average of two independent determinations. Acid concentrations were measured by titrating aliquots of indicator solutions; the primary determination was equivalents of acid per kilogram of solution, and this was then converted to equivalents of acid per liter when needed by calculations using the recently measured[12] densities of these solutions.

Principal features of the ultraviolet spectra of the carbazole bases and their conjugate acids are given in Table II.

Relative Heats of Formation of Cyclic Oxonium Ions in Sulfuric Acid[1]

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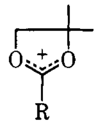
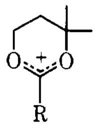
Contribution from the Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37916. *Received November 13, 1970*

Abstract: The relative heats of formation of a series of 2-substituted 4,4-dimethyl-1,3-dioxolenium ions have been measured calorimetrically in concentrated sulfuric acid. The relative heats of formation of some tetrahydrofuryl, -pyryl, and 1,3-dioxenium ions have also been measured. A significant Baker–Nathan order has been observed. Replacement of a methyl group by phenyl or vinyl results in a less exothermic heat of formation for the ion. The effects of substituents and ring size on the relative thermodynamic stabilities of the cations are discussed. Linear relationships between the relative heats of formation of dioxolenium ions and the chemical shift of the ring protons and solvolysis rates of *trans*-2-aroyloxycyclohexyl tosylates have been observed.

As part of our studies of the thermodynamics of formation of organic intermediates, we have been investigating the relative heats of formation of cationic intermediates formed *via* anchimeric assistance. One of the best established and most thoroughly studied members of this class of ions is the 1,3-dioxolenium ion (I). Our studies of this ion have led us to gather data on the six-membered ring analog II, and the tetrahydrofuryl (III) and -pyryl (IV) ions.


I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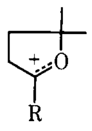
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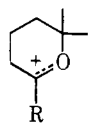
IV

The first demonstration of a dioxolenium ion as an intermediate in a solvolysis reaction was due to Winstein[2] who observed participation by the acetoxy group in the solvolysis of *trans*-2-acetoxycyclohexyl tosylate. The early solvolytic studies of this intermediate have been reviewed.[3] More recently a variety of preparations of stable 1,3-dioxolenium salts have been reported.[4-10] Several groups have also studied the nmr spectra of these ions in strong acids. Pittman[11] has prepared a variety of 2-substituted 3,3-dimethyldioxolenium ions in strong acids. Hart and Tomalia have studied the nmr spectra of a variety of dioxolenium ions in acidic media[8] including several dications.[12] A variety of five- and six-membered ring unsaturated monooxonium ions have been prepared by Brouwer using a procedure analogous to that of Pittman[11,13] and their nmr spectra reported.[14] Dioxolenium ions are important intermediates in carbohydrate chemistry and have been observed from acetylated carbohydrates in liquid hydrogen fluoride.[15] Pedersen has also studied dioxolenium ions in anhydrous hydrogen fluoride.[16]

A great deal of information about the spectra, formation, and chemical reactivity of cyclic five- and six-membered ring mono- and dioxonium ions is available but thermodynamic data on this series have not been available. This series of compounds seemed to provide a system in which thermodynamic stability and chemical reactivity could be compared. The effect of substituents and ring size on the thermodynamic stability is also of interest. To these ends we have measured calorimetrically the relative heats of formation of a series of ions having the general structures illustrated in I–IV.

Experimental Section

The calorimeter and its operation have been described previously.[17] The sulfuric acid was Baker Analyzed Reagent grade. Several bottles of this acid were mixed, stirred, and rebottled to ensure constant composition throughout the work. The strength of the acid was determined by measuring the heat of solution of water in the acid and determining the strength from Giauque's data.[18] The methallyl esters were prepared by treating the necessary carboxylic acid with methallyl chloride in trimethylamine using the procedure of Mills.[19] Reaction of an acid chloride with

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(1) A preliminary report of this work has appeared: J. W. Larsen, S. Ewing, and M. Wynn, *Tetrahedron Lett.*, 539 (1970).

(2) S. Winstein, E. Grunwald, R. Buckles, and C. Hanson, *J. Amer. Chem. Soc.*, **70**, 816 (1948), and references therein.

(3) B. Capon, *Quart. Rev., Chem. Soc.*, **18**, 45 (1964).

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(10) S. Kabuss, *Angew. Chem., Int. Ed. Engl.*, **7**, 64 (1968).

(11) C. U. Pittman, Jr., and S. P. McManus, *Tetrahedron Lett.*, 339 (1969).

(12) H. Hart and D. A. Tomalia, *ibid.*, 1347 (1967).

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(17) E. M. Arnett, R. P. Quirk, and J. J. Burke, *J. Amer. Chem. Soc.*, **92**, 1260 (1970).

(18) W. F. Giauque, E. W. Hornung, J. E. Kunzler, and T. R. Rubin, *ibid.*, **82**, 62 (1960).

Table I. Relative Heats of Protonation (kcal/mol) in Fluorosulfonic Acid at 25°

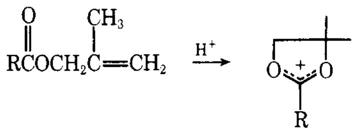
Compound	$\Delta\bar{H}_{\mathrm{S,CCl_4}}$	$\Delta H_{\mathrm{R^+,FSO_3H}}$
$(C_6H_5)_2C{=}CH_2$	$+0.10 \pm 0.07$	-14.7 ± 0.2[a]
$H_3CC({=}O)CH_3$	$+0.79 \pm 0.02$	-19.1 ± 0.1[b]
$CH_3C({=}O)OEt$	$+0.10 \pm 0.00$	-17.4 ± 0.1[b]
$C_6H_5C({=}O)Cl$	$+0.72 \pm 0.10$	-6.0 ± 0.5[b]
Et_2O	-0.42 ± 0.01	-19.1 ± 0.7[c]
EtOH	$+3.8$[d]	-19.1[c]
H_2O	$+4.2$	-16.4[c]
Et_3N	-0.64 ± 0.08	-49.2 ± 0.3[c]
$C_6H_5NH_2$	-0.31 ± 0.02[d]	-34.0 ± 0.4[c]
$CH_3C({=}O)OCH_2C(CH_3){=}CH_2$	$+0.72 \pm 0.03$	-31.5 ± 0.4
$C_6H_5C({=}O)OCH_2C(CH_3){=}CH_2$	$+0.62 \pm 0.11$	-28.6 ± 0.2
p-$MeOC_6H_4C({=}O)OCH_2C(CH_3){=}CH_2$	$+0.67 \pm 0.08$	-32.6 ± 0.8

[a] E. M. Arnett and J. V. Carter, unpublished data. [b] E. M. Arnett, R. P. Quirk, and J. W. Larsen, *J. Amer. Chem. Soc.*, **92,** 3977 (1970). [c] Reference 17. [d] Ethylene chloride was used as the standard state rather than carbon tetrachloride.

methallyl alcohol was also used in several cases.[20] All liquids were purified by careful distillation through a spinning band column and were dried over 4A molecular seives. Most solids were distilled and stored in a desiccator over P_2O_5. The structures of all esters were verified by nmr, ir, and in most cases mass spectrometry. The nmr spectra of all ions were observed and, except where noted, were clean. That is, the spectra contained no peaks not attributed to the ion. All enthalpy values reported are the average of at least six determinations except where noted.

Results and Discussion

With a variety of methods available for preparing dioxolenium ions, a choice of the method best suited for a calorimetric study was necessary. Ideally, a reaction giving the desired ions rapidly ($t_{1/2} < 10$ sec), cleanly, and from readily prepared and purified starting materials should be selected. Such a process for preparation of dioxolenium ions had been developed by Pittman.[11] It is shown below. This reaction is very fast, and



yielded no product other than the desired ion which could be observed in the nmr. For several species, slow addition of the ester to the periphery of a rapidly stirred acid solution was necessary to obtain the ion cleanly. These are the conditions used in the calorimeter. As before,[21] the reported relative heats of formation are heats of transfer from carbon tetrachloride to sulfuric acid.

Heats of protonation of a wide variety of functional groups have been measured in fluorosulfonic acid. These data provide a quantitative scale of the stability of the cations formed relative to their precursors. Some of these data, including values for several dioxolenium ions, are shown in Table I. They range from −6.0 kcal/mol for the heat of protonation of benzoyl chloride to −49.2 kcal/mol for the protonation of triethylamine. At about −30 kcal/mol, the dioxolenium ions are indeed very stable species. Their heat of formation is nearly twice that obtained by protonating ethyl acetate and more than twice that for protonation of 1,1-diphenylethylene to give the very stable diphenylmethyl carbonium ion.

In Table II, the effect of substituents on the relative heats of formation of 2-substituted 4,4-dimethyldioxolenium ions is shown. Some of the differences between the substituent effects normally observed in solvolysis reactions and those observed in this system are striking. In particular, the fact that the heat of formation of the ion becomes less exothermic when methyl is replaced by phenyl or vinyl is opposite to the effects normally observed in solvolysis reactions.[23] Substitution of cyclopropyl for methyl has no effect on the heat of formation of the dioxolenium ion from the ester precursors. In addition a significant Baker–Nathan order is observed. We have recently discussed the large Baker–Nathan orders observed with several different systems in strong acid solutions in terms of the destablizing effect of increasing substituent size on a cation in solution and the increasing endothermicity of the heat of transfer from carbon tetrachloride to sulfuric acid due to the higher cohesive energy density (or Hildebrand solubility parameter δ) of sulfuric acid.[22] While this system provides another example of a large Baker–Nathan order, these data provide no new insight into the source of this large substituent effect.

In solvolysis reactions, replacing a methyl group by cyclopropyl, vinyl, or phenyl is expected to result in an increase in the rate of the reaction.[23] In this system, the heat liberated on conversion of the unsaturated ester to the dioxolenium ion is decreased or unchanged by these substituents. In the case of the vinyl groups, this is probably due to the resonance interactions in the initial ester being greater than in the cation. Apparently cyclopropyl stabilizes both the ester and cation to the same extent. This hypothesis could be tested by measuring the heats of combustion of the esters. Interpretation of the effect due to the phenyl is more difficult. One can balance the inductive electron withdrawal with the resonance stabilization to achieve the desired effect. Alternatively, the phenyl group is quite large and is expected to have a destabilizing effect on the cation due to its larger size superimposed on whatever resonance stabilization it might provide. Also one can balance the resonance stabilization of the starting material with the stabilization of the product. This system does not permit a test between these alternatives and a system which

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(19) R. H. Mills, M. W. Farrar, and O. S. Weinkauff, *Chem. Ind.* (*London*), 2144 (1962).

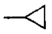
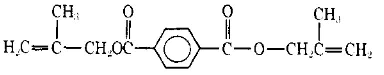
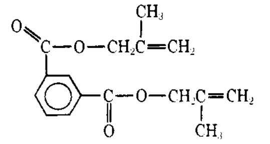
(20) A. I. Vogel, "Practical Organic Chemistry," 3rd ed, Wiley, New York, N. Y., 1966.

(21) E. M. Arnett and J. W. Larsen, "Carbonium Ions," Vol. I, G. A. Olah and P. von R. Schleyer, Ed., Interscience, New York, N. Y., 1969, and ref 22.

(22) J. W. Larsen, *J. Amer. Chem. Soc.*, **92,** 5136 (1970).

(23) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962.

Table II. Relative Heats of Formation of 2-Substituted Dioxolenium Ions (I) in 99.5% Sulfuric Acid at 25°

R	$\Delta \bar{H}_{\mathrm{S,CCl_4}}$, kcal/mol	ΔH_{R^+}, kcal/mol
H	+0.99 ± 0.06	−20.1 ± 0.6
CH_3	+0.72 ± 0.03	−23.7 ± 0.2
Et	+0.67 ± 0.03	−23.0 ± 0.2
n-Pr	+0.26 ± 0.06	−22.8 ± 0.2
i-Pr	+0.07 + 0.02	−23.2 ± 0.5[a]
tert-Bu	+0.26 ± 0.02	−22.1 ± 0.6
$CH{=}CH_2$	+0.45 ± 0.02	−19.2 ± 0.7
	+0.10 ± 0.01	−23.6 ± 0.3
C_6H_5NH	+6.40 ± 0.16	−25.5 ± 0.9
C_6H_5	+0.62 ± 0.11	−22.1 ± 0.3
$C_6H_5HC{=}CH$	+0.95 ± 0.07	−24.0 ± 0.2
p-BrC_6H_4	+0.44 ± 0.04[a]	−20.7 ± 0.1
p-$CH_3C_6H_4$	+0.28 ± 0.05	−21.9 ± 0.6
p-EtC_6H_4	+0.79 ± 0.04	−22.9 ± 0.1
p-$MeOC_6H_4$	+0.67 ± 0.08	−24.8 ± 0.3
p-ClC_6H_4	+0.41 ± 0.03[a]	−21.1 ± 0.2
m-ClC_6H_4	+0.38 ± 0.02	−20.1 ± 0.4
p-$NO_2C_6H_4$	+7.45 ± 0.36	[b]
m-$NO_2C_6H_4$	+1.43 ± 0.09	−21.7 ± 0.5
3,4,5-Tri-$MeOC_6H_2$	+1.07 ± 0.06	−26.4 ± 0.2
	+9.27 ± 0.37	−38.1 ± 1.0
	+7.48 ± 0.48	−37.6 ± 0.8

[a] Average of three measurements. [b] Exothermic drift. Extrapolation to infinite dilution yields a ΔH_{R^+} of 14 ± 2 kcal/mol.

does is currently under investigation. It should be noted that the apparent destabilization by phenyl compared to methyl has been observed in a variety of systems.[22]

Hart[8] has reported that the chemical shifts of the four ring protons in 2-aryl-1,3-dioxolenium ions are a linear function of the σ value for the substituent on the aromatic ring. A comparison of Hart's chemical shifts and the relative heats of formation of the corresponding 4,4-dimethyl cations is shown in Figure 1. As can be seen, there is a rough correlation if only the aromatic derivatives are used. The data for the ions bearing aliphatic substituents are scattered. The nitro compound is well removed from the line. This is almost certainly due to a strong interaction between the nitro group and the sulfuric acid solvent. The para nitro derivative gave a heat of solution in sulfuric acid which became steadily more exothermic. It is apparent that there is a limited rough correlation between heat of formation and chemical shift for aromatic derivatives, but it is equally apparent that large changes in substituent can invalidate this relationship.

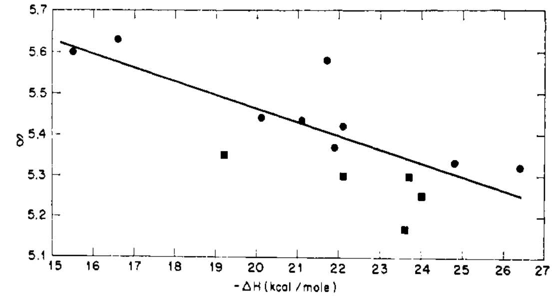


Figure 1. Relative heat of formation of 2-substituted 4,4-dimethyl-1,3-dioxolenium ions in 99.5% H_2SO_4 *vs.* the chemical shift of the ring protons of the corresponding dioxolenium ion in FSO_3H: ■, aliphatic substituent; ●, aromatic substituent.

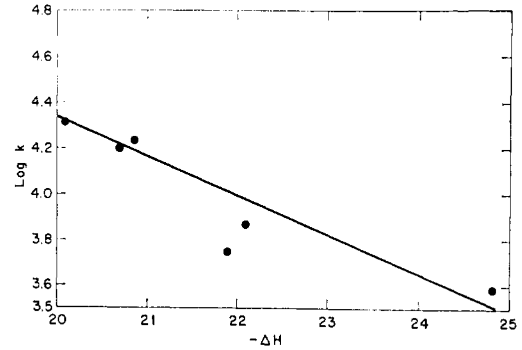


Figure 2. Relative heat of formation of 2-aryl-4,4-dimethyl-1,3-dioxolenium ions in 99.5% H_2SO_4 *vs.* log *k* for acetolysis of the corresponding *trans*-2-aryoloxycyclohexyl tosylate.

Gash and Yuen[24] have measured the acetolysis of *trans*-2-aroyloxycyclohexyl tosylates. A plot of log *k vs.* our relative heats of formation for the correspondingly substituted 2-aryl-4,4-dimethyldioxolenium ions is shown in Figure 2. There is a reasonable correlation between the free energy of activation for the anchimerically assisted solvolysis and the relative heats of formation of the substituted dioxolenium ion. It is noteworthy that the enthalpy of activation for the solvolysis is constant within experimental error while the heat of forma-

(24) K. B. Gash and G. Y. Yuen, *J. Org. Chem.*, **34**, 720 (1969).

Table III. Relative Heats of Formation of a 1,3-Dioxenium Ion and Monooxonium Ions in 99.5% Sulfuric Acid at 25°

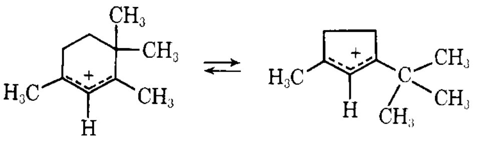
Precursor	Ion	$\Delta\bar{H}_{\mathrm{S,CCl_4}}$, kcal/mol	ΔH_{R^+}, kcal/mol	$\Delta\Delta H_{\mathrm{hydrog}}$
$CH_3C(=O)OCH_2C(CH_3)=CH_2$	V	$+0.72 \pm 0.03$	-23.7 ± 0.2	0
$CH_3C(=O)O(CH_2)_2C(CH_3)=CH_2$	VI	-0.06 ± 0.02	-25.1 ± 0.1[a]	0
$CH_3C(=O)CH_2CH_2C(CH_3)=CH_2$	VII	$+0.46 \pm 0.05$	-27.7 ± 0.2	0
$CH_3C(=O)CH_2CH_2CH=C(CH_3)CH_3$	VIII	$+0.06 \pm 0.07$	-27.0 ± 0.4	-1.5
$CH_3C(=O)CH_2CH_2CH=CH_2$	IX	$+0.26 \pm 0.03$[b]	-26.3 ± 0.1[b]	$+1.7$

[a] The nmr of this cation was not free of other products. Average of the first two points used. Starting with the third point the heats became increasingly exothermic. [b] Average of three points.

tion of the dioxolenium ions is changing by *ca.* 4 kcal/mol.

Using the data from Table III, it is possible to compare the thermodynamic stabilities of a variety of five- and six-membered ring mono- and dioxonium ions. A thorough nmr study of these ions has been made by Brouwer.[15] It will be assumed throughout this discussion that there are no significant differences in steric or inductive effects in the open-chain esters used to form the cyclic ions. Using data from Table III, it is apparent that the six-membered ring ion VI is thermodynamically more stable than the five-membered ring V. This situation is complicated by the chemical instability of VI. The nmr spectrum of VI in concentrated sulfuric acid changes very rapidly going to a mixture of unidentified products. Even when the spectrum is recorded within 2 min of mixing, it indicates only about half of the ester is in the form of VI. There is, however, no drift in the temperature *vs.* time curves recorded in the calorimeter. Thus, the decomposition of VI is either not occurring at the low concentration (*ca.* 10^{-3} *M*) used in the calorimeter, or the decomposition is isoenthalpic. The heat of reaction does become more exothermic with increasing concentration at slightly higher ion concentrations. It is possible to estimate the relative heat of formation of VI and this value is given in Table III. The nmr of VI shows a triplet at 5.0, a sharp singlet at 1.8, a singlet at 2.3, and complex absorption from 2.45 to 3.1 ppm with areas of 1.7:3:5.7:undetermined.

The situation at first glance is elegant confirmation of Eliel's statement that "the five-membered ring is easier to close but is [thermodynamically] less stable."[25] However, as Eliel points out, this situation is strongly affected by the substituents on the rings. This system is also complicated by the coplanarity of the O⎓C⁺⎓O grouping. Sorensen[26] has studied in detail the rearrangement of several substituted cyclohexenyl cations to cyclopentenyl cations such as the system shown below for which $\Delta G = -1.40$ and $\Delta H = -1.45 \pm 0.5$. He



observed the five-membered ring to be more stable and suggested charge delocalization as the most probable explanation. The oxonium ions are substituted quite differently than in Sorensen's system and we feel that the substituents are playing a major role in determining the relative stability of the five- and six-membered rings. Construction of a Dreiding model of the five-membered ring ion reveals two eclipsed methyl–hydrogen interactions. These are not present in the six-membered ring, although there is a 1,3-axial methyl–hydrogen interaction partially (if not largely) relieved by the twisting in the rest of the ring caused by the three coplanar atoms. If 1.3 kcal/mol is used for the eclipsed H–CH_3 interaction in the five-membered ring,[25,27] conformational factors favor the six-membered ring ion over the five by about 2.2 kcal/mol. Experimentally, the larger ring is favored by about 1.5 kcal/mol. This analysis is rendered somewhat uncertain by the chemical instability of VI. It is apparent that the two ring systems are of nearly the same stability and that the unsubstituted five-membered ring may be slightly more stable, as observed by Sorensen in a related system.

It is possible to carry out a similar analysis of the five- and six-membered ring monooxonium ions VII and VIII. Since these were formed from precursors differing in the stability of the double bond, a correction was made using the data reported in Wheland.[28] The numerical values of the corrections are given in Table III. In this case the formation of the six-membered ring is more exothermic than the five- by 0.8 kcal/mol. Replacing an oxygen by a methylene introduces two eclipsed H–H interactions in the five-membered ring which are not present in the six. Correcting for all such nonbonding interactions as before leads to the prediction that the smaller unsubstituted ring will be more stable than the unsubstituted six-membered ring by about 4 kcal/mol. This value includes corrections for all nonbonded intereactions including the two eclipsed H–H interactions in the five-membered ring. Using Turners'[29] data for the heats of hydrogenation of ethylcyclopentene and methylcyclohexene and the heats of formation for the saturated analogs,[30] the five-membered ring olefin is calculated to be less stable than the six- by 4.7 kcal/mol (assuming equal heats of solution in acetic acid for the hydrocarbon pairs). This value includes the eclipsed H–H interactions in 1-methylcyclopentene and so only the presence of the methyl groups must be accounted for when a comparison with the oxonium ion is made. Correcting only for these interactions it appears that the six-membered ring oxonium ion is favored by 3 kcal/mol, 1.7 kcal/mol less than the difference observed with the olefins. There appears to be

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(25) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill, New York, N. Y., 1962, p 199.

(26) T. Sorensen, *J. Amer. Chem. Soc.*, **91**, 6398 (1969).

(27) K. Pihlaja and S. Luoma, *Acta Chem. Scand.*, **22**, 2401 (1968).

(28) G. W. Wheland, "Resonance in Organic Chemistry," Wiley, New York, N. Y., 1955, p 78.

(29) R. B. Turner and R. H. Garner, *J. Amer. Chem. Soc.*, **80**, 1424 (1958).

(30) D. R. Stull, E. F. Westrum, Jr., and G. C. Sinke, "The Chemical Thermodynamics of Organic Compounds," Wiley, New York, N. Y., 1969.

a significant difference between the effect of the $-C{=}O^{+}-$ group and the $-C{=}C-$ group. The energy differences between the five- and six-membered rings are similar to those observed by Sorensen.[26]

The substituent effect indicated by the relative heat of formation of the 1,3-dimethyltetrahydrofuranonium ion IX is not easy to rationalize. The heat of formation is 3.1 kcal/mol less exothermic than that of the corresponding 1,3,3-trimethyl-substituted ion VII after correcting for the difference in energy of the olefinic bond in the starting esters. Thus replacing a hydrogen in the 3 position by a methyl increases the stability of the ion by 3.1 kcal/mol in spite of a steric interaction expected to decrease the stability by *ca.* 0.4 kcal/mol. Thus there must be a net inductive and/or resonance stabilization of about 3.5 kcal/mol. Replacing the 2-hydrogen in 4,4-dimethyldioxolenium ion by a methyl group results in an increased stabilization of 3.6 kcal/mol (see Table I). It is hard to see why a 3-methyl group in the monooxonium ion should have as large a stabilizing effect as a 2-methyl group in the dioxolenium ion.

It is also of interest that formation of the monooxonium ions from ketones is more exothermic than formation of the dioxonium ions by 2–4 kcal/mol. The ion with the charge spread over two oxygen atoms is expected to be thermodynamically more stable. We believe this apparent contradiction is due to a greater increase in the stabilization of the ground-state ester than of the ion when a methylene group is replaced by an oxygen. The difference in heats of formation (gas phase) of 2-pentanone and ethyl acetate is 44.04 kcal/mol[30] with ethyl acetate being more stable. If replacing the methylene group in the 5 position in ion VII by an oxygen yielding ion V increases the stability of the ion by *ca.* 40 kcal/mol, the relative heats of formation will be as observed. The heat of protonation of ethyl acetate is larger than that for 2-pentanone, by 0.6 kcal/mol,[31] and can be rationalized on the same basis. Arnett[31] has rationalized the decrease in heat of protonation as alkyl groups are replaced by phenyl using a similar argument.

There are many unexpected substituent effects on the stability of the oxonium ions discussed here. It is obvious that many factors not explicitly considered in the rationalization of substituent effects on solvolytic reactivities must be playing a significant role in stable ions in strong acid media. The substituent effects on the stabilities of cations observed in strong acids are large, and the development of the calorimetric technique means that a variety of systems not readily studied using acidity function techniques can be handled nicely. Our studies of the relative heats of formation of a variety of cationic systems are proceeding in order to explore some of these substituent effects.

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(31) Table I, footnote *b*.

Protolysis Kinetics of *N*-Benzyl-*N'*-methylurea

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Abstract: Protolysis of the title compound is specific acid–base catalyzed and the rate constants are reported. Both NH groups are base catalyzed to the same extent, but differ under acid catalysis. Acid and base catalysis of the title compound is explained qualitatively on the basis of polar substituent effects (σ^*) and steric effects (E_s). The energy of activation for protolysis was only obtainable under basic conditions and is reported. The protolysis kinetics of *N*-methylpropionamide under identical conditions is reported and is used as a comparison.

The study of proton exchange kinetics of NH-bearing compounds has provided a number of examples of compounds differing in mechanism and rates of protolysis.[1–6] Steric and polar influences of proton exchange, however, have not been extensively studied. This paper reports our study of the protolysis kinetics of *N*-benzyl-*N'*-methylurea, a compound whose two NH groups exhibit protolysis kinetic differences as a result only of influences by their respective substituents. The title compound allows one to qualitatively assess steric and polar influences on NH exchange rates. To our knowledge no similar study has been reported, nor has the protolysis of a disubstituted urea previously been reported.

In this paper the technique employed was to follow by high-resolution pmr the rate of collapse of the NCH_3 and NCH_2 doublets as a function of pH. The methyl and methylene doublets arise from coupling by the protons of the urea nitrogens which becomes discernible under slow proton exchange conditions. *N*-Methylpropionamide was also studied under the same conditions for comparison. Rate constants for acid- and base-catalyzed protolysis of the title compound and the

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