Stable Carbonium Ions. LX.[1] Protonated α,β-Unsaturated Carboxylic Acids and Their Cleavage to Alkenyloxocarbonium Ions

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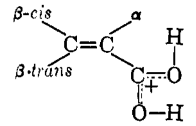
Abstract: The O protonation of acrylic, α-methylacrylic, β-methylacrylic, and β,β-dimethylacrylic acids in SO_2–SbF_5–FSO_3H solution has been observed by nmr spectroscopy at −20 and −95°. The kinetics of cleavage to alkenyloxocarbonium ions were measured and compared with those of protonated saturated carboxylic acids.

There has been considerable interest in the observation of protonated carbonyl compounds,[3] especially in regard to the existence of stereoisomerism. Investigation of protonated ketones,[3a] aldehydes,[3b] and carboxylic acids[3c,h] have been recently reported. The base strengths of 2-butenoic (crotonic), 3-methylbutenoic (β,β-dimethylacrylic), and sorbic acids were reported by Deno and coworkers.[4a] They also reported the nmr spectra of these α,β-unsaturated acids as well as that of 2-methyl-2-butenoic (tiglic) acid and methylacrylic acid[4b] and investigated the protonated acids and the corresponding acyl cations in sulfuric acid and oleum solutions.

We extended our investigation to the protonation of α,β-unsaturated carboxylic acids as it might be expected to give indications concerning the stereoisomerisms of the protonated forms. In the strong acid system FSO_3H–SbF_5–SO_2 all the unsaturated acids studied were completely protonated, and the change in the OH chemical shifts as a function of the temperature proved to be a valuable method for investigating the stereoisomerism of the protonated compounds. Furthermore, by heating the SbF_5–FSO_3H solutions of α,β-unsaturated carboxylic acids to 0–40°, it was possible to study the kinetics of their cleavage to alkenyloxocarbonium ions under nonequilibrium conditions.

Table I. Pmr Chemical Shifts and Coupling Constants of Protonated α,β-Unsaturated Carboxylic Acids in FSO_3H-SbF_5- SO_2 Solution[a]



Acid			OH (−90°)	OH (−20°)
Acrylic	α	−6.60 to −7.06[b]	*syn* −12.06	
		(−5.66 to	*anti* −12.53[c]	−11.95[d]
	β-*cis*	−6.91)		
	β-*trans*	−7.25 to −7.88		
α-Methylacrylic	α	−2.43 (−1.95)		
	β-*cis*	−7.35 (−6.25)	*syn* ...	
	β-*trans*	−7.05 (−5.66)	*anti* −12.10	−11.96
β-Methylacrylic (crotonic)	α	−6.60 (−5.83)		
	β-*cis*	−8.55 (−7.11)	*syn* −11.60[h]	
	β-*trans*	−2.41 (−1.90)	*anti* −12.06	−11.50[g]
β,β-Dimethylacrylic	α	−6.40 (−5.72)[e]		
	β-*cis*	−2.63 (−2.18)[i]	*syn* ...	
	β-*trans*	−2.50 (−1.93)[f]	*anti* −11.43	−11.26[j]

[a] In parentheses are the chemical shifts of α,β-unsaturated acids at room temperature in $CDCl_3$. [b] At −20° unless otherwise noted and in ppm from external TMS (sealed capillary tube). [c] Doublet, J_{OH-CH} = 2 Hz. [d] Doublet, J_{OH-CH} = 0.7 Hz. [e] Complex multiplet. [f] Doublet, J_{CH_3-CH} = 1.2 Hz. [g] Doublet, J_{CH-OH} = 0.8 Hz. [h] Doublet, J_{CH-OH} = 1.6 H. [i] Doublet, J_{CH_3-CH} = 1.0 Hz. [j] Doublet, J_{OH-CH} = 1.2 H .

$$R_2C{=}CRCO_2H \xrightarrow[-20 \text{ or } -95°]{FSO_3H\text{-}SbF\text{-}SO_2} R_2C{=}CRCO_2H_2^+ \xrightarrow[0\text{-}40°]{SbF_5\text{-}FSO_3H} R_2C{=}CRCO^+ + H_3O^+$$

Results and Discussion

The following simple aliphatic α,β-unsaturated carboxylic acids have been investigated: acrylic, α-methylacrylic, β-methylacrylic (crotonic), and β,β-dimethylacrylic acids. All the protonated acids give well-resolved spectra which were obtained at −20 and at −95°. The chemical shifts and coupling constants are summarized in Table I. It should be noted that the

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[1] Part LIX: G. A. Olah and M. Calin, *J. Am. Chem. Soc.*, **90**, 401 (1968).

[2] National Institutes of Health Postdoctoral Research Investigator, 1966–1967.

[3] (a) G. A. Olah, M. Calin, and D. H. O'Brien, *J. Am. Chem. Soc.*, **89**, 3586 (1967); (b) G. A. Olah, D. H. O'Brien, and M. Calin, *ibid.*, **89**, 3582 (1967); (c) G. A. Olah and A. M. White, *ibid.*, **89**, 4752 (1967); (d) G. A. Olah and M. Calin, *ibid.*, **89**, 4736 (1967); (e) *ibid.*, part LV, in press; (f) M. Brookhart, G. C. Levy, and S. Winstein, *ibid.*, **89**, 1735 (1967); (g) S. Winstein, *Chem. Eng. News*, **45** (15), 54 (1967); (h) H. Hogeveen, A. F. Bickel, C. W. Hilbers, E. L. Mackor, and C. MacLean, *Chem. Commun.*, 898 (1966); (i) H. Hogeveen, *Rec. Trav. Chim.*, **86**, 289 (1967).

[4] (a) N. C. Deno, C. U. Pittman, Jr., and J. Wisotsky, *J. Am. Chem. Soc.*, **86**, 4370 (1964); (b) N. C. Deno, G. W. Holland, Jr., and T. Schulge, *J. Org. Chem.*, **32**, 1496 (1967), footnote 15.

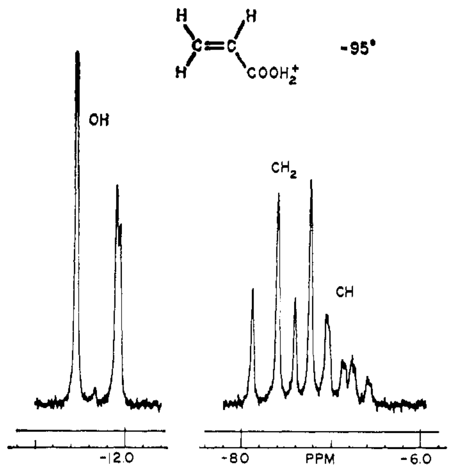


Figure 1.

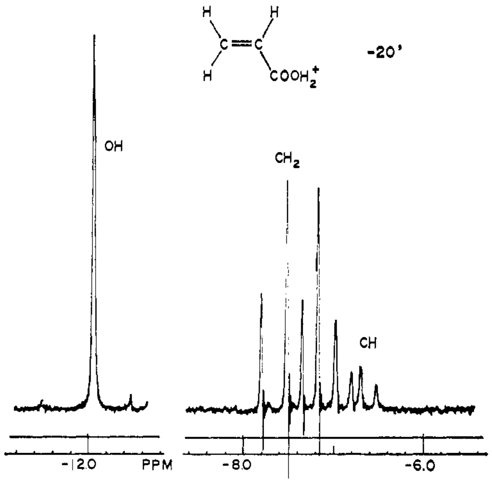


Figure 2.

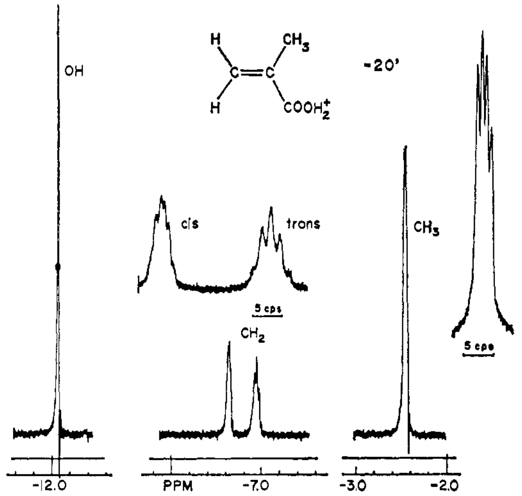


Figure 3.

OH resonance occurs at higher field than in protonated saturated carboxylic acids.[3c]

The nmr spectrum of protonated acrylic acid at −95° (Figure 1) shows the α- and β-hydrogens as a multiplet from −6.60 to −7.88 ppm. The α-hydrogen appears as four peaks from −6.60 to −7,06 ppm and

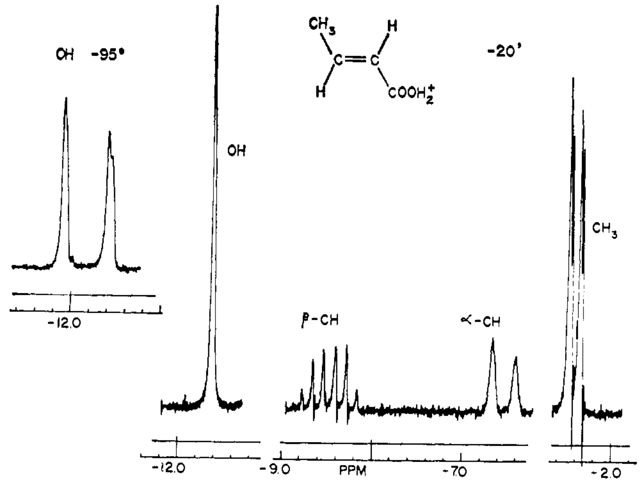


Figure 4.

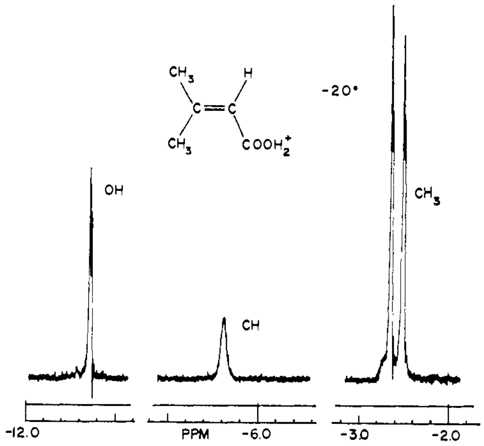


Figure 5.

the β-hydrogens as four peaks from −7.25 to −7,88 ppm. The α-hydrogen has a fine structure caused by the coupling (2 Hz) to one of the protons on oxygen. The protons on oxygen (2 H) appear as two peaks at −12.06 and −12.53 ppm with the upfield peak resolved into a doublet due to the coupling to the α-hydrogen. At higher temperature (−20°) (Figure 2), the two peaks collapse into a sharp doublet centered at −11.95 ppm.

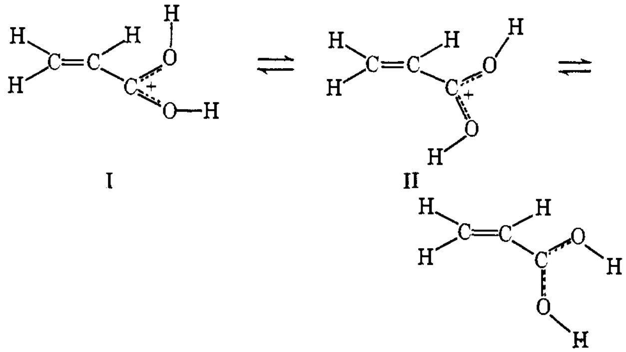
Protonated α-methylacrylic acid (Figure 3) at −20° shows the methyl hydrogens as a multiplet at −2.43 ppm and the two β-hydrogens at −7.05 and −7.35 ppm, the upfield peak being resolved into a multiplet. The proton on oxygen (2 H) appears as a sharp singlet at −11.96 ppm. No temperature dependence of the spectrum was observed by cooling the sample to −90°.

The nmr spectrum of protonated crotonic acid (Figure 4) at −20° shows the methyl hydrogens as a pair of doublets, at −2.41 ppm, being differently coupled to the α- and β-hydrogens. The couplings to α- and β-hydrogens are 1.5 and 6,8 Hz, respectively. The α-hydrogen appears as two multiplets centered at −6.60 ppm and the β-hydrogen as two quartets centered at −8.55 ppm. The proton on oxygen (2 H) appears at 11.50 ppm as a sharp doublet ($J_{\mathrm{CH\text{-}OH}} = 0.8$ Hz). By cooling the sample to −95° the OH resonance appears as two peaks, a singlet at −12.08 ppm and a doublet at −11,60 ppm. The coupling of one OH to the α-hydrogen is 1.6 Hz,

Protonated β,β-dimethylacrylic acid (Figure 5) at

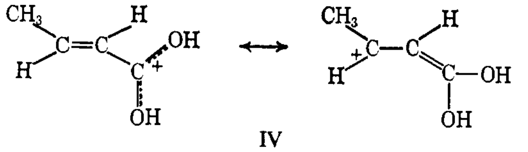
$-20°$ shows the methyl hydrogens as a pair of doublets centered at -2.56 ppm. The methyl groups of *cis* and *trans* isomers have different chemical shifts and they are coupled to the α-hydrogen (1.0 and 1.2 Hz, respectively). The proton on oxygen (2 H) appears as a sharp doublet at -11.26 ppm being split by the α-hydrogen (1.2 Hz). Double irradiation of the α-hydrogen changes the methyl and OH resonance to singlets. Lowering the temperature to $-95°$, it was not possible to resolve the OH resonance into two peaks. At this temperature the OH resonance appears as a broad peak.

Structure of Protonated α,α-Unsaturated Acids. The isomerism observed for protonated carboxylic acids should also be considered in this case. Three isomers for protonated α,β-unsaturated acids can be drawn.



I II III

If it is assumed that the barrier to rotation around the C–C(OH)$_2$ bond is very small and only observable around the C–O bond, then I is the only structure which accounts for two nonequivalent OH groups. Structures II and III would exhibit only one OH resonance. It should be remembered that the positive charge is delocalized not only through the two oxygens, but also through the conjugated π system. Indeed, from the nmr data it can be seen that the β-hydrogen in protonated crotonic acid is more downfield shifted than the α-hydrogen, a fact which accounts for the existence of IV as a contributing resonance form. If IV is an important contributing form, the barrier to rotation around the C–C(OH)$_2$ bond should be considered instead or together with that around the C–O bond. Although IV should not be neglected (at least for β-substituted acids which could lead to secondary and tertiary carbonium ions), it is unlikely that this has a large contribution to the structure of protonated species. The nmr data could be satisfactorily explained considering the hindered rotation around the C–O partial double bond.



IV

At low temperature ($-95°$) I is the isomer observed for protonated acrylic and crotonic acids. This is based on the multiplicity of the OH resonance and their fine structure. Only one of the OH absorptions shows a coupling to the α-hydrogen. Coupling through four bonds having a partial double-bond character had been encountered in protonated aliphatic ketones[3a] and alicyclic ketones,[3e] and also in protonated aldehydes[3b] but not in protonated carboxylic acids.[3c] This allylic type coupling was shown[3e] to be at maximum for the *syn* isomer and for a dihedral angle of 90°. It can be said that only the *syn* OH group in I is coupled to the α-hydrogen and thus appears as a doublet at lower field than the *anti*-OH group. These assumptions do not consider a change of the coupling in the case where two of the four bonds are partial double bonds, which could be the case here. A partial double bond with a barrier to rotation around C–C(OH) could also imply that the whole system is planar, which is unlikely in view of the allylic spin–spin coupling of the proton on oxygen to the α-hydrogen. At higher temperature, it is interesting to observe that the OH resonance is well resolved into a sharp doublet. Rotation around the C–O bond becomes possible, and the coupling observed is an average of that of the *syn* and *anti* isomers. It is remarkable that proton exchange is still very slow at $-20°$.

Protonated methylacrylic acid shows only one resonance for the proton on oxygen. The possible explanation is that the steric hindrance of the *syn* proton with the α-methyl group in I is too high, and III is the preferred conformation. This also assumes that there is free rotation around the C–C(OH) bond. The appearance of one peak for the OH of protonated β,β-dimethylacrylic acid can be explained in other terms. The fact that IV would lead to a tertiary carbonium ion makes it more possible as an important contributing form. Therefore, the barrier to rotation around the C–O bond is lower, and at $-90°$ we observe only one broad peak.

If the SbF$_5$–FSO$_3$H[5] solutions of α,β-unsaturated acids were allowed to warm up to between 0 and 40°, dehydration occurs to give the corresponding alkenyloxocarbonium ions, which are the only species observed by nmr spectroscopy.

$$R_2C{=}CRCO_2H_2^+ \xrightarrow[k]{SbF_5\text{–}FSO_3H} R_2C{=}CRCO^+ + H_3O^+$$

Stable crystalline salts of these ions have been recently obtained[6] by ionizing alkenoyl fluorides in antimony pentafluoride. The pmr parameters of alkenyloxocarbonium ions have been extensively analyzed[6] and will not be further discussed here. It should be added that we observe the same chemical shifts as those published in our previous studies.[6] The cleavage of α,β-unsaturated acids in SbF$_5$–FSO$_3$H solution is analogous to that observed for the cleavage of protonated saturated carboxylic acids.[3c] Indeed, first-order kinetics are observed for all protonated acids. The rate of dehydration of the protonated species and appearance of alkenyloxocarbonium ions was followed by integration of selected peaks in the nmr spectrum. The relative

Table II. Relative Rates of Dehydration of Protonated α,β-Unsaturated Carboxylic Acids to Oxocarbonium Ions[a]

$CH_3CO_2H_2^+$	1.00[b]
$(CH_3)_2C{=}CHCO_2H_2^+$	0.48
$CH_2{=}C(CH_3)CO_2H_2^+$	0.12
$CH_3CH{=}CHCO_2H_2^+$	0.09

[a] Rates at +1° referred to acetic acid. [b] From ref 3c.

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(5) By allowing a solution of β,β-dimethylacrylic acid in SbF$_5$–FSO$_3$H–SO$_2$ solutions to warm up, the protonated acid reacted with SO$_2$ to give an unidentified product. The other protonated acids investigated do not react with SO$_2$ under the same conditions, and oxocarbonium ions are the only species observed.

(6) G. A. Olah and M. Comisarow, *J. Am. Chem. Soc.*, **89**, 2964 (1967).

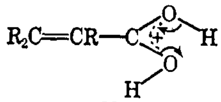
Table III. Activation Parameters Calculated at 0°

	$\Delta H^{\ddagger}$ [a]	$\Delta S^{\ddagger}$ [b]	No. of points on plot
$CH_3CO_2H_2^+$ [c]	16.3	−13.1	5
$(CH_3)_2C{=}CHCO_2H_2^+$	16.7	−8.8	4
$CH_2{=}CH(CH_3)CO_2H_2^+$	19.0	+1.7	5
$CH_3CH{=}CHCO_2H_2^+$	19.8	+3.7	4

[a] $\Delta H = E_a - RT$ (kcal/mole). [b] $\Delta S = 4576 \log A/T - 49.203$; time in seconds and entropy in standard units (eu). [c] From ref 3c.

rates of cleavage compared to that of protonated acetic acid under the same conditions are given in Table II.

From the rate of cleavage and activation parameters (the Arrhenius parameters are summarized in Table III), little could be said about the transition states. A cyclic symmetrical transition state V as proposed for the acidolysis of esters[7] is also likely for the dehydration of protonated unsaturated carboxylic acids.



V

Experimental Section

Materials. All alkenoic acids were commercial materials of reagent grade and were used without further purification.

Nmr Spectra. Varian Associates Model A-56/60A and HA 60-IL nmr spectrometer with variable-temperature probes were used for all spectra. The coupling constants are accurate to within 0.1 Hz.

Preparation of Protonated Acids. Samples of protonated acids were prepared by dissolving 1.5 ml of SbF_5–FSO_3H (1:1 *M*) in an equal volume of sulfur dioxide and cooling to −78°. The acid (~0.3 g) was dissolved in 2 ml of sulfur dioxide, cooled to −78°, and dropwise added to the acid solution. The kinetics were measured using the published procedure for the carboxylic acids.[3c] The excess of acid (SbF_5–FSO_3H) indicated by the intense peaks at −10.9 ppm and that of H_3O^+ at −10.5 ppm were deleted from the spectra for simplicity (Figures 1–5).

Acknowledgment. Support of the work by a grant of the National Institutes of Health is gratefully acknowledged.

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[7] G. A. Olah, D. H. O'Brien, and A. M. White, *J. Am. Chem. Soc.*, **89**, 5694 (1967).

Kinetics of Reactions of 2-Hexyl Halides and 2-Hexyl *p*-Bromobenzenesulfonate with Sodium Methoxide in Methanol. Evidence That Orientation of Olefin-Forming Elimination Is Not Determined by the Steric Requirements of Halogen Leaving Groups[1,2]

Richard A. Bartsch[3] and J. F. Bunnett[4]

Contribution from the Metcalf Chemical Laboratories, Brown University, Providence, Rhode Island.
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Abstract: The kinetics of the elimination and substitution reactions of $NaOCH_3$ with the four 2-hexyl halides and 2-hexyl *p*-bromobenzenesulfonate have been measured by a precise gas–liquid partition chromatographic technique, and activation parameters have been evaluated. The 2-hexenes:1-hexene ratio diminishes steadily from iodine to fluorine, and 1-hexene is the predominant olefin from 2-hexyl fluoride. The 2-hexene *trans*:*cis* ratio diminishes steadily in the same order. These effects are in accord with the theory of the variable E2 transition state, but cannot be attributed to steric repulsions between the (solvated) leaving group and β-alkyl substituents. Novel linear free energy relationships obtain, for all the 2-hexyl halides, between log *k*(1-hexene) and log *k*(*cis*-2-hexene) or log *k*(*trans*-2-hexene), but the data for 2-hexyl brosylate do not conform to these relationships.

Recent observations have challenged theories of orientation in olefin-forming elimination that had enjoyed wide if not universal acceptance. Saunders's discovery that 2-fluoropentane forms mainly 1-pentene on reaction with sodium ethoxide in ethanol[5] is difficult to reconcile with the hypothesis[6,7] that Hofmann orientation[8] is determined by steric interactions. Demonstration that orientation may be drastically changed, and indeed reversed, by varying the base–solvent system[10,11] contradicts the theory[12,13] that Hofmann

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[1] Based on the Ph.D. Dissertation of R. A. Bartsch, June 1967. This dissertation will be abstracted by *Dissertation Abstracts*, and copies will be available from University Microfilms, Ann Arbor, Mich.

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[3] Jesse M. Metcalf Fellow, 1964–1965; ICI (Organics) Fellow, 1965–1966.

[4] University of California, Santa Cruz, Calif.

[5] W. H. Saunders, Jr., S. R. Fahrenholtz, E. A. Caress, J. P. Lowe, and M. Schreiber, *J. Am. Chem. Soc.*, **87**, 3401 (1965).

[6] H. C. Brown, *J. Chem. Soc.*, 1248 (1956).

[7] H. C. Brown and R. L. Klimisch, *J. Am. Chem. Soc.*, **88**, 1425 (1966).

[8] When H and X are eliminated from adjacent carbons to form a double bond, the carbon which carries leaving group X is designated α, and those adjacent to it β. Formation of the double bond toward the less substituted β-carbon is known as *Hofmann* orientation, while elimination toward the more substituted β-carbon is called *Saytzeff* orientation.[9]

[9] J. F. Bunnett, *Angew. Chem. Intern. Ed. Engl.*, **1**, 225 (1962); *Angew. Chem.*, **74**, 731(1962).

[10] H. C. Brown, I. Moritani, and Y. Okamoto, *J. Am. Chem. Soc.*, **78**, 2193 (1956).