The concentrations of alcohol and persulfate will not correspond to their initial values, however, since certain amounts will have undergone reaction, and certain quantities of alcohol and sulfur tetroxide will be bound in the complex. Therefore, we set $[\mathrm{ROH}] = [\mathrm{ROH}]_0 - X$ and $[\mathrm{S_2O_8^=}] = [\mathrm{S_2O_8^=}]_0 - X$. Making this substitution in eq. 16 and neglecting the presumably small term in X^2, we find for X

$$X = \frac{k_1[\mathrm{ROH}]_0[\mathrm{S_2O_8^=}]_0}{k_{-1}[\mathrm{SO_4^=}] + k_2 + k_1([\mathrm{ROH}]_0 + [\mathrm{S_2O_8^=}]_0)} \quad (17)$$

Finally, setting the over-all rate equal to k_2X and dividing through by k_1, we obtain the rate expression

$$\text{initial rate} = \frac{k_2[\mathrm{ROH}]_0[\mathrm{S_2O_8^=}]_0}{[\mathrm{ROH}]_0 + [\mathrm{S_2O_8^=}]_0 + (k_2 + k_{-1}[\mathrm{SO_4^=}])/k_1} \quad (18)$$

which, as was stated above, is quite similar in form to the empirical expression (eq. 8), predicting a limiting rate with respect to both alcohol and persulfate, and yet differs sufficiently from eq. 8 to make it incorrect. Indeed, it is rather difficult to see how a rate equation of the exact required form can be derived from purely mechanistic considerations.

Analogy with Enzyme Kinetics.—A very interesting fact which remains to be pointed out is that eq. 8 is similar to, and eq. 18 identical with, the complete Briggs and Haldane equation for variation of the rate of enzymatic reactions with initial concentration of enzyme and substrate[13]

$$\text{initial rate} = \frac{k_2S_0E_0}{S_0 + E_0 + (k_2 + k_{-1})/k_1} \quad (19)$$

where S_0 and E_0 are, respectively, the initial substrate and enzyme concentrations, and $(k_2 + k_{-1})/k_1$ is the Michaelis constant, K_m.

Thus persulfate oxidations seem to follow kinetic laws similar to those obeyed by enzyme systems, with the persulfate concentration taking the place of the enzyme concentration in these equations, although, needless to say, the persulfate is not regenerated and hence does not actually function catalytically as does an enzyme.

[13] See, for example, K. J. Laidler, "Chemical Kinetics," McGraw-Hill Book Co., New York, N. Y., 1950, p. 281.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS]

Kinetic Studies of Thiourea Derivatives. IV. The Methylated Thioureas. Conclusions[1]

BY WILLIAM H. R. SHAW AND DAVID G. WALKER

RECEIVED APRIL 30, 1958

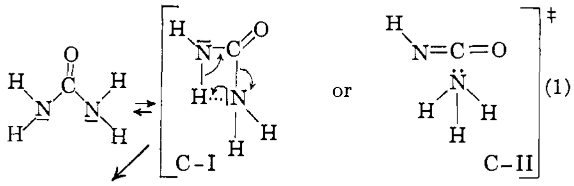
Kinetic data on urea, thiourea and the methylated thioureas have been assembled and compared. The dissociations of these compounds in low *p*H water solutions at elevated temperatures are all first-order, ionic strength independent reactions. Transition states formed by hydrogen transfer and loosening of a C–N bond are assumed. For thiourea and its methyl derivatives these activated complexes are visualized as being composed of two parts: an amine or ammonia-like fragment, and an isothiocyanate-like fragment (either isothiocyanic acid-like or methyl isothiocyanate-like). One important generalization presented is that if transition states with identical amine fragments are compared, substitution of methyl for hydrogen in the thiocyanate fragment increases the rate by a factor of 2.2. If the rate-determining step is assumed to involve rupture of a C–N bond by removal of the nucleophilic amine fragment from the electrophilic isothiocyanate fragment, a consistent interpretation is possible. Under this assumption the relative reactivities of all the methylated thioureas can be rationalized in terms of hyperconjugative electron release by methyl groups and steric strain. The observation that urea is 244 times more reactive than thiourea is attributable to the sulfur atom's superior ability to withdraw electrons. Other aspects of the kinetic behavior of these compounds are discussed.

Introduction

Results of kinetic studies with urea,[2] thiourea[3] and the methylated thioureas,[4-6] in aqueous media at elevated temperatures have been reported. These data have now become extensive enough to warrant their collection, comparison and detailed examination for significant interrelationships.

Discussion

It has been suggested that urea and its derivatives decompose *via* intramolecular hydrogen transfer and dissociation of the activated complex. Applied to urea the postulated mechanism can be formulated as



$$\mathrm{NH_3} + \mathrm{HNCO} \rightleftarrows \mathrm{NH_4^+} + \mathrm{NCO^-} \quad (2)$$

Similar mechanisms have been proposed for thiourea, the dimethylthioureas and trimethylthiourea. Two slightly different activated complexes are represented in the above scheme. Within the framework of the assumed mechanism they are indistinguishable *a priori* since both represent different configurations that might be encountered along the reaction coördinate. A discussion of the relative merits of the two representations will be presented in a subsequent paragraph after pertinent data on derivatives has been reviewed.

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[1] Presented before the Division of Physical and Inorganic Chemistry, 133rd National Meeting of the American Chemical Society held in San Francisco, California, April, 1958.

[2] W. H. R. Shaw and J. J. Bordeaux, THIS JOURNAL, **77**, 4729 (1955).

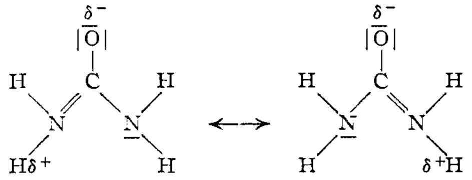
[3] W. H. R. Shaw and D. G. Walker, *ibid.*, **78**, 5769 (1956).

[4] W. H. R. Shaw and D. G. Walker, *ibid.*, **79**, 2681 (1957).

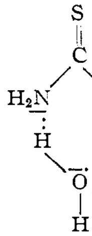
[5] W. H. R. Shaw and D. G. Walker, *ibid.*, **79**, 3683 (1957).

[6] W. H. R. Shaw and D. G. Walker, *ibid.*, **79**, 4329 (1957).

The Hydrogen Transfer.—It seems correct to assume that the hydrogen transfer is not, in general, rate limiting. This assumption is supported by several pieces of evidence. In aqueous media, the isomerizations of urea,[2] thiourea[3] and *unsym*-dimethylthiourea are *p*H independent over a very wide range. The primary steps in the dissociations of *sym*-dimethylthiourea[5] and trimethylthiourea[6] are also most probably *p*H independent. In these last two instances, however, additional reactions by the products tend to make interpretation of the data more complex. Resonance forms[7] such as would also suggest that protons on the nitrogen atoms are relatively free to migrate. The observation that urea is rapidly deuterated in heavy water is likewise important evidence that the hydrogens are quite labile. Thus the contention that hydrogen transfer is not, in general, rate limiting seems amply justified.



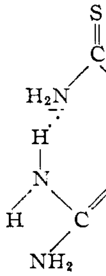
On the basis of the arguments outlined above, the hydrogen transfer may be either intermolecular or intramolecular. Unequivocal distinction between these two possibilities cannot, as yet, be made. If intermolecular hydrogen transfer involving solvent participation is assumed, as possible transition state, C-III, for the thiourea isomerization might be written as



C-III

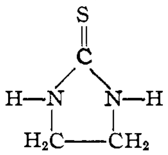
This is to be compared with the transition states C-I and C-II postulated for intramolecular hydrogen transfer.

The thiourea isomerization also has been studied in the melt. In these molten mixtures of thiourea and ammonium thiocyanate, Kappanna[8] finds that the reaction is first order with respect to thiourea. The frequency factor and activation energy calculated by this investigator agree with those reported for the reaction in water solutions.[3] If a transition state analogous to C-III is assumed for reaction in the melt it should be formulated as C-IV. Such a transition state would imply a reaction that is second order with respect to thiourea. Since this implication is contrary to the experimental findings, transition state C-IV would appear to be less acceptable than C-I and C-II. By analogy then C-I and C-II might be considered better representation than C-III. In any event, after the configuration represented by C-III has proceeded along its corresponding reaction coördinate, an intermediate state similar to C-II would probably occur. Additional information about the complexity of the transition state has very recently become available from isotopic studies. Yankwich and Veazie[9] have published important results on the carbon isotope effect in the decomposition of urea. Their study was made over a temperature range of 60–96° in aqueous acid, and the ratio of isotopic rate constants for C^{12}-urea and C^{13}-urea was examined as a function of temperature. These investigators conclude that a "four atom or more complex model" is required to explain their data. The original paper should be consulted for details. Since the complexes considered all involve at least four atoms and since C-I and C-II are convenient simple representatives that do not conflict with the experimental observations—we shall employ them in the discussions that follow.



C-IV

Before proceeding further it is necessary to inquire if hydrogen transfer is even of major importance in the rate-determining step. One previously unreported finding would seem to indicate that this process can be made rate limiting although in general it seems to be unimportant in determining the rate of decomposition. Measurements were made with ethylenethiourea in water solutions at 100° by the titration technique[6] previously described. In neutral solution this compound was approximately $^1/_{25}$ as reactive as *sym*-dimethylthiourea. Examination of models reveals that intramolecular hydrogen transfer in this cyclic derivative should be difficult. In fact, the observed reactivity of ethylenethiourea is most likely *entirely* due to a hydrolytic reaction rather than to a simple decomposition. Tetramethylthiourea is also very slowly hydrolyzed in neutral solutions and does not exhibit simple decomposition. In the absence of water it can, however, be distilled[10] at 245° without decomposition. If the slight reactivity of tetramethylthiourea and of ethylenethiourea can be attributed to hydrolysis, it is important to inquire whether this is the rate-determining process when other thiourea derivatives react in aqueous media.



Hydrolysis as a Rate-limiting Process.—For urea, thiourea and *unsym*-dimethylthiourea over a

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(7) G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, p. 361.

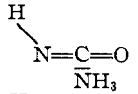
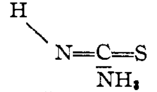
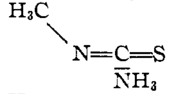
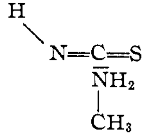
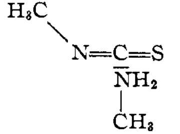
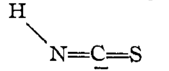
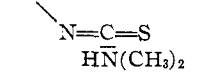
(8) A. N. Kappanna, *J. Indian Chem. Soc.*, **4**, 217 (1927).

(9) P. E. Yankwich and A. E. Veazie, THIS JOURNAL, **80**, 1835 (1958).

(10) M. Delepine, *Bull. soc. chim. France*, **7** [4], 988 (1910).

TABLE I

THE DISSOCIATION OF UREA, THIOUREA AND THE METHYLATED THIOUREAS IN WATER SOLUTIONS

Reactant and reaction numeral	Assumed transition state	Postulated primary products	Cor.[a] first-order constant, sec.$^{-1}$ × 10^7	Obsd. products and stoichiometry
I Urea		HNCO, NH_3	208	NH_4^+ and NCO^- in equal amts.
II Thiourea		HNCS, NH_3	0.85	NH_4^+ and NCS^- in equal amts.
III Methylthiourea		H_3C–NCS, NH_3	1.84	$CH_3NH_3^+$, COS, NH_4^+
IV Methylthiourea		HNCS, CH_3NH_2	0.57	NCS^- and $CH_3NH_3^+$ Over-all stoichiometry for III and IV $(CH_3NH_3^+) = (NH_4^+) + (NCS^-)$
V *sym*-Dimethyl thiourea		CH_3NCS. CH_3NH_2	1.25	$CH_3NH_3^+$ and COS
VI *unsym*-Dimethylthiourea		HNCS, $(CH_3)_2NH$	16.8	$(CH_3)_2NH_2^+$ and NCS^- in equal amts.
VII Trimethylthiourea		CH_3NCS, $(CH_3)_2NH$	37.7	$(CH_3)_2NH_2^+$ and $CH_3NH_3^+$ in equal amts.

[a] Obtained by dividing the empirical first-order constants in Table II by suitable statistical factors. The reaction numerals and corresponding statistical factors are: I, 2; II, 2; III, 1; IV, 1; V, 2; VI, 1; and VII, 1.

relatively wide *p*H range the answer to the question posed in the preceding paragraph is clear. Hydrolysis is unimportant as a rate-determining step. The products formed and their stoichiometry clearly establish the rate-determining process as a simple dissociation. In strongly alkaline solutions, however, there is evidence for a base-catalyzed parallel reaction that culminates in the production of sulfide ion (in the case of thiourea and its derivatives) and other products. This reaction quite likely involves hydrolysis. The distinction between hydrolysis and dissociation is not always easy to make. With *sym*-dimethylthiourea for example, dissociation would give methylamine and methyl isothiocyanate. The last-named compound reacts rapidly with water to produce methylamine and carbon oxysulfide. Thus in acid media the ultimate products expected from a rate-determining dissociation are methylamine and carbon oxysulfide. These are the same products anticipated from a direct rate-determining hydrolysis. Thus, in this case, the two mechanisms cannot be distinguished by analysis of the products formed in acid solution. With *unsym*-dimethylthiourea, on the other hand, no such ambiguity exists. True dissociation should not produce ammonia; hydrolysis should. From *p*H 1 to *p*H 11 no ammonia was detected by our sensitive tests in reacted solutions of this compound. At *p*H 12.6, however, ammonia was observed and an increased rate of dimethylamine production noted. These observations are in quantitative agreement with the reaction

$$Me_2N\text{-}CS\text{-}NH_2 + H_2O \xrightarrow{OH^-} Me_2NH + COS + NH_3 \quad (3)$$

Similar considerations apply to thiourea. Consequently, by analogy the rate limiting reaction of *sym*-dimethylthiourea in acidic media is most probably a dissociation and not a hydrolysis. Related reasoning can be applied to trimethylthiourea.

Products and the Possibility of Methyl Migration.—In summary, dissociation occurs when a hydrogen atom bonded to N in a thiourea derivative is free to migrate to N′. The correct products can be predicted by assuming an intramolecular hydrogen transfer accompanied by rupture of the C–N′ bond. A mobile hydrogen on N′ is, of course, also free to migrate to N with rupture of the C–N bond. These two different modes of hydrogen transfer may or may not result in different products[4] depending upon other substituents present on N and N′. If no labile hydrogen is present (*e.g.*, tetramethylthiourea) decomposition does not take place, but hydrolysis is still possible.

Migration of methyl groups does not occur under our experimental conditions. This conclusion is based on the following evidence. In the dissociation of *sym*-dimethylthiourea no dimethylamine is observed. With *unsym*-dimethylthiourea no methylamine is obtained. With tetramethylthiourea no methylamine is produced. These qualitative observations, the experimentally determined stoichiometries, possible formulas for activated complexes and other data are presented in Table I.

Complicating Reactions.—The isomerization of thiourea and *unsym*-dimethylthiourea are free from complicating reactions by the products over an extremely wide range. Reaction IV (Table I) shown by methylthiourea behaves in a similar fashion. Thus all reactions that produce NCS^- show this behavior. These findings can be explained by assuming that complicating reverse reactions must take place through un-ionized thiocyanic acid. Since this acid is strong, such reactions do not occur to a significant degree in the cases considered above.

In strongly acid media some hydrolysis of NCS^- is observed and increased ammonia production from this source is noted. This reaction has been observed with thiourea and methylthiourea. The increased reactivity of *unsym*-dimethylthiourea made shorter reaction times possible and the hydrolysis of NCS^- was not detected.

In the isomerization of urea, cyanate ion[11] is formed. This ion is much more easily hydrolyzed by acid than the thiocyanate ion; and, in acid solutions, no cyanate was detected in our reaction mixtures.[2,12] Amell[13] recently has presented extensive data for the hydrolysis of cyanic acid. He concludes that hydrolysis must proceed *via* a rate-limiting reaction of un-ionized HNCO with water. Our observations[3-6] that, in relatively very low *p*H media, a small but significant hydrolysis of NCS^- takes place can be rationalized on a similar basis. Since HNCS is much stronger than HNCO and since hydrolysis must proceed through the un-ionized acid, the relatively great stability of the NCS^- ion in water solution can be explained.

In sharp contrast to the reactions producing NCS^-, those involving methyl isothiocyanate as a primary product exhibit complex *p*H dependence. This complexity has been explained on the basis of reverse reactions (syntheses of the parent compounds) and other reactions by the products.[4-6]

At high *p*H the base-catalyzed parallel reaction noted above (see section on Hydrolysis) takes place with urea,[14] thiourea[3] and the methylated thioureas.[4-6] With thiourea and its derivatives sulfide ion is produced. This desulfurization could lead to formation of a cyanamid or a carbodiimide[15] as intermediates that subsequently undergo further reaction perhaps to a urea which in turn dissociates. A detailed discussion must await the collection of more data in basic media.

The Collected Results.—Frequency factors, activation energies and first-order reaction rate constants at 100° are reported in Table II. It is interesting to note that for all these reactions A is greater than *ekT/h* indicating a positive entropy of activation.[16] If the cyclic complex C-I is postulated. the positive entropy of activation can be explained by assuming that the activated complex is less solvated than the reactant. This explanation has been presented previously.[3] It is also reasonable to select C-II instead and attribute the positive entropy of activation to a general loosening of the structure of the reactant. If this alternative is pursued, it also must be assumed that the solvation of reactant and activated complex are very similar or that solvation is relatively unimportant. Since C-II has been postulated for the synthetic reaction,[2,17] we shall, for simplicity, employ it in the ensuing discussion.

With urea, thiourea and *sym*-dimethylthiourea hydrogen transfers from N to N′ accompanied by rupture of the CN′ bond, and similar transfers from N′ to N accompanied by rupture of the CN bond give the same products. Thus there are two different reaction paths leading to the same products. This is not true for the other thiourea derivatives listed in Table I. For purposes of comparison it becomes apparent, therefore, that the empirical first-order constants at 100° reported in Table II should be divided by a suitable statistical factor. These factors and statistically corrected rate constants are included in Table I (footnote *a*).

TABLE II

ARRHENIUS PARAMETERS[a] AND EMPIRICAL FIRST-ORDER RATE CONSTANTS

Reactant	Reaction numeral[e]	First-order rate constant at 100°, sec.$^{-1}$ × 10^7	A,[c,d] sec.$^{-1}$ × 10^{-14}	E,[c,d] kcal./mole	Av. %[b] dev.
Urea	I	415 ± 30	5.77	32.7	5
Thiourea	II	1.70 ± 0.05	1.53	35.8	3
Methylthiourea	III	1.84 ± .15	0.337	34.5	7
Methylthiourea	IV	0.57 ± .07	9.87	37.9	3
sym-Dimethylthiourea	V	2.50 ± .16	3.69	36.3	9
unsym-Dimethylthiourea	VI	16.8 ± 1.5	3.90	34.6	10
Trimethylthiourea	VII	37.7 ± 4.0	4.98	34.4	4

[a] Based on the usual form of the law: $k = A \exp(E/RT)$. [b] Rate constants were calculated from these parameters at all reaction temperatures studied. The calculated constants were then compared with the experimental constants and the average per cent. deviation calculated as a measure of the goodness-of-fit of the data to the Arrhenius expression. [c] The frequency factors and activation energies are reported to three figures solely for purposes of calculation of rate constants at various temperatures from the A and corresponding E recorded in the table. Because of the limited temperature range studied and experimental error it is possible to select a variety of A's and corresponding E's that will give an adequate fit. [d] In line with comments above the frequency factors are, by a conservative estimate, good to approximately a factor of 10, and the activation energy to ±1 kcal. [e] See Table I for details.

Interrelationships.—As a drastic simplification it can at first be assumed that the dominant factor governing the rate of reaction is the rupture of a C–N bond. If activated complexes like those postulated in Table I are involved, rupture of this bond entails removal of a nucleophilic amine fragment from an electrophilic isothiocyanate fragment.

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(11) J. Walker and F. J. Hambley, *J. Chem. Soc.*, **105**, 609 (1895).

(12) W. H. R. Shaw and J. J. Bordeaux, *Anal. Chem.*, **27**, 138 (1955).

(13) A. R. Amell, THIS JOURNAL, **78**, 6234 (1956).

(14) R. C. Warner, *J. Biol. Chem.*, **142**, 709 (1942).

(15) H. G. Khorana, *Chem. Revs.*, **53**, 145 (1943). See also D. C. Schroeder, *ibid.*, **55**, 181 (1955).

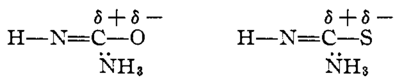
(16) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., New York, N. Y., 1941, p. 417.

(17) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 257.

Thus the strength of this bond depends on the nucleophilicity of N and the electrophilicity of C. Substituting methyl for hydrogen on the amine fragment should increase the nucleophilicity of N since the methyl group is a weak electron donor.[18,19] Referring now to Table I on the basis of this reasoning, IV should be less reactive than II. This conclusion is in line with the statistically corrected constants. Substitution of a methyl for hydrogen on the isothiocyanate fragment should have a different effect. This substitution should lead to a decreased electrophilicity of carbon causing II to be less reactive than III. Since the magnitude of the electronic shift initiated by the methyl group diminishes with increasing distance from this group, the effect should be relatively small. Applying this same reasoning gives: IV < V, VI < VII.

If the only important effect were the hyperconjugative release of electrons by methyl groups VI should be less reactive than IV. Just the opposite order is observed. This result can be attributed to steric strain arising from interaction of the two methyl groups with the isothiocyanate fragment. Similar arguments have been presented previously by Brown[20] in his stimulating papers on the base strengths of amines. Other references[21] are also relevant. R. W. Taft,[22] for example, lists strain energies for the formation of amine–borontrimethyl addition compounds. The steric strains for ammonia, methylamine and dimethylamine derivatives are estimated as 0, 0 and 1.7 kcal., respectively. If it is assumed that the increased reactivity of *unsym*-dimethylthiourea compared to thiourea is entirely due to release of steric strain, it might be possible to crudely estimate this strain from the difference in activation energies (Table II). This difference is 1.2 kcal., a result that compares favorably with the 1.7 kcal. value reported for the formation of the dimethylamine–borontrimethyl addition compound mentioned above. This comparison is open to criticism on several counts and should be regarded as suggestive but not rigorous.

Further examination of Tables I and II reveals that urea is about 244 times more reactive than thiourea. The argument presented above and consideration of the two transition states



$$\mathrm{H{-}N{=}}\underset{\dot{\mathrm{N}}\mathrm{H_3}}{\overset{\delta+}{\mathrm{C}}}\mathrm{{-}}\overset{\delta-}{\mathrm{O}} \qquad \mathrm{H{-}N{=}}\underset{\dot{\mathrm{N}}\mathrm{H_3}}{\overset{\delta+}{\mathrm{C}}}\mathrm{{-}}\overset{\delta-}{\mathrm{S}} \qquad (4)$$

I′ II′

lead to a simple conclusion: the molecule forming the transition state having the highest $\delta+$ on carbon will be the least reactive. From the electronegativities[23] of O and S one would conclude that urea should be less reactive than thiourea. In complex molecules, however, the use of these simple electronegativities to predict electron distribution is a highly questionable procedure.[24] There is an increasing body of evidence supporting the contention that, in many instances, S has a greater ability to withdraw electrons than O. The observation that thiourea is a stronger base than urea[25] can be interpreted on this basis. Measurements of the dipole moments and ultraviolet spectra of these two molecules have been similarly explained.[26] Ingold[27] has compared the =S group with the =O. He concludes that S has a greater tendency than O to decrease its covalency because of its higher Mendeleeff period number. Thus the =S group is more electron attracting than the =O group as a result of the —M effect. Consequently on the basis of the evidence outlined above, it seems very reasonable to assume that the $\delta+$ on C in II′ is greater than the $\delta+$ on C in I′. Therefore—as observed—thiourea should be less reactive than urea.

Another important conclusion can be drawn from Table I. Starting with II, alternate structures differ from each other by substitution of a CH_3-group for H- on the isothiocyanate fragment in the transition state. The amine fragments in these neighboring transition states are the same. More succinctly the structures bear the relationship

$$\mathrm{III/II = V/IV = VII/VI} \qquad (5)$$

The rate constants stand in the ratios

$$\frac{1.84}{0.85} = 2.16;\ \frac{1.25}{0.57} = 2.19;\ \frac{37.7}{16.8} = 2.22 \qquad (6)$$

and on the basis of the deviations reported (Table II), only two significant figures should be considered. This rather remarkable result must mean that substitution of a methyl group for a hydrogen atom on the isothiocyanate fragment increases the rate constant by a factor of approximately 2.2 when molecules leading to transition states with the same amine fragment are compared. Thus given this factor and rate constants for molecules with transition states such as II, IV and VI, it is possible to predict rate constants for the molecules with transition states: III, V and VII. Predictions such as

$$\mathrm{VII/III = VI/II} \qquad (7)$$

also can be made. These are, of course, all implied in the basic relationship (eq. 5). If substitution of CH_3- for H- on the isothiocyanate fragment is assumed to contribute a constant amount to the free energy of activation, $\Delta F^{\ddagger}$, then these generalizations can be obtained theoretically.

Although the arguments presented above are consistent with the data, a somewhat different approach can be used to rationalize the observations. This approach stems from a consideration of the resonance energy lost in going from reactant to activated complex.

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[18] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, New York, 1953, p. 65.

[19] J. W. Baker, "Hyperconjugation," Oxford University Press, London, 1952, p. 5.

[20] H. C. Brown, *et al.*, in "Determination of Organic Structures by Physical Methods," E. A. Braude and F. C. Nachod, Eds., Academic Press, Inc., New York, N. Y., 1955, p. 641.

[21] G. S. Hammond in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, pp. 454–460.

[22] R. W. Taft in ref. 21, p. 635.

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Urea has a resonance energy of approximately 41 kcal.,[28] and at least in the solid state is a completely planar molecule.[29] This planarity is destroyed when the activated complex is formed. Thus the activation process should require enough energy to compensate for the loss of resonance energy involved in activated complex formation. This resonance energy loss will be given by the difference in resonance energy between reactant and complex. If it is assumed that the activated complex involved in the urea decomposition possesses resonance energy approximately equal to that of an alkyl isocyanate, *i.e.*, about 8 kcal.[28]; then the loss in resonance energy should be $41 - 8 = 33$ kcal.[30] This value compares favorably with the 32 kcal. activation energy reported for the decomposition of urea in aqueous solutions (Table I).

Resonance energies for thiourea and the thiourea derivatives are not available, but some qualitative observations can be made. It seems reasonable to assume that methylation should destroy planarity and decrease the resonance energy. The lowered activation energies of *unsym*-dimethylthiourea and trimethylthiourea might be rationalized on this basis. In the absence of resonance energy data for these compounds, however, rigorous comparisons cannot be made.

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[28] Ref. 18, p. 116. Ref. 7, p. 100, gives 33 and 30 kcal. Ref. 23, p. 138, gives 37 kcal.

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[30] Use of the other values[28] for resonance energies of urea and the alkyl isocyanates gives these values for the loss in resonance energy: 40 and 37 kcal. (based on ref. 7), 30 kcal. (based on ref. 23).

[CONTRIBUTION FROM WASHINGTON UNIVERSITY]

Electron Spin Resonance Spectra of the Anions of Benzene, Toluene and the Xylenes[1]

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The preparation and electron spin resonance spectra of the anions of benzene, toluene, *o*-xylene, *m*-xylene and *p*-xylene are reported. The distribution of spin density is compared with predictions of molecular orbital theory.

Introduction

Although the reaction between alkali metals and hydrocarbons has been known for some time, only recently has it been shown to involve the transfer of one or two electrons from the alkali metal to the hydrocarbon.[3–6] The scope of this reaction apparently includes all aromatic hydrocarbon systems of two or more conjugated rings. Until recently the only examples of single ring aromatic systems forming negative ions were those of nitrobenzenes.[3] The preparation of benzene negative ion at room temperature was reported by Paul,[7] but confirmation of his experiment has not been obtained.

Experimental Procedure

All samples were prepared under high-vacuum conditions by techniques similar to those described by Paul, Lipkin and Weissman.[6] A typical preparation proceeded as follows. After the alkali metal had been distilled to form a mirror at the bottom of the apparatus, about 2 ml. of dimethoxyethane and 0.1 ml. of hydrocarbon were distilled onto the metallic film. With the contents frozen, the sample tube was sealed from the vacuum system and warmed in a Dry Ice–acetone bath.

As the sample warmed and melted the characteristic color of the hydrocarbon anion formed at the surface of the metal and gradually diffused throughout the solution. The reaction proceeds rather rapidly with benzene and toluene, more slowly with the xylenes. On warming from −80°, these solutions gradually lose their color with accompanying formation of fine grey precipitates. At room temperature the solutions have a yellow to orange color whose intensity increases with time of contact between solution and metal. The yellow and orange solutions are not paramagnetic. Recooling the solutions restores the anion color as well as the paramagnetism.

Dimethoxyethane alone in contact with potassium at −80° yields a deep blue solution.[8] The color fades with precipitation of metallic potassium at room temperature. The deep blue solution exhibits a weak spin resonance absorption line about two oersteds in breadth.

E.S.R. Observations and Discussion

The e.s.r. absorption spectra were taken on a spectrometer operating at approximately 9,000 Mc./sec. The magnetic field was modulated at 90 cycles/sec. Low temperatures were obtained by boiling liquid nitrogen and conducting the cold gas through a transfer tube into a sleeve dewar in the resonant cavity. The temperature in the cavity was controlled by regulating the boiling rate of the liquid nitrogen.

The spectrum of benzene negative ion consists of seven equally spaced lines with interval between lines 3.75 oersteds and intensity ratios approximately 1:6:15:20:15:6:1. The pattern corresponds to splitting by six equivalent protons. The

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