For trimethylsilylbenzene as a representative example the 1:1 stoichiometry of the CT complexes was demonstrated by a Benesi–Hildebrand[36] plot of the concentration dependence of the CT extinction: the equilibrium constant K of the 1:1 complex I_2–trimethylsilylbenzene amounts to 0.287 l./mole, the molar extinction ϵ_m is 9800 l./mole cm. The corresponding values for the TCNE–trimethylsilylbenzene complex are K = 0.275 l./mole and ϵ_m = 2850 l./mole cm.

The CT band analysis was based on CT band contours observed in CT spectra in which CT bands I and II were well separated. The CT band shapes fulfill reasonably eq 10 given by Briegleb and Czekalla[37] in which the wave number $\tilde{\nu}_l$ corresponds to the longer wavelength absorption, $\tilde{\nu}_h$ to the shorter wavelength absorption with $\epsilon = \epsilon_m/2$, and $\tilde{\nu}_h$ to the CT band maximum.

$$\frac{\tilde{\nu}_h - \tilde{\nu}_l}{2(\tilde{\nu}_m - \tilde{\nu}_l)} \approx 1.2 \qquad (10)$$

Ionization Energies. Ionization potentials were determined using a Krupp Mat CH4 mass spectrometer equipped with a Fox ion source.[38] The values obtained in addition to the ionization energies of monosubstituted benzene derivatives published in ref 12 are given in Table VI. They were also used for calculating the regression $IE/\tilde{\nu}_m{}^{CT}$ (Figure 1).

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[36] H. A. Benesi and J. H. Hildebrand, *J. Amer. Chem. Soc.*, **71**, 2703 (1949).

[37] G. Briegleb and J. Czekalla, *Z. Phys. Chem.*, **24**, 37 (1960).

[38] R. I. Reed, "Mass Spectroscopy," Academic Press, London, 1965.

Concerning the Reactivity of Amines toward Carbonium Ions Derived from Ortho Esters[1]

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Abstract: First-order rate constants for decomposition of a series of *para*-substituted methyl orthobenzoates in aqueous solutions of semicarbazide, methoxyamine, and hydroxylamine are independent of amine concentration under conditions in which substantial fractions of the ortho esters yield amine adducts as products. Analysis of product composition as a function of amine concentration indicates that products are derived from the partitioning of the carbonium ion derived from ortho ester between amine, generating an amine adduct as product, and water, generating the carboxylic ester as product. Relative rate constants for attack of amine and water on such carbonium ions are correlated by a single straight line in a Brønsted plot with a slope of 0.4. This slope is independent, within experimental error, of the nature of the polar substituent in the parent ortho ester. The mode of partitioning of the tetrahedral intermediate generated from the addition of methoxyamine to the carbonium ion derived from methyl orthobenzoate does not depend on the concentration of an acetate buffer.

Reaction of amines with ortho esters appears to be a rather general process. Both early and recent developments relevant to such reactions have been reviewed.[3,4] Largely as a result of the efforts of Roberts and his associates, it is clear that reaction of simple amines with ortho esters may generate either imidates or amidines depending on substrate structure, the ratio of reactants, and the presence or absence of acid catalysts.[5–7] Reactions of more complicated amines yield a variety of products including heterocycles.[4]

In addition to their synthetic value, the reaction of amines with ortho esters has, in one case, provided evidence relevant to the mechanism of hydrolysis of the latter species. Fullington and Cordes observed that rate constants for decomposition of methyl orthobenzoate in aqueous solutions of semicarbazide and hydroxylamine are independent of amine concentration even though substantial amounts of amine-derived reaction products were formed.[8] This finding corroborated earlier suggestions, based on a variety of experimental approaches, that ortho esters hydrolyze by a pathway not involving the participation of solvent as a nucleophilic reagent in the transition state.[9]

In this investigation, we have extended our earlier studies to examine both the influence of basicity on rate constants for reaction of amines with ortho ester derived carbonium ions and the influence of carbonium ion stability on their selectivity to nucleophilic attack by amines.

Experimental Section

Materials. Methyl ortho-*p*-hydroxybenzoate, methyl ortho-*p*-methoxybenzoate, methyl ortho-*p*-methylbenzoate, methyl orthobenzoate, methyl ortho-*p*-chlorobenzoate, and methyl ortho-*p*-nitrobenzoate were prepared and purified as described elsewhere.[10] Organic amines were recrystallized or redistilled before use with the following exceptions: hydrazine, 97% (anhydrous), which was obtained from Matheson Coleman and Bell, and 2,2,2-trifluoroethylamine hydrochloride, which was obtained from Pennisular Chemresearch Co., were used without further purification. Sub-

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[1] Supported by Grant No. 08232 from the National Institutes of Health.

[2] Career Development Awardee of the National Institutes of Health.

[3] H. W. Post, "The Chemistry of the Aliphatic Ortho Esters," Reinhold Publishing Corp., New York, N. Y., 1943.

[4] E. H. Cordes in "The Chemistry of the Carboxylic Acid Group," S. Patai, Ed., Interscience Publishers, in press.

[5] (a) R. M. Roberts, *J. Amer. Chem. Soc.*, **72**, 3603 (1950); (b) R. M. Roberts, R. H. DeWolfe, and J. H. Ross, *ibid.*, **73**, 2277 (1951); (c) R. M. Roberts and R. H. DeWolfe, *ibid.*, **76**, 2411 (1954).

[6] E. C. Taylor and W. A. Ehrhart, *J. Org. Chem.*, **28**, 1108 (1963).

[7] R. H. DeWolfe, *ibid.*, **27**, 490 (1962).

[8] J. G. Fullington and E. H. Cordes, *ibid.*, **29**, 970 (1964).

[9] For a review, see: E. H. Cordes, *Progr. Phys. Org. Chem.*, **4**, 1 (1967).

[10] K. Koehler and E. H. Cordes, to be published.

limed ferric chloride was used in the preparation of the 10% solutions of ferric chloride in 0.7 *N* hydrochloric acid. Hydroxamic acids were prepared according to the method of Hauser and Renfrow.[11] Benzohydroxamic acid and *p*-methoxybenzohydroxamic acid were recrystallized several times from benzene and *p*-hydroxybenzohydroxamic acid was recrystallized from ethyl acetate. Inorganic salts employed were reagent grade. Glass-distilled water was used throughout.

Kinetic measurements were carried out spectrophotometrically with a Zeiss PMQ II spectrophotometer equipped with a thermostated cell holder maintained at 25°. The kinetics of aminolysis of methyl orthobenzoate with hydroxylamine and semicarbazide were followed by observing the increase in optical density at 245 mμ as a function of time. In all cases pseudo-first-order rate behavior was observed. First-order rate constants were evaluated from slopes of plots of log ($OD_\infty - OD_t$) against time in the usual manner or by the Guggenheim method.[12] Infinite time values were obtained by checking the reactions at an estimated ten half-times and at appropriate intervals thereafter until the optical density remained constant. Values of pH were determined with a glass electrode and a Radiometer PHM 4c pH meter. Ionic strength was maintained at 0.50 *M* with LiCl except where noted.

Product ratios for ortho ester decomposition in the presence of amines were determined by (1) measurement of the concentration of ester at infinite time by the hydroxylamine–ferric chloride method and (2) spectrophotometric measurement of the concentration of ester or adduct at infinite time. The results are expressed as per cent ester formed compared to control experiments in which only ester is formed (*i.e.*, in the absence of added nucleophiles). In all cases, the experiments run in the presence of added amine were allowed to proceed for at least ten half-times (estimated from the known second-order rate constants for hydrolysis of the ortho esters) before assaying. Whenever possible, the control experiments were run at the same pH as the experiments with added nucleophiles.

The ortho ester stock solutions used yielded final ester concentrations of up to 6×10^{-4} *M* (at 100% ester production). The hydroxylamine–ferric chloride method of Lipmann and Tuttle[13] as modified by Pletcher, *et al.*, was used to determine ester concentration.[14] The solutions of hydroxylamine free base were always prepared immediately prior to use. Linearity of the assay through the anticipated ester concentration ranges was confirmed by determining standard curves for both the corresponding esters of the ortho esters and the hydroxamic acids of the esters. The standard curves were linear over the entire range of ester concentration used in these experiments.

When the spectra for adduct and ester are sufficiently distinct, it is possible to unambiguously obtain the optical density due to the ester product alone and thus the ester concentration. In some cases it is also possible to determine adduct concentration independently. It is possible to run the spectrophotometric determinations of ester adduct at substrate concentrations 10 times lower than those used with the hydroxylamine–ferric chloride method.

Results

In Table I, first-order rate constants for the decomposition of several *para*-substituted methyl orthobenzoates in aqueous solutions of semicarbazide, methoxyamine, and hydroxylamine are listed. The first-order rate constants are independent of amine concentration over the ranges investigated.

The stability of the adduct (presumably the corresponding imidate) formed from the decomposition of methyl orthobenzoate in the presence of (1) 0.50 *M* hydroxylamine, pH 5.46, and (2) 0.50 *M* acetate buffer, pH 5.04, was investigated. In each case, after the initial hydrolysis of the ortho ester (approximately 1–2 hr) the concentration of ester as determined by the hydroxylamine–ferric chloride method remained relatively unchanged.

Table I. First-Order Rate Constants for the Decomposition of Several *para*-Substituted Methyl Orthobenzoates[a]

$(NH_2NHCONH_2)_{total}$ (*M*)	$(CH_3ONH_2)_{total}$ (*M*)	$(NH_2OH)_{total}$ (*M*)	pH	k_{obsd} (min^{-1})
Methyl Ortho-*p*-hydroxybenzoate				
0.01			3.94	1.94
0.02			3.93	2.05
0.05			3.92	1.89
0.10			3.93	1.85
0.20			3.94	1.45
0.30			3.95	1.73
0.40			3.96	1.41
0.50			3.97	1.38
0.70			3.99	1.43
1.00			3.98	1.41
	0.005		4.58	0.377
	0.010		4.60	0.392
	0.015		4.60	0.407
	0.025		4.61	0.407
	0.050		4.61	0.396
	0.075		4.62	0.378
	0.100		4.62	0.378
	0.500		4.67	0.347
		0.025	5.41	0.0554
		0.050	5.41	0.0587
		0.10	5.41	0.0653
		0.50	5.45	0.0554
Methyl Orthobenzoate				
0.10			3.74	1.040
0.20			3.74	0.990
0.40			3.76	0.924
0.50			3.79	0.867
0.70			3.79	0.866
0.90			3.80	0.855
		0.10	5.45	0.0248
		0.20	5.45	0.0225
		0.40	5.46	0.0228
		0.50	5.47	0.0204
		0.70	5.45	0.0216
		0.90	5.44	0.0255
Methyl Ortho-*p*-chlorobenzoate				
0.01			3.88	0.151
0.02			3.88	0.163
0.05			3.87	0.227
0.10			3.88	0.264
0.20			3.89	0.298
0.30			3.91	0.282
0.40			3.92	0.292
0.50			3.94	0.309
0.70			3.95	0.296
1.00			3.95	0.315
	0.005		4.56	0.0597
	0.010		4.56	0.0630
	0.015		4.57	0.0608
	0.025		4.57	0.0619
	0.050		4.58	0.0597
	0.075		4.58	0.0597
	0.10		4.58	0.0619
Methyl Ortho-*p*-nitrobenzoate				
0.005			3.76	1.29
0.010			3.73	1.28
0.020			3.71	1.29
0.030			3.71	1.28
0.040			3.70	1.28
0.050			3.70	1.31
0.070			3.70	1.35
	0.010		5.46	0.00256
	0.025		5.46	0.00256
	0.050		5.45	0.00278
	0.150		5.46	0.00268

[a] In aqueous solutions of semicarbazide, methoxyamine, and hydroxylamine at 25° and ionic strength 0.50.

The experiment in acetic acid buffer showed no change in ester concentration after 36 hr, while the

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Table II. Product Composition for the Acid-Catalyzed Decomposition of a Series of *para*-Substituted Methyl Orthobenzoates[a]

Amine (M)[b]	pH	% ester[c]
Methyl Ortho-*p*-hydroxybenzoate		
Semicarbazide		
0.025	3.69	58.4[f]
0.050	3.69	53.5
0.150	3.69	39.0
0.250	3.69	28.0
0.350	3.71	20.5
0.01	3.94	81.2[f]
0.02	3.93	81.4
0.05	3.92	80.5
0.10	3.93	78.0
0.20	3.93	76.1
0.30	3.95	74.4
0.40	3.96	71.6
0.50	3.97	72.6
0.70	3.99	68.6
1.00	3.98	66.4
0.10	3.94	73.0[d,g]
0.02	3.93	68.6
0.05	3.92	63.4
0.10	3.93	47.8
0.20	3.93	34.8
0.30	3.95	27.8
0.40	3.96	20.5
0.50	3.97	17.5
0.70	3.99	6.8
1.00	3.98	4.6
Methoxyamine		
0.005	4.58	89.4[f]
0.010	4.60	88.8
0.015	4.60	87.0
0.025	4.61	86.2
0.050	4.61	81.2
0.075	4.62	78.4
0.10	4.62	76.6
0.50	4.67	68.0
Hydroxylamine		
0.005	5.41	86.2[f]
0.025	5.41	78.5
0.050	5.41	71.5
0.10	5.41	66.2
0.50	5.45	59.2
Methyl Ortho-*p*-methoxybenzoate		
Semicarbazide		
0.010	3.67	94.2[e]
0.025	3.64	89.6
0.050	3.64	84.4
0.150	3.64	69.4
0.250	3.66	59.6
Methoxyamine		
0.025	4.60	84.3[e]
0.05	4.60	73.4
0.15	4.61	50.8
0.25	4.62	37.6
0.35	4.62	31.8
0.45	4.62	27.8
Hydroxylamine		
0.01	5.40	83.9[e]
0.025	5.40	68.8
0.050	5.40	55.5
0.15	5.40	32.4
0.25	5.40	24.3
0.35	5.40	20.8
Methyl Ortho-*p*-methylbenzoate		
Semicarbazide		
0.01	3.72	95.2[e]
0.025	3.69	93.8
0.05	3.68	90.4
0.15	3.69	76.7
0.25	3.70	67.2
Methoxyamine		
0.025	4.65	88.7[e]
0.05	4.65	76.7
0.15	4.65	56.3
0.25	4.67	39.4
0.35	4.67	32.4
0.45	4.65	28.9
Hydroxylamine		
0.010	5.44	89.5[e]
0.025	5.44	75.4
0.050	5.44	62.0
0.15	5.45	35.2
0.25	5.45	26.8
0.35	5.46	22.6
Methyl Orthobenzoate		
Semicarbazide		
0.10	3.71	81.2[e]
0.20	3.80	71.7
0.30	3.81	64.2
0.40	3.82	62.2
0.50	3.83	54.1
0.60	3.84	51.2
0.80	3.84	47.3
1.00	3.84	44.7
0.10	4.34	75[e]
0.20	4.36	60
0.30	4.40	51
0.40	4.38	53
0.50	4.39	44
0.60	4.40	40
0.80	4.40	36
1.00	4.42	34
0.05	5.13	85.2[e]
0.10	5.16	71.2
0.20	5.20	57.7
0.30	5.25	49.3
0.40	5.28	45.7
0.05	5.13	87.4[e]
0.10	5.17	73.8
0.20	5.23	57.7
0.30	5.26	52.2
0.40	5.07	45.7
Methoxyamine		
0.10	4.68	59.5[e]
0.20	4.69	53.5
0.30	4.71	40.5
0.40	4.71	30.3
0.50	4.70	25.0
0.05	4.65	68.0
0.10	4.65	61.9
0.20	4.66	44.9
0.30	4.67	38.8
0.50	4.64	28.6
Hydroxylamine		
0.10	5.46	48.8[e]
0.20	5.46	36.6
0.30	5.47	28.5
0.40	5.47	26.3
0.50	5.47	21.9
0.60	5.46	21.2
0.80	5.45	17.5
0.90	5.45	10.2
Methyl Ortho-*p*-chlorobenzoate		
Semicarbazide		
0.04	3.68	89[e]
0.10	3.65	80.5
0.20	3.70	74
0.30	3.70	66.9
0.50	3.73	61.1
0.025	3.69	51.5[f]
0.05	3.69	46.3
0.15	3.69	26.2

Table II (*Continued*)

Amine (M)[b]	pH	% ester[c]
0.01	3.88	77.1
0.02	3.88	73.8
0.05	3.87	69.6
0.10	3.88	63.0
0.20	3.89	50.7
0.30	3.91	40.0
0.40	3.92	31.3
0.50	3.94	24.2
0.70	3.95	12.6
Methoxyamine		
0.05	4.65	71.9[e]
0.10	4.65	58.1
0.20	4.66	41.2
0.30	4.68	34.8
0.50	4.67	25.2
0.005	4.56	95.8[f]
0.01	4.56	95.2
0.015	4.57	91.4
0.025	4.57	87.0
0.05	4.58	89.3
0.075	4.58	82.4
0.10	4.58	81.0
0.50	4.62	62.1
Hydroxylamine		
0.05	5.43	67.7[e]
0.10	5.43	52.5
0.20	5.43	38.6
0.30	5.44	34.8
0.50	5.43	28.4

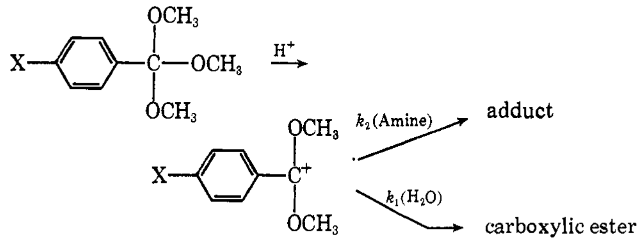
[a] In aqueous solutions of semicarbazide, hydroxylamine, and methoxyamine at 25° and ionic strength 0.5. [b] Amine concentrations expressed as total amine in solution. [c] Per cent of ortho ester yielding ester as product. [d] These percentages are uncertain due to probable inaccuracy in estimating 100% adduct. [e] Determined by the hydroxylamine–ferric chloride method. [f] Determined by spectrophotometric estimation of ester concentration. [g] Determined by spectrophotometric estimation of adduct concentration.

experiment in hydroxylamine solution showed an increase of 25% after 26 hr. Since the product distribution experiments were usually terminated after 5 or 6 hr, little significant error can be attributed to the formation of ester *via* hydrolysis of the amine adduct. The stability of the adduct formed from the decomposition of methyl orthobenzoate in the presence of methoxyamine (0.5 M, pH 4.67) similarly demonstrated that the imidate is stable over the time range of the experiments reported here.

By observing the appearance and slow disappearance of the adduct peak, it is possible to estimate the rates of decomposition of the adducts. p-Hydroxy, p-chloro, and unsubstituted methyl orthobenzoates were added to a 1 M aqueous solution of semicarbazide at pH 3.93 and 25° and the kinetics of disappearance of the adduct peaks were observed (adduct followed at 290, 280, and 245 mμ, respectively). Thus, at pH 3.93 and 25° the first-order rate constants for the decomposition of the semicarbazide adducts of p-OH, p-Cl, and unsubstituted methyl orthobenzoates are 0.0158, 0.00866, and 0.00825 (min^{-1}), respectively.

Both the stability of the infinite time values for the decomposition of methyl orthobenzoates in the presence of amines and previous control experiments[8] indicate that the methyl benzoates formed in these experiments do not react with amines at appreciable rates under these experimental conditions.

These considerations suffice to justify the methods described in the Experimental Section as reliable means for the estimation of product distributions at the completion of ortho ester decomposition in the presence of amines. From the product distributions, relative rate constants for attack of water and amine on the derived carbonium ions may be calculated using the following model



Validity of this model requires that the reactions of the carbonium ion with water and amine be essentially irreversible. While there is no way to be certain that this is strictly true, the model does predict the product distribution as a function of amine concentration and is thus susceptible to experimental test. Assuming that the concentration of carbonium ion at any time is negligible, it is easy to show that [15,16]

$$\frac{1}{f_e} = 1 + \frac{k_2}{k_1}(\text{amine})_{\text{free base}} \tag{1}$$

in which f_e is the fraction of ortho ester which yields ester as product. Plots of $1/f_e$ against $(\text{amine})_{\text{free base}}$ are, in fact, linear with intercepts of unity in accord with the model (see Figure 1). Relative rate constants for reaction of water and amine with the carbonium ions were evaluated from the slopes of these plots.

Product distributions for the acid-catalyzed decomposition of *para*-substituted methyl orthobenzoates in the presence of aqueous amine solutions are collected in Table II. Although the first-order rate constants for the decomposition of methyl orthobenzoate were found to be independent of semicarbazide concentration over the range 0.10–1.0 M, over this same range of amine concentrations the fraction of methyl orthobenzoate yielding methyl benzoate decreases from 0.75 (1.0 at 0 M amine) to 0.34. At the highest semicarbazide concentration, 66% of the methyl orthobenzoate yields the semicarbazide adduct, probably the corresponding benzimidate. Similar results were obtained for the other amines and ortho esters listed in Table II.

The product distribution for the decomposition of methyl ortho-p-hydroxybenzoate in semicarbazide solutions determined by observing the optical density of the adduct is uncertain due to the difficulty encountered in estimating the optical density of a solution in which all of the methyl ortho-p-hydroxybenzoate decomposes to yield adduct. Similarly, due to difficulty in obtaining consistent results for the product distributions obtained by following ester appearance, the value of k_2/k_1 for the addition of semicarbazide must be considered only approximate.

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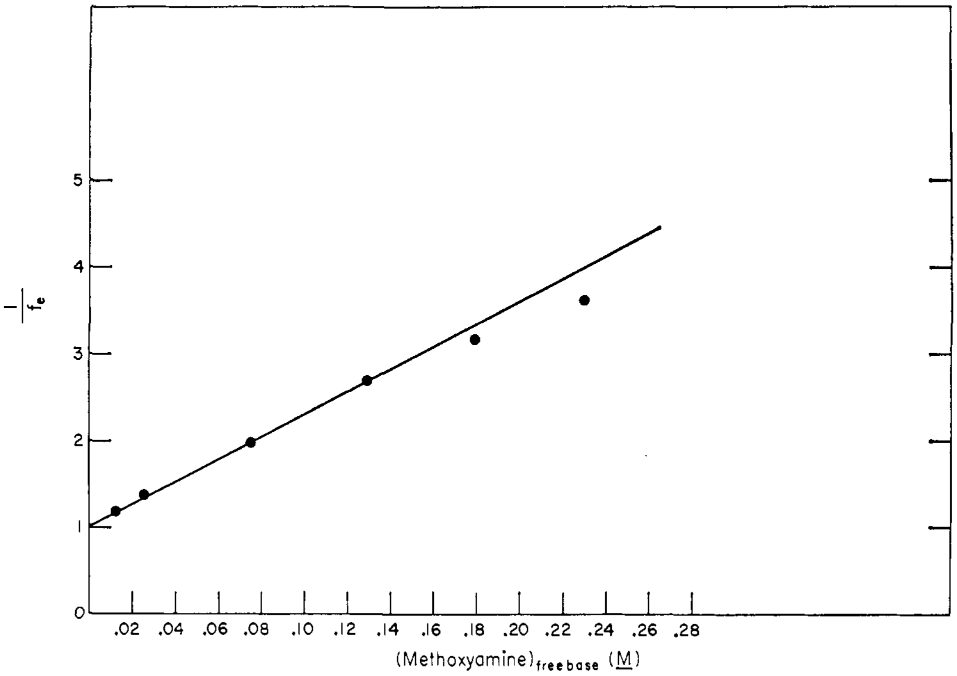

Figure 1. Plot of $1/f_e$ as a function of (amine)$_{\text{free base}}$ for the decomposition of methyl ortho-*p*-methoxybenzoate in the presence of aqueous solutions of methoxyamine at 25°.

The addition of other amines to methyl orthobenzoate was investigated by the hydroxylamine–ferric chloride method; however, the results indicated that either adduct formation did not occur or that adduct hydrolysis was faster than ortho ester decomposition. Aniline, *p*-methoxyaniline, benzimidazole, and N,O-dimethylhydroxylamine showed no evidence of addition. The hydroxylamine–ferric chloride test failed as a method for determining ester concentrations in the presence of N-methylhydroxylamine, phenylhydrazine, and hydrazine. 2,2,2-Trifluoroethylamine may yield some stable adduct in a reaction with methyl ortho-*p*-methylbenzoate but the extent of addition is difficult to quantitate. In these cases, the optical density at 540 mμ was found to be either time dependent or dependent on amine concentration. The first-order rate constant for ester formation from methyl orthobenzoate in the presence of 0.2 *M* N,O-dimethylhydroxylamine at pH 4.75 in aqueous solution at 25° determined by the hydroxylamine–ferric chloride method (0.068 min^{-1}) is, within experimental error, identical with that determined in the absence of amine at the same pH.

In Figure 1 a plot of $1/f_e$ *vs.* (amine)$_{\text{free base}}$ is shown for the decomposition of methyl ortho-*p*-methoxybenzoate in the presence of methoxyamine. This plot is typical of those used to determine values of k_2/k_1. The scatter observed is almost certainly the result of measuring very small differences where the per cent ester *vs.* amine curve begins to approach unity.

Values for the ratio k_2/k_1, the ratio of rate constants for the reaction of carbonium ion with amine and water, determined from slopes of plots of $1/f_e$ *vs.* (amine)$_{\text{free base}}$ (Figure 1) are collected in Table III. The values of k_2/k_1 increase with increasing amine basicity for the series: semicarbazide, methoxyamine, hydroxylamine.

Plots of the logarithm of k_2/k_1 as a function of the values of pK_a for the conjugate acids of the amines are shown in Figure 2. These plots have been constructed from the data of Table III with the exception that the concentration of water is taken as unity rather than 55 *M*. A plot for the *p*-hydroxy substrate is not included since only two reliable points are available; behavior of this substrate is, however, consistent with that observed for the others. In each case, the data generate a good straight line from which the Brønsted exponent, β, has been calculated. These values are collected in Table IV. The differences observed are not significant.

Table III. Relative Rate Constants for Reaction of Amines and Water with Carbonium Ions Derived from a Series of *para*-Substituted Methyl Orthobenzoates[a]

Amine	pK_a	k_2/k_1[c]
Methyl Ortho-*p*-hydroxybenzoate		
Methoxyamine	4.60	248
Hydroxylamine	5.97	1330
Methyl Ortho-*p*-methoxybenzoate		
Semicarbazide	3.65	352
Methoxyamine	4.60	722
Hydroxylamine	5.97	2700
Methyl Ortho-*p*-methylbenzoate		
Semicarbazide	3.65	222
Methoxyamine	4.60	605
Hydroxylamine	5.97	2930
Methyl Orthobenzoate		
Semicarbazide	3.65	147[b]
Methoxyamine	4.60	400[b]
Hydroxylamine	5.97	1330[b]
Methyl Ortho-*p*-chlorobenzoate		
Semicarbazide	3.65	228[b]
Methoxyamine	4.60	588
Hydroxylamine	5.97	1820

[a] Calculated from the data of Table II; in aqueous solutions at 25°. [b] Average of several determinations. [c] Corrected to a concentration of water of 55 *M*.

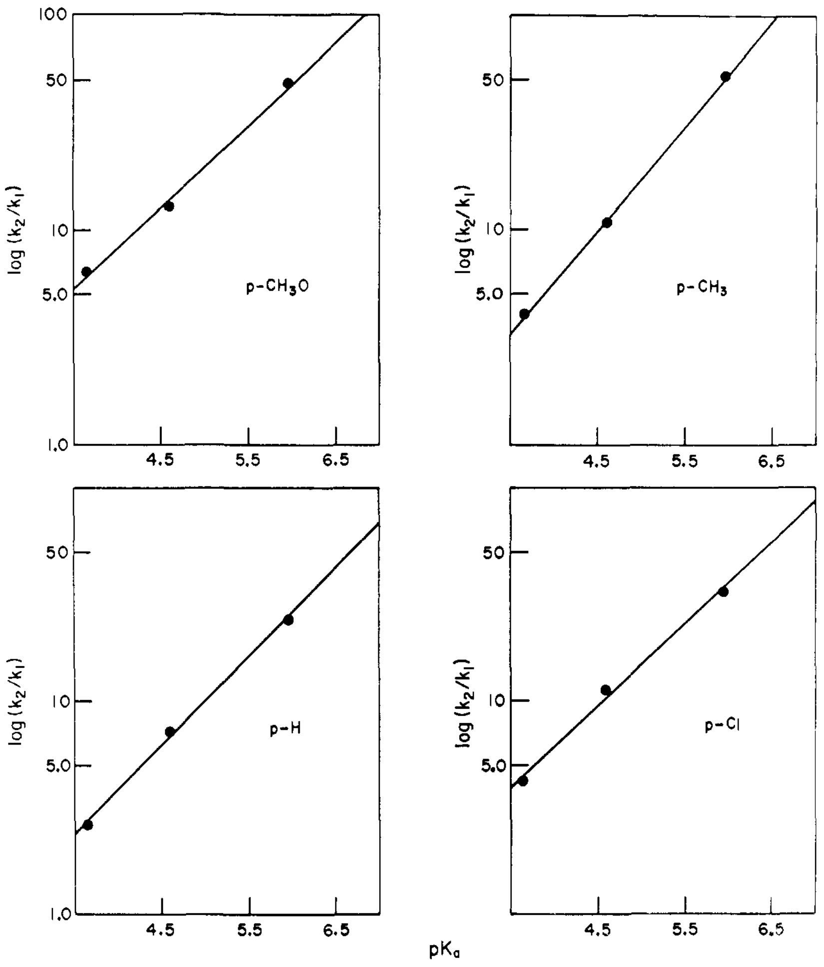

Figure 2. Plots of log (k_2/k_1) *vs.* pK_a for decomposition of a series of *para*-substituted methyl orthobenzoates. Values of pK_a and k_2/k_1 ratios are taken from Table IV.

Product compositions for the decomposition of methyl orthobenzoate in the presence of aqueous solutions of methoxyamine at several concentrations of acetic buffer are listed in Table V. In each experiment the amine concentration was varied from 0.005 to 0.05 *M*.

Table IV. Brønsted Values for the Reaction of Carbonium Ions Generated from a Series of Methyl Orthobenzoates with Semicarbazide, Methoxyamine, and Hydroxylamine

Substrate	β
Methyl ortho-*p*-methoxybenzoate	0.38
Methyl ortho-*p*-methylbenzoate	0.49
Methyl orthobenzoate	0.41
Methyl ortho-*p*-chlorobenzoate	0.39

Discussion

In each case investigated, rate constants for ortho ester decomposition are independent of amine concentration under conditions in which appreciable fractions of the ortho esters yield amine adducts as products. Furthermore, the observed product distributions are consistent with a reaction pathway involving a partitioning of the intermediate carbonium ions between water and amine, yielding acid and imidate, respectively. These findings are in accord with those obtained previously in an investigation of more limited scope and reaffirm the conclusion that ortho ester hydrolysis occurs without the nucleophilic participation of solvent in the transition state.[8]

The Brønsted β values for addition of the three amines studied to dialkoxycarbonium ions, near 0.4 (Table IV), are markedly less than values observed for reaction of amines with less reactive substrates. Thus, the addition of amines to phenyl acetate, *p*-nitrophenyl acetate, 2,4-dinitrophenyl acetate, and 1-acetoxy-4-methoxypyridinium cation yields Brønsted plots with β values near 0.8.[17] A sharp leveling off of rate with increasing basicity of the amine occurs in the reactions of 2,4-dinitrophenyl acetate and 1-acetoxy-4-methoxypyridinium cation. The reaction becomes less sensitive to basicity in the reactions of strongly basic amines with very reactive esters. The β value for the attack of amines on methyl formate is approximately 0.7.[18]

The lower sensitivity of the rates of addition of amines to dialkoxycarbonium ions compared to esters presumably reflects a smaller degree of substrate organization in arriving at the transition state for the former reactions in accord with the considerations of Hammond.[19] A more quantitative statement cannot

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

(18) G. M. Blackburn and W. P. Jencks, *ibid.*, **90**, 2638 (1968).

(19) G. S. Hammond, *ibid.*, 77, 334 (1955).

Table V. Product Compositions for the Decomposition of Methyl Orthobenzoate in the Presence of Aqueous Solutions of Methoxyamine[a]

Methoxyamine (*M*)[b]	pH	Acetate (*M*)	f_e[c]
0.005	4.59	0	0.980
0.010	4.59		0.960
0.015	4.58		0.892
0.025	4.58		0.859
0.05	4.58		0.757
0.005	4.57	0.001	0.980
0.010	4.57		0.960
0.015	4.58		0.933
0.025	4.58		0.907
0.050	4.59		0.790
0.005	4.55	0.0025	1.0
0.010	4.56		0.933
0.015	4.56		0.927
0.025	4.57		0.866
0.050	4.58		0.778
0.005	4.50	0.010	1.0
0.010	4.53		0.947
0.015	4.53		0.927
0.025	4.55		0.878
0.050	4.57		0.764
0.005	4.50	0.10	0.994
0.010	4.51		0.960
0.015	4.51		0.932
0.025	4.51		0.906
0.050	4.53		0.798
0.005	4.55	0.25	1.0
0.010	4.55		0.994
0.015	4.55		0.954
0.025	4.56		0.927
0.05	4.57		0.811

[a] At several concentrations of acetate buffer at 25° and ionic strength 0.50 *M*. [b] Total amine. [c] Fraction of methyl orthobenzoate yielding methyl benzoate as determined by the hydroxylamine–ferric chloride method.

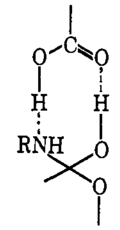
be made owing to the lack of rate constants for the reactions of amines with the dialkoxycarbonium ions.

While the transition from carboxylic ester to dialkoxycarbonium ion is sufficient to change the sensitivity of the reaction to amine basicity, the transitions from one to another of the dialkoxycarbonium ions studied here are insufficient to provide clear evidence for such an effect. The various values of β are all near 0.4. Multiple structure–reactivity relationship considerations indicate that values of β ought to be related to values of polar substituents constants, σ, for these reactions as follows[20]

$$\frac{\sigma_i}{\beta_i - \beta_0} = C$$

From the available data, one can conclude only that the value of *C* must be small.

Acetate, phosphate, and carbonate buffers, among others, have been observed to affect the partitioning of the tetrahedral intermediate formed during the hydrolysis of imidates.[21] It has been suggested that the influence of these buffers on the product distributions is the consequence of bifunctional catalysis of these buffers in which the neutral carbinolamine and buffer interact in the following way



Presumably, the addition of an amine to the dialkoxycarbonium ion generated during the ortho ester hydrolysis yields a similar tetrahedral intermediate with the exception that neither oxygen atom has a dissociable proton. Thus, the mechanism depicted above ought to be impossible in our system. The failure to observe any influence of an acetate buffer (Table V) on the product distribution during ortho ester aminolysis thus provides mild supporting evidence for this formulation.

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(20) (a) E. H. Cordes and W. P. Jencks, *J. Amer. Chem. Soc.*, **84**, 4319 (1962); (b) W. P. Jencks, *Progr. Phys. Org. Chem.*, **2**, 63 (1964).

(21) (a) G. L. Schmir and B. A. Cunningham, *J. Amer. Chem. Soc.*, **87**, 5692 (1965); (b) B. A. Cunningham and G. L. Schmir, *ibid.*, **88**, 551 (1966); (c) R. K. Chaturvedi and G. L. Schmir, *ibid.*, **90**, 4413 (1968); (d) G. L. Schmir, *ibid.*, **90**, 3478 (1968).

The Role of *p*-Phenylene Groups in Nematic Liquid Crystals[1]

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Abstract: Many compounds forming nematic mesophases contain *p*-phenylene units. It is shown that these perform a dual function, providing rigid linear groupings and contributing to the polarizability of the molecule. These conclusions are based on a comparison with compounds where benzene rings are replaced by cyclohexane or bicyclo[2.2.2]octane.

Liquid crystals form a state of matter intermediate between crystalline solids and isotropic liquids;[3,4] such mesophases behave mechanically as liquids but differ from normal liquids in that the molecules in them are oriented, having lost two degrees of rotational free-

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