The Behavior of Isopropenyl Acetate in Strong Sulfuric and Deuteriosulfuric Acids

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Because of the many important contributions that have appeared in recent years on the behavior of organic systems in strong sulfuric acid solutions,[1-4] we have become interested in the nature of protonated esters in concentrated sulfuric acid. While ordinary esters produce n.m.r. spectra that remain stable over a period of many hours,[5] several simple vinyl esters upon contact with concentrated sulfuric acid underwent rapid decomposition as evidenced by the dark brown to black color of the solution and the lack of any distinct n.m.r. absorption. In sharp contrast, isopropenyl acetate dissolves in cold concentrated sulfuric acid with only slight discoloration of the solution. The n.m.r. spectrum (Figure 1) shows four sharp singlets which do not change intensity over a period of many hours.[6] The same spectrum in deuteriosulfuric acid solution within a few minutes after its preparation shows the complete absence of peak a and peak c, and, during the next 24 hr., exhibits a steady decrease in area ratio d/b as indicated in Table I. These results point to an interesting fragmentation process and indirectly provide evidence for the existence of at least four distinct ionic species. Further information can be deduced on relative rates of interconversion of several of these ionic species.

TABLE I

DEUTERIUM EXCHANGE IN CONCENTRATED DEUTERIOSULFURIC ACID

Isopropenyl acetate[a]		Acetone + acetic anhydride	
Time, hr.	N.m.r. area ratio d/b	Time, hr.	N.m.r. area ratio d/b
0	1.095	0	2.955
5	0.886	5	2.040
8	0.740	8	1.750
24	0.333		
45	0.355		

[a] Figure 2.

Discussion

First, consider the gross features of the isopropenyl acetate spectrum in concentrated sulfuric acid (Figure 1). Singlets a, b, and c, which appear 0.02, 0.59, and 0.65 p.p.m. downfield of their counterparts in carbon tetrachloride solution have been assigned to the vinyl, acetyl, and olefinic methyl protons, respectively, in the oxygen-protonated isopropenyl acetate (V).[7] Note the apparent irregularity in the area ratio b/c of 1.72 (in carbon tetrachloride, b/c = 1.0) and the appearance of an additional peak at 7.10. The 0.65-p.p.m. deshielding of the acetyl protons of V relative to those in the unprotonated molecule in carbon tetrachloride corresponds closely with the 0.67-p.p.m. value for the acetyl group of ethyl acetate measured under the same conditions.[5] Finally, the fine structure observed on the 5.38 absorption in carbon tetrachloride (not shown) and attributed to allylic coupling is absent in the sulfuric acid solution because of the higher viscosity of this medium and/or rapid proton exchange. Rapid exchange has been demonstrated to occur, *vide infra.*

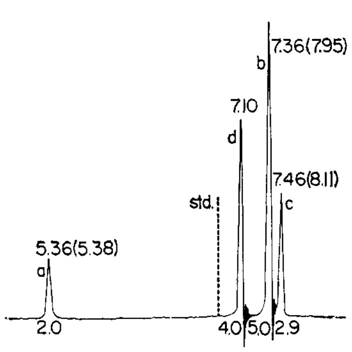
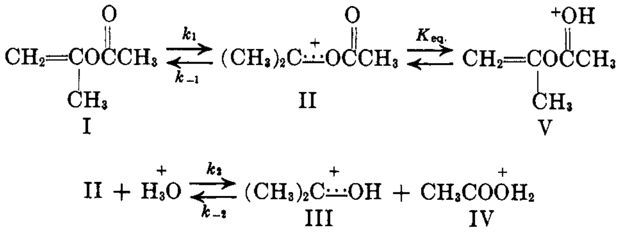


Figure 1.—N.m.r. spectrum (60 Mc.p.s.) of isopropenyl acetate in concentrated sulfuric acid. Chemical shift values in τ units are related to tetramethylsilane *via* an internal tetramethylammonium chloride standard at 6.9 (dotted line).[1b] Values in parentheses refer to the spectrum in carbon tetrachloride. Areas relative to a value of 2.0 for peak a are shown at the base of each peak.

The above assignment of peaks a, b, and c is quite reasonable except for the apparent abnormality in the relative area of peak b, but this difficulty can be resolved by a detailed consideration of the origin of peak d. Initial contemplation led us to propose that singlet d originated from the *gem*-dimethyl protons of ion II, which is formed by vinyl protonation of I, but this explanation is untenable since discrete absorptions from ions II and V would require that an unprecedented slow equilibrium be established between them. Unequivocal evidence that ion II or an equilibrium mixture of ions II and V is not responsible for the absorption at 7.10 can be obtained by use of a deuteriosulfuric acid medium.



$$\underset{\text{I}}{\mathrm{CH_2{=}\underset{\displaystyle\overset{|}{CH_3}}{C}O\overset{\displaystyle O}{\overset{\|}{C}}CH_3}} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \underset{\text{II}}{\mathrm{(CH_3)_2\overset{+}{C}\cdots O\overset{\displaystyle O}{\overset{\|}{C}}CH_3}} \overset{K_{\mathrm{eq.}}}{\rightleftarrows} \underset{\text{V}}{\mathrm{CH_2{=}\underset{\displaystyle\overset{|}{CH_3}}{C}O\overset{\displaystyle {}^{+}OH}{\overset{\|}{C}}CH_3}}$$

$$\mathrm{II} + \mathrm{H_3\overset{+}{O}} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \underset{\text{III}}{\mathrm{(CH_3)_2\overset{+}{C}\cdots OH}} + \underset{\text{IV}}{\mathrm{CH_3CO\overset{+}{O}H_2}}$$

The spectrum in deuteriosulfuric acid ($\geq 98\%$ deuterium) at room temperature taken within 5 min. of the time of preparation (Figure 2, 0 hr.) shows the complete exchange of peaks a and c, clearly indicative of a rapid reversible equilibrium between I and II. Since the

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[1] (a) N. C. Deno, H. G. Richey, Jr., J. D. Hodge, and M. J. Wisotsky, *J. Am. Chem. Soc.*, **84**, 1498 (1962); (b) N. C. Deno, H. G. Richey, Jr., N. Friedman, J. D. Hodge, J. J. Houser, and C. U. Pittman, Jr., *ibid.*, **85**, 2991 (1963); (c) N. C. Deno, N. Friedman, J. D. Hodge, and J. J. Houser, *ibid.*, **85**, 2995 (1963); (d) N. C. Deno, J. Bollinger, N. Friedman, K. Hafer, J. D. Hodge, and J. J. Houser, *ibid.*, **85**, 2998 (1963).

[2] (a) H. Hart and R. W. Fish, *ibid.*, **82**, 5419 (1960); **83**, 4460 (1961); (b) H. Hart and J. S. Fleming, *Tetrahedron Letters*, 983 (1962).

[3] M. E. Reach and T. C. Waddington, *J. Chem. Soc.*, 600 (1962).

[4] J. F. Bunnett, *J. Am. Chem. Soc.*, **82**, 499 (1960); **83**, 4956, 4968, 4973, 4978 (1961).

[5] These observations together with more detailed information on the nature of protonated esters and thioesters will be published separately.

[6] Except for slight peak broadening in >96% sulfuric acid, the spectrum remained essentially unchanged.

[7] No implication should be made from structure V about the exact position of the proton. However, it is important to recognize that chemical shift data for various saturated esters in concentrated sulfuric acid is consistent with a nearly equal distribution of positive charge among both oxygen atoms and the carbonyl carbon atom as evidenced by the nearly equal downfield shifts in sulfuric acid of protons on the carbon atoms adjacent to the oxygen and to the carbonyl group.[5]

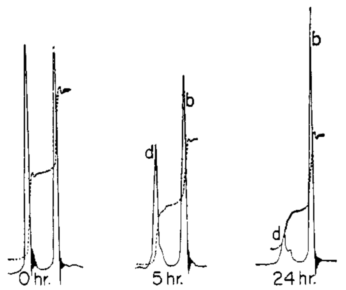
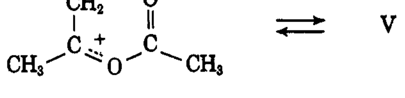


Figure 2.—N.m.r. spectrum (60 Mc.p.s.) of isopropenyl acetate in concentrated deuteriosulfuric acid at 0, 5, and 24 hr. from the time of preparation. The integrator trace is shown as a dotted line.

deuterium exchange undoubtedly takes place *via* ion II, the assignment of peak d to the six *gem*-dimethyl protons of II is irreconcilable with the observed lack of deuterium exchange of this singlet under conditions where a and c exchange rapidly.

The assignment of peak d as well as the explanation for the apparent abnormality in the area of peak b can can be made if one assumes that ion II is capable of slow fragmentation, *i.e.*, $k_2 \ll k_1$, to protonated acetone and acetic acid in the presence of small amounts of water. That protonated acetone could account for singlet d was confirmed from an independent spectrum of acetone in concentrated sulfuric acid. A singlet at 7.10 is observed and shows signs of relatively slow exchange in a deuteriosulfuric acid medium over a period of 8 hr. at room temperature (see Experimental). The singlet at 7.36 (peak b in Figure 1) is assigned to the acetyl protons of protonated acetic acid plus the acetyl protons of ion V (or an equilibrium mixture of II and V) and corresponds closely to the value of 7.33 recently reported by Deno.[8] He also demonstrated that the acetylium ion, which would be the product of direct fragmentation of II, does not exist in 96% sulfuric acid. A comparison of area d/(area b − area c) compensates for that fraction of area b which is attributed to ion V or the equilibrium mixture of II and V and gives a value of 2.0 as required by the formation of ions III and IV in equimolar quantities.

Although protonation of simple olefins with dilute acid has been shown not to be a rapid reversible reaction,[9] one would not expect olefin protonation to be slow under the conditions of our experiments. From a geometric standpoint one can easily visualize an intramolecular proton transfer from methyl to oxygen *via* highly favorable six-membered ring transition state to form the oxygen-protonated ion V. This mode of proton transfer may account for the rapidity of proton exchange but is not required to explain the results.



One can now account for the slow decrease in area ratio d/b (Figure 2, Table I). After 8 hr. the d/b ratio was reduced by *ca.* 32%. Since deuterium exchange takes place with protonated acetone III to the extent of only 18 ± 3% under identical conditions over the same period of time (see Experimental) but occurs more rapidly *via* ion II, one need only assume that k_{-2} is significant and therefore provides for the slow formation of ion II from the initially produced ions III and IV. Thus, $k_{-2} < k_2 \ll k_{-1}$. An interesting test of this hypothesis was made by generating ions III (peak d) and IV (peak b) (from acetone and acetic anhydride) together in deuteriosulfuric acid. While each of these ions independently showed 18 ± 3 and 6% exchange, respectively, relative to an internal tetramethylammonium chloride standard over a period of 8 hr., the ion mixture exhibited a regular decrease in area ratio d/b over that same time span (Table I).[10] The slight increase in ratio d/b after 45 hr. is undoubtedly due to the slow deuterium exchange into the acetyl group of the protonated acetic acid (see Experimental). Such exchange would only become noticeable when the exchange of protons on ion III *via* ion II has become very slow owing to the low concentration of undeuterated ion III.

The initial origin of the acetone is open to question. In order that signals from protonated acetone III be observed in a deuteriosulfuric acid medium, ion III must have a rapid path for its initial formation. Since it has already been demonstrated that protons on the isopropenyl group of the starting ester exchange very rapidly with the medium *via* ion II, any acetone formed by slow fragmentation of II should be highly deuterated.

Experimental

All n.m.r. spectra were obtained on a Varian A-60 n.m.r. spectrometer. Chemical shift values are reported in τ units. For those spectra obtained in concentrated sulfuric acid solution, reference to tetramethylsilane is made by direct measurement of the peak position relative to an internal tetramethylammonium chloride standard which has been shown to be τ 6.9 .[1b]

Deuteriosulfuric acid was prepared by direct distillation of sulfur trioxide from a small amount of oleum (20% excess sulfur trioxide) into deuterium oxide. The fuming deuteriosulfuric acid product was found by n.m.r. analysis to be ≥99% deuterated. Deuterium oxide was carefully added to the n.m.r. sample tubes which contained the fuming acid until the excess sulfur trioxide was destroyed. After the tubes were cooled to 0–10°, the organic material was carefully added dropwise and thoroughly mixed to avoid a local temperature increase. Samples in concentrated sulfuric acid were prepared according to the latter part of the above procedure.

A sample of acetone in concentrated deuteriosulfuric acid showed a decrease in the methyl peak area (relative to internal tetramethylammonium chloride) of 15.8 and 20.9%, respectively, in two runs at *ca.* room temperature. The relative area of the acetone to internal standard signal was 1.20 ± 0.03 and 1.01 ± 0.01 at the beginning and end of the 8-hr. period, respectively. A similar measurement on glacial acetic acid showed a decrease in the acetate peak area of 6.3% over an 8-hr. period. The relative area of the acetate to internal standard signal was 0.96 ± 0.01 and 0.90 ± 0.01 at the beginning and end of the 8-hr. period, respectively. In concentrated sulfuric acid, neither glacial acetic acid nor acetone showed a decrease in signal area relative to internal tetramethylammonium chloride over an 8-hr. period.

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[8] N. C. Deno, C. U. Pittman, Jr., and M. J. Wisotsky, *J. Am. Chem. Soc.*, **86**, 4370 (1964).

[9] (a) R. W. Taft, Jr., *ibid.*, **74**, 5372 (1952); (b) E. L. Purlee and R. W. Taft, Jr., *ibid.*, **78**, 5807 (1956).

[10] Since the absolute concentrations of ions III and IV were not known and since the formation of ion II (step k_{-2}) is a second-order process, one should not expect the fractional decrease in area d/b with time measured in the isopropenyl acetate spectrum and measured for the independently generated ions to be exactly the same. However, the changes are of the same order of magnitude; compare the 32.4 and 40.8% decreases in the two d/b ratios over an 8-hr. period (Table I).

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Unsaturated Heterocyclic Systems. XVII.[1] The Reaction of 2(1H)-Pyridone with Hexafluoro-2-butyne

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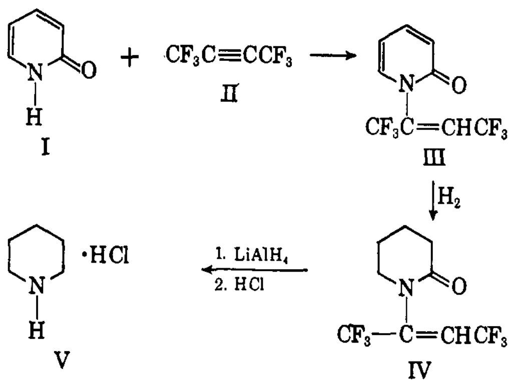
The 2(1H)-pyridone molecule (I) represents a *cis*-dienoid ring system which has yet to enter into a Diels–Alder reaction.[3] Because of the remarkable capability of hexafluoro-2-butyne (II) to react with dienes such as benzene, durene, and naphthalene,[4] we have attempted a diene synthesis utilizing I as the diene and II as the dienophile.

When 2(1H)-pyridone (I) was heated with a slight excess of hexafluoro-2-butyne (II) in an autoclave at 175° for 12 hr., there resulted a mobile black liquid. Chromatography of this material on Florisil afforded a 61% yield of a solid 1:1 adduct, m.p. 55–56°. On the basis of the following data, we have shown that this adduct (III) did not result from a diene synthesis, but rather was formed by a 1,2 addition of the amide proton to the triple bond.



The infrared spectrum of III exhibited the usual pyridone carbonyl band at 1675 cm.$^{-1}$, but lacked the characteristic band of the amide proton below 3000 cm.$^{-1}$. The presence of the intact pyridone ring was inferred from the ultraviolet absorption pattern [$\lambda_{\max}^{\text{EtOH}}$ 274 mμ (ε 4400) and 302 mμ (ε 5000)]. A large measure of further support came from the n.m.r. spectrum which, although quite complex in the aromatic region, was in full agreement with structure III.

Catalytic reduction of III over platinum in ethyl acetate proceeded readily with the uptake of 2 moles of hydrogen. The interesting aspect of this reaction was the rapidity of the reductive process[5] which we have attributed to the electronic influence of the two trifluoromethyl groups. Lithium aluminum hydride reduction of IV produced the corresponding enamine in 53% yield. Direct hydrochloric acid hydrolysis of this enamine gave rise in good yield to piperidine hydrochloride (V), which was identical by the usual criteria with an authentic sample. The isolation of V established beyond doubt the integrity of the heterocyclic ring in the above reactions.

The possibility was considered that reaction of II with N-methyl-2(1H)-pyridone, a system in which a 1,2 addition of the above type is structurally forbidden, might lead to a Diels–Alder adduct. Attempts to condense these components under a wide range of temperatures afforded only uncharacterizable black tars.

Experimental[6]

1-[3,3,3-Trifluoro-1-(trifluoromethyl)propenyl]-2(1H)-pyridone (III).—A mixture of 48 g. (0.5 mole) of 2(1H)-pyridone and 97 g. (0.6 mole) of hexafluoro-2-butyne was placed in an autoclave blanketed with nitrogen, and heated at 175° for 12 hr. There resulted a mobile black liquid which was chromatographed on Florisil.[7] Elution with hexane–ether (9:1) afforded 78.0 g. (60.5%) of a pale yellow oil which crystallized on cooling and scratching. Three recrystallizations of this material from hexane–ether gave pure III as long white blades, m.p. 55–56°, ν^{Nujol} 1675 cm.$^{-1}$ (pyridone carbonyl), $\lambda_{\max}^{\text{EtOH}}$ 224 mμ (ε 4400) and 302 mμ (ε 5000).

Anal. Calcd. for $C_9H_5F_6NO$: C, 42.03; H, 1.96; F, 44.33; N, 5.45; mol. wt., 257. Found: C, 42.18; H, 2.28; F, 44.26; N, 5.66; mol. wt., 297 (osmometric in DMF).

1-[3,3,3-Trifluoro-1-(trifluoromethyl)propenyl]-2-piperidone (IV).—A solution of 20.8 g. (0.08 mole) of III in 130 ml. of ethyl acetate containing 1 g. of platinum oxide was hydrogenated in a Parr apparatus at an initial pressure of 50 p.s.i. The uptake of hydrogen proceeded rapidly and was complete in 1 hr. The catalyst was removed by filtration and the filtrate was evaporated. The colorless residue was distilled to give 19.0 g. (91.4%) of IV as a colorless liquid, b.p. 90–94° (13 mm.), $n^{26}\text{D}$ 1.3970. Redistillation afforded the analytical sample, b.p. 90° (14 mm.), $n^{26}\text{D}$ 1.3970, ν^{Nujol} 1680 cm.$^{-1}$ (amide carbonyl), ultraviolet end absorption only.

Anal. Calcd. for $C_9H_9F_6NO$: C, 41.39; H, 3.47; F, 43.65; N, 5.36. Found: C, 41.90; H, 3.79; F, 45.46; N, 5.34.

Reduction and Acid Hydrolysis of IV.—To a stirred slurry of 2.66 g. (0.07 mole) of lithium aluminum hydride in 150 ml. of anhydrous ether was added dropwise a solution of 18.5 g. (0.071 mole) of IV in 50 ml. of ether at such a rate to maintain gentle reflux. When the addition was completed, the mixture was refluxed with stirring for 2 hr. With external ice cooling, there was added 3 ml. of water, 3 ml. of 25% sodium hydroxide solution, and 8 ml. of water, in that order. The precipitated salts were filtered and washed thoroughly with ether. The filtrate was evaporated and the residue was distilled to give 9.3 g. (53.1%) of colorless enamine, b.p. 44–46° (14 mm.), $n^{26}\text{D}$ 1.3910.[8]

The enamine was dissolved in 50 ml. of ethanol and the solution was treated with 10 ml. of concentrated hydrochloric acid. The mixture was refluxed for 1 hr., cooled, and evaporated to dryness. The residue was recrystallized from ethanol–ether to give 3.8 g. (83.4%)[9] of piperidine hydrochloride. Recrystalli-

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[1] Part XVI: L. A. Paquette, *Tetrahedron*, in press.

[2] Department of Chemistry, The Ohio State University, Columbus, Ohio.

[3] For a recent attempt to effect such a reaction between N-methyl-2(1H)-pyridone and maleic anhydride, see B. S. Thyagarajan and K. Rajagopalan, *Tetrahedron*, **19**, 1483 (1963).

[4] C. G. Krespan, B. C. McKusick, and T. L. Cairns, *J. Am. Chem. Soc.*, **82**, 1515 (1960); **83**, 3428 (1961).

[5] Whereas III underwent complete reduction within 1 hr. at room temperature and an initial hydrogen pressure of 50 p.s.i., N-methyl-2(1H)-pyridone has been reported to require 17 hr. for the theoretical uptake of hydrogen in acetic acid solution: N. J. Leonard and E. Barthel, Jr., *ibid.*, **71**, 3098 (1949).

[6] Melting points are corrected and boiling points are uncorrected.

[7] Florisil is a magnesia–silica gel adsorbent manufactured by the Floridin Co., Tallahassee, Fla.

[8] Infrared and gas chromatographic analyses of this sample indicated the presence of approximately 8% unreacted IV.

[9] This yield is based on the assumption that the enamine was of 100% purity.