases. This behavior is probably due to consumption of iodine by a solvent impurity (*vide infra*) and to partial hydrolysis of a reaction intermediate.

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Competition of H_2O with I^- for an intermediate would lead to some production of $(\text{CH}_3)_2\text{SO}$, thereby decreasing the observed rate of formation of iodine. Hydrolysis of $(\text{CH}_3)_2\text{SNH}_2^+$



independent of the presence of I^- can be ruled out. Allowing a mixture of $(\text{CH}_3)_2\text{SNH}_2\text{ClO}_4$ and HClO_4 at typical initial concentrations to stand for 2400 sec before addition of I^- to start reaction 2 does not alter the initial rate observed. Furthermore, preliminary measurements of the rate of hydrolysis in aqueous solution containing $[\text{H}^+] = 0.10 M$ and $[(\text{CH}_3)_2\text{SNH}_2\text{ClO}_4] = 5 \times 10^{-3} M$ showed that the half-time for hydrolysis is greater than 10 hr at 25° at these concentrations.

The highly aqueous $X_{\text{DMSO}} = 0.150$ and 0.300 solvents apparently contain a trace impurity which reacts with I_3^- at a moderate rate. This impurity seems to be produced when water and DMSO are mixed, despite precautions taken to remove the heat which occurs during mixing. When $X_{\text{DMSO}} = 0.150$, plots of A vs. t show an inhibition of I_3^- production during the first 2000 sec as I_3^- presumably reacts with the trace impurity. After 2000 sec, the A vs. t plots are linear. Initial addition of $(1-1.5) \times 10^{-5} M$ I_3^- greatly reduces the inhibitory effect. The resulting initial rates are in agreement with the values obtained without prior addition of I_3^- . However, the values of k_I obtained at $X_{\text{DMSO}} = 0.150$ and 0.300 should be regarded as less reliable than those in the less aqueous solvents.

The effect of added Cl^- and Br^- as potential catalysts for the reaction was studied. The results of addition of KCl and KBr in $X_{\text{DMSO}} = 0.700$ and of KCl in $X_{\text{DMSO}} = 0.300$ are shown in Table II. No catalysis was observed since there was no significant increase in the k_I values.

The reduction of $(\text{CH}_3)_2\text{SNH}_2\text{ClO}_4$ and consequent formation of I_3^- is catalyzed by thiourea. In a typical run, the initial rate of triiodide production is increased by a factor of 2.6 in the presence of $7.5 \times 10^{-3} M$ $(\text{H}_2\text{N})_2\text{CS}$ in an $X_{\text{DMSO}} = 0.700$ solution containing $5.5 \times 10^{-4} M$ $(\text{CH}_3)_2\text{SNH}_2\text{ClO}_4$, $4.16 \times 10^{-3} M$ HClO_4 , and $5.40 \times 10^{-2} M$ KI . Values of $(d[\text{I}_3^-]/dt)_0$ obtained at several initial concentrations of $(\text{CH}_3)_2\text{SNH}_2\text{ClO}_4$, HClO_4 , KI , and $(\text{H}_2\text{N})_2\text{CS}$ are shown in Table III. The data are in accord with the two-term rate law

$$d[\text{I}_3^-]/dt = [(\text{CH}_3)_2\text{SNH}_2^+][\text{H}^+]\{k_I[\text{I}^-] + k_{\text{TU}}[(\text{H}_2\text{N})_2\text{CS}]\} \quad (5)$$

in which k_{TU} is the third-order rate constant for the thiourea-catalyzed path. At 25.17° in $X_{\text{DMSO}} = 0.700$, $k_{\text{TU}} = 0.51 \pm 0.04 M^{-2} \text{sec}^{-1}$, determined by assuming $k_I = 0.046 M^{-2} \text{sec}^{-1}$.¹¹ For the several concentrations employed, the contribution of the catalytic term to the total rate varies from 34 to 67%. Thiourea catalyzes the reaction in $X_{\text{DMSO}} = 0.500$, also. In a series of runs with $[\text{H}^+]_0 = 3.72 \times 10^{-3} M$, $[\text{I}^-]_0 = 6.01 \times 10^{-2} M$, $[(\text{CH}_3)_2\text{SNH}_2\text{ClO}_4]_0 = 9.25 \times 10^{-4} M$, and $[(\text{H}_2\text{N})_2\text{CS}]_0$ in the range $(2.50-9.95) \times 10^{-3} M$, the value of k_{TU} is $0.34 \pm 0.04 M^{-2} \text{sec}^{-1}$.

(11) Thiourea also catalyzes the reduction of solvent dimethyl sulfide by H^+ and I^- as described in ref 3. Initial rates for runs summarized in Table III have been corrected by subtracting the small (0.5-1.3%) contributions to I_3^- production due to reaction of the solvent.

Table II. Kinetic Data for the Reduction of S,S-Dimethylsulfiminium Perchlorate in 1.00–0.150 Mole Fraction of DMSO at 25.17° and 0.120 M Ionic Strength

$10^4[(\text{CH}_3)_2\text{SNH}_2\text{ClO}_4]_0, M$	$10^2[\text{I}^-]_0, M$	$10^3[\text{H}^+]_0, M$	$10^2k_1, M^{-2} \text{sec}^{-1}$	
1.00 Mole Fraction of DMSO ^a				
4.55	4.98	1.14–4.54	16.0 ± 0.6^b	
2.3–9.06	4.99	2.90	16.3 ± 0.3^b	
0.900 Mole Fraction of DMSO ^a				
5.00	5.98	1.28–5.12	10.7 ± 0.4^b	
4.90	2.9–11.6	3.24	11.0 ± 0.2^b	
0.700 Mole Fraction of DMSO				
2.7–14.5	6.00	4.19	4.6 ± 0.1^c	
3.64	5.96	3.42	4.5 ± 0.1^b	$[\text{Cl}^-] = (2.6\text{--}12.9) \times 10^{-3} M$
6.68	5.97	4.52	4.7 ± 0.1^b	$[\text{Br}^-] = (5.1\text{--}15.1) \times 10^{-3} M$
9.78	2.00	3.84	4.3 ± 0.2	$[\text{Cl}^-] = 0.020 M$
0.300 Mole Fraction of DMSO				
11.6	5.98	2.02–8.07	2.5 ± 0.2^b	
9.87	7.00	1.97–7.88	2.7 ± 0.2^b	
6.82	3.1–19.2	3.92	2.6 ^d	
13.3	8.33	4.80	2.5	
13.3	8.33	4.80	2.5	$[\text{Cl}^-] = 0.030$
0.150 Mole Fraction of DMSO				
4.97	5.84	3.18	8.1	
4.97	5.84	3.18	8.4 ^e	
4.55	5.80	3.18	8.3	
4.55	5.80	3.18	8.5 ^e	
4.55	8.70	3.18	8.4 ^f	

^a In this solvent, initial rates were corrected for concomitant I_3^- production from the reaction of dimethyl sulfoxide with HI .^g ^b Value of k_1 based on the average of three runs in the concentration range indicated. ^c Average of five runs. ^d Values of k_1 range from $2.2 \times 10^{-2} M^{-2} \text{sec}^{-1}$ in 0.031 M KI to $3.0 \times 10^{-2} M^{-2} \text{sec}^{-1}$ in 0.192 M KI. A small ionic strength correction was applied in 0.192 M KI. ^e $1 \times 10^{-5} M \text{KI}_3$ added prior to reaction. ^f $1.5 \times 10^{-5} M \text{KI}_3$ added prior to reaction.

Table III. Kinetic Data for the Thiourea-Catalyzed Reduction of S,S-Dimethylsulfiminium Perchlorate in $X_{\text{DMSO}} = 0.700$ at 25.17° and 0.120 M Ionic Strength

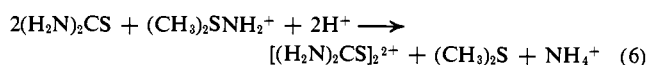
$10^4[(\text{CH}_3)_2\text{SNH}_2\text{ClO}_4]_0, M$	$10^2[\text{I}^-]_0, M$	$10^3[\text{H}^+]_0, M$	$10^3[(\text{H}_2\text{N})_2\text{CS}]_0, M$	$k_{\text{TU}},^a M^{-2} \text{sec}^{-1}$
5.16	5.40	4.16	2.50	0.52
5.16	5.40	4.16	5.01	0.52
5.50	5.40	4.16	7.51	0.53
5.50	5.40	4.16	10.0	0.51
3.93	5.97	1.51	7.55	0.49
3.93	5.97	3.02	7.55	0.53
3.93	5.97	6.05	7.55	0.52
5.25	11.7	3.19	7.50	0.59 ^b
4.32	7.02	3.19	7.50	0.58 ^b
4.32	4.67	3.19	7.50	0.53 ^b
5.46	5.80	3.15	7.59	0.47 ^b
5.46	11.6	3.15	7.59	0.52 ^b
4.86	5.82	2.93	7.82	0.50 ^b
4.52	6.02	3.13	7.38	0.47 ^c

^a Based on eq 5, using $k_1 = 0.046 M^{-2} \text{sec}^{-1}$. ^b In these runs, $(\text{CH}_3)_2\text{SNH}_2\text{ClO}_4$, HClO_4 , and $(\text{H}_2\text{N})_2\text{CS}$ were mixed and allowed to react before addition of KI. Initial production of I_3^- was noted in these runs. ^c In this run, $(\text{H}_2\text{N})_2\text{CS}$, KI, and HClO_4 were mixed and allowed to react before addition of $(\text{CH}_3)_2\text{SNH}_2\text{ClO}_4$. No initial production of I_3^- occurred.

As indicated in Table III, some of the runs involved mixing of $(\text{CH}_3)_2\text{SNH}_2\text{ClO}_4$, HClO_4 , and $(\text{H}_2\text{N})_2\text{CS}$ prior to initiation of reaction 2 by the addition of KI. In these runs a very rapid ($t_{1/2} < 10 \text{ sec}$) initial production of I_3^- was noted, followed by production of I_3^- at the normal rate anticipated from eq 5. With $(\text{CH}_3)_2\text{SNH}_2\text{ClO}_4$ added to a stock solution of HClO_4 and thiourea 100–1000 sec prior to addition of KI, concentrations of triiodide initially produced varied from 0.4×10^{-5} to $1.5 \times 10^{-5} M$. This premature formation of

I_3^- was peculiar to runs in which $(\text{CH}_3)_2\text{SNH}_2^+$, H^+ , and $(\text{H}_2\text{N})_2\text{CS}$ are premixed; no other combination of reactants results in this behavior.

The observations above, together with the separate thiourea path in eq 5, indicate that thiourea reacts with $(\text{CH}_3)_2\text{SNH}_2^+$ in acid solution. The reaction, which occurs independent of the presence or absence of I^- , is tentatively formulated as



The products and kinetics of this reaction were examined briefly by a spectral analysis at 235 m μ in aqueous solution.¹² There is no evidence for products other than $[(\text{H}_2\text{N})_2\text{CS}]_2^{2+}$, such as $(\text{H}_2\text{N})_2\text{CSS}(\text{CH}_3)_2^{2+}$. Addition of iodide ion to a solution containing $[(\text{H}_2\text{N})_2\text{CS}]_2^{2+}$ results in the formation of triiodide ion, thus accounting for the premature formation of I_3^- in the kinetic studies described above. Thiourea reacts according to eq 6 with a half-life of 4000 sec in water for solutions containing approximately $8 \times 10^{-3} M \text{HClO}_4$ and $1 \times 10^{-3} M (\text{CH}_3)_2\text{SNH}_2\text{ClO}_4$, typical of the pre-reaction mixtures involved in $X_{\text{DMSO}} = 0.700$. Since the concentration of thiourea in the pre-reaction mixtures was usually $200 \times 10^{-5} M$, the rapid production of $[(\text{H}_2\text{N})_2\text{CS}]_2^{2+}$ equivalent to $10^{-5} M \text{I}_3^-$ is readily accounted for, even though some difference in rate will occur on going from water to $X_{\text{DMSO}} = 0.700$ solvent.

Kinetic data for reaction 6 (Table IV) have been analyzed using the rate expression

$$-d[(\text{H}_2\text{N})_2\text{CS}]/dt = k_{\text{TU}}^{\text{H}^+\text{or}}[(\text{CH}_3)_2\text{SNH}_2^+][(\text{H}_2\text{N})_2\text{CS}][\text{H}^+] \quad (7)$$

(12) It was impossible to observe any spectral change due to this reaction in DMSO solvents since DMSO has a cutoff near 260 m μ .

Table IV. Kinetic Data for the Reaction of Thiourea with S,S-Dimethylsulfiminium Perchlorate at 25.17° in Water

$10^3[(\text{CH}_3)_2\text{SNH}_2\text{ClO}_4]_0, M$	$10^2[\text{H}^+]_0, M$	$10^3[(\text{H}_2\text{N})_2\text{CS}]_0, M$	$k_{\text{TU}}^{\text{H}_2\text{O}}, M^{-2} \text{sec}^{-1}$
3.66	1.22	7.7	21.4
3.66	1.82	7.7	21.9
3.66	3.04	7.7	22.3
2.02	2.00	8.1	22.5
3.03	2.00	8.1	22.7
5.05	2.00	8.1	22.6

Assuming that $k_{\text{TU}} = 0.51 M^{-2} \text{sec}^{-1}$ represents the rate constant for attack of thiourea on $(\text{CH}_3)_2\text{SNH}_2^+$ in $X_{\text{DMSO}} = 0.700$, the reactivity in water, relative to that in $X_{\text{DMSO}} = 0.700$, is $k_{\text{TU}}^{\text{H}_2\text{O}}/k_{\text{TU}} = 43$.

Reduction of S,S-Dimethylsulfiminium Perchlorate in Water. The iodide ion reduction of $(\text{CH}_3)_2\text{SNH}_2\text{ClO}_4$ proceeds more rapidly in water than in DMSO-water solvents. With H^+ and I^- in large excess over $(\text{CH}_3)_2\text{SNH}_2^+$, it was possible to follow the conversion of $(\text{CH}_3)_2\text{SNH}_2^+$ to products as a pseudo-first-order process. Plots of $\ln(A_\infty - A)$ vs. time were found to be linear for at least two half-lives. The concentrations of I_3^- produced, as judged by A_∞ values, were found to be in good agreement with values based on initial concentrations of $(\text{CH}_3)_2\text{SNH}_2^+$. There was a tendency for A_∞ values to be 2–3% larger for solutions containing 0.07–0.10 M I^- than for solutions containing 0.03–0.06 M I^- . The effect of air oxidation was eliminated by making small blank corrections. The slopes of the log plots were proportional to $[\text{H}^+]$ and $[\text{I}^-]$, indicating that rate law 3 holds in aqueous solutions. The data are summarized in Table V, with values of k_1 based on eq 3. The following activation parameters were derived from values of the third-order rate constant at 10.37, 25.17, and 29.73°: $\Delta H^\ddagger = 12.2 \pm 0.4 \text{ kcal/mole}$ and $\Delta S^\ddagger = -19 \pm 1 \text{ eu}$.

Table V. Kinetic Data for the Iodide Ion Reduction of S,S-Dimethylsulfiminium Perchlorate in Water at 0.120 M Ionic Strength^a

Range of initial concentrations			
$10^3[\text{H}^+]_0, M$	$10^2[\text{I}^-]_0, M$	Temp, °C	$k_1, M^{-2} \text{sec}^{-1}$
3.04–4.95	5.87–8.95	10.37	0.176 ± 0.003^b
0.80–6.27	2.99–10.9	25.17	0.56 ± 0.02^c
0.70–1.53	5.32–11.3	29.73	0.74 ± 0.02^d

^a $[(\text{CH}_3)_2\text{SNH}_2\text{ClO}_4]_0 = (2.75\text{--}4.05) \times 10^{-5} M$. ^b Average of four runs. ^c Average of ten runs. ^d Average of six runs.

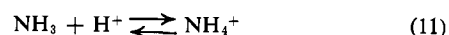
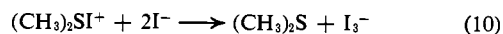
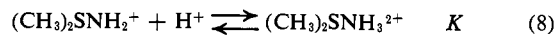
The deuterium solvent isotope effect was evaluated at 25.17° in 99.8% D_2O . With $[(\text{CH}_3)_2\text{SNH}_2\text{ClO}_4]_0 = 2.58 \times 10^{-5}$ and $2.73 \times 10^{-5} M$, $[\text{H}^+]_0 = 7.02 \times 10^{-3}$ and $6.5 \times 10^{-3} M$, and $[\text{I}^-]_0 = 0.0600$ and $0.100 M$, values of $k_1^{\text{D}_2\text{O}}$ were, respectively, 2.1 and $2.0 M^{-2} \text{sec}^{-1}$. Thus, $k_1^{\text{H}_2\text{O}}/k_1^{\text{D}_2\text{O}} = 0.27 \pm 0.02$.

Reduction of S,S-Diethylsulfiminium Sulfate in Water. For comparative purposes, the kinetics of the iodide ion reduction of $(\text{C}_2\text{H}_5)_2\text{SNH}_2^+$ were examined. The techniques and data treatment employed were identical with those described above. The rate law assumed was of the same form as that in eq 3. An average value of $k_1^{\text{Et}} = 0.193 \pm 0.004 M^{-2} \text{sec}^{-1}$ was obtained for four runs in which $[(\text{C}_2\text{H}_5)_2\text{SNH}_2^+]_0 = (2.78\text{--}2.90) \times 10^{-5} M$, $[\text{H}^+]_0 = (1.57\text{--}7.68) \times 10^{-2} M$, and $[\text{I}^-]_0 = (4.00\text{--}$

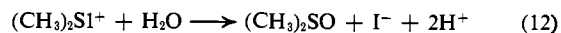
$8.00) \times 10^{-2} M$. The relative reactivity of the ethyl compared with the methyl compound is $k_1^{\text{Et}}/k_1^{\text{Me}} = 0.193/0.56 = 0.34$.

Discussion

Any mechanism proposed for reaction 2 must lead to rate law 3 and be consistent with the following observations: (1) $\Delta S^\ddagger = -19 \text{ eu}$; (2) $k_1^{\text{H}_2\text{O}}/k_1^{\text{D}_2\text{O}} = 0.27$; (3) a minimum in the rate exists in the region of solvent composition $X_{\text{DMSO}} = 0.300\text{--}0.500$; (4) $k_1^{\text{Et}}/k_1^{\text{Me}} = 0.34$; (5) thiourea catalyzes reaction 2, but Cl^- and Br^- do not. The simplest mechanism which satisfies the criteria above is



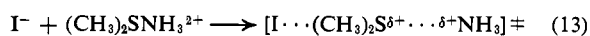
which involves a rate-determining step 9 preceded by a rapid equilibrium 8 in which $K \ll 1$. (The kinetic data do not relate to steps 10 and 11 which are suggested as a reasonable path for completing the reaction.) The over-all reaction is not significantly reversible in acid solution because of the nearly complete protonation of the NH_3 produced. The kinetic data also are consistent with iodide ion displacement on nitrogen with $(\text{CH}_3)_2\text{S}$ as the leaving group. This point is discussed below. Since the iododimethylsulfonium ion is subject to hydrolysis,¹³ reaction 12 potentially can com-



pete with reaction 10. In aqueous solution such competition is insignificant since theoretical yields of I_3^- are obtained. However, as pointed out in the Results section, some hydrolysis may occur in $X_{\text{DMSO}} = 0.150$ and 0.300 and at low $[\text{I}^-]$ in $X_{\text{DMSO}} = 0.500$.

The value of $\Delta S^\ddagger = -19 \text{ eu}$ results from a combination of reactions 8 and 9. Negative ΔS^\ddagger values in the range -10 to -30 eu are expected for bimolecular processes such as (9).^{14a} Unless the unknown ΔS° for reaction 8 were large and negative, the ΔS^\ddagger observed is not inconsistent with the mechanism proposed.^{14b}

The mechanism involves specific hydrogen ion transfer preceding the rate-determining step for which one would expect $k_{\text{H}_2\text{O}}/k_{\text{D}_2\text{O}} = 0.5\text{--}1.0$.¹⁵ The observed effect of 0.27 is somewhat greater than expected. A possible explanation for this behavior involves recognition of the fact that the leaving group in D_2O is very likely to be ND_3 , rather than NH_3 . Equilibrium reaction 8 should lead to essentially complete deuteration of the $-\text{NH}_2$ group. Although the system is too complex to allow a quantitative prediction of the secondary deuterium isotope effect created by ND_3 , the effect observed clearly is in the right direction. The slow step assumed



(13) H. Böhme and E. Boll, *Z. Anorg. Allgem. Chem.*, **290**, 17 (1957).

(14) (a) L. L. Schaleger and F. A. Long, *Advan. Phys. Org. Chem.*, **1**, 1 (1963). (b) A value of $\Delta S^\circ = +6 \text{ eu}$ has been reported for the equilibrium $\text{H}_2\text{NC}_2\text{H}_4\text{NH}_3^+ + \text{H}^+ \rightleftharpoons \text{H}_2\text{NC}_2\text{H}_4\text{NH}_3^{2+}$: D. H. Everett and B. R. W. Pinsent, *Proc. Roy. Soc. (London)*, **A215**, 416 (1952). This reaction is of the same charge type as reaction 8, although ΔS° for the latter will be more negative because of the more highly concentrated positive charge.

(15) C. A. Bunton and V. J. Shiner, Jr., *J. Am. Chem. Soc.*, **83**, 3207 (1961).

involves partial conversion of an ammonium-like nitrogen to an ammonia-like nitrogen. This should lead to an increase in the N-H stretching frequencies.¹⁶ The approximate relation¹⁷

$$k_H/k_D = e^{(0.187/T)\Sigma(\nu_H - \nu_H^*)} \quad (14)$$

therefore suggests that $k_H/k_D < 1$. This additional secondary effect will be superimposed on the effect arising from a shift to the right in the protonation equilibrium step 8.

As shown in the plot of $\log k_I$ vs. mole fraction of DMSO in Figure 1, the rate decreases markedly with increasing DMSO content and goes through a broad minimum at $X_{\text{DMSO}} = 0.300\text{--}0.500$. This behavior parallels the proton-donating ability of the solvent mixture. Since DMSO is known to be more basic than H_2O ,¹⁸ equilibrium reaction 8 becomes less favorable upon addition of DMSO to the system. Wolford has measured the ability of acidic DMSO-water media to protonate *m*-nitroaniline.¹⁹ His pK_a values for *m*-nitroaniline are shown in Figure 1 where it is clear that the solvent effect on rate generally parallels the effect of solvent on *m*-nitroaniline basicity.^{20,21}

Substitution occurring at sulfur (reaction 9) should be moderately susceptible to an increase in steric hindrance with an increase in the size of the groups bound to sulfur. Values of $k^{\text{C}_2\text{H}_5}/k^{\text{CH}_3}$ are available for a variety of bimolecular reactions closely related to the present system. Typical values of $k^{\text{C}_2\text{H}_5}/k^{\text{CH}_3}$ (in parentheses) are: (0.26) racemization of *p*- $\text{CH}_3\text{C}_6\text{H}_4\text{SOR}$ by HCl in aqueous dioxane,^{2f} (0.50) $\text{RSSO}_3^- + {}^{35}\text{SO}_3^{2-}$ in water,^{2f} (0.65) $\text{RCH}_2\text{Br} + \text{Li}^{82}\text{Br}$ in acetone,^{2f} (0.62) reduction of RSOC_6H_5 by HI in aqueous perchloric acid,^{2g} (0.62) $\text{R}_2\text{S} + \text{CH}_3\text{I}$ in methanol,²² and (0.45) $\text{R}_2\text{S} + \text{Pt}(\text{py})_2\text{Cl}_2$ in methanol.²² The value of $k_I^{\text{C}_2\text{H}_5}/k_I^{\text{CH}_3} = 0.34$ observed in the present study, involving replacement of *two* methyl groups, therefore is similar to values arising from other systems involving a sulfur center in the transition state. This similarity suggests that displacement occurs at sulfur, rather than at nitrogen. If displacement at nitrogen is assumed in the activated complex, the steric effect would be that due to increased size of the leaving group, SR_2 . The direction of the leaving group effect is uncertain because increased size raises the transition state energy, but the steric relief arising from partial expulsion of the leaving group should also increase with size.

It is well known that sulfur centers are susceptible to nucleophilic attack. Thus, the transition state implied

(16) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, pp 104, 84: $\text{NH}_4^+(\text{s}) \nu_1 \cong 3040 \text{ cm}^{-1}$ and $\text{NH}_3(\text{s}) \nu_1 \cong 3223 \text{ cm}^{-1}$.

(17) A. Streitwieser, Jr., R. H. Jagow, R. C. Fahey, and S. Suzuki, *J. Am. Chem. Soc.*, **80**, 2326 (1958).

(18) DMSO is 1.5 ± 0.5 log units more basic than H_2O : I. M. Koltzoff, M. K. Chantooni, and S. Bhowmik, *ibid.*, **90**, 23 (1968).

(19) R. K. Wolford, *J. Phys. Chem.*, **68**, 3392 (1964).

(20) A similar correlation between rate and indicator basicity in DMSO-water solvents has been observed for rate-determining proton transfer in the hydrolysis of ethyl vinyl ether: M. M. Kreevoy and J. M. Williams, Jr., *J. Am. Chem. Soc.*, **90**, 6809 (1968).

(21) Possible deprotonation of $(\text{CH}_3)_2\text{SNH}_2^+$ to $(\text{CH}_3)_2\text{S}=\text{NH}$ in DMSO can be ruled out as the cause of the rate minimum in $X_{\text{DMSO}} = 0.300\text{--}0.500$. Although DMSO is more basic than H_2O , the free imine base is formed only under highly basic conditions.⁴ Furthermore, deprotonation would not be consistent with the simple first-order hydrogen ion dependence observed throughout the solvent range.

(22) R. G. Pearson, H. Sobel, and J. Songstad, *J. Am. Chem. Soc.*, **90**, 319 (1968).

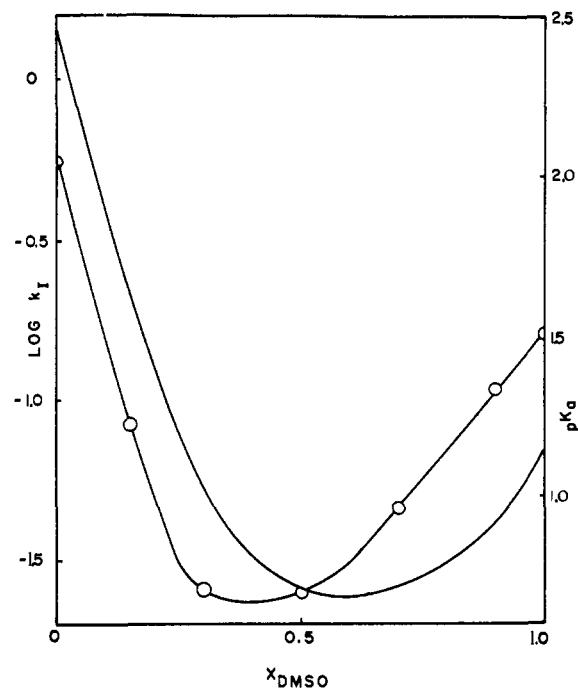
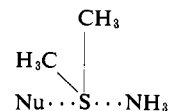
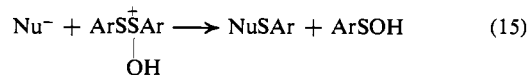


Figure 1. $\log k_I$ (open circles) and pK_a of *m*-nitroaniline (solid line) plotted as a function of mole fraction of dimethyl sulfoxide in the solvent.

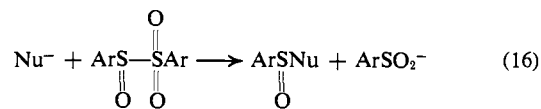
in eq 9 may be generalized to



The experimental results in this study suggest that thiourea catalyzes reaction 2 by nucleophilic attack on sulfur. This center is medium soft by virtue of its possessing three bond pairs and one lone pair, in addition to a partial positive charge.²³ Accordingly, nucleophiles which are more basic and less polarizable than iodide and thiourea are expected to exhibit relatively little reactivity at such a center. Indeed, chloride and bromide were found to be without effect on the reaction.²⁴ It is of interest to compare the results for *S,S*-dimethylsulfiminium ion with those obtained for nucleophilic displacement reactions at other sulfur centers. The racemization of optically active sulfoxides is subject to nucleophilic catalysis with a reactivity order $\text{I}^- > \text{Br}^- > \text{Cl}^-$.^{2h,i} At sulfinyl sulfur (a soft center)



the reactivity order $\text{I}^- > \text{Br}^- \gg \text{Cl}^-$ is observed,^{2a} and at sulfinyl sulfur (a medium soft center)



the reactivity order thiourea $\sim \text{I}^- > \text{Br}^- > \text{Cl}^-$ is observed.^{2b} In contrast, only the harder base nucleo-

(23) J. O. Edwards and R. G. Pearson, *ibid.*, **84**, 16 (1962).

(24) The upper limit of reactivity of Cl^- or Br^- which could have been detected in this study is approximately 10% of that of I^- .

philes such as F^- and OAc^- show an appreciable reactivity at sulfonyl sulfur.^{2b}

The presumed transition state for reaction 1 is probably similar to that for reaction 2 shown above, with H_2O rather than NH_3 as the leaving group. The sulfur center in $(CH_3)_2SOH_2^{2+}$ is a borderline soft acid in which the reactivity order for the halides is inverted by dipolar aprotic solvents (e.g., $Cl^- > Br^- > I^-$ in DMSO).³ The relative softness of sulfur in $(CH_3)_2SNH_3^{2+}$ is greater than that in $(CH_3)_2SOH_2^{2+}$ as judged by the observed solvent effects. Even in $X_{DMSO} = 0.700$ where Cl^- is only poorly solvated, Cl^- is unreactive toward $(CH_3)_2SNH_3^{2+}$. The preference of this center for soft

base nucleophiles is great enough that inversion in the reactivity order does not occur.^{2b} No quantitative comparison of the rates of reduction of $(CH_3)_2SO$ and $(CH_3)_2SNH_3^{2+}$ can be made because the order with respect to $(CH_3)_2SO$ is indeterminable in DMSO solvents.³ However, the ratio of the third-order rate constants $k_{(CH_3)_2SNH_3^{2+}}/k_{(CH_3)_2SO} = 2800$ in $X_{DMSO} = 0.500$ indicates that iodide is more reactive at the softer sulfur center.

Acknowledgment. We are grateful to the National Science Foundation for support of this work under Grants GP-2968 and 7981.

(25) R. G. Pearson and J. Songstad, *J. Am. Chem. Soc.*, **89**, 1827 (1967)

Hydrogen-Carbon-13 Spin-Spin Coupling in Transition Metal Hydride Complexes¹

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Abstract: Analysis of the proton nmr spectra of $K_3[HR(CN)_5]$ (1), $K_3[HRh(CN)_5]$ (2), *trans*-[HPtCN(P(C₂H₅)₃)₂] (4), $HMn(CO)_5$ (5), *cis*- $HMn(CO)_4P(C_2H_5)_3$ (6), $Na[HW_2(CO)_{10}]$ (7), and $Na[HMnO_2(CO)_{10}]$ (8) either naturally abundant or isotopically enriched in ¹³CN or ¹³CO has yielded values of ¹H-M-¹³C spin-spin coupling constants for representative transition metal carbonyl and cyano hydrides. The utility of these coupling constants in structural investigations of hydride complexes of the transition metals is discussed briefly, with particular reference to compounds 2, 5, and 6.

Proton nmr spectroscopy is well established as a technique of general usefulness in structural investigations of hydride complexes of the transition metals.² With few exceptions, metal hydride complexes are diamagnetic,³ and the resonances due to the hydride ligands characteristically occur in a high-field region of the spectrum which contains no interfering absorptions due to solvents or to other ligands. Consequently, hydride resonances are relatively easily detected even at the low concentrations frequently required for these studies.

For the large and important class of metal hydride complexes which contain phosphines or phosphites as ligands, straightforward analysis of ¹H-³¹P spin-spin coupling constants provides a simple and apparently reliable method for establishing the relative stereochemistry of the hydride- and phosphorus-containing ligands.⁴ The determination of stereochemistry for metal hydride complexes which do *not* contain phosphorus remains a difficult problem. Although ir spectroscopy is useful in studies of metal carbonyl hydrides of appropriate symmetry, and single-crystal X-ray dif-

fraction studies are being carried out on increasing numbers of complexes, development of alternative spectroscopic approaches to stereochemical studies of transition metal hydrides would constitute a valuable addition to the range of techniques applicable to the examination of these materials.

The work reported in this paper was initiated in the hope that ¹H-¹³C spin-spin coupling constants could be utilized in transition metal carbonyl and cyano hydrides in a manner analogous to that with which ¹H-³¹P coupling constants are used in metal phosphine hydrides, to provide information concerning the stereochemical arrangement of hydride and carbonyl or cyanide groups coordinated to a common metal atom. The natural abundance of ¹³C is 1.1%; its nuclear spin is 1/2. The ¹H nmr spectrum of the transition metal hydride containing carbon monoxide or cyanide ligands would thus be expected to consist of the superposition of strong resonances due to species containing only ¹²CO or ¹²CN ligands, and additional weaker satellite peaks due to ¹H-¹³C spin-spin coupling in species containing one or more ¹³C-containing ligands.⁵

(1) Supported by the National Science Foundation, Grant GP-7266.
(2) Reviews: (a) A. P. Ginsburg, *Transition Metal Chem.*, **1**, 111 (1965); (b) M. L. H. Green and D. J. Jones, *Advan. Inorg. Chem. Radiochem.*, **7**, 146 (1965).

(3) The reported paramagnetic hydrides are $Cp_2Ti_2H_2$: H. Brintzinger, *J. Amer. Chem. Soc.*, **88**, 4305, 4307 (1966); $Li_3[Cr_2H_3(C_5H_5)_3]$, F. Hein and R. Weiss, *Naturwiss.*, **46**, 321 (1959).

(4) A *trans* H-M-P stereochemistry is normally characterized by $J(H,P)$ of 80-160 Hz, while a *cis* stereochemistry results in $J(H,P)$ of 10-40 Hz.²

(5) The analysis of ¹³C satellites has been extensively exploited in determination of ¹H-¹³C coupling constants in organic molecules.⁶ To our knowledge, the only such coupling reported for a metal hydride has been the *cis* coupling (*vide infra*) of $[HW_2(CO)_{10}]^-$.⁷

(6) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 2, Pergamon Press, Oxford, 1966, p 1011 *ff*.

(7) R. G. Hayter, *J. Amer. Chem. Soc.*, **88**, 4376 (1966).