23 was prepared by pyrolysis, under the usual conditions, of impure **21** (110 mg, prepared by path b above) which yielded, after $AgNO_3$ tlc (benzene), 88 mg of product. Preparative vpc gave a sample: mp 76–76.5°; nmr δ ($CDCl_3$) 3.08 (t, $J = 7.5$ Hz, 2 H), 5.95–6.7 (m, 4 H), 6.95–7.80 (m, 6 H); ir 3.27, 3.29, 3.38, 3.42, 7.45, 9.12, 9.88 μ; uv λ_{max} (log ϵ) 243 (4.41), 325 (3.84); mass spectrum m/e (%) 194 (P + 2, 3), 193 (P + 1, 12), 192 (P, 80), 191 (P − 1, 100), 165 (90); exact mass (using the intense P − 1 peak) 191.0867 (calcd for $C_{15}H_{11}$, 191.0860).

1,8-Divinylnaphthalene (18) was prepared by the method of Mitchell and Sondheimer[22] in 79% yield, mp 43–45° (methanol), lit. 47–47.5°.

Cyclic voltammetry experiments were performed on a Princeton Applied Research Model 1170 electrochemistry system, using a Sargent-Welch sce reference electrode and a hanging mercury drop working electrode. The solvent was dimethyl sulfoxide dried over Linde 4A molecular sieves, containing 0.1 *M* tetrabutylammonium perchlorate (MCB). We did not correct for ir drop, and ΔE_p values of 68–80 mV were observed at the 200-mV/sec scan rates employed.

Esr spectra were simulated using a program similar to Stone and Maki,[23] but modified (originally by Professor J. Harriman) to plot on a Calcomp plotter and employ a Univac 1108 computer for calculations. The values quoted in Table I are those used in the simulations which best fit the experimental spectra. Splittings were calibrated with Fremy's salt.

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[22] R. H. Mitchell and F. Sondheimer, *Tetrahedron*, **24**, 1397 (1968).

[23] E. W. Stone and A. H. Maki, *J. Chem. Phys.*, **38**, 1999 (1963).

Cation–Anion Combination Reactions. XI. Reactions of Cations with Amines[1]

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Abstract: The reactions of a wide variety of amines, and of sulfite and hypochlorite ions, with triarylmethyl, tropylium, and aryldiazonium ions in aqueous solution have been studied using stop-flow spectrophotometry. With the exceptions of methoxylamine and hydrazine, all of the nucleophiles studied show constant selectivities toward the various cations. Thus, these nucleophiles follow the relationship: $\log k_n = N_+ + \log k_0$, which we have previously shown to correlate the rates of cation–anion combination reactions. Values of N_+ newly assigned are: glycine, 4.95; ethylenediamine, 5.04; hydrazine, 5.60; ethylamine, 4.88; glycylglycine, 4.28; phenylhydrazine, 4.36; glycine ethyl ester, 3.99; 2-ammonioethylamine, 3.94; semicarbazide, 3.32; methoxylamine, 3.96; 2,2,2-trifluoroethylamine, 3.04; hydroxylamine, 4.95; diethylamine, 5.87; piperidine, 6.25; methylhydrazine, 5.70; hydroperoxide ion, 8.4; hypochlorite ion, 7.0; and sulfite ion, 7.6. With an extensive range of nucleophiles for which we now have N_+ values, it is possible to examine the application of the correlation of reactivities of reactions of carbonyl compounds. We find that the reactions of acetoxy- and acetylpyridinium ions with nucleophiles are excellently correlated by the N_+ values.

The previous papers in this series[1a] have described the results of our studies of the reactions of nucleophiles with aryldiazonium ions, tropylium ions, and triarylmethyl cations. The entire body of rate data was shown to be well correlated by

$$\log k_n/k_0 = N_+ \tag{1}$$

where k_n is the rate constant for reaction of a given nucleophilic system (*i. e.*, a given nucleophile in a given solvent) with a cation, k_0 is a constant characteristic only of the cation, and N_+ is a parameter characteristic of the given nucleophilic system independent of the cation. Values of N_+ were obtained by setting $N_+ = 0$ for water in water, and by the use of *p*-nitro(Malachite Green) as the standard cation.

All of the reactions were studied under closely analogous conditions of low ionic strength and 23°. Most of the nucleophiles studied were mononegative ions, only water and methanol being included as examples of neutral nucleophiles.

The purpose of the present work is to extend our studies to include nucleophiles of various charge type, particularly amines, and to initiate an attempt to extend eq 1 to reactions of electrophiles other than simple organic cations. For the latter purpose, we shall utilize the extensive data which have been reported by Jencks[2] for the reactions of nucleophiles with carbonyl compounds.

Bruice[3] has recently reported studies of the reactions of primary amines with Malachite Green [bis(*p*-dimethylaminophenyl)phenylmethyl cation] in aqueous solution. The use of high ionic strength (1.0 *M*) and a temperature of 30°, unfortunately, made direct comparisons with our studies somewhat uncertain.

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[1] (a) Previous paper in this series: C. D. Ritchie and P. O. I. Virtanen, *J. Amer. Chem. Soc.*, **94**, 4966 (1972); see also C. D. Ritchie, *Accounts Chem. Res.*, **5**, 348 (1972). (b) This work was supported by Grant GP-29164 from National Science Foundation, and by Grant GM-12832 from National Institutes of Health, U. S. Public Health Service.

[2] W. P. Jencks and M. Gilchrist, *J. Amer. Chem. Soc.*, **90**, 2622 (1968).

[3] J. E. Dixon and T. C. Bruice, *ibid.*, **93**, 3248 (1971).

We have repeated the study of these reactions under conditions analogous to those of our earlier work and have extended the study to the reactions of amines and sulfite ion with tropylium ion, *p*-dimethylaminophenyltropylium ion, *p*-nitro(Malachite Green) [bis(*p*-dimethylaminophenyl)-*p*-nitrophenlymethyl cation], and several aryldiazonium ions.

Results

The rate and equilibrium constants determined in the present study are reported in Table I.

The reactions of amines are represented by

$$R^+ + BH \rightleftarrows RB + H^+ \qquad (2)$$

where BH is a primary or secondary amine. Details of the reactions are discussed individually for each of the cation classes below. All of the reactions were studied by stop-flow spectrophotometry under pseudo-first-order conditions. The use of excess amine allowed us to use the amine–conjugate acid pair as a buffer in the solutions for the amine reactions. Ionic strength of the solutions was determined by the concentration of the ammonium ion salt present in the buffer. Studies of the dependence of rate on amine concentration were carried out by varying the concentration of amine while keeping the concentration of conjugate acid constant.

Reactions of Triarylmethyl Cations. The reactions of Malachite Green and of *p*-nitro(Malachite Green) with primary amines are found to be accurately first order with respect to amine concentration in all cases. Under the conditions used, the reactions of the cations with water and hydroxide ion were negligibly slow, and the observed rates were independent of pH.

The extents of reactions of the cations were dependent on amine concentration and hydroxide ion concentration as expected from eq 2. Since R is electron withdrawing relative to hydrogen, the product RB is expected to be less basic than the reactant BH. Bruice[3] has determined the p*K*'s of several of the products of the Malachite Green reactions and confirms this expectation. Under the conditions used in our experiments, with the solutions buffered at a pH close to the p*K* of the conjugate acid of the reactant amine, there will be negligible protonation of the products except in the special cases discussed below. The measurement of the extent of reaction of the cation at "infinite" time, then, allows the direct calculation of the equilibrium constant for eq 2 from the known pH and amine concentration.

The measurement of the equilibrium constants is complicated in the cases of amines whose conjugate acids have p*K*'s of less than *ca.* 6. The product, RB, contains dimethylamino groups which have basicities very nearly equal to that of dimethylaniline[4] (p*K* of conjugate acid = 5.2). Thus, at pH lower than *ca.* 6, the dimethylamino groups will be significantly protonated. In our studies, this consideration applies only in the two cases of reactions of semicarbazide and of methoxylamine. In these cases, we have assumed a p*K* value of 5.2 for the dimethylammonio groups in order to calculate the equilibrium constants for eq 2.

Because of the small equilibrium constants expected for the reactions of Crystal Violet [tris(*p*-dimethyl-

Table I. Rate and Equilibrium Constants for Reactions of Nucleophiles with Cations According to Eq 2 (23°)

Nucleophile	k, M^{-1} sec^{-1}	K	Ionic strength, M
Malachite Green			
Glycinate	9.0	1.0×10^{-8}	8×10^{-2}
	$(8.6)^a$	$(2.3 \times 10^{-8})^a$	1.0
Ethylenediamine	1.1×10	2.8×10^{-8}	5×10^{-3}
	$(1.8 \times 10)^a$		1.0
Hydrazine	4.0×10		5×10^{-2}
	$(6.2 \times 10)^a$	$(5.3 \times 10^{-6})^a$	1.0
Ethylamine	7.6	1.8×10^{-8}	5×10^{-3}
	$(1.6 \times 10)^a$	$(1.4 \times 10^{-8})^a$	1.0
Glycylglycinate	1.9	2.8×10^{-8}	5×10^{-2}
	$(2.2)^a$	$(2.0 \times 10^{-8})^a$	1.0
Phenylhydrazine	2.3	2.1×10^{-5}	5×10^{-2}
	$(6.5)^a$		1.0
Glycine ethyl ester	9.7×10^{-1}	8.1×10^{-9}	1×10^{-1}
	$(9.3 \times 10^{-1})^a$	$(1.3 \times 10^{-8})^a$	1.0
EthylenediamineH$^+$	8.7×10^{-1}	3.7×10^{-8}	4×10^{-1}
Semicarbazide	2.1×10^{-1}	1.2×10^{-5}	7×10^{-1}
	$(6.0 \times 10^{-1})^a$	$(3.3 \times 10^{-5})^a$	1.0
Methoxylamine	9.1×10^{-1}	3.2×10^{-5}	5×10^{-1}
	$(1.2)^a$		1.0
2,2,2-Trifluoroethylamine	1.1×10^{-1}	4.3×10^{-8}	1×10^{-2}
	$(1.4 \times 10^{-1})^a$		1.0
Methylhydrazine	2.0×10	$<10^{-7}$	4×10^{-1}
substd N	$(3.2 \times 10)^a$		1.0
Unsubstd N	2.3	4.0×10^{-7}	5×10^{-2}
Sulfite ion	4.0×10^{3}	$>10^{6}$	1×10^{-3}
	$(2.8 \times 10^{2})^b$		1.0
Hypochlorite ion	1.0×10^{3}		5×10^{-4}
	$(5.0 \times 10)^b$		1.0
p-Nitro Malachite Green			
Hydrazine	4.1×10	3.3×10^{-5}	1×10^{-2}
Methoxylamine	9.4×10^{-1}		2×10^{-2}
Glycylglycinate	2.2	3.5×10^{-7}	3×10^{-2}
Sulfite ion	1.1×10^{4}		1×10^{-3}
Crystal Violet			
Sulfite ion	4.7×10^{2}	8.0×10^{3}	1×10^{-3}
p-Dimethylaminophenyltropylium Ion			
Piperidine	1.0×10^{5}		1×10^{-3}
Diethylamine	4.2×10^{4}		3×10^{-3}
Methylhydrazine	3.0×10^{4}		1×10^{-2}
Glycinate	5.1×10^{3}	7.8×10^{-6}	5×10^{-3}
Ethylenediamine	3.8×10^{3}		3×10^{-3}
Hydrazine	3.0×10^{3}		5×10^{-2}
Ethylamine	2.8×10^{3}		3×10^{-3}
Glycylglycinate	1.3×10^{3}	7.5×10^{-6}	3×10^{-3}
Phenylhydrazine	5.7×10^{2}	2.3×10^{-4}	1×10^{-2}
Glycine ethyl ester	5.4×10^{2}	7.5×10^{-6}	5×10^{-3}
EthylenediamineH$^+$	2.1×10^{2}	1.2×10^{-5}	1×10^{-1}
Semicarbazide	8.0×10	6.0×10^{-5}	1×10^{-1}
Methoxylamine	4.4×10	3.5×10^{-4}	2×10^{-1}
2,2,2-Trifluoroethylamine	4.2×10	2.3×10^{-6}	2×10^{-2}
Sulfite ion	9.6×10^{5}		1×10^{-3}
Tropylium Ion			
Hydrazine	3.0×10^{5}		3×10^{-3}
Glycylglycinate	1.4×10^{5}		2×10^{-3}
Glycine ethyl ester	2.8×10^{4}		3×10^{-3}
EthylenediamineH$^+$	2.5×10^{4}		5×10^{-3}
Semicarbazide	7.3×10^{3}		3×10^{-3}
Methoxylamine	4.7×10^{3}		1×10^{-2}
2,2,2-Trifluoroethylamine	7.3×10^{3}		1×10^{-3}
p-Nitrobenzenediazonium Ion			
Sulfite ion	4.5×10^{8}		1×10^{-3}
p-Cyanobenzenediazonium Ion			
Sulfite ion	4.3×10^{8}		1×10^{-3}
p-Chlorobenzenediazonium Ion			
Sulfite ion	2.4×10^{7}	5.1×10^{5}	1×10^{-3}
		$(2.7 \times 10^{5})^c$	1.0

[a] Values obtained at 30°; see ref 3. [b] Value obtained at 30°; see ref 5. [c] From ref 7.

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[4] C. D. Ritchie, E. S. Lewis, and W. F. Sager, *J. Amer. Chem. Soc.*, 84, 2349 (1962).

aminophenyl)methyl cation] with amines, we have not attempted to study the reactions of this cation.

High precision in the measurements of equilibrium constants was not attempted. At worst, the observed precision was ±50% and was usually considerably better. We believe that the values reported in Table I are accurate to better than a factor of 2.

Second-order rate constants determined over a range of amine concentrations (generally one-third to three times the ionic strengths shown in Table I) showed a precision of *ca.* ±10%, and there is no reason to believe that the accuracies of the values reported in the table are any worse.

Rate and equilibrium constants for the reactions of amines with Malachite Green at 30° and 1.0 *M* ionic strength, reported by Bruice,[3] are shown in Table I for comparison with the values obtained in the present study. Bruice reports activation enthalpies of *ca.* 9 kcal/mol for these reactions. This leads us to expect that the rate constants at 30° will be *ca.* 45% higher than those at 23°. Consideration of this effect, as well as the differences in ionic strength, brings the results into quite reasonable agreement.

Attempts to study the reactions of piperidine and diethylamine with Malachite Green were unsuccessful. At the high pH required for the study of these reactions, the reaction with hydroxide ion was a complicating factor. The observed rates of disappearance of Malachite Green in the presence of the amines were only slightly greater than could be attributed to the hydroxide ion reaction, and no break in the kinetic traces, expected for equilibrium formation of amine product, could be seen. We believe that the equilibrium constants for the reactions of secondary amines with Malachite Green are too small to observe at reasonable concentrations of amines.

The reaction of Malachite Green with methylhydrazine is somewhat complex. At high concentrations of methylhydrazine, there is a fast reaction that nearly reaches equilibrium before significant incursion of an ensuing slower reaction. Both reactions are first order with respect to methylhydrazine concentration. The rate constant for the fast reaction is *ca.* 20 M^{-1} sec^{-1}, and that for the slower reaction is 2.3 M^{-1} sec^{-1}. At lower concentrations of methylhydrazine, only the slower reaction is observed, and an equilibrium constant of 4×10^{-7} was determined for this reaction. A reasonable interpretation of these data, which is also consistent with other data to be reported below, is that the first reaction involves addition of Malachite Green to the methyl-substituted nitrogen, and the second, slower but more favorable, reaction involves addition to the unsubstituted nitrogen. We have not, however, subjected this hypothesis to further tests.

Bruice[3] studied the rate and equilibrium for the reaction of methylhydrazine with Malachite Green in separate experiments. The rate studies utilized high concentrations of amine, and the equilibrium studies utilized lower concentrations of amine and allowed longer time before observation. A rate constant of 32 M^{-1} sec^{-1} and an equilibrium constant of 1.6×10^{-7} are reported for 30°. Considering the temperature difference, as discussed above, Bruice's value for the rate constant is in good agreement with our value for the faster reaction, and his value for the equilibrium constant is in good agreement with our value for the slower reaction.

The unusually high rate and equilibrium constants found for the "α-effect" amines, and commented on by Bruice,[3] led us to question whether the products of the reactions of these amines are the same as those for other amines and other nucleophiles which we have previously studied. Although such a reaction has not been observed for Malachite Green, the occurrence of nucleophilic aromatic attack would not be highly surprising. We have, therefore, closely examined the spectra of the products of the reactions of hydrazine and of methoxylamine with Malachite Green. The spectra from 260 to 400 nm are virtually superimposable on the spectrum of Malachite Green carbinol. We conclude that the products are analogous to those for reactions of Malachite Green with other nucleophiles.

The reactions of sulfite ion with triarylmethyl cations were studied in unbuffered solutions of sodium sulfite. Some difficulty was encountered in these solutions, apparently resulting from a slow decomposition of sulfite ion. The addition of *ca.* 10^{-5} *M* hydroquinone to the solutions eliminated the problem, and we were able to obtain consistent second-order rate constants over a range of sulfite ion concentrations. Control experiments showed that the cations did not react with the hydroquinone under the reaction conditions.

Bruice[5] has reported a rate constant of 2.8×10^2 M^{-1} sec^{-1} for the reaction of sulfite ion with Malachite Green at 30° and 1.0 *M* ionic strength. If this rate is "corrected" to infinite dilution by use of the Debye-Hückel limiting law ($\log \gamma_\pm = -1.1$) for the activity coefficient of a 2:1 salt, we obtain a value of 3.0×10^3 M^{-1} sec^{-1}, in reasonable agreement with our value of 4.0×10^3 M^{-1} sec^{-1} at 23° and 10^{-3} *M* ionic strength.

The reaction of hypochlorite ion with Malachite Green was studied by methods analogous to those reported by Bruice.[5] The reactions were carried out in unbuffered solutions of sodium hypochlorite used immediately after preparation from a concentrated master solution. Use of hypochlorite concentrations from 5×10^{-2} to 5×10^{-4} *M* gave reasonably constant values of the second-order rate constant. At 23° and an ionic strength of *ca.* 10^{-3} *M*, we obtain a value of 1.0×10^3 M^{-1} sec^{-1}. Bruice reports a value of 50 M^{-1} sec^{-1} at 30° and 1.0 *M* ionic strength. We do not presently understand the source of the large discrepancy in these measurements.

Reactions of Tropylium Ions. The study of the reactions of *p*-dimethylaminophenyltropylium ion followed closely along the lines discussed above for the reactions of Malachite Green. The accuracies of the rate constants reported in Table I are estimated at ±10%, and those for the equilibrium constants at better than a factor of 2, as above. The reactions of methylhydrazine and of secondary amines showed none of the complicating factors found in the reactions of Malachite Green.

The fast reaction of tropylium ion with hydroxide ion allowed us to study only reactions of this cation with weakly basic amines.

Reactions of Aryldiazonium Ions. The reactions of aryldiazonium ions with amines are known to produce

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(5) J. E. Dixon and T. C. Bruice, *J. Amer. Chem. Soc.*, **93**, 6592 (1971).

triazenes.[6] The triazenes derived from reactions of primary amines may tautomerize or may react with another mole of diazonium ion to produce bisdiazoamines.[6] Although we were hopeful that the first step of these reactions could be observed kinetically, the hope was not borne out. Observations of the disappearance of the absorption of the diazonium ion, or of the appearance of absorption at longer wavelengths, around 310 nm, gave kinetic traces with rate increasing with time. The curves could not be simulated by analog computation programmed for a scheme involving formation of a single unstable intermediate.

We, therefore, turned our attention to the reactions of secondary amines which are not expected to be quite so complex. In accordance with this expectation, we isolated a product from the reaction of benzenediazonium ion with diethylamine which was identified as the expected triazene on the basis of its nmr spectrum. The ultraviolet spectrum of the product shows two strongly overlapping peaks with maxima at 285 and 313 nm. Attempts to study the equilibrium constant for formation of the product were frustrated by the incursion of a side reaction at low amine concentrations which produced absorption at 400–430 nm, and a loss of absorption due to diazonium ion and triazene. Stop-flow experiments showed that the rate of production of absorption at 400 nm, when it occurs, is the same as the rate of the loss of absorption at 261 nm, the wavelength of maximum diazonium ion absorption.

At higher concentrations of amine, no absorption at 400 nm is produced even after several hours. The kinetics of disappearance of absorption at 261 nm, or of the appearance of absorption at 310 nm, using amine concentrations above 10^{-3} M, show good first-order behavior. The reaction is not, however, first order with respect to amine concentration. At amine concentrations from 5×10^{-2} to 1×10^{-1} M, the rate is nearly independent of amine concentration. At lower amine concentrations, the rate appears to become close to first order with respect to amine, but the incursion of the above mentioned side reaction prevents studies over a wide enough range to verify this behavior.

Kinetic studies of the reaction of *p*-chlorobenzenediazonium ion with diethylamine were complicated by a fast equilibrium reaction of the diazonium ion with hydroxide ion at the pH required for the studies. Under conditions such that the equilibrium formation of diazotate consumed only a small fraction of the diazonium ion, we were able to observe a slower subsequent reaction with a first-order rate constant of 3×10^{-1} sec^{-1}, independent of amine concentration in the range from 1×10^{-3} to 7×10^{-3} M.

On the basis of the above observations, we have decided that the probability of obtaining the desired rate constants for the simple combination step, with any reasonable effort, is small. We have, therefore, abandoned our study of these reactions.

Lewis[7] reported studies of the reactions of aryldiazonium ions with sulfite ion. Using conventional spectrophotometry, the equilibrium constants for formation of *syn*-diazosulfonates and the rates for syn–anti isomerization and reduction of the product by sulfinate ion were measured.[7] The rate of formation of the *syn*-diazosulfonates was instantaneous on the time scale of conventional spectrophotometry, however.

We have studied the rates of formation of *syn*-diazosulfonates in acetate buffered solutions of sodium sulfite from *p*-nitro-, *p*-cyano-, and *p*-chlorobenzenediazonium ions using stop-flow spectrophotometry. The formation of *syn*-diazosulfonate is so fast in all cases that no interference by the further reactions reported by Lewis[7] is observed. In the case of the reaction of *p*-chlorobenzenediazonium ion, we have measured the equilibrium constant for the reaction, and find reasonable agreement with the value reported by Lewis. The results are shown in Table I.

Discussion

In our previous studies, we have emphasized the constancy of selectivities of cations of widely varying reactivities toward nucleophiles, as embodied in eq 1. The pertinent rate ratios found in the present study are shown in Table II along with previously reported data for the reactions of water and hydroxide ion. Also shown, for contrast, are the equilibrium constant ratios.

Table II. Rate and Equilibrium Constant Ratios for Cation–Nucleophile Reactions in Water

Nucleophile	k_{DT}[a]	R_{DT}^{T}[b]	R_{MG}^{DT}[c]	R_{PNMG}^{DT}[d]	K_{MG}^{DT}[e]
Sulfite ion	9.6×10^5		240	87	
Glycinate	5.1×10^3		570		920
Ethylenediamine	3.8×10^3		350		
Ethylamine	2.8×10^3		370		
Hydroxide ion	1.7×10^3	160	770	304	0.33
Glycylglycinate	1.3×10^3	110	680	590	270
Phenylhydrazine	5.7×10^2		250		11
Glycine ethyl ester	5.4×10^2	52	560		920
EthylenediamineH$^+$	2.1×10^2	120	240		320
Semicarbazide	8.0×10	91	380		5
$CF_3CH_2NH_2$	4.2×10	170	380		
Hydrazine	3.0×10^3	100	75	73	
Methoxylamine	4.4×10	107	49	47	11
Water	2.0×10^{-2}	140	95	110	0.33

[a] Rate constants for reactions of *p*-dimethylaminophenyltropylium ion, M^{-1} sec^{-1}. [b] Rate constant ratios for tropylium and *p*-dimethylaminophenyltropylium ions. [c] Rate constant ratios for *p*-dimethylaminophenyltropylium and Malachite Green ions. [d] Rate constant ratios for *p*-dimethylaminophenyltropylium and *p*-nitro(Malachite Green) ions. [e] Equilibrium contant ratios for *p*-dimethylaminophenyltropylium and Malachite Green ions.

The rate ratios shown in Table II, with the exceptions of those for reactions of hydrazine, methoxylamine, and water, are remarkably constant and are in good agreement with those that we have previously found for the reactions of other nucleophiles with these cations.[1a] The reactions of sulfite ion are also in accord with eq 1, and the constancy of rate ratios for such widely different cations as aryldiazonium and triarylmethyl ions is even more striking. For example, the rate ratios for reactions of hydroxide ion and sulfite ion, $k_{SO_3^{2-}}/k_{OH^-}$, for the various cations are: *p*-dimethylaminophenyltropylium ion, 560; *p*-nitro(Malachite Green), 2000; Malachite Green, 1800; Crystal Violet, 2300; *p*-nitrobenzenediazonium ion, 800; *p*-cyanobenzenediazonium ion, 1100; and *p*-chlorobenzenediazonium ion, 1700. The absolute rate constants for reactions of

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[6] H. Zollinger, "Azo and Diazo Chemistry," Wiley-Interscience, New York, N. Y., 1961.

[7] E. S. Lewis and H. Suhr, *Chem. Ber.*, **92**, 3031 (1959).

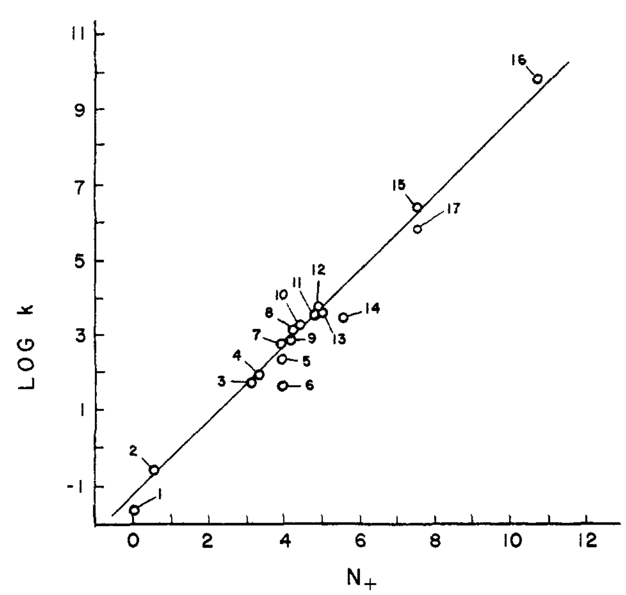

Figure 1. Rates of reactions of *p*-dimethylaminophenyltropylium ion plotted according to eq 1. The points are identified as follows: (1) H_2O; (2) CH_3OH; (3) 2,2,2-trifluoroethylamine; (4) semicarbazide; (5) 2-ammonioethylamine; (6) methoxylamine; (7) glycine ethyl ester; (8) glycylglycine; (9) phenylhydrazine; (10) hydroxide ion; (11) ethylamine; (12) glycine; (13) ethylenediamine; (14) hydrazine; (15) methoxide ion (in methanol solution); (16) thiophenoxide ion (in methanol solution); (17) sulfite ion.

Crystal Violet and *p*-nitrobenzenediazonium ion with any given nucleophile differ by six powers of ten.

In his discussion of the reactions of amines with Malachite Green, Bruice[3] has focused attention on the fact that all of the "α-effect" amines show both greater rate and equilibrium constants for their reactions than do other amines of similar basicity. He concludes that the "α-effect" on rates stems from the same source as the effect on equilibria. The data shown in Table II do not bear out this similarity in rate and equilibrium behaviors of "α-effect" amines. Both semicarbazide and phenylhydrazine show equilibrium constant ratios for reaction with *p*-dimethylaminophenyltropylium ion and Malachite Green which are close to that shown by methoxylamine. The rate constant ratios for semicarbazide and phenylhydrazine, however, are similar to those for "normal" amines, and quite different from those for methoxylamine and hydrazine.

There is a great deal of evidence that the equilibrium constants for reactions of Malachite Green with nucleophiles are quite sensitive to steric effects. Some of this evidence has been discussed in previous papers.[1a] In the present study, the small equilibrium constants found for the reactions of secondary amines, and the behavior of methylhydrazine, with Malachite Green provide further confirmation of the importance of such steric effects. The extremely small equilibrium constant ratio for the formation of carbinols from Malachite Green and *p*-dimethylaminophenyltropylium ion, shown in Table II, can also be most reasonably ascribed to small steric effects relative to other nucleophiles.

It seems most likely, then, that the small equilibrium constant ratios for the reactions of all of the "α-effect" amines with Malachite Green and *p*-dimethylaminophenyltropylium ion result from less steric strain in the products of the Malachite Green reactions with these amines than in those from reactions with "normal" amines. This effect, however, does not influence the rates of reactions of semicarbazide, hydrazine, or hydroxide ion with Malachite Green. Thus, it seems unlikely that the small rate constant ratios found for reactions of hydrazine, methoxylamine, and water with the two cations can be attributed to steric effects. We can offer no rational explanation for the deviant behavior of these three nucleophiles.

In order to evaluate N_+ for the nucleophiles involved in the present study, we make use of eq 3

$$\log k_n^{MG} = -4.00 + N_+ \qquad (3)$$

where k_n^{MG} is the rate constant for the reaction of Malachite Green with the nucleophilic system having N^+ as its nucleophilic parameter. The constant, −4.00, was evaluated from our earlier studies.[1a] The values of N_+ from eq 3 are shown in Table III. Also included in the table are N_+ values for several additional nucleophiles whose rates of reactions with Malachite Green have been determined by Bruice.[5]

Table III. N_+ Values from Eq 3

Nucleophile	Log k_n^{MG}	N_+
Glycinate	0.95	4.95
Ethylenediamine	1.04	5.04
Hydrazine	1.60	5.60
Ethylamine	0.88	4.88
Glycylglycinate	0.28	4.28
Phenylhydrazine	0.36	4.36
Glycine ethyl ester	−0.01	3.99
EthylenediamineH^+	−0.06	3.94
Semicarbazide	−0.68	3.32
Methoxylamine	−0.04	3.96
$CF_3CH_2NH_2$	−0.96	3.04
SO_3^{2-}	3.6	7.6
Hydroxylamine[a]	0.8[a]	4.8
Hydroperoxide ion[b]	4.4[b]	8.4
Hypochlorite ion	3.0	7.0

[a] Reference 5 reports log k = 0.95 at 30°. The value at 23° is estimated as 0.15 unit lower, as discussed in text. [b] Reference 5 reports log k = 4.11 for hydroperoxide ion, and 1.70 for hypochlorite ion, both at 1.0 M ionic strength and 30°. Values shown in this table are "corrected" to zero ionic strength by the limiting Debye-Hückel expression, and to 23° as discussed in text.

The correlation of the rates of reactions of *p*-dimethylaminophenyltropylium ion by eq 1 is shown in Figure 1. The correlation is excellent, and even the deviation of the points for reactions of hydrazine, methoxylamine, and water, discussed above, are small in comparison to the range of 12 powers of ten in rate constants included in the plot.

We have presented arguments and evidence, which we believe to be quite strong, that the N_+ values are measures of the energies required to desolvate the nucleophiles, with the higher N_+ values associated with lower energies required.[1a] Hydroxide ion is a special case, apparently functioning as a general base in the reaction of the cation with water.[8] General base catalysis has not been observed for the reactions of the amines in the present study, although it is possible that a small general base-catalyzed component could have escaped detection.

In the previous paper of this series, we suggested that the differences in reactivities of the various cations

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[8] C. D. Ritchie, *J. Amer. Chem. Soc.*, **94**, 3275 (1972).

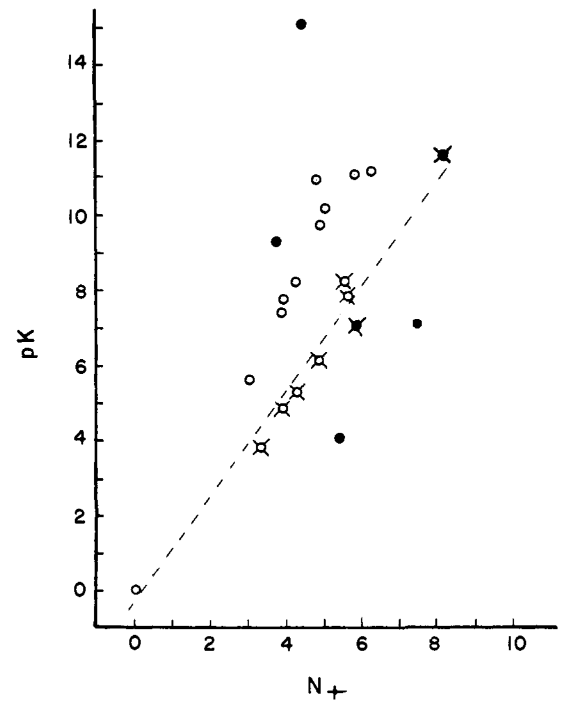

Figure 2. N_+ values plotted *vs.* p*K*: (●) anions, (○) amines, and (×) "α-effect" nucleophiles. Values are from Table III and ref 1a.

likely resulted from electrostatic effects. The present data, which show that positively charged, neutral, negatively charged, and dinegatively charged nucleophiles all give constant rate ratios for the various cations, casts considerable doubt on that suggestion. At the present time, however, we can offer no alternative that is consistent with the existing data.

The independence of relative reactivities of the wide variety of nucleophiles on the nature of the cation, found in both earlier and the present studies, strengthens our earlier arguments that the N_+ values are measures of some inherent property of the nucleophiles. We still believe that this inherent property is most rationally identified as the energy required to partially desolvate the nucleophile.

We have commented[1a] on the absence of any correlation between N_+ values and any previously discussed measures of nucleophilic reactivity.[9] In the past, because of the lack of any generally applicable measure of nucleophilic reactivity, many investigators have discussed reactivities in comparisons with Brønsted basicities, frequently limiting discussion to closely similar structures of nucleophiles.[2] Figure 2 shows a plot of N_+ *vs.* p*K* for the nucleophiles whose reactions we have studied in aqueous solution.

The plot is clearly a scatter diagram when all classes of nucleophiles are considered together. Some order may be perceived when only limited classes, such as primary amines, are considered. One interesting point to note in Figure 2 concerns the "α-effect" nucleophiles. It is most curious that the points for all such nucleophiles, including both neutral and ionic reagents, define a reasonably good straight line (dotted line in Figure 2) which passes through the point for water. This may be pure coincidence, but in view of the similarities in behavior of water, hydrazine, and methoxylamine toward the cations in the present study, already discussed above, it is, at least, a striking observation.

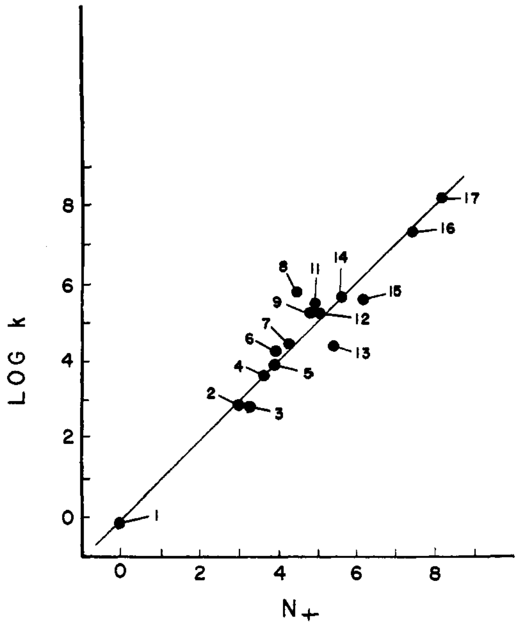

Figure 3. Rates of reactions of 1-acetoxy-4-methoxypyridinium perchlorate plotted according to eq 1. Points are identified as follows: (1) H_2O; (2) 2,2,2-trifluoroethylamine; (3) semicarbazide; (4) cyanide ion; (5) $H_2NCH_2CH_2NH_3^+$; (6) glycine ethyl ester; (7) glycylglycine; (8) hydroxide ion; (9) ethylamine; (10) glycine; (11) hydroxylamine; (12) ethylenediamine; (13) azide ion; (14) hydrazine; (15) piperidine; (16) methoxide ion; (17) hydroperoxide ion.

Several of the perplexing points which we have discussed here are the subjects of further research in our laboratories. At the present time, we would like to turn attention to the possible application of eq 1 to nucleophilic reactivities with carbonyl compounds.

Since N_+ values are derived from reactions in which relative rates are believed to be governed by desolvation of the nucleophiles, the arguments may be turned around to suggest that reactions in which desolvation of nucleophiles is the dominant factor in determining relative rates will be correlated by eq 1, and *vice versa*. The argument, coupled with the realization that desolvation of reagents is a necessary step for most reactions in solution,[10] leads to the hope that eq 1 might be useful in the identification and evaluation of factors other than desolvation in reactions where such factors are important. We begin to explore the possibilities using the extensive data which have been reported by Jencks and Gilchrist[2] for the reactions of esters with nucleophiles in aqueous solution.

The correlation of the rates of reactions of 1-acetoxy-4-methoxypyridinium perchlorate (AMPP) with nucleophiles is shown in Figure 3. The N_+ values for piperidine and diethylamine, 6.25 and 5.87, respectively, were obtained from the rates of reactions of these amines with *p*-dimethylaminophenyltropylium ion and the correlation is shown in Figure 1. Other N_+ values are either from Table III or from our earlier work.[1a]

With the exceptions of the points for hydroxide ion and azide reactions, the correlation is remarkably good.

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(9) R. G. Pearson, H. Sobel, and J. Songstad, *J. Amer. Chem. Soc.*, **90**, 319 (1968).

(10) C. D. Ritchie in "Solute-Solvent Interactions," J. F. Coetzee and C. D. Ritchie, Ed., Marcel Dekker, New York, N. Y., 1969.

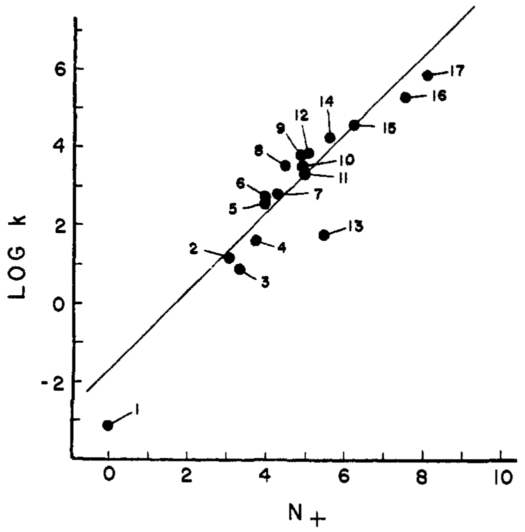

Figure 4. Rates of reactions of 2,4-dinitrophenylacetate plotted according to eq 1. Point identification is the same as that in Figure 3.

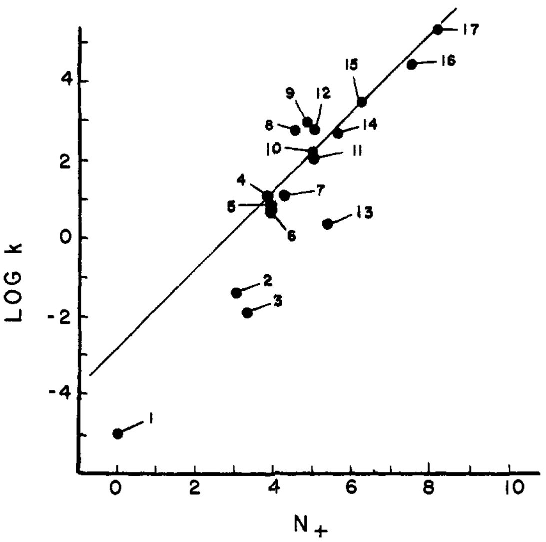

Figure 5. Rates of reactions of p-nitrophenylacetate plotted according to eq 1. Point identification is the same as that given in Figure 3.

Data correlated include anions, neutral, and "α-effect" reagents. The correlation is so good, in fact, that we suspect that the two deviant points indicate some fundamental differences in the reactions of these reagents from others.

Fersht and Jencks[11] have studied the rates of reactions of nucleophiles with several acetylpyridinium ions and have noted that plots of the logs of the rates of reactions of these compounds *vs.* those for reactions of 1-acetoxy-4-methoxypyridinium ion give good straight lines *with unit slope.* Thus, the reactions of the acetylpyridinium ions with nucleophiles are also correlated by eq 1. The rate of reaction of 1-acetoxy-4-methoxypyridinium ion with any given nucleophile is slower by a factor >300 than the rate for 1-acetyl-4-methylpyridinium ion with the same nucleophile.

Figure 4 shows the plot of the data for reactions of 2,4-dinitrophenylacetate according to eq 1. Although the quality of the correlation is not as good as that of Figure 3, it is still quite good considering the range of structural variation of nucleophiles included. It is important to note again that the slope of the line shown in each of the figures is the unit slope line required by eq 1.

Figure 5 shows the plot of the data for reactions of p-nitrophenylacetate according to eq 1. The overall correlation is rather poor, but it appears that the data for reactions of water, semicarbazide, trifluoroethylamine, and azide ion nearly define a separate line of unit slope. It may be pertinent that these are the four weakest Brønsted bases involved in the study.

A number of possibilities concerning mechanism are suggested by the correlations of these reactions, but we resist, for the present time, the temptation to speculate further. We are content, at this time, that the excellent correlation of the reactivities of nucleophiles with acetoxy- and acetylpyridinium ions, and the reasonable correlation of the data for reactions of 2,4-dinitrophenylacetate, indicate the general utility of eq 1 in approaching the problem of nucleophilic reactivities.

Experimental Section

Materials. The preparation of the carbonium ion and diazonium ion salts has been described in earlier papers.[1a] Commercial samples of ethylamine hydrochloride, ethylenediamine hydrochloride, glycine, glycylglycine, hydrazine sulfate, methylhydrazine sulfate, glycine ethyl ester hydrochloride, phenylhydrazine hydrochloride, and methoxylamine hydrochloride were recrystallized from ethanol-water mixtures and dried *in vacuo* over P_2O_5. Commercial piperidine was distilled at atmospheric pressure, neutralized with hydrochloric acid in ethanol-water solution, precipitated by addition of acetone, collected, and dried *in vacuo* over P_2O_5. Diethylamine (Baker AR), semicarbazide hydrochloride (Baker AR), and 2,2,2-trifluoroethylamine (Columbia Organic Chemicals) were commercial samples used without further purification. Water was distilled under argon.

Water, reagents, and solutions were kept under an argon atmosphere after preparation.

Equipment. The stop-flow spectrophotometer used in this work has been described previously.[1a] Conventional spectrophotometric studies utilized a Cary Model 14 spectrophotometer. All measurements were carried out in an air-conditioned room maintained at 23 ± 1°.

Kinetic and Equilibrium Studies. The details of the measurements were similar to those which we have described previously.[1a] A weakly acidic solution of the cation in water was mixed with an equal volume of the nucleophile solution in the stop-flow apparatus. The reactions were followed at the wavelengths of maximum absorption of the cations. Amine solutions were prepared by dissolving either the amine or amine salt in water and partially neutralizing by the addition of either hydrochloric acid or sodium hydroxide. The pH of the solutions were calculated from the known[3] pK's of the conjugate acids of the amines and the buffer ratio prepared. Solutions of sulfite ion were prepared for reactions with the triarylmethyl and tropylium ions by dissolving sodium sulfite in unbuffered solution containing *ca.* 10^{-5} M hydro-

Table IV. Reaction of Benzenediazonium Ion with Diethylamine

$[ArN_2^+]_0$	λ	[Amine]	$[OH^-]$	k_{obsd}, sec^{-1}
2.2×10^{-5}	310	8.9×10^{-2}	1.1×10^{-2}	3.08
2.2×10^{-5}	310	4.2×10^{-2}	7.7×10^{-3}	2.71
2.2×10^{-5}	310	6.9×10^{-3}	3.1×10^{-3}	1.29
2.6×10^{-5}	261	3.0×10^{-3}	2.0×10^{-3}	0.51
2.6×10^{-5}	310	3.0×10^{-3}	2.0×10^{-3}	0.50
2.6×10^{-5}	261	3.2×10^{-4}	6.8×19^{-4}	0.086[a]
2.6×10^{-5}	310	3.2×10^{-4}	6.8×10^{-4}	0.10[a]
2.4×10^{-5}	310	1.1×10^{-4}	3.9×10^{-4}	0.046[a]

[a] In these reactions, and several at lower amine concentrations, absorption at 400–430 nm is produced; see Results section.

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(11) A. R. Fersht and W. P. Jencks, *J. Amer. Chem. Soc.*, **92**, 5442 (1970).

quinone. Sulfite solutions for reactions with diazonium ions were prepared in acetic acid buffers, and the concentration of sulfite ion was calculated from the known pH of the buffer and p*K* of hydrosulfite ion. All rates were studied over at least a tenfold range of concentrations of nucleophile, and many over a 100-fold range.

In the measurements of equilibrium constants, the change in absorbance of the cations at high and low concentrations of added nucleophile were measured to determine the extent of reaction of the cation at low nucleophile concentration. The equilibrium constants were calculated as described in the Results section.

Reaction of Benzenediazonium Ion with Diethylamine. Aqueous solutions of benzenediazonium ion and diethylamine, both at 0.03 *M*, were mixed in equal volumes. After several minutes, dilute sodium hydroxide was added to the solution, and the product was extracted into ether. Evaporation of the ether at room temperature left a brownish oil. Gas chromatography on Carbowax at 210° showed a single peak which has retention time different from diethylamine, biphenyl, and azobenzene.

The nmr spectrum in carbon tetrachloride solution exhibited a triplet at δ 1.3, a quartet at 3.8, and a multiplet at 7.4, with relative intensities of 6:4:5, respectively. The ultraviolet spectrum of the oil showed strongly overlapping bands with maxima at 285 and 313 nm.

The kinetics of the reaction were followed by techniques analogous to those described above for reactions of other cations. The results are summarized in Table IV.

Cationic Olefin Complexes of Copper(I). Structure and Bonding in Group Ib Metal–Olefin Complexes

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Contribution No. 2157 from the Department of Chemistry, Indiana University, Bloomington, Indiana 47401. *Received July 20, 1972*

Abstract: A variety of new structural types of cationic copper(I)–olefin complexes have been isolated and characterized. The nmr spectrum of the olefin changes with coordination to copper(I). An analysis of the chemical shifts indicates that the nature of the olefin–metal bond varies predictably with the number and the geometric arrangement of the coordinated C═C bonds. The bonding in olefin complexes of other group Ib metals is also discussed in the light of these results.

Olefin complexes of copper(I) salts are known for a variety of olefinic ligands, but these complexes, with few exceptions, have been limited to copper(I) halides.[1-3] The presence of halide, however, limits the range of π-olefin structures possible, since it is extensively involved as a bridging ligand between copper(I) nuclei, and the resultant polynuclear copper(I) halide clusters often dominate the structures. Furthermore, copper(I) and nickel(0) are isoelectronic, yet despite the number of polyolefin complexes of nickel(0) that are extant, there are few isostructural analogs of copper(I) halide.[2,4] Competition between halide ions and olefin or ligand sites on copper(I) is no doubt an important factor in determining the stability of these complexes.

Salts of copper(I) with noncoordinating anions are generally considered to be unstable due to the tendency of copper(I) to disproportionate to copper(II) and copper metal. We have found that benzene, a rather weak π ligand, provides sufficient stabilization of copper(I) to allow its isolation as a stable crystalline trifluoromethanesulfonate (triflate) salt **1**,[5] which is an excellent reagent for the preparation of cationic olefin complexes of copper(I).

We wish to report a general method for the preparation and the properties of a wide variety of new structural types of copper(I)–olefin complexes. The use of the poorly coordinating triflate anion allows these cationic complexes to be readily soluble in organic solvents in contrast to other previously known complexes.[6,7] Their unique solubility and stability thus enable structural studies to be carried out by nuclear magnetic resonance (nmr). For example, the olefin–metal bond is pictured in the Dewar–Chatt model as consisting of σ and π components, the relative contributions of which vary from one complex to another.[8] Analysis of the changes in the olefin nmr spectra which occur on coordination can be employed to deduce factors which influence the contributions from σ and π components in a variety of olefin–copper(I) complexes. These results are compared with the bonding in other group Ib metal–olefin complexes involving silver(I) and gold(I).

Results and Discussion

Benzene–Copper(I) Triflate. A crystalline, air-sensitive complex of copper(I) triflate and benzene [$(CuOTf)_2C_6H_6$] can be isolated from the reaction of trifluoromethanesulfonic anhydride with copper(I) oxide in benzene. This colorless copper(I)–benzene complex is stable to about 100° when heated carefully in a sealed evacuated tube. Benzene is released quantitatively from **1** only when heated above 120°. Complex **1** probably has a structure with local C_{2h} symmetry about the benzene ring analogous to that found in the 1:1 benzene–$AgClO_4$ complex.[9] One of the degenerate highest occupied molecular orbitals of benzene which

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