Concerning the Behavior of Aqueous Thenoyltrifluoroacetone

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King and Reas have reported a stable crystalline monohydrate ($TTA \cdot H_2O$) of thenoyltrifluoroacetone (TTA).[1] Zebroski has found the chemistry of TTA and $TTA \cdot H_2O$ to be markedly different. The addition of solid $TTA \cdot H_2O$ to dilute aqueous sodium hydroxide results in a rapid and nearly complete cleavage to acetylthiophene and the salt of trifluoroacetic acid. On the other hand, the same treatment of solid anhydrous TTA produces essentially complete conversion to the enolate ion.[2]

We have found that the addition of an aqueous solution of TTA to an appreciable excess of base gives very nearly the same results as the addition of solid $TTA \cdot H_2O$ or its aqueous solution. This result supports the conclusion of the previous investigators,[1,2] based upon spectral and bromination data, that the principal species in an aqueous solution of TTA is $TTA \cdot H_2O$ (keto hydrate). We have been able to interpret several apparently anomalous results on this basis.

The potentiometric titration of an acidified aqueous solution of TTA with sodium hydroxide solution requires in the low *p*H region (<3) of the titration curve, an appreciable excess of base over the added mineral acid. An aqueous solution of TTA, however, gives a titration curve resembling that of a typical weak acid. These results suggested that an acid-catalyzed cleavage to trifluoroacetic acid and acetylthiophene occurred in the former case. We have eliminated this possibility, however, by obtaining a nearly quantitative recovery of TTA (as $TTA \cdot H_2O$) from a one molar aqueous HCl solution of TTA which stood for 24 hours at 50°. The formation of the strong acid in the titration of an acidified aqueous TTA solution must therefore be the result of the cleavage of the $TTA \cdot H_2O$ present obtained by momentary local concentrations of high *p*H during the addition of base.

Further, the titration of an aqueous TTA solution with strong base, although deceitful from the appearance of the titration curve, is not a simple neutralization of a weak acid by strong base. The titration curve cannot be reproduced by back-titration with strong acid. Instead a typical back-titration shows that about half of the diketone is converted to a strong acid.[3] Spectral data indicate cleavage occurs during the addition of base since there is only partial conversion to enolate ion.

Either TTA or $TTA \cdot H_2O$ can, however, be converted to enolate ion in a buffer of *p*H 8. Essentially complete enolization results from addition of either (1) aqueous TTA solutions; (2) dry ethanol solution of anhydrous TTA; (3) solid $TTA \cdot H_2O$; or (4) solid anhydrous TTA to a buffer of *p*H 8.

Preliminary work has indicated the rate of enolization of aqueous TTA solutions takes place appreciably more rapidly at *p*H 8 than in solutions of *p*H below 4.[4] The latter rates have been determined by rates of bromination,[5] the former by the rates of appearance of the absorption band due to enolate ion. At *p*H 8 the rate is first order with respect to β-diketone, but also dependent upon the salt component of the buffer and its concentration. Results indicating that $TTA \cdot H_2O$ enolizes at a slower rate than TTA have also been obtained. Quantitative rate studies are in progress.

If aqueous TTA solutions are allowed, even momentarily, to become more basic than *p*H 9, cleavage of the $TTA \cdot H_2O$ (the principal species present) results, *i.e.*, above *p*H 9 the rate of cleavage of $TTA \cdot H_2O$ becomes the same order or exceeds its rate of enolization. By conducting experiments in such a manner as to reduce the hydration of TTA, cleavage in strongly basic solution can however be reduced and enolization increased. When a dry ethanol solution of anhydrous TTA is added to an equivalent amount of aqueous sodium hydroxide about 85% of the TTA is converted to enolate ion and 15% is cleaved. Similar treatment of aqueous TTA results in better than 95% cleavage, thus indicating that in the previous experiment an appreciable amount of enolate ion is formed before the TTA from the alcohol solution hydrates.

The only way we have found to obtain complete conversion to enolate ion in strongly basic aqueous solution is by the addition of solid anhydrous TTA. When added to either an equivalent or an excess of aqueous sodium hydroxide, this substance gives 100% enolate ion.[6] In this case protons must be removed at the surface of the solid phase before the TTA has hydrated, with the result that TTA goes into solution as enolate ion. Back-titration of enolate ion gives a value of 4.2×10^{-7} for the apparent ionization constant for aqueous TTA.

The data presented indicate not only that $TTA \cdot H_2O$ is much more susceptible to cleavage than TTA, but also that the conversion to enolate ion protects the diketone from cleavage in basic solution.[7] Further, the cleavage of $TTA \cdot H_2O$ at high *p*H's rather than enolization represents an important case in which the rupture of a C–C bond proceeds at a markedly faster rate than the breaking of a C–H bond. The great rapidity with which the cleavage must occur is remindful of the strong activating influence of the CF_3 group in base-catalyzed ester hydrolysis.

Experimental

Materials.—The TTA used (m.p. 44–45°) was obtained from the Dow Chemical Company and the $TTA \cdot H_2O$ was prepared from it by the method of King and Reas.[1]

Spectral Data.—The ultraviolet spectra of a slightly acidified aqueous solution of TTA (or $TTA \cdot H_2O$) is closely equivalent to that of acetylthiophene with maxima in the regions 260–270 mμ and 285–295 mμ.[2] Similar results have been obtained by us in 50% (vol.) aqueous dioxane. The spectral data (in agreement with other information) there-

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[1] E. L. King and W. H. Reas, This Journal, **73**, 1806 (1951).

[2] E. Zebroski, Atomic Energy Commission Report BC-63 (1947); Ph.D. Thesis, University of California.

[3] Titration results are not generally reproducible but depend upon the rate of addition of base and of stirring. See also ref. 2.

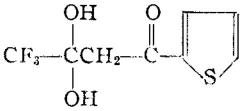
[4] Compare ref. 2.

[5] (a) J. C. Reid and M. Calvin, This Journal, **72**, 2948 (1950); (b) unpublished work of the present authors.

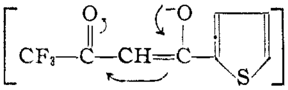
[6] The quite slow disappearance of enolate ion from these solutions (see ref. 2) seems best accounted for on the basis of a slow hydrolysis of enolate ion to $TTA \cdot H_2O$ followed by cleavage, rather than a direct cleavage of enolate ion.

[7] See, for similar results, R. G. Pearson and E. A. Mayerle, This Journal, **73**, 926 (1951).

fore indicate that TTA·H_2O is the principal species in an aqueous TTA solution and that its structure is[1,2]



The optical density at 340 mμ of aqueous solutions of TTA obtained by addition of TTA in the forms indicated below to aqueous buffer solutions (phthalate, phosphate and borate buffers have been used) increases exponentially with *p*H reaching a maximum at approximately *p*H 8. Very nearly equivalent results were obtained by adding the ketone as TTA(s), TTA·H_2O(s), TTA(aq.) or TTA(s) dissolved in a small volume of dry ethanol. Typical optical densities[8] at 340 mμ for 1.00×10^{-4} *M* solutions are (cell length 1 cm.): *p*H 4.0, 0.04; *p*H 5.0, 0.11; *p*H 6.0, 0.58; *p*H 8.0, 1.95. The addition of TTA(s) to an excess of aqueous sodium hydroxide gives an optical density of 2.00 at otherwise equivalent conditions.[8] The absorption at 340 mμ must be due to the formation of enolate ion and the relatively high maximum and extinction (ϵ molar 20,000) require that the enolate ion be the unhydrated species[2,9]



The buffer solution results indicate that TTA·H_2O or TTA can be essentially completely converted to enolate ion at *p*H 8. However, when aqueous solutions of TTA are added to buffer solutions of *p*H 9 or greater the optical densities at 340 mμ fall markedly below that expected for complete enolization. Addition of an aqueous TTA solution to a 0.066 *N* sodium hydroxide solution gave an absorption of only 0.059 at 340 mμ for a 1.00×10^{-4} *M* solution.[8] Nearly equivalent results are obtained with TTA·H_2O(s) or TTA·H_2O(aq.). Since sodium trifluoroacetate and acetylthiophene do not absorb appreciably at 340 mμ, the 97–98% of TTA which should have, but was not, converted to enolate ion must have cleaved to these products. This is confirmed by titration data given below and by the work of Zebroski.[2] In the latter work it was found that TTA·H_2O (solid or in aqueous solution) was 96% hydrolyzed by sodium hydroxide to the above cleavage products and the remaining 4% was converted to enolate ion. Spectral data also indicate that in the titration of aqueous TTA solutions with sodium hydroxide, even though the equilibrium *p*H is held below 8, appreciable hydrolysis occurs. Samples withdrawn during a titration did not give results similar to those above for buffer solutions, but instead gave optical densities much smaller than that corresponding to the equilibrium *p*H of the solution.

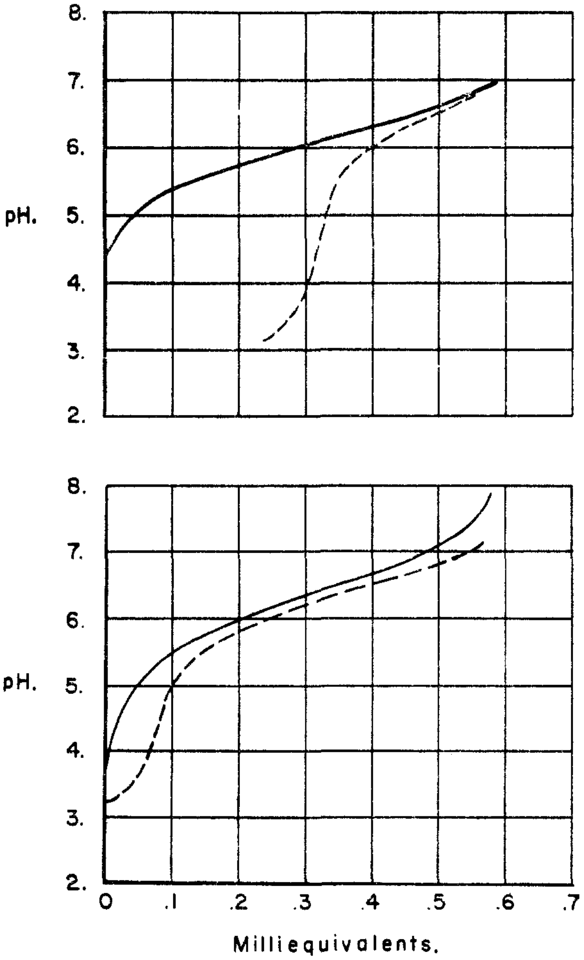


Fig. 1.

When 1 ml. of a solution of TTA in dry ethanol was added to 99 ml. of 0.066 *N* sodium hydroxide, the optical density of a 1.00×10^{-4} *M* at 340 mμ was 1.85.[9]

Titration Data.—Titrations were made with a Beckman "G" *p*H meter using type "E" glass and calomel electrodes. In the upper half of Fig. 1 is shown by the full line a typical curve for the titration of an aqueous TTA solution with sodium hydroxide. In the present case the titration was carried only to an equilibrium *p*H of 6.95 and then back-titrated, as shown by the dashed line, with HCl solution. Since data given above demonstrate that TTA·H_2O (the principal species in aqueous TTA solutions) can be converted to enolate ion without interfering hydrolysis if the *p*H is not made to exceed 8, the fact that the back-titration follows a completely different course than the original (in the present case indicating about 50% of the ketone is converted to the strong trifluoroacetic acid) confirms the spectral evidence showing that cleavage occurs during the addition of base. Back-titration of a solution obtained by adding aqueous TTA to an excess of base shows no more than 5% of the TTA remained unhydrolyzed, as acid equivalent to only 5% of the diketone titrated in the *p*H region above 3.

In the lower half of Fig. 1 is given by the dashed line the back-titration curve for a solution prepared by addition of 1 ml. of a dry ethanol solution of TTA to 99 ml. of an aqueous solution containing sodium hydroxide slightly less than that required for complete neutralization of the TTA. The results indicate that about 15% of the diketone is converted to the trifluoroacetic acid, the remainder being converted from enolate ion to diketone. The full line in the lower half of Fig. 1 gives the back-titration curve (HCl) for a solution prepared by dissolving 0.567 milliequiv. wt. of TTA(s) in a solution containing 0.572 millieq. wt. NaOH. The results indicate no hydrolysis occurs when TTA(s) is dissolved in the base since the theoretical amount of enolate ion was titrated in the high *p*H region. Making a small correction for ionic strength an apparent pK_a of 6.38 is obtained from this curve from the *p*H corresponding to one-half neutralization of the enolate ion. This value is in good agreement with the *p*H corresponding to one-half maximum optical density at 340 mμ obtained from a plot of the buffer solution data referred to above. Other investigators[5a,10] have reported lower pK's based upon the *p*H obtained when one-half of the diketone present is titrated directly with base, but this method is not accurate since it ignores the hydrolysis which accompanies the titration.

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[8] The optical densities given here are maximum values (obtained in every case within a few minutes after reaction was initiated) and were constant for a period of several hours. With long standing the optical densities of the solutions decrease—see ref. 6.

[9] (a) R. N. Jones, *Chem. Revs.*, **32**, 1 (1943); (b) J. R. Platt and H. B. Klevens, *Rev. Modern Phys.*, **16**, 182 (1944).

[10] L. Van Uitert, Master's Thesis, The Pennsylvania State College, 1951.