caps and attached to a flat fused-silica esr cell. The appropriate volume of 10 M sodium hydroxide was then placed in the remaining arm and both solutions were deoxygenated using nitrogen for 10–20

min. The solutions were then mixed (total volume 2 ml) and the appropriate gas was bubbled or syringed into the system. Spectra were recorded on either a Varian E-3 or 4500 esr spectrometer.

Cation–Anion Combination Reactions. VIII.[1]
Reactions of Tropylium Ions in Methanol Solution

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Abstract: Rate and equilibrium constants for the reactions of tropylium ion and of several aryltropylium ions with nucleophiles in methanol solution have been determined by stop-flow spectrophotometry. The pK_R values, rate constants for reaction with methanol, and rate constants for reaction with methoxide ion, respectively, for the cations studied are tropylium ion, 2.15, 150 sec^{-1}, —; phenyltropylium ion, 2.92, 71 sec^{-1}, 1.8 × 10^8 M^{-1} sec^{-1}; p-chlorophenyltropylium ion, 2.30, 92 sec^{-1}, 1.9 × 10^8 M^{-1} sec^{-1}; p-methoxyphenyltropylium ion, 4.09, 13 sec^{-1}, 6.8 × 10^7 M^{-1} sec^{-1}; p-dimethylaminophenyltropylium ion, 6.68, 0.22 sec^{-1}, 2.3 × 10^6 M^{-1} sec^{-1}. The reactions of all of these cations with azide ion reached equilibrium at rates too fast to measure by our techniques. Equilibrium constants for formation of the aryltropyl azides are phenyltropylium ion, 1.8 × 10^6 M; p-chlorophenyltropylium ion, 4.8 × 10^6 M; p-methoxyphenyltropylium ion, 8.8 × 10^5 M; p-dimethylaminophenyltropylium ion, 1.9 × 10^3 M. The reaction rates of all of the cations with thiophenoxide ion are very nearly diffusion controlled. In the case of p-dimethylaminophenyltropylium ion the equilibrium and rate constants for formation of the thiophenyl ether are 9.1 × 10^8 M and 6.4 × 10^9 M^{-1} sec^{-1}, respectively. Although the reactivities of these cations differ greatly from those of Malachite Green derivatives, the selectivities of the different cations are the same.

The work leading to the present series of papers was initiated in an effort to understand the peculiar order of nucleophilic reactivities observed toward derivatives of Malachite Green cations.[2] An initial hypothesis that the order of reactivity is characteristic of any cation–anion combination reaction has been tested by studies of aryldiazonium ion reactions. These studies indeed provided substantial support for the hypothesis.[3]

In order to provide additional data bearing on the question of nucleophilic reactivity in cation–anion combination reactions, we then turned our attention to a third class of cations, the tropylium and aryltropylium ions. The immediately preceding paper of this series[1a] detailed our studies of the reactions of these cations in aqueous solution. The present paper reports the results of the conclusion of our studies of the tropylium ions, detailing the reactions with several nucleophiles in methanol solution.

Results

The pK_R values and the rate constants for reactions of the cations with methanol and with methoxide ion are reported in Table I. In the cases of the p-dimethylaminophenyltropylium ion and the p-methoxyphenyltropylium ion, the use of dichloroacetic acid–dichloroacetate and trichloroacetic acid–trichloroacetate buffers, respectively, furnished pH ranges in which the

(1) (a) Previous paper in this series: C. D. Ritchie and H. Fleischhauer, *J. Amer. Chem. Soc.*, **94**, 3481 (1972). (b) This work was supported by Grant GM-12832 from NIH-PHS and Grant GP-29164 from National Science Foundation.
(2) C. D. Ritchie, G. A. Skinner, and V. G. Badding, *ibid.*, **89**, 2063 (1967).
(3) C. D. Ritchie and P. O. I. Virtanen, *ibid.*, **94**, 1589 (1972).

Table I. Reactions of Cations in Methanol at 23 ± 1°

Cation	pK_R	k_{MeOH} sec^{-1}	k_{MeO} M^{-1} sec^{-1}
p-(CH$_3$)$_2$NC$_6$H$_4$C$_7$H$_6^+$	6.68	0.22	2.3 × 10^6
p-CH$_3$OC$_6$H$_4$C$_7$H$_6^+$	4.09	13	6.8 × 10^7
C$_6$H$_5$C$_7$H$_6^+$	2.92	71	1.8 × 10^8
p-ClC$_6$H$_4$C$_7$H$_6^+$	2.30	92	1.9 × 10^8
C$_7$H$_7^+$	2.15	1.5 × 10^2	
p-Nitro(MG)^a	6.79^b	5.4 × 10^{-4}	6.0 × 10^{3b}

^{a} p-Nitro(Malachite Green), bis(p-dimethylaminophenyl)-p-nitrophenylmethyl cation. ^{b} Data from ref 2.

equilibria could be studied by techniques analogous to those previously reported for aqueous solutions.[1a] For all of the other cations, however, the pK_R values are so low that we were forced to use dilute solutions of perchloric acid and treat the data according to the Benesi–Hildebrand equation to obtain values for K_R and the molar absorptivities of the cations.

Rate constants were obtained at pH high enough that the reactions were complete and corrections for the reverse rates were not necessary. Measurements over a range of pH established the expected relationship: $k_{obsd} = k_{MeOH} + k_{MeO}\text{-}(MeO^-)$, where k_{obsd} is the observed pseudo-first-order rate constant at a given pH.

Previously reported data for the reaction of p-nitro-(Malachite Green) with methanol and methoxide ion[2] are also shown in Table I. The rate constant for reaction of p-nitro(Malachite Green) with methanol was determined in the present study, using techniques analogous to those for the tropylium ions.

In our studies of the reactions of the tropylium ions with azide ion in methanol, we have succeeded in mea-

Table II. Reactions of Cations with Azide and Thiophenoxide Ions in Methanol at 23 ± 1°

Cation	$K_{N_3}{}^a$	$k_{N_3}{}^b$	$K_{PhS}{}^c$	$k_{PhS}{}^d$
p-(CH₃)₂NC₆H₄C₇H₆⁺	1.9 × 10³	>2 × 10⁵	9.1 × 10³	6.4 × 10⁹
p-CH₃OC₆H₄C₇H₆⁺	8.8 × 10⁵	>9 × 10⁷		
C₆H₅C₇H₆⁺	1.8 × 10⁶	>1 × 10⁸		
p-ClC₆H₄C₇H₆⁺	4.8 × 10⁶	>2 × 10⁸		
p-Nitro(MG)ᵉ	1.6 × 10³	6.2 × 10⁴	1.6 × 10⁶	9.4 × 10⁶

[a] Units of M^{-1}, formation constant of product from azide ion. [b] Second-order rate constant for formation of azide product, units of M^{-1} sec⁻¹. [c] Formation constant of thiophenyl ether, units of M^{-1}. [d] Second-order rate constant for formation of thiophenyl ether in units of M^{-1} sec⁻¹. [e] p-Nitro(Malachite Green). Data from ref 2 and 3.

Table III. Relative Rate and Equilibrium Constants for Cation–Anion Combination Reactions

Cation	$K_{MeO}/K_{OH}{}^a$	$k_{MeO}/k_{OH}{}^b$	$K_{PhS}/K_{OH}{}^c$	$k_{PhS}/k_{OH}{}^d$
p-(CH₃)₂NC₆H₄C₇H₆⁺	3.8 × 10³	1.3 × 10³	2.0 × 10²	3.8 × 10⁶
p-CH₃OC₆H₄C₇H₆⁺	3.8 × 10⁴	1.7 × 10³		
C₆H₅C₇H₆⁺	7.2 × 10⁴	2.3 × 10³		
p-ClC₆H₄C₇H₆⁺	1.5 × 10⁵	1.4 × 10³		
p-Nitro(MG)ᵉ	4.2 × 10	1.1 × 10³	5.0 × 10⁻³	1.7 × 10⁶

[a] Equilibrium constants for reactions with methoxide ion in methanol and hydroxide ion in water. [b] Rate constants for reactions with methoxide ion in methanol and hydroxide ion in water. [c] Equilibrium constants for reactions with thiophenoxide ion in methanol and with hydroxide ion in water. [d] Rate constants for reactions with thiophenoxide ion in methanol and with hydroxide ion in water. [e] p-Nitro-(Malachite Green). Data from ref 3.

suring equilibrium constants, but not the rate constants. In all cases where azide ion concentration was high enough to form measurable amounts of product, the reactions were complete before the first observation. Lower limits on the rate constants can be calculated from the assumption that mixing time is ca. 2 msec. The reactions were necessarily studied at pH where reaction of the cations with solvent is a complicating feature, but this reaction is enough slower than the azide reaction that approximate corrections can be applied, except in the case of tropylium ion. The differences in the initially observed absorbances of the cations in the presence and absence of azide ion showed the expected dependence on azide ion concentration and allowed the calculation of the equilibrium constants. In the cases of the phenyl- and p-chlorophenyl-substituted ions, the reaction with solvent is fast enough that a significant amount of this reaction occurs before observation is possible, and this could cause an error of as much as 20% in the calculation of the equilibrium constants for the azide reactions. The data obtained are reported in Table II.

Because of the very rapid formation of methyl ethers at the pH required for study of thiophenoxide ion reactions, we were able to study only p-dimethylaminophenyltropylium ion reacting with this anion. The data are reported in Table II.

Attempts to study reactions of the tropylium ions with cyanide ion in methanol and with azide and cyanide ions in dimethyl sulfoxide solutions were unsuccessful. The reactions with cyanide ion in methanol were too slow to be observed in the presence of the reactions to form methyl ethers, and the cations in dimethyl sulfoxide appeared to react with the traces of water (ca. 10 ppm) which could not be eliminated.

Discussion

The present data considered along with previously reported data on reactions of the tropylium ions in water[1a] and on reactions of other cations in water and methanol lead to some interesting conclusions on reactivity–selectivity relationships and on the nature of the transition states for cation–anion combination reactions. Some of the pertinent combined data are shown in Table III.

The relative rate and equilibrium constants for reactions of hydroxide ion in water and methoxide ion in methanol with the various cations are even more striking than our previous data in showing the constant selectivity of cations toward entirely different nucleophilic systems. Reasonably assuming that hydroxide and methoxide have nearly the same steric requirements, and that the solvation of alcohol vs. methyl ether products does not depend on the structure of the cation, the variations in the equilibrium constant ratios for methoxide and hydroxide reactions for the various cations must be attributed to differences in the solvation of the cations. Since the rate constant ratio is independent of the cation, then, we must conclude that the solvation of the cationic moiety at the transition states for the reactions is not seriously disturbed from that of the reactant cation.

In the case of the thiophenoxide ion reactions, we believe that there is a steric destabilization of the thiophenyl ether of p-nitro(Malachite Green) relative to that of the aryltropylium ions which affects the equilibrium constant, but obviously does not affect the rate constant since the rate ratio for thiophenoxide and hydroxide ion reactions in the case of p-nitro(Malachite Green) is very close to that in the case of the aryltropylium ions. The evidence for the steric effect in the case of thiophenoxide ion equilibrium is based on a comparison of the relative equilibrium constants for p-nitro(Malachite Green) and p-dimethylaminophenyltropylium ion reacting with methoxide ion, azide ion, and thiophenoxide ion, all in methanol solution. The equilibrium constant for reaction of azide ion in methanol with p-dimethylaminophenyltropylium ion is very nearly the same as that for the reaction with p-nitro-(Malachite Green), as shown in Table II. Similarly, in Table I, we see that the equilibrium constants for reaction of methoxide ion with these two cations are

nearly the same. With thiophenoxide ion, however, the equilibrium constant for reaction with p-nitro(Malachite Green) is more than two powers of ten smaller than that for reaction of p-dimethylaminophenyltropylium ion.

Since this steric effect does not affect the rate constant for the reaction of p-nitro(Malachite Green) with thiophenoxide ion, we must conclude that the cationic and anionic moieties have not approached each other closely enough at the transition state for crowding to begin. This conclusion is in accord with, and virtually required by, the previous conclusion that cationic solvation at the transition state is not far different from that of the reactant cation.

The above conclusions begin to lead to a description of the transition state which sounds suspiciously like a solvent-separated ion pair. The following paper in this series[4] contains a more complete discussion based on all of our accumulated data on cation–anion combination reactions.

Experimental Section

Materials. The tropylium and aryltropylium salts used in the present study were available from the earlier work.[1a]

Dichloroacetic acid and triethylamine were commercial products distilled before use. Sodium azide, thiophenol, chloroacetic acid, and trichloroacetic acid were commercial products used without further purification.

Methanol was purified by the ion-exchange technique described in earlier work.[5] Stock solutions of potassium methoxide were prepared by treating freshly cut potassium with methanol under an argon atmosphere. Anhydrous perchloric acid in methanol was prepared by ion-exchange techniques previously described[5] and the solutions were stored at −20°. The acid and base solutions were standardized as previously described.[5]

All operations were carried out under an argon atmosphere using glove bags and gas tight syringes for transfers of reagents.

Equipment. The stop-flow apparatus has been described in previous papers.[2] Reactions were carried out in an air conditioned room maintained at $23 \pm 1°$. A Cary Model 14 spectrophotometer was used for the equilibrium constant determinations.

Determination of pK_R Values in Methanol. In the cases of p-methoxyphenyltropylium and p-dimethylaminophenyltropylium ions, solutions of the cations in dilute perchloric acid and in buffers of trichloroacetic acid–potassium trichloroacetate (for p-methoxyphenyltropylium ion), or dichloroacetic acid–potassium dichloroacetate (for p-dimethylaminophenyltropylium ion), were prepared and the absorbances of the solutions measured. The calculations of the pH of the solutions were made from the known concentrations of added acid and potassium methoxide and the pK values of

the buffer acids in methanol: 6.41 for dichloroacetic acid and 4.98 for trichloroacetic acid.[6] Ionic strength was kept below 2.0×10^{-3} M, but was not maintained constant. The calculation of the pK_R values was analogous to the previous determinations in aqueous solution.[1a]

The equilibrium constants for tropylium, phenyltropylium, and p-chlorophenyltropylium ions could not be made in buffer solutions of reasonable ionic strength because of the low pK_R values for these cations. In these cases, the spectra were obtained in dilute solutions of perchloric acid, ranging in concentration from 5×10^{-4} to 1×10^{-2} M. The pK_R values were calculated from Benesi–Hildebrand plots of $1/(H^+)$ vs. the reciprocal of the observed absorbance.

Kinetic Measurements. Reactions of the cations with methanol were studied in buffers of chloroacetic acid–chloroacetate (for p-dimethylaminophenyltropylium ion), dichloroacetic acid–dichloroacetate (all four other cations), or trichloroacetic acid–trichloroacetate (for the three least stable cations). In all cases, the buffer ratio was adjusted so that the reverse reaction contributed no more than a few per cent to the observed rate.

Reactions of the tropylium ions with methoxide ion were carried out in buffers prepared by partial neutralization of triethylamine ($pK = 10.88$[2]) with perchloric acid. Subtraction of the previously determined rate constant for methanol reaction from the observed rate constant at known pH allowed the calculation of the second-order rate constants for methoxide reaction. The reaction of tropylium ion with methanol was so fast, and the spectral changes so small, that we were not able to obtain a reliable value for the rate constant for methoxide reaction.

In both series of rate measurements, the ionic strength was kept below 3×10^{-3} M, but was not maintained constant. No variation with ionic strength beyond experimental error was observed for any of the determinations.

Except in the case of p-dimethylaminophenyltropylium ion, the reactions with azide ion were studied in dichloroacetic acid–dichloroacetate buffers. Equilibrium constants were calculated from the differences in absorbances of the cations in methanol and in azide solutions as initially observed on the stop-flow traces. Variations in absorbances with variations in azide ion concentrations were consistent with those expected from the equilibrium expression.

For p-dimethylaminophenyltropylium ion, the azide solutions were buffered by partial neutralization of sodium azide with perchloric acid. The calculations of the equilibrium constants utilized the pK_a value of 8.91 previously reported for hydrazoic acid in methanol.[2] Ionic strength was maintained at 2.0×10^{-3} M.

The reaction of p-dimethylaminophenyltropylium ion with thiophenoxide ion was studied in solutions buffered with dichloroacetic acid–dichloroacetate. The value of 11.27 for the pK_a of thiophenol in methanol at ionic strength of 1.7×10^{-3} M, which we had previously reported,[3] was used in the calculation of the rate and equilibrium constant.

Reaction of p-nitro(Malachite Green) with methanol was determined by the same techniques used for p-dimethylaminophenyltropylium ion, except that the reaction was slow enough to be followed by conventional spectrophotometry using the Cary Model 14 spectrophotometer.

(4) C. D. Ritchie and P. O. I. Virtanen, *J. Amer. Chem. Soc.*, **94**, 4966 (1972).

(5) C. D. Ritchie and P. D. Heffley, *ibid.*, **87**, 5402 (1965).

(6) These values were determined in our laboratories by Mr. A. Lopata using techniques previously described in ref 5.