

than is the "model" compound *p*-fluorophenyltriethoxysilane³⁷ and indeed is more highly shielded than any of the silanes measured. This is a consequence of high-electron density on the silicon atom resulting from a

(37) The shielding parameter of the "model" compound was obtained in CCl_4 ,¹⁵ whereas **5**, which is insoluble in CCl_4 , was measured in acetone.

partial $\text{N}^+ \rightarrow \text{Si}^-$ donor-acceptor bond. Evidence for some $\text{N}^+ \rightarrow \text{Si}^-$ interaction in the "tritych" compounds (**5**, $\text{R} = \text{C}_6\text{H}_5$) includes diminished basicity of the N and association in solution,^{38a} high dipole moment (5.98D),^{38b} a Si-N distance of 2.19 Å (1.3 Å less than the van der Waals radii), and distorted trigonal-bipyramidal geometry about the silicon atom.^{38c}

Acknowledgments. We thank Dr. D. Williams, and A. Bond, G. Ronk, and R. Robinson for their assistance in obtaining spectroscopic data, and Dr. R. H. Baney for helpful suggestions.

(38) (a) See Frye, *et al.*, Table I, footnote a; (b) M. G. Voronkov *Pure Appl. Chem.*, **13**, 35 (1966); (c) J. W. Turley and F. P. Boer, *J. Amer. Chem. Soc.*, **90**, 4026 (1968).

Cation–Anion Combination Reactions. V. Correlation of Reactivities of Nucleophiles with Diazonium Ions and with Triarylmethyl Cations^{1a,b}

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Received April 30, 1971

Abstract: New data concerning rates and equilibria of reactions of diazonium ions with azide, cyanide, methoxide, and thiophenoxide ions in methanol solution and reactions of three triarylmethyl cations with thiophenoxide ion in methanol are presented. The new data and previously reported data on reactions of nucleophilic systems with both diazonium ions and triarylmethyl cations clearly show that the selectivities of the two different cation classes are nearly identical. The data cannot be accommodated by current concepts of nucleophilicities or of reactivity–selectivity relationships.

In the previous papers of this series, we have reported the results of our studies of the reactions of aryldiazonium ions with hydroxide, cyanide, and azide ions in aqueous solution and have made comparisons with the earlier results of studies of reactions of triarylmethyl cations with the same nucleophiles. The present paper deals with reactions of aryldiazonium ions and of triarylmethyl cations with nucleophiles in methanol solution.

The reactions of Malachite Green (MG, bis(*p*-dimethylaminophenyl)phenylmethyl cation), *p*-Nitro Malachite Green (PNMG, bis(*p*-dimethylaminophenyl)-*p*-nitrophenylmethyl cation), and Crystal Violet (CV, tris(*p*-dimethylaminophenyl)methyl cation) with azide and methoxide ions in methanol solution were studied earlier. We now report the results of studies of reactions of MG, PNMG, and CV with thiophenoxide ion, and reactions of a series of aryldiazonium ions with azide, cyanide, methoxide, and thiophenoxide ions, all in methanol solution.

As we have explained in the earlier papers of this series, the goal of the studies of cation–anion com-

bination reactions is an understanding of the factors affecting the relative nucleophilicities of anions in this type reaction. We believe that the present results have brought us quite close to this goal and allow an unusual insight into the general problems of nucleophilicity and solvent effects.

Results

Reactions of Diazonium Ions with Azide Ion in Methanol. The reactions of aryldiazonium ions with azide ion produce aryl azides and aryl pentazoles as the initial observable products.^{2,3} In the present studies, we have followed the rates of disappearance of the diazonium ions in low buffered concentrations of azide ion in methanol solution. The measured rate constants are the sum of the rate constant for formation of aryl azide and that for formation of aryl pentazole. The techniques are detailed in the Experimental Section.

In all cases studied, the decomposition of the aryl pentazole to aryl azide was sufficiently slower than the formation reaction that it did not interfere with calculations of the fast reaction rate constants. In only one case, that of *p*-benzoylbenzenediazonium ion, did we measure the rate constant for decomposition of the

(1) (a) Previous paper in this series: C. D. Ritchie and D. J. Wright, *J. Amer. Chem. Soc.*, **93**, 6574 (1971). (b) This work was supported by a grant from National Institutes of Health, U. S. Public Health Service, Grant GM-12832, and National Science Foundation Grant No. GP-10414. (c) On leave from Department of Chemistry, University of Oulu, Oulu, Finland.

(2) I. Ugi and R. Huisgen, *Chem. Ber.*, **90**, 2914 (1957).

(3) C. D. Ritchie and D. J. Wright, *J. Amer. Chem. Soc.*, **93**, 2429 (1971), and earlier references cited there.

aryl pentazole. In this case, the slow increase in absorbance at the aryl azide absorption maximum amounted to 12% of the final total absorption and the rate constant for the increase is found to be $7.9 \times 10^{-2} \text{ sec}^{-1}$. In aqueous solution, the slow increase in absorption was found to be 20% of the final value, and a rate constant of $1.9 \times 10^{-2} \text{ sec}^{-1}$ was determined.³

The second-order rate constants for disappearance of diazonium ions in solutions with azide concentrations between 10^{-9} to 10^{-8} M in methanol are shown in Table I.

Table I. Second-Order Rate Constants for the Reactions of X-Substituted Benzenediazonium Ions with Azide Ion in Methanol Solution at $23 \pm 1^\circ$, $\mu = 6 \times 10^{-4} \text{ M}$

X	$k, \text{ M}^{-1} \text{ sec}^{-1}$	Log k	σ_x^a
<i>p</i> -OCH ₃	1.4×10^6	6.15	-0.27
<i>p</i> -CH ₃	9.7×10^6	6.99	-0.17
H	4.6×10^7	7.66	0
<i>p</i> -Cl	2.1×10^8	8.32	0.23
<i>p</i> -Br	2.8×10^8	8.45	0.23
<i>m</i> -Cl	1.1×10^9	9.04	0.37
<i>p</i> -CO ₂ H	6.5×10^8	8.81	0.41
<i>p</i> -C ₆ H ₅ CO	7.1×10^8	8.85	0.50
<i>p</i> -CN	2.7×10^9	9.43	0.66
<i>p</i> -NO ₂	6.7×10^9	9.83	0.78

^a Hammett substituent constants are the normal values taken from a list by C. D. Ritchie and W. F. Sager, *Progr. Phys. Org. Chem.*, **2**, 323 (1964).

Least-squares treatment of the data in Table II, excluding the *p*-CH₃O substituent, gives a Hammett ρ value of 2.83. The ρ value for aqueous solution reactions was found to be 3.4.³ The fact that the ρ value in methanol is lower than the value in aqueous solution is a strong indication that a change in rate-determining step has occurred on changing from water to methanol. After an initial argument based on misleading data,³ we arrived at the conclusion that the rate-determining step of the reaction in water was the decomposition of the diazoazide intermediate² involved in these reactions.^{1a} The ρ value now found for the azide reaction in methanol is comparable to the ρ value of 2.4 found for the reactions of aryldiazonium ions with benzenesulfinate ions in methanol solution.⁴ The small ρ value and the additional observation that the rate constant for reaction of *p*-nitrobenzenediazonium ion with azide ion must be quite close to the diffusion-controlled limit are strong evidence that the rate-determining step of the reaction in methanol solution is the attack of azide ion on the diazonium ion.

Reactions of Aryldiazonium Ions with Methoxide Ion. The reactions of aryldiazonium ions in buffered solutions of methoxide ion in methanol rapidly reach an equilibrium with a stoichiometry involving reaction of 1 mol of methoxide ion with 1 mol of diazonium ion. Subsequent slow reactions of the initially formed product make it very difficult to measure the equilibrium constant for the fast reaction by conventional methods. The subsequent reactions are slow enough, however, that the use of stop-flow techniques allows the study of the initial reaction before complication by the second stages. Our present observations along

with earlier investigations of the slow reactions⁵ clearly indicate that the initial reaction involves formation of the *syn*-diazomethoxide, probably followed by slow isomerization to the *anti*-diazomethoxide and reaction of the equilibrium concentration of diazonium ion in other ways.⁵

We have been able to measure both rate and equilibrium constants for the initial reaction only in the cases of the *p*-nitro- and *p*-cyanobenzenediazonium ions. We were able to obtain a reliable value for the equilibrium constant for the reaction of *m*-chlorobenzenediazonium ion, but the rate of reaction with the high concentration of methoxide ion required to convert an appreciable amount of diazonium ion to product was too fast to be measured by the stop-flow technique. The values obtained are reported in Table II.

Table II. Rate and Equilibrium Constants for the Formation of *syn*-Diazomethoxides in Methanol at $23 \pm 1^\circ$

$\text{X-C}_6\text{H}_4\text{N}_2^+ + \text{CH}_3\text{O}^- \rightleftharpoons \text{syn-X-C}_6\text{H}_4\text{N}_2\text{OCH}_3$		
X	$k, \text{ M}^{-1} \text{ sec}^{-1}$	$K, \text{ M}^{-1}$
<i>p</i> -NO ₂ ^a	3.0×10^8	5.6×10^7
<i>p</i> -CN ^b	2.0×10^8	8.6×10^6
<i>m</i> -Cl ^b		4.2×10^5

^a $\mu = 3 \times 10^{-3} \text{ M}$. ^b $\mu = 5 \times 10^{-4} \text{ M}$.

The short half-lives, the necessity of working under conditions where the reactions are not complete to the right, and the rather small changes in absorbance between reactants and products severely limit the precision and accuracy of the measured rate constants. The precision of a series of measurements with various concentrations of methoxide ion was no worse than $\pm 20\%$, and we believe that the accuracy is no worse than *ca.* $\pm 50\%$. Approximately the same error limits apply to the equilibrium constants.

Reactions of Aryldiazonium Ions with Cyanide Ion. Only in the cases of *p*-nitro- and *p*-cyanobenzenediazonium ion were we able to observe the rates of formation of the *syn*-diazocyanides. Unfavorable equilibrium constants requiring rate studies at high cyanide concentrations are responsible for the rates too fast to measure by stop-flow, and require basic solutions where reaction with methoxide ion is a further complicating feature.

The formation constant of $2.2 \times 10^7 \text{ M}^{-1}$ and rate constant of $2.2 \times 10^6 \text{ M}^{-1} \text{ sec}^{-1}$ were obtained for *p*-cyanobenzenediazocyanide. A rate constant of approximately $5 \times 10^6 \text{ M}^{-1} \text{ sec}^{-1}$ for formation of *p*-nitrobenzenediazocyanide was estimated. A more accurate value could not be obtained because of small changes in absorbance between reactants and products. The small absorbance changes also made equilibrium measurements extremely difficult, and we were not able to obtain a reliable value for the equilibrium constant.

Reactions of Aryldiazonium Ions with Thiophenoxide Ion. The reactions of all of the aryldiazonium ions with thiophenoxide ion were followed by observing the increase in absorption at 350 nm due to the thioether. At relatively high concentrations of thiophenoxide ion,

(4) C. D. Ritchie, J. Saltiel, and E. S. Lewis, *J. Amer. Chem. Soc.*, **83**, 4601 (1961).

(5) J. F. Bunnett and H. Takayama, *ibid.*, **90**, 5173 (1968); personal communication from Professor Bunnett, July 1970.

all of the diazonium ions except the three with the least electron-withdrawing substituents show an initial rapid reaction which reaches completion before the incursion of a succeeding slower reaction producing further increase in absorption at 350 nm. There is little doubt that the reactions being observed are analogous to other reactions of diazonium ions; that is, the initial rapid reaction is the formation of the *syn*-diazo thioether and that the slower reaction is the *syn*-anti isomerization.⁶ Under conditions where the thiophenoxide ion concentration is low enough that the reactions are not complete, only the *p*-nitro- and *p*-cyanobenzenediazonium ions show clear breaks between the first and second reactions. Thus, it was possible to obtain reliable values for the equilibrium constants of the initial reaction in these two cases only. Rate constants for the slow reaction are reported in Table III.

Table III. Rate Constants for the *Syn*-Anti Isomerization of Aryldiazothiophenyl Ethers in Methanol at $23 \pm 1^\circ$

$$\text{syn-X-C}_6\text{H}_4\text{N}_2\text{SC}_6\text{H}_5 \longrightarrow \text{anti-X-C}_6\text{H}_4\text{N}_2\text{SC}_6\text{H}_5$$

X	k , sec ⁻¹	Log k	σ
<i>p</i> -NO ₂	0.064	-1.19	0.78
<i>p</i> -CN	0.066	-1.18	0.66
<i>p</i> -C ₆ H ₅ CO	0.20	-0.70	0.50
<i>p</i> -COOH	0.20	-0.70	0.41
<i>m</i> -Cl	0.14	-0.85	0.37
<i>p</i> -Br	0.28	-0.55	0.23
<i>p</i> -Cl	0.37	-0.43	0.23

The effect of substituents on the *syn*-anti isomerization of the diazo thioethers is the opposite of that for the isomerization of diazotates⁷ and diazocyanides.⁸ We have previously speculated that the failure to observe *syn*-anti isomerization in the case of diazo sulfones might be due to rapid isomerization facilitated by *d*-orbital participation of sulfur.⁴ Such participation would be expected to lead to the substituent effects which we find for the diazo thioethers.

The reactions of benzenediazonium ion, and of the *p*-CH₃ and *p*-OCH₃ substituted ions, with thiophenoxide ion, follow first-order kinetics over the entire course of reaction. In these cases, we are possibly observing a rate-determining formation of the *syn*-

Table IV. Rate and Equilibrium Constants in Methanol at $23 \pm 1^\circ$

$$\text{X-C}_6\text{H}_4\text{N}_2^+ + \text{C}_6\text{H}_5\text{S}^- \rightleftharpoons \text{syn-X-C}_6\text{H}_4\text{N}_2\text{SC}_6\text{H}_5$$

X	k , ^a M ⁻¹ sec ⁻¹	K , ^b M ⁻¹
<i>p</i> -NO ₂	8.7×10^9	1.9×10^{10}
<i>p</i> -CN	7.0×10^9	1.8×10^{10}
<i>p</i> -C ₆ H ₅ CO	6.2×10^9	
<i>p</i> -COOH	7.2×10^9	
<i>m</i> -Cl	5.2×10^9	
<i>p</i> -Br	4.0×10^9	
<i>p</i> -Cl	6.0×10^9	
H	1.4×10^9	
<i>p</i> -CH ₃	1.4×10^9	
<i>p</i> -OCH ₃	5.7×10^8	

^a $\mu = 6 \times 10^{-4}$ M. ^b $\mu = 2 \times 10^{-3}$ M.

(6) A. Hantsch and A. Freese, *Chem. Ber.*, **28**, 3237 (1895).

(7) E. S. Lewis and H. Suhr, *ibid.*, **91**, 2350 (1958).

(8) E. S. Lewis and H. Suhr, *ibid.*, **92**, 3243 (1959).

diazo thioether followed by a rapid isomerization to the *anti*-diazo thioether. The rate and equilibrium constants for the thiophenoxide reactions are reported in Table IV.

Reactions of Triarylmethyl Cations with Thiophenoxide Ion. The reactions of MG, PNMG, and CV with thiophenoxide ion were followed by observing the disappearance of absorption of the cations in the visible range. Both rate and equilibrium constants were determined for MG and PNMG. In the case of CV, the unfavorable equilibrium constant made it impossible to measure the rate constant by the stop-flow method. The data for the reactions are reported in Table V.

Table V. Reactions of Malachite Green Derivatives with Thiophenoxide Ion in Methanol at $23 \pm 1^\circ$

Cation	k , M ⁻¹ sec ⁻¹	K , M ⁻¹
<i>p</i> -Nitro Malachite Green ^a	9.4×10^6	2.6×10^6
Malachite Green ^a	1.0×10^6	7.7×10^4
Crystal Violet ^b		3.2×10

^a $\mu = 1.0 \times 10^{-2}$ M. ^b $\mu = 5.0 \times 10^{-3}$ M.

Discussion

Data for the rates and equilibria of reactions of PNMG and of *p*-nitrobenzenediazonium ion with those nucleophilic systems for which we have been able to obtain data for both cations are summarized in Table VI. Other substituted diazonium ions and the other triarylmethyl cations show virtually identical relative rates for reactions with the various nucleophiles.

Figure 1 is a plot of the logarithms of the rate constants for the PNMG reactions *vs.* the logarithms of the rate constants for the *p*-nitrobenzenediazonium ion reacting with each of the nucleophilic systems. The line drawn in the figure has unit slope up to diffusion-controlled reaction rates (estimated as $k_{\text{diffusion}} = 10^{10}$ M⁻¹ sec⁻¹) of the diazonium ion.

The striking conclusion from Figure 1 is that the selectivities of the triarylmethyl cations toward the various nucleophiles are virtually identical with the selectivities of the aryldiazonium ions, even though the rates with any given nucleophile differ by factors of greater than 10^4 . The correlation is even more astounding when we note that there is no correlation of equilibrium constants between the two sets of reactions, nor is there any correlation of rate and equilibrium constants for either set of reactions.

Neither the Edwards-Pearson correlation of nucleophilicities⁹ (sometimes referred to as the oxibase scale)¹⁰ nor the older Swain-Scott parameters¹¹ give the observed order with azide reacting faster than cyanide ion in both water and methanol solutions. The fact that the line in Figure 1 shows no sign of curvature up to diffusion-controlled reactions is counter to the current concepts of reactivity-selectivity relationships in carbonium ion reactions.¹²

Full interpretation of the present results must await further data now being collected in our laboratories.

(9) J. O. Edwards, *J. Amer. Chem. Soc.*, **76**, 1540 (1954); **78**, 1819 (1956); J. O. Edwards and R. G. Pearson, *ibid.*, **84**, 16 (1962).

(10) R. E. Davis, *ibid.*, **87**, 3010 (1965); **91**, 91, 97, 104 (1969).

(11) C. G. Swain and C. B. Scott, *ibid.*, **75**, 141 (1953).

(12) R. A. Sneen, J. V. Carter, and P. S. Kay, *ibid.*, **88**, 2594 (1966).

Table VI. Rate and Equilibrium Constants for Cation-Anion Combination Reactions

Anion	Cation			
	PNMG		<i>p</i> -NO ₂ C ₆ H ₄ N ₂ ⁺	
	<i>k</i> , M ⁻¹ sec ⁻¹	<i>K</i> , M ⁻¹	<i>k</i> , M ⁻¹ sec ⁻¹	<i>K</i> , M ⁻¹
H ₂ O in H ₂ O ^{a,d}	1.8 × 10 ⁻⁴		2.7	
OH ⁻ in H ₂ O ^d	5.6	3.2 × 10 ⁸	5.4 × 10 ⁵	(2.6 × 10 ²) ^b
CN ⁻ in H ₂ O ^d	1.1	>10 ⁸	1.7 × 10 ⁴	6.0 × 10 ⁴
MeO ⁻ in MeOH	6.0 × 10 ^{3 d}	1.4 × 10 ^{10 d}	3.0 × 10 ⁸	5.6 × 10 ⁷
N ₃ ⁻ in MeOH	6.2 × 10 ^{4 d}	1.6 × 10 ^{3 d}	6.7 × 10 ⁹	
CN ⁻ in MeOH	<10 ^{3 d}		5.0 × 10 ⁶	(6.0 × 10 ⁷) ^c
C ₆ H ₅ S ⁻ in MeOH	9.4 × 10 ⁵	2.6 × 10 ⁶	8.7 × 10 ⁹	1.9 × 10 ¹⁰

^a Pseudo-first-order rate constants are given. ^b Estimated with the questionable assumption that the acidities of the syn and anti diazo hydroxides are the same. ^c Estimated as *ca.* three times the equilibrium constant for the *p*-cyanobenzendiazonium ion. ^d Values reported in previous papers of this series.

One obvious conclusion may be noted, however. The rate-rate correlation in the absence of any correlation of equilibria strongly indicates that specific interactions between the nucleophiles and cations are not present at the transition states for these reactions. The im-

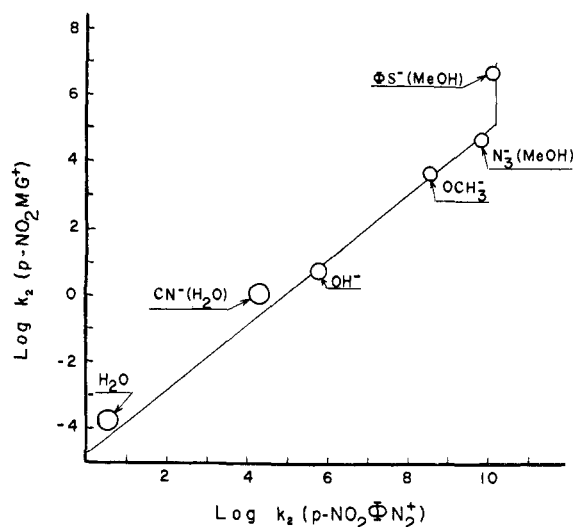


Figure 1. Plot of rate data from Table VI. The line shown has unit slope.

plication is that the observed nucleophilic order is an inherent property of the nucleophiles alone. We suggest that this inherent property is related to the solvation of the nucleophiles, but resist the strong temptation to speculate further at this time.

Experimental Section

Materials. Preparation of the aryldiazonium fluoroborates and of the triarylmethyl fluoroborates has been described in an earlier paper.^{1a}

Dichloroacetic acid and triethylamine were commercial products distilled at atmospheric pressure before use. Dabco (triethylenediamine) was recrystallized from heptane. Sodium azide, sodium and potassium perchlorate, potassium cyanide, trichloroacetic acid, and thiophenol were commercial products used without further purification.

Methanol was purified and dried by treatment with molecular sieves followed by ion exchange as previously described.¹³ Stock solutions of potassium methoxide were prepared by reacting freshly cut potassium with methanol. Anhydrous perchloric acid in methanol was prepared by ion exchange of sodium perchlorate solutions¹³ and was stored at -20°. All operations were carried out under an argon atmosphere.

(13) C. D. Ritchie and P. D. Heffley, *J. Amer. Chem. Soc.*, **87**, 5402 (1965).

Equipment. The stop-flow spectrometer used in the current studies has been described previously.¹⁴ A Cary Model 14 spectrophotometer was used to obtain spectra. The studies were carried out in an air-conditioned room maintained at 23 ± 1°.

Reactions of Aryldiazonium Ions with Azide Ion. Sodium azide was weighed with a Cahn electrobalance into a small Teflon cup. The cup and sample were placed in a volumetric flask and flushed with argon and the flask was sealed with a rubber septum through which the methanol was injected with a gas-tight syringe. Upon dissolution of the sodium azide, accurate amounts of trichloroacetic acid and potassium methoxide solutions were added to provide the desired buffer, and the flask was filled to the mark with methanol. The buffered azide solutions were mixed with the aryldiazonium ion solutions on the stop-flow apparatus.

Fresh solutions of trichloroacetic acid in methanol were used for each experiment, and the concentration of acid was determined by titration with barium hydroxide in water before and after the kinetic runs to allow correction for the slow reaction of trichloroacetic acid with methanol. Ionic strength was maintained at 6.0 × 10⁻⁴ M in all experiments.

Calculations of the second-order rate constants from the observed pseudo-first-order reactions of the diazonium ions with buffered azide ion utilized the p*K*_a values of 4.98 for trichloroacetic acid in methanol¹⁵ and 8.91 for hydrazoic acid in methanol.¹⁴ A summary of typical experimental data for several of the diazonium ions is contained in Table VII.

For the *p*-benzoylbenzenediazonium ion reaction, the rate constant for decomposition of the aryl pentazole was measured by following the slow increase in absorbance at 298 nm after the first reaction was complete. The rate constant was found to be 7.9 × 10⁻² sec⁻¹, and the increase in absorbance was found to be 12% of the final absorbance.

Reactions of Aryldiazonium Ions with Methoxide Ion. Attempts to obtain the spectrum of the product of reaction of *p*-nitrobenzenediazonium ion in buffered solutions in methanol by conventional spectrophotometry were unsuccessful. Nonreproducible, time-dependent spectra were observed. Stop-flow studies of the reaction using Dabco (triethylenediamine) buffers gave consistent results for both equilibria and rate constants calculated at various wavelengths for observation. Several experiments using triethylamine, and one experiment using acetate, buffers gave results in close agreement with those obtained with Dabco buffers.

In the definitive set of experiments, five buffers of Dabco-DabcoH⁺ were prepared from stock solutions of Dabco and perchloric acid in methanol solutions. Each of the buffers contained 3.0 × 10⁻³ M DabcoH⁺ and an amount of Dabco to give buffer ratios (B/BH⁺) of 5.0, 3.0, 2.0, 1.0, and 0.50, respectively. These buffer solutions were mixed with 5.95 × 10⁻⁵ M *p*-nitrobenzenediazonium fluoroborate in methanol on the stop-flow apparatus. In separate experiments, the reaction of each buffer solution was observed at 250, 260, 280, 290, and 300 nm. Benesi-Hildebrand plots of the initial and final absorbance for each buffer and each wavelength were constructed to determine the equilibrium constant for the reaction of diazonium ion with methoxide relative to the basicity constant for Dabco. Plots of the observed pseudo-

(14) C. D. Ritchie, G. A. Skinner, and V. G. Badding, *ibid.*, **89**, 2063 (1967).

(15) Determined by Mr. Alexander Lopata using the techniques which have previously reported in ref 13 and 14. These and other acidity constants in methanol solution will be published in a future paper.

Table VII. Sample Data for the Reactions of Substituted Benzenediazonium Ions with Azide Ion in Methanol at $23 \pm 1^\circ$

Substituent	Total azide, $M \times 10^4$	TCA, ^a $M \times 10^4$	TCA ⁻ , ^b $M \times 10^4$	$10^4(N_3^-)$	$10^3k_1^c$	k_2^d
<i>p</i> -OCH ₃ ^e	1.22	1.50	6.22	59.8	83.7	1.4×10^6
	0.96	2.94	5.96	22.9	32.5	1.4×10^6
	0.98	5.68	5.98	12.1	15.2	1.3×10^6
	0.98	13.0	5.98	5.25	8.89	1.7×10^6
	0.95	40.8	5.95	1.62	2.61	1.6×10^6
<i>p</i> -Cl ^f	1.06	1.58	6.06	47.3	10,100	2.1×10^8
	0.95	5.81	5.95	11.5	1,950	1.7×10^8
	1.02	5.72	6.02	12.5	2,660	2.1×10^8
<i>p</i> -C ₆ H ₅ CO ^g	0.96	1.63	5.97	41.2	21,300	5.2×10^8
	0.98	5.72	5.98	12.0	8,420	7.0×10^8
	1.05	29.1	6.05	3.24	2,350	7.2×10^8

^a Trichloroacetic acid. ^b Potassium trichloroacetate. ^c Units of sec^{-1} for the observed pseudo-first-order rate constants. ^d Second-order rate constants in units of $M^{-1} \text{sec}^{-1}$. ^e Reaction followed at 312 nm. ^f Reaction was followed in different experiments at both 253 and 280 nm. ^g Reaction followed at 298 nm.

first-order rate constants *vs.* buffer ratio gave both forward and reverse rate constants from which the relative equilibrium constant could also be calculated. The values obtained from the equilibrium and rate measurements were in excellent agreement. Using the pK_a of 9.48¹⁵ for DabcoH⁺ and the pK_a value of 16.92¹⁶ for methanol leads to the values of $5.6 \times 10^7 M^{-1}$ for the equilibrium constant for the formation of the *syn*-diazomethyl ether, and of $3.0 \times 10^8 M^{-1} \text{sec}^{-1}$ for the forward rate constant.

Similar studies of *p*-cyanobenzenediazonium ion using triethylamine—triethylammonium perchlorate ($pK_a = 10.88^{14}$) buffers and observation at 270 nm gave the equilibrium constant of $8.6 \times 10^6 M^{-1}$ and the rate constant of $2.0 \times 10^8 M^{-1} \text{sec}^{-1}$ for the formation of the *syn*-diazomethyl ether.

In the case of *m*-chlorobenzenediazonium ion, studies using the triethylamine buffers allowed the determination of an equilibrium constant of $4.2 \times 10^6 M^{-1}$ for formation of the *syn*-diazomethyl ether, but the high buffer ratios required for appreciable conversion resulted in rates too fast to measure on the stop-flow apparatus. A lower limit of $4 \times 10^7 M^{-1} \text{sec}^{-1}$ can be placed on the value of the second-order rate constant.

Reactions of Aryldiazonium Ions with Cyanide Ion. The reaction of *p*-cyanobenzenediazonium ion with cyanide ion was studied by the use of cyanide solutions buffered with Dabco–DabcoH⁺ at pH 9.48. At this pH, the fast reaction of the diazonium ion with methoxide does not interfere with the cyanide reaction. There is, however, a slower reaction with methoxide ion, probably the formation of the *anti*-diazomethyl ether, which must be corrected for. Using the solutions of cyanide buffered at cyanide ion concentrations of 1.5×10^{-8} to $1.5 \times 10^{-7} M$ (the pK_a of 13.01 for hydrocyanic acid in methanol¹⁵ was used to calculate the cyanide concentration), the reaction with methoxide ion amounted to less than a 10% correction to the rate, and *ca.* 10% correction to the equilibrium constant. These corrections were obtained by studies of the reaction of the diazonium ion in buffered solution with and without cyanide present. The corrected data were treated in the same manner as described above for the methoxide reactions to give a value of $2.2 \times 10^7 M^{-1}$ for the equilibrium constant, and of $2.2 \times 10^6 M^{-1} \text{sec}^{-1}$ for the rate constant, for the formation of the *syn*-diazocyanide. The reaction was followed at 270 nm. Ionic strength was maintained at $2.5 \times 10^{-3} M$ with potassium perchlorate.

The reaction of *p*-nitrobenzenediazonium ion with cyanide ion produced extremely small changes in absorbance. The best observations were carried out at 261 nm, but we were not able to obtain accurate data. An estimate of $5 \times 10^6 M^{-1} \text{sec}^{-1}$ could be obtained for the rate constant, which is probably accurate to better than $\pm 50\%$.

Reactions of Aryldiazonium Ions with Thiophenoxide Ion. Reactions of the entire series of diazonium ions with thiophenoxide ion were studied in solutions of thiophenoxide buffered by dichloroacetic acid ($pK_a = 6.41$)¹⁵–dichloroacetate or trichloroacetic acid ($pK_a = 4.98$)–trichloroacetate. The pK_a of thiophenol in methanol was determined by spectrophotometry, using wavelengths of 267 and 273 nm, on solutions of thiophenol in triethylamine–triethylammonium perchlorate buffers. The values of 11.28 and

10.97, at ionic strengths of 1.0×10^{-3} and $1.0 \times 10^{-2} M$, respectively, were obtained for the pK_a . These values yield the value of -4.5 for the slope $d(pK)/d\sqrt{\mu}$, in good agreement with the Debye–Hückel theoretical slope of *ca.* -4.0 . Values of 11.30 and 11.22 at ionic strengths of 6.0×10^{-4} and $2.0 \times 10^{-3} M$, respectively, were used in the calculations involving reactions with diazonium ions.

The reactions of all of the aryldiazonium ions with thiophenoxide ion resulted in a large increase in absorption at 350 nm, and this wavelength was used in all studies. The reactions of all of the diazonium ions, with the exceptions of the H-, *p*-CH₃-, and *p*-OCH₃-substituted compounds, under conditions where the thiophenoxide ion concentration is relatively high, clearly show two stages of conversion. An initial rapid increase in absorption is followed by a much slower further increase. This is almost certainly analogous to other reactions in which there is a rapid formation of the *syn*-diazo compound, followed by a slower isomerization to the *anti* isomer.⁶ Studies at various concentrations of thiophenoxide ion show that the slower reaction rate is independent of thiophenoxide ion concentration, and that the initial reaction involves the reaction of 1 mol of diazonium ion with 1 mol of thiophenoxide ion. At concentrations of thiophenoxide ion low enough to allow measurement of the equilibrium for the initial reaction, only the *p*-nitro and *p*-cyano compounds still gave kinetic traces that could be well separated into the first and second stages. Thus, we were able to obtain reliable values for the equilibrium constants in only these two cases. Treatment of the data as described for other reactions above yielded the rate and equilibrium constants reported in Tables III and IV.

Reactions of the *p*-CH₃-, *p*-OCH₃-, and H-substituted diazonium ions with thiophenoxide ion followed pseudo-first-order kinetics to completion. Since the data obtained for the slow reaction of the compounds listed above show that the rate of this second reaction increases as the electron-withdrawing ability of the substituent decreases, it appears possible that the three present compounds react to form the *anti* diazothio ether by slow formation of the *syn* isomer followed by rapid isomerization. The second-order rate constants obtained for these compounds are reported in Table IV.

Reactions of *p*-chloro- and *p*-bromobenzenediazonium ions with thiophenoxide ion do not follow pseudo-first-order kinetics over the entire course of the reaction. The rate studies show clearly that under the conditions used there are two consecutive reactions which are not well separated. We have been able to use the initial parts (*ca.* 25% reaction) of the kinetic runs to obtain consistent rate constants for the initial reaction, but have not been able to determine the equilibrium constants. The data are reported in Table IV.

Reactions of Triarylmethyl Cations with Thiophenoxide Ion. PNMG reactions were studied in thiophenoxide solutions buffered by triethylamine–triethylammonium perchlorate. MG reactions were studied both in buffered solutions and solutions of thiophenol–thiophenoxide prepared by adding potassium methoxide to an excess of thiophenol. Reactions of CV were studied in the thiophenoxide–thiophenol solutions only. Reactions were followed by observing the disappearance of absorption in the visible spectra of the cations.

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In the case of PNMG and MG, treatment of the data as for the other reactions already described led to both rate and equilibrium constants for formation of the triarylmethyl thioethers. In the case of CV, the unfavorable equilibrium required studies at such

high thiophenoxide concentrations that the rate became too fast to measure. In the case of MG and PNMG, the values reported in Table V were obtained at an ionic strength of $1.0 \times 10^{-3} M$. The CV data were obtained at an ionic strength of $5.0 \times 10^{-3} M$.

Reactions of Thiols with Schiff Bases in Nonaqueous Solvents. Addition Equilibria, Cleavage, and Reduction

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Abstract: The addition of thiols to the C=N bond of Schiff bases in nonaqueous solvents has been shown to involve an easily studied mobile equilibrium analogous to semimercaptal formation. A study involving substituted Schiff bases has shown that electron-withdrawing groups in either the aniline-derived ring or benzaldehyde-derived ring favors adduct formation. A Hammett plot of the equilibrium constants for the reaction of 1-butanethiol with Schiff bases substituted in the para position of the benzaldehyde-derived ring against σ^+ constants gave a straight line of slope +0.86. Strong electron-withdrawing substituents in the aniline-derived ring caused a facile cleavage of the Schiff base with resultant mercaptal formation. The reaction of benzaldehyde with *p*-toluenethiol to form the corresponding mercaptal was shown to be catalyzed by electron-withdrawing para substituted anilines. Evidence is presented to indicate that the catalysis may be due to intermediate Schiff base formation. The reduction of Schiff bases by *p*-toluenethiol at higher temperatures has been shown to be catalyzed by a free-radical initiator, thus suggesting a free-radical mechanism.

The addition of water, alcohols, thiols, and amines to the carbonyl group has been studied rather extensively.^{2,3} Equilibrium measurements have shown that the tendency of thiols to add to the carbonyl group is considerably greater than that of hydroxyl compounds or of most amines.⁴ Similarly, the addition equilibria of water and alcohols to imines^{5,6} has received attention, but interestingly little has been done involving the addition equilibria of thiols to carbon-nitrogen double bonds. This is somewhat surprising in view of the relative stability of the adducts that can be obtained. For example, Stacy, Day, and Morath⁷ have previously demonstrated that stable crystalline adducts readily form from the simple addition of thiols to Schiff bases. That these adducts are simple 1:1 adducts involving addition of the thiol to the carbon-nitrogen bond shall be further demonstrated in this work.

Indications that a mobile equilibrium existed between reactants and adducts were first given by the ease with which these adducts reverted to thiol and Schiff base under the influence of base.⁷ Also, the crystalline adducts were shown to give a positive nitroprusside test even after repeated recrystallization.⁸ We have also noted that the adducts readily react with heavy metal ions such as divalent lead or mercury to produce mercaptides.

Further indications that a facile dissociation was taking place in solution was given by some of the chemical reactions of the adducts. For example, Stacy, Day, and Morath⁹ have shown that the acetylation of the *p*-toluenethiol adduct of *N*-benzylideneaniline proceeds with some difficulty. They generally obtained only small amounts of the anticipated *N*-acetyl derivative. The major products are now best interpreted as being formed from free thiol and Schiff base due to prior dissociation of the adduct. Reaction of the adducts with phenyl isocyanate and phenyl isothiocyanate¹⁰ leads to a similar conclusion. A complex mixture of products was obtained when the adducts were allowed to react with phenyl isocyanate alone, but when the reaction was run in the presence of triethylamine (a potent catalyst for the reaction of thiols with isocyanates¹¹), the only products obtained were *N*-benzylideneaniline and the phenyl isocyanate derivative of the thiol. All of this, taken together, suggested a ready dissociation of adducts to thiol and Schiff base.

More recent work dealing with chain tautomerism of thiazolidines has further demonstrated the existence of a reversible equilibrium for the addition of thiols to the C=N bond.¹² In this case, the authors showed that equilibrium greatly favors the ring tautomer but they demonstrated that the open-chain tautomer was a probable intermediate in many different reactions involving the incipient thiol or imino function. Spectral studies^{12,13} of the thiazolidine system have not been able to detect the presence of the open-chain tautomer,

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