[CONTRIBUTIONS FROM THE CHEMISTRY DEPARTMENT, STATE UNIVERSITY OF NEW YORK, COLLEGE OF FORESTRY]

Reactions of Methyl Radicals with Substrates Acting as Hydrogen Donors and as Methyl Radical Acceptors

BY R. P. BUCKLEY, F. LEAVITT AND M. SZWARC

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It is shown that the mechanism proposed by Levy and Szwarc, describing reactions of methyl radicals with solvents which are hydrogen donors and olefinic or aromatic compounds which are methyl radical acceptors, can be extended to systems in which either of these two components act in a dual fashion: as a hydrogen donor and as a methyl radical acceptor. Furthermore, it is shown that for acceptors of methyl radicals which are simultaneously hydrogen atom donors, the equation derived by Levy and Szwarc does not lead to a ratio of rate constants of addition to an olefin and of abstraction of a hydrogen from a solvent (this ratio is denoted by k_2/k_1), but to a quantity $(k_2/k_1)_{\text{exp}}$ which varies with the molar ratio of olefin and solvent. It is shown that $(k_2/k_1)^{-1}_{\text{exp}}$ is a linear function of molar fraction of the olefin/molar fraction of the solvent. The intercept of such a straight line gives the "true" value of k_2/k_1 and its slope the relative rates of hydrogen abstraction from and methyl radical addition to the olefin. These deductions are confirmed by experiments, and the significance of the derived rate constants is further discussed.

In a series of papers[1-4] it was shown that methyl radicals, generated in a solution composed of an aliphatic hydrocarbon HS and an aromatic or olefinic compound A, undergo two competing reactions. They abstract hydrogen atoms from the solvent HS

$$\mathrm{CH_3 + H{\cdot}S \xrightarrow{k_1} CH_4 + S{\cdot}} \tag{1}$$

or they add to the aromatic or olefinic molecules A

$$\mathrm{CH_3 + A \xrightarrow{k_2} A{\cdot}CH_3} \tag{2}$$

If the stationary concentration of radicals is maintained at a sufficiently low level, then reactions 1 and 2 account for *all* the methyl radicals which diffused out into solution. Under these conditions the ratio of the rate constants k_2/k_1 is given by the simple expression[2,4]

$$k_2/k_1 = \{(\mathrm{A{\cdot}CH_3 formed})/(\mathrm{CH_4\ formed})\} \times X_{\mathrm{HS}}/X_{\mathrm{A}}$$

in which X_{HS} and X_{A} denote the mole fractions of the solvent HS and of the aromatic or olefinic compound A, (CH_4 formed), the amount of methane formed in the reaction, and ($A{\cdot}CH_3$ formed), the amount of methyl radicals consumed by reaction 2. The primary product of reaction 2, *i.e.*, $A{\cdot}CH_3$, is itself a radical and therefore is not the final product of the over-all process. Under experimental conditions chosen in those investigations, $A{\cdot}CH_3$ disappears by a reaction involving either another radical $A{\cdot}CH_3$ or a solvent radical S·. Therefore, the amount of $A{\cdot}CH_3$ originally formed can be determined by measuring the difference in the amounts of methane formed in the presence and in the absence of A in experiments which otherwise are identical.

The kinetic scheme proposed above applies to those systems in which the solvent HS is *only* the hydrogen donor, while the aromatic or olefinic compound A acts *only* as methyl radical acceptor. However, the situation is more complex when one or the other component of the solution can act dually: as a hydrogen donor and as a methyl radical acceptor. It is the purpose of this communication to discuss the kinetic behavior of such systems, and to illustrate the conclusions on suitably chosen examples.

Systems Involving Solvents Which Are Acceptors of Methyl Radicals.—In our studies methyl radicals are generated by the decomposition of acetyl peroxide. It was shown previously that the decomposition of a dilute solution of acetyl peroxide in a non-polar solvent produces one methyl radical for each molecule of carbon dioxide formed in the reaction.[5] Moreover, if the solvent is an aliphatic hydrocarbon then all the methyl radicals formed by the decomposition yield either methane or ethane,[6] *i.e.*, the ratio $(CH_4 + 2C_2H_6)/CO_2$, is essentially unity (see *e.g.*, Table I in ref. 1). However, if the decomposition takes place in toluene solution, then the ratio $(CH_4 + 2C_2H_6)/CO_2$ is substantially less than unity, *e.g.*, its average value calculated from ten experiments carried out at 65° was found to be 0.858 ± 0.010. Since this ratio is not affected by the concentration of the peroxide, if the latter is less than 10^{-2} *M*, one concludes that the "missing" methyl radicals are not lost in reaction 3

$$\mathrm{C_6H_5{\cdot}CH_2 + CH_3{\cdot} \longrightarrow C_6H_5{\cdot}CH_2{\cdot}CH_3} \tag{3}$$

but that their disappearance is due to the reaction analogous to reaction 2, namely

$$\mathrm{CH_3 + C_6H_5{\cdot}CH_3 \longrightarrow adduct} \tag{4}$$

Assuming that all the "missing" methyl radicals are consumed by reaction 4 we calculate k_4/k_1 as $\{1 - (CH_4 + 2C_2H_6)/CO_2\}/(CH_4/CO_2)$. Since (CH_4/CO_2) was found to be 0.742 ± 0.08 (again the average from the same ten experiments), hence, $k_4/k_1 = 0.19$, *i.e.*, the probability of the interaction between a methyl radical and a toluene molecule leading to a hydrogen atom abstraction is about five times greater than the probability of the addition.[7]

Let us now consider the effect of reaction 4 on the determination of the relative rate constant k_2. In the absence of compound A (*i.e.*, in pure toluene solution) the amount of methane formed is given by $q(k_1/(k_1 + k_4))$, where q denotes the difference between the total number of methyl radicals generated by the decomposition and the number dimerized in a cage recombination. The amount of

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[1] M. Szwarc, *J. Polymer Sci.*, **16**, 367 (1955).

[2] M. Levy and M. Szwarc, THIS JOURNAL, **77**, 1949 (1955).

[3] A. Rembaum and M. Szwarc, *ibid.*, **77**, 4468 (1955).

[4] F. Leavitt, M. Levy, M. Szwarc and V. Stannett, *ibid.*, **77**, 5493 (1955).

[5] M. Levy and M. Szwarc, *ibid.*, **76**, 5981 (1954).

[6] It was shown that ethane is formed by a "cage" recombination of methyl radicals, see A. Rembaum and M. Szwarc, THIS JOURNAL, **77**, 3486 (1955).

[7] In this section toluene is the solvent, and equation 1 is represented as: $\mathrm{CH_3 + C_6H_5{\cdot}CH_3 \rightarrow CH_4 + C_6H_5{\cdot}CH_2}$.

methane formed in presence of compound A is given by the expression

$$(\mathrm{CH_4\ formed}) = q[k_1(X_{\mathrm{HS}}/\{(k_1 + k_4)X_{\mathrm{HS}} + k_2X_{\mathrm{A}})\}]$$

Hence

$$(\mathrm{A{\cdot}CH_3\ formed}) = (\mathrm{CH_4\ ``lost"})$$

$$= q(k_1/(k_1 + k_4)) - qk_1(X_{\mathrm{HS}}/\{(k_1 + k_4)X_{\mathrm{HS}} + k_2X_{\mathrm{A}}\}$$

$$= q(k_1k_2(X_{\mathrm{A}}/\{(k_1 + k_4)X_{\mathrm{HS}} + k_2X_{\mathrm{A}}\}) \times (k_1 + k_4)$$

Therefore

$$(\mathrm{A{\cdot}CH_3\ formed})/(\mathrm{CH_4\ formed}) = k_2(X_{\mathrm{A}}/\{(k_1 + k_4)X_{\mathrm{HS}}\})$$

and

$$k_2/(k_1 + k_4) = \{(\mathrm{A{\cdot}CH_3\ formed})/(\mathrm{CH_4\ formed})\}(X_{\mathrm{HS}}/X_{\mathrm{A}})$$

One concludes therefore, that the technique applied in studies involving aliphatic hydrocarbons as solvents is also valid when the solvents used are not only hydrogen donors but also methyl radical acceptors. The relative rate constant k_2 is given by the same expression, the only difference being in the interpretation of the results, namely, $k_1 + k_4$ instead of k_1 appears in the denominator.

Levy and Szwarc[2] demonstrated that $(k_1 + k_4)_{\mathrm{toluene}}$ is about three times greater than $(k_1)_{\mathrm{isoöctane}}$ Remembering that $(k_4/k_1)_{\mathrm{toluene}}$ is 0.19, we calculate $(k_4)_{\mathrm{toluene}}/(k_1)_{\mathrm{isoöctane}}$ to be 0.48. The latter value is not much greater than $(k_2)_{\mathrm{benzene}}/(k_1)_{\mathrm{isoöctane}}$, found to be[2] 0.29 at 65°. It was shown by Heilman[8] that the rate of addition of methyl radicals to substituted benzenes is only slightly enhanced by a substituent. Hence, the present result showing the methyl affinity of toluene to be about 1.65 greater than the methyl affinity of benzene seems to be plausible. It is interesting to mention at this juncture the work of Hey and his school[9] who showed that substituents enhance only slightly the rate of addition of phenyl radicals to the substituted benzenes.

Systems in Which the Olefinic or Aromatic Component Acts Also as a Hydrogen Atom Donor.—Let us consider a system in which molecule A adds methyl radicals and also serves as a hydrogen donor. The reactions of methyl radicals with the solvent molecules and the A molecules are represented by the three equations

$$\mathrm{CH_3 + HS \xrightarrow{k_1} CH_4 + S\cdot} \qquad (1)$$

$$\mathrm{CH_3 + A \xrightarrow{k_5} CH_4 + A'} \qquad (5)$$

$$\mathrm{CH_3 + A \xrightarrow{k_2} CH_3A} \qquad (2)$$

The ($\mathrm{CH_4}$ formed) is proportional to $(k_1X_{\mathrm{HS}} + k_5X_{\mathrm{A}})$, while the ($\mathrm{A{\cdot}CH_3}$ formed) is proportional to k_2X_{A}. Hence

$$(\mathrm{CH_4\ formed})/(\mathrm{A{\cdot}CH_3\ formed}) = k_1X_{\mathrm{HS}}/k_2X_{\mathrm{A}} + k_5/k_2$$

After rearrangement this expression acquires the form

$$\left\{\frac{(\mathrm{A{\cdot}CH_3\ formed})}{(\mathrm{CH_4\ formed})} \times \frac{X_{\mathrm{HS}}}{X_{\mathrm{A}}}\right\}^{-1} = \left(\frac{k_2}{k_1}\right)^{-1} + \frac{k_5}{k_2} \times \left(\frac{X_{\mathrm{A}}}{X_{\mathrm{HS}}}\right)$$

The left-hand side represents the reciprocal of the expression previously used in calculation of k_2/k_1, and denoted now as $(k_2/k_1)_{\mathrm{exp}}$. We conclude, therefore, that plotting of the reciprocal of $(k_2/k_1)_{\mathrm{exp}}$ *versus* $X_{\mathrm{A}}/X_{\mathrm{HS}}$ should lead to a straight line. The intercept of this line equals the reciprocal of k_2/k_1 and its slope gives k_5/k_2, *i.e.*, the probability of hydrogen abstraction to the probability of $\mathrm{CH_3}$ addition, both reactions referring to molecules A.

Such linear relations were tested by investigating a series of compounds which are not too powerful methyl radical acceptors and at the same time sufficiently good hydrogen donors.

Methyl Affinity of Allyl Acetate.—Allyl acetate is a not too reactive monomer and a self-inhibitor of its own polymerization. Studies of the polymerization of allyl acetate by Bartlett and Altschul[10] demonstrated that the molecular weight of polyallyl acetate is abnormally low, and from the kinetics of polymerization they deduced that the termination is due to the abstraction of a hydrogen atom from the monomer, the latter reaction competing efficiently with the propagation step.

Our studies of methyl affinities of allyl acetate were carried out in isoöctane solution at 65 and 85°. The results are listed in Table I and the plot of reciprocal of $(k_2/k_1)_{\mathrm{exp}}$ *versus* $X_{\mathrm{A}}/X_{\mathrm{HS}}$ is shown in Fig. 1. The expected linear relationship seems to be well obeyed and the data listed in Table II are derived from the intercepts and the slopes of the respective straight lines.

Table 1

Allyl Acetate[a]

T, °C.	Mole % of the monomer	$\mathrm{CH_4/CO_2}$	(k_2/k_1)exp.
65	1.02	0.500	58.5
65	2.05	.420(?)	43.6(?)
65	3.03	.331	55.1
65	5.05	.258	39.7
65	7.05	.225	33.8
85	1.02	.548	45.3
85	2.05	.401(?)	49.0(?)
85	3.03	.385	34.8
85	4.09	.335	32.9
85	6.06	.280	29.0
85	8.05	.270	22.6

[a] These experiments were carried out in 10^{-2} M solution of acetyl peroxide (for 65° runs) and 10^{-3} M solution of the peroxide (for 85° runs). $\mathrm{CH_4/CO_2}$ in pure isoöctane is 0.802 for 65° and 0.804 for 85°.

Table II

Allyl Acetate

Temp., °C.	k_2/k_1	Methyl affinity	k_5/k_2	k_5/k_1
65	8.4	29	0.23	1.9
85	5.7	14	.28	1.6

The values for k_2/k_1 thus obtained seem to be reasonable although somewhat lower than the corresponding value of k_2/k_1 for propylene; the latter was found to be 22 at 65° (unpublished results of Buckley from our laboratories). It would appear that the acetate group deactivates the propylene molecule. Also, the values of k_5/k_1 are reasonable if we compare them with the corresponding value obtained for toluene, about 2.5, since it is expected that the ease of abstraction of a hydrogen atom from the methyl group of toluene, propylene or the methylene group of allyl acetate should be comparable.

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[8] W. Heilman, Thesis, Syracuse Univ., New York, 1956.

[9] D. H. Hey, *et al.*, *J. Chem. Soc.*, 3412 (1953), and related papers.

[10] P. D. Bartlett and R. Altschul, This Journal, **67**, 812, 816 (1945).

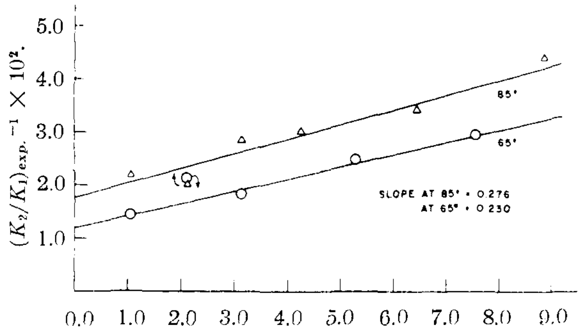

Fig. 1.—Allyl acetate $(K_2/K_1)_{exp.}^{-1}$ *versus* [monomer]/[solvent].

The temperature dependence of k_5/k_2 seems to indicate that the activation energy of hydrogen abstraction is higher than that of methyl radical addition. Furthermore, the temperature dependence of k_5/k_1 would indicate that the hydrogen abstraction from allyl acetate requires a lower activation energy than the hydrogen abstraction from isoöctane. All these conclusions appear to be reasonable.

Methyl Affinities of Butene-2's and Isobutene.—The investigation of these olefins showed again the concentration dependence of $(k_2/k_1)_{exp}$ expected for compounds exhibiting the dual behavior of hydrogen donors and methyl radical acceptors. All the experiments were carried out at 65° in isoöctane solution. From the data illustrated in Fig. 2 the following values were obtained.

	k_2/k_1	k_5/k_2	k_5/k_1
cis-Butene-2	3.3	0.95	3.1
trans-Butene-2	6.9	.7	4.7
Isobutene	36	.06	2.2

The values of k_5/k_1 are the most significant. Their magnitude is comparable to the k_5/k_1 for toluene (this ratio was denoted in the beginning of this paper by k_4/k_1) and the k_5/k_1 for allyl acetate. Furthermore, it appears that the crowding of the methyl groups in *cis*-butene-2 and in isobutene hinders the hydrogen atom abstraction, while this reaction is uninhibited in *trans*-butene-2.

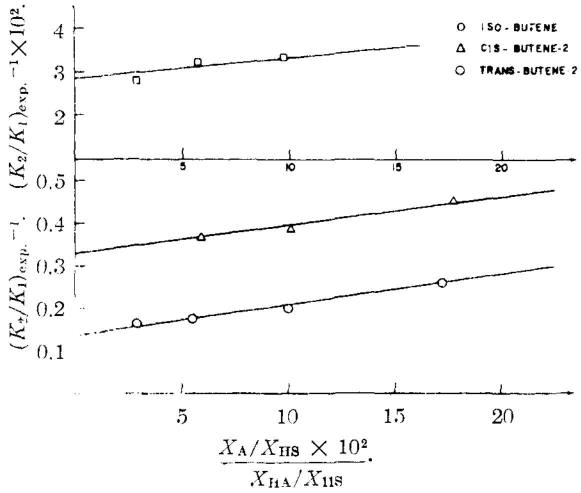

Fig. 2.

Methyl Affinity of Vinyl Phenyl Acetate.—Vinyl phenyl acetate has been chosen for these studies since it has been expected that the hydrogen atom abstraction from its methylene group should be extraordinarily easy. Indeed, the results, listed in Table III, and the plot of $(k_2/k_1)^{-1}_{exp}$ as a function of X_A/X_{HS}, shown in Fig. 3, confirm this expectation. The k_2/k_1 values for vinyl phenyl acetate are 92 at 65° and 62 at 85°, both being higher than the respective values for vinyl acetate.[1] The k_5/k_1 values are 55 at 65° and 51 at 85° indicating the enormous ease of abstraction of a hydrogen atom from vinyl phenyl acetate molecule. It is desirable to compare the values of the relative rate constants of hydrogen atom abstraction for the following molecules

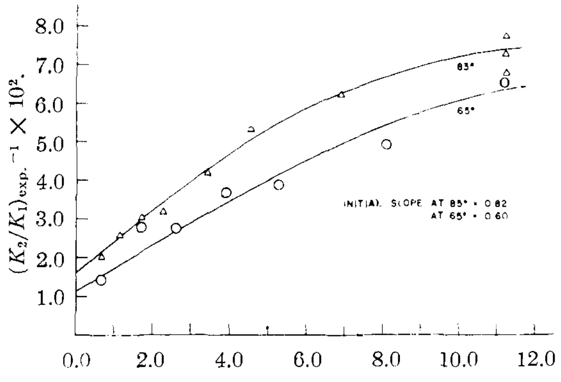

Fig. 3.—Vinyl phenyl acetate $(K_2/K_1)_{exp.}^{-1}$ *versus* [monomer]/[solvent].

TABLE III

VINYL PHENYL ACETATE IN ISOÖCTANE SOLUTION[a]

T, °C.	Mole % of the monomer	CH_4/CO_2	(k_2/k_1)exp
65	0.66	0.550	69
65	1.64	.502	36
65	2.52	.415	36
65	4.99	.342	26
65	10.1	.295	15
65	15.1	.306	9.1
85	0.66	.605	49.5
85	1.10	.565	38
85	1.64	.518	33
85	2.19	.474	31
85	3.29	.446	24
85	4.39	.435	18.5
85	6.47	.383	15.5
85	10.1	.330	12.7
85	10.1	.305	14.6
85	10.1	.319	13.6

[a] For details of experimentation see Table I.

Isoöctane	Toluene	Methyl ethyl ketone	Vinyl phenyl acetate
C_8H_{18}	$Ph{\cdot}CH_3$	$CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_3$	$CH_2{:}CH{\cdot}O{\cdot}CO{\cdot}CH_2Ph$
1	2.5	9	51

One notices that the hydrogen abstraction is facilitated by the presence of a phenyl group and even more by the presence of a carbonyl group. Since 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 $CH_2{:}CH{\cdot}O{\cdot}\underset{\cdot}{C}O{\cdot}\underset{\cdot}{C}H{\cdot}Ph$ 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.

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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