Solvent Effects on the Reactions of Stabilized Carbonium Ions with Nucleophiles[1]

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Abstract: The rates and equilibria of reactions of three derivatives of malachite green [4,4′-bis(dimethylamino)triphenylmethyltetrafluoroborate] with several nucleophiles in water, methanol, dimethyl sulfoxide, and dimethylformamide solvents have been studied. In all solvents azide ion reacts much faster with the carbonium ions than does cyanide ion, although the equilibrium constants for formation of the covalent product are greater in the case of cyanide. The rate constants for reactions of the carbonium ions with the nucleophiles are found to be more sensitive to changes in solvent than are the equilibrium constants. Both forward and reverse rate constants are changed in the same direction by a change of solvent. It is argued that this latter observation requires the consideration of solvent reorientation as an essential part of the activation process.

Ideas concerning solvent effects on reactivity have undergone drastic revision since the classical concept of the solvent as a continuous dielectric medium. In spite of many recently proposed theories of the nature of the effect of solvents on reactivities in solution which focus attention on some particular aspect of the solvent such as ionizing power,[2] dipolar association,[3] or hydrogen bonding ability,[4] we feel that a much more fundamental question requires attention. In somewhat naive terms, this question may be phrased as follows. Can the reactions of molecules in solution be discussed meaningfully in terms of only those molecules which are observed to undergo the chemical change, or is it necessary to take account of the entire system, including the solvent motion along the reaction coordinate?

In studies on quite different systems, both Caldin[5] and Robertson[6] have been led to revive an earlier suggestion[7] that solvent reorganization may make an appreciable contribution to energies of activation in solution. Essentially, the concept suggested is that initial-state solvation has been broken down to some extent without compensation by complete final-state solvation. This concept would require the consideration of the motion of solvent molecules in discussions of reactions in solution, and is counter to the common assumption that all solvent is in the most stable state at all points along the reaction coordinate.

We have felt that pertinent information concerning the question posed above can best be gained by a study where the mechanism of reaction is least complicated. In the present paper, we report the results of a study of solvent effects on reactions of stabilized carbonium ions with the anionic nucleophiles cyanide, azide, hydroxide, and methoxide. Malachite green [4,4′-bis(dimethylamino)triphenylmethyl tetrafluoroborate] and its 4′′-substituted derivatives, crystal violet [4,4′,4′′-tris(dimethylamino)triphenylmethyl tetrafluoroborate)] and *p*-nitro malachite green [4,4′-bis(dimethylamino)-4′′-nitrotriphenylmethyl tetrafluoroborate], have been shown in a variety of studies[8-14] to react with nucleophiles at the methyl carbon to form covalent derivatives. The reactions are generally kinetically straightforward and are easily followed by spectrophotometry at low concentrations because of the very high extinction coefficients ($\epsilon \approx 10^5$ M^{-1} cm^{-1}) in the 590–650-mμ range.

Results

The reactions of malachite green, *p*-nitro malachite green, and crystal violet with hydroxide ion and water in aqueous solution were studied in buffer solutions of triethylamine–triethylammonium chloride under pseudo-first-order conditions. In the case of crystal violet, the rates in the high pH range were studied in unbuffered solutions of standard potassium hydroxide. Plots of the observed pseudo-first-order rate constants *vs.* concentrations of hydroxide ion are shown in Figures 1–3. From the slopes and intercepts of these plots, we obtain the values for the second-order rate constants for reaction with hydroxide ion, and the pseudo-first-order rate constants for reaction with water which are reported in Table I.

The reactions with hydroxide ion and with water are found to be rather insensitive to inert salt effects. Addition of potassium perchlorate in concentrations up to 10^{-2} M has no measurable effect on the rates of the reactions. Taft has similarly reported[15] that the addition of potassium chloride in concentrations of 0.05–1.0 M causes less than a 10% change in the rate

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[1] This work was supported by a grant from Army Research Office (Durham), DA-ARO(D)-31-G376.

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[3] R. W. Taft, Jr., G. B. Klingensmith, E. Price, and I. R. Fox, paper presented at Symposium on Linear Free Energy Correlations, Durham, N. C., Oct 1964; see also, *J. Am. Chem. Soc.*, **87**, 3620 (1965).

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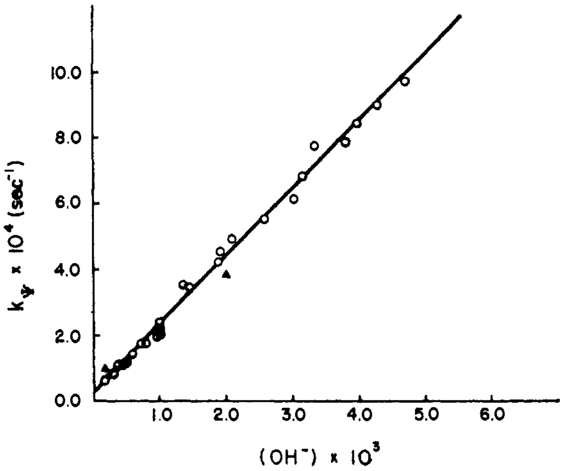

Figure 1. Plot of pseudo-first-order rate constants for reaction of crystal violet with water and hydroxide ion in water: O, present work; ●, data from ref 15; ▲, data from ref 14.

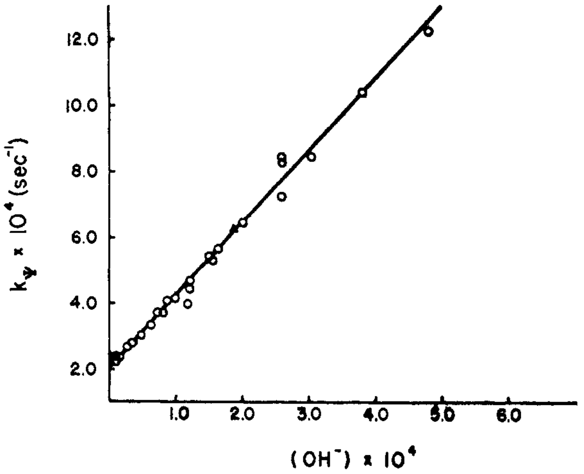

Figure 2. Plot of pseudo-first-order rate constants for reaction of malachite green with water and hydroxide ion in water: O, present work; ●, data from ref 15; ▲, data from ref 14.

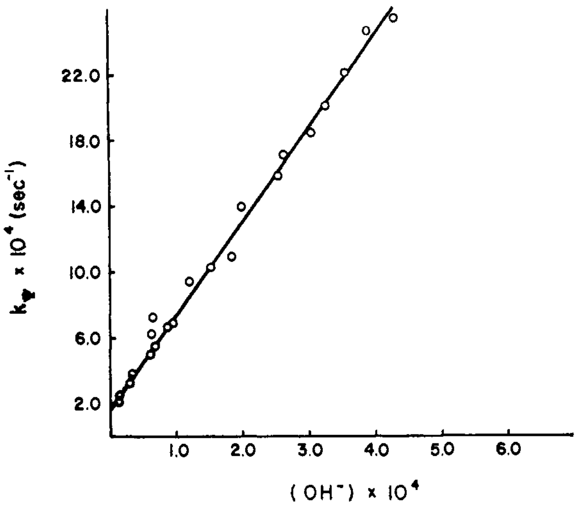

Figure 3. Plot of pseudo-first-order rate constants for reaction of *p*-nitro malachite green with water and hydroxide ion in water.

constant for the reaction of malachite green with hydroxide ion.

Table I. Rate Constants for Reactions with Hydroxide Ion and Water in Aqueous Solution at 25.0°

Cation	k_{OH^-}, M^{-1} sec^{-1}	$k_{H_2O} \times 10^4$, sec^{-1}	pK^a
Crystal violet (λ_{max} 590 mμ)	2.05×10^{-1}	0.35	9.36
Malachite green (λ_{max} 615 mμ)	2.18	2.11	6.84
p-Nitro malachite green λ_{max} 641 mμ)	5.64	1.80	5.50
Crystal violet in D_2O	2.2×10^{-1}	0.35	...

[a] Values taken from ref 8.

The rate constants reported in Table I may be compared with a number of previously reported values. For the reaction of malachite green with hydroxide ion at 25°, values of 1.59[15] and 1.36[14] M^{-1} sec^{-1} have been reported. Values of the first-order rate constant for the reaction with water from the same sources are 2.2×10^{-4} and 3.8×10^{-4} sec^{-1}, respectively. The discrepancies of these values with those reported in Table I are primarily due to the determination of the slope and intercept of the plot of observed rate constant *vs.* concentration of hydroxide. The actually observed rates, as shown in Figures 1 and 2, are in reasonable agreement. The same explanation applies to the comparison of the rate constants reported for crystal violet. Ekström,[13] however, has reported values considerably lower than these for all three of the carbonium ions studied here. His measurements were carried out at 20° rather than the 25° used in the present study, but it is most unlikely that a 5° temperature difference could explain the large discrepancies.

The rates of reaction of the carbonium ions with cyanide ion in aqueous solution were determined by measuring the increase in rate of reaction of the dyes on increase of cyanide ion concentration at constant pH and buffer concentration. The pH of all solutions used in these determinations was accurately adjusted to 10.61. Since hydrogen cyanide has a pK of 9.14 in aqueous solution, only about 3% of the cyanide ion added is converted to the conjugate acid. The rate constants obtained from these measurements were found to decrease with increasing cyanide ion concentration. The addition of potassium perchlorate to the solutions was also found to retard the reaction. The data are presented in Table II.

The salt effects noted are of the magnitude expected from Debye–Hückel theory for the neutralization of two unit charges. Rate constants extrapolated to zero ionic strength were calculated from a visual fit of the data plotted in Figure 4. The lines shown have slopes of -0.10 M^{-1}.

We have also attempted to measure the rates of reaction of the dyes with azide ion in aqueous solution, but have been prevented from doing so because of solubility problems. The equilibrium for formation of the triarylmethyl azide is too unfavorable to allow measurements at concentrations of less than 10^{-2} M azide, and, at much higher concentrations of azide, salting out of the dyes is evident.

The reactions of crystal violet with deuterioxide ion, deuterium oxide, and cyanide ion in D_2O were studied by the same methods as outlined above for aqueous

Table II. Reactions of Carbonium Ions with Cyanide Ion in Aqueous Solution at 25.0° [a]

Cation	Total salt,[b] $M \times 10^3$	Cyanide, $M \times 10^3$	$k_{CN^-} \times 10$, M^{-1} sec^{-1}	$\mu^{1/2} \times 10^2$, M
Crystal violet	8.33	5.0	0.630	9.14
	8.33	5.0	0.666	9.14
	8.33	5.0	0.675	9.14
	10.01	6.67	0.665	10.0
	10.8	7.50	0.675	10.4
	13.3	10.0	0.690	11.5
	15.0	11.7	0.633	12.3
	16.6	13.3	0.631	12.9
	18.3	15.5	0.663	13.5
	20.8	17.5	0.617	14.4
	23.3	20.0	0.630	15.3
Malachite green	8.33	5.00	5.33	9.14
	10.3	5.00	5.10	11.5
	18.3	5.00	4.74	13.5
	23.3	5.00	4.53	15.3
	3.66	0.333	5.98	6.05
	3.83	0.500	5.61	6.19
	4.33	1.00	4.61	6.58
	5.33	2.00	5.75	7.31
	6.00	2.67	5.75	7.75
	6.66	3.33	5.60	8.16
	8.33	5.00	5.37	9.14
	10.0	6.67	5.11	10.0
	11.7	8.33	5.09	10.8
	13.3	10.0	4.96	11.5
	15.0	11.67	4.96	12.3
p-Nitro malachite green	8.33	5.00	8.88	9.14
	13.3	5.00	8.15	11.5
	4.33	1.00	9.9	6.58
	5.33	2.00	9.25	7.31
	6.66	3.33	8.96	8.16
	8.33	5.00	9.17	9.14
	10.0	6.67	8.67	10.0
	11.7	8.33	8.36	10.8
	13.3	10.0	8.21	11.5

[a] Extrapolated rate constants: crystal violet, 8.8×10^{-2} M^{-1} sec^{-1}; crystal violet in D_2O, 8.5×10^{-2} M^{-1} sec^{-1}; malachite green, 6.9×10^{-1} M^{-1} sec^{-1}; *p*-nitro malachite green, 1.13 M^{-1} sec^{-1}. [b] Total salt concentration is 3.33×10^{-3} M buffer salt, plus potassium cyanide concentration shown, plus potassium perchlorate.

solution. The values obtained for the rate constants are reported in Tables I and II. The solvent isotope effect on all three of these reactions is remarkably small.

All of the reactions discussed above were conveniently studied by conventional spectrophotometric techniques, the half-times for the reactions varying from several minutes to several hours. In all of the studies in nonaqueous solutions discussed below, however, the reactions are too fast for conventional techniques, and we have used a stop-flow apparatus patterned after the one described by Gibson.[16] In our apparatus, the solutions contact only glass, Teflon, and stainless steel. The apparatus is described in the Experimental Section.

Before presenting the results obtained in the nonaqueous solvents, we would like to emphasize the extreme importance of rigorously purified solvents, and of carrying out all operations in an inert, dry atmosphere. Contamination of solutions by moisture or traces of acids can cause astonishing decreases in the rates of some of these reactions, particularly those with cyanide ion.

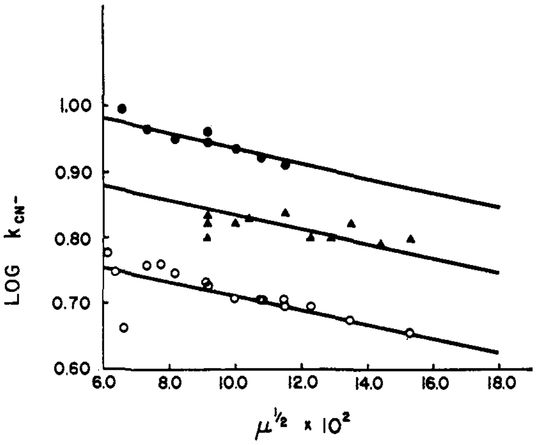

Figure 4. Plot of log k^{CN^-} *vs.* square root of ionic strength for reaction of carbonium ions with cyanide ion in water: ○, malachite green (1 + log *k* is shown); ▲, crystal violet (2 + log *k* is shown); ●, *p*-nitro malachite green (1 + log *k* is shown).

The reactions of the three carbonium ions with methoxide ion in anhydrous methanol were studied by reaction of solutions of the dye with dilute solutions of standardized sodium methoxide. The rates of the reactions showed a very strong salt effect at sodium methoxide concentrations above 10^{-3} M. It was found that the assumption of a dissociation constant for sodium methoxide ion pair of 1.03×10^{-2} M brings the rate constants obtained over a wide range of concentrations into agreement with each other. Since at least one determination of rate was made at concentrations of sodium methoxide below 10^{-3} M for each dye, the accuracy of the reported rate constants is not very dependent on this choice for the ion pair dissociation constant. The values obtained for the rate constants are shown in Table III.

Table III. Rate and Equilibrium Constants in Methanol Solution at 25.0° [a]

Cation	$k_{OCH_3^-} \times 10^{-3}$ [b]	pK_R [c]	$k_{N_3^-}$ [d]	$K_{N_3^-}$ [e]
Malachite green	1.25	8.80	...	$>10^{-2}$
Crystal violet	0.065	...	...	$>10^{-2}$
p-Nitro malachite green	6.0	6.79	6.2×10^4	6.2×10^{-4}
m-Chloro malachite green	2.9	7.75	...	...
m-Nitro malachite green	7.4	6.84	...	...

[a] pK_{HN_3} in methanol = 8.91; p*K* (triethylammonium ion) in methanol = 10.88; p*K* (tribenzylammonium ion) in methanol = 6.40; λ_{max} in methanol: crystal violet, 592 mμ; malachite green, 623 mμ; *p*-nitro malachite green, 648 mμ. [b] Rate constant in M^{-1} sec^{-1} for the reaction with methoxide ion. [c] Equilibrium constant for the reaction $Ar_3C^+ + MeOH \rightleftarrows Ar_3COMe + H^+$ at 25.0°. [d] Rate constant in M^{-1} sec^{-1} for reaction with azide ion. [e] Equilibrium constant for the reaction $Ar_3CN_3 \rightleftarrows Ar_3C^+ + N_3^-$.

In a previous study,[12] we have reported the rates of reactions of several malachite green derivatives with methoxide ion using rates relative to the basicity of triethylamine in methanol. From the present data in conjunction with the previous measurements, therefore, we can evaluate the pK_b of triethylamine as 6.04. Using the solvent ionization constant of $pK_s = 16.92$

(16) Q. H. Gibson and L. Milnes, *Biochem. J.*, **91**, 161 (1964).

reported by Koskikallio,[17] we thus obtain a pK_a value of 10.88 for triethylammonium ion in methanol. In water, the pK_a is 10.87,[18] and, as we have pointed out previously,[19] would be expected to remain the same in methanol.

In the earlier study, we found that the rate of reaction of the carbonium ions with methanol is negligible, and this conclusion is confirmed by the present study.

Also in the earlier work,[12] we determined the pK_R values of several malachite green derivatives relative to tribenzylammonium ion in methanol. We have now measured the pK_a of tribenzylammonium ion in methanol by the differential potentiometric method described in another paper[19] and find a value of 6.40 at 25.0°. This value may now be used to convert the previously reported relative pK_R values to absolute values. These values are shown in Table III.

The reaction of azide ion with *p*-nitro malachite green in methanol was studied by observation of the first 50–100 msec of reaction of the carbonium ion with a methanol solution of 3.12×10^{-4} *M* sodium methoxide with 1.04×10^{-2} to 9.73×10^{-4} *M* added sodium azide. The reaction with azide under these conditions is fast enough that equilibrium is established before any appreciable reaction with methoxide ion occurs. From the stop flow traces shown in the Experimental Section, both the equilibrium constant and rate constant for the formation of the triarylmethyl azide can be evaluated. The values obtained for these constants are shown in Table III.

The equilibrium constants for formation of the triarylmethyl azides from malachite green and crystal violet are too small to allow measurements even at concentrations of 10^{-2} *M* in sodium azide.

We have measured the ionization constant for hydrazoic acid in anhydrous methanol by titration of sodium azide with methanolic perchloric acid using the potentiometric method described elsewhere.[20] We obtain a p*K* value of 8.9 at 25.0°, which is in excellent agreement with the value of 8.9 reported by Parker.[21]

In this work, in order to provide a convenient buffer solution for calibration of glass electrodes in methanol, we have measured a pH of 8.987 for a 1.465×10^{-2} *M* solution of potassium hydrogen phthalate in anhydrous methanol at 25.0°.

Unfortunately, we have not been able to measure the rates of reactions of the carbonium ions with cyanide ion in methanol because of the basicity of cyanide ion in this solvent. From titrations of tetraethylammonium cyanide in methanol, we have estimated that K_b for cyanide is approximately 10^{-3} *M*. We cannot, therefore, prepare solutions of reasonable concentration in which the amount of cyanide exceeds the amount of methoxide present. On the basis of one experiment, however, it appears that cyanide reacts more slowly than does methoxide. A solution containing 7.8×10^{-3} *M* sodium methoxide and 5.5×10^{-3} *M* tetraethylammonium cyanide was found to react with crystal violet at the same rate as does the solution without cyanide present. We can, therefore, set an upper limit on the rate constant for reaction of cyanide ion with crystal violet in methanol of *ca.* 6 M^{-1} sec^{-1}.

In attempts to measure the rates of reactions of malachite green and *p*-nitro malachite green with azide ion in dimethyl sulfoxide solution, the solutions reached equilibrium concentrations of the dyes during mixing. In all cases, we were able to show that changes in azide ion concentration caused a change in equilibrium concentration of the dye consistent with the expected reaction to produce the triarylmethyl azide. For malachite green, we have determined a dissociation constant for the triarylmethyl azide of 2.9×10^{-5} *M*. The corresponding constant for *p*-nitro malachite green is 5.0×10^{-6} *M*. Since mixing time in the stop flow is less than 5 msec, we can set a lower limit on the rate constants for formation of product of *ca.* 10^7 M^{-1} sec^{-1}. Crystal violet showed no measurable reaction with sodium azide solutions up to *ca.* 10^{-3} *M*. The equilibrium is therefore too unfavorable in this case to allow measurements at reasonable concentrations.

We have reported the pK_a of hydrazoic acid in dimethyl sulfoxide elsewhere as 7.9.[22]

Reactions of the carbonium ions with cyanide ion in dimethyl sulfoxide were studied by the use of solutions of tetraethylammonium cyanide. Sodium cyanide cannot be dissolved even to concentrations of 10^{-4} *M* in *pure* solvent.[23] The reactions with the carbonium ions are completely to product in the most dilute solutions studies (*ca.* 5×10^{-5} *M* cyanide). All three carbonium ions gave excellent second-order behavior in reactions with cyanide ion.

The rate constants obtained in dimethyl sulfoxide are summarized in Table IV. The p*K* of HCN in dimethyl sulfoxide is reported in a separate paper[22] as 12.9.

Table IV. Reactions of Carbonium Ions in Dimethyl Sulfoxide Solution at 25.0°

Cation	$k_{N_3^-}$[a]	$K_{N_3^-}$[b]	k_{CN^-}[a]
Crystal violet (λ_{max} 602 mμ)	. . .	$>10^{-2}$	1.2×10^3
Malachite green (λ_{max} 634 mμ)	$>10^7$	2.9×10^{-5}	1.7×10^4
p-Nitro malachite green (λ_{max} 656 mμ)	$\gg 10^7$	5.0×10^{-6}	7.5×10^4

[a] Forward rate constant in units of M^{-1} sec^{-1}. [b] Dissociation constant in units of *M*.

The reactions of all three carbonium ions with azide ion in dimethylformamide solution were also found to reach equilibrium on mixing. Consistent equilibrium constants over a range of concentrations were again obtained, and lower limits on the rates of reactions set at 10^7 M^{-1} sec^{-1}.

The reactions of the dyes with cyanide ion in dimethylformamide were studied in the same manner as

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(17) J. Koskikallio, *Suomen Kemistilehti*, **30B**, 111, 155 (1957).

(18) R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959, pp 64, 65.

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

(20) C. D. Ritchie and G. H. Megerle, *ibid.*, **89**, 1452 (1967).

(21) B. W. Clare, D. Cook, E. C. F. Ko, Y. C. Mac, and A. J. Parker, *ibid.*, **88**, 1911 (1966).

(22) C. D. Ritchie and R. E. Uschold, *ibid.*, **89**, 1721 (1967).

(23) In both dimethylformamide and dimethyl sulfoxide, which have been rigorously purified, the solubilities of salts such as sodium cyanide or sodium azide are much lower than previous reports in the literature would lead one to believe. The presence of small amounts of water (*ca.* 100 ppm) in the solvents causes marked increases in the solubilities of salts.

described above for dimethyl sulfoxide solutions.[23] The reactions again went completely to product in the most dilute solutions studied and consistent second-order rate constants were obtained over wide ranges of cyanide ion concentrations. The data are shown in Table V.

Table V. Reactions of Carbonium Ions in Dimethylformamide at 25.0°

Cation	$k_{N_3^-}$[a]	$K_{N_3^-}$[b]	k_{CN^-}[a]
Crystal violet (λ_{max} 597 mμ)	$>10^7$	1.5×10^{-3}	7.2×10^3
Malachite green (λ_{max} 628 mμ)	$>10^7$	4.4×10^{-6}	1.1×10^5
p-Nitro malachite green (λ_{max} 650 mμ)	$>10^7$	$<10^{-6}$	4.3×10^5

[a] Second-order rate constants in units of M^{-1} sec^{-1}. [b] Dissociation constant of triarylmethyl azide in units of M.

Table VI. Summary of Rate and Equilibrium Constants at 25.0°

		Crystal violet		Malachite green		*p*-NO$_2$ malachite green		
Nucleophile	Solvent	k_2[a]	K_d[b]	k_2[a]	K_d[b]	k_2[a]	K_d[b]	pK_a[c]
Azide	Methanol	...	$>10^{-2}$	...	$>10^{-2}$	6.2×10^4	6.1×10^{-4}	8.91
	DMSO	...	$>10^{-2}$	$>10^7$	2.9×10^{-5}	$>10^7$	5.0×10^{-6}	7.9
	DMF	$>10^7$	1.5×10^{-3}	$>10^7$	4.4×10^{-6}	$>10^7$	$<10^{-6}$	
Cyanide	Water	8.8×10^{-2}	$<10^{-6}$	0.69	$<10^{-6}$	1.13	$<10^{-6}$	9.14
	D$_2$O	8.5×10^{-2}	$<10^{-6}$	...	...	...	...	...
	DMSO	1.2×10^3	$<10^{-6}$	1.7×10^4	$<10^{-6}$	7.5×10^4	$<10^{-6}$	12.9
	DMF	7.2×10^3	$<10^{-6}$	1.1×10^5	$<10^{-6}$	4.3×10^5	$<10^{-6}$	
Hydroxide	Water	0.205	2.3×10^{-5}	2.2	6.9×10^{-8}	5.6	3.2×10^{-9}	15.74[e]
Water[d]	Water	6.3×10^{-7}	...	3.8×10^{-6}	...	3.2×10^{-6}	...	−1.74
Methoxide	Methanol	65.0	...	1.25×10^3	7.6×10^{-9}	6.0×10^3	7.4×10^{-11}	18.31[e]
Deuterioxide	D$_2$O	0.22	...	...	...	...	...	...
D$_2$O[d]	D$_2$O	7.0×10^{-7}	...	...	...	...	...	...

[a] Second-order rate constants in units of M^{-1} sec^{-1}. [b] Dissociation constants in units of M for the reaction $Ar_3CA \rightleftarrows Ar_3C^+ + A^-$. [c] p$K$ of the conjugate acid of the nucleophile referred to standard state in the solvent in which it is measured. [d] The pseudo-first-order rate constants for reaction with solvent have been divided by the concentration of solvent in order to place them on approximately the same scale with the others. [e] Corrected for solvent concentration.

The various rate and equilibrium constants obtained in this study are summarized in Table VI. Rate constants for reactions with solvent and dissociation constants of solvents have been placed on approximately the same scale as the other second-order rate constants.

Discussion

We should like to call first and particular attention to the reactions of the carbonium ions with azide ion and with hydroxide and methoxide ions, the processes for which we have been able to measure both rate and equilibrium constants.

In the reactions with hydroxide and methoxide, the dissociation constants of products are decreased by a factor of 9 for malachite green and of 40 for *p*-nitro malachite green on going from water to methanol. The rate constants for formation of products, however, increase by the much larger factors of 6 × 10^2 and 10^3, respectively. In the same solvent, the nucleophilicities of hydroxide and methoxide are known to be quite similar.[24] The change in rate observed here, then, must be ascribed to a solvent effect. These observations can be stated in terms of rate constants for the dissociation of the products since

$$k_d = k_2 K_d \tag{1}$$

where k_d is the rate constant for dissociation of the product, k_2 is the second-order rate constant for formation of the product, and K_d is the dissociation constant for the product. Thus, for *p*-nitro malachite green, the change from solvent water to solvent methanol causes an *increase* by a factor of 24 in the rate of dissociation of product, and for malachite green, an increase by a factor of 63.

The same type of greater increase in rate of formation than in formation constant is observed for the reaction of azide ion in going from methanol to dimethyl sulfoxide. In this case, however, we may only set a lower limit on the increase in rate constant because the reaction becomes too fast to measure in dimethyl sulfoxide. Since in all of the reactions studied here malachite green reacts about five times slower with any anionic nucleophile than does *p*-nitro malachite green, and since malachite green reacts with azide in dimethyl sulfoxide with a rate constant greater than 10^7, a *lower limit* on the rate constant for reaction of *p*-nitro malachite green may confidently be set at 5 × 10^7. Thus the rate constant for formation of triarylmethylazide from *p*-nitro malachite green increases by *at least* a factor of 300 on going from methanol solvent to dimethyl sulfoxide solvent. The dissociation constant, however, only decreases by a factor of 120. From eq 1, therefore, the rate of dissociation of the triarylmethylazide is increased by a factor of at least 9 on changing solvent from methanol to dimethyl sulfoxide.

The above observations become even more pointed when we note that changes in rates of reactions caused by substituents in the 3′′ or 4′′ position of malachite green are less than the changes produced in the equilibrium constants. We have previously reported Hammett ρ values for both the rate and equilibrium constants for formation of the methyl ethers of malachite green derivatives as 0.94 and 2.64, respectively. The present data show that similar ratios of ρ values for rates and equilibria pertain to the reactions with hydroxide and azide ions. Since the ρ values for the rates of formation of product are only about one-third of the ρ values for equilibria, the charge distribu-

(24) I. R. Alet and D. B. England, *J. Chem. Soc.*, 5259 (1961).

tion at the transition state is changed from that of the reactant ion by only one-third of the total change from reactant to covalent product. From the substituents' viewpoint, then, the transition state is intermediate between reactants and products. From the solvent effects discussed above, however, it is obvious that from the solvents' viewpoint the transition state is not simply intermediate between reactants and products. Both the forward and reverse rates are changed in the same direction by a change of solvent.

The postulation of an ion-pair-like transition state with localized charge on the carbonium ion portion[25] does not appear to be consistent with the present data. The solvolyses of alkyl tosylates which presumably involve ion-pair-like transition states show solvent effects on rates which are the opposite of those observed for the rates of dissociation in the present study.[2]

We believe that the present observations are uniquely explained by the postulate of solvent reorganization being a significant contributor to the activation process. The physical situation which we presently envision is that solvent molecules which are hydrogen bonded or otherwise associated with the ions in the reactant state, and which are associated with other solvent molceules, perhaps in "ice-berg" formation, in the final covalent state, are at least partially free and in the process of reorientation at the transition state.[6]

If we assume that the rate of dissociation of product would be the same in water and methanol if solvent reorganization were not a factor, then we can estimate the difference in energy required for solvent reorganization in water and methanol. From the data given above, this energy difference would be *ca.* 3 kcal/mole. The total solvent reorganization energy would be expected to be a great deal higher than this difference. It would be most interesting to be able to actually obtain the rates of reaction of malachite green and particularly of *p*-nitro malachite green with azide ion in dimethyl sulfoxide and dimethylformamide. The only technique which appears to be applicable to these measurements in nonaqueous solvents is Caldin's recently developed microwave T-jump apparatus.[26]

The solvent isotope effects on the reactions of crystal violet with lyoxide ion and cyanide ion also provide some support for the importance of solvent reorganization. Both of the bases are expected to be considerably more basic in D_2O than in water, and, on this basis alone, we should expect to find that the reactions in D_2O are faster than in water. As pointed out by Robertson,[6] however, D_2O is more structured than is water. The additional energy required for solvent reorganization in heavy water would therefore be expected to decrease both forward and reverse rates of reaction as has been observed for solvolysis reactions.[6] The observed extremely small solvent isotope effects are probably the result of these two compensating factors.

It should be pointed out that the solvent effect discussed above is quite different from that discussed by Parker.[4,21] Parker's interpretation of solvent effects on nucleophilicities stresses the similarity of effects on rates and equilibria as one changes from hydrogen bonding to nonhydrogen bonding solvents. His interpretation places complete emphasis on initial-state solvation. The concept discussed in the present paper does not exclude consideration of this effect, but rather places emphasis on the difference between transition-state and *final-state* solvation. The changes in equilibrium constants on change of solvent observed in the present work are probably partly due to hydrogen bonding to the anionic nucleophiles (see below); *the rate constant changes, however, cannot be explained on this basis alone*, since both forward and reverse rates are affected in the same direction.

The presence of some effect on the rates and equilibria other than hydrogen bonding differences appears to be indicated by a comparison of the change in the equilibrium constant for dissociation of *p*-nitro malachite green azide on going from methanol to dimethyl sulfoxide with the change in the acidity of hydrazoic acid for the same change in solvent. If we assume that the activity coefficient ratio for the carbonium ion to triarylmethyl azide is unaffected by a change from methanol to dimethyl sulfoxide, then we must say that the activity coefficient of azide ion is 120 times greater in dimethyl sulfoxide than in methanol. If this were true, then the difference in the acidity of hydrazoic acid in the two solvents would require that the activity coefficient ratio for the proton and hydrazoic acid be 1200 times smaller in dimethyl sulfoxide than in methanol. Actually, dimethyl sulfoxide is 100 times more basic than methanol in sulfuric acid.[27] Even if the activity coefficient of the proton were 100 times lower in dimethyl sulfoxide, because of this basicity difference, we would also expect that the greater basicity of dimethyl sulfoxide would somewhat reduce the activity coefficient of hydrazoic acid by hydrogen bonding. Actually, from data reported for the acidity of ammonium ions in dimethyl sulfoxide, one can estimate that the activity coefficient ratio for the proton to hydrazoic acid should be about 50.[22] We are thus led to the conclusion that the activity coefficient ratio for the carbonium ion to triarylmethyl azide must be changed by a change of solvent.

We believe that the most reasonable explanation for the change in activities of carbonium ion and covalent product is in terms of the dispersion effect recently discussed by Grunwald.[28] The greater polarizability of dimethyl sulfoxide than that of methanol should result in increased interaction with the carbonium ion relative to that with the covalent product. (The extremely high oscillator strengths of the carbonium ions studied here would make them particularly susceptible to this effect, and would help explain the very great reactivity with the highly polarizable azide ion.) The observations of shifts in the wavelengths of maximum absorbance noted in Tables I–V are consistent with this type of interaction since one would expect the dispersion interaction to be greater in the excited state than in the ground state of the dyes. The wavelengths of maximum absorbance decrease with solvent in the order DMSO $>$ DMF $>$ MeOH $>$ H_2O, which is the expected order for the dispersion effect. It seems probable that this effect is

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[25] See, for example, C. W. Looney and W. T. Simpson, *J. Am. Chem. Soc.*, **76**, 6293 (1954).

[26] E. F. Caldin and J. E. Crooks, paper presented at the American Chemical Society Division of Physical Chemistry, 1965 Summer Symposium on Relaxation Techniques in Chemical Kinetics in Solution, Buffalo, N. Y., June 1965.

[27] E. M. Arnett, *Progr. Phys. Org. Chem.*, **1**, 223 (1963).

[28] E. Grunwald and E. Price, *J. Am. Chem. Soc.*, **86**, 4517 (1964).

primarily responsible for the differences in rates and equilibria between dimethyl sulfoxide and dimethylformamide solvents, since electrostatic effects are expected to be quite similar in the two solvents.

The order of nucleophilicities of hydroxide, azide, and cyanide ion toward the carbonium ions studied here is the reverse of the usual nucleophilicities in SN2 type reactions. In the present work, azide reacts faster than does methoxide, which is faster than cyanide. In typical SN2 reactions, cyanide reacts about eight times faster than hydroxide, and hydroxide reacts about twice as fast as does azide.[29] Apparently, polarizability and the α effect are primary factors in nucleophilicity toward these stabilized carbonium ions. It is also interesting to note that the relative nucleophilicities of azide and cyanide ions are not changed by solvent. Azide ion appears to react at least 10^4 times more rapidly than does cyanide in all of the solvents studied. It also appears, however, that the relative acidities of hydrazoic acid and hydrocyanic acids are not drastically changed by a change of solvent. In water, the difference in p*K*'s is 4.4 units, and in dimethyl sulfoxide, the difference is 5.0 units. One would suspect, therefore, that there is no great difference in the hydrogen bonding of water to azide and cyanide ions. It is apparent, then, that the greater reactivity of azide ion is not due to solvent hydrogen bonding strengths.

Experimental Section

Materials. The tetrafluoroborate salts of malachite green, *p*-nitro malachite green, and crystal violet were prepared as previously described.[12] After extensive recrystallization from water, the compounds exhibited identical spectral properties with those previously reported by us, and in close agreement with those reported by others.[5-14] Elemental analysis of malachite green tetrafluoroborate gave 66.69% C, 6.10% H, and 6.69% N (theoretical for $C_{23}H_{25}N_2BF_4$: 66.4% C, 6.01% H, and 6.73% N).

Triethylamine (Eastman White Label) was used without further purification.

Tribenzylamine was recrystallized from ethanol before use.

Sodium azide (Eastman Practical Grade) was recrystallized several times from ethanol and dried at 120° for several hours. Potentiometric titration of the salt with perchloric acid in methanol solution required 98.5% of the theoretical amount of acid.

Potassium cyanide (Baker Analyzed Reagent) was used without further purification.

Tetraethylammonium cyanide[30] was recrystallized from dry acetonitrile under an argon atmosphere and dried under vacuum at room temperature. Potentiometric titration of the salt with *p*-toluenesulfonic acid in dimethyl sulfoxide solution required precisely the theoretical amount of titrant. The dried salt was stored under argon in a desiccator.

Sodium perchlorate and potassium perchlorate were obtained in reagent grade quality and were used without further purification.

Hydrochloric acid solutions were standardized by potentiometric titration of analytical grade sodium carbonate in water.

Potassium hydroxide solutions were standardized by potentiometric titration of a National Bureau of Standards sample of potassium hydrogen phthalate.

Sodium methoxide solutions were prepared by reacting freshly cut sodium with methanol purified as described below. The solutions were standardized by potentiometric titration with perchloric acid in methanol which, in turn, had been standardized with potassium hydrogen phthalate in methanol.[19] All operations were carried out under an inert atmosphere, and the solutions were stored under argon.

Solvent Purification. All solvents were purified and stored under a dry inert atmosphere. Water was doubly distilled from potassium permanganate.

Methanol was purified by the ion-exchange technique previously described.[19] Potentiometric titration of the solvent with methoxide and with perchloric acid showed much less than 5×10^{-6} *M* acidic or basic impurities. Karl Fisher titration shows less than 10 ppm water present.

Deuterium oxide (Columbia Organic Chemicals Co., 99.5% isotopic purity) was purified by an ion-exchange technique similar to that described for methanol. The solvent used was shown to contain less than 5×10^{-6} *M* acidic or basic impurities, and near-infrared analysis showed better than 99.5% isotopic purity.

Dimethylformamide was dried with molecular sieves and vacuum distilled from phosphorus pentoxide as previously described.[24] Potentiometric titration of the solvent with methanolic sodium methoxide and with picric acid in dimethylformamide reveals less than 5×10^{-6} *M* acidic or basic impurities. Karl Fisher titration shows less than 10 ppm water present. The solvent was used within 48 hr following preparation.

Dimethyl sulfoxide was purified by a procedure furnished by Steiner,[31] in which the solvent is dried with molecular sieves, topped by distillation under vacuum, and finally distilled from freshly prepared potassium amide under vacuum in a rotary evaporator. The distillation temperature is kept well below 50°. The distillate is held under vacuum for several hours to remove traces of ammonia. Potentiometric titration of the solvent with dimsyl ion solutions and with *p*-toluenesulfonic acid in dimethyl sulfoxide[22] shows less than 5×10^{-6} *M* acidic or basic impurities, and Karl Fisher titration shows less than 10 ppm water.

Apparatus. A Cary Model 14 spectrophotometer equipped with a specially designed thermostated cell holder was used to record spectral data and for kinetic measurements on those reactions with half-lives greater than about 1 min. The thermostated cell holder consisted of a brass block through which thermostated water was circulated. Cylindrical spectrophotometer cells of 0.01–10.0 cm fit snugly into a bore of the block. Checks of the temperature of solutions in the cells showed that a temperature variation of less than 0.1° from that of the circulating liquid could be maintained between 5 and 35°.

A Beckman KF3 aquameter was used for the Karl Fisher titrations.

Potentiometric titrations and pH measurements were carried out by the use of either a Beckman 1019 research pH meter for nonaqueous solutions, or a Beckman Model G pH meter for aqueous solutions. Measurements in aqueous solutions utilized a Beckman Type E2 glass electrode and a saturated calomel reference electrode. The electrode systems for use in nonaqueous solutions have been described elsewhere.[19,22,24]

For the study of the kinetics of reactions having half-lives of less than 1 min, a small-scale stop-flow apparatus was used. The apparatus was patterned closely after the one described by Gibson and Milnes.[16] Hamilton Co. gastight syringes (2.5 ml) were used for the driving syringes. Seals between various parts of the apparatus were made with Teflon gaskets kept under pressure. Valve tips and mixing chambers were also fabricated from Teflon. In the finished apparatus, the reaction solutions contact only glass, Teflon, and stainless steel. (It is important that no epoxy seals are used since they are rapidly softened by the solvents used in the present study. Lucite is, of course, also unsuitable for use with these solvents. We have had some indications that Kel-F is attacked to some extent by strongly basic solutions in dimethyl sulfoxide.)

The observation chamber of the apparatus has a 2.0-cm light path 2.0 mm in diameter fitted with Teflon-gasketed quartz windows. This chamber is interchangeable with one with a 2.0-mm light path. The light source is a Bausch and Lomb high-intensity grating monochromator, Model No. 33-86-25-02, with beam condenser, modified to use a GE No. 1958 tungsten-iodine high-intensity lamp, and to operate from a stabilized DC power supply (Electro, Model NFB). A Corning filter, C53-74, was used to remove higher order spectra. Light intensity was measured with a 1P-28 phototube whose output was fed through a cathode follower-emitter (R. W. Dykstra, Sauk Village, Ill.) to an oscilloscope (Tektronix Type 564 MODO8, time base No. 2B67, differential amplified No. 2A63).

Each kinetic run on the stop-flow apparatus requires approximately 0.5–1.0 ml of solution after the apparatus has been thoroughly flushed with the reactants. A total of about 10.0 ml of each reactant solution is generally sufficient for flushing and

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(29) J. O. Edwards and R. G. Pearson, *J. Am. Chem. Soc.*, **84**, 16 (1962).

(30) We are grateful to Drs. S. Andreades and O. Webster of DuPont for a generous sample of this material and for purification procedures.

(31) E. C. Steiner, to be published. We are grateful to Dr. Steiner for permission to quote this procedure.

several measurements. Mixing time in the apparatus is estimated to be less than 5 msec with a good sharp push on the driving block.

The entire valve block, delivery block, driving syringes, and observation chamber are thermostated by circulating water from a constant temperature bath.

Kinetics in Aqueous Solutions. The rates of all the reactions of malachite green and *p*-nitro malachite green, and some of the reactions of crystal violet, with water and hydroxide ion were studied in solutions buffered with triethylamine and its hydrochloride salt. The usual technique was to prepare a solution *ca.* 0.25 M in amine and a separate solution of 0.25 M hydrochloric acid. These solutions were then mixed, with dilution, to produce a solution of the desired pH and a total buffer concentration of *ca.* 10^{-2} M (amine + amine hydrochloride). The solution was then placed in a thermostat set at 25.0°. A measured volume of this solution was then mixed with an equal volume of a thermostated solution of the carbonium ion. One portion of the resulting solution was placed in the spectrophotometer cell and the absorbance of the solution at the wavelength of maximum absorbance of the dye followed with time. The pH of the remaining portion was measured at the start and at the end of the kinetic run. All solutions were kept under a nitrogen atmosphere. The initial dye concentrations ranged from 3×10^{-6} to 5×10^{-5} M.

In the case of crystal violet, a number of runs were made in the high pH region by use of standard solutions of potassium hydroxide. The pH of the solutions was measured as described above.

The second-order rate constants for reactions with hydroxide ion, and the pseudo-first-order rate constants for reaction with water were determined from the slopes and intercepts, respectively, of plots of the observed pseudo-first-order rate constants *vs.* concentration of hydroxide ion. Figures 1, 2, and 3 show the plots obtained. The lines shown in the figures were determined by the method of least squares.

A fivefold increase in buffer concentration was found to cause about a 10% increase in the observed rate at a given pH. We believe that this is due to the presence of small amounts of impurities in the triethylamine.

The effect of inert salts on the rates of the reactions was examined by adding up to 10^{-2} M potassium perchlorate to solutions at constant pH and buffer concentration. No measurable effect was observed for any of the reactions.

The reactions of cyanide ion with the dyes were studied by adding measured quantities of potassium cyanide to solutions containing a constant buffer concentration and a constant pH of 10.61. The rate constant for reaction with cyanide was obtained by subtraction of the pseudo-first-order rate constant observed in the absence of cyanide from that in the presence of cyanide. The effect of inert salts was examined by adding various amounts of potassium perchlorate to solutions of constant pH, buffer, and cyanide ion concentrations. Typical results of these experiments are shown in Table II and Figure 4.

In the aqueous solutions, precipitation of the dyes at salt concentrations much above 10^{-2} M prevented further examination of salt effects. The same factor prevented the study of the reactions of the dyes with azide ion in aqueous solutions. At concentrations of azide about 10^{-2} M, it appeared that there was a slight reaction with *p*-nitro malachite green, but precipitation of the dye was enough of a problem that accurate measurements could not be made. A very rough estimate for the dissociation constant of *p*-nitro malachite green azide in water can be given as 5×10^{-2} M. We would not be surprised, however, if this value is as much as a factor of 10 too low; it is unlikely that it is too high.

Reactions of Crystal Violet in D_2O. The reactions of crystal violet with deuterium oxide and deuterioxide ion in deuterium oxide were studied in unbuffered solutions of sodium deuterioxide. Deuterioxide ion concentrations ranged from 2×10^{-3} to 8.5×10^{-3} M. Treatment of the data was as described for aqueous solutions.

The rate constant for reaction with cyanide ion in D_2O was determined in the same manner as for the reaction in water. The concentration of deuterioxide ion in these runs was 1.61×10^{-3} M.

Reactions in Methanol Solution. The reactions of the dyes with methoxide ion in methanol were studied in unbuffered solutions of sodium methoxide at concentrations between 8×10^{-5} and 7.8×10^{-3} M. The reactions showed half-times of *ca.* 0.1 to 10 sec, and were studied on the stop-flow apparatus. Solutions were prepared and transferred to gastight syringes in an argon-filled glove bag. The gastight syringes fit into adapters on the valve block of the stop-flow apparatus, and transfer of solutions could be accomplished without opportunity for contamination from the atmosphere. The stop-flow apparatus is thoroughly flushed with the reactants by twice filling the driving syringes and emptying through the flow path. The time base of the oscilloscope was adjusted during the flushing operations so that approximately 95% of the reaction was followed on a single trace.

The second-order rate constants obtained for the reactions with methoxide ion were found to decrease with increasing methoxide concentration. Addition of sodium perchlorate to the reaction solutions was also found to retard the rates. The assumption of an ion-pair dissociation constant of 1.03×10^{-2} M for sodium methoxide was found to be consistent with the data. A typical set of data for the reaction of malachite green with methoxide is shown in Table VII.

Table VII. Reaction of Malachite Green with Methoxide Ion in Methanol at 25.0°

$Na,^+$ M $\times 10^3$[a]	OCH_3^-, M $\times 10^3$[b]	k_{obsd},[c] sec^{-1}	10^{-3} $k_{2(obsd)}$[d]	10^{-3} $k_{2(cor)}$[e]
1.56	1.56	1.79	1.15	1.31
0.624	0.624	0.686	1.10	1.17
0.312	0.312	0.378	1.21	1.26
0.156	0.156	0.180	1.15	1.19
2.67	1.56	1.52	0.974	1.20
5.43	1.56	1.18	0.757	1.12
7.80	7.80	6.61	0.848	1.27

[a] Total sodium ion concentration added. [b] Total sodium methoxide concentration. [c] Pseudo-first-order rate constant obtained from plot of log A *vs.* time. [d] Second-order rate constant obtained by dividing k_1 by total sodium methoxide concentration. Units are M^{-1} sec^{-1}. [e] Second-order rate constant obtained by dividing k_1 by the concentration of free methoxide ion calculated from a dissociation constant for the sodium methoxide ion pair of 1.03×10^{-2} M. Units are M^{-1} sec^{-1}.

The reaction of crystal violet with a solution of 7.8×10^{-3} M sodium methoxide and 5.5×10^{-3} M tetraethylammonium cyanide was found to proceed at the same rate as that in the absence of the cyanide.

The reaction of *p*-nitro malachite green with azide ion in methanol was studied in solutions containing 3.12×10^{-4} M sodium methoxide. The reaction with methoxide at this concentration has a half-time of 0.37 sec. It was observed that when sodium azide is added to the solution, the initial absorbance shown on a time scale of 0.2 sec/div on the oscilloscope was decreased from that observed in the absence of azide, and that further decrease in absorbance is slower than in the absence of azide. The changes in initial absorbance with changes in azide concentration observed in these traces gave an equilibrium constant of $6.2\ (\pm 0.3) \times 10^{-4}$ M for the dissociation constant of the triarylmethyl azide.

In the absence of azide ion, a decrease in absorbance from 1.310 to 1.191 is observed in the first 50 msec of reaction of *p*-nitro malachite green with the 3.12×10^{-4} M methoxide solution. It was, therefore, possible to observe the reaction of azide with the dye, without appreciable interference from the simultaneous reaction with methoxide, by the following general technique.

The vertical scale of the oscilloscope was adjusted so that 0.0–0.20 v corresponded to 0–100% transmittance. A trace of the reaction was then obtained on the usual time scale (usually 0.2–0.5 sec/div) and the initial transmittance noted. The vertical oscilloscope base was then adjusted to 20 mv for full-scale deflection, and the time base was adjusted to 5–10 msec/div. The base-line output was adjusted by means of a vernier control incorporated into the emitter follower circuit so that the zero line on the oscilloscope corresponded to the previously observed initial transmittance. A second trace of the same reactants was then obtained. From this latter trace, the second-order rate constant for the reaction of azide could be obtained by the usual method for pseudo-first-order reversible reactions. A typical example of the traces obtained is shown in Figures 5 and 6. The two traces in Figure 6 are for consecutive traces on the same reactants. The flat portion of the fast traces represents the portion of continuous flow immediately preceding the stop.

In attempts to measure the reaction of malachite green with sodium azide in methanol, it was found that sodium azide concentrations up to 1.26×10^{-2} M caused no decrease in the initial absorbance of the dye, and that the rate of reaction with methoxide

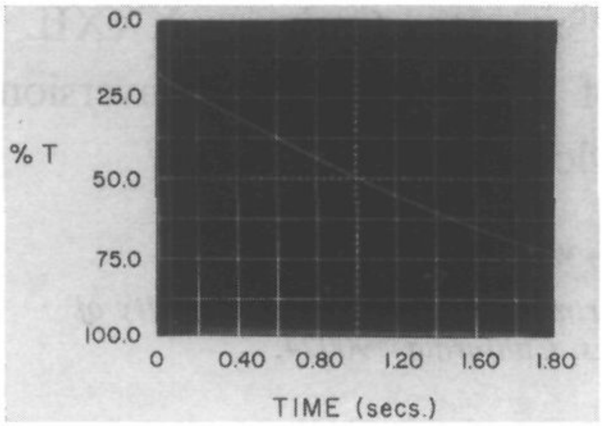

Figure 5. Oscilloscope trace for slow time scale of reaction of *p*-nitro malachite green with methoxide ion in methanol in the presence of azide ion.

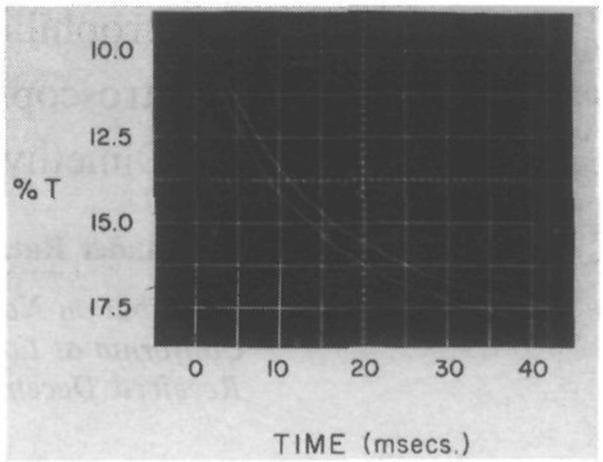

Figure 6. Oscilloscope trace for fast time scale of reaction of *p*-nitro malachite green with azide ion in methanol.

was affected only to the extent calculated for the effect of the added sodium ion on the formation of sodium methoxide ion pair.

Reactions of crystal violet with azide ion in methanol were not attempted.

Reactions of Cyanide and Azide in Dimethylformamide and Dimethyl Sulfoxide. The general technique for the study of reactions in dimethylformamide and in dimethyl sulfoxide was as follows. Master solutions of the dye (*ca.* 10^{-5} *M*) and of the salt (sodium azide or tetraethylammonium cyanide) were prepared by weighing the sample on a Cahn electrobalance and dissolving in a measured volume of the solvent. The reactions were studied in a manner analogous to that described above for methanol solutions. All reactions were performed under pseudo-first-order conditions, and tenfold ranges of concentrations of nucleophiles were studied to verify the order of the reactions.

For the azide reactions in both dimethylformamide and dimethyl sulfoxide, the solutions had reached equilibrium before stopping, even in the lowest concentrations of azide which would cause measurable changes in absorbance. Consistent values for the equilibrium constants were obtained over a range of azide concentrations in every case. Minimum values for the forward rate constants were calculated on the basis of mixing requiring 5 msec, and that the reactions were 75% complete in this time. Actually, absolutely no change in absorbance could be observed in any case, and the reaction was quite probably more than 95% complete within 5 msec. Thus, the lower limits reported in Tables IV and V are very conservative values.

In dimethyl sulfoxide solution, reaction of crystal violet with 10^{-3} *M* azide solutions could not be detected. The limited solubility of sodium azide in *pure* dimethyl sulfoxide[23] prevented studies at higher concentrations.

The reactions of the dyes with cyanide ion in both solvents were found to be complete at the concentrations of 10^{-4} to 10^{-3} *M* cyanide which were studied.

We have found that the slightest contamination of dimethyl sulfoxide or dimethylformamide solutions of cyanide by exposure to the atmosphere results in drastically reduced rates of reactions with the dyes.

Since dimethyl sulfoxide is known to carry various materials in solution through the skin, extreme caution should be exercised in handling solutions of azide or cyanide in this solvent. We have used rubber gloves in handling containers with these solutions, and have taken special pains to clean up thoroughly after each experiment.

p*K* Measurements in Nonaqueous Solvents. The measurements of p*K* values for various acids reported in the results section have been carried out by methods described in other papers from our laboratories.[19,20,22,24]

Acknowledgments. Although primary financial support of this work was through the Army Research Office (Durham), as acknowledged in footnote 1, we also wish to express our gratitude to the National Science Foundation (GP-2635) and the Public Health Service (GM12832) for grants supporting other phases of our work which resulted in many of the solvent purification techniques, p*K* measurement methods, and in construction of the stop-flow apparatus, which were necessary parts of the present research project. In addition, thanks are due to Mr. Htain Win for preparation of the carbonium ion salts and some early exploratory measurements in nonaqueous solutions; to Mr. G. H. Megerle for help in the purification of dimethylformamide; and to Mr. R. E. Uschold for help in the purification of dimethyl sulfoxide. We are also grateful to Professor R. G. Wilkins for helpful discussions on the construction of the stop-flow apparatus.

The Cary Model 14 spectrophotometer used in the present work was purchased through Grant No. GM-11036 from the Public Health Services. The Graduate School, State University of New York at Buffalo, furnished funds for the purchase of the Beckman KF3 aquameter.