both these groups are present in the molecule of vinyl phenylacetate, the high reactivity of its hydrogen might be justified.

Closer inspection of Fig. 3 indicates some curvature for higher values of X_A/X_{HS}. The reason for this curvature is not quite clear. It might be due to the change in the character of the decomposition as a result of the change of the environment (from non-polar to polar solvent), or it might be due to the accumulation of $CH_2{:}CH{\cdot}O{\cdot}CO{\cdot}\dot{C}H{\cdot}Ph$ radicals, recombination of which might be hindered by steric reasons, thus causing a partial recombination with methyl radicals. This complication throws some doubt on the derived values of k_2/k_1 and k_5/k_1 of vinyl phenyl acetate, which should be taken therefore with some reservation.

General Conclusions.—All the examples quoted above show that the mechanism proposed by Levy and Szwarc[2] can be modified to enclose the cases in which either the solvent or the compound A act in a dual fashion: as a hydrogen atom donor and as a methyl radical acceptor. The agreement between theory and experiment can be considered as an additional argument favoring Levy and Szwarc's mechanism. Moreover, it is now obvious that whenever k_2/k_1 remains constant and independent of the X_A/X_{HS} ratio, the abstraction of a hydrogen atom from the molecule A is negligible as compared with methyl radical addition to this molecule.

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SYRACUSE, NEW YORK

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

A Study of Thiourea and Substituted Thiourea Analogs by the Bjerrum Titration Method

BY J. L. WALTER, C.S.C., J. A. RYAN AND T. J. LANE, C.S.C.

RECEIVED JUNE 28, 1956

The relative basicity of a number of substituted thiourea compounds has been described. Also the determination of the relative stabilities of some of their metal complexes has been attempted by the Calvin–Bjerrum potentiometric procedure.

Since thiourea and several of its analogs have been used successfully as analytical reagents,[1,2] it was thought desirable to study the acid dissociation constants of the reagents and the stability constants of several of their metal complexes, using the Calvin–Bjerrum potentiometric titration procedure. The relatively low basicity of these compounds and their susceptibility to oxidation in the presence of traces of oxidizing agents proved to be quite interesting.

Experimental

Materials.—Stock solutions of approximately 0.01 *M* metal ions were prepared by dissolving their reagent grade perchlorates in water. The copper(II) and cobalt(II) solutions were standardized by electrodeposition. The nickel(II) solution was standardized by precipitation with dimethylglyoxime.

The standardization procedure for sodium hydroxide and perchloric acid, and the purification of dioxane have been described by Freiser, Charles and Johnston.[3] To ensure against any oxidizing impurities in the dioxane, it was kept over sodium at all times and distilled as needed.

The urea, thiourea, allylthiourea, phenylthiourea and 1,3-diethylthiourea were products of Eastman Kodak. The other compounds listed in Table I were purchased from K and K. Laboratories, Long Island, N. Y. All compounds were recrystallized from suitable ethanol or ethanol–water solutions until melting point determinations established purity.

Apparatus and Procedure.—The titration apparatus and procedure is essentially the same as that described by Freiser, Charles and Johnston.[3]

Fifty-five milliliters of dioxane, 50 ml. of 0.01 *N* perchloric acid and 5 ml. of 0.01 *M* metal perchlorate solution were added to a weighed quantity of the compound studied. In all titrations the amount of reagent used was approximately 0.4 mmole in order that the acid concentration might be sufficient to ensure complete protonation of the reagent present. The low solubility of several of the substituted thiourea compounds necessitated the use of a 50% by volume dioxane–water solvent.

The standard base (0.1 *N* NaOH) was added in small increments to the stirred solution. For the titration of the reagent alone, 5 ml. of water was substituted for the metal perchlorate solution.

All potentiometric measurements of *p*H were made using the Beckman Model G *p*H meter equipped with a glass-saturated calomel electrode pair.

The pK_a values were calculated from the known concentrations of the reagent and of the hydrogen ion at the stoichiometric midpoint of the titration. The acid dissociation constants of reagents of the type used in this work may be defined in terms of the equation

$$RH^+ \rightleftarrows R + H^+$$

It follows that

$$K_a = (H^+)(R)/(RH^+)$$

where K_a is the acid dissociation constant of the protonated reagent RH^+, and R refers to the simple reagent. In the case of reagents which have a weakly basic nitrogen the terms R and RH^+ were evaluated from the equations[4]

$$R = \frac{1/2 \text{ total moles reagent}}{\text{volume (liters)}} + H^+$$

$$RH^+ = \frac{1/2 \text{ total moles reagent}}{\text{volume (liters)}} - H^+$$

These equations were employed in all of the dissociation constant calculations.

Discussion

Acid Dissociation Constants.—Thiourea and its substituted analogs are neutral in reaction, but react toward acids as monoacidic bases. There has been a suggestion that the normal state of the

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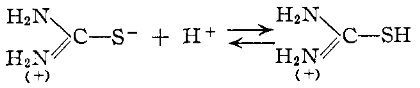
(1) F. J. Welcher, "Organic Analytical Reagents," Vol. IV, D. Van Nostrand, New York, N. Y., 1948.

(2) J. H. Yoe and L. A. Sarver, "Organic Analytical Reagents," John Wiley and Sons, Inc., New York, N. Y., 1941.

(3) H. Freiser, R. G. Charles and W. D. Johnston, THIS JOURNAL, **74**, 1383 (1952).

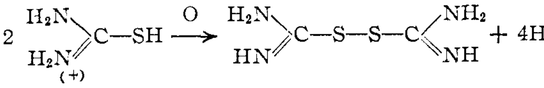
(4) W. D. Johnston, Ph.D. Thesis, University of Pittsburgh, 1952

thiourea is that of the zwitterion I.[5] This deduction is supported by the action of oxidizing agents on thiourea. In the presence of a mineral acid nearly every oxidizing agent gives a salt of formamidine disulfide (III), a typical product of the oxidation of a compound containing the thiol group. This again suggests that thiourea in the presence of acids is the cation II derived from the zwitterion I.



$$(H_2N)(\underset{(+)}{H_2N}){>}C{-}S^- + H^+ \rightleftarrows (H_2N)(\underset{(+)}{H_2N}){>}C{-}SH \qquad (1)$$

I II



$$2\,(H_2N)(\underset{(+)}{H_2N}){>}C{-}SH \xrightarrow{O} (H_2N)(HN{=}){>}C{-}S{-}S{-}C{<}(NH_2)({=}NH) + 4H^+ \qquad (2)$$

III

Another support for the existence of reaction (2) was observed in some of the preliminary titrations. These titrations were made in 50% dioxane–water solvent using dioxane which had been stored for several days after purification. From these titrations there were obtained acid dissociation constants which were considerably larger than those obtained from titrations utilizing freshly distilled dioxane, and also in these former titrations, equilibrium was not attained at the expected end point.

Complete neutralization of all acid present in the system, whether present as the free acid or as the protonated form of the reagent, occurs at about a volume of 5.3 ml. of base. Figure 1 (curve A) shows that as the pH begins to rise at that point, a further liberation of hydrogen ion occurs. This would seem to indicate the production of protons from a reaction such as (2) since a titration of the stored dioxane (without thiourea) indicated no presence of an acid constituent (Fig. 1, curve B). The most predominant oxidizing agent present in the impure dioxane was probably a peroxide. All K values presented here were obtained from titrations utilizing freshly purified dioxane.

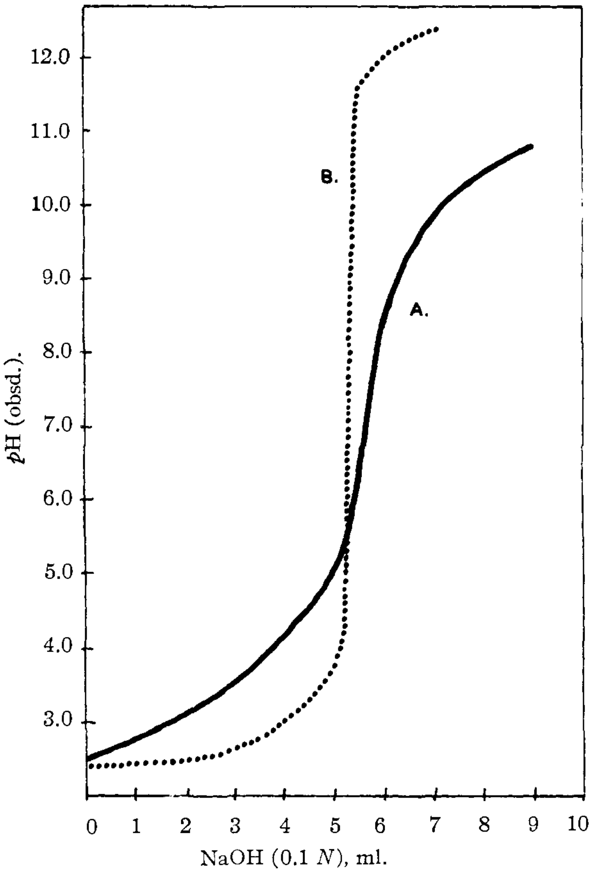
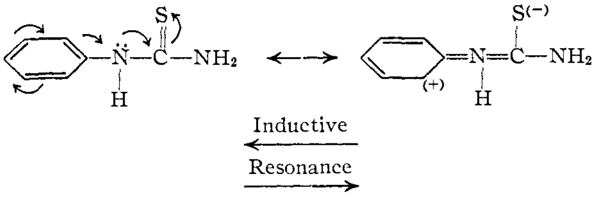


Fig. 1.—Titration of: (A) phenylthiourea in the presence of 50 ml. of 0.01 N perchloric acid + 50 ml. of dioxane (stored for several days); (B) of 50 ml. of 0.01 N perchloric acid + 50 ml. of dioxane (stored for several days.)

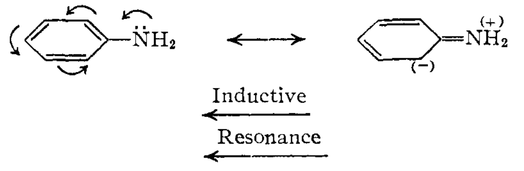
The pK_a values obtained are given in Table I. As was expected, thiourea (pK = 2.03) was found to be more basic than the corresponding urea (pK = 1.40), however the lack of a greater separability between pK values for the substituted thiourea compounds was not expected.

Considering the inductive and hyperconjugative effects exhibited by the alkyl substituent on thiourea, it can be predicted that the order of increasing basicity should be H < allyl < ethyl < methyl < diethyl. The results given in Table I show this to be the case.

From the prevailing −I, +E effects of the aromatic substituents on thiourea it might be expected that the aromatic substituted thiourea compounds would be slightly less basic than the alkyl substituted compounds which exhibit only a +I effect. When these two effects are present in an aromatic compound, it has been found that about half the decrease or increase in basic strength is due to an inductive effect and the other half is due to a resonance effect.[6] When the effects are opposed, as in the case here, not much change in basic strength is noted, (phenylthiourea pK = 2.8, methylthiourea pK = 2.9) IV, but if they operate in the same direction, as in aniline, there is a marked effect of the basic strength, (aniline pK = 4.58, methylamine pK = 10.6) V.



IV



V

The order of increasing basicity found in the group of aromatic substituted thiourea compounds

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(5) N. V. Sidgwick, "Organic Chemistry of Nitrogen," Oxford, 1936, pp. 290–1.

(6) Braude and Nachod, "Determination of Organic Structures by Physical Methods," Chap. 14, Academic Press, New York, N. Y., 1955.

TABLE I

ACID DISSOCIATION CONSTANTS OF THIOUREA ANALOGS IN 50% BY VOLUME DIOXANE AT 25°

	pK_a		pK_a
1 Thiourea	2.03	7 *o*-Tolylthiourea	2.78
2 Urea	1.40	8 *m*-Tolylthiourea	2.70
3 Allylthiourea	2.48	9 *p*-Tolylthiourea	2.72
4 Ethylthiourea	2.85	10 Ethylenethiourea	2.70
5 Methylthiourea	2.90	11 *sym*-Diethylthiourea	2.91
6 Phenylthiourea	2.80	12 *sym*-Diphenylthiourea	2.91

studied was (Table I): *m*-tolyl $\leqslant$ *p*-tolyl $<$ *o*-tolyl $<$ phenyl $<$ diphenyl. This order is approximately satisfactory with the exception of phenyl. It would be expected that the *ortho*- and *para*-tolyl groups would contribute more to the basicity of thiourea than a phenyl group.

Stability Constants.—Values of n, the average number of reagent molecules bound to the metal, equalled four at the start of the titration in the case of each of the compounds studied with the metals copper(I), cobalt(II) and nickel(II). This indicated that at even the lowest pH limit, complete complexing had occurred. This was not too surprising, however, since a comparison of the acid dissociation constants of the various ligands indicated that with this lack of ligand basicity, the competition between the metal and proton for the ligand was not very keen, so that the metal would tend to add to the ligand immediately upon combination. Acid dissociation constants should be at least 3.5–4.0 to enable the successful determination of stepwise formation constants.

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[CONTRIBUTION FROM THE DEPARTMENT OF MINING AND METALLURGY, UNIVERSITY OF BRITISH COLUMBIA]

Kinetics of the Reaction between Formic Acid and Thallium(III) in Aqueous Solution

BY H. N. HALVORSON AND J. HALPERN[1]

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Formic acid and thallic perchlorate were found to react in aqueous perchloric acid solution as follows: $Tl^{+++} + HCOOH \rightarrow Tl^{+} + 2H^{+} + CO_2$. The kinetics of this reaction were investigated between 65 and 85° and shown to be consistent with a mechanism involving the following sequence of steps (1) $Tl^{+++} + HCOOH \overset{K}{\rightleftarrows} Tl{\cdot}HCOOH^{+++}$; (2) $Tl{\cdot}HCOOH^{+++} \xrightarrow{k} Tl^{+} + 2H^{+} + CO_2$. The first step is a rapid equilibrium while the second step is rate determining. The equilibrium constant (K) and the unimolecular rate constant (k) were found to have the following values: $K = 16.2$ liter mole^{-1} and $k = 1.0 \times 10^{13} \exp[-26600/RT]$ sec.$^{-1}$. The inhibiting effects of Cl^{-} and $SO_4^{=}$ were attributed to the fact that these ions compete with HCOOH to form complexes with Tl^{+++}. Spectrophotometric measurements were also made which provide evidence for the existence of the $Tl{\cdot}HCOOH^{+++}$ complex and quantitative support for the proposed mechanism.

Introduction

Following recent studies in this Laboratory[2] on the homogeneous reactions between molecular hydrogen and metal ions such as Cu^{++}, Ag^{+}, Hg^{++}, Hg_2^{++} and MnO_4^{-}, in aqueous solution, it seemed of interest to examine also some analogous reactions involving other molecular reducing agents whose oxidation, like that of hydrogen, involves the disruption of covalent bonds. Formic acid is one of the simplest examples of such a reducing agent and was therefore selected for study initially. Previous investigations have been reported on the reactions of formic acid with a number of oxidants in aqueous solution including the metal ions Co^{+++},[3] Hg^{++} and Hg_2^{++}.[4] In the present paper, a kinetic study of the reaction between formic acid and thallic perchlorate, in aqueous perchloric acid solution, is described.

Experimental

Reagents.—A stock solution of thallic perchlorate was prepared as follows. A solution of Analar grade thallous sulfate in aqueous perchloric acid was oxidized with sodium bromate and the resulting thallium(III) was precipitated as thallic oxide with ammonia. The precipitate was washed thoroughly, then redissolved in perchloric acid and reprecipitated with ammonia (this procedure was repeated three times to ensure removal of foreign anions). The final stock solution of thallic perchlorate, obtained by dissolving the purified oxide in perchloric acid solution, contained 0.3 M Tl^{+++}, 0.006 M Tl^{+} and 9 M $HClO_4$ and did not change over a period of four months. A second batch of thallic perchlorate solution, prepared by the same procedure, gave identical results.

Analar grade formic acid was used. Attempts to purify it further by redistillation did not alter the results. With the exception of the various perchlorate salts, which were obtained from G. F. Smith Chemical Co., all other chemicals were Baker and Adamson reagent grade products. Distilled water was used in the preparation of all solutions.

Analytical Procedures.—The Tl^{+} content of the solution was determined, following addition of HCl, by titration with standard (0.01 N) $KBrO_3$ using Brilliant Ponceau 5R (G. F. Smith Chemical Co. product) as indicator. It was established that the results were unaffected by the presence of HCOOH and of Tl^{+++}. To determine the total thallium content of the solution the Tl^{+++} was first reduced with SO_2. The excess SO_2 was then removed by boiling and the solution titrated with $KBrO_3$ as described above.

Kinetic Measurements.—The experiments were conducted in stoppered flasks immersed in a thermostated (±0.05°) water-bath. Most of the measurements were made at 74.0°. The reacting solution was prepared by mixing, in suitable proportions, standardized stock solutions (pre-heated to the reaction temperature) of the various separate components, *i.e.*, Tl^{+++}, HCOOH and $HClO_4$. To follow the reaction, samples of the solution were withdrawn

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[1] Department of Chemistry, University of British Columbia.

[2] E. Peters and J. Halpern, *J. Phys. Chem.*, **59**, 793 (1955); A. H. Webster and J. Halpern, *ibid.*, **60**, 280 (1956); G. J. Korinek and J. Halpern, *ibid.*, **60**, 285 (1956); J. Halpern, *Quart. Revs.* (*London*), in press.

[3] C. E. H. Bawn and A. G. White, *J. Chem. Soc.*, 339 (1951).

[4] A. R. Topham and A. G. White, *ibid.*, 105 (1952).