

AN ABSTRACT OF THE THESIS OF

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Title: KINETICS AND MECHANISMS OF NUCLEOPHILIC
DISPLACEMENT REACTIONS WITH S-METHYL-S-
PHENYLSULFIMINIUM PERCHLORATE

Abstract approved: Redacted for privacy
U James H. Krueger

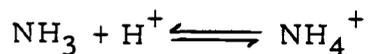
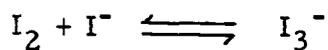
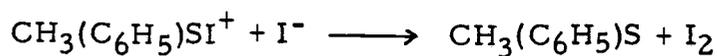
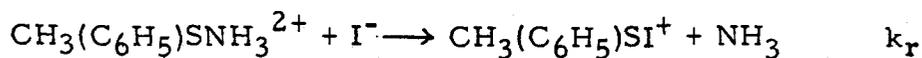
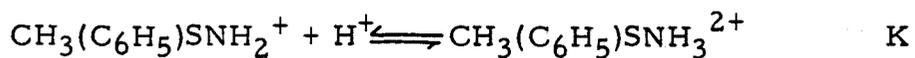
The compound S-methyl-S-phenylsulfiminium perchlorate has been synthesized and characterized. The kinetics of the reaction

$$\text{CH}_3(\text{C}_6\text{H}_5)\text{SNH}_2^+ + 3\text{I}^- + 2\text{H}^+ \rightarrow \text{CH}_3(\text{C}_6\text{H}_5)\text{S} + \text{I}_3^- + \text{NH}_4^+$$

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 $d[\text{I}_3^-]/dt = k_1[\text{CH}_3(\text{C}_6\text{H}_5)\text{SNH}_2^+][\text{H}^+][\text{I}^-]$. In aqueous solution at 20.0° and 0.120 M ionic strength, $k_1 = 0.960 \pm 0.044 \text{ M}^{-2}\text{sec}^{-1}$. The activation parameters ΔH^\ddagger and ΔS^\ddagger , calculated from transition-state theory, are $12.3 \pm 0.2 \text{ kcal/mole}$ and $-16.7 \pm 0.2 \text{ eu}$, respectively. The reaction is catalyzed by thiourea but not by bromide, chloride, or thiocyanate ions. Thiourea has been shown to react with S-methyl-S-phenylsulfiminium perchlorate, and this reaction has been studied briefly. It is tentatively concluded that sulfur in the S-methyl-S-phenylsulfiminium perchlorate is a medium-soft acid center on the

Pearson HSAB scale.

The mechanism proposed for the reaction with iodide ion involves a rate-determining step preceded by a rapid equilibrium in which $K \ll 1$.



The kinetic data also are consistent with iodide-ion displacement on nitrogen with $\text{CH}_3(\text{C}_6\text{H}_5)\text{S}$ as the leaving group. However, this nitrogen-attack mechanism can be ruled out for this reaction.

Kinetics and Mechanisms of
Nucleophilic Displacement Reactions with
S-Methyl-S-Phenylsulfiminium Perchlorate

by

Richard Junji Kiyokane

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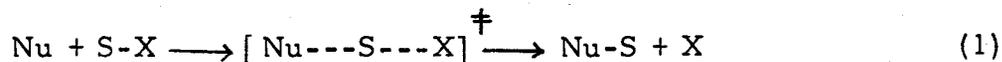
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KINETICS AND MECHANISMS OF NUCLEOPHILIC DISPLACEMENT REACTIONS WITH S-METHYL- S-PHENYLSULFIMINIUM PERCHLORATE

I. INTRODUCTION

Nucleophilicity

In a nucleophilic displacement reaction, one electron-pair donor replaces another in a substrate. The general reaction is



where Nu is a nucleophile, S-X is the substrate, and X is a leaving group.

Nucleophilic displacement reactions can occur by a variety of mechanisms. The simplest type of S_N2 substitution proceeds without an intermediate; the rate-determining step is the bimolecular collision of the nucleophile with the substrate.

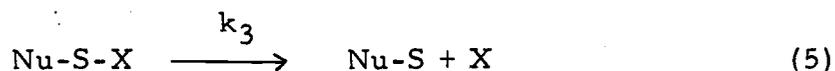
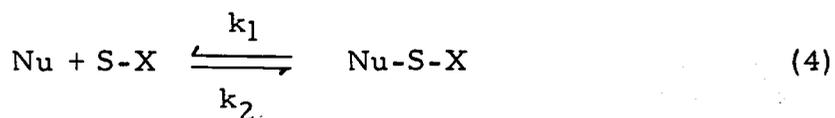
The second type of mechanism, S_N1, is a two-step process



in which the first step is a bond-breaking step that forms an electron-deficient intermediate.

Another two-step mechanism involves addition of the nucleophile to the substrate, followed by loss of the leaving group. The

general reaction is



In examining the reaction of a particular substrate with a series of nucleophiles, many factors have been found to govern the order of activated-complex stabilities. Basicity and polarizability are important factors which determine nucleophilic orders (1). Experimental data for a number of substrates show that the reactivities of some substrates depend almost entirely on the basicity of the nucleophile while some substrate reactivities depend largely on polarizability. Pearson (2-5) has classified the former type of substrates as hard-acid centers and the latter type as soft-acid centers. Hard-acid centers prefer to bind to "hard" or nonpolarizable bases and soft-acid centers prefer to bind to "soft" or polarizable bases. The correlation of basicity with nucleophilic character stems from the fact that substitution reactions are generalized acid-base reactions. In equation (1) Nu and X are bases and S is an acid. Substrates which resemble the proton in having a high positive charge density and a low number of electrons in the outer orbitals of the central atom depend on the basicity of the nucleophile and are thus characterized as hard-acid centers (1).

Soft-acid centers are characterized by their polarizability. A polarizable nucleophile can approach a substrate more closely and yet by its "softness" minimize the effect of the electron-electron repulsion. Therefore, substrates with a low positive charge density and with many electrons in the outer orbitals of the central atom depend on the polarizability of the nucleophile (1).

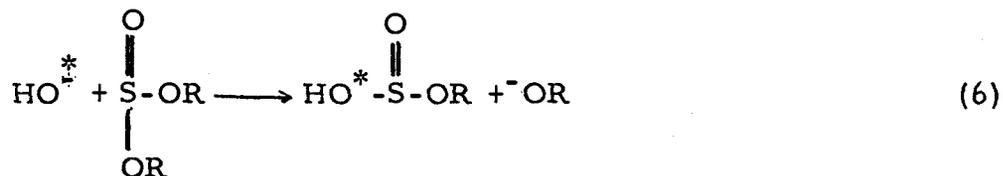
Other factors, such as solvent effects and steric hindrance, can be important and have been described in several publications (6-9).

Nucleophilic Displacement on Tricoordinate,
Tetravalent Sulfur

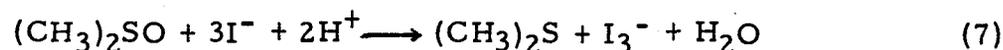
Nucleophilic displacement at sulfur centers is a relatively recent subject of considerable interest (10-16). Mechanistic aspects of nucleophilic displacement at tricoordinate, tetravalent sulfur compounds, which include sulfoxides R_2SO , sulfinyl halides $RS(=O)-X$, sulfilimines R_2SNR , sulfonium salts R_3S^+ , and sulfinate esters $R_2S(=O)-OR$, have been studied extensively in recent years to better understand the nature of sulfur centers.

An example of attack at tetravalent sulfur which has been studied in detail, is the hydrolysis of sulfite esters studied by Bunton, Tillett, and co-workers (10, 11-16) and by Davis (10, 17). The rate law is first order both in the neutral ester and in hydroxide ion indicating a bimolecular reaction. The reaction was found to involve

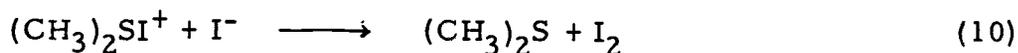
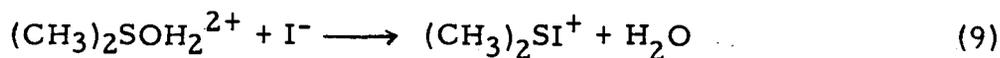
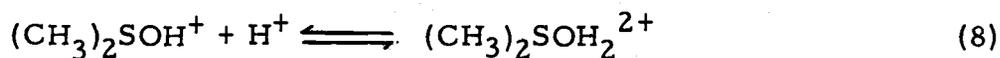
S-O scission, and the rate-determining step is an irreversible S_N2 attack on the sulfur center by hydroxide ion.



The oxidation of iodide ion by dimethyl sulfoxide in various aqueous acidic solutions has been studied by Krueger (18).

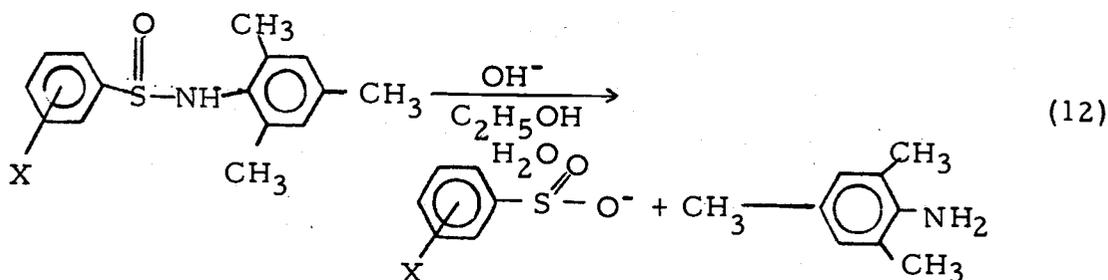


The reaction was found to be second-order in hydrogen-ion and first-order in iodide-ion concentration. The mechanism proposed is the following



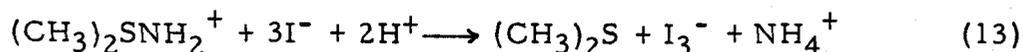
in which 9 is the slow step preceded by a rapid and reversible formation of $(\text{CH}_3)_2\text{SOH}_2^{2+}$.

The hydrolysis of arenesulfinamides in basic, aqueous ethanol has been studied by Biasotti and Andersen (19). In particular, the base hydrolysis of nine meta and para substituted N-mesitylarene-sulfinamides in aqueous ethanol has been reported.



Overall second-order rate constants were obtained: first-order in base and first-order in sulfonamide.

In 1962 a new type of tricoordinate, tetravalent sulfur compound was made available for kinetic study with the synthesis of R_2SNH_2^+ compounds by Appel and Büchner (20, 21). The first detailed kinetic work on this type of tricoordinate, tetravalent sulfur compound was done by Krueger (22). Specifically, the iodide-ion reduction of S,S-dimethylsulfiminium perchlorate was studied.



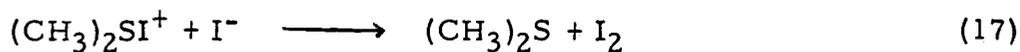
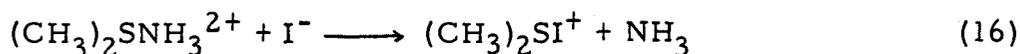
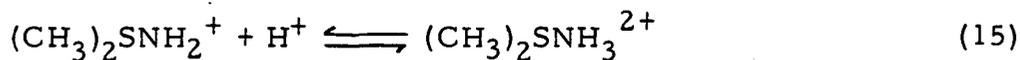
The kinetics of the above reaction have been measured spectrophotometrically in water and in DMSO-water solvents over the range

$X_{\text{DMSO}} = 0-1.00$. The rate law reported was

$$d[\text{I}_3^-]/dt = k_{\text{I}}[(\text{CH}_3)_2\text{SNH}_2^+][\text{H}^+][\text{I}^-]$$
(14)

In aqueous solution at 25° and 0.120 M ionic strength, $k_{\text{I}} = 0.56 \pm 0.02 \text{ M}^{-2}\text{sec}^{-1}$, $\Delta H^\ddagger = 12.2 \pm 0.4 \text{ kcal/mole}$, and $\Delta S^\ddagger = -19 \pm 1 \text{ eu}$. The deuterium solvent-isotope-effect observed was $k_{\text{H}_2\text{O}}/k_{\text{D}_2\text{O}} = 0.27$. The reaction was found to be 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 sulfur center in this compound was tentatively proposed to be a relatively soft-acid center on Pearson's HSAB scale.

In conclusion, upon surveying the literature, one finds that an understanding of the factors which influence reactivity at sulfur centers has been hampered greatly by a lack of quantitative rate data which relate to a single type of sulfur center. Since a general synthetic route was known for the preparation of compounds of the type R_2SNH_2^+ , the synthesis of $\text{Me}(\text{Ph})\text{SNH}_2^+$ was attempted in this study (20, 21). (Hereafter, CH_3 and C_6H_5 will be denoted as Me and Ph, respectively.) It was thought that the presence of an aromatic group would allow a spectroscopic means for studying the kinetics and mechanisms of nucleophilic displacement reactions at this type of sulfur center. As a result, a wider range of nucleophiles could be studied to determine the nature of this sulfur center. Also,

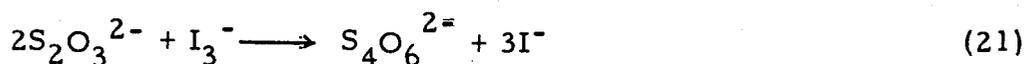
information on the resulting steric and electronic effects could be obtained. Therefore, in this study, we have undertaken an examination of nucleophilic displacement reactions of S-methyl-S-phenylsulfonium perchlorate to provide additional data for another tricoordinate, tetravalent sulfur center.

II. EXPERIMENTAL

Synthesis of S-Methyl-S-Phenylsulfiminium Perchlorate

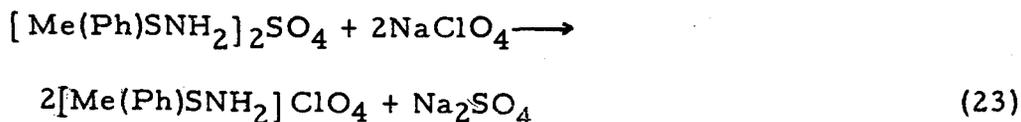
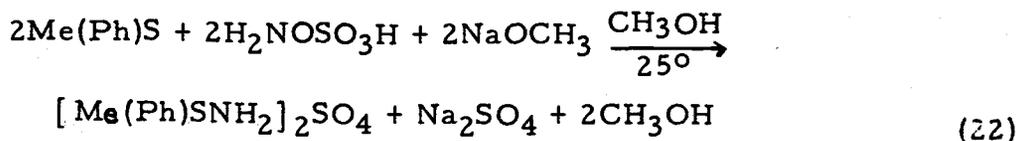
Hydroxylamine-O-sulfonic acid was prepared by the reaction of chlorosulfonic acid (Matheson, Coleman, and Bell reagent) with hydroxylamine sulfate (Matheson, Coleman, and Bell reagent) according to the procedure by Sommer and co-workers (23). The hydroxylamine sulfate was dried in an oven at 110° for 24 hours before it was used.

The product was usually about 94% pure. No further purification was attempted. The purity of the hydroxylamine-O-sulfonic acid was determined by an iodometric method involving the reaction of triiodide ion with thiosulfate ion.



A weighed sample and a large excess of potassium iodide (B & A reagent) were added to 1 M sulfuric acid which had previously been boiled and purged with dry nitrogen. The iodine produced was immediately titrated with standardized sodium thiosulfate (B & A reagent).

The compound, S-methyl-S-phenylsulfiminium perchlorate, was synthesized by the route shown in the following equations.



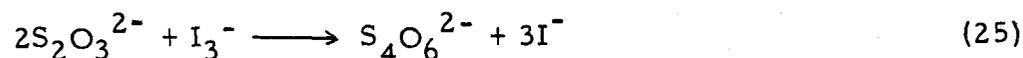
Drying of the methanol was accomplished by reaction with magnesium turnings and refluxing overnight with constant stirring. Then the methanol was fractionally distilled and only the middle fraction at 65° was collected. Approximately 11.4 grams of sodium methoxide (Matheson, Coleman, and Bell reagent) were dissolved in 150 ml of ice-chilled dry methanol (Matheson, Coleman, and Bell reagent) and placed in an ice bath. Next, 22.7 grams of 94% pure hydroxylamine-O-sulfonic acid were dissolved in 150 ml of ice-chilled dry methanol and placed in an ice bath.

Methylphenylsulfide (Aldrich Chemical Company) was used without any purification. Approximately 24 ml of methylphenylsulfide were measured out into a 100 ml graduated cylinder and placed in a 500 ml three-neck round bottom flask. The hydroxylamine-O-sulfonic acid - methanol and sodium methoxide - methanol solutions were simultaneously added to the methylphenylsulfide by means of two 250 ml equalizing funnels in 15 portions of approximately 10 ml. Immediately the solution turned yellow and a large quantity of white precipitate was formed. The white precipitate was found to be sodium

sulfate. Thirty minutes were allowed before the addition of each portion during which time the mixture was constantly stirred with a magnetic stirrer. Also, the hydroxylamine-O-sulfonic acid - methanol and sodium methoxide - methanol solutions were kept cool with towels wet in ice-chilled water. After the addition of the last portion, the pH was determined with Universal pH paper and was found to be neutral. The solution was allowed to stir for another hour and again the pH was found to be neutral.

Once the stirring was stopped, the precipitate was allowed to settle, and the yellow solution was decanted into a 500 ml round bottom flask. The volume of the solution was reduced using a rotary evaporator. During the evaporation process, additional white precipitate (sodium sulfate) was formed and was periodically removed from the yellow solution. This evaporation process was continued until the final volume of the solution was about 40 ml.

Attempts to crystallize the $[\text{Me}(\text{Ph})\text{SNH}_2]_2 \text{SO}_4$ salt were unsuccessful. Therefore, by changing the salt to the perchlorate form, it was thought that the crystallization would be facilitated. A 1-ml aliquot of this yellow solution was analyzed iodometrically.



Based on this analysis, a corresponding number of grams of sodium perchlorate, dissolved in methanol, were added to approximately 10 ml of the yellow solution. A fine white precipitate (sodium sulfate) immediately resulted. After the solution was allowed to stand for 24 hours, the white precipitate was filtered and discarded. The solution was reduced in volume to approximately 40 ml and a ten-fold excess of anhydrous ethyl ether (Baker Analyzed reagent) was added slowly and immediate precipitation occurred. The precipitate was washed with more ethyl ether, filtered, and dried under vacuum over phosphorus pentoxide for 24 hours. Although no difficulty was experienced, this perchlorate salt is a potentially hazardous compound. It should be prepared only in small quantities and handled with care.

The white powdery solid was analyzed iodometrically (equations 24, 25) and was found to be about 75-80% pure. Purification was effected in the following manner. Initially, about 1.5 grams of the solid were dissolved in 1 ml of dry methanol and a ten-fold excess of dry chloroform (reagent) was slowly added and the solution was allowed to remain in an ice bath for 24 hours. The resulting white solid, containing sodium sulfate, was filtered out and discarded and an eight-fold excess of anhydrous ethyl ether was added to the remaining solution. The resulting white solid was filtered and the methanol-ether recrystallization was repeated. Finally, after the second recrystallization, the white solid was collected and dried under vacuum over

phosphorus pentoxide for 24 hours.

The white solid was analyzed iodometrically and was found to be 95-98% pure. Elemental analysis, which was performed by Galbraith Laboratories, Knoxville, Tenn., gave the following results for $[\text{Me}(\text{Ph})\text{SNH}_2]\text{ClO}_4$. Calculated: C, 35.1; H, 4.2; N, 5.8. Found: C, 34.8; H, 4.3; N, 5.9. The melting point of this compound was found to be $60^\circ - 61^\circ$.

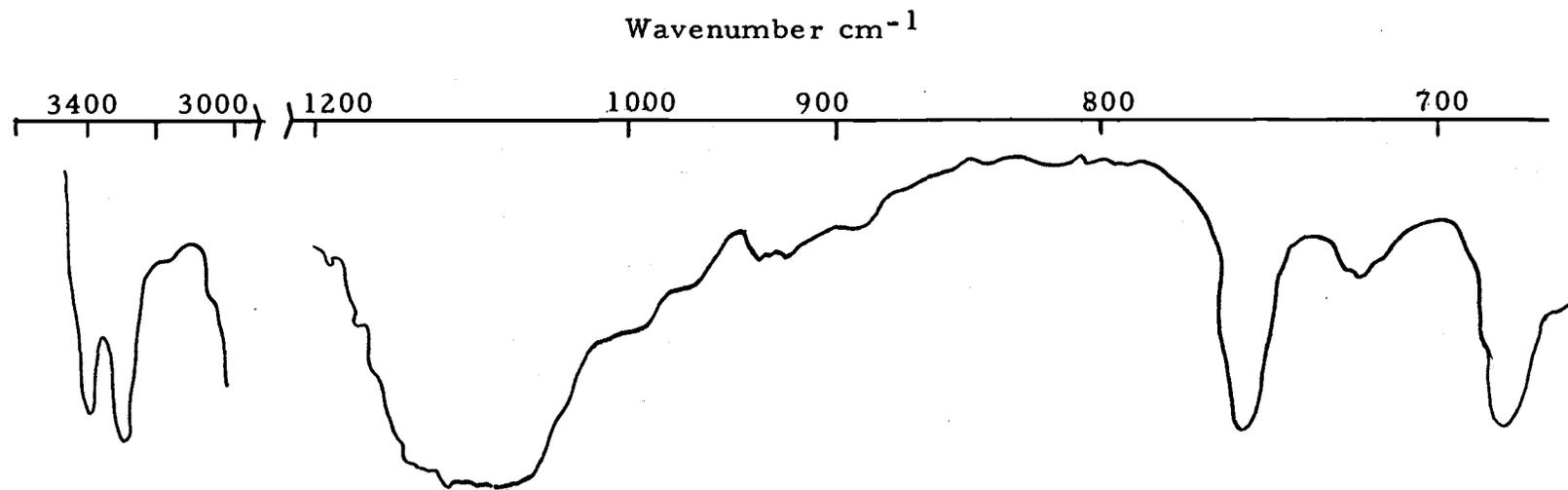
Infrared spectra were taken in Nujol and in Kel-F 10 and are shown in Figures 1 and 2 along with the peak assignments. An nmr spectrum along with the peak assignments is shown in Figure 3. A uv spectrum of this compound is shown in Figure 4. The compound has a maximum at 265 nm and a molar absorption coefficient at 265 nm of $8.02 \times 10^2 \text{ M}^{-1} \text{ cm}^{-1}$.

Potassium Iodide and S-Methyl-S-Phenylsulfiminium Perchlorate Reaction

Reagents

Reagent grade potassium iodide and sodium perchlorate were finely powdered and dried in an oven at 110° for 24 hours.

The S-methyl-S-phenylsulfiminium perchlorate was periodically checked for purity by iodometric titration with standardized sodium thiosulfate. In all kinetic runs, the purity was 95-98%. The S-methyl-S-phenylsulfiminium perchlorate has been found to decompose upon



NH_2 - 3360, 3270 cm^{-1}

ClO_4^- - 1050-1170 cm^{-1}

C_6H_5 - 752, 682 cm^{-1}

Figure 1. Infrared spectrum of S-methyl-S-phenylsulfiminium perchlorate in Nujol.

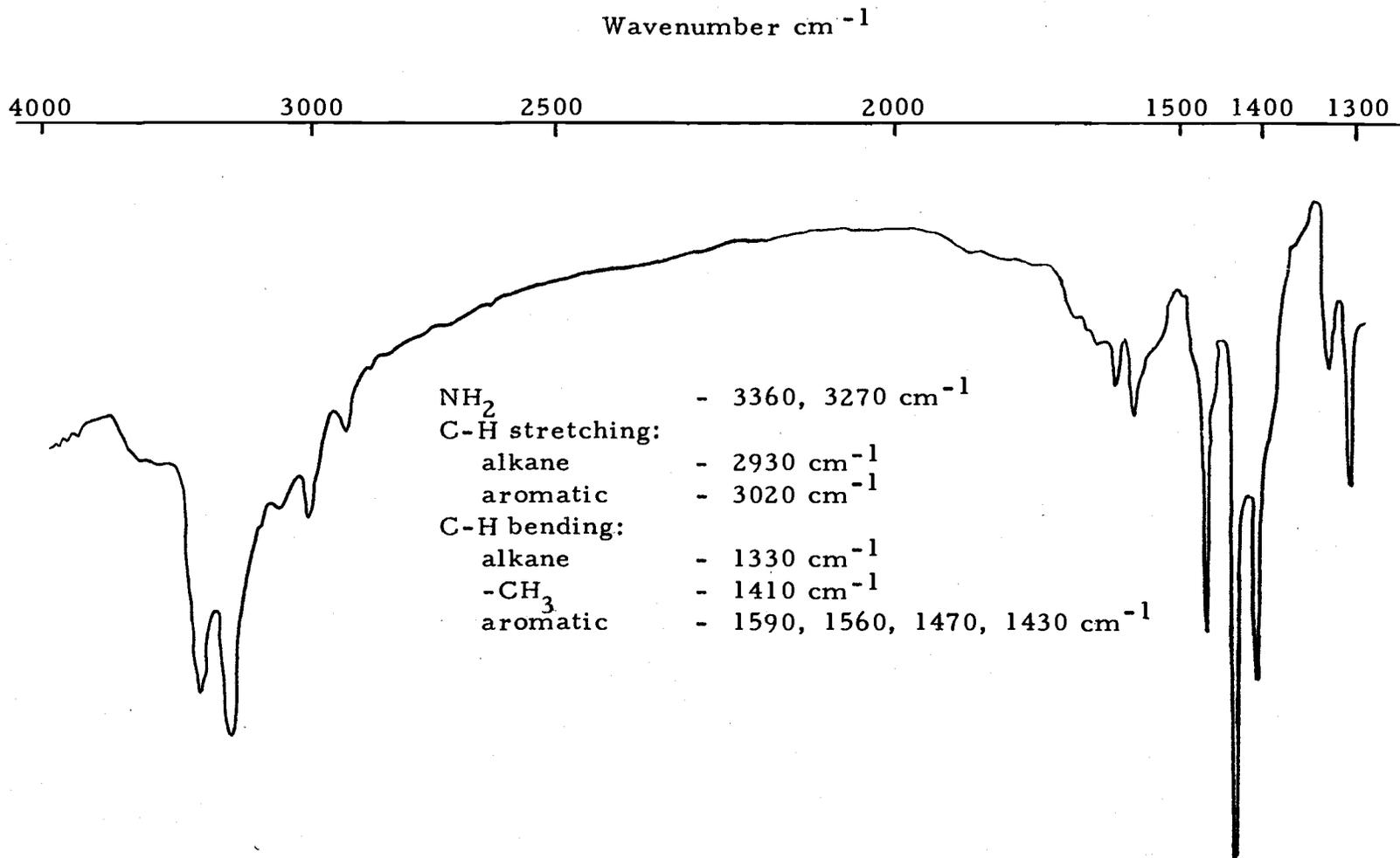


Figure 2. Infrared spectrum of S-methyl-S-phenylsulfiminium perchlorate in Kel-F 10.

(a) CH₃ 2.85 ppm

(b) C₆H₅ 6.63 ppm

a b
[Me(Ph)SNH₂]⁺ClO₄⁻

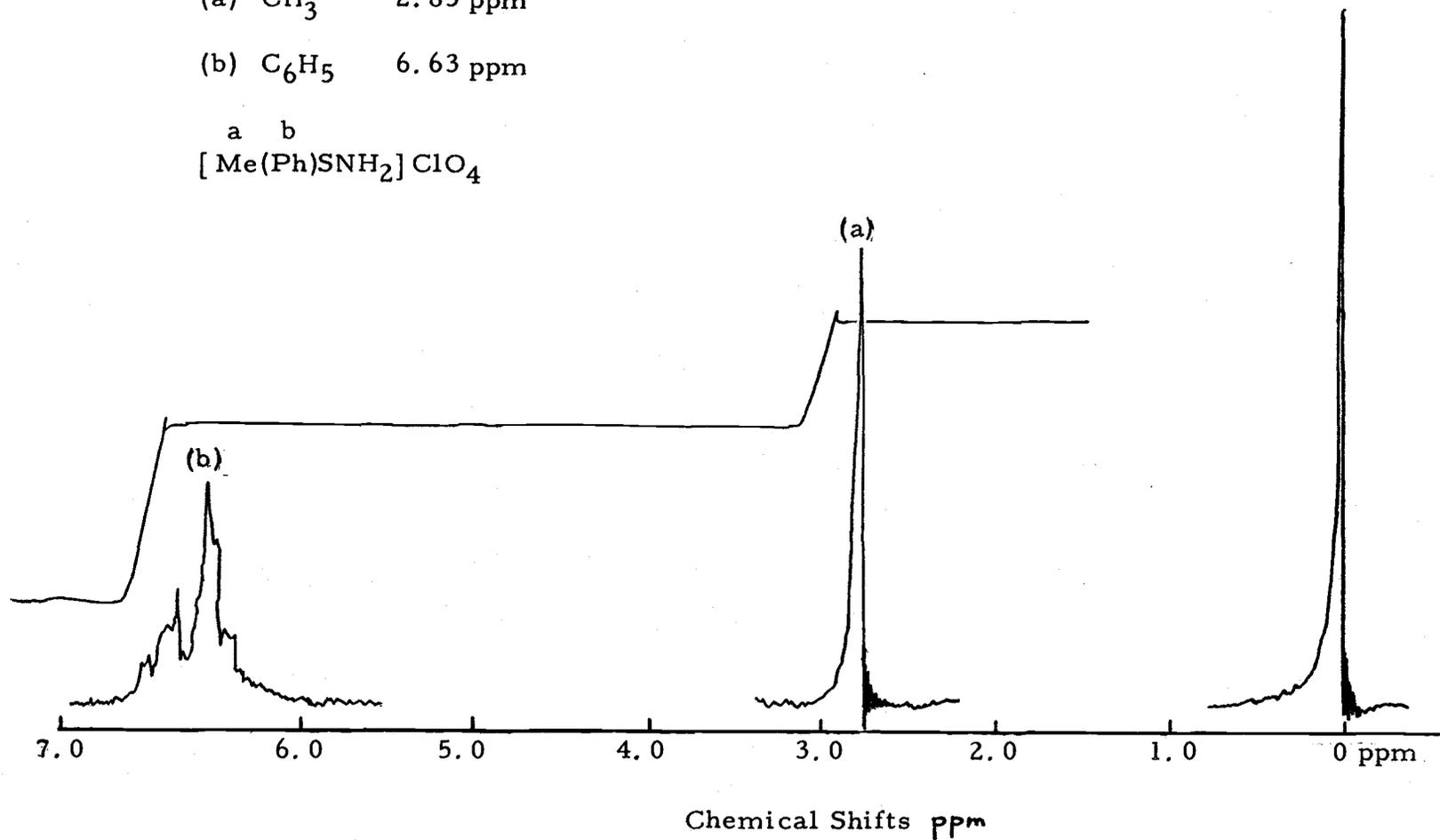


Figure 3. Varian A-60 nmr spectrum of S-methyl-S-phenylsulfiminium perchlorate in D₂O and 3-trimethylsilyl-1-propanesulfonate as an internal standard.

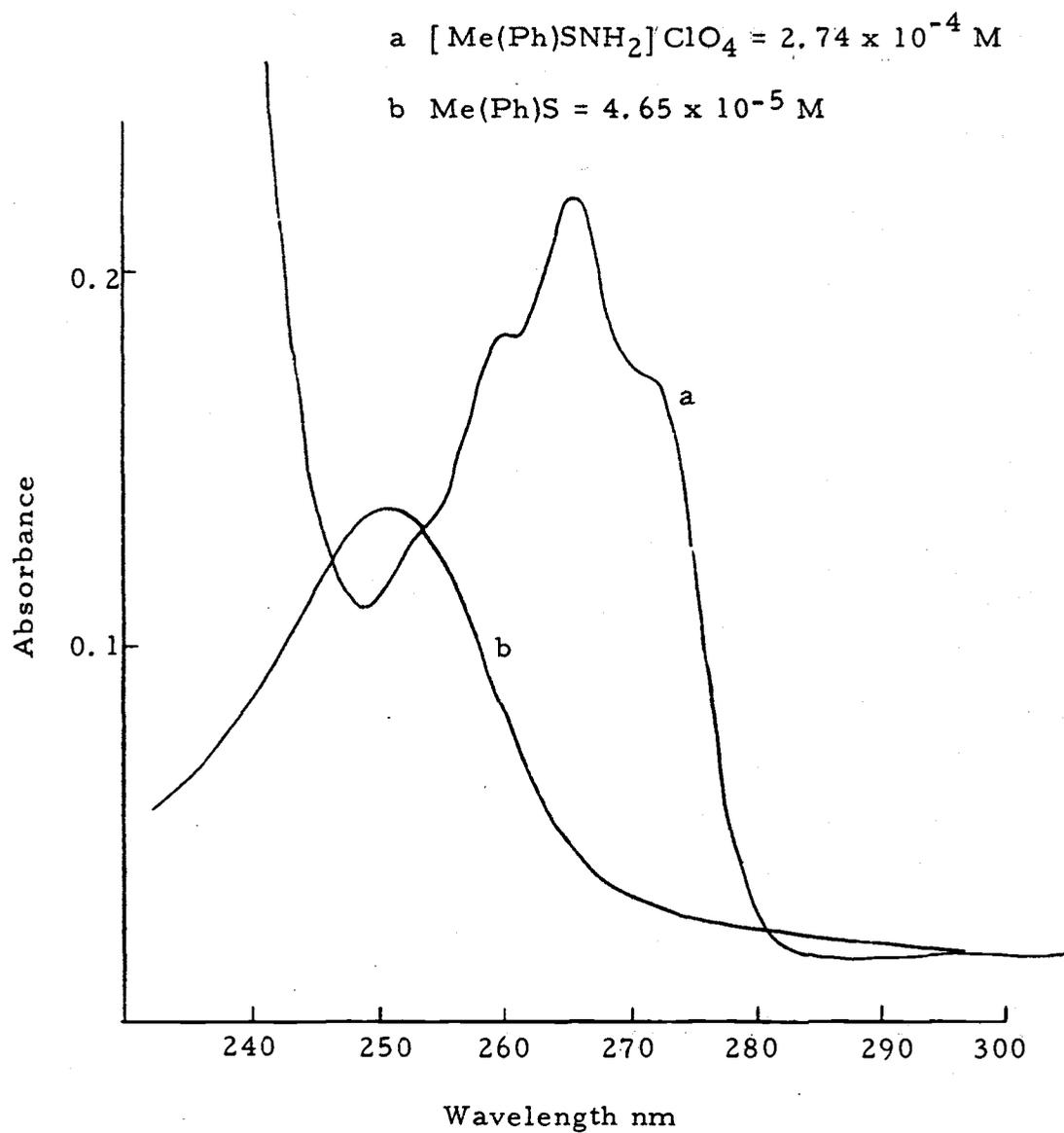


Figure 4. UV spectrum of S-methyl-S-phenylsulfiminium perchlorate and methylphenylsulfide in water.

long standing. In aqueous solution, S-methyl-S-phenylsulfiminium perchlorate appears to be quite stable. The absorbance at 265 nm of an aqueous solution of this compound showed no change during a period of several weeks.

In all cases, the solvent employed was doubly distilled water. All the acid solutions were prepared from 72% perchloric acid (Mallinckrodt Analytical reagent). The concentrations of the acid solutions were accurately determined by titration with standardized sodium hydroxide solution with phenolphthalein as an indicator.

Kinetic Measurements

All kinetic measurements in this study were performed using a Cary Model 16 spectrophotometer. The reaction was followed at a wavelength of 265 nm, which is the maximum absorbance of the S-methyl-S-phenylsulfiminium perchlorate. A single run was made at 353 nm to indicate that the analysis was not dependent on the wavelength. All reactions were run under pseudo-first-order conditions with the iodide-ion and hydrogen-ion concentrations in large excess over the S-methyl-S-phenylsulfiminium perchlorate concentration.

The potassium iodide, S-methyl-S-phenylsulfiminium perchlorate, sodium perchlorate, and perchloric acid solutions were prepared separately in volumetric flasks and immersed in a constant temperature bath.

To start a kinetic run, the prepared solutions were transferred to a previously thermostated 50-ml glass-stoppered Erlenmeyer flask by means of 5-ml pipets. The stirred reaction mixture was quickly transferred to a 1-cm glass-stoppered silica cell which was then immediately placed back into the cell compartment of the spectrophotometer. Absorbance readings were taken automatically by a recorder and a final reading was taken at about ten half-lives which was regarded as the absorbance at infinite time.

The ionic strength was maintained at 0.120 M using sodium perchlorate. A few runs were performed in which the ionic strength was maintained by using potassium perchlorate. These experiments revealed that no appreciable ion pairing was occurring. The effect of bromide, chloride, and thiocyanate ions, as potential catalysts for the iodide-ion reduction of S-methyl-S-phenylsulfiminium perchlorate was also studied. The potassium salts of these ions were all reagent grade and used without further purification.

Potassium Iodide and S-Methyl-S-Phenylsulfiminium
Perchlorate Reaction in DMSO-Water Solvent

Reagents

Crown-Zellerbach commercial grade DMSO was distilled twice at 72° (10mm pressure). The center 60% in each distillation was retained for use. DMSO-water solvent mixtures were prepared on a

volume basis by slow addition of doubly distilled water to DMSO at a mixing temperature of approximately 10°. The volumes of DMSO and water were measured by means of pipets.

Kinetic Measurements

The reaction was followed by measuring the absorbance at 365 nm of triiodide ion, the only significantly absorbing species at this wavelength. The molar absorption coefficient in DMSO-water for triiodide ion at 365 nm is $25,800 \text{ M}^{-1} \text{ cm}^{-1}$ (22, 18). In DMSO-water mixtures, iodine is completely converted to triiodide ion when the initial iodide-ion concentration is greater than 0.05 M (22).

The method of initial rates was employed to determine the third-order rate constants in mole fraction DMSO: 0.500, 0.700, and 1.00. The kinetic method employed in this study was similar to that in the aqueous system except a blank run which did not contain the electrophile, S-methyl-S-phenylsulfiminium perchlorate, was made along with the regular kinetic run. Ionic strengths were controlled at 0.120 M with sodium perchlorate.

Reaction of Thiourea and S-Methyl-S-Phenylsulfiminium Perchlorate in Water Solvent

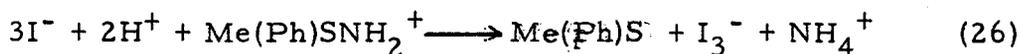
This reaction was followed by measuring the increase in absorbance at 265 nm. The reaction was set up as pseudo-first-order

with the initial thiourea and acid concentration in at least 20-fold excess of that of the initial concentrations of the S-methyl-S-phenyl-sulfiminium perchlorate. The procedure employed was similar to that of the system described previously.

III. RESULTS

Potassium Iodide and S-Methyl-S-Phenylsulfiminium
Perchlorate ReactionStoichiometry

The reaction of S-methyl-S-phenylsulfiminium perchlorate with potassium iodide in acidic solution gave methylphenylsulfide, triiodide ion, and ammonium ion as products according to the following equation:



The stoichiometry of this reaction was verified by analysis of iodine produced and hydrogen ion consumed. S-methyl-S-phenylsulfiminium perchlorate was added to a solution containing known excess amounts of perchloric acid and potassium iodide. The water used to make up the solutions was boiled and purged with prepurified nitrogen to minimize air oxidation. After the reaction was complete, three to four hours, the iodine produced was titrated with standardized sodium thiosulfate and subsequently the remaining acid was titrated with standardized sodium hydroxide to the methyl red end point. The results for a solution initially containing 0.245 mmoles of S-methyl-S-phenylsulfiminium perchlorate, 1.22 mmoles of perchloric acid, and 2.51 mmoles of potassium iodide, were (moles H^+ consumed)/(moles

iodine produced) = 1.98.

The spectral stoichiometry was also verified for this reaction. The reaction was followed at a wavelength of 265 nm, which is the maximum absorbance of the S-methyl-S-phenylsulfiminium perchlorate. Potassium iodide has a molar absorption coefficient at 265 nm of $8.69 \text{ M}^{-1} \text{ cm}^{-1}$. The value of the molar absorption coefficient of potassium iodide was very difficult to obtain due to the fact that the absorbance of a solution of potassium iodide decreased with time. Recrystallized potassium iodide was used in these determinations. The initial absorbance value was finally used to determine the molar absorption coefficient which therefore may be in slight error. The products, triiodide ion and methylphenylsulfide, absorb at 265 nm also. Triiodide ion has a molar absorption coefficient of $9.18 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ and methylphenylsulfide has a molar absorption coefficient of $2.58 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$. Table 1 gives the results of the determination of the spectral stoichiometry. The experimental infinity absorbances agree within + 5% of the calculated values.

Table 1. Results of the spectral stoichiometric analysis of the S-methyl-S-phenylsulfiminium perchlorate and potassium iodide reaction in 0.021 M perchloric acid.

$10^2[\text{KI}], \text{ M}$	$10^5[\text{Me(Ph)SNH}_2^+], \text{ M}$	Experimental infinity absorbance	Calculated infinity absorbance
2.12	4.61	0.720	0.727
3.02	4.61	0.808	0.804
3.02	4.40	0.750	0.780
4.03	4.40	0.833	0.869
4.24	4.78	0.914	0.931

Determination of the Rate Law

The reaction was run under pseudo-first-order conditions, with the hydrogen-ion and iodide-ion concentrations in large excess over the S-methyl-S-phenylsulfiminium perchlorate concentration. Plots of $\log(A_t - A_\infty)$ versus time, shown in Figure 5, were found to be linear for at least two half-lives. The slopes of the log plots were found to be proportional to the hydrogen-ion and iodide-ion concentrations indicating that the following rate law holds in aqueous solutions.

$$d[\text{I}_3^-]/dt = k_I[\text{Me(Ph)SNH}_2^+][\text{H}^+][\text{I}^-] \quad (27)$$

Kinetic data for this system are summarized in Table 2, along with the values of k_I based on the above rate law. The third-order rate constant for this system was found to be $0.960 \pm 0.044 \text{ M}^{-2}\text{sec}^{-1}$ at

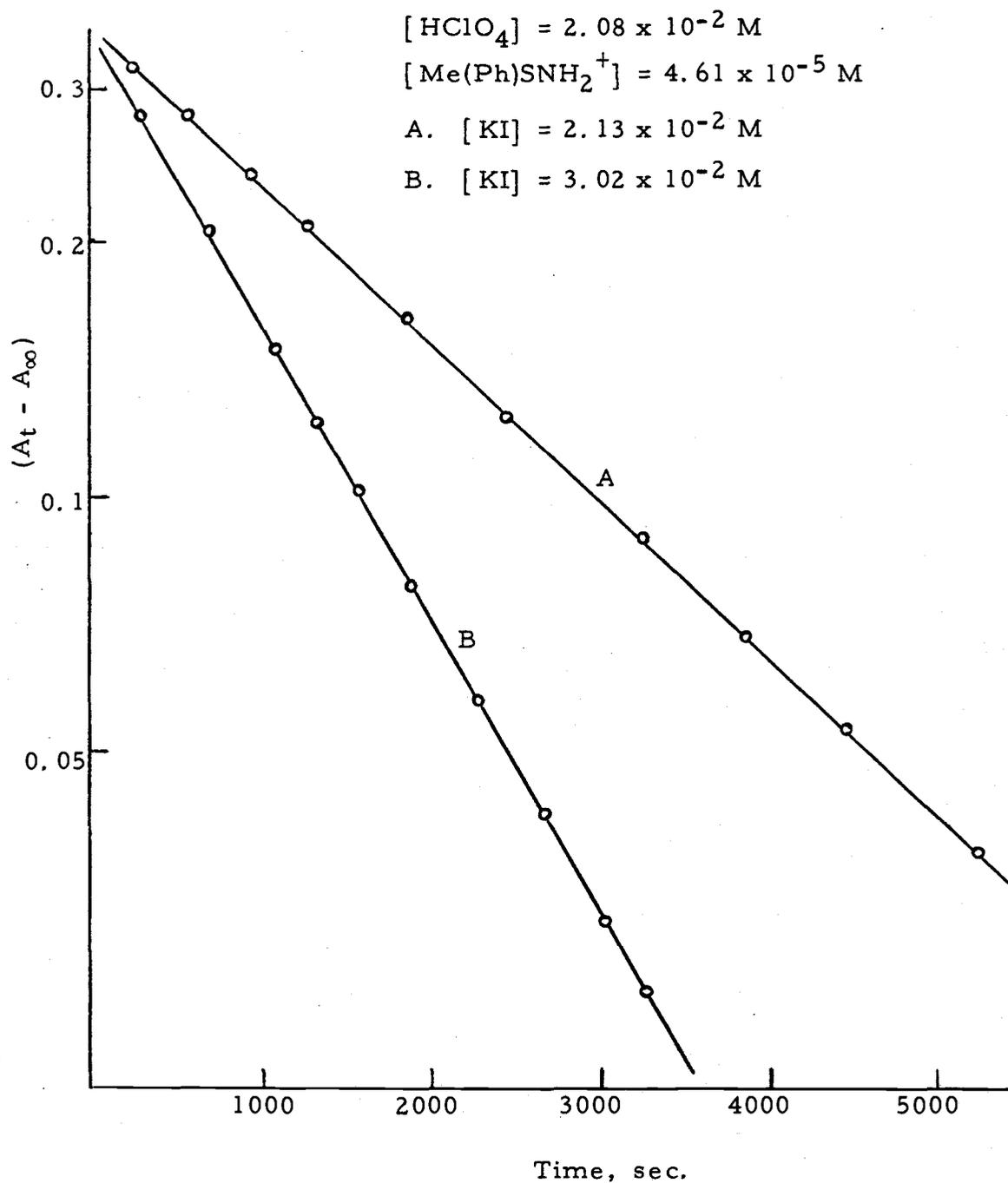


Figure 5. $\text{Log}(A_t - A_\infty)$ versus time plots for the S-methyl-S-phenylsulfiminium perchlorate and potassium iodide reaction at 0.120 M ionic strength and 20.0° in water solvent.

Table 2. Kinetic data for the reaction of S-methyl-S-phenylsulfiminium perchlorate and potassium iodide at 0.120 M ionic strength and 20.0° in water solvent.

$10^2[\text{KI}], \text{ M}$	$10^2[\text{HClO}_4], \text{ M}$	$10^5[\text{Me(Ph)SNH}_2^+], \text{ M}$	$k_I, \text{ M}^{-2}\text{sec}^{-1}$	
0.53	10.00	4.40	0.981	
1.31	2.08	1.33	0.971	
2.13	2.08	4.61	0.971	
3.01	2.08	2.84	0.958	
3.02	2.08	4.61	0.977	
3.02	2.08	4.40	0.963	
3.04	1.04	4.61	0.938	
4.03	2.08	4.40	0.967	
4.13	3.93	4.95	0.958	
4.17	3.93	4.80	0.965	
4.22	3.93	4.80	0.934	
4.22	2.08	2.84	0.970	
4.24	2.08	4.78	0.949	
6.08	0.42	2.39	0.964	
6.08	1.96	2.19	0.936	
8.06	0.98	2.19	0.953	
8.07	0.98	2.19	0.965	
1.15	4.04	4.67	0.980	$\mu = 0.052 \text{ M}^a$
1.15	4.04	4.67	0.973	$\mu = 0.360 \text{ M}^a$
3.02	1.01	4.78	0.964	$[\text{Br}^-] = 0.150 \text{ M}$
2.05	1.01	4.61	0.970	$[\text{SCN}^-] = 0.089 \text{ M}$
4.13	3.93	4.95	0.958	$[\text{Cl}^-] = 0.040 \text{ M}$

^aionic strength

$$k_I = 0.960 \pm 0.044 \text{ M}^{-2}\text{sec}^{-1} \quad (\pm 0.044 = 1 \text{ std. dev.})$$

20.0° and 0.120 M ionic strength.

Temperature Effect

Values of the activation parameters, ΔH^\ddagger and ΔS^\ddagger , were derived using values of the third-order rate constant at 10.4°, 20.0°, 29.7°, 30.0°, and 40.2°. The summary of this temperature-dependence study is found in Table 3. According to transition-state theory,

$$\ln(k_I/T) = \ln(k/h) - \Delta H^\ddagger/RT + \Delta S^\ddagger/R \quad (28)$$

ΔH^\ddagger is obtained from the slope of the $\log(k_I/T)$ versus $(1/T)$ plot. The $\log(k_I/T)$ versus $(1/T)$ plot for this system is shown in Figure 6. The ΔH^\ddagger and ΔS^\ddagger values were found to be 12.3 ± 0.2 kcal/mole and -16.7 ± 0.2 eu, respectively. The slope and intercept of the $\log(k_I/T)$ versus $(1/T)$ plot was determined by SIMLIN, a computer program for simple correlation and regression. Figure 6 also shows the uncertainty in the slope due to the error limits of the third-order rate constants.

Ionic Strength Effect

The ionic strength was varied from 0.042 M to 0.360 M in several kinetic runs. Third-order rate constants showed no change within experimental error. The results of this study are shown in Table 2. In a few runs, potassium perchlorate, rather than sodium perchlorate, was used to control the ionic strengths in order to see if

Table 3. Temperature-dependence of the S-methyl-S-phenylsulfiminium perchlorate and potassium iodide reaction at 0.120 M ionic strength.

Temperature(°C)	$10^2[\text{KI}], \text{M}$	$10^2[\text{HClO}_4], \text{M}$	$10^5[\text{Me(Ph)SNH}_2^+], \text{M}$	$k_I, \text{M}^{-1}\text{sec}^{-1}$
10.4	2.08	4.04	4.67	0.443
	3.00	4.04	4.67	0.458
				Ave 0.451 (<u>+ 0.008</u>)
29.7	2.08	0.81	4.67	1.87
	2.09	1.01	4.67	1.93
				Ave 1.90 (<u>+ 0.03</u>)
30.0	2.13	2.08	4.78	1.93
	2.42	2.08	4.78	2.04
				Ave 1.98 (<u>+ 0.06</u>)
40.2	1.28	2.08	3.15	3.74
	1.51	2.08	3.15	4.13
	1.37	2.08	3.80	4.08
				Ave 3.98 (<u>+ 0.24</u>)

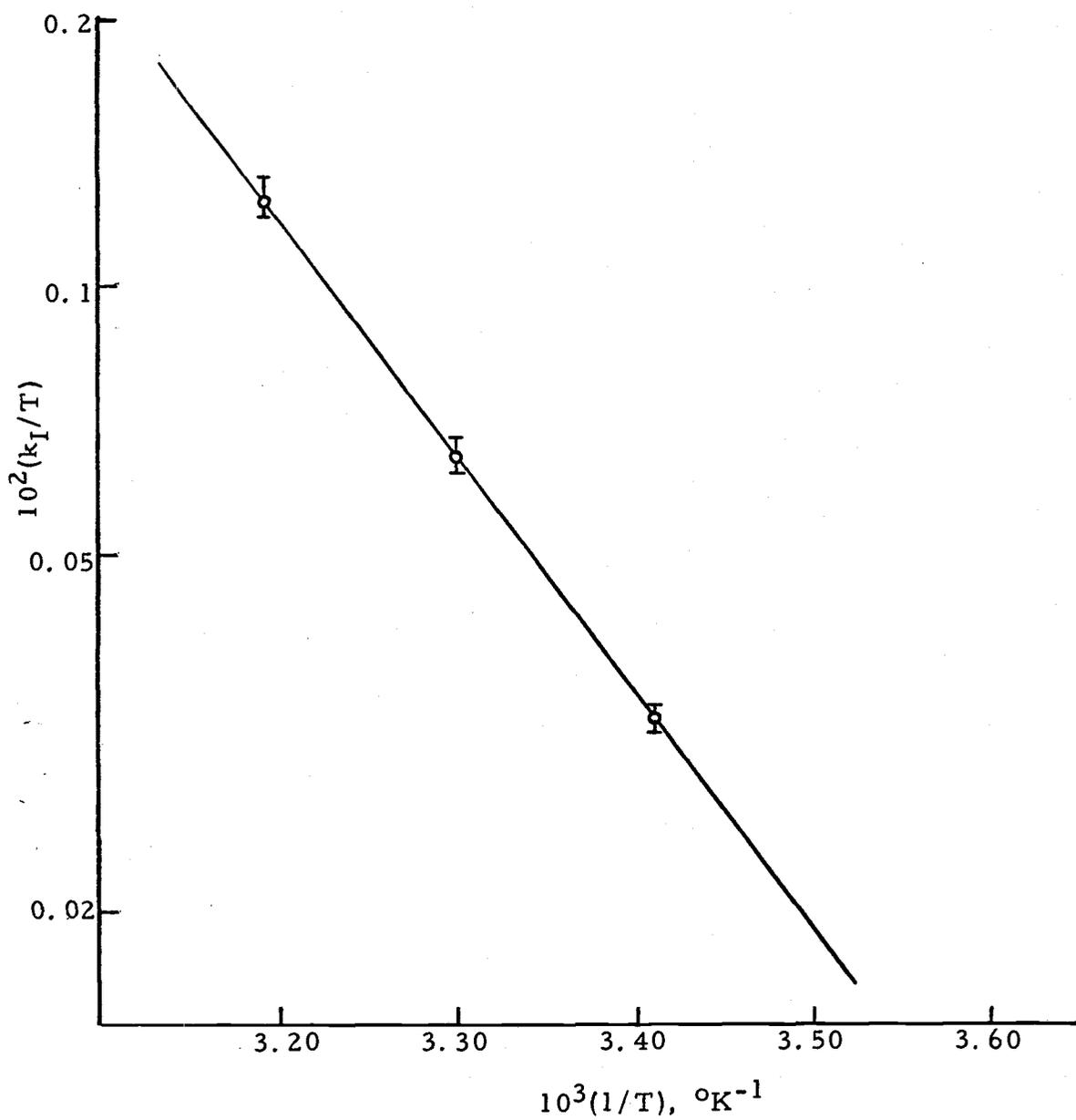


Figure 6. Temperature-dependence plot of the third-order rate constant for the S-methyl-S-phenylsulfiminium perchlorate and potassium iodide reaction.

there was any appreciable ion pairing occurring with sodium perchlorate. Third-order rate constants for these runs were found to be the same within experimental error.

Catalysis Study

The potential catalysis of the reaction of S-methyl-S-phenylsulfiminium perchlorate and potassium iodide by bromide, chloride, and thiocyanate ion was studied briefly. The results are shown in Table 2. Third-order rate constants for these kinetic runs showed no catalysis exhibited by these ions within experimental error.

Potassium Iodide and S-Methyl-S-Phenylsulfiminium Perchlorate Reaction in DMSO-Water Solvent

Kinetic Measurements

The reaction was followed by measuring the absorbance of triiodide ion at 365 nm. In DMSO-water solvents, the triiodide ion is the only significantly absorbing species at 365 nm and the molar absorption coefficient of this species at 365 nm is $25,800 \text{ M}^{-1}\text{cm}^{-1}$ (18, 22).

When the iodide-ion concentration is greater than 0.05 M in solvents of $X_{\text{DMSO}} \geq 0.500$, iodine is completely converted (>99%) to the triiodide ion. Initial rates of appearance of triiodide ion were measured for the first 1-3% of the reaction. Plots of absorbance versus time were linear for solvents containing 0.500-1.00 mole fraction of DMSO.

However, in most cases, for the initial 90 seconds of the reaction, the absorbance-versus-time plot was slightly curved. This curvature was attributed to a temperature effect even though care was taken to set the water bath at a temperature low enough to compensate for the increase in temperature during the mixing process. Two typical plots of absorbance versus time for 0.700 mole fraction of DMSO are shown in Figure 7. The slopes of these plots were taken as the initial rates, with an uncertainty of $\pm 2\%$. Since dimethyl sulfoxide is known to oxidize iodide ion in acidic solutions, the third-order rate constants reported in Table 4 were all corrected for this competing reaction. The correction procedure was to subtract the initial slope of the blank kinetic run which did not contain the electrophile, S-methyl-S-phenylsulfiminium cation, from the initial slope of the kinetic run. Third-order rate constants were calculated using this corrected initial slope. The corrections in all cases were approximately 1-3%.

Initial rates were measured as a function of initial concentrations of hydrogen ion, iodide ion, and S-methyl-S-phenylsulfiminium cation. The rate law for this reaction was rigorously established in 0.700 mole fraction DMSO.

$$d[I_3^-]/dt = k_I [Me(Ph)SNH_2^+][H^+][I^-] \quad (29)$$

The values of k_I were obtained by dividing the observed initial rate by the initial concentrations of S-methyl-S-phenylsulfiminium perchlorate,

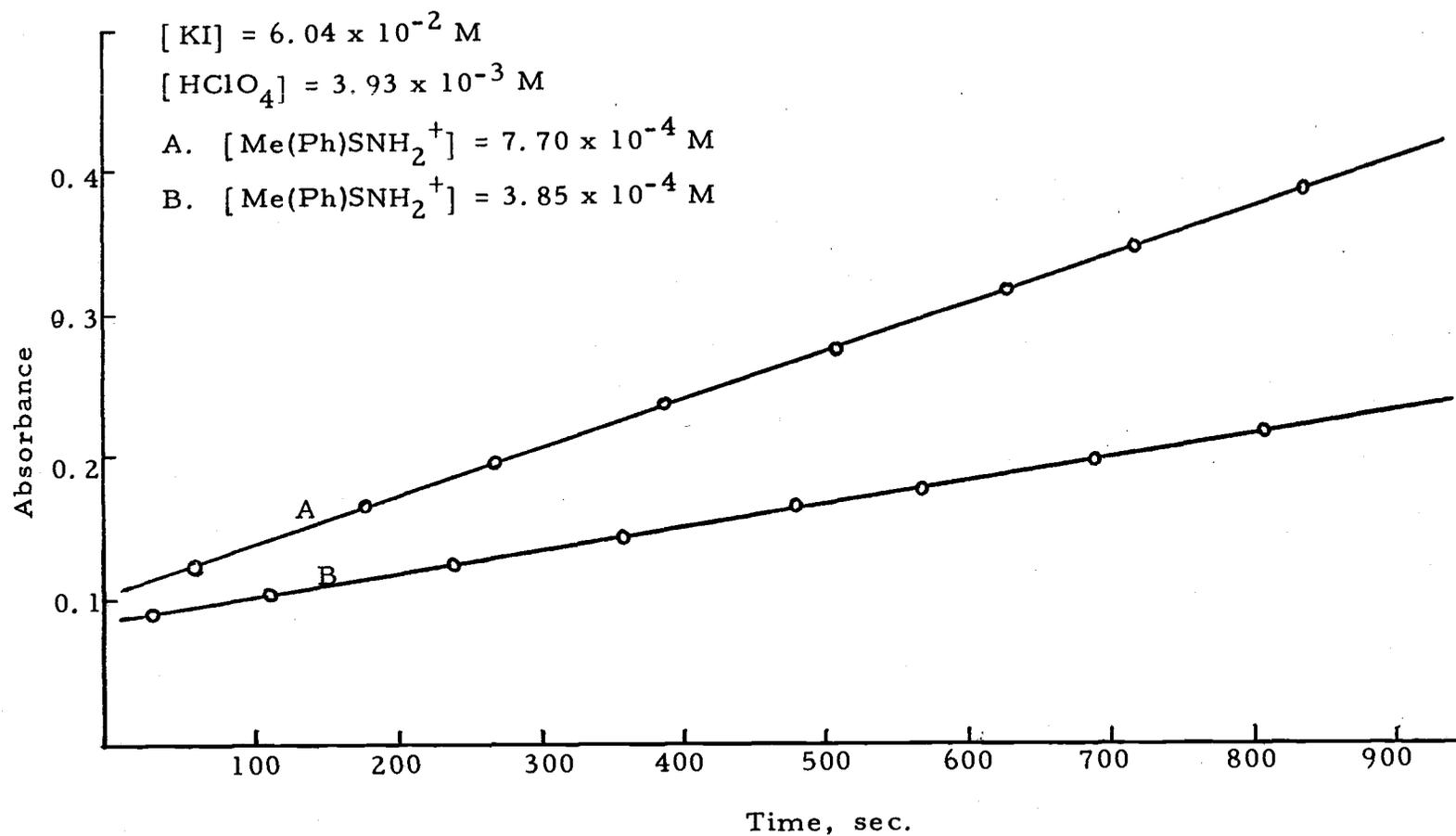


Figure 7. Plots of absorbance versus time for the reaction of S-methyl-S-phenylsulfiminium perchlorate and potassium iodide in 0.700 mole fraction DMSO.

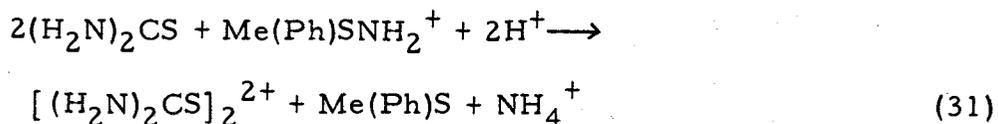
Table 4. Kinetic data for the reaction of S-methyl-S-phenylsulfiminium perchlorate and potassium iodide in 0.500-1.00 mole fraction DMSO at 20.0° and 0.120 M ionic strength.

$10^2[\text{KI}], \text{M}$	$10^2[\text{HClO}_4], \text{M}$	$10^4[\text{Me(Ph)SNH}_2^+], \text{M}$	$10^2k_I, \text{M}^{-2}\text{sec}^{-1}$	
Mole fraction DMSO = 0.500				
2.10	7.86	3.73	2.18	
1.01	7.86	3.73	2.27	
			Ave 2.22	(+ 0.05)
Mole fraction DMSO = 0.700				
0.60	3.93	3.84	3.76	
0.60	1.96	3.84	3.50	
3.13	0.393	3.84	3.84	
5.61	0.393	4.29	3.38	
6.04	0.393	3.85	3.21	
6.04	0.393	7.70	3.39	
6.26	0.393	3.84	3.47	
7.00	0.393	2.03	3.60	
			Ave 3.51	(+ 0.21)
6.03	0.393	3.85	3.22	$[\text{Br}^-] = 0.010 \text{ M}$
6.03	0.393	3.85	3.21	$[\text{Br}^-] = 0.006 \text{ M}$
0.00	0.393	2.03	no reaction	$[\text{Br}^-] = 0.300 \text{ M}$ 265 nm
5.61	0.393	4.29	3.38	$[\text{Cl}^-] = 0.016 \text{ M}$
Mole fraction DMSO = 1.00				
5.15	0.314	1.91	14.1	
5.15	0.314	1.91	10.9	$[\text{Cl}^-] = 0.016 \text{ M}$

hydrogen, and iodide ions. Kinetic data for this reaction in 0.500, 0.700, and 1.00 mole fraction DMSO are summarized in Table 4 along with the third-order rate constants. The ionic strength was varied in several runs at 0.700 mole fraction DMSO. No change was observable in the rate constants.

Catalysis Study

The effect of added chloride and bromide ions as potential catalysts for the reaction was studied. Results of the addition of potassium chloride, and potassium bromide in 0.700 mole fraction DMSO are summarized in Table 4. No catalysis was observed since there was no observable increase in the k_I values within experimental error. A kinetic run at 0.700 mole fraction DMSO was also carried out with bromide ion alone. The reaction was followed at 265 nm. There was no reaction occurring based on the lack of change in absorbance at 265 nm. In 1.00 mole fraction DMSO, the presence of chloride ions apparently lowered the rate constant by 15%. The molar absorption coefficient for triiodide ion was found to be different for solutions that contained chloride or bromide ions. Although the rate constants were calculated using the appropriate molar absorption coefficients, we are unable to account for the apparent decrease in rate.



The products and kinetics of this reaction were examined briefly by a spectral analysis at 265 nm. The molar absorption coefficient of thiourea at 265 nm is $2.82 \times 10^2 \text{ M}^{-1}\text{cm}^{-1}$ and the molar absorption coefficients of the proposed products, Me(Ph)S and $[(\text{H}_2\text{N})_2\text{CS}]_2^{2+}$, are $2.58 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$ and $1.29 \times 10^2 \text{ M}^{-1}\text{cm}^{-1}$, respectively. The $[(\text{H}_2\text{N})_2\text{CS}]_2\text{Cl}_2$ used to obtain its molar absorption coefficient at 265 nm was prepared by Krueger (22) by the method of Preisler and Berger (24). Infinity absorbances in all the kinetic runs agreed very well with the calculated infinity absorbances. Also, after the attainment of the infinity absorbance, 20 ml of the reaction mixture were extracted with approximately 21 ml of ethyl ether. The absorbance of the ether layer corresponded to the expected absorbance for the product, methylphenylsulfide at 265 nm. The uv scan of this ether layer showed the characteristic spectrum of methylphenylsulfide.

The reaction was conducted under pseudo-first-order conditions with the perchloric acid and the thiourea concentrations in excess of the S-methyl-S-phenylsulfiminium perchlorate concentration. Plots of $\log(A_t - A_\infty)$ versus time, shown in Figure 8, were found to be linear. The kinetic data for this reaction, along with the third-order rate constants, are tabulated in Table 5. Slopes of the log plots were

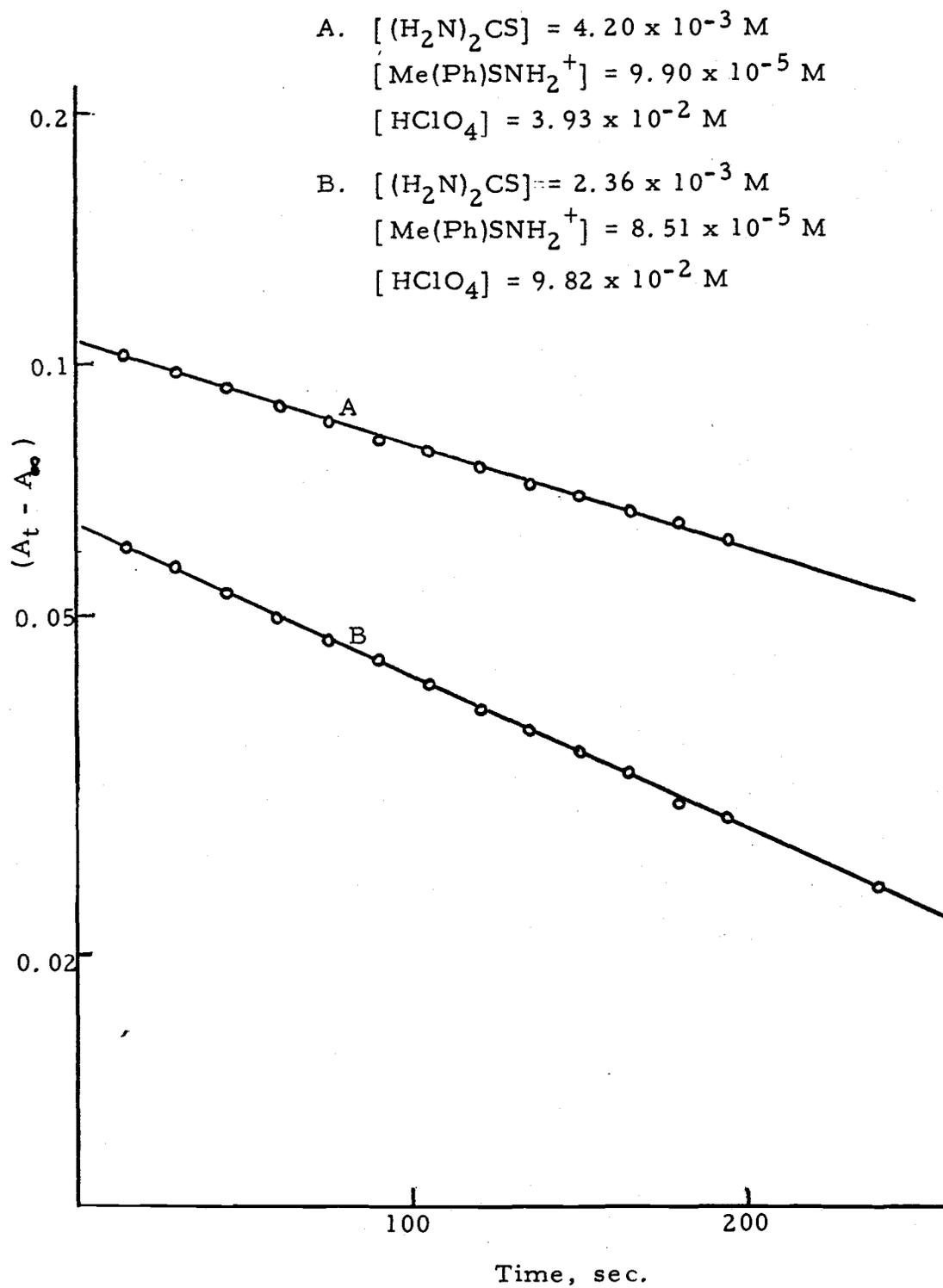


Fig. 2. $\log(A_t - A_\infty)$ versus time plots for the S-methyl-S-phenyl-
 perchlorate and thiourea reaction at 0.120 M
 perchlorate in water solvent.

Table 5. Kinetic data for the reaction of thiourea and S-methyl-S-phenylsulfiminium perchlorate at 20.0° in water solvent.

$10^3[(\text{H}_2\text{N})_2\text{CS}], \text{M}$	$10^2[\text{HClO}_4], \text{M}$	$10^5[\text{Me}(\text{Ph})\text{SNH}_2^+], \text{M}$	$k_{\text{TU}}, \text{M}^{-2}\text{sec}^{-1}$
4.20	3.93	9.90	17.6
4.71	3.93	8.51	17.4
4.33	9.82	9.90	17.6
4.20	9.82	9.90	17.2
4.71	9.82	9.90	18.1
2.36	9.82	8.51	18.3
2.02	9.82	8.51	18.3
4.20	10.15	9.90	17.9
4.71	11.45	9.90	18.4
2.36	19.65	8.51	17.9

$$k_{\text{TU}} = 17.9 \pm 0.4 \text{ M}^{-2}\text{sec}^{-1}$$

found to be proportional to the hydrogen-ion and thiourea concentrations thus giving the following rate-law expression.

$$-d[(H_2N)_2CS]/dt = k_{TU}[Me(Ph)SNH_2^+][(H_2N)_2CS][H^+] \quad (32)$$

The rate constant found for this reaction at 20.0° and 0.120 M ionic strength is $17.9 \pm 0.4 \text{ M}^{-2}\text{sec}^{-1}$.

Assuming that $k_{TU} = 0.43 \text{ M}^{-2}\text{sec}^{-1}$ represents the rate constant for attack of thiourea on S-methyl-S-phenylsulfiminium ion in 0.700 mole fraction DMSO, the reactivity in water, relative to that in 0.700 mole fraction DMSO, is $17.9/0.43 = 42$.

Other Nucleophiles Studied

Hydroxide ion has been found to react with S-methyl-S-phenylsulfiminium perchlorate in water at pH ~ 12. Experiments at pH ~ 12 with high concentrations of reactants present were performed in order to determine the products of the reaction. Ammonia was detected as a product but no hydroxylamine was found. There was no definite detection of methylphenylsulfoxide.

In a typical kinetic run in which the S-methyl-S-phenylsulfiminium perchlorate concentration was $4.03 \times 10^{-4} \text{ M}$ and the pH ~ 12, the spectrum of S-methyl-S-phenylsulfiminium perchlorate changed over into one being a mixture of two species, S-methyl-S-phenylsulfiminium perchlorate and methylphenylsulfide. Methylphenylsulfoxide

may also be present. Also, absorbances of two intermediates were noted at 277 nm and 285 nm, which disappeared after about ten minutes. By adjusting the hydroxide-ion concentration in the range of 0.003-0.01 M, spectral changes occurred in a matter of minutes. These spectrum changes are shown in Figure 9.

Thiosulfate ion showed little or no reactivity with S-methyl-S-phenylsulfiminium perchlorate in neutral or basic solution. In a typical kinetic run in neutral solution, in which the S-methyl-S-phenylsulfiminium perchlorate concentration was 1.32×10^{-4} M and thiosulfate-ion concentration was 9.10×10^{-3} M, there was no absorbance change at 250 nm. Runs done in solutions of pH > 9 revealed similar results.

The nucleophile, 2-aminoethanethiol, has been briefly studied. This nucleophile is very weakly reactive with S-methyl-S-phenylsulfiminium perchlorate in solutions of pH 10-11 and in solutions of pH 1-2 is completely unreactive. The reaction was studied at 250 nm.

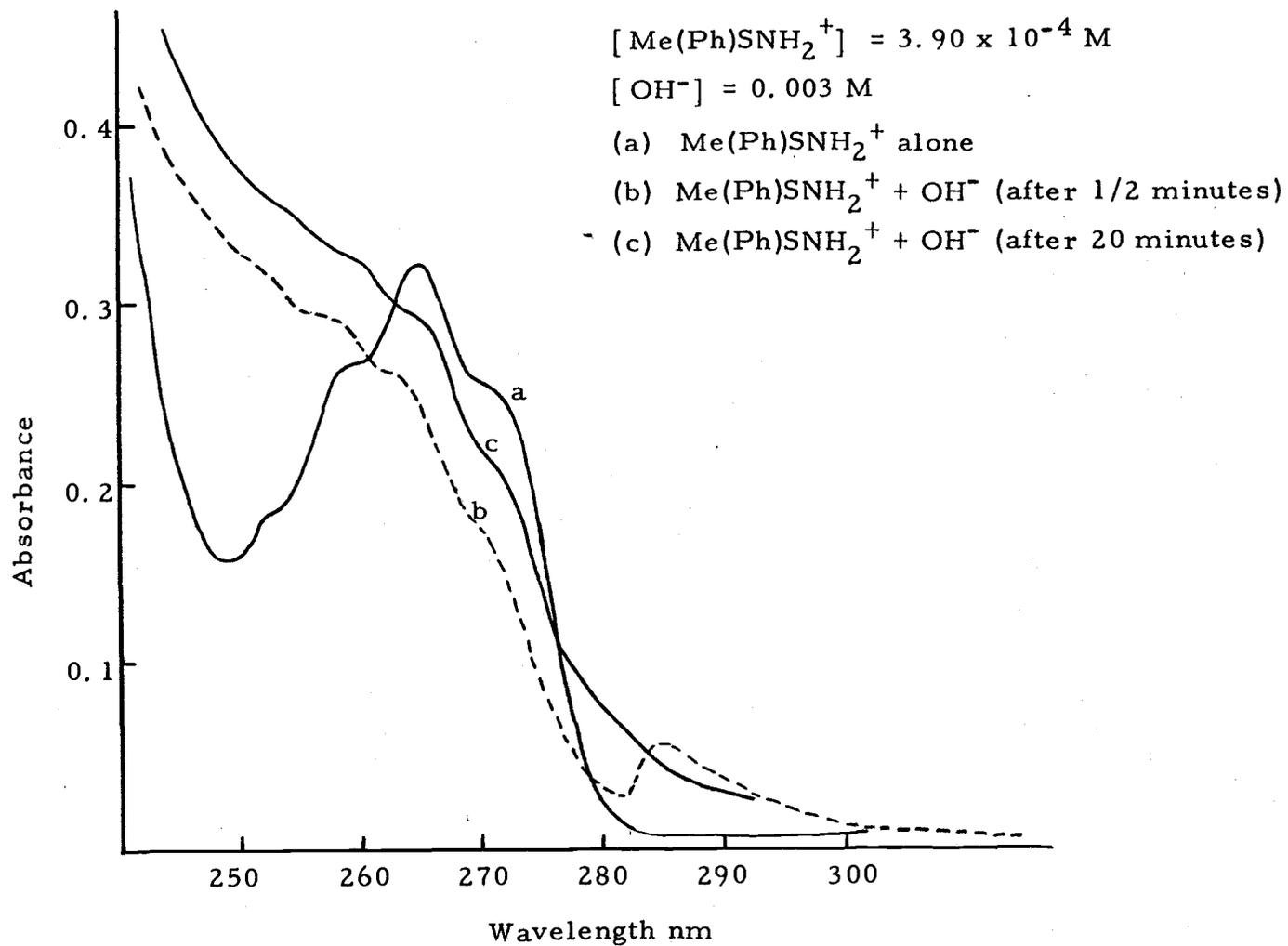
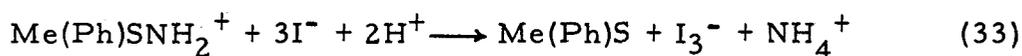


Figure 9. UV spectral changes in the hydroxide ion and S-methyl-S-phenylsulfiminium perchlorate reaction.

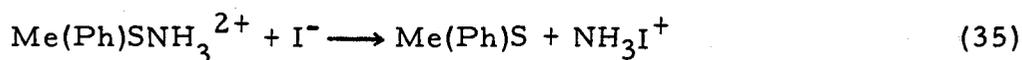
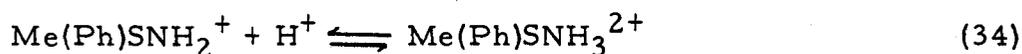
IV. DISCUSSION

The kinetics of the reaction

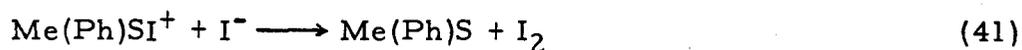
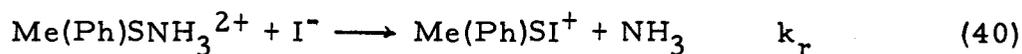
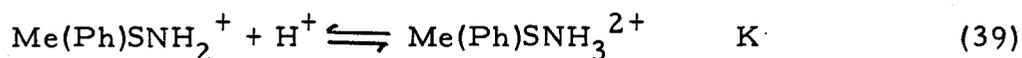


have been measured spectrophotometrically in water and in DMSO-water solvents over the range $X_{\text{DMSO}} = 0-1.00$. There are two plausible mechanisms that can be envisioned for this reaction. One involves an attack of the nucleophile, iodide ion, on the sulfur acid center and the other on the nitrogen acid center.

The nitrogen-attack mechanism is



and the sulfur-attack mechanism is



Let us first examine the nitrogen-attack mechanism. The iodide-ion displacement occurs on the nitrogen with Me(Ph)S as the leaving group. The mechanism involves specific hydrogen-ion transfer (step 34) preceding the rate-determining step (step 35). This protonation would presumably facilitate the attack of the negative iodide ion by purely electrostatic considerations.

As shown in the plot of $\log k_I$ versus mole fraction of DMSO in Figure 10, the rate decreases greatly with increasing DMSO content, goes through a broad minimum at $X_{\text{DMSO}} = 0.300-0.500$, and then increases markedly. This behavior parallels the proton-donating ability of the solvent mixture. Since DMSO is known to be more basic than H_2O (25), reaction 34 becomes less favorable upon addition of DMSO to the system. Wolford has measured the ability of acidic DMSO-water media to protonate *m*-nitroaniline (26). The pK_a values for *m*-nitroanilinium which were obtained by Wolford, are shown in Figure 10. The solvent effect on the rate clearly parallels the effect of the solvent on *m*-nitroaniline basicity. Kreevoy and Williams have also observed a similar correlation between rate and indicator basicity in DMSO-water solvents for the rate-determining proton transfer in the hydrolysis of ethyl vinyl ether (27). The possibility of deprotonation of Me(Ph)SNH_2^+ to Me(Ph)S = NH in DMSO is ruled out as the cause of the rate minimum in $X_{\text{DMSO}} = 0.300-0.500$ because the free imine base is formed only under highly basic conditions

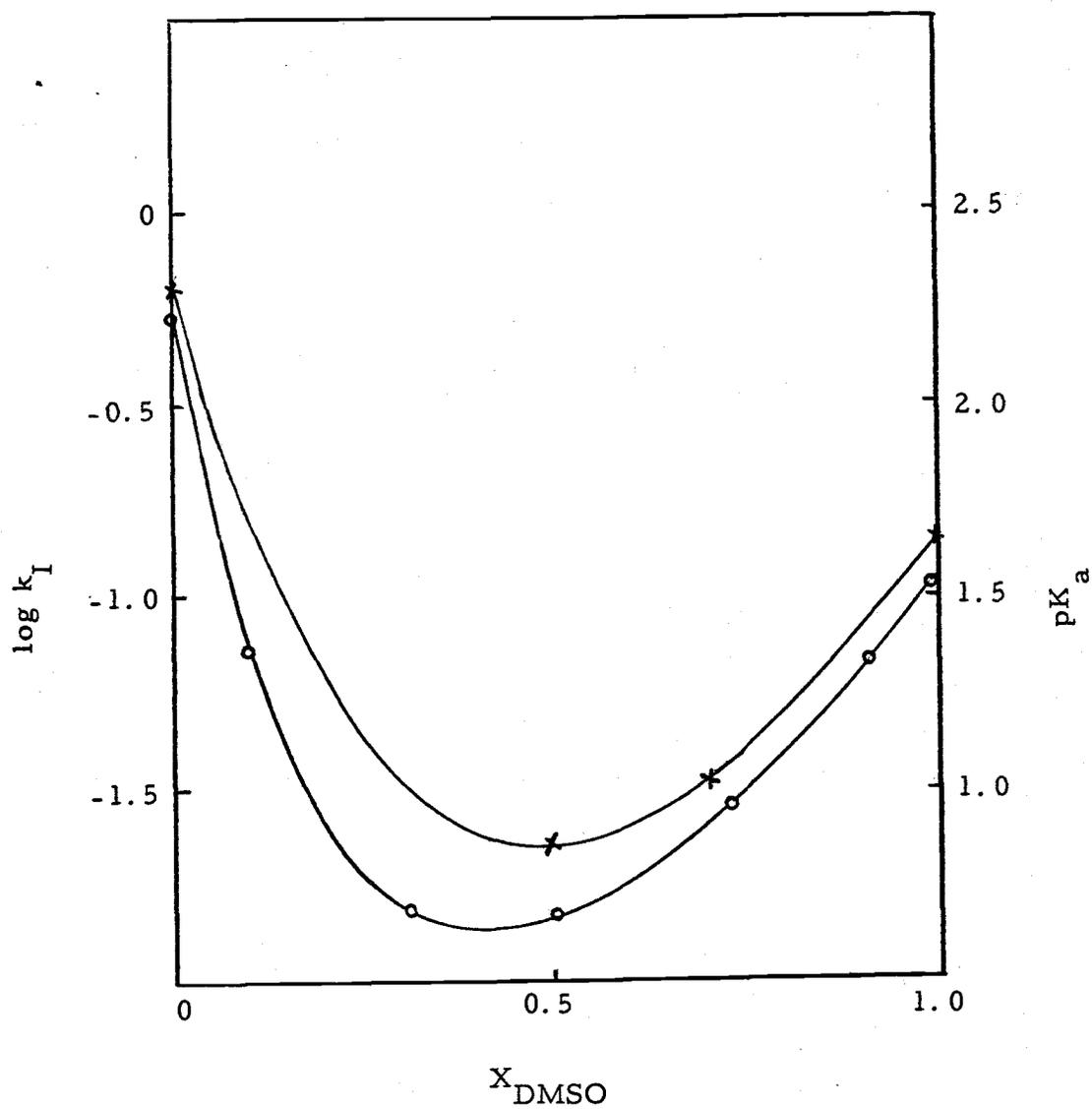
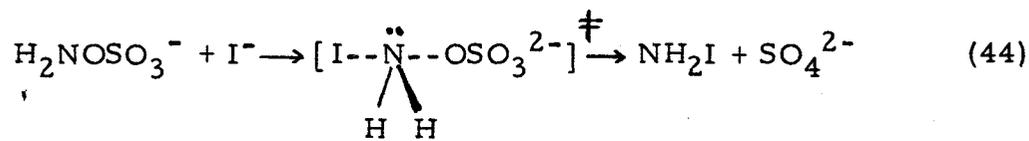


Figure 10. $\log k_I$ (crosses) and pK_a of m-nitroanilinium (open circles) plotted as a function of mole fraction of dimethyl sulfoxide in the solvent.

(20). In addition this deprotonation step would not be consistent with the simple first-order hydrogen-ion dependence observed in this system. The marked increase in the rate beyond $X_{\text{DMSO}} = 0.500$ also arises in part from the decreasing dielectric constant of the solvent (28). Therefore, from the above discussion one can see the importance of the protonation equilibrium.

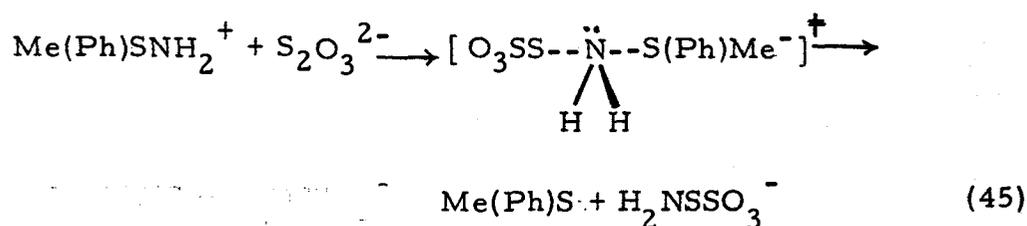
Let us now discuss several points against the nitrogen-attack mechanism and see how this mechanism can be ruled out. In the study of the hydroxylamine-O-sulfonic acid reaction with iodide ion,



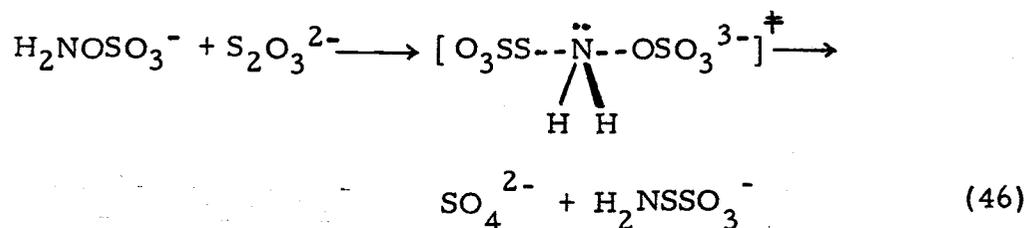
which is thought to involve nitrogen attack (30), the presence of hydrogen ion has been shown to retard the reaction (29). Since protonation is crucial to the reaction in the case of the S-methyl-S-phenylsulfiminium cation, the nitrogen-attack mechanism seems less likely for its reaction with iodide. Because the steric relief arising from the partial expulsion of the leaving group increases with an increase in size of the leaving group, Me(Ph)S may be a better leaving group than SO_4^{2-} , rendering the above argument invalid. However, it is very difficult to assess the bond strength by this criterion alone, for the increased size of the leaving group also raises the transition state energy. Moreover, since an $\text{S}_{\text{N}}2$ mechanism is

invoked for these reactions, the reactions become very much less sensitive to the size of leaving groups involved (31).

Another important point against the nitrogen-attack mechanism is that Me(Ph)SNH_2^+ has been shown not to react with $\text{S}_2\text{O}_3^{2-}$ and $\text{H}_2\text{NCH}_2\text{CH}_2\text{S}^-$ in neutral and basic solution. Unlike iodide ion, these nucleophiles must be studied in neutral or basic solution, in which case, displacement at sulfur, requiring a NH_2^- leaving group, is very unlikely. However, the nitrogen-attack mechanism as in 45 would be reasonable with Me(Ph)S as a leaving group.



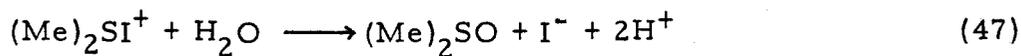
Such a reaction involving hydroxylamine-O-sulfonic acid with $\text{S}_2\text{O}_3^{2-}$ has been demonstrated (29) as shown in 46.



Therefore, the lack of reactivity of the nucleophiles with Me(Ph)SNH_2^+ indicates that the nitrogen-attack mechanism is not the case in this study. In conclusion, based on the hydrogen-ion requirement for the reaction of hydroxylamine-O-sulfonic acid analogies, the

nitrogen-attack mechanism can be eliminated in favor of the sulfur-attack mechanism.

Let us now focus our attention to the sulfur-attack mechanism. The mechanism involves a rate-determining step 40 preceded by a rapid equilibrium 39 in which $K \ll 1$. Steps 41-43 do not relate to the kinetic data obtained but are suggested as a reasonable path for the completion of the reaction. The overall reaction is not significantly reversible in acid solution because of the nearly complete protonation of the NH_3 produced. Iododimethylsulfonium ion is subject to hydrolysis (22, 32),



and, similarly, iodomethylphenylsulfonium ion may also be subject to hydrolysis. Therefore, a reaction analogous to reaction 47 potentially can compete with reaction 41. However, in aqueous solution such competition is insignificant since theoretical yields of I_3^- are obtained.

The value of $\Delta S^\ddagger = -16.7 \pm 0.2$ eu is a result of reactions 39 and 40. Negative values of ΔS^\ddagger in the range of -10 to -30 eu are expected for bimolecular reactions (33). Unless the ΔS° for reaction 39 were large and negative, the ΔS^\ddagger observed can be associated largely with reaction 40. For a reaction similar to that in step 39,

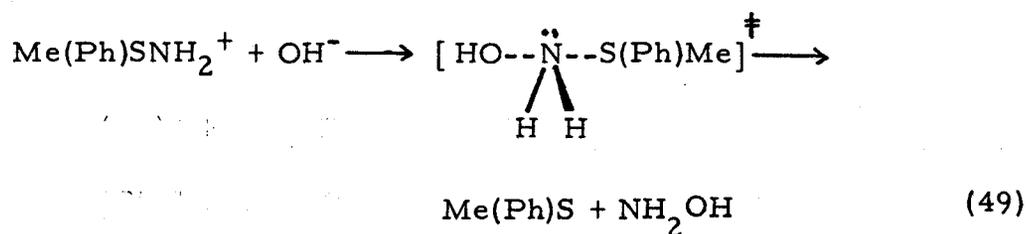


a value of ΔS° of +6 eu has been reported (34). This reaction is of the same charge type as reaction 39, although ΔS° for the latter will be more negative because of the more highly concentrated positive charge (22).

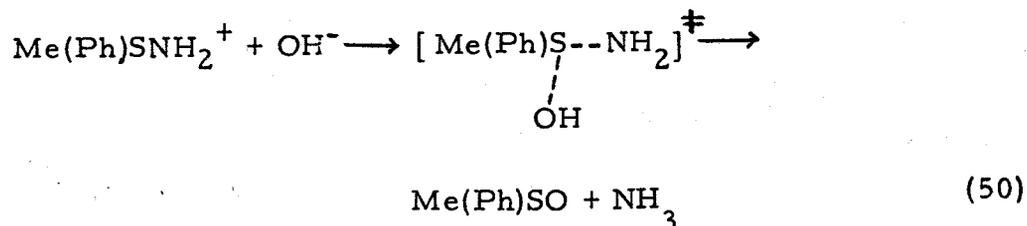
Substitution occurring at the sulfur center should be susceptible to an increase in steric hindrance with an increase in the size of the groups bound to sulfur. However, in the case of S-methyl-S-phenylsulfiminium perchlorate, the presence of the aromatic group bound to sulfur would also reveal an electron-withdrawing effect, making the sulfur center more positive. In the case of the iodide-ion reduction of S,S-dimethylsulfiminium and S,S-diethylsulfiminium perchlorates, the ratio $k_{C_2H_5}/k_{CH_3}$ was found to be equal to 0.34 (22). Values of $k_{C_2H_5}/k_{CH_3}$ are available in the literature for closely related systems and are found to be comparable to that found in the above case. Typical values of $k_{C_2H_5}/k_{CH_3}$ are: 0.26 for the racemization of p-CH₃C₆H₄-SOR by HCl in aqueous dioxane (35), 0.45 for the R₂S + Pt(py)₂Cl₂ reaction in methanol (36), and 0.62 for the R₂S + CH₃I reaction in methanol (36). Therefore, in the S,S-dimethylsulfiminium perchlorate reaction with iodide ion, it was concluded that sulfur attack was more plausible than nitrogen attack (22). Taking a ratio of the rate constant obtained for the S-methyl-S-phenylsulfiminium perchlorate reaction with iodide ion in this study and the rate constant for the S,S-dimethylsulfiminium perchlorate reaction with iodide ion obtained by Krueger,

$k_{\text{Me(Ph)}}/k_{(\text{Me})_2}$, the resulting value is 2.8. In addition, the ratio $k_{\text{Me(Ph)}}/k_{(\text{Me})_2}$ for the reactions with thiourea as the nucleophile is equal to approximately 1.3. Therefore, steric hindrance, which may still have an effect, is overridden by an electronic effect in which the aromatic group withdraws electrons from the sulfur center making it a more positive center and thus rendering it more susceptible for the attack of the negative iodide ion. If displacement occurs at nitrogen, then the steric effect would be that due to the increased size of the leaving group, R_2S . The direction of the leaving-group effect is uncertain. However, for an $\text{S}_{\text{N}}2$ mechanism, the leaving-group effect is not very large. Therefore, the nitrogen-attack mechanism is less likely.

In examining the hydroxide-ion reaction with S-methyl-S-phenylsulfiminium perchlorate at $\text{pH} \sim 12$, the sulfur-attack mechanism is supported. If nitrogen attack occurs as shown in equation 49,



methylphenylsulfide and hydroxylamine are the expected products. However, as reported in the Results section ammonia, but not hydroxylamine, was detected as a product. Therefore, the nitrogen-attack mechanism is not possible. If sulfur attack occurs,



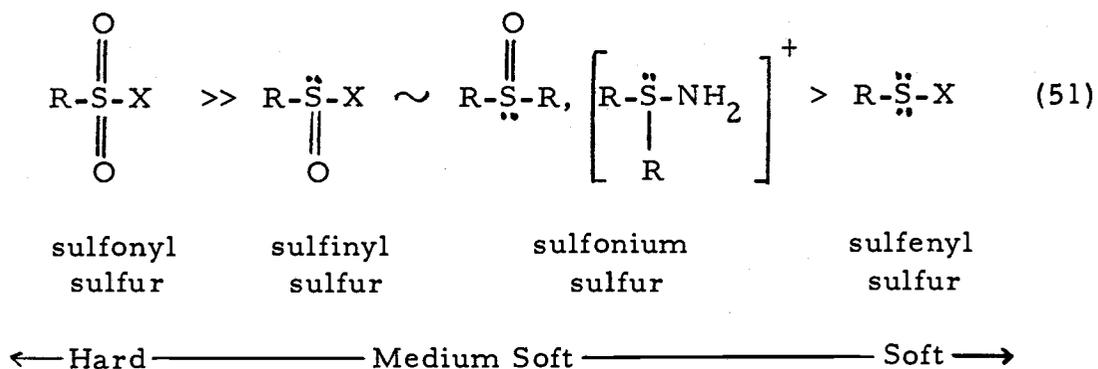
methylphenylsulfoxide and ammonia are the products. Although methylphenylsulfoxide was not proven to be a product of the reaction, sulfoxide production has been shown to occur with R_2SNH_2^+ compounds (20). Also, sulfonium compounds of the type $\text{R}_2\text{SN} \begin{array}{l} \text{R} \\ \text{Ts} \end{array}$ where Ts is $\text{p-CH}_3\text{C}_6\text{H}_4$ have been found to base-hydrolyze to give the sulfoxides (37).

In conclusion, all the kinetic data obtained for this system are consistent with an $\text{S}_{\text{N}}2$ mechanism with the attack on the sulfur acid center.

Let us now examine the nature of the sulfur acid center in the compound S-methyl-S-phenylsulfiminium perchlorate. This center can be characterized as medium-soft because it possesses three bond pairs, one lone pair of electrons, and also a partial positive charge (4). Thiourea, a soft base nucleophile, catalyzes reaction 33 by nucleophilic attack on sulfur as expected. In contrast, nucleophiles which are more basic and less polarizable than iodide ion and thiourea are expected to be relatively less reactive at such a center. Accordingly, chloride, bromide, and thiocyanate ions were found to be without effect on the reaction even in DMSO-water solvents where the

reactivity of harder base nucleophiles toward hard-acid centers is enhanced. The sulfur center in S-methyl-S-phenylsulfiminium perchlorate was found to react weakly with hydroxide ion at $\text{pH} \sim 12$. In contrast, hard-acid sulfur centers react very rapidly with OH^- at $\text{pH} < 12$. For example, the base hydrolysis of the chlorosulfonate anion, ClSO_3^- , is very rapid and occurs at $\text{pH} < 12$.

In comparing the type of mechanisms that occur with other similar sulfur compounds, one finds that the general mechanism is in all cases $\text{S}_{\text{N}}2$ with attack on the sulfur. Therefore, comparisons of the nature of this center with other electrophilic-sulfur centers can be made. A relative scale of "hardness" of these various centers is shown in the following diagram.



Therefore, from the data available for sulfonium sulfur, S-methyl-S-phenylsulfiminium perchlorate, is similar to sulfinyl sulfur and is thus characterized as a medium-soft acid center on the Pearson HSAB scale.

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