appreciable sorting out of solvent molecules from the mixture were taking place under the influence of the charged centers,[32] the reverse would be expected. The changes in pK with changing solvent composition shown in Table IIIs (supplementary material) do not seem to depend on the nature of the charged groups, as they might if very specific solvating properties were of overriding importance. This indicates that the macroscopic dielectric constant may not be a bad parameter for mixed solvents but that the results obtained using it in the KW treatment are only very approximate.

Calculations using D_{eff} derived by Tanford's method are beset by uncertainty because of our ignorance of the correct value for d of the variously substituted ammonium groups. The results obtained with d = 1.72 Å for the trimethylammonium group[33] were in poorer agreement with experimental ΔpK values than those shown in Table II.

Acknowledgments. We are grateful to the National Research Council for financial support and to Coopération Franco-québécoise for financing the exchanges between our laboratories, in particular for the mission of J.K. to Paris where the dissociation constants were measured. We thank Dr. Bo-Long Poh for checking many calculations and Mrs. Annie Corlaville for NMR measurements.

Supplementary Material Available: First and second dissociation constants of some amino acids and derivatives in water and water–Me_2SO mixtures at 20 °C, Table III (2 pages). Ordering information is given on any current masthead page.

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Dioxolenium Ion Trapping in the Hydrolysis of Cyclic Ortho Esters: The Rate-Determining Step

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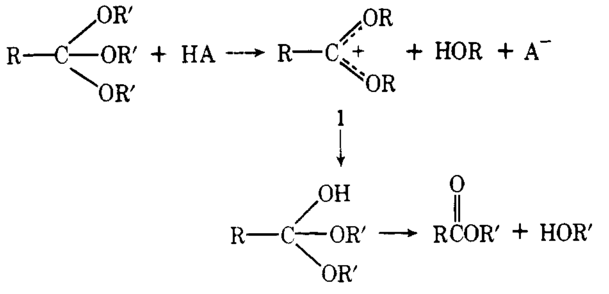
The dioxolenium ion formed during the acid-catalyzed hydrolysis of 2-(p-methoxyphenyl)-2-methoxy-1,3-dioxolane in NH_3OH^+/NH_2OH aqueous buffer solutions at 25 °C is trapped efficiently by hydroxylamine without producing a corresponding increase in reaction rate; this indicates that trapping occurs after the rate-determining step and that dioxolenium ion formation is rate limiting in this hydrolysis reaction. Quantitative treatment of the data gives $N_+(NH_2OH) = 1.44 \pm 0.04$, much lower than the standard value of 5.05, but this discrepancy could be due to reversibility of the hydroxylamine trapping reaction.

The effect of phenyl substitution at the proacyl carbon atom of simple acyclic ortho esters is anomalous in that it leads to rate reductions instead of the accelerations expected in a carbonium ion forming reaction such as this (eq 1). We demonstrated recently that this unusual behavior is produced by steric inhibition of resonance in the dialkoxy carbonium ion intermediate of this reaction, **1**; when steric hindrance is removed by forming the alkoxy groups into a small ring, as in the 1,3-dioxolenium ion **3**, phenyl substitution does give the anticipated rate acceleration.[1]

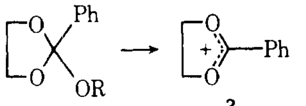
This explanation is based upon an argument which requires dialkoxy carbonium ion formation to be the rate-determining step of these hydrolyses under the conditions of the study, i.e., at acidities less than pH ~ 6. All of the available evidence in-



(1)

R = H, Ph

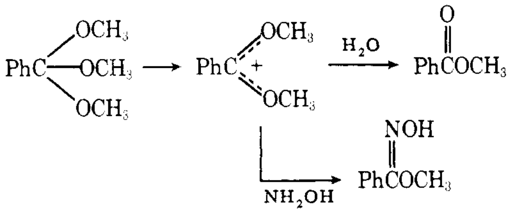
dicates that this is so for simple acylic ortho esters,[2] and a recent study[3] suggests that the situation is no different for the 2-alkoxy-1,3-dioxolanes, **2**, which produce dioxolenium ions, eq 2. In order to provide additional evidence on this point, we carried out the present investigation.



(2)

2 3

Our study uses the effect of an added nucleophile, hydroxylamine, on the course and velocity of the hydrolysis reaction. Nucleophiles such as this are known to react readily with carbonium ions,[4] and hydroxylamine has been used before to trap the dialkoxycarbonium ion generated during the hydrolysis of trimethyl orthobenzoate and thereby to divert some of the reaction to nucleophile addition product (eq 3).[5]



(3)

If trapping such as this occurs after the rate-determining step, it cannot affect the rate of the reaction. If, on the other hand, it takes place before the rate-determining step, i.e., if some reaction step subsequent to dialkoxycarbonium ion formation is rate limiting, then the velocity of this additional trapping reaction will add to the rate of formation of product, and a rate increase commensurate with the amount of trapping will be realized.

Experimental Section

Materials. 2-(*p*-Methoxyphenyl)-2-methoxy-1,3-dioxolane was prepared by the reaction of 2-(*p*-methoxyphenyl)-1,3-dioxolenium fluoroborate with methoxide ion, as described before.[6] Benzohydroxamic acid was synthesized by a standard method,[7] and the syn and anti forms of its methyl esters (methyl *N*-hydroxybenzimidate) were prepared from benzonitrile via the imino ester hydrochloride.[8] All other substances were best available commercial grades. Deionized water was purified further by distillation from alkaline potassium permanganate in glass apparatus.

Kinetics. Reaction rates were determined spectroscopically by monitoring the increase in absorbance of carboxylate and benzimidate ester products at 240–260 nm; the details have been published before.[1]

Product Analysis. Carboxylic acid ester product concentrations were determined by a modification of the method of Lipmann and Tuttle[9] which involved converting the ester into a benzohydroxamic acid, through the action of hydroxylamine, and estimating this acid spectroscopically as its ferric chloride complex. The procedure adopted involved combining 2 mL of test solution with 1 mL of hydroxylamine reagent in a 5-mL volumetric flask. The hydroxylamine reagent was prepared by dissolving 2.8 g of hydroxylamine hydrochloride in 5 mL of water and adding 15 mL of 3.5 M aqueous NaOH; it is of limited stability and is best made up just before use. The test solution–hydroxylamine reagent mixture was allowed to react at room temperature for 2 min. It was then neutralized to pH 7 (pH paper) with about 0.5 mL of 3 M aqueous HCl and 1 mL of 5% ferric chloride in 0.1 M aqueous HCl was added. The mixture was swirled gently and the brown precipitate which formed was dissolved by adding a very small amount of 3 M aqueous HCl. The mixture was then diluted to 5.00 mL with water and its absorbance was immediately measured at 540 nm.

This procedure was verified using methyl benzoate. It also produced good quantitative results with 2-hydroxyethyl benzoate, but methyl *N*-hydroxybenzimidate gave no response.

Analyses were performed on spent reaction mixtures of 2-(*p*-methoxyphenyl)-2-methoxy-1,3-dioxolane in dilute NH_3OH^+–NH_2OH buffer solutions. The amount of *N*-hydroxybenzimidate ester formed was obtained by difference, using substrate concentrations estimated by this analysis on reaction mixtures in which the NH_3OH^+–NH_2OH buffer was replaced with dilute perchloric acid.

Results

Rates of reaction of 2-methoxy-2-(*p*-methoxyphenyl)-1,3-dioxolane were measured in NH_3OH^+–NH_2OH buffers by monitoring the increase in UV absorbance at 240–260 nm. The substrate has negligible absorbance in this region, whereas both benzoate esters and alkyl *N*-hydroxybenzimidates absorb strongly; this method of following the reaction therefore measures the rate of appearance of both the hydrolysis reaction product and the product of hydroxylamine trapping of the dialkoxycarbonium ion. This conclusion is reinforced by the fact that the extinction coefficient in the vicinity of λ_{max} for methyl benzoate is about 20% greater than that for methyl *N*-hydroxybenzimidate, and the final absorbance for a series of kinetic runs in hydroxylamine buffers at constant substrate concentration increased some 20% as the hydroxylamine concentration was lowered from high (0.10 M) to zero (extrapolated) values.

Data obtained in this way conformed to the first-order rate law within the experimental uncertainty, and observed first-order rate constants, k_{obsd}, were determined from plots of ln $(A_\infty - A)$ vs. time. These rate constants increased slightly with increasing buffer concentration (Table I), which is consistent with the weak general acid catalysis that the hydrolysis of these ortho esters usually shows.[1,6] Least-squares analysis of the relationship between k_{obsd} and buffer acid concentration gave general acid catalytic coefficients at two different buffer ratios, 1.0 and 0.2, which were not significantly different, indicating general base catalysis to be absent. The intercepts of these relationships, when combined with hydronium ion concentrations calculated from the acidity constant of NH_3OH^+, $pK_a = 5.97$,[10] gave hydronium ion catalytic coefficients whose average value, $k_{H^+} = (2.11 \pm 0.22) \times 10^4$ M^{-1} s^{-1},[11] is in good agreement with measurements made on the same substrate in acetic acid and biphosphate ion buffers, $k_{H^+} = 1.93 \times 10^4$ M^{-1} s^{-1}.[6] The average value of the catalytic coefficient for the hydroxylammonium ion is $k_{HA} = (1.27 \pm 0.06) \times 10^{-2}$ $M^{-1} s^{-1}$.[11] It is interesting that this is less than the catalytic coefficient for this reaction catalyzed by the biphosphate ion, $k_{HA} = 6.9 \times 10^{-2}$ M^{-1} s^{-1}, even though NH_3OH^+ is a stronger acid than $H_2PO_4^-$, for that is the behavior expected on the basis of electrostatic interactions in the transition states of these reactions.[12]

Product compositions were determined upon completion of the reactions in hydroxylamine buffers under conditions similar to those used for the kinetics. The results are summarized in Table II.

Discussion

The data of Table II show that the presence of hydroxylamine causes a substantial reduction in the amount of carboxylic acid ester product formed during the hydrolysis of 2-(*p*-methoxyphenyl)-2-methoxy-1,3-dioxolane. Hydroxylamine is thus an efficient trapping agent for the dioxolenium ion generated during this process: at concentrations of the

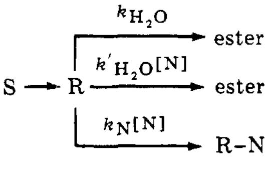
Table I. Rates of Hydrolysis of 2-Methoxy-2-(*p*-methoxyphenyl)-1,3-dioxolane in Hydroxylamine Buffer Solutions at 25 °C

$10^2[NH_3OH^+]$, M	$10^2 k_{obsd}$, s^{-1}
$[NH_3OH^+]/[NH_2OH] = 0.92$; $\mu = 0.20$ M	
1.84	1.84, 1.86, 1.87
3.66	1.86, 1.89
7.31	1.93, 1.94
9.15	1.94, 1.94, 1.96
$k_{obsd} = (1.83 \pm 0.01) \times 10^{-2} + (1.21 \pm 0.12) \times 10^{-2}[NH_3OH^+]$	
$k_{H^+} = 1.87 \times 10^4$ M^{-1} s^{-1}	
$[NH_3OH^+]/[NH_2OH] = 0.20$; $\mu = 0.60$ M	
2.00	0.510, 0.512
4.00	0.540, 0.540, 0.543
6.00	0.562, 0.568, 0.575
8.00	0.585, 0.588
10.00	0.609, 0.610
$k_{obsd} = (4.91 \pm 0.03) \times 10^{-3} + (1.21 \pm 0.06) \times 10^{-2}[NH_3OH^+]$	
$k_{H^+} = 2.29 \times 10^4$ M^{-1} s^{-1}	
$[NH_3OH^+]/[NH_2OH] = 0.91$; $\mu = 0.60$ M	
1.90	2.14, 2.14, 2.15
3.79	2.14, 2.14, 2.14
5.69	2.18, 2.18, 2.18
9.48	2.24, 2.24, 2.24
$k_{obsd} = (2.10 \pm 0.01) \times 10^{-2} + (1.38 \pm 0.13) \times 10^{-2}[NH_3OH^+]$	
$k_{H^+} = 2.17 \times 10^4$ M^{-1} s^{-1}	

order of 0.5 M, it diverts some 95% of the reaction from its normal course.

If this trapping had occurred before the rate-determining step, the additional reaction path so provided would have added to the overall rate of product formation in proportion to the amount of new product formed. For 95% trapping, this would have amounted to a 20-fold (95/5) acceleration. The change in rate actually observed was only 24% in the case of the experiments done at a buffer ratio of 0.2 and only 21% (extrapolated to 0.5 M NH_2OH) for the series at buffer ratio 1.0. These changes, moreover, are not related to hydroxylamine concentration, as they should be if the effect were caused by this species, and they are completely explicable in terms of the general acid catalysis expected for this reaction in these buffers. Trapping must therefore occur after the rate-determining step, and dioxolenium ion formation must be the rate-limiting step of this reaction.[13]

A quantitative analysis of the data can be based upon the reaction scheme of eq 3, elaborated to take into account possible general base catalysis by hydroxylamine of water attack on the dioxolenium ion (eq 4).[4,15] This leads to an expression,



(4)

eq 5, which predicts that the carboxylic acid ester to nucleophile addition product ratio, [ester]/[R–N], will be a linear function of the reciprocal of the nucleophile concentration.

$$\frac{[\text{ester}]}{[\text{R–N}]} = \frac{k'_{H_2O}}{k_N} + \frac{k_{H_2O}}{k_N}\frac{1}{[N]} \qquad (5)$$

Figure 1 shows that this is indeed the case, and linear least-squares analysis gives a relationship with the correlation coefficient $r = 0.999$.

It is interesting that this relationship has an experimentally insignificant intercept, $k'_{H_2O}/k_N = -0.05 \pm 0.02$, for this means that hydroxylamine serves much better as a nucleophile in this reaction than as a general base catalyst for water attack. From the slope of this relationship, it is also apparent that hydroxylamine is a much better nucleophile than water: $k_N/k_{H_2O} = 27.3 \pm 0.4$.

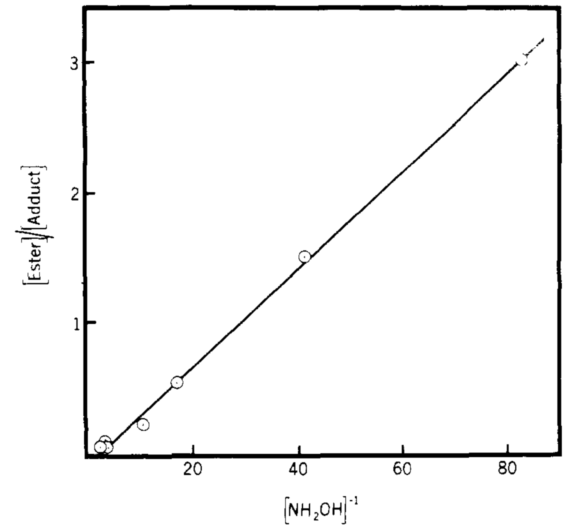


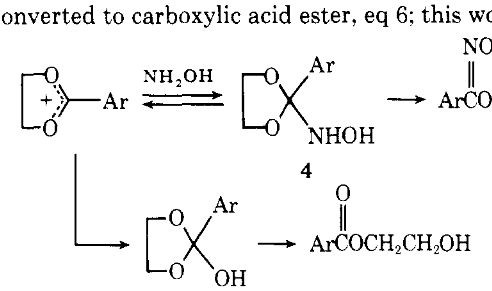
Figure 1. Linear relationship between the product ratio and the reciprocal of hydroxylamine concentration in hydroxylamine trapping of the dioxolenium ion formed during the hydrolysis of 2-(*p*-methoxyphenyl)-2-methoxy-1,3-dioxolane in aqueous NH_3OH^+/NH_2OH buffers at 25 °C.

Table II. Product Composition in the Hydrolysis of 2-Methoxy-2-(*p*-methoxyphenyl)-1,3-dioxolane in Hydroxylamine Buffer Solutions at 25 °C

$10^2[NH_3OH^+]$	$10^2[NH_2OH]$	f[a]
$[NH_3OH^+]/[NH_2OH] = 0.20$; $\mu = 0.60$ M		
2.0	10	0.20
6.0	30	0.10
10.0	50	0.06
$[NH_3OH^+]/[NH_2OH] = 1.0$; $\mu = 0.60$ M		
1.2	1.2	0.75
2.4	2.4	0.60
6.0	6.0	0.35
30	30	0.05

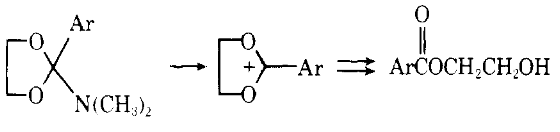
[a] Fraction of substrate appearing as carboxylic acid ester product.

However, an even greater nucleophilic superiority over water might have been expected. The reactivity of nucleophiles in reactions such as this has recently been quantified, and the results have been expressed as N_+ parameters;[4,16] these are logarithms of rate constant ratios for reaction by a given nucleophile to reaction by the reference substance, water. The present data thus lead to $N_+ = \log(27.3 \pm 0.4) = 1.44 \pm 0.04$, which is significantly less than the standard value for hydroxylamine, $N_+ = 5.05$.[16] It is possible, however, that the presently determined product ratios are not a true indication of the relative rates of hydroxylamine and water attack on the dioxolenium ion. The product of hydroxylamine attack, for example, the *N*-hydroxyamide acetal **4**, could revert back to dioxolenium ion, which could then react with water and be converted to carboxylic acid ester, eq 6; this would increase



(6)

the amount of carboxylic acid ester in the reaction product at the expense of *N*-hydroxybenzimidate ester. The fact that hydroxylamine adds reversibly to carbonyl compounds at neutral pH, and that oximes are formed only by slow further reaction of the adduct,[17] offers some support for this hypothesis. Further evidence comes from a recent study of the hydrolysis of tertiary amide acetals, **5**, closely related to the hydroxylamine adduct **4**, which shows that in neutral and acidic solution these substances react by strongly preferential loss of the amino group to give carboxylic acid ester products (eq 7).[18]



(7)

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Registry No.—2-Methoxy-2-(*p*-methoxyphenyl)-1,3-dioxolane, 66137-63-1; hydroxylamine, 7803-49-8; methyl benzoate, 93-58-3; (*E*)-methyl *N*-hydroxybenzimidate, 68525-45-1; (Z)-methyl *N*-hydroxybenzimidate, 68525-46-2; 2-hydroxyethyl benzoate, 94-33-7.

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The Pyrrolo[3,4-*c*]pyrazole System, a New 10π-Electron Heteropentalene[1]

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Nitration of ethyl 1-methyl-5-phenyl-4-(2-pyridyl)pyrrole-2-carboxylate, prepared from 2-phenyl-*N*-(ethyloxalyl)sarcosine, 2-ethynylpyridine, and Ac_2O at 95–100 °C, and treatment of the nitro compound with $(EtO)_3P$ at reflux gave ethyl 8-methyl-9-phenylpyrrolo[3′,4′:2,3]pyrazolo[1,5-*a*]pyridine-7-carboxylate, a new 10π-electron triazapentalene. Reaction with dimethyl acetylenedicarboxylate occurred at the azomethine ylide giving a stable 1:1 cycloadduct; a similar reaction occurred with *N*-phenylmaleimide, except that under the more drastic reaction conditions employed the elements of CH_3NH_2 were extruded from the initial 1:1 adduct. The synthesis of a variety of substituted thiophenes by similar cycloaddition and nitration procedures is also described.

The title ring system **1**, a 10π-electron azapentalene which cannot be represented by a classical, noncharge-separated structure, belongs to a group of heteropentalenes which up to now has included only polyaza derivatives with or without nitrogen atoms at the points of fusion of the bicyclic system.[2] The sulfur analogue of **1**, the thieno[3,4-*c*]pyrazole system **2**, is a "nonclassical" thiophene[2,3] showing many of the interesting properties of the parent thieno[3,4-*c*]thiophene system including cycloadditions at the thiocarbonyl ylide dipole.[2,3,4a] These properties were present to some degree in the thiazolo[3,4-*b*]indazole system **3**, a structural analogue of **2** with a bridgehead nitrogen atom.[4b] Thus **1** represents an extremely interesting heteropentalene, intermediate between the very reactive "nonclassical" thiophenes on one hand and the considerably less reactive polyazapentalenes at the other extreme. A study of its synthesis and properties is thus of considerable interest to this area of chemistry and this publication describes the first successful synthesis of **1** and its behavior in cycloaddition reactions.

There are two principal routes to **1**: either formation of a pyrrole nucleus onto a preformed pyrazole ring, or ring closure of a substituted pyrrole to form the pyrazole ring. The difficulty in forming a pyrrole nucleus of this type led us to favor the latter approach, involving N–N bond formation as in **4**, a scheme which was successful[4b] in the synthesis of **3**. Synthetic procedures described in the literature for azapentalenes are best suited to the synthesis of polyaza derivatives. Thus tetraazapentalenes are formed by the dimerization of either oxalonitrilebis(phenylimine)[5] or arylazoethynylarenes,[5,6] by the reductive cyclization of 4-azoxypyrazoles with $P(OEt)_3$,[7,8] or by oxidative ring closure of 5-benzyl-4-arylazapyrazoles.[8] The corresponding hexaazapentalenes are readily formed on thermolysis of 4-azido-5-phenylazo-1,2,3-triazoles.[9] These ring systems are very stable and their lack of reactivity is in marked contrast to that observed with several of the "nonclassical" thiophene systems,[2,3] the multiplicity of nitrogen atoms while assisting in their synthesis apparently depresses their reactivity.

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