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Reaction of Substituted Malachite Green Cations with Cyanide Ion

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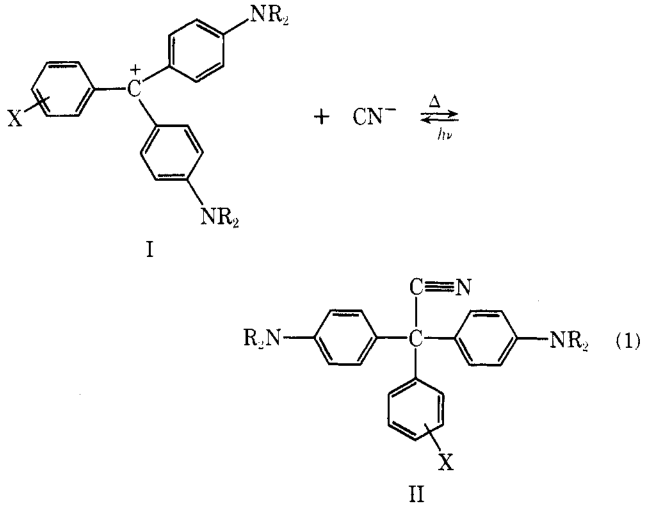
The reaction rate constants and the activation parameters for the reaction of cyanide ion with a variety of substituted triarylmethane carbocations have been measured in dimethyl sulfoxide (Me_2SO) containing 8% water by volume. The reaction is second order overall and first order with respect to each reactant. The nucleophilicity system parameter ($N_+ = 8.1$) indicates a nucleophilic system much like that found in pure Me_2SO. The slope of the Hammett plot ($\rho = 0.647$) and the large negative "salt effect" closely resemble the results found for reactions of these carbocations in water, indicating a similar transition state structure and mechanism.

The reaction of the stable triarylmethyl cations (i.e., primarily dye cations) with a variety of nucleophiles in a number of solvents has been studied extensively.[1] The reaction of the cyanide nucleophile with this class of dye carbocation (I) has been shown to be a kinetically straightforward anion–cation recombination, which can be easily followed by spectrophotometry at low concentrations because of the very high extinction coefficients of the cations (ϵ 10^5 M^{-1}). The relatively slow reaction to form the covalent triarylmethane leuconitrile (II) has been treated as a nucleophilic attack involving an ion pair at the transition state.[2] More recently it has been considered as a reaction involving the reorganization of the solvent structure around a one solvent separated ion pair,[3] as a critical factor at the transition state.

The present work will examine the reactions of cyanide ion with a variety of substituted triarylmethane cations (eq 1) in dimethyl sulfoxide containing 8% water by volume, in order to measure the activation parameters of these reactions and to determine further applicability of the linear free energy relationship to a series of triarylmethanes[4] carrying a larger number of substituents than the series studied by previous investigators.



Results

The reactions of the carbonium ions with cyanide ions in dimethyl sulfoxide (Me_2SO) containing 8% water were studied by irradiating a solution containing the leuconitrile of the dye and potassium cyanide. The irradiation, which was carried out in a spectrophotometer, produced the desired dye cation in concentration of ca. 10^{-6} *M*. The reaction kinetics with excess cyanide (ca. 10^{-5}–10^{-3} *M*) are pseudo-first-order with respect to the dye, to at least 90% completion. The plots of the pseudo-first-order rate constants (k_{ps}) are linear in all cases with respect to the cyanide ion concentration over a wide range (20–500 ×), Figure 1. As would be expected, all the carbonium ions were found to follow excellent second-order kinetics in their reactions with cyanide ion.

Certain salts have been shown to cause retardation of the pseudo-first-order rates of this reaction, as shown by an inverse relation between k_{ps} and salt concentration.[2,5] Although we also found that some salts have a strong retarding effect on the rate (vide infra), potassium cyanide did not display such as effect, nor did it cause side reactions.

An 8% aqueous Me_2SO resolution containing potassium cyanide, even at the low concentrations used in the kinetic studies, will contain hydroxyl ions formed by the hydrolysis of the salt. The concentration of these ions was measured using apparatus similar to that described by Ritchie and Unschold.[6] The hydroxide ion concentration in this solvent was found to be similar to the calculated concentrations assuming a mixture of solvents. Over the range of potassium cyanide concentrations studied, the hydroxyl ion concentration is smaller than that of the cyanide ion by as much

Table I
Second-Order Rate Constants

Registry no.	Compd X	R_2	Temp, °C	n[a]	k_2[b]	r[c]
7438-46-2	p-$N(CH_3)_2$	CH_3	15.00	5	44.37 (16.15)	0.992
			20.00	9	61.69 (10.29)	0.985
			28.00	3	104.3 (2.6)	0.9996
			30.00	3	134.7 (16.5)	0.998
			35.05	7	134.3 (58.5)	0.985
			40.00	3	190.2 (71.0)	0.994
			45.00	4	244.7 (41.7)	0.955
			50.00	8	669.1 (362.4)	0.950
57049-32-8	p-Phenoxy	CH_3	17.40	6	244.0 (51.5)	0.978
			30.00	7	404.3 (96.4)	0.982
			50.00	5	1133. (92.)	0.983
42297-53-0	p-CH_3O	CH_3	18.70	9	169.9 (37.2)	0.950
			40.00	7	592.7 (55.9)	0.990
			60.00	5	1908. (215.)	0.956
17717-39-4	p-CH_3	CH_3	17.50	8	194.4 (49.8)	0.962
			35.00	9	575.6 (112.9)	0.978
			50.80	7	1447. (204.)	0.967
10309-95-2	H	CH_3	20.00	3	259.6 (5.0)	0.985
			30.00	7	619.6 (32.5)	0.987
			40.00	3	1225. (63.)	0.999
42297-52-9	m-CH_3O	CH_3	17.50	6	159.7 (31.1)	0.989
			30.00	9	365.6 (81.9)	0.943
			35.00	7	641.6 (122.1)	0.975
			50.00	9	951.0 (43.9)	0.956
34101-54-7	m-CF_3	CH_3	17.40	6	604.4 (268.8)	0.985
			30.00	11	912.7 (219.6)	0.969
			50.00	5	2709. (329.)	0.973
34101-55-8	p-CF_3	CH_3	18.65	7	725.7 (111.3)	0.975
			30.00	2	1194. (23.)	d
			35.35	4	1581. (257.)	0.989
			50.10	3	2324. (8.)	0.910
25501-72-8	o-Cl	CH_3	17.00	4	18.00 (6.28)	0.962
			30.00	8	68.29 (13.57)	0.989
			50.00	3	130.0 (17.9)	0.994
			60.00	5	243.5 (35.7)	0.970
57049-33-9	H	H	19.50	7	263.3 (18.1)	0.980
			40.00	7	577.8 (14.7)	0.993
			60.00	15	1427. (475.)	0.907

[a] Number of runs. [b] Maximum of errors in parentheses. [c] Linear correlation coefficient for k_{ps} against CN^-. [d] Only one concentration measured at this temperature.

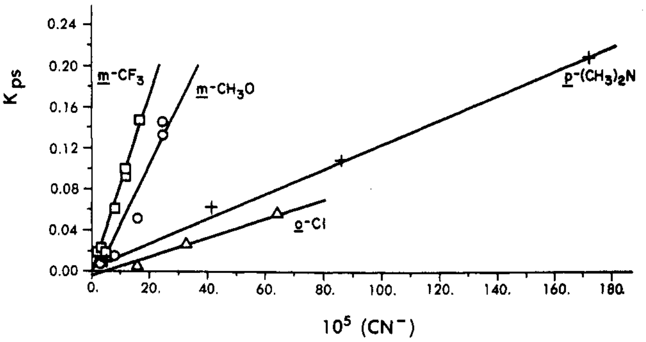


Figure 1. Dependence of the pseudo-first-order rate constants at 30°C for the conversion of I to II upon the concentration of cyanide ion. Experimental points are given for X = m-CF_3 (□), p-CH_3O (○), p-$(CH_3)_2N$ (+), and o-Cl (△).

as a factor of 25 at 10^{-3} M potassium cyanide, and approaches the cyanide ion only at very low (10^{-5} M) concentrations.

The expected effect of these ions, an increase in values of k_{ps}, was not apparent at the lowest cyanide concentrations ($<10^{-4}$ M), where the concentration of the hydroxyl ion approaches that of cyanide ion. A control run using the reaction of malachite green cation with hydroxide showed the relative nucleophilicity of hydroxide ion in 8% aqueous Me_2SO to be less than that of cyanide ion by a factor of ca. 5. Thus, the effect of hydroxide ion or any other nucleophile was not found; good linear correlation was obtained between k_{ps} and cyanide ion concentration for all the dyes at a given temperature. Thus, the kinetics of the reactions of the carbonium ions with cyanide could be studied without the use of buffer solutions, which themselves could cause difficulties by introducing their own salt effects.

At the higher temperatures with the more reactive compounds, there were indeed some indications of an increase in the rate constant leading toward plot curvature (k_{ps} vs. CN^-). However, this curvature did not cause unacceptable linear correlations, nor cause deviations from the excellent second-order kinetics at these concentrations. It is of interest that the cyanide ion concentrations studied ranged from 20-fold in the case of the most reactive compounds to 500-fold in the case of the least reactive dye cation. Over this extremely large range the data showed excellent correlation with the expected second-order kinetics and results were consistent with the rate law in eq 2.

$$\text{rate} = k_2\,[\text{dye cation}^+]\,[CN^-] \qquad (2)$$

The second-order rate constants (k_2) determined at a number of temperatures, are reported in Table I together with the linear correlation coefficients for the plot of k_{ps} against counterion concentration at each temperature.

Our rate constant values for the reaction of two of the dyes with cyanide, are, as expected from the earlier work by Ritchie,[5] substantially smaller than the rate constants in pure anhydrous Me_2SO by at least one order of magnitude, and larger than the rate in water by three orders of magnitude. In particular, when the rate constants at 25° for the

Table II
Activation Parameters for the Reaction of Triarylmethyl Cations with Cyanide Ion

Dye cation	Substituent X	Substituent R	r^a	E_a, kcal mol^{-1}	Log A	k_2 at 30°
Crystal violet	p-N(CH$_3$)$_2$	CH$_3$	0.986	11.0	10.0	134.7
	p-Phenoxy	CH$_3$	0.996	8.74	8.95	404.3
New green	p-CH$_3$O	CH$_3$	0.999	11.0	10.5	341.6^b
	p-CH$_3$	CH$_3$	0.9999	11.2	10.7	431.7^b
Malachite green	H	CH$_3$	0.999	14.5	13.2	619.6
	m-CH$_3$O	CH$_3$	0.988	10.4	10.1	365.6
	m-CF$_3$	CH$_3$	0.985	8.65	9.26	912.7
	p-CF$_3$	CH$_3$	0.997	6.81	7.97	1153.
	o-Cl	CH$_3$	0.976	11.5	9.96	68.29
Doebner's violet	H	H	0.998	7.14	7.75	400.3^b

[a] Weighted linear correlation coefficient. [b] Calculated from the Arrhenius plot.

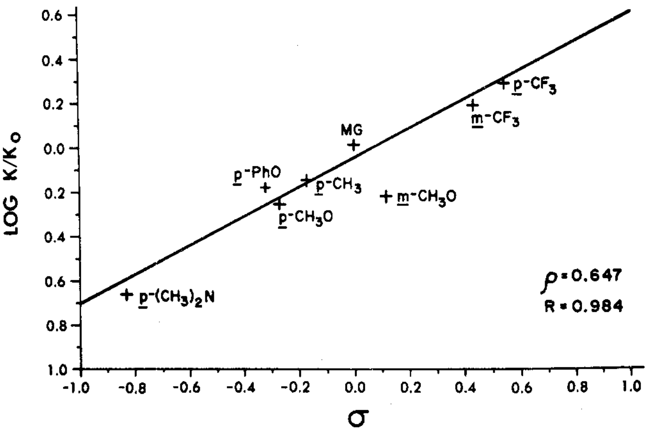


Figure 2. Correlation of the rates of combination at 30°C with the Hammett σ substitution parameters.

malachite green and crystal violet cations were calculated from their Arrhenius plots (395.4 and 86.8 M^{-1} sec^{-1}, respectively), and were used with Ritchie's rate values for the reaction of these cations with water (3.8×10^{-6} and 6.3×10^{-7} M^{-} sec^{-1})[5], the values for N_+, the nucleophilicity system parameter of Ritchie,[3] were obtained.

$$N_+ = \log(k_n/k_{H_2O}) = \log\left(\frac{395.4}{3.8 \times 10^{-6}}\right) = 8.0 \quad (3)$$

$$\log\left(\frac{86.8}{6.3 \times 10^{-7}}\right) = 8.1 \quad (4)$$

These are consistent values which indicate a nucleophilic system much like that found by Ritchie with pure Me$_2$SO ($N_+ = 8.6$),[7,8] but with a reduced nucleophilicity, attributable to the presence of water, which solvates anions more effectively than the aprotic solvent.[10]

The activation parameters for the reaction of the carbocations examined are collected in Table II, together with the weighted linear correlation coefficients. The E_a values are slightly lower than those reported for other reactions of these dye cations indicating that the transition state is energetically favored in the present solvent system.[9]

Figure 2, the Hammett plot, shows that the reaction rate depends upon the electron density on the central carbon atom; electron-donating substituents decrease the rate while electron-withdrawing substituents increase it. The slope ($\rho = 0.647$) is very similar to that of the reaction of these dye cations with cyanide in water (0.693),[11] but less than that found in pure DMF or Me$_2$SO (1.11 and 1.12, respectively[11]).

The effect of salts upon the rate of reaction of the p-trifluoromethyl derivative of malachite green was also studied (Figure 3). This work was carried out at salt concentrations much higher than those for which theoretical treatments are applicable, but the plots of log k_2 against $\mu_{1/2}$ were linear for most salts. A "salt effect" was expected from the simple electrostatic treatment. It was found to be the same as reported for the reaction in aqueous solutions.[5] The large negative effect is much like that seen earlier by Bunton and Huang[1] at high salt concentrations for the reaction of trianisylmethane cation with hydroxide ion. Like them we found that the effect is most pronounced with lithium perchlorate, but our data, unlike theirs, indicate that NaNO$_3$ has a greater effect than LiCl, which has no detectable effect. The observed order upon the rate constant was LiClO$_4$ < NaNO$_3$ < KBr < Mg(ClO$_4$)$_2$ < no salt = LiCl, whereas Bunton and Huang reported the order LiClO$_4$ < LiCl < NaNO$_3$ < no salt.

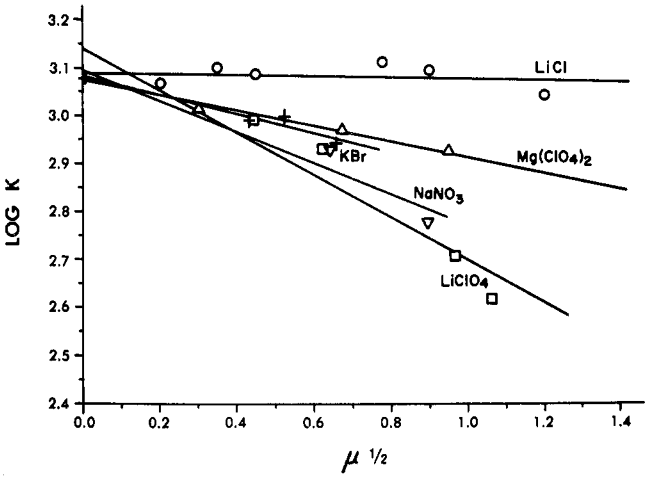


Figure 3. Effect of salts upon the reaction of p-CF$_3$ malachite green cation with cyanide ion at 30°C. Symbols follow: ○, LiCl; △, Mg(ClO$_4$)$_2$; +, KBr; ▽, NaNO$_3$; and □, LiClO$_4$.

The results of this work are consistent with earlier investigations of nucleophilic attack upon stable carbocations. The activation parameters, the slope of the Hammett plot, and the large negative salt effects closely resemble the results found for the reaction of the triarylmethyl cations in water, indicating similar transition state structure and mechanism in the formation of leuconitrile from the dye cation.

Experimental Section[16]

Materials. Water was doubly distilled from potassium permanganate. Dimethyl sulfoxide (Fisher spectroanalyzed) was purged with nitrogen and used without further purification. The solvent was dimethyl sulfoxide containing 8% water by volume.

Potassium cyanide (ROC/RIC 99.5% grade) was used without further purification. The other inorganic salts were commercial reagent grade samples and were dried before use.

The leuconitriles of the triarylmethane dyes were prepared by

Table III
Physical Constants of the Triarylmethane Compounds

Substituents		Leucocarbinol		Dye		Leuconitrile[e]	
		mp, °C		95% EtOH	8% Me_2SO	mp, °C	
X	R	Obsd	Lit.	λ_{max} (10^5 ϵ)	λ_{max} (10^5 ϵ)	Obsd	Lit.
H	CH_3	160–162	163[b]	622 (10.63)	631.5 (9.63), 431 (1.84)[a] 631.5 (9.66), 431 (1.57)[h]	176–177	176–177[f]
p-$(CH_3)_2N$	CH_3		190[b]	589 (11.3)	603 (11.0)[h]	293	294–295.6[g]
p-CH_3O	CH_3	129–130	154[b]	610.5 (9.89)	621.5 (8.62), 466.5 (2.59)[a]	230–232	
p-Phenoxy	CH_3	147–148		616 (10.3)	628 (9.25), 458 (2.59)[a]	154–155	
p-CH_3	CH_3	157–159	151[b]	618 (10.6)	629 (9.82), 442.6 (1.59)[a]	211–212	
m-CH_3O	CH_3	149–151	151[b]	637 (9.89)	636.5 (8.79), 437.2 (1.42)[a]	145.5–147.5	
m-CF_3	CH_3	*d*	145–146[c]	634 (9.66)	641 (4.62), 428 (0.960)[i]	164–165	
p-CF_3	CH_3	187–188	181–182[c]	636 (9.93)	646.5 (7.49), 427 (1.16)[a]	201–202	
o-Cl	CH_3			640 (12.6)	642 (6.04)[h]	200.5	
H	H			564 (10.2)	584 (6.96), 404 (1.52)[h]	226–227	

[a] By acidification of alcohol. [b] Reference 4a. [c] Reference 4b. [d] Isolated as an oil. [e] Correct analyses were found for all new compounds (±0.4% for C, H, and N). [f] Reference 13. [g] L. Harris, J. Kamimsky, and R. G. Simard, *J. Am. Chem. Soc.*, 57, 115 (1935). [h] By irradiation of leuconitrile. [i] By chloranil oxidation.

treatment of dye cation with excess cyanide ion in dimethyl sulfoxide.[12]

The dye cation or its leucocarbinol (1 g) was dissolved in 25 ml of Me_2SO on the steam bath, and a double excess of hydrochloric acid (ca. 0.5 ml in 5 ml of water) was added. The resulting solution of dye was treated with 0.7 g (0.108 mol) of potassium cyanide and the mixture was stirred until the solution decolorized. At this time, the mixture was filtered, the filter pack washed with 10 ml of hot 95% ethanol, and the filtrate heated. Water (ca. 10 ml) was added slowly with stirring, to fog the resulting solution. The fogged mixture was then digested on the hot plate and cooled to give crystals. The crystals were separated, washed with water, and repeatedly recrystallized from a chloroform–ethanol mixture to give a constant melting point. Physical constants for the leuconitriles are shown in Table III.

Those dyes which were not commercially available could be obtained as their leucocarbinols (1) by the addition of the appropriate phenylsodium salt to Michler's ketone in toluene,[13] (2) by the addition of the phenyllithium salt in ether.[4b] When these one-step routes were unsuccessful, as in the case of Doebner's violet[14] and the *m*-trifluoromethyl compound, (3) the conventional condensation–oxidation method used by Ritchie[4a] was employed.

The dye cations were produced by three different methods and their absorbances then measured. The methods were (1) acidification of the dye leucocarbinol in 95% ethanol with a slight excess of hydrochloric acid; (2) irradiation[15] of the easily purified dye leuconitriles of Doebner's violet and the commercially obtained dyes; or (3) utilization of the quantitative[4c] chloranil oxidation to produce the cation in situ from the pure leucobase of the *m*-trifluoromethyl compound. The extinction coefficients (Table III) were determined by Beer's law linear regressions on the absorbance data of the cations and agree well with previously reported values.[4]

The spectra of the dye cations were then measured in 8% aqueous Me_2SO at different concentrations over the range used for kinetic studies. The extinction coefficients at the λ_{max} were determined by the same methods used with ethanol for the compounds. The absorption of the cations does not deviate from Beer's law in the concentration range measured. All spectra were measured on a Cary 17I spectrophotometer and the linear regressions on the data for the Beer's law were carried out on a Hewlett-Packard 9810A calculator.

Apparatus. Measurements of hydroxyl ion in aqueous Me_2SO were carried out using a Beckman Research pH meter, Model 1019, with H-cell similar to that described by Ritchie and Unschold,[6] a silver billet electrode (Beckman no. 39261), and Beckman E-2 electrode (no. 39099). The meter was operated on the millivolt scale and standardized with solutions of potassium hydroxide in 8% Me_2SO over a range of 10^{-5}–10^{-3} *M* base. In these cases good adherence to the Nerst equation was observed.

For the kinetic measurements, a Cary Model 17I spectrometer was equipped with a special compartment cover, and a thermostatted cell which could be kept ±0.05°C by means of water circulated from a constant-temperature bath. The cover contained a 100-W Hanovia high-pressure quartz mercury-vapor light source mounted in front of a parabolic reflector, with provision to insert a flint glass filter to remove the short-wavelength light. The cover had light-baffled venting and provision for air circulation to prevent overheating of the cell compartment and to prevent large ozone concentrations. In addition a heavy duty solenoid was mounted on this cover to close the shutter of the spectrophotometer detector to protect the detector when the mercury lamp was on.

Kinetics. Stock solutions of the leuconitriles and of the salts were prepared in Me_2SO containing 8% water by volume. These solutions were used to prepare reaction mixtures with concentrations of approximately 5×10^{-5} *M* in leuconitrile and with the desired concentrations of counterion (10^{-5}–10^{-3} *M*). The reaction was initiated by approximately 1-min irradiation with the mercury vapor lamp which produced the dye cation in a 5- or 10-cm thermostatted cell with less than a 10% conversion of the leuconitrile. At the completion of the decoloration reactions (i.e., when the absorbance had returned to zero) no absorbances that could be attributed to side products produced by irradiation were evident. Only after repeated or lengthy exposure of a solution did the absorbances due to decomposition become significant.

The change in absorbance was measured from the time the initiating lamp turned off until the reaction was completed. Three or more repetitions at each set of concentrations were carried out using fresh solutions. These were followed by measuring the change of absorbance at the wavelength of maximum absorbance of the dye at a known chart speed. These values were converted to concentrations using a digitizer and a Hewlett-Packard 9810A desk calculator, which was also used to calculate the rate constants using a linear regression technique. The data, when treated as pseudo-first-order, and as second order with respect to dye and cyanide concentrations, gave excellent correlations for up to 3 half-lives and greater than 90% completion of reaction. Correlation coefficients of at least 0.98 (usually 0.999) were obtained with data averaged from each set of replications. The second-order rate constant was calculated as the mean of all the rate constants obtained at a given temperature.

Acknowledgment. We wish to thank Drs. J. H. Cornell and M. Nakashima for their valuable discussions of the work with M. L. Herz. Our thanks also to Mr. T. Metcalf for his assistance in measuring the effect of salts on the reaction.

Registry No.—Leucocarbinol (X = H; R = CH_3), 510-13-4; leucocarbinol (X = p-$(CH_3)_2N$; R = CH_3), 467-63-0; leucocarbinol (X = p-CH_3O; R = CH_3), 10165-76-1; leucocarbinol (X = p-PhO; R = CH_3), 57049-34-0; leucocarbinol (X = p-CH_3; R = CH_3), 10249-42-0; leucocarbinol (X = m-CH_3O; R = CH_3), 10165-77-2; leucocarbinol (X = m-CF_3; R = CH_3), 28316-15-6; leucocarbinol (X = p-CF_3; R = CH_3), 28316-16-7; leucocarbinol (X = o-Cl; R = CH_3), 596-42-9; leucocarbinol (X = H; R = H), 57049-35-1; leuconitrile (X = H; R = CH_3), 4468-56-8; leuconitrile (X = p-$(CH_3)_2N$; R = CH_3), 4439-06-9; leuconitrile (X = p-CH_3O; R = CH_3), 57049-36-2; leuconitrile (X = p-phenoxy; R = CH_3), 57049-37-3; leuconitrile (X = p-CH_3; R = CH_3), 57049-38-4; leuconitrile (X = m-CH_3O; R = CH_3), 57049-39-5; leuconitrile (X = m-CF_3; R = CH_3), 57049-40-8; leuconitrile (X = p-CF_3; R = CH_3), 57049-41-9; leuconitrile (X = o-Cl; R = CH_3), 57049-42-0; leuconitrile (X = R = H), 57049-43-1; potassium cyanide, 151-50-8.

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Catalysis of the Reaction of Morpholine with Phenyl Benzenethiolsulfonate by Halide Ions and Thiocyanate. Possible Evidence for an Intermediate on the Reaction Coordinate in a Substitution at Sulfenyl Sulfur[1a]

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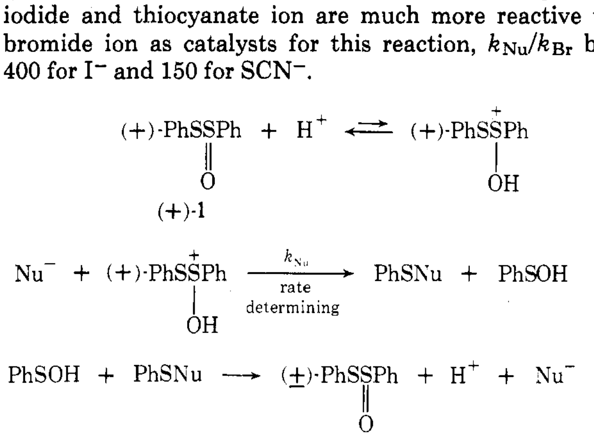
The reaction of morpholine with phenyl benzenethiolsulfonate (2) in aqueous dioxane to form the sulfenamide can be catalyzed by the addition of bromide, iodide, or thiocyanate ions. Data on their catalytic effectiveness can be used to measure the rates of attack of each of these three nucleophiles on the sulfenyl sulfur of 2. One finds that SCN^- is 6.3 times more reactive than I^- and 19 times more reactive than Br^-. This reactivity pattern is markedly different than the one previously observed for attack of the same nuclophiles on the sulfenyl sulfur of $PhSS^+(OH)Ph$; there (k_{Nu}/k_{Br}) is SCN^-, 150; I^-, 400; Br^-, (1.0). It is shown that this marked change in reactivity pattern can be easily explained if nucleophilic attack on the sulfenyl sulfur of 2 by these nucleophiles involves an addition–elimination mechanism with an intermediate (4) on the reaction coordinate, and with loss of $PhSO_2^-$ from 4 being rate determining, while in the case of $PhSS^+(OH)Ph$ attack of the nucleophile is instead rate determining.

In aqueous dioxane optically active phenyl benzenethiolsulfinate, (+)-1, undergoes an acid- and nucleophile-catalyzed racemization via the mechanism shown in eq 1.[2] Both iodide and thiocyanate ion are much more reactive than bromide ion as catalysts for this reaction, k_{Nu}/k_{Br} being 400 for I^- and 150 for SCN^-.



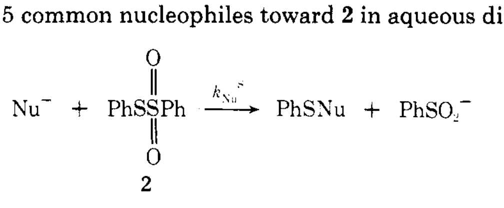
$$(+)\text{-PhS}\underset{\underset{\displaystyle O}{\|}}{S}\text{Ph} + H^+ \rightleftharpoons (+)\text{-PhS}\underset{\underset{\displaystyle OH}{|}}{\overset{+}{S}}\text{Ph} \qquad (1a)$$

(+)-1

$$Nu^- + (+)\text{-PhS}\underset{\underset{\displaystyle OH}{|}}{\overset{+}{S}}\text{Ph} \xrightarrow[\text{rate determining}]{k_{Nu}} \text{PhSNu} + \text{PhSOH} \qquad (1b)$$

$$\text{PhSOH} + \text{PhSNu} \longrightarrow (\pm)\text{-PhS}\underset{\underset{\displaystyle O}{\|}}{S}\text{Ph} + H^+ + Nu^- \qquad (1c)$$

Phenyl benzenethiolsulfonate (2) undergoes nucleophilic substitution reactions (eq 2) easily with many nucleophiles, and we have recently reported[3] kinetic data on the reactivity of 15 common nucleophiles toward 2 in aqueous dioxane.



$$Nu^- + \text{PhS}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}\text{Ph} \xrightarrow{k_{Nu}^{S}} \text{PhSNu} + \text{PhSO}_2^- \qquad (2)$$

2

Thiocyanate ion and the halide ions were not among the nucleophiles studied, however, because of several complications. First, benzenesulfenyl halides undergo hydrolysis easily in aqueous dioxane, and under some conditions[4] the hydrolysis product, the sulfenic acid PhSOH, can react readily with 2 to produce 1; this has the potential for greatly complicating the kinetics. Second, the reaction of $PhSO_2^-$ with PhSX (reverse of eq 2 for Nu = X) can be fast enough compared to hydrolysis of PhSX so that, even if subsequent reactions of PhSOH produce no kinetic complications, reversal of attack of X^- on 2 can be kinetically significant, and one cannot equate $k_X{}^S$ with the rate of disappearance of 2, since attack of X^- on 2 will not be rate determining.

These several complications to determining the reactivity of halides and thiocyanate toward 2 can be circumvented if one can find some other nucleophile to add to the reaction medium which, at the concentration employed, is reactive enough toward PhSX compared to water or $PhSO_2^-$ so that it will capture essentially every PhSX produced by eq 2 before they can react with either water or $PhSO_2^-$. This added nucleophile should also react with PhSX to give a product which will be stable under the reaction conditions. The only other requirement is that the nucleophile added to trap PhSX must not itself react directly with 2 at too rapid a rate. If it does, the contribution of the X^--induced disappearance of 2 to the overall rate will be too small to be detected.

It appeared to us that morpholine might meet all the re-