[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA]

The Hydration of Thenoyltrifluoroacetone in Benzene Solution[1]

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This work is an investigation of the formation of the hydrate of thenoyltrifluoroacetone and in particular its stability in benzene solution. Eleven per cent. of the thenoyltrifluoroacetone in a benzene solution which is in equilibrium with an aqueous solution is present as a hydrate. This has been shown by a study of the solubility of water in benzene solutions of thenoyltrifluoroacetone. The rate of the enol ⇄ hydrate reaction in benzene solution is low. This leads to curious phenomena in experiments in which the distribution of thenoyltrifluoroacetone between aqueous and benzene phases is studied at short time intervals. The rapidly established distribution coefficients to be expected have been calculated and agree with those observed. The phenomena observed in this work is of importance in studies of the rate of metal ion chelate distribution.

In the course of studying the activity coefficient of thenoyltrifluoroacetone, hereafter referred to as TTA, in benzene solution by means of solvent distribution studies,[3] unusual behavior was observed. In all experiments partial transfer of TTA between the phases occurred very rapidly followed by a much slower establishment of final distribution equilibrium. Particularly curious were experiments in which the concentration of TTA in the aqueous phase decreased and then increased before reaching the equilibrium value. These observations are consistent with a rapid establishment of distribution equilibrium coupled with a slow reaction of TTA with one of the solvents to form a species which has an appreciable solubility in the other solvent.

The stability of the hydrate of TTA in benzene solution is the subject of this work. Aside from the studies of the two phase distribution, studies of the spectrum of TTA in benzene and water and measurements of the solubility of water in a benzene-TTA solution have been made.

Experimental Work

Materials.—The TTA used in this experimental work was prepared and purified (by vacuum distillation) by Dr. J. C. Reid. Reagent grade thiophene free benzene was used. In some studies the benzene was dried, while in others it was used with no further treatment.

The Solid Hydrate, TTA·H_2O.—If solid TTA is allowed to stand in contact with an aqueous solution, the color changes from amber to white. The equivalent weight of the air dried material which had been in contact with a dilute aqueous acid solution was determined. This was done by dissolving the solid in 95% alcohol, treating with a known slight excess of base, allowing to stand for a time sufficient for the slow neutralization to occur and then back titrating the excess base with a standard acid. In two samples, the equivalent weight was found to be 240 and 241. The value calculated for TTA·H_2O is 240.2.

The existence of a dihydrate of hexafluoroacetylacetone has recently been shown by Schultz and Larsen.[4]

The Solubility of Water in Benzene Solutions of TTA.—The approximate solubilities of water in benzene and in benzene solutions of TTA have been determined in order to establish the extent to which a hydrate of TTA exists in a benzene solution in equilibrium with an aqueous phase. This was done by measuring the volume of water which dissolved in measured volumes of the benzene solutions.

A short piece (approx. 5 cm.) of heavy walled capillary tubing of known bore closed at one end was sealed to the bottom of a 100-ml. Pyrex centrifuge tube. This tip was partially filled with water or dilute acid and its depth measured to the nearest 0.2 mm. A measured volume of benzene solution was added and the entire tube sealed. The aqueous phase was shaken out of the capillary tip and then equilibrated with the benzene phase at room temperature using a mechanical shaker. At various times the tube was centrifuged to send all of the aqueous phase into the capillary. It was possible to determine the amount of water which had dissolved in the benzene by again measuring the depth of the aqueous phase. The solubility of water in benzene determined in this way was found to be 0.024 mole/l. in two independent experiments; in one of these experiments the reagent-grade thiophene free benzene was used without further drying, while in another this benzene was dried over $CaSO_4$ before use. This value is in acceptable agreement with the values 0.021 and 0.026 mole/l. determined by Black, Joris and Taylor[5] at 20° and 26°. The solubility of water in solutions of TTA has been corrected for this solubility in benzene. The results of these experiments are presented in Table I. It is seen that 12% of the TTA in a benzene solution in equilibrium with an aqueous phase is present as the hydrate if the species in solution involves one H_2O molecule per TTA molecule. Under the conditions of these experiments, the hydrate is not formed rapidly as it took about two to three days for equilibrium to be established.

TABLE I

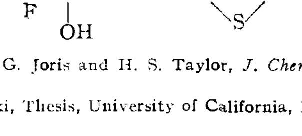
SOLUBILITY OF WATER IN BENZENE SOLUTIONS OF TTA

Concn. TTA (in moles/l.)	Excess solubility of water (moles/l.)	$\frac{\text{Moles } H_2O}{\text{Mole TTA}}$
0.51	0.060[a]	0.12
0.90	0.114,[a] 0.106[b]	.12
1.53	.198,[a] .197[b]	.13

[a] Aqueous phase was pure water. [b] Aqueous phase was 0.13 *M* HCl.

The Spectrum of TTA.—The absorption spectrum of TTA in a dilute aqueous acid solution has been determined. A plot of ϵ, the molar extinction coefficient ($\epsilon = (cl)^{-1} \log I_0/I$; c is concn. in moles/liter and l is cell length in cm.) as a function of wave length is given in Fig. 1. It is seen that maxima are present at 267 and 292 mμ, while the solution is relatively transparent at wave lengths greater than 340 mμ. The absorption has been shown to obey Beer's law[3] and to be independent of hydrogen ion concentration over the pH range 1–4.[6] A solution of TTA in benzene on the other hand absorbs strongly at wave lengths greater than 340 mμ. The values of ϵ for benzene solutions are also plotted in Fig. 1.

It appears, therefore, that the principal species in the two solvents are different. It seems reasonable to assume that essentially all of the TTA in an aqueous solution is the hydrate. E. Zebroski[6] has concluded from the spectrum of an aqueous solution that the structure of the hydrate is



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[1] This research was carried out in the Radiation Laboratory and Chemistry Department of the University of California under the auspices of the Manhattan District, Corps of Engineers, during 1945 and 1946.

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[3] E. L. King and W. H. Reas, THIS JOURNAL, **73**, 1804 (1950).

[4] B. G. Schultz and E. M. Larsen, *ibid.*, **71**, 3250 (1949).

[5] C. Black, G. Joris and H. S. Taylor, *J. Chem. Phys.*, **16**, 537 (1948).

[6] E. Zebroski, Thesis, University of California, 1947.

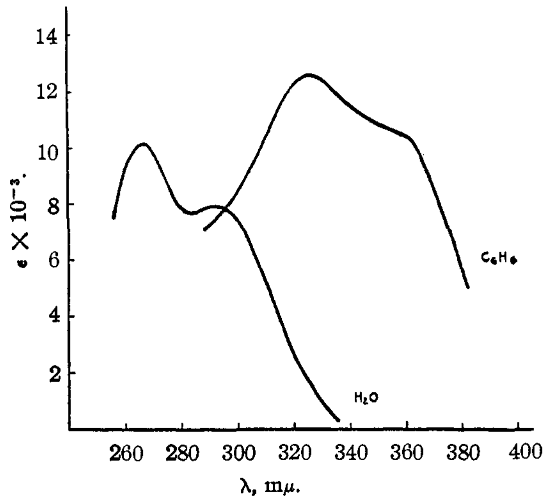

Fig. 1.—Molar extinction coefficient of TTA in benzene and dilute aqueous hydrochloric acid.

J. C. Reid and M. Calvin[7] have reported that approximately 1.6% of the TTA in an aqueous solution is present in the enol form as determined by the method of K. Meyer. On the other hand, in a dry benzene solution of TTA, the principal species appears to be the enol. Reid and Calvin have reported that 94.5% of the TTA in a benzene solution is enol. In this work comparable results were obtained, although there were some unexplained variations in the analyses; in some solutions less than 90% of the TTA was present as the enol. The difference between the percentage of enol and 100% may be the percentage of keto present. A few per cent. of hydrate may be present in an undried solution of TTA in benzene due to traces of water in the solvent, the solid used, or both.

In view of the difference in the absorption of the principal forms, a spectral study offers an additional means of establishing the fraction of TTA present as the hydrate in a benzene solution in equilibrium with an aqueous phase. The spectra of solutions of TTA in benzene which have been equilibrated with a small volume of an aqueous phase have been measured. Another solution of TTA in benzene was allowed to stand in contact with $CaSO_4$ for a day. The concentration of enol in this dried solution was measured by determining the Cu^{II} which reacted rapidly with an aliquot of the solution to form the copper chelate compound. The spectrum of this solution was also measured. The values of the extinction coefficients are presented in Table II. The extinction coefficients for the "wet" solutions are lower in the wavelength region in which the hydrate is transparent. One can calculate the percentage of the TTA present as the TTA hydrate in the "wet" benzene solutions by assuming that all of the material not present as enol is hydrate. The equation, % hydrate = $100\,(1 - (\bar{\epsilon}_w/\epsilon_e))$, has been used to give the values which are presented in Table II. It is seen that approximately 10% of the TTA present in a benzene solution saturated with water is present as the hydrate. This is in acceptable agreement with the value, 12%, determined in more concentrated solutions by the water solubility studies.

TABLE II

LIGHT ABSORPTION OF WET AND DRY SOLUTIONS OF TTA IN BENZENE

Wave length in mμ	Molar extinction coefficients "wet"-TTA-C_6H_6 solution 1.75 × 10^{-5} moles/l.	5.25 × 10^{-6} moles/l.	Dry solution 9.04 × 10^{-6} moles/l.[a]	% TTA hydrate in "wet" solution
380	4990	5030	5520	9.2
370	7520	7580	8400	10.1
360		9500	10500	9.5
350	9800	9900	10900	9.6
330	11100	11200	12500	10.8

[a] This is the concentration of enol; the molar extinction coefficients are calculated using this concentration.

The interesting question of how rapidly a benzene solution of TTA hydrate approaches equilibrium has been investigated qualitatively by a spectral study. A weighed portion of solid $TTA \cdot H_2O$ was dissolved in benzene and a dilution made to give a solution 3.4 × 10^{-5} mole/liter. The spectrum of this solution was measured at various times; the results are presented in Fig. 2. It is seen that the conversion of hydrate to enol proceeds very slowly in benzene solution.

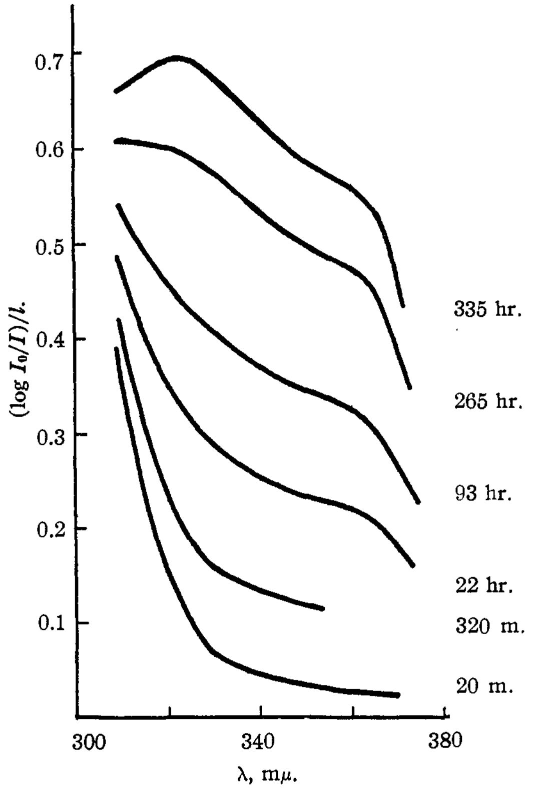

Fig. 2.—Spectrum of solution prepared by dissolving $TTA \cdot H_2O$ in benzene as function of time (concn. of solution was 3.4 × 10^{-5} moles/l.).

The rate of conversion of enol to hydrate in an aqueous solution is rapid. This was demonstrated by measuring the spectrum of an aqueous solution prepared by dissolving a small volume of a benzene solution of TTA in a dilute acid solution and within a few minutes measuring its spectrum. The observed spectrum was that of the hydrate.[8]

The Distribution of TTA between Water and Benzene.—As mentioned earlier, the behavior of TTA in short duration distribution experiments is unusual. In all of the experiments performed, there appears to be a rapid distribution equilibrium followed by a much slower process. The most reasonable slow process occurring in the system being studied is the enol $\rightleftarrows$ hydrate reaction. Final equilibrium is not established rapidly because the ratio of the amounts of these two species is different initially than it is at equilibrium in the two-phase system.

The results of several experiments in which the distribution was studied at short times as a function of time are presented in Fig. 3 (a–e). In all cases the analytical procedure used was the measurement of the extinction at 292 mμ of a diluted aliquot of the aqueous phase. The concentrations were calculated using ϵ = 7960[3].

Data which have already been discussed (the equilibrium distribution coefficient,[3] the amount of TTA hydrate present in a benzene solution in equilibrium with an aqueous phase and the absence of appreciable amounts of enol in the aqueous phase) allow a calculation of the rapid distribution to be expected if no forms of TTA other than the enol and

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[7] J. C. Reid and M. Calvin, THIS JOURNAL, **72**, 2948 (1950).

[8] E. Zebroski[6] has performed a similar experiment with the same result.

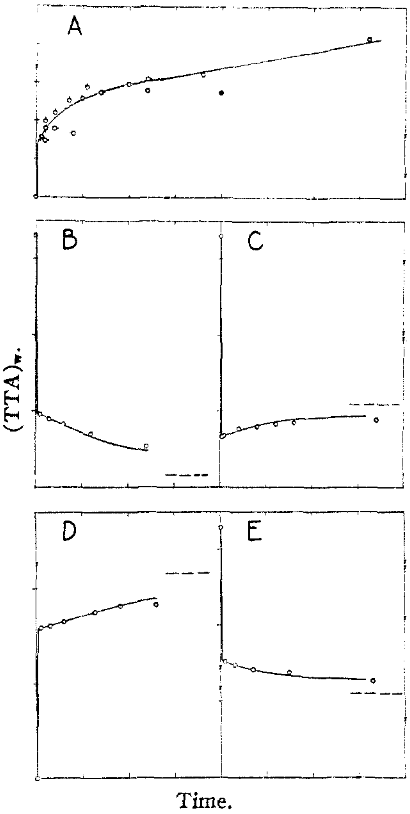

Fig. 3.—Concentration of TTA in aqueous phase in distribution experiments as function of time. Figures a-e correspond to similarly lettered experiments in Table III. (In all cases divisions on time scale = 5 min. The ordinate is concn. of TTA in moles/l. One scale division is 0.010 mole/l. (b, c, e); 0.005 mole/l. (d) and 0.002 mole/l. (a). Horizontal dashed lines reyresent the equilibrium concentration.)

hydrate exist. The complete absence of the keto form of TTA in both phases is not proved by the data presented here. The determinations of enol in a benzene solution of TTA reported by Reid and Calvin[7] and duplicated in this work indicate that no more than 5% keto could be present in the benzene solution. This value is an upper limit because in a solution of TTA in benzene which has not been dried there appears to be present 2–3% of the TTA as the hydrate. This follows from a comparison of the rapid distribution established when dried and undried solutions of TTA in benzene are shaken with dilute acid containing no TTA. If this rapid distribution were due to the hydrate distributing itself, there must be present in the undried and dried benzene solutions 3% and 0.7% hydrate, respectively. One could assume that the other 2% of TTA in an ordinary benzene solution which is not present as the enol is present as the keto form. The keto/enol ratio would be expected to be greater in the aqueous phase than in the benzene phase.[9] If the change in this ratio in going from benzene to water is comparable to that observed for acetylacetone, the resulting amount of keto in the aqueous phase would be less than one per cent. The presence of these small amounts of the keto form of TTA in the two solvents does not influence markedly the calculations of the distribution to be expected in the types of experiments presented in Fig. 3 (a–e), and therefore the calculations will be carried out on the basis that only the enol and the hydrate exist. In these calculations it will be assumed: (1) in an aqueous solution, the TTA is entirely in the form of the hydrate, (2) in a benzene solution saturated with water, 11% of the TTA is present as the hydrate, and (3) in a benzene solution which has neither been dried nor equilibrated with water there is present 3% hydrate. Since in all of the experiments except one, the concentration of TTA in the benzene is ~ 0.5 molar the over-all distribution coefficient of 48.2 will be used.[3] If one assumes the activity coefficients of the enol and hydrate in the benzene phase to be equal, this leads to a distribution coefficient for the hydrate $D_H = (TTA \cdot H_2O)_B/(TTA \cdot H_2O)_W = 5.3$, where $(TTA \cdot H_2O)_B$ and $(TTA\ H_2O)_W$ are the concentrations of the hydrate in the benzene and water (in moles/liter), respectively. The corresponding distribution coefficient for the enol is approximately ∞ since essentially no enol exists in the aqueous phase.

The results of calculations carried out using these assumptions are presented in Table III. The observed values of the rapidly established concentration of TTA in the aqueous phase are taken from the curves of Fig. 3 (a–e). The agreement between the observed and calculated values is evidence for the essential correctness of the over-all picture. It is seen that the unusual observation of the concentration crossing the equilibrium value and approaching equilibrium from the other side (see c, Fig. 3 and Table III) is just what is expected on the basis of the picture presented here.

TABLE III

RAPID DISTRIBUTION OF TTA BETWEEN BENZENE AND WATER

	$\frac{\text{Vol. } C_6H_6}{\text{Vol. } H_2O}$	Concentration (in moles/l.) Before distribution Benzene[e]	Aqueous[e]	Rapidly established concn. in aqueous phase Calcd.	Obs.
A	1.0	0.015 h[b]	0.00		
		.495 e		(0.0024)[d]	0.0025
A′	1.0	.090 e[c]	.00	.00	1.2×10^{-4} [f]
B	0.5	.00	.033	.0102	.0100
C	1.0	.015 h[b]	.033		
		.495 e		.0075	.0065
D	0.67	.056 h[a]	.00		
		.454 e		.0081	.0078
E	0.67	.056 h[a]	.033		
		.454 e		.0155	.0154

[a] Benzene phase pre-equilibrated with an aqueous soln. [b] Benzene phase neither dried nor equilibrated with water. [c] Benzene phase dried over $CaSO_4 \cdot {}^1/_2H_2O$. [d] Amount of hydrate in benzene chosen to give agreement here (3%). [e] h = hydrate, e = enol. [f] This experiment not included in Fig. 3.

The final distribution equilibrium, although slowly established, is realized more rapidly than is the hydrate $\rightleftarrows$ enol equilibrium in benzene. It appears, therefore, that the mechanism by which final equilibrium is established involves the hydrate $\rightleftarrows$ enol change occurring predominantly in the aqueous phase. The very low concentration of enol in an aqueous solution leads to a slow equilibration despite the relative rapidity of this change (hydrate $\rightleftarrows$ enol) in an aqueous solution and the rapid distribution of the two species between the two solvents.

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[9] Branch and Calvin, "The Theory of Organic Chemistry," Prentice-Hall, New York, N. Y., 1941, p. 297.