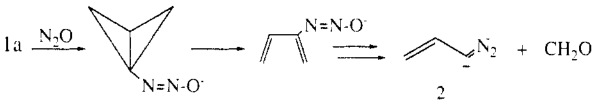
The structure of the $(P\text{-}1)^-$ ion obtained from bicyclobutane was shown to be **1a** based on its reactivity and hydrogen/deuterium exchange behavior.[10] Deuterium oxide is a sufficiently strong Brønsted acid to react with the ion by deuteron transfer to afford OD^-. In contrast, addition of ND_3, which is less acidic, to the $(P\text{-}1)^-$ results in one exchange of hydrogen for deuterium. This is consistent only with the proposed structure **1a**. Ions **1b** and **1c**, independently produced by proton abstraction from methylenecyclopropane or 1-methylcyclopropene[9c,11] and 1,3-butadiene, undergo up to 5 H/D exchanges with D_2O and ND_3, respectively. Therefore, neither **1b** or **1c** can be the ion produced by proton abstraction from bicyclobutane.[12]

The acidity of **1** was measured with the bracketing technique. This is the simplest method for measuring acidities and involves adding progressively stronger and stronger bases to an acid until proton transfer occurs. The reliability of the process is greatly enhanced if the other direction is also examined by adding successively potent acids to the conjugate base of interest. Both directions were studied, and the results, summarized in Table I, allow us to assign $\Delta H_{acid} = 398 \pm 2$ kcal mol^{-1} to bicyclobutane. This is in excellent agreement with a calculated value of 400 kcal mol^{-1} using AM1[14] and a linear correction, which is required to reliably reproduce hydrocarbon acidities.[15]

In the liquid phase it has been observed that there is a linear correlation between acidity, pK_a, and ^{13}C–^{1}H coupling constants.[16] We have found this relationship to be equally true for gas-phase acidities of small hydrocarbons.[17] It will break down for compounds whose conjugate bases are resonance stabilized and for larger molecules where polarization effects are important. Nevertheless, this relationship may be of value in predicting acidities and finding accessible alkyl anions.

The electron affinity (EA) of **1a** was bracketed and found to be 0.77 ± 0.33 eV (17.8 ± 7.6 kcal mol^{-1}, see Table I). Even with the relatively large uncertainty, this is the largest EA reported to date for an alkyl anion. When combined with the acidity, a bridgehead C–H bond dissociation energy of ~102 kcal mol^{-1} is obtained.[18] The C–H bond energy in cyclopropane[19] is 106 kcal mol^{-1} so the ~10 kcal mol^{-1} difference in electron affinities[3] can be attributed to the enhanced acidity of bicyclobutane.

The reactivity of **1a** with nitrous oxide, carbon disulfide, and isoamyl nitrite has been briefly explored. All three reactions occur quite readily. Addition of N_2O to **1a** produces two ionic products of m/z 67 and 97, which correspond to the vinyldiazomethane anion (**2**) and an adduct, in approximately a 9:1 ratio (eq 2). The



(2)

mechanism is presumably the same, after isomerization of the initial adduct, as in the known reaction between the $(P\text{-}1)^-$ of 1,3-butadiene and N_2O.[20] Carbon disulfide and isoamyl nitrite both react in a manner that is consistent with what has previously been described.[21,22] The major product with the former compound is an ion of m/z 85 which corresponds to sulfur atom transfer. The latter reagent reacts with **1a** to afford NO_2^- (m/z 46) and an ion which corresponds to $C_4H_4NO^-$ (m/z 82) as the major products. Smaller amounts of CN^- (m/z 26), 3-methyl-1-butoxide (m/z 87), and an ion of m/z 42 are also produced.

Further investigations into the chemistry of the bicyclobutyl anion and other small ring anions are in progress and will be presented in due course.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. Support from the University of Minnesota Graduate School Grant-In-Aid of Research and the McKnight-Land Grant Professorship programs is gratefully acknowledged. We owe a particular debt to Charles DePuy, Veronica Bierbaum, Barney Ellison, David Smith, Nigel Adams, and Harley Steinbrenner for their unselfish and detailed advice in constructing the flowing afterglow used in this investigation.

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(12) Ions **1b** and **1c** can also be ruled out based on their reactivity with N_2O and O_2. The former ion reacts with N_2O to afford CN^- as the major product,[13] while **1c** and O_2 undergo a rapid reaction to afford a variety of products. Another isomer which was considered is the vinyl anion obtained by proton abstraction from cyclobutene. This ion undergoes 1 H/D exchange with ND_3[13] but reacts readily with O_2 to afford O_2^- and with N_2O to produce both the vinyldiazomethane anion (**2**, m/z 67) and cyclobutanone enolate or the enolate of methyl vinyl ketone (m/z 69).[9c]

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(17) A plot of gas-phase acidities versus ^{13}C–^{1}H coupling constants is linear: $y = -0.296x + 455.3\ r = 0.98$. The data points are CH_4 (416.6, 125), C_2H_4 (406, 156), c-C_3H_6 (412, 161), **1** (398, 202), and C_2H_2 (379.6, 249) where the acidities (ref 9a) and coupling constants (Muller, N.; Pritchard, D. E. *J. Chem. Phys.* **1959**, *32*, 767 and 1471 and ref 5), in that order, are given in the brackets.

(18) BDE (A–H) = $\Delta H_{acid}(AH) - IP(H^{\bullet}) + EA\ (A)$ where $IP(H^{\bullet})$ = 313.6 kcal mol^{-1} (see ref 9a).

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Evidence for Free Monomeric Thiometaphosphate Anion in Aqueous Solution

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Phosphoryl- and thiophosphoryl-transfer reactions have been extensively studied, particularly in relation to enzyme-catalyzed processes.[1] Despite this close scrutiny the mechanisms of these reactions have still not been unambiguously established. Of particular interest has been the series of studies pertinent to the "freeness" of monomeric metaphosphate in reactions of phosphate monoesters.[2] We have recently made a comparative study of model phosphoryl- and thiophosphoryl-transfer reactions with principally stereochemical methods.[3] On the basis of these studies we believe that there are significant differences between the phosphoryl- and thiophosphoryl-transfer reactions in aqueous

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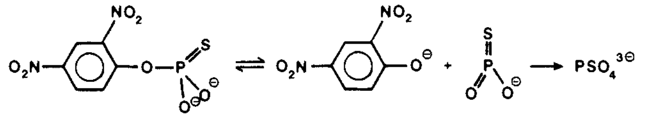
Scheme I



solution. We report here the effects of pressure on the rate of hydrolysis of 2,4-dinitrophenyl thiophosphate dianion that provide strong evidence for a dissociative mechanism involving monomeric thiometaphosphate as an intermediate, in contrast to the corresponding reaction of the phosphate ester.[4]

Although monomeric metaphosphate anion has been widely accepted as an intermediate with finite lifetime in the hydrolysis of phosphate monoesters,[5] more recent studies are not consistent with a fully dissociative mechanism. For example, the alcoholysis of 2,4-dinitrophenyl [^{16}O,^{17}O,^{18}O]phosphate dianion in aqueous methanol occurs with inversion of configuration which is inconsistent with a symmetrically solvated intermediate.[6] This observation alone does not however rule out the fleeting existence of a metaphosphate intermediate that does not survive long enough to allow the leaving group to diffuse away or for the species to tumble before being captured. le Noble et al. reported that the volume of activation for the hydrolysis of 2,4-dinitrophenyl phosphate dianion is -4.8 cm^3 mol^{-1} (i.e., the reaction is accelerated by pressure).[4] It is argued that the activation volume for a reaction may distinguish dissociative from associative reaction mechanisms,[7] although the interpretation of small negative volumes of activation in mechanistic terms has been questioned.[8] In the dissociative pathway bond breakage is complete before bond making thus involving an expansion in the transition state, whereas in the associative mechanism bond making and bond breaking proceed together with bond formation usually dominating, thus involving a shrinkage at the transition state. Typically associative reactions have volumes of activation in the range -5 to -10 cm^3 mol^{-1}, whereas dissociative reactions show activation volumes exceeding $+10$ cm^3 mol^{-1}.[7] Our stereochemical studies on the thiophosphoryl-transfer reactions of 4-nitrophenyl thiophosphate have suggested that monomeric thiometaphosphate may be sufficiently kinetically and thermodynamically stable to participate as an intermediate even in reactions in aqueous solution.[3] Following the work of le Noble[4,7] we would predict that thiophosphoryl-transfer reactions in aqueous solution will show a volume of activation with the opposite sign to that recently reported for the corresponding phosphoryl-transfer reaction.

We have investigated the rate of hydrolysis of 2,4-dinitrophenyl thiophosphate dianion (Scheme I) as a function of pressure.[9] The rate constant for release of 2,4-dinitrophenoxide from the thiophosphate dianion was observed to be reduced by presure with a volume of activation of $+11$ cm^3 mol^{-1} (Figure 1). Although the error bars on the plot are significant, the sign of the volume of activation is clearly positive and differs from that reported by le Noble for the corresponding phosphate ester.[4] Since in the latter case an associative reaction mechanism has been deduced on the basis of a number of studies,[2,4] it is likely that the change in sign for the reaction of the corresponding thiophosphate signals a change in mechanism. A dissociative reaction would give rise to an expansion in the transition state which would be expected to be further amplified by the effects of the greater charge delocalization at the transition state (electrostriction effects). The difference in activation volumes for the reactions of 2,4-dinitrophenyl phosphate and the corresponding thiophosphate is large (16 cm^3 mol^{-1}) and lends some support to the claim that this parameter is a good mechanistic indicator.[3,4,8] These observations are consistent with the conclusions drawn from the stereochemical studies as discussed above and provide further direct evidence for the participation of monomeric thiometaphosphate ion as an intermediate in the hydrolysis of aryl thiophosphate dianion in aqueous solution. Confirmation that thiophosphoryl- and phosphoryl-transfer reactions follow different and distinct mechanistic pathways in aqueous solution may be pertinent to the use of the former to probe enzyme-catalyzed reactions.[1b,c]

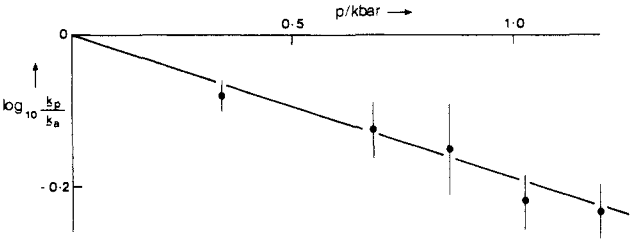


Figure 1. Pseudo-first-order rate constants as a function of pressure for the hydrolysis of 2,4-dinitrophenyl thiophosphate dianion in aqueous solution (pH 12.7, 25 °C).

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Remarkably Similar Solution and Solid-State Structures for Two Divergently Reactive Lithium Enolates Derived from Vinylogous Urethanes

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The synthetic utility of the lithium enolate **1** generated from the vinylogous urethane **2** in anti-selective aldol reactions has been demonstrated.[1] An attempt to develop enantioselection for this anti-aldol process led us to generate the lithium enolate **3** from the vinylogous urethane **4**—the anticipation being that these structurally similar enolate species would augment each other in

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