[CONTRIBUTION FROM THE PENNSYLVANIA STATE UNIVERSITY AND THE UNIVERSITY OF MICHIGAN]

# Polarographic Behavior of Thenoyltrifluoroacetone (TTA) and Related Compounds. Alkaline Cleavage of TTA. Complexation of TTA with Borate. Analytical Determination of TTA

BY PHILIP J. ELVING AND CLARENCE M. CALLAHAN[1]

RECEIVED NOVEMBER 29, 1954

Thenoyltrifluoroacetone (TTA) gives two polarographic waves in chloride, acetate and ammonia buffers; the presence of only one wave in borate buffer is attributed to the complexation of TTA with buffer component. By correlating the half-wave potentials and behavior of TTA with those of thiophene, acetylthiophene, thenoylacetone, acetylacetone and trifluoroacetylacetone, the complex polarographic wave pattern exhibited by TTA is explained by the different nature of the electrode processes involved. The first TTA wave results from the reduction of the carbonyl group entity adjacent to the trifluoromethyl group, and is kinetic-controlled, due to conversion of the hydrated TTA to the reducible enolate form. The second wave is the result of a one- to two-electron diffusion-controlled process in which the thenoyl carbonyl group is reduced to the pinacol, the carbinol or both as the *p*H varies. In alkaline solution the first wave may also involve reduction of the thenoyl carbonyl to pinacol, and the second wave only reduction to carbinol. The current of each wave is a linear function of concentration; optimum analytical results are secured using the sum of both waves in acetate buffer. The alkaline fission of TTA in ammonia buffer was followed polarographically; the data indicated a zero-order reaction. The complex resulting from interaction between boron species and the carbonyl group adjacent to the trifluoromethyl group is possibly due to the formation of either a four-member ring involving boron and the two hydroxyl oxygens on the carbon of the hydrated carbonyl group, or a five-member ring between boron and one hydroxyl group oxygen and one fluorine of the trifluoromethyl group.

2-Thenoyltrifluoroacetone, first prepared by Reid and Calvin[2] and usually referred to as TTA, forms complex molecules with various metal ions. As the extent of complexation is *p*H-dependent, mixtures of ions which are ordinarily very difficult to separate can be resolved by the the use of TTA as a selective extractant. The possibility exists of determining metals indirectly by measurement of the TTA in the metal–TTA complex.

The present investigation was undertaken to determine the general electrochemical behavior of TTA at the dropping mercury electrode. TTA presents a number of possible electroreducible structures, *e.g.*, the trihalogenated carbon atom $\alpha$ to a carbonyl group, the carbonyl group $\alpha$ to an unsaturated cyclic structure, the $\beta$-diketone structure, and the conjugated double bond system, which through keto–enol tautomerism should materially increase the number of electroreducible structures in the molecule.

In order to identify the two polarographic waves generally given by TTA with the electrochemical reduction of particular groups in TTA, the latter was considered to be a possible derivative or composite of thiophene, acetylthiophene, thenoylacetone, acetone, acetylacetone and trifluoroacetylacetone. It was assumed that if one of the component units of a composite structure produces a polarographic wave when the component unit exists as a discrete molecule, it will produce this or a related wave when it is a part of the composite structure with, of course, due consideration being given to the influence of the rest of the molecule.

By thus correlating the polarographic data of TTA with those of compounds which may be considered as precursors of its structure, it was possible to assign each TTA wave in a particular buffer to certain electroreductions and, on the added basis of the known chemistry of TTA, to formulate reactions to account for the observed reductions. Suitable explanations were postulated for the apparently anomalous behavior observed in some buffer systems, particularly in reference to cleavage in alkaline solution and complexation with borate. The applicability of polarographic measurement for the detection and estimation of TTA was investigated.

## Experimental

**Chemicals.**—The TTA was a research sample, kindly furnished by the Dow Chemical Company, and a sample of 99.5% purity obtained from Midcontinent Chemicals Corp. Acetone, methyl ethyl ketone, acetylacetone and thiophene were redistilled prior to use. Acetylthiophene was kindly furnished by Dr. Robert W. Taft. Trifluoroacetylacetone was redistilled from a sample prepared in this Laboratory.

TTA is sparingly soluble in water. Acetone and methyl ethyl ketone were unsuitable as stock solution solvents for TTA since, as subsequently discussed, they produce a well-defined wave in ammonia buffer, when present in decimolar or larger concentration. Ten per cent. ethanol was found to be a suitable solvent. The requisite weight of TTA was first dissolved in 95% ethanol; distilled water was then added, with shaking, to the desired volume. The final test solution had a concentration of 1% ethanol which had little or no effect on the polarographic properties.

Buffer systems, prepared from analytical reagent grade chemicals, were used at the *p*H indicated: No. 1, 1.0 *M* KCl with added HCl, 1.0; No. 2, 1.0 *M* NaOAc with added HOAc, 5.0 to 5.2; No. 3, 1.0 *M* $NH_4Cl$ with added $NH_3$, 8.2 and 9.2; No. 4, 0.05 *M* $Na_2B_4O_7$, 0.90 *M* KCl and added NaOH, 9.2 and 10.0; No. 5, 0.22 *M* $Na_2HPO_4$ with added NaOH, 12.0. The concentrations were such as to give an ionic strength level of 0.9 in the final test solution.

The nitrogen used for purging was deoxygenated and equilibrated in reference to vapor pressure by bubbling it successively through an alkaline pyrogallol solution, sulfuric acid, water and a portion of the test solution.

**Apparatus.**—Polarographic curves were obtained with a calibrated Fisher Elecdropode, recording maximum galvanometer deflection. The capillary (Corning marine barometer tubing) had an *m* value of 1.14 mg./sec. at open circuit in 0.1 *M* KCl solution. All $E_{1/2}$ values are against the S.C.E. at 25.0° unless other temperatures are specified. The S.C.E. and sample were in a water-jacketed constant-temperature H-cell.[3] A Beckman Model G *p*H meter was used.

**Procedure.**—Stock solutions were made by dissolving the requisite weight of the ketone in 25 ml. of ethanol and diluting with distilled water to volume in a 250-ml. volumetric flask. The test solution was prepared by pipetting 5.00 ml. of a stock solution into a 50-ml. volumetric flask and

---

(1) This work is based in part on the M.S. thesis of C. M. Callahan, The Pennsylvania State College, 1952.

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

(3) J. C. Komyathy, F. Malloy and P. J. Elving, *Anal. Chem.*, **24**, 431 (1952).

diluting with the desired buffer. The test solution was deoxygenated for 10 minutes and then electrolyzed at a constant head of mercury (67 cm.). The nitrogen atmosphere was maintained throughout the electrolysis.

**Observed Behavior of TTA.**[4]—At *p*H 1.0 the first wave is so small and poorly defined that $E_{1/2}$ cannot be accurately located; the second wave is larger, but, unfortunately, has a pronounced maximum. Because of these limitations, no further work was done in this buffer system. At *p*H 5.2, two well-defined waves are produced; *i* of the second wave is more than twice that of the first wave. In the ammonia buffer (*p*H 8.2) two well-defined waves are produced; *i* of the first wave is now appreciably larger than that of the second wave. In the same buffer at *p*H 9.2, $E_{1/2}$ shift to more negative values and *i* of the second wave is nearly twice that of the first wave. In borate buffer at *p*H 9.2, the first wave is absent. Phosphate buffer (*p*H 12.0) also gives only the second wave whose *i* is considerably diminished.

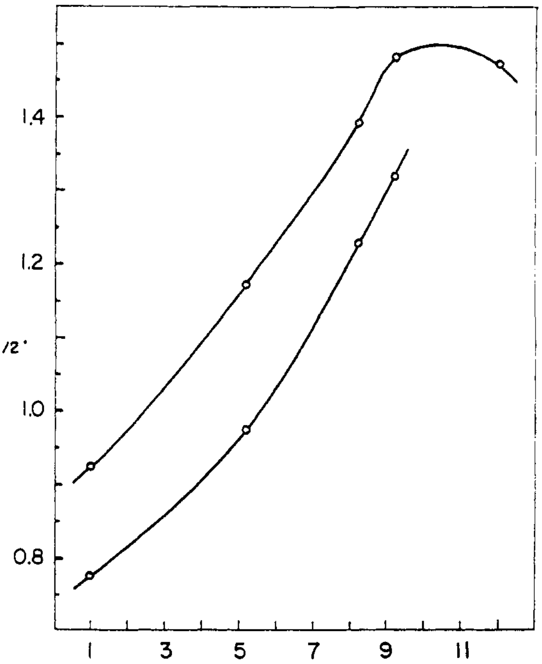


Fig. 1.—Variation of the half-wave potentials of the waves of thenoyltrifluoroacetone with *p*H.

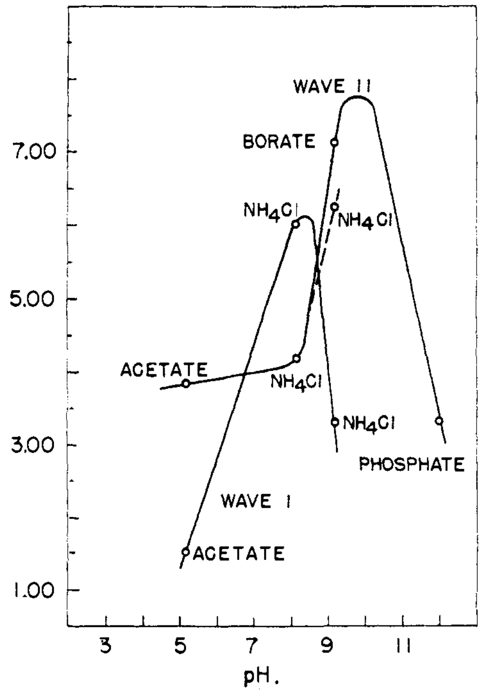


Fig. 2.—Variations of the current-concentration ratio with *p*H for the waves of 0.5 m*M* solutions of thenoyltrifluoroacetone.

TABLE I

POLAROGRAPHIC CHARACTERISTICS OF TTA AND RELATED COMPOUNDS AT 25°

| Cpd. and concn. | Buffer no. | *p*H | Wave I[a] $-E_{1/2}$, v. | Wave I[a] *i/c* | Wave II[a] $-E_{1/2}$, v. | Wave II[a] *i/c* |
|---|---|---|---|---|---|---|
| Thenoyltrifluoroacetone | 1 | 1.0 | 0.78 | 0.62 | 0.92 | 5.2 |
| $C$ = 0.40 to 0.80 m*M* | 2 | 5.2 | 0.98 | 1.5 | 1.17 | 3.8 |
| | 3 | 8.2 | 1.23 | 6.1 | 1.39 | 4.2 |
| | 3 | 9.2 | 1.32 | 3.3 | 1.45 | 6.2 |
| | 4 | 9.2 | No wave | | 1.48 | 7.2 |
| | 5 | 12.0 | No wave | | 1.47 | 3.3 |
| Thiophene: $C$ = 0.5 m*M* | 1 to 4 | 1 to 10 | No wave | | No wave | |
| Acetylthiophene | 1 | 1.0 | No wave | | 0.96 | 4.0 |
| $C$ = 0.5 m*M* | 2 | 5.1 | No wave | | 1.25 | 3.5 |
| | 3 | 8.2 | No wave | | 1.41 | 7.1 |
| | 4 | 10.0 | No wave | | 1.49 | 5.5 |
| Thenoylacetone | 2 | 5.0 | No wave | | 1.15 | 4.8 |
| $C$ = 0.64 to 0.69 m*M* | 3 | 8.2 | 1.25 | 5.0 | 1.45 | 1.9 |
| | 4 | 9.2 | 1.35 | 1.9 | 1.50 | 2.9 |
| Trifluoroacetylacetone | 1 | 1.0 | No wave | | No wave | |
| $C$ = 1.07 m*M* | 2 | 5.0 | 1.22 | 1.0 | No wave | |
| | 3 | 8.2 | 1.43 | 1.7 | No wave | |
| | 4 | 9.2 | No wave | | No wave | |
| Acetylacetone | 1, 2, 4 | | No wave | | No wave | |
| $C$ = 0.38 *M* | 3 | 8.2 | No wave | | 1.21 | 0.009 |
| Acetone | 1, 2, 4 | | No wave | | No wave | |
| $C$ = 1.37 *M* | 3 | 8.2 | No wave | | 1.44 | 0.006 |
| Methyl ethyl ketone | 3 | 8.2 | No wave | | 1.43 | 0.003 |
| $C$ = 1.10 *M* | | | | | | |

[a] Each set of values is generally an average of two runs.

TABLE II

EFFECT OF *p*H AND BUFFER ON THE POLAROGRAPHIC CONSTANTS OF THENOYLTRIFLUOROACETONE AT VARIOUS CONCENTRATIONS IN 1% ETHANOL–WATER SOLUTION AT 25°

| Buffer no. | *p*H | TTA concn., m*M* | Wave I[a] $-E_{1/2}$, v. | Wave I[a] $I$[b] | Wave II[a] $-E_{1/2}$, v. | Wave II[a] $I$[b] | Combined waves $I$ |
|---|---|---|---|---|---|---|---|
| 2 | 5.2 | 0.2 | 0.98 | 1.04 | 1.17 | 2.74 | 3.8 |
| 2 | 5.2 | 0.5 | 0.98 | 1.06 | 1.17 | 2.71 | 3.8 |
| 2 | 5.2 | 0.8 | 0.98 | 1.00 | 1.17 | 2.78 | 3.8 |
| 2 | 5.2 | 1.2 | 0.98 | 1.05 | 1.17 | 2.72 | 3.8 |
| 3 | 8.2 | 0.2 | 1.24 | 4.49 | 1.39 | 3.01 | 7.5 |
| 3 | 8.2 | 0.5 | 1.24 | 4.28 | 1.40 | 3.00 | 7.3 |
| 3 | 8.2 | 0.8 | 1.23 | 4.20 | 1.40 | 3.14 | 7.3 |
| 3 | 8.2 | 1.2 | 1.23 | 4.09 | 1.41 | 2.90 | 7.0 |
| 4 | 9.2 | 0.2 | No wave | | 1.48 | 5.21 | 5.2 |
| 4 | 9.2 | 0.5 | No wave | | 1.47 | 5.14 | 5.1 |
| 4 | 9.2 | 0.8 | No wave | | 1.47 | 5.15 | 5.2 |
| 4 | 9.2 | 1.2 | No wave | | 1.47 | 4.66 | 4.7 |

[a] Each set of values is an average of 4 to 8 runs, 6 being the usual number. [b] $I = i/Cm^{2/3}t^{1/6}$. Note that only wave II is diffusion-controlled.

***p*H-Dependence.**—Both TTA waves shift to more negative $E_{1/2}$ with increase in *p*H (Fig. 1);

---

(4) Detailed tables of polarographic data, upon which the discussion is based, are available from the authors; essential data for the conclusions reached are given in Tables I and II, and Figs. 1 and 2.

above $pH$ 9.0, $E_{1/2}$ may be constant. The waves of acetylthiophene, thenoylacetone and trifluoroacetylacetone also show this $pH$ dependence, indicating reduction mechanisms similar to those of TTA.

**Current-controlling Processes.**—Temperature coefficients and variation with drop-time, *i.e.*, head of mercury, for the first wave current (buffers 2 and 3) indicate at least a partially kinetic-controlled process which is explained by subsequent equation 6. The behavior of the second wave (buffers 2, 3 and 4) indicates diffusion-control.

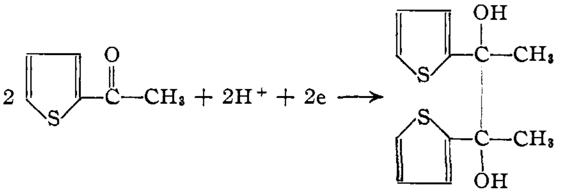
***n*-Values.**—Values of $n$, the number of electrons transferred per molecule of TTA reduced, based on the Ilkovic equation, are open to some question due to the uncertainty in the actual TTA diffusion coefficient; the latter can be estimated from the Stokes–Einstein equation as $6.15 \times 10^{-6}$ cm.$^2$ sec.$^{-1}$. Use of this value gives $n$ values for the second diffusion-controlled wave of 1.6 ($pH$ 5), 1.7 ($pH$ 8), 2.5 ($pH$ 9, ammonia buffer) and 2.9 ($pH$ 9, borate).

A more exact determination of $n$ was attempted by coulometric measurement,[5] in which any equilibrium involving a reducible species would be displaced toward that species as it was reduced. A number of one and two millimolar solutions of TTA were electrolyzed at $-1.40$ v. in acetate buffer at $pH$ 5.0; $n$ was found to be approximately 4. Polarograms of the reduced solution showed that the first wave had disappeared, and that only a greatly diminished second wave remained; the $pH$ was unchanged.

Values of $\alpha$ calculated from the slopes of the polarographic waves are approximately one in all buffers and at all concentrations.

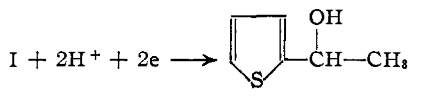
**Behavior of Compounds Related to TTA. Thiophene.**—Since thiophene produced no wave in any of the buffer systems or in 0.1 $M$ lithium chloride, it may be concluded that the thiophene ring is not reducible under the experimental conditions used and that the thiophene radical in TTA is probably not reduced.

**Acetylthiophene.**—2-Acetylthiophene (I), which differs from thiophene in possessing a carbonyl group conjugated to the ring, produces one wave in each of the buffer systems. Hence, it may be assumed that the wave is produced by the reduction of the carbonyl group $\alpha$ to the thiophene ring, probably by one or both of the following reactions



I II

(1)



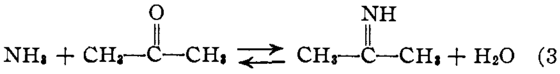
(2)

Aromatic ketones are generally polarographically reduced to the pinacol *via* a free radical mechanism with more or less carbinol being produced in the intermediate $pH$ region due to the further reduction of the free radical.[6] Equation 1 is lent further credence by the preparative electrolytic reduction of ketones[7] in which pinacols are produced. On the basis of the $i_d/C$ ratios, we may assume that the electrode process involves a one-electron reduction to the free radical which dimerizes to pinacol in acidic solution and a further one-electron reduction of the free radical to the carbinol in basic solution; the diminution of the carbinol wave in more alkaline medium is characteristic of ketones.

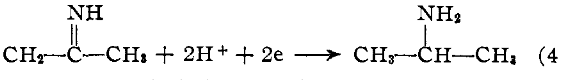
**Thenoylacetone.**—Thenoylacetone (TA) differs from TTA in that hydrogen rather than fluorine is present in the terminal methyl group. The waves given by TA may be ascribed to the same processes as produced the acetylthiophene wave with the following modifications. The presence of the acetyl group in TA shifts the reduction potential of the keto group $\alpha$ to the thiophene ring to more positive potentials. In addition, the wave representing the reduction of the free radical to carbinol occurs at a sufficiently more negative potential in alkaline solution that it is clearly separated from the first wave representing the reduction of carbonyl to free radical. The somewhat greater magnitude of the second wave as compared to the first wave at $pH$ 9 may be due to some reduction of the acetone carbonyl group which is activated in the free radical.

**Trifluoroacetylacetone.**—This compound produces one wave in acetate and ammonia buffers, whose $E_{1/2}$ values compare closely with those of the second TTA wave. However, other factors such as absence of the wave in borate buffer and the behavior of the other compounds would indicate the wave as being actually similar in origin to the first TTA wave. Such a wave, as subsequently discussed, would also depend on activation of the acetone carbonyl group due to the inductive effect of the fluorine atoms; the more negative $E_{1/2}$ compared to that of the first TTA wave would be due to the lesser possibilities of conjugation in trifluoroacetylacetone. Absence of a second wave is due to lack of the activation effect of the thiophene ring in the reduction product of the first wave.

**Acetylacetone, Acetone, Methyl Ethyl Ketone.**—Acetylacetone gives one wave in ammonia buffer and none in the other buffer systems; this behavior is similar to that of acetone and methyl ethyl ketone. The wave appears to be due to a different reaction than those for TTA and may be ascribed to the reduction of the imino group formed from the ketone and free ammonia in ammonia buffers. Zuman[8] reported a wave for acetone at $-1.6$ v. in ammonium sulfate–ammonia buffer at $pH$ 9.3, which he attributed to reduction of the imino group of the ketimine in equilibrium with acetone and ammonia



$$NH_3 + CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \rightleftharpoons CH_3-\overset{\overset{NH}{\|}}{C}-CH_3 + H_2O \quad (3)$$



$$CH_3-\overset{\overset{NH}{\|}}{C}-CH_3 + 2H^+ + 2e \longrightarrow CH_3-\overset{\overset{NH_2}{|}}{C}H-CH_3 \quad (4)$$

Zuman concluded that the wave height is influ-

---

(5) J. J. Lingane, THIS JOURNAL, **67**, 1916 (1945).

(6) J. T. Leone, Ph.D. Thesis (in preparation), University of Michigan, 1954.

(7) D. H. Hey and W. A. Waters, *Chem. Revs.*, **21**, 169 (1937).

(8) P. Zuman, *Nature*, **165**, 485 (1950).

Table III

Comparative $E_{1/2}$ and $i_d/C$ Values for TTA and Related Compounds[a]

Buffer and $p$H; wave origin[b]; values of $E_{1/2}$ (volts) and $i/C$[c] ($\mu$a/m$M$)

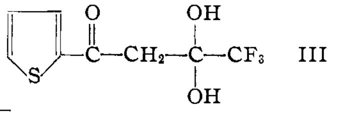
| Compound | Chloride, $p$H 1 | | | Acetate, $p$H 5 | | | Ammonia, $p$H 8 | | | Borate, $p$H 9 | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | A | B | C[d] | A | B | C | A | B | C | A | B | C |
| Thiophene | nw | nw | nw | nw | nw | nw | nw | nw | nw | nw | nw | nw |
| Acetylthiophene | nw | 0.96<br>(4.0) | nw | nw | 1.25<br>(3.5) | nw | nw | nw | 1.41<br>(7.1) | nw | nw | 1.49<br>(5.5) |
| Thenoylacetone | | | | nw | 1.15<br>(4.8) | nw | nw | 1.25<br>(5.0) | 1.45<br>(1.9) | nw | 1.35<br>(1.9) | 1.50<br>(2.9) |
| Trifluoroacetylacetone | nw | nw | nw | 1.22<br>(1.0) | nw | nw | 1.43<br>(1.7) | nw | nw | nw | nw | nw |
| TTA | 0.68<br>(0.62) | 9.92<br>(5.2) | nw | 0.98<br>(1.5) | 1.17<br>(3.8) | nw | —1.23—<br>(6.1) | | 1.39<br>(4.2) | nw | nw | 1.48<br>(7.2) |
| | | | | | | | Ammonia, $p$H 9 | | | Phosphate, $p$H 12 | | |
| | | | | | | | —1.32—<br>(3.3) | | 1.45<br>(6.2) | nw | nw | 1.47<br>(3.3) |

[a] A blank indicates that the compound was not studied in the particular buffer; nw indicated no wave observed. [b] A, reduction of acetyl or trifluoroacetyl carbonyl group; B, reduction of thenoyl carbonyl group to pinacol; C, further reduction of thenoyl carbonyl group to carbinol. [c] $i/C$ values are given in parentheses beneath $E_{1/2}$ values. [d] The discharge of background electrolyte or hydrogen ion may obscure this wave.

enced by the concentration of available free ammonia and is a linear function of the acetone concentration; he reported well-defined waves in millimolar acetone solution. In the present work, in ammonium chloride–ammonia buffer of $p$H 8.2, acetone gave a well-defined wave at −1.44 v. and methyl ethyl ketone a similar wave at −1.43 v. The discrepancy with Zuman's value may be attributed to differences in the $p$H and ionic strength of the buffers used. The difficulty of detecting small concentrations of acetone and methyl ethyl ketone in the present case is believed to be due to the fact that the equilibrium of equation 3 is far to the left at $p$H 8.2.

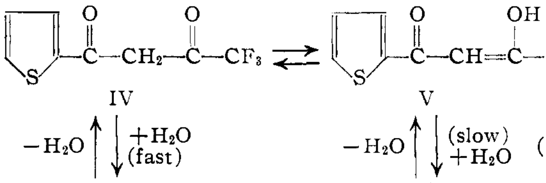
**Reduction Mechanism of TTA.**[9]—From correlation of the behavior and half-wave potentials (Table III) of TTA and related compounds, it is probable that at $p$H 1 and 5 the first TTA wave, which shows kinetic character, is due to the reduction of the carbonyl group in the trifluoroacetyl portion, and the second wave to the reduction of the carbonyl group in the thenoyl portion to pinacol. In alkaline solution ($p$H 8) the first wave probably represents a coalescence of the waves originating in the two processes just indicated, while the second observed wave represents the further reduction to the carbinol of the free radical representing the first stage in thenoyl carbonyl group reduction. The causes of the behavior observed as $p$H increases are subsequently discussed.

In order to assign mechanisms for the electrode reactions, it is necessary to consider the various TTA species present in aqueous solution. Spectral studies[10,11] of the aqueous TTA solution indicate that the compound exists primarily as the hydrate



III (5)

Only 1.6% of TTA in aqueous solution is present in the enol form; however, 94.5% enol is present in dry benzene solution.[2] Stabilization of the hydrate is due both to the strong inductive effect of the adjacent fluorine atoms, which is conducive to the production of a positive carbon capable of adding a hydroxyl ion, and to possible formation of a strong hydrogen bond between the oxygen and fluorine on adjacent carbon atoms. This push–pull effect would explain the stabilization of similar hydrates such as those of chloral. An equilibrium is indicated,[12] in which the hydrated form, III, is the principal species present



(6)

Since hydration is not possible in dry benzene, the principal species present is the enol, V, stabilized by hydrogen bonding either of the O–H–O or O–H–F type, or possibly both. Since hydration represses enolization and the hydrated form presents only one reducible carbonyl, the presence of two waves, one kinetic controlled and one diffusion controlled, in acidic and ammonia buffers must be due (1) to the reduction of the small amount of the keto–enol species of the $\gamma$-carbonyl that remains unhydrated and is produced during the life-time of the mercury drop (equation 6), and (2) to the reduction of the carbonyl group $\alpha$ to the thiophene ring. Since an acidic environment favors the keto modification and an alkaline medium the enolic, the small first wave in acidic media is due to repression of the enolic species as well as to hydration of the TTA. The shift to the enolic form in going from $p$H 1 to 8 accounts for the increase in the first wave. The latter at $p$H 8 also includes the reduction of the thenoyl carbonyl to the pinacol; the $i_d/C$ value of 4.2 for the second wave indicates a 1.9 or greater $i_d/C$ contribution from the acetone carbonyl.

---

[9] In the subsequent discussion, enol is used for either the enol or enolate forms; the $pK_a$ of TTA, which Cook and Taft[10] evaluate as 6.38, indicates the enolate ion to be the predominant species in alkaline solution.

(10) E. H. Cook and R. W. Taft, This Journal, **74**, 6103 (1952).

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

(12) H. M. Irving, *Quart. Revs.*, **5**, 200 (1951).

It is possible that the second wave observed for TTA also contains a contribution due to the reduction of the free radical produced from the one-electron reduction of the acetone carbonyl.

As the *p*H increases, *i* of the first wave passes through a maximum (Fig. 2), due in part to competition between the increases in enol formation and in alkaline cleavage of the hydrated TTA to acetylthiophene and trifluoroactate[10,13]

$$\mathrm{III} + \mathrm{OH}^- \longrightarrow \mathrm{I} + \mathrm{CF_3COO^-} + \mathrm{H_2O} \qquad (7)$$

In addition, the wave representing reduction of the thenoyl carbonyl to the free radical, which may dimerize to the pinacol, shifts toward and finally merges with the wave representing the further reduction of the free radical to carbinol. Thus, the first wave at *p*H 9 in ammonia buffer may represent reduction of the acetone carbonyl in the enol form, while the second wave represents reduction of the thenoyl carbonyl to the carbinol. In borate buffer, only the latter process is observed; the same process is observed but in the expected diminished magnitude in phosphate buffer of *p*H 12.

Relative values of *n* (calculated from the Ilkovic equation) are in general agreement with the mechanism described. The coulometric *n* value of 4 found in acetate buffer indicates that the polarographic waves reflect at least some reduction of the two carbonyl groups to the carbinol.

The variation suggested in the origin of the first wave from *p*H 5 (thenoyl carbonyl reduction) to *p*H 8 (reduction of both carbonyl groups) is supported by the temperature coefficient of the current, which is 7% at *p*H 5 and 4% at *p*H 8; the coefficients for the second wave are 1 to 2%.

**Alkaline Cleavage of TTA.**—In alkaline solution, the magnitude of *i* depends on the length of time the stock TTA solution has been mixed with the buffer. Such variation is not observed in acidic solution, while the aqueous stock solutions themselves were quite stable for several months. In ammonia buffer (*p*H 8.2) the first wave eventually disappears, while the second wave remains relatively unchanged (Table IV). The diminution of the first wave follows a zero-order rate given by the equation $k = x/t = 0.0063$ μa. min.$^{-1}$, until *i* has been reduced to 45% of its initial value.

The gradual disappearance of the first TTA wave in the ammonia buffer is due to cleavage of the compound. The alkaline environment shifts the equilibrium (equation 6) in the direction of the enolate. Since the hydrated TTA form is cleaved in the alkaline buffer,[10,11,13,14] the rate-controlling step is probably hydrolysis of the enolate to the hydrated form, which is then cleaved as fast as it is formed. The rate of cleavage is very much greater at *p*H 9 as compared to *p*H 8.[10] The alkaline cleavage is accelerated by light.

The second wave originally represents the reduction to the carbinol of the free radical reduction product of the TTA thenoyl carbonyl group. As TTA is cleaved, the acetylthiophene formed contributes to the second wave, slightly increasing its magnitude; acetylthiophene itself is apparently destroyed at a very much slower rate.

**Complexation of TTA with Borate.**—The absence of the first TTA wave in borate buffer is ascribed not only to hydrolysis of the TTA, but more largely to complexation of the borate with the ketone through the hydroxyl groups of the hydrated TTA.

TABLE IV

CLEAVAGE OF TTA IN AMMONIA BUFFER OF *p*H 8.2 AT 25°

| | Wave I[a] | | Wave II |
|---|---|---|---|
| Time, min. | *i*, μa. | $k = x/t$, μa. min.$^{-1}$ | *i*, μa. |
| 31 | 4.45 | 0.0064 | 3.35 |
| 81 | 4.16 | .0061 | 3.22 |
| 128 | 3.88 | .0060 | 3.30 |
| 249 | 3.15 | .0060 | 3.35 |
| 323 | 2.55 | .0065 | 3.51 |
| 588 | 1.98 | .0045 | 3.69 |
| 839 | 1.22 | .0041 | 3.64 |
| 1488 | 0.65 | .0027 | 3.72 |
| 1683 | 0.60 | .0024 | 3.53 |
| 1826 | 0.34 | .0024 | 3.25 |
| 2160 | No wave | | 3.01 |
| 2876 | No wave | | 2.75 |

[a] The value of *i* extrapolated to zero time is 4.65 for the first wave.

The presence of both TA waves in borate buffer tends to eliminate the possibility of boron complexing with the β-diketone grouping, since the waves would be expected to be suppressed if complexation occurred. This type of complexation also appears unlikely in TTA whose second wave appears to be normal. A complex that included the carbonyl of the thenoyl group should at least materially reduce the size of the second TTA wave as well as probably shift $E_{1/2}$ to a more negative potential; this does not occur.

Dropwise addition of hydrochloric acid to a borate solution (originally *p*H 9.2) of TTA causes the reappearance and growth of the first TTA wave. The $E_{1/2}$ values for both waves shift, as one might expect, with increasing acidity. This clearly indicates the complex formed to be reversible, even though quite stable as shown by the total absence of the first wave. It also indicates that alkaline fission is not the only cause of the disappearance of the first wave in alkaline borate solution.

The complexation is explicable on the basis of the species present in aqueous borate–TTA solution. Borax dissociates into boric acid and sodium metaborate; addition of sodium hydroxide converts the boric acid to sodium metaborate. Thus, the buffer effectively consists of boric acid, metaborate and tetraborate.[15] Boric acid has very feeble ability for complex formation with non-ionizable organic polyoxy compounds, while alkali borate shows strong complexing activity.[16] The order of activity is $H_3BO_3 << Na_2B_4O_7 < KBO_2$. Stable complexes are formed between borate and polyhydric alcohols. This property has long been used in boric acid titration. Reppere and La Mer[17] also found strong indication of complexation between borate or metaborate and polyhydroxy alcohols

---

(13) L. Wish and R. A. Bolomey, This Journal, **72**, 4486 (1950).

(14) R. G. Pearson and E. A. Mayerle, *ibid.*, **73**, 926 (1951).

(15) J. H. Hibben, *Am. J. Sci.*, **35A**, 113 (1938).

(16) Y. Tsuzuki, *Bull. Chem. Soc. Japan*, **13**, 337 (1938); **16**, 23 (1941); Y. Tsuzuki and Y. Kemura, *ibid.*, **15**, 27 (1940).

(17) R. E. Reppere and V. K. La Mer, *J. Phys. Chem.*, **47**, 204 (1943).

with at least two adjacent carbon atoms containing alcoholic groups; the formation of orthoboric or metaboric esters was excluded.

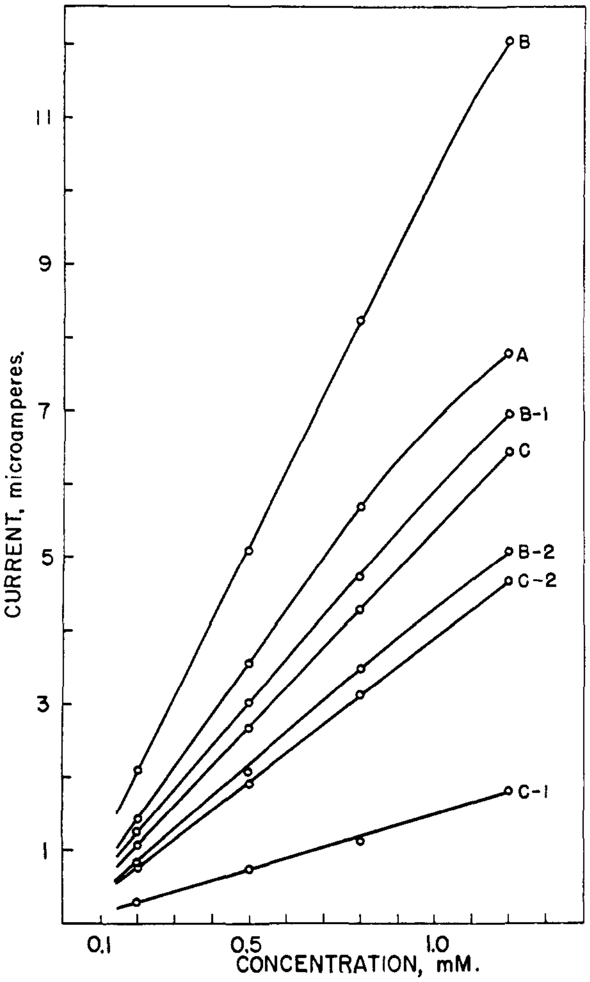
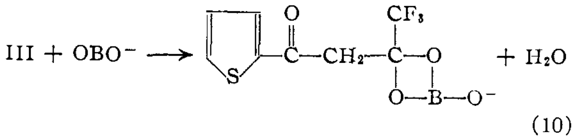


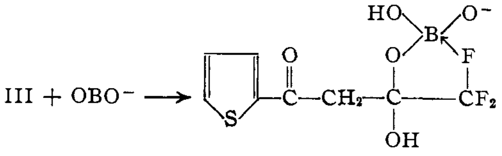
Fig. 3.—Variation of the current of thenoyltrifluoroacetone with concentration: A, wave in borax buffer, *p*H 9.2; B, combined waves in ammonia buffer, *p*H 8.2; B1, wave I in ammonia buffer, *p*H 8.2; B2, wave II in ammonia buffer, *p*H 8.2; C, combined waves in acetate buffer, *p*H 5.2; C1, wave I in acetate buffer, *p*H 5.2; C2, wave II in acetate buffer, *p*H 5.2.

Since Raman spectra[18] indicate that the metaborate ion is linear or slightly bent,[15] it is possible that, on mixing, the metaborate present in the alkaline borate buffer immediately forms a stable complex with the hydrated TTA (eq. 10).



(10)

The question of the stability of a four-membered ring naturally arises. Since the ring is quite heterocyclic, its formation is not improbable but may be unusual. Another possible boron complex would involve an hydroxyl group and an adjacent fluorine atom



(11)

The remaining hydroxyl group could then be similarly complexed.

**Polarographic Determination of TTA.**—From the data for TTA in the concentration range of 0.2 to 1.2 millimolar in the various buffers in 1% ethanol (Table II), it is possible to evaluate the accuracy of the polarographic method for the determination of TTA.

Values of $i/C$ for the two waves increase with increasing *p*H, passing through maxima in the alkaline region (Fig. 2). Values of $i$ *vs.* concentration for the sum of the two waves as well as for the individual waves in different buffers are plotted in Fig. 3. In borate buffer a slight deviation of $i$ *vs.* $C$ from linearity is noticeable at high concentration. Generally, the relations in ammonia and acetate buffers are linear up to 1.2 m$M$, the largest concentration measured; use of the sum of the two waves gives the best result.

For the quantitative determination of TTA, either acetate or ammonia buffer is satisfactory; the latter produces the larger $i$ and hence may minimize the relative error. The chief disadvantage of ammonia buffer is the cleavage of TTA in alkaline media; this can be minimized by not mixing the TTA sample with the buffer until immediately before electrolysis, and by making the buffer as nearly neutral as is consistent with good buffering practice, *i.e.*, *p*H 8.2. Although $i$ values in acetate buffer are small, they are easily reproducible, using ordinary techniques, to 2 or 3% of the mean value.

The feasibility of determining TTA in the presence of the related ketones can be evaluated by comparing the data in Tables I to III.

**Acknowledgment.**—The authors wish to thank the Atomic Energy Commission and the Office of Naval Research which supported the research project upon which this work was done, and Miss Philomena Grodzka for help with several supplementary experiments.

STATE COLLEGE, PENNSYLVANIA
ANN ARBOR, MICHIGAN

[18] J. R. Nielson and N. E. Ward, *J. Chem. Phys.*, **5**, 201 (1937).