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The SN1 Hydrolysis of Isothioureas. 1

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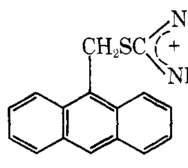
The hydrolysis of certain arylmethylisothioureas in water was studied. Evidence is presented which indicates that 9-anthrylmethylisothiourea (**1**), 10-methyl-9-anthrylmethylisothiourea (**2**), and 7(10)-benzanthrylmethylisothiourea (**3**) hydrolyze under acidic conditions by an SN1 mechanism. Support for this mechanism arises from a significant thiourea ("common ion") effect and from differences in the reactivity of **1–3**, which can only be rationalized on the basis of a carbonium ion mediated mechanism.

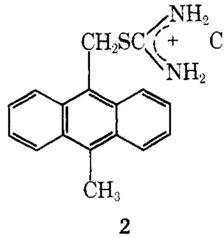
Recently there has been much interest in investigating the mechanistic details of hydrolysis reactions in pure water.[1] The development of sensitive conductance methods has allowed the accurate determination of hydrolysis rates for organic halides and sulfonates in water, which otherwise would have been difficult to study by conventional titrimetric methods. Most hydrolytic investigations have been conducted in mixed solvent systems, which avoided the analytical difficulties associated with the low aqueous solubilities of organic nonelectrolytes and moderated the high reactivity of many organic halides. Despite the development of more sensitive analytical techniques, low solubility remains as a major barrier to the systematic study of the hydrolysis of many compounds in water. Thus, correlations of reactivity with structure have been conducted in partially aqueous solvent systems, and comparison of results from different investigators is difficult because of the wide variety of solvent systems employed.

This report describes our investigations into the hydrolysis of certain arylmethylisothioureas in water. The isothiouronium moiety represents a new type of leaving group for an SN1 reaction. The proposed SN1 mechanism for these isothioureas is shown in Scheme I.

The compounds studied as their hydrochloride salts are 9-anthrylmethylisothiourea (**1**), 10-methyl-9-anthrylmethylisothiourea (**2**), and 7(10)-benzanthrylmethylisothiourea (**3**). These isothioureas are moderately soluble in water at a pH below their pK_a where they exist in the cationic isothiouronium form. Isothioureas normally decompose to thiols in alkaline media,[2] but no information is available on their stability in acidic media.



1



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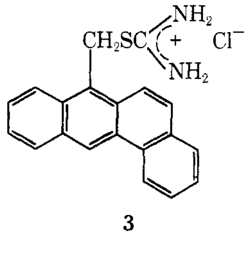
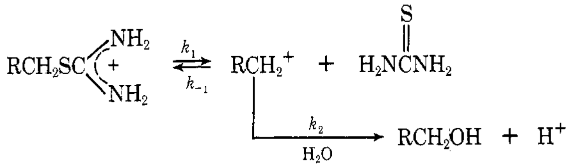


3

Scheme I



Experimental Section

9-Anthrylmethylisothiourea Hydrochloride (1). 9-Anthraldehyde was synthesized by the Vilsmeier method.[3] Reduction of 9-anthraldehyde with sodium borohydride in refluxing methanol gave 9-hydroxymethylanthracene.[4] The 9-hydroxymethylanthracene was dissolved in benzene and chlorinated by passing hydrogen chloride gas into the solution. The 9-chloromethylanthracene was not isolated because direct addition of excess thiourea in ethanol to this solution with refluxing gave **1** as a yellow precipitate. The isolated solid **1** was mixed with a small amount of water and ultrasonified to dissolve any excess thiourea which may have contaminated the product. The slurry was filtered and, after drying, **1** melted with decomposition at 213–215 °C. Anal. Calcd for $C_{16}H_{17}ClN_2OS$ (monohydrate): C, 59.9; H, 5.34; H_2O, 5.61. Found: C, 60.13; H, 5.25; H_2O, 5.20.

10-Methyl-9-anthrylmethylisothiourea Hydrochloride (2). 10-Methyl-9-chloromethylanthracene was synthesized by chloromethylation of 9-methylanthracene.[5] The resulting chloromethyl compound, after recrystallization, was refluxed with a slight excess of thiourea in benzene. A yellow precipitate of **2** formed, which was isolated and washed with water in a manner similar to **1**. After drying, **2** melted with decomposition at 208–210 °C. Anal. Calcd for $C_{17}H_{17}ClN_2S$: C, 64.44; H, 5.41. Found: C, 64.31; H, 5.50.

7(10)-Benzanthrylmethylisothiourea Hydrochloride (3). The procedure of Wood and Fieser[6] was followed in synthesizing **3**. Chloromethylation of benzanthracene produced 7(10)-chloromethylbenzanthracene,[7] which was reacted with thiourea to give **3**, which melted with decomposition at 212–215 °C (reported 213–214 °C).

Other Isothioureas. Benzylisothiourea hydrochloride (**4**) was available commercially and was used as received. 1-Naphthylmethylisothiourea hydrochloride (**5**) was synthesized by reacting 1-chloromethylnaphthalene with thiourea.[8] 9-Phenanthrylmethylisothiourea hydrochloride (**6**) was obtained similarly by reacting 9-chloromethylphenanthrene with thiourea.

Kinetic Methods. Two methods were used to follow the hydrolysis of isothioureas. One method depended on hydrogen ion production, while the other depended on a change in the uv-visible absorption spectrum as hydrolysis proceeded.

The production of hydrogen ion was followed with a pH stat by recording the volume of 0.01 M potassium hydroxide required to maintain the reaction solution at pH 5. The reaction solution temperature was maintained by circulating oil from a constant temperature bath through a stoppered jacketed beaker. The stopper contained holes for the pH-electrode, buret tip, and thermometer, but otherwise was tight fitting to minimize evaporation at the high temperature (50–80 °C) of most of the kinetic studies. First-order rate constants were obtained from semilogarithmic plots of the titrant volumes ($V_\infty - V_t$) by graphical estimation and least-square computer fits.

Rates of hydrolysis were determined spectrophotometrically using the absorbance measured at the spectral peaks of the arylmethylisothioureas between 350 and 405 nm. These studies were conducted by extracting the hydrolysis end products (arylmethyl alcohols) with ethyl ether from reaction solution samples, leaving the intact cationic isothioureas in the aqueous phase. From semilogarithmic plots of the remaining absorbance at one of the spectral maxima, as a function of time, were obtained first-order rate constants. This method was generally preferred over the pH-stat method at low temperatures because the lower reaction rates required sampling over long periods of time to accurately establish the rate.

Reaction solutions usually contained 0.001 M KCl, but for others, dilute acetate or succinate buffers were used. The aqueous medium did not affect the kinetics, unless the pH was outside of the range from 2 to 7 or high buffer or salt concentrations were used. The apparent solubility of these isothioureas became a problem in the presence of inorganic salt concentrations greater than 0.05 M. Apparently, these isothioureas form insoluble salts upon the addition of organic or inorganic salts at concentrations greater than 0.05 M, whereas the free base precipitated out of solution above pH 7.

Thiourea Effect. Evidence for a carbonium ion intermediate can be obtained by observing a common-ion effect.[9] For the hydrolysis of isothioureas, thiourea can be considered to be the "common ion". Reagent grade thiourea was initially added to reaction solutions, and the hydrolysis reaction followed by the uv or pH-stat method. For the general SN1 mechanism in Scheme I the rate expression is

$$\frac{d[\mathrm{RX}]}{dt} = \frac{k_1k_2[\mathrm{RX}][\mathrm{H_2O}]}{k_2[\mathrm{H_2O}] + k_{-1}[\mathrm{X}]} = \frac{k_1[\mathrm{RX}]}{1 + \alpha[\mathrm{X}]} = k_{\mathrm{obsd}}[\mathrm{RX}]$$

where RX = isothiourea, X = thiourea, $\alpha = k_{-1}/k_2[\mathrm{H_2O}]$, k_{obsd} = observed rate constant, k_1 = initial rate constant at [X] = 0. Solving for α, which is a measure of the magnitude of the common-ion effect, gives

$$\alpha = \frac{1}{[\mathrm{X}]}\left[\frac{k_1}{k_{\mathrm{obsd}}} - 1\right] = \frac{k_1 - k_{\mathrm{obsd}}}{k_{\mathrm{obsd}}[\mathrm{X}]}$$

Generally the more stable the intermediate carbonium ion in question, the larger α is.

Results and Discussion

9-Anthrylmethylisothiourea Hydrochloride (1). Initial kinetic studies with 1 were conducted by the uv–visible spectral method with dilute (0.01–0.02 M) acetate or succinate buffers. Such dilute buffer concentrations were required because of the solubility problem mentioned previously. Initial studies were also made by the pH-stat method, which required no buffer. It was apparent that the hydrolysis rate was independent of pH or buffer type under acidic conditions. Therefore, further kinetic studies by the uv–visible spectral method were made in the absence of buffer with the solution being initially adjusted to pH 5 with dilute HCl so that the results could be directly compared to studies made by the pH-stat method. The rate constants for hydrolysis at various temperatures and the activation parameters are summarized in Table I.

Table I. Hydrolysis Rate Constants for Arylmethylisothiourea Hydrochlorides (1, 2, 3)

	$10^4 k$, s^{-1}		
Temp, °C	9-Anthryl (1)	10-Methyl-9-anthryl (2)	7(10)-Benzanthryl (3)
81			3.50
77	23.00		2.10
72			1.30
67	7.00		0.74
62			0.34
57	1.70	51.10	0.18
52		26.50	
47	0.43	13.50	
37	0.10	4.50	
27	0.03	1.10	
17		0.24	
E_a, kcal/mol	28.2	25.4	28.6
S_a, cal/mol K	+7.8	+5.8	+4.3

The addition of thiourea to reaction solutions of 1 produced dramatic reductions in the observed rate of hydrolysis. The observed rate constants are summarized in Table II for three temperatures. In addition to the observed rate reductions, it is apparent that the magnitude of the retardation is greater at lower temperatures for a particular thiourea concentration. The first measurement of α for an SN1 halide hydrolysis was conducted on benzhydryl halides,[10] for which values of 10–10^2 were obtained. For 1, α ranges from 200 to 500 (Table II), which is the same order of magnitude as α for the SN1 hydrolysis of triphenylmethyl chloride.[11] Such large values of α for 1 lend strong support to the proposed SN1 mechanism.

Support for the proposed carbonium ion mediated hydrolysis of 1 also is obtained from the fact that the 9-anthrylmethyl carbonium ion produced by dissociation of the thiouronium moiety has been shown to be quite stable by both hydrolysis studies on arylmethyl chlorides[12] and by theoretical molecular orbital calculations.[13] The high stability of the 9-anthrylmethyl carbonium ion arises from its ability to effectively delocalize its positive charge away from the methylene carbon from which the leaving group has departed.

10-Methyl-9-anthrylmethylisothiourea Hydrochloride (2). Hydrolysis of 2 proceeds to 10-methyl-9-hydroxymethylanthracene which is similar to 9-hydroxymethylanthracene obtained from the hydrolysis of 1. A significant increase in hydrolysis rate (15–20-fold) was observed for 2 compared to that for 1 (Table I).

An unusual feature of the semilogarithmic hydrolysis plots of 2 was significant curvature after initial linear portions. This behavior has been observed for the hydrolysis of 9-anthrylmethyl halides[14,15] and can be attributed to a mass-law effect. This nonlinear behavior has only been seen previously for highly reactive 9-anthrylmethyl halides because of the high stability of their carbonium ion. Such an effect for 2, in our work, is essentially the observation of a thiourea ("common ion") effect at a very low thiourea concentration. Thus the observed curvature as hydrolysis progresses is due to an increasing thiourea concentration producing an increasing retardation in rate.

Addition of thiourea to reaction solutions of 2 produced larger reductions in the observed hydrolysis rate constants than were observed for 1. These rate constants are summarized in Table II. In a typical hydrolysis study, the initial concentration of 2 was 6×10^{-4} M, which would produce 6×10^{-4} M thiourea upon complete hydrolysis. Since 1×10^{-3} M thiourea produces an initial rate reduction of one-half, it is apparent that even the thiourea produced after partial hydrolysis can cause an appreciable reduction in the observed hydrolysis rate.

The high reactivity of 2 is easily rationalized by the proposed SN1 mechanism and cannot be accounted for by an SN2 mechanism. The accelerative effect of a *p*-methyl group on a typical SN2 reaction can only be expected to be a factor of 2 or 3.[16] For an SN1 reaction, on the other hand, the accelerative effect of a *p*-methyl group is usually an order of magnitude or higher. This acceleration results from the greater

Table II. Thiourea Effect on Arylmethylisothiourea Hydrochlorides at Various Temperatures (1, 2)[a]

Thiourea concn, M	$10^4 k_{obsd}$, s^{-1}			
	9-Anthryl (1)			10-Methyl-9-anthryl (2), 52 °C
	57 °C	66 °C	77 °C	
0	1.700	5.70	23.0	26.5
0.001				12.9 (1050)
0.005				3.5 (1320)
0.010	0.280 (500)	1.40 (350)	6.7 (250)	1.4 (1800)
0.100	0.033 (480)	0.18 (310)	1.1 (220)	0.2 (1210)

[a] The numbers in parentheses are α values ($k_{-1}/k_2[H_2O]$).

Table III. Molecular Orbital Calculations on Arylmethyl Carbonium Ions

Ar in $ArCH_2^+$	Reactivity $10^4 k$, s^{-1}, at 62 °C	Charge on $-CH_2^+$	
		CNDO	Huckel ($\omega = 1.1$)
Phenyl		+0.410	+0.411
1-Naphthyl		+0.310	+0.309
9-Phenanthryl		+0.292	+0.295
9-Anthryl	3.61		+0.191
7(10)-Benzanthryl	0.336		+0.201
10-Methyl-9-anthryl	77.8		+0.175

electronic sensitivity of an S_N1 reaction, mediated by a positively charged carbonium ion that is resonantly stabilized by an aromatic nucleus. The *p*-methyl group has the ability to increase the resonance stability of the carbonium ion through hyperconjugation.[17]

This type of interaction has been accounted for by the use of the Hammett σ^+ substituent constants, proposed for reactions in which a developing positive charge interacts with a π electron or aromatic system.[18] For a pure S_N1 reaction a ρ of at least -4 is required and the σ^+ value for a *p*-methyl group is -0.31. Combining these values gives

$$\log\left(\frac{k_{p\text{-}CH_3}}{k_{mono}}\right) = \rho\sigma+ = (-4)\,(-0.31) = 1.24$$

$$\frac{k_{p\text{-}CH_3}}{k_{mono}} = 10^{1.24} = 17.4$$

This ratio is in agreement with the observed factor of 15–20 obtained for the increase in hydrolysis rate of 2 over 1.

The thiourea effect for 2, as mentioned previously, is two to three times higher than for 1. Values for α, shown in Table II, range from 1000 to 1800 which indicate an even higher carbonium ion stability than the 9-anthrylmethyl carbonium ion. These α values approach the highest observed for an S_N1 reaction, which are in the range of 1000–4000 for 4,4′-disubstituted diphenylmethyl chlorides.[19] This information supports the concept that structural changes which enhance the stability of a carbonium ion also increase α and thus α appears to be a reflection of the stability of the intermediate carbonium ions.

From an alternate point of view, α can be considered to be a measure of the discrimination of the carbonium ion for nucleophiles. Thus α, which is a ratio of k_{-1} to k_2 [H_2O], is a measure of the ability of the 9-anthrylmethyl carbonium ion to discriminate between thiourea and water as nucleophiles. To correct for the concentration of water, α should be multiplied by 55.5, which then would make α the ratio of two true second-order rate constants. With this correction, the magnitude of α becomes 10^4–10^5. This value reflects the ratio of the nucleophilicities of thiourea and water for the 9-anthrylmethyl carbonium ion, which is approximately the same magnitude as the ratio of their nucleophilicities in a standard S_N2 reaction.[20] This suggests that the 9-anthrylmethyl carbonium ion is stable enough so that α becomes a measure of the intrinsic nucleophilicities of thiourea and water.

7(10)-Benzanthrylmethylisothiourea Hydrochloride (3). The hydrolysis rate of 3 was determined by the pH-stat method and the rate constants and activation parameters are summarized in Table I. Essentially the same activation energy is obtained for 3 as 1 with its lower reactivity arising from a less positive activation entropy.

The lower reactivity of 3 compared to 1 and 2 is in agreement with the poorer ability of the benzanthryl aromatic system to delocalize a charge away from the exocyclic methylene carbon of the carbonium ion. The rate of S_N1 hydrolysis of arylmethyl halides has been shown to be dependent upon their ability to delocalize the positive charge away from the exocyclic atom from which the leaving group has departed.[21] Hydrolysis rates for limiting S_N1 hydrolyses can then be compared to parameters calculated from molecular orbital theory. Recent work[22] has shown a linear correlation between σ^+ substituent constants and the charge on the exocyclic $-CH_2$ group of polycyclic arylmethyl carbonium ions. Such correlations indicate that a lower charge on this $-CH_2$ group corresponds to a higher S_N1 reactivity because of greater charge delocalization through the π-electron system.

Molecular orbital calculations on the carbonium ions produced by the polycyclic arylmethylisothioureas investigated in this study show the same correlations. Omega–Huckel[23,24] and CNDO/2[25] calculations were used to calculate the charges on the arylmethyl carbonium ions and each gave comparable results for the smaller aromatic systems. The Omega–Huckel method was used exclusively for the larger carbonium ions because of the limited size of the CNDO/2 computer program.[26] For the 10-methyl-9-anthrylmethyl carbonium ion, a heteroatom model[27] was used which accounted for the stabilizing effect of the *p*-methyl group. The charges for representative aromatic systems obtained from these calculations are shown in Table III along with the hydrolysis rate constants at 62 °C. The lower reactivity of 3 compared to 1 as mentioned above is in keeping with the higher charge on the exocyclic $-CH_2$ group of the intermediate carbonium ion. The higher reactivity of 2 also correlates with its lower localized charge.

The other arylmethyl systems shown in Table III were investigated as their respective isothioureas. The benzyl-, 1-naphthylmethyl-, and 9-phenanthrylmethylisothioureas were subjected to hydrolytic conditions but none showed hydrolysis characteristic of 1–3. Referring to the charges in Table III calculated for these hypothetical carbonium ions, it is evident that a significantly higher positive charge is localized on their exocyclic methylene groups as compared to 1–3. Thus the nonreactivity of these three compounds can be ascribed to the lower stability of the carbonium ion produced and the higher energy requirement to remove the thiourea moiety from the higher localized charge. Using as a comparison the hydrolysis rates of the corresponding arylmethyl halides indicates that

9-anthrylmethyl chloride hydrolyzes 10^3–10^5 times faster than 9-phenanthrylmethyl chloride.[28] If this large reactivity difference can be applied to the relative reactivity for isothiourea hydrolysis, a rate of hydrolysis is predicted that would be practically undetectable for 9-phenanthrylmethylisothiourea under our experimental conditions.

Such large differences in reactivity for arylmethylisothioureas indicates that nucleophilic assistance does not make a significant contribution to this type of hydrolysis. If water was acting as a direct nucleophile in displacing the isothiourea moiety, there should not be such large differences in reactivity among different arylmethyl systems. The polycyclic aromatic ring should not alter greatly the ability to undergo an SN2 hydrolysis since the exocyclic methylene group electronically and sterically is only slightly altered with different aromatic rings. As an example, in the SN2 reaction in which chloride is displaced by iodide in anhydrous acetone, the difference in reactivity between 9-phenanthrylmethyl chloride and 9-anthrylmethyl chloride is only a factor of 10.[29] Such a mechanism would not, therefore, account for the large observed difference in the hydrolytic reactivity of the comparable isothioureas. Only an SN1 mechanism can account for such variation in reactivity because of pronounced differences in the carbonium ion stability of the various arylmethyl systems studied.

Conclusions

This investigation was undertaken in an attempt to determine the mechanism of hydrolysis of certain arylmethylisothioureas. Evidence has been presented to show that this hydrolysis proceeds by an SN1 mechanism with thiourea as the leaving group. Substituent effects and the observed activation parameters lend strong support to this proposal. As a comparison, the only well-characterized hydrolysis, in pure water, involving a sulfur leaving group (i.e., carbon–sulfur bond cleavage), is that of *tert*-butyldimethylsulfonium iodide,[30] which has an activation energy of 31.56 kcal/mol and an activation entropy of +15.74 cal/(mol K). This hydrolysis reaction was shown to be SN1 and its activation energy and entropy are of the same sign and approximately the same magnitude as those for the hydrolysis of **1**–**3**. Although comparisons of activation parameters are insufficient evidence on which to base a mechanism, they provide further support for our proposed carbonium ion mediated hydrolysis.

Alterations in the arylmethyl group, to which the isothiourea moiety is attached, altered reactivity in a predictable fashion if an SN1 mechanism is operative and molecular orbital calculations correlated well with the predicted order of reactivity of the arylmethylisothioureas. The arylmethylisothioureas that would produce arylmethyl carbonium ions with high charge delocalization showed much higher hydrolytic reactivity and the unreactivity of other arylmethylisothioureas (i.e., benzyl-, 1-naphthylmethyl-, and 9-phenanthrylmethyl-) can also be understood on the basis of these molecular orbital calculations.

This investigation has thus shown that thiourea is a new leaving group for SN1 solvolyses. Because of their moderate aqueous solubility, the arylmethylisothioureas offered the opportunity of studying an SN1 hydrolysis in a purely aqueous medium. The generally higher stability of the isothiourea compounds compared to the corresponding arylmethyl halides allowed study of the hydrolytic reactivity of the 9-anthrylmethyl ring system in a purely aqueous environment. These ring systems have only been studied previously in organic solvents of low water content, because of their high hydrolytic reactivity as halides. The following paper will report on the effect of modifications of the leaving group on hydrolytic reactivity and on the reactivity of an allylic isothiourea.[31]

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Registry No.—**1**, 2962-76-7; **2**, 59474-01-0; **3**, 59574-02-1; 9-hydroxymethylanthracene, 1468-95-7; 10-methyl-9-chloromethylanthracene, 25148-26-9.

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