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VINYL ETHER HYDROLYSIS. 25. EFFECT OF α- AND β-TRIMETHYLSILYL SUBSTITUTION

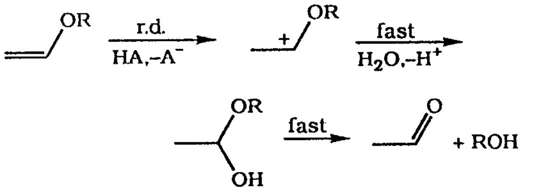
A. J. KRESGE* AND J. B. TOBIN

Department of Chemistry, University of Toronto, Toronto, Ontario M5S 1A1, Canada

Rates of hydrolysis catalyzed by dilute perchloric acid were measured for the vinyl ethers $MeOC(SiMe_3){=}CH_2$, $EtOC(SiMe_3){=}CH_2$, *cis*-$EtOCH{=}CHSiMe_3$, $MeOC(t\text{-}Bu){=}CH_2$ and $EtOC(t\text{-}Bu){=}CH_2$ in wholly aqueous solution and for $MeOCH{=}CH_2$, $MeOC(SiMe_3){=}CH_2$ and $MeOC(t\text{-}Bu){=}CH_2$ in ethanol–water (4 : 1), in order to assess the effects of silyl substitution on the stability of the carbocations formed in the rate-determining step of these reactions. The results for α-substitution give the reactivity order $H < SiMe_3 < t\text{-}Bu$, with a greater spread (10^3) in wholly aqueous solution than in the mixed solvent (10^2). The β-trimethylsilyl substituent shows a modest 100-fold acceleration over hydrogen; the diminished magnitude of this effect relative to the 10^{12}-fold acceleration found recently in a cyclohexyl solvolysis reaction is attributed to the imposition of a conformation in the transition state of vinyl ether hydrolysis that is far from optimum for hyperconjugative electron donation.

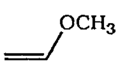
INTRODUCTION

There is much current interest in the effect of silyl substituents on carbocation stability.[1] Not all of the reactions which have been used to investigate this phenomenon, however, are mechanistically well defined, and this has led to uncertainties in the interpretation of some of the experimental data. Vinyl ether hydrolysis would seem to be free from this difficulty: it is a mechanistically simple cation-producing reaction which occurs, with no known exception, by rate-determining proton transfer from a catalyzing acid to the substrate:[2]



(1)

This mechanistically clear reaction has in fact already been used to probe the effect of α-silyl groups on carbocation stability in a comparative study of the rates of hydrolysis of methyl vinyl ether (**1**), methyl α-trimethylsilylvinyl ether (**2**) and methyl α-*tert*-butylvinyl ether (**3**).[3] We have now extended that work, which was done in acetone–water (4 : 1) solvent, to a wholly aqueous medium and also to ethanol–water solvent. We have also examined the corresponding ethyl vinyl ethers and, in order to probe the effect of β-silyl substitution, we have investigated ethyl *cis*-β-trimethylsilylvinyl ether (**4**).



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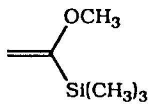

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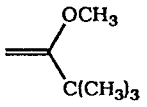

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EXPERIMENTAL

Materials. Methyl and ethyl α-trimethylsilylvinyl ethers were prepared by treating the α-lithio derivatives of methyl and ethyl vinyl ethers, respectively, with trimethylsilyl chloride;[4] the spectral and physical properties of these substances agreed well with literature values.[4,5] Ethyl *cis*-β-trimethylsilylvinyl ether was obtained by hydrogenation of trimethylsilylethoxyacetylene[6] using a Lindlar catalyst; its properties were also consistent with literature values.[7]

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* Author for correspondence.

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Methyl α-*tert*-butylvinyl ether was synthesized from pinacolone by treating the latter with trimethyl orthoformate and a catalytic amount of *p*-toluenesulfonic acid in methanol solution.[8] Its ^1H NMR spectrum [$CDCl_3$ solution: $\delta = 1{\cdot}09$ (s, 9H), $3{\cdot}52$ (s, 3H), $3{\cdot}78$ (d, 1H, $J = 2{\cdot}4$ Hz), $3{\cdot}92$ (d, 1H, $J = 2{\cdot}4$ Hz)] was consistent with its structure, and the parent peak in its high-resolution mass spectrum, $m/z = 114{\cdot}1041$, agreed with the expected value of $114{\cdot}1045$. We were unable to prepare ethyl α-*tert*-butylvinyl ether by the same method, and we therefore synthesized it by *O*-alkylation of the potassium enolate of pinacolone, using potassium hydride in hexamethylphosphoramide (HMPA)–tetrahydrofuran (THF) (20 : 80) to make the enolate and ethyl *p*-toluenesulfonate to effect the alkylation. The ^1H NMR spectrum of the vinyl ether [$CDCl_3$ solution: $\delta = 1{\cdot}08$ (s, 9H), $1{\cdot}28$ (t, 3H, $J = 7$ Hz), $3{\cdot}68$ (q, 2H, $J = 7$ Hz), $3{\cdot}74$ (d, 1H, $J = 2.2$ Hz), $3{\cdot}90$ (d, 1H, $J = 2.2$ Hz)] was also consistent with its structure and the parent peak in its high-resolution mass spectrum, $m/z = 128{\cdot}1203$, agreed with the expected value of $128{\cdot}1201$.

All other materials were best available commercial grades. Samples of methyl and ethyl α-trimethylsilylvinyl ethers used for kinetic measurements were purified by distillation, those of methyl and ethyl α-*tert*-butylvinyl and ethyl β-trimethylsilylvinyl ethers by gas chromatography and methyl and ethyl vinyl ether were used as received from commercial suppliers.

Kinetics. Rates of vinyl ether hydrolysis were determined spectroscopically, mostly by monitoring the decrease in absorbance of the strong vinyl ether absorption band at 205–210 nm; some determinations for ethyl α-trimethylsilylvinyl ether were also made by following the appearance of product absorbance at 354 nm. Measurements of the slower reaction rates were performed using Cary Model 118 and 2200 spectrometers, and measurements of the faster reactions were made with a Hi-Tech Scientific Model SF-S1 stopped-flow spectrometer; the temperature of the reaction solutions was controlled at $25{\cdot}0 \pm 0{\cdot}1$ °C. For the slower reactions vinyl ether substrates were supplied as acetonitrile stock solutions; these were diluted 300-fold so that the final reaction mixtures contained $0{\cdot}3\%$ acetonitrile and were *ca* 2×10^{-4} M in substrate. For the faster reactions, wholly aqueous solutions were loaded into both syringes of the stopped-flow apparatus, and the final reaction mixtures were therefore wholly aqueous; substrate concentrations in the reaction mixtures were again *ca* 2×10^{-4} M. The data obeyed the first-order rate law well, and observed first-order rate constants were obtained by least-squares fitting to appropriate linear or exponential functions.

The solvent for rate measurements in ethanol–water (4 : 1) was prepared by diluting $10{\cdot}0$ ml of aqueous perchloric acid to a final volume of $50{\cdot}0$ ml with freshly distilled absolute ethanol. In all cases the ionic strength was maintained at $0{\cdot}10$ M by adding sodium perchlorate as needed.

RESULTS

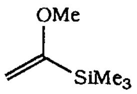
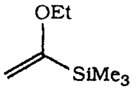
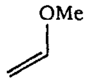
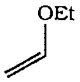
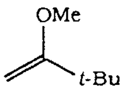
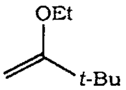
Rates of hydrolysis of methyl and ethyl α-trimethylsilylvinyl ethers, ethyl β-trimethylsilylvinyl ether and methyl and ethyl α-*tert*-butylvinyl ethers were determined in dilute aqueous perchloric acid solutions at constant ionic strength ($0{\cdot}10$ M). Measurements were made at different acid concentrations, generally six or more spanning at least an order of magnitude, and five or six replicate determinations were usually made at each concentration. Observed first-order rate constants so obtained proved to be accurately proportional to acid concentration in all cases, and bimolecular hydrogen-ion catalytic coefficients were obtained by linear least-squares analysis. The kinetic data are summarized in a supplementary table (S1) (this and other supplementary tables referred to below are available from the authors on request) and the catalytic coefficients are listed in Table 1.

Rates of hydrolysis of methyl vinyl, methyl α-trimethylsilylvinyl and methyl α-*tert*-butylvinyl ethers were also measured in dilute ethanol–water (4 : 1) solutions of perchloric acid. Here again, replicate determinations were made over a range of acid concentrations, and observed first-order rate constants once more proved to be linear functions of acid concentration. These data are summarized in a supplementary table (S2) and the hydrogen-ion catalytic coefficients obtained by least-squares analysis are listed in Table 1.

A solvent isotope effect for the hydrolysis of ethyl α-trimethylsilylvinyl ether was supplied by measuring rates of hydrolysis of this substrate in D_2O solution. The data, again covering a range of acid concentrations, are summarized in a supplementary table (S3). Linear least-squares analysis gave the catalytic coefficient $k_{D^+} = 10{\cdot}0 \pm 0{\cdot}2\ l\,mol^{-1}\,s^{-1}$, which, when combined with its H_2O counterpart, provides the isotope effect $k_{H^+}/k_{D^+} = 3{\cdot}36 \pm 0{\cdot}07$.

All of the rate determinations described above were performed by monitoring the disappearance of vinyl ether through the decrease in its strong UV absorption band at 205–210 nm. In order to determine whether products appeared at the same rate as the substrate disappeared, some measurements were also made on ethyl α-trimethylsilylvinyl ether by monitoring the increase in ketone-product absorbance at its maximum, 354 nm. This absorption band is weak, however, and substrate concentrations exceeding the solubility of ethyl α-trimethylsilylvinyl ether in water were needed in order to obtain good kinetic data. Acetonitrile–water (1 : 2) solvent was therefore used instead of a wholly aqueous medium. Rate measurements were made at both wavelengths, 204 and 354 nm, in this solvent over a range of

Table 1. Summary of rate constants for the hydrolysis of vinyl ethers catalyzed by dilute perchloric acid at 25 °C[a]

Substrate	k_{H^+} ($l\,mol^{-1}\,s^{-1}$) H_2O	$EtOH-H_2O$ (4 : 1)	CH_3CN-H_2O (1 : 2)
	11·5	0·184	—
	33·6	—	10·2
	225	—	—
	0.760[b]	0.0346	—
	1.75[c]	—	—
	779	7.86	—
	2100	—	—

[a] Ionic strength = 0·10 M.

[b] From Ref. 9.

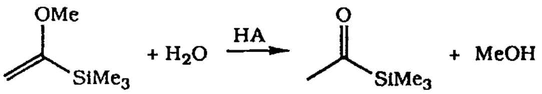
[c] From Ref. 10.

acid concentrations. The data so obtained are summarized in a supplementary table (S4). Observed first-order rate constants were accurately proportional to acid concentration, and linear least-squares analysis gave identical hydrogen-ion catalytic coefficients, k_{H^+} = 10·2 ± 0·2 $l\,mol^{-1}\,s^{-1}$, for the two wavelengths.

DISCUSSION

Reaction mechanism

It is well known that acid-catalysed hydrolysis of α-silylvinyl ethers gives the corresponding silyl-substituted ketones as reaction products; the hydrolysis of methyl α-trimethylsilylvinyl ether is in fact the basis of a standard method for preparing acetyltrimethylsilane:[4]



(2)

The present study shows that acylsilanes are produced in this reaction at the same rate as the vinyl ether reactants are consumed: the specific rate of hydrolysis of ethyl α-trimethylsilylvinyl ether measured by monitoring disappearance of the vinyl ether was found to be identical with that measured by following the appearance of the acylsilane product. This is consistent with the behaviour of other vinyl ethers not containing silyl substituents, e.g. the prototype substance ethyl vinyl ether;[10] this means that none of the intermediates generated in this process [cf. equation (1)] builds up to any significant extent during the course of this reaction, as required if the initial carbocation-forming step is to be rate determining.

Additional evidence that the hydrolysis of silyl-substituted vinyl ether follows the conventional reaction mechanism of equation (1) comes from the hydrogen-ion isotope effect measured for ethyl α-trimethylsilylvinyl ether, $k_{H^+}/k_{D^+} = 3{\cdot}36$. Large isotope effects in the normal direction ($k_{H^+}/k_{D^+} > 1$) such as this are characteristic of rate-determining proton transfer from catalyst to substrate, in contrast to the inverse isotope effects ($k_{H^+}/k_{D^+} < 1$) generally found for reactions in which proton transfer occurs in a rapid and reversible pre-equilibrium step.[11] The magnitude of the presently measured isotope effect is, in fact, consistent with the value of $k_{H^+}/k_{D^+} = 3{\cdot}25$ predicted for a vinyl ether of this reactivity from a correlation of hydrogen-ion isotope effects for the hydrolysis of a large group of vinyl ethers known to occur by the rate-determining proton transfer mechanism.[9]

α-Silyl substitution

The rate constants summarized in Table 1 show that α-trimethylsilyl substitution accelerates vinyl ether hydrolysis relative to α-hydrogen but retards it relative to α-*tert*-butyl. This is the case for both the methyl and ethyl ether series studied here and also for the methyl series examined in an earlier study using a different solvent system.[3] A similar ordering has been found in other cation-forming reactions,[1] and also by theoretical calculations of carbocation stability.[12] This order is believed to be the result of the electropositive nature of silicon, which gives it an electron-donating inductive effect compared to hydrogen, coupled with an inferior ability of carbon—silicon bonds to undergo hyperconjugative electron donation (**5**) compared with carbon—carbon bonds (**6**) because of the greater length

$$\overset{+}{C}H_2-\overset{CH_3}{\overset{|}{Si}}Me_2 \longleftrightarrow CH_2{=}\overset{CH_3^+}{Si}Me_2$$

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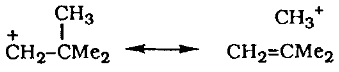


$$\overset{+}{C}H_2-\overset{CH_3}{\overset{|}{C}}Me_2 \longleftrightarrow CH_2{=}\overset{CH_3^+}{C}Me_2$$

6

of carbon—silicon over carbon—carbon bonds and the relative weakness of carbon—silicon multiple bonding.[1]

Although the reactivity order for the present α-substituted vinyl ethers is the same for all conditions investigated, there is an interesting difference in the spread of relative reactivities between the wholly aqueous and the mixed aqueous–organic solvent systems studied. In the wholly aqueous solvent, rate constants for the methyl ethers along the series α-H, α-$Si(CH_3)_3$, α-$C(CH_3)_3$ give the relative reactivities 1 : 15 : 1000, and those for the ethyl ethers in this medium are similar, 1 : 19 : 1200. In the mixed solvents, on the other hand, this relative reactivity scale is considerably compressed: in ethanol (4 : 1) the methyl ethers give 1·0 : 5·3 : 230 and in acetone–water (4 : 1) 1·0 : 1·8 : 100.[3]

This difference may be understood in terms of the effect that switching from an aqueous to a mixed aqueous–organic solvent has on the rate of vinyl ether hydrolysis. The data in Table 1 show that such a change is rate retarding, consistent with previous experience,[13] and that the retardation increases along the series α-H, α-$Si(CH_3)_3$, α-$C(CH_3)_3$: the ratios of rate constants in water to those in ethanol–water (4 : 1) for these substances are 22, 63 and 99, respectively. This is also the order of increasing hydrophobicity of these vinyl ethers, which suggests that the retardation is the result of improved initial state solvation by the non-aqueous component of the solvent mixture. This increasing retardation is, of course, opposite to the order of increasing reactivity of these substrates, and it will therefore serve to reduce the relative reactivity as water is replaced with an organic solvent.

It would seem, therefore, that differences in reactivity along the series under discussion are due not only to electrical effects of the substituents involved, but also to differential solvent effects on the reactions taking place.

β-Silyl substitution

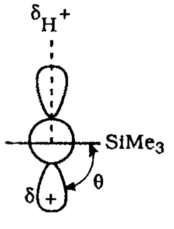
The data in Table 1 show that silyl substitution in the β-position of vinyl ethers also accelerates the rate of hydrolysis. This again is consistent with previous experimental observations on other cation-forming reactions[1] and also with theoretical calculations.[12] The effect here is believed to be a combination of inductive electron donation and a particularly effective hyperconjugation which now involves carbon—carbon multiple bond formation (**7**).

$$\overset{+}{C}H_2-\overset{SiMe_3}{\overset{|}{C}}H_2 \longleftrightarrow CH_2{=}\overset{SiMe_3^+}{C}H_2$$

7

The acceleration found here, however, is small compared with previous experimental results and theoretical predictions. The present data give a rate factor of 130, which is equivalent to the free energy of activation difference $\delta\Delta G^{\ddagger} = 2{\cdot}9\ \mathrm{kcal\,mol^{-1}}$, whereas previous studies show an acceleration of 10^{12}-fold for the solvolytic generation of a cyclohexyl cation,[14] and high-level calculations predict carbocation stabilizations of 16, 22 and 38 kcal mol^{-1} for tertiary, secondary and primary carbocations, respectively.[12b,15]

This difference can be attributed to a transition-state conformation in the vinyl ether hydrolysis reaction that is unfavorable for hyperconjugation. Hyperconjugative stabilization will be maximum when the hyperconjugating bond and the vacant p-orbital of the cationic center being stabilized are coplanar and the dihedral angle between these bonds, θ, is zero. This situation was achieved in the cyclohexyl system which showed the very large rate acceleration, and it is also the conformation to which the calculated large stabilization refers. In vinyl ether hydrolysis, however, this dihedral angle is considerably larger than $\theta = 0°$: it starts at $\theta = 90°$ in very early, reactant-like transition states (**8**) and never drops to less than $\theta = 60°$ even in very late, product-like transition states (**9**).



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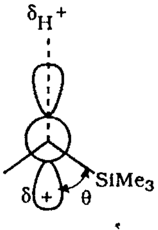

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It is possible to evaluate the hyperconjugative contribution to the present observed effect on the basis of the generally held assumption that hyperconjugative interactions vary as $(\cos\theta)^2$, while inductive effects are conformationally independent. This gives the relationship

$$\delta\Delta G^{\ddagger} = I + (\cos\theta)^2 H \tag{3}$$

in which I and H are the inductive and hyperconjugative contributions to the overall effect, $\delta\Delta G^{\ddagger}$. A value for the dihedral angle may be set from the expectation that this angle will vary between its $\theta = 90°$ and 60° limits in proportion to the Brønsted exponent, α, for the reaction: such exponents are commonly used measures of transition-state structure. Taking $\alpha = 2/3$ as a typical value for the hydrolysis of a vinyl ether of the present reactivity[16] then leads to $\theta = 70°$ and that, coupled with the relationship $H/I = 5{\cdot}2$ found in the cyclohexyl systems,[14] then provides the solution $I = 1{\cdot}8$ kcal mol^{-1}, $H = 9{\cdot}3$ kcal mol^{-1} and $(\cos\theta)^2H = 1.1$ kcal mol^{-1}.

It is interesting that the sum of the inductive and the conformationally maximum hyperconjugative interactions given by this analysis, $I + H = 11{\cdot}1$ kcal mol^{-1}, is two thirds of that for the cyclohexyl system, $I + H = 16{\cdot}9$ kcal mol^{-1}. This implies that two-thirds as much positive charge is generated on the substrate at the transition state of the present vinyl ether hydrolysis reaction as at the transition state of the cyclohexyl solvolysis system, which, if the latter reaction generates a full positive charge, is consistent with the measure of transition state structure, $\alpha = 1/3$, used in the present calculation. This, however, requires that a conformationally correct silyl group be fully as effective in vinyl ether hydrolysis as in cyclohexyl solvolysis, with no diminution of silyl hyperconjugative stabilization through additional conjugative electron donation from the vinyl ether's alkoxy group. This would seem to be at variance with the known strong ability of alkoxy groups to stabilize adjacent positive charge, as seen, for example, in the much greater reactivity of vinyl ethers over simple alkenes.

ACKNOWLEDGMENTS

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