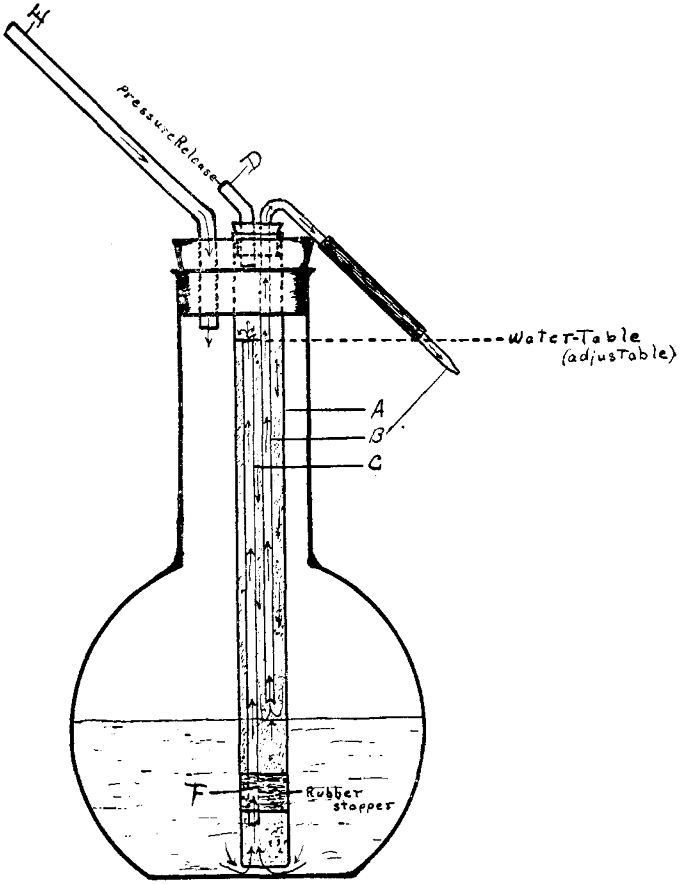

4. The tube A (12 mm.) projects up through the stopper and to the bottom of the bottle.

5. The intake C should be 4 mm. or as small as possible and still give sufficient flow. Its height determines the height of the water-table.

Note.—All calibrations are outside measurements. F. C. CLAPP.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

RELATIONS BETWEEN THE CONSTANTS OF DIBASIC ACIDS AND OF AMPHOTERIC ELECTROLYTES.

BY ELLIOT QUINCY ADAMS.

Received April 4, 1916.

This paper comprises some remarks on the ionization of polybasic acids, of their acid esters, of polyacid bases, and of amphoteric electrolytes.

The fact that the two dissociation constants of a dibasic acid seldom differ by a factor *less* than four or five appears in all experimental studies of such constants,[1] and Walker[2] observed that the constants of acid esters of symmetrical dibasic acids are never[3] more than half those of the acids from which they are derived. In the following discussion it will be shown that these results are to be expected.

The term amphoteric is applied to two classes of compounds—hydroxyl compounds, like $Zn(OH)_2$, which may lose either hydroxyl or hydrogen ion—and compounds like the amino acids which may gain or lose hydrogen ion; and in the latter case the practice of expressing the "base constant" of such electrolytes in terms of hydroxide ion concentration has very greatly obscured the results.[4]

In this paper the constants for amino acids and amines will be expressed in terms of hydrogen ion concentration, *e. g.*, for aniline[5] $K = (C_6H_5NH_2)(H^+)/(C_6H_5NH_3^+)$.

The first point to be investigated will be the relation between the two ionization constants of a dibasic acid. The ionization of such an acid is represented in Fig. 1 in which the two ionizable hydrogens are distinguished by being written, respectively, before and after the symbol A of the negative radical. K_1, K_2, K_3, K_4 are the respective constants for the reactions $HAH = H^+ + AH^-$, $HAH = HA^- + H^+$, $HA^- = H^+ + A^{--}$, $AH^- = A^{--} + H^+$, namely, $K_1 = (H^+)(AH^-)/(HAH)$, etc. (It follows that $K_1K_4 \equiv K_2K_3$.)

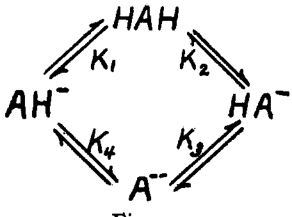

Fig. 1.

Expressions for the first and second ionization constants as ordinarily defined, K' and K''—since $(AH^-) + (HA^-)$ is the total concentration of intermediate ion—may be derived as follows:

$$K' = \frac{[(AH^-) + (HA^-)](H^+)}{(HAH)} = K_1 + K_2 \qquad (1)$$

$$K'' = \frac{(A^{--})(H^+)}{(AH^-) + (HA^-)} = \frac{1}{1/K_4 + 1/K_3} = \frac{K_3K_4}{K_3 + K_4} \qquad (2)$$

From these general equations may be derived the simpler equations for certain special cases.

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[1] Cf. E. E. Chandler, THIS JOURNAL, 30, 707 (1908).

[2] J. Walker, *J. Chem. Soc.*, 61, 715–7 (1892).

[3] Adipic acid (*Loc. cit.*) is only an apparent exception, for the fall in the observed constant on dilution shows clearly, as Walker himself pointed out, the presence of some conducting impurity.

[4] As will be shown later.

[5] In the following equation $(C_6H_5NH_2)$ means the aggregate concentration of aniline and all of its hydrates, just as (H^+) means the aggregate concentration of hydrogen ion and all of its hydrates, etc.

The simplest of these is that in which the acid is symmetrical and the hydrogens independent of each other's ionization. Then $K_1 = K_2 = K_3 = K_4 = K$ and Equations 1 and 2 become

$$K' = 2K; \; K'' = {}^1/_2K. \qquad (3)\ (4)$$

The condition of symmetry is easily satisfied, that of adequate separation of the hydrogens not so easily, for in the "straight chain" of five or six carbon atoms ring formation is possible and hence the ends of the chain may be near one another even when no ring is formed. In the derivatives of triphenylmethane the rigidity of the benzene rings may be trusted to keep *para*-substituents in the several rings apart; and the best examples of Equations 3, 4 are found in such derivatives. Thus the two constants for phenolphthalein[1] as determined colorimetrically by Rosenstein[2] are $K' = 11.5 \times 10^{-10}$, $K'' = 2.83 \times 10^{-10}$, whence $K'/K'' = 4.06$. while the first two constants of crystal violet as determined spectrophotometrically by Adams and Rosenstein[3] and expressed in terms of acid concentration (although crystal violet is a base) are 1.62×10^{-2} and 6.6×10^{-2}, whence K'/K'' for the yellow salt, regarded as a dibasic acid, is 4.08. The extreme closeness to 4 is accidental, as the ratio, in the second case at least, is uncertain to five per cent. or more.

Chandler[4] has shown that the ratio of the constants for dibasic organic acids approaches this value at high concentrations.

For *independently* ionizable hydrogens in an unsymmetrical acid $K_3 = K_1$, $K_4 = K_2$ and Equation 2 becomes

$$K'' = \frac{K_1K_2}{K_1 + K_2}. \qquad (5)$$

If the hydrogens are not sufficiently separated to ionize independently, we may generalize from the behavior of oxalic acid and its immediate homologs, whose first constants are markedly greater and whose second constants are distinctly less than the ionization constants of the corresponding fatty acids; and state the principle that a negative group in-

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[1] Un-ionized phenolphthalein and its singly charged ion are colorless, and are therefore supposed to be entirely in the lactone form; the doubly charged ion is pink and consists of a mixture, in tautomeric equilibrium, of the ion of colorless phenolphthalein and that of an unsymmetrical quinoid phenol-acid, $O:C_6H_4:C(C_6H_4OH)-C_6H_4CO_2H$. Since the ratio of the two constants. determined experimentally, agrees with that for a symmetrical dibasic acid. the quinoid ion can constitute only a few per cent., at most, of the tautomeric mixture.

[2] L. Rosenstein, THIS JOURNAL, 34, 1117 (1912); cf. phenol, $K = 1.1 \times 10^{-10}$.

[3] E. Q. Adams and L. Rosenstein, THIS JOURNAL, 36, 1452 (1914). In crystal violet the quinoid basic group is not involved in the change from the violet to the green and yellow forms. The two remaining nitrogens are equivalent, hence the yellow ion is symmetrical with respect to the two hydrogens which it is able to lose.

[4] E. E. Chandler, THIS JOURNAL, 30, 707 (1908).

creases and a negative charge diminishes the ionizability of any hydrogen in the molecule, whence $K_3 < K_1$, $K_4 < K_2$ and Equation 2 becomes

$$K'' < \frac{K_1K_2}{K_1 + K_2}. \qquad (6)$$

Dividing (1) by (6)

$$\frac{K'}{K''} > \frac{(K_1 + K_2)^2}{K_1K_2} > \frac{(K_1 + K_2)^2}{K_1K_2} - \frac{(K_1 - K_2)^2}{K_1K_2}$$

but

$$\frac{(K_1 + K_2)^2}{K_1K_2} - \frac{(K_1 - K_2)^2}{K_1K_2} = \frac{4K_1K_2}{K_1K_2} = 4,$$

whence

$$\frac{K'}{K''} > 4. \qquad (7)$$

That is to say, the first ionization constant will in general be more than four times[1] the second, the limiting ratio of 4 being found in *symmetrical* acids whose hydrogens are widely separated (and, therefore, *independently ionizable*).

For a *tribasic* acid it may be shown in similar fashion that the limiting ratio between successive constants is 3; indeed the calculation may be made for an acid with any number of hydrogens.

The truth of the conclusion for dibasic acids may be seen in Table I. The data are taken, unless otherwise indicated from Scudder,[2] and are, in general, at 25°.

The acid esters of dibasic acids will differ from the acids in two ways: by the loss of one hydrogen and by the effect on the other hydrogen of the substitution. If the second effect—which will be in general a decrease in the "polar character" of the molecule and, therefore, of the ionization—be neglected, then, as Wegscheider[3] showed, the ionization constant for the *acid* ester of a *symmetrical* dibasic acid will be one-half the first constant of the acid, and the *sum* of the constants for the two isomeric acid esters of an unsymmetrical dibasic acid will be *equal* to the first constant of the acid. Table II shows in how far this expectation is borne out.

To amphoteric electrolytes Equations 1, 6 and 7 derived above, apply directly if the constant of the basic part of the molecule be expressed in terms of hydrogen ion concentration. Much of the supposedly anomalous behavior of amphoteric electrolytes is due to the neglect of the possibility that the constants so expressed will be related in such a

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[1] Cf. E. E. Chandler, *Loc. cit.*

[2] Scudder, "The Electrical Conductivity and Ionization Constants of Organic Compounds," Van Nostrand (1914).

[3] R. Wegscheider, *Monatsh. Chem.*, **16,** 153 (1895).

TABLE I.

Acid.	K′.	K″.	K′/K″.
$(CO_2H)_2$	0.10	4.9×10^{-5}	2000
$CH_2(CO_2H)_2$	1.6×10^{-3}	2.0×10^{-6}	800
$(CH_2)_2(CO_2H)_2$	6.8×10^{-5}	2.7×10^{-6}	25
$(CH_2)_3(CO_2H)_2$	4.7×10^{-5}	2.9×10^{-6}	16.2
$(CH_2)_4(CO_2H)_2$	3.6×10^{-5}	2.8×10^{-6}	12.9
$(CH_2)_5(CO_2H)_2$	3.4×10^{-5}	[1] 2.6×10^{-6}	13.1
$(CH_2)_6(CO_2H)_2$	3.0×10^{-5}	[2] 2.3×10^{-6}	13.0
$(CH_2)_7(CO_2H)_2$	2.7×10^{-5}	[3] 2.4×10^{-6}	11.3
$(CH_2)_8(CO_2H)_2$	2.6×10^{-5}	2.6×10^{-6}	10.0
$H(CH_2)_7CO_2H$	1.4×10^{-5}		
cis-$C_2H_2(CO_2H)_2$	1.3×10^{-2}	[4] 2.6×10^{-7}	50000
trans-$C_2H_2(CO_2H)_2$	1.0×10^{-3}	[5] 2.2×10^{-5}	45
o-$C_6H_4(CO_2H)_2$	1.2×10^{-3}	[6] 3.1×10^{-6}	390
m-$C_6H_4(CO_2H)_2$	2.9×10^{-4}	[7] 2.4×10^{-5}	12
$C_8H_{14}(CO_2H)_2$	2.3×10^{-5}	[8] 0.7×10^{-6}	33
cis-p-$C_6H_{10}(CO_2H)_2$	3.0×10^{-5}	3.0×10^{-6}	10
trans-p-$C_6H_{10}(CO_2H)_2$	4.6×10^{-5}	2.5×10^{-6}	18
[9] H_2SO_4	0.45	1.7×10^{-2}	26
[9] H_2SO_4	1.7×10^{-2}	5.0×10^{-6}	3400
[9] H_2CO_3	3.0×10^{-7}	1.3×10^{-11}	23000

way that the constant determined in acid solution is the acid constant and that in alkaline solution the basic constant.

Aminoacetic acid, for example, has the constants $K_A = 1.8 \times 10^{-10}$, $K_B = 2.8 \times 10^{-12}$, which become in the notation used in this article $K'' = 1.8 \times 10^{-10}$, $K' = \dfrac{1.0 \times 10^{-14}}{K_B} = 3.7 \times 10^{-3}$, which are to be compared with the constants for methylamine $K = \dfrac{1.0 \times 10^{-14}}{4.1 \times 10^{-14}} = 2.4 \times 10^{-11}$, N-benzoyl aminoacetic acid, $K = 2.2 \times 10^{-4}$, acetic acid, $K = 1.8 \times 10^{-5}$, N-acetyl aminoacetic acid, $K = 2.3 \times 10^{-4}$, chloroacetic acid, $K = 1.6 \times 10^{-3}$, showing that aminoacetic acid is at once an acid stronger than monochloroacetic acid and a base nearly as strong as methylamine.

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[1] By inversion; by partition $= 4.4 \times 10^{-6}$.

[2] By inversion; by conductivity $= 1.9 \times 10^{-6}$; by partition $= 3.7 \times 10^{-6}$.

[3] By conductivity; by partition $= 3.3 \times 10^{-6}$.

[4] By conductivity; by partition 2.0×10^{-7}; by inversion 3.9×10^{-7}, 5.5×10^{-7}.

[5] By partition and inversion; by conductivity 3.0×10^{-5}.

[6] By partition; by conductivity 3.9×10^{-6}; by inversion 1.7×10^{-6}, 2.2×10^{-6}.

[7] By conductivity; by partition 2.7×10^{-5}; by inversion 1.0×10^{-5}.

[8] These values are given for *d*-, *l*-, and *dl*-camphoric acids. Chandler (*Loc. cit.*) gives for the second constant of *d*-camphoric acid (by conductivity) $K'' = 14 \times 10^{-6}$, but he uses $K' = 2.3 \times 10^{-4}$ in his calculations (apparently by mistake). As camphoric acid is an unsymmetrical acid it was rather surprising to find for it constants whose ratio is less than 2.

[9] *Landolt-Börnstein Tabellen* (1912 edition).

TABLE II.

Symmetrical Acids.

Acid.	K′.	Ester.	K.
$CH_2(CO_2H)_2$	1.6×10^{-3}	Ethyl	0.46×10^{-3}
$(CH_2)_2(CO_2H)_2$	6.8×10^{-5}	Methyl	3.2×10^{-5}
		Ethyl	3.0×10^{-5}
$(CH_2)_4(CO_2H)_2$	4.2×10^{-5}	Ethyl	2.5×10^{-5}
$(CH_2)_6(CO_2H)_2$	3.0×10^{-5}	Ethyl	1.5×10^{-5}
$(CH_2)_8(CO_2H)_2$	2.8×10^{-5}	Ethyl	1.4×10^{-5}
cis-$C_2H_2(CO_2H)_2$	1.3×10^{-2}	Ethyl	0.11×10^{-2}
trans-$C_2H_2(CO_2H)_2$	1.0×10^{-3}	Ethyl	0.48×10^{-3}
o-$C_6H_4(CO_2H)_2$	1.2×10^{-3}	Methyl	0.66×10^{-3}
		Ethyl	0.55×10^{-3}
d-$(CHOHCO_2H)_2$	9.7×10^{-4}	Methyl	4.6×10^{-4}
$(CH_3)_2C(CO_2H)_2$	7.6×10^{-4}	Methyl	3.1×10^{-4}
m-$(CHCH_3CO_2H)_2$	1.4×10^{-4}	Methyl	0.45×10^{-4}
dl-$(CHCH_3CO_2H)_2$	2.1×10^{-4}	Methyl	0.6×10^{-4}
3,6-$Cl_2C_6H_2(CO_2H)_2$(1,2)	3.4×10^{-2}	Ethyl	1.5×10^{-2}

Unsymmetrical Acids.

Acid.	K′.	Ester.	K_1.	K_2.
$C(CH_3)_2CH_2(CO_2H)_2$	8.0×10^{-5}	Methyl	2.3×10^{-5}	2.6×10^{-5}
3-$NO_2C_6H_3(CO_2H)_2$(1,2)	1.3×10^{-2}	Methyl	1.7×10^{-2}	0.3×10^{-2}
4-$NO_2C_6H_3(CO_2H)_2$(1,2)	7.7×10^{-3}	Methyl	3.0×10^{-3}	5.2×10^{-3}
2-$NO_2C_6H_3(CO_2H)_2$(1,4)	1.9×10^{-2}	Methyl	0.08×10^{-2}	2.0×10^{-2}
2-$BrC_6H_3(CO_2H)_2$(1,4)	6.2×10^{-3}	Methyl	0.37×10^{-3}	5.0×10^{-3}
4-$(OH)C_6H_3(CO_2H)_2$(1,2)	1.2×10^{-3}	Methyl	0.15×10^{-3}	0.20×10^{-3}
2-$(OH)C_6H_3(CO_2H)_2$(1,4)	2.7×10^{-3}	Methyl	0.25×10^{-3}	2.77×10^{-3}
o-$C_6H_4(CO_2H)(CH_2CO_2H)$	1.9×10^{-4}	Methyl	0.43×10^{-4}	0.76×10^{-4}
		Ethyl	0.46×10^{-4}	0.71×10^{-4}
(3,4)$(CH_3O)_2C_6H_2(CO_2H)_2$(1,2)	1.17×10^{-3}	Methyl	[1]0.17×10^{-3}	1.30×10^{-3}
		Ethyl	0.15×10^{-3}	1.01×10^{-3}
		Propyl	0.15×10^{-3}	0.93×10^{-3}

Since K′ is several million times as great as K″, and is unquestionably the measure of the ionization of the carboxyl, aminoacetic acid will be almost exclusively the "inner salt," $N^+H_3CH_2CO_2^-$, with less than one part per million of true amino acid, $NH_2CH_2CO_2H$. In the case of the aminobenzoic acids (see below) this fraction becomes about 1%. It should be pointed out that aminoacetic acid appears to be an exception to the general rule that a negative charge diminishes the ionization of any hydrogen in the molecule, for whereas acetic acid, CO_2HCH_3, loses its hydrogen more readily than acid malonate ion, $CO_2HCH_2CO_2^-$, methylammonium ion, $N^+H_3CH_3$, loses hydrogen ion less readily than aminoacetic acid, $H^+N_3CH_2CO_2^-$. The aminobenzoic acids do not show this anomaly, for, as bases, they are stronger than aniline.

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[1] The data are from Scudder, but the designations α and β have been interchanged in the case of the methyl and propyl esters to agree with Wegscheider, as Scudder quotes Wegscheider and assigns no reason for the changes.

Comparing the aminobenzoic acids with benzoic acid, $K = 6.7 \times 10^{-5}$ and aniline $K = 1.0 \times 10^{-14}/4.6 \times 10^{-10} = 2.2 \times 10^{-5}$, and with their respective N-acetyl derivatives:

Acid.	$K_B = 1.0 \times 10^{-14}/K'$.	K'.	$K_A = K''$.	K(acetyl-).
o-Aminobenzoic	1.37×10^{-12}	7.3×10^{-3}	1.1×10^{-5}	2.4×10^{-4}
m-Aminobenzoic	1.22×10^{-11}	0.82×10^{-3}	1.6×10^{-5}	0.85×10^{-4}
p-Aminobenzoic	2.33×10^{-12}	4.3×10^{-3}	1.2×10^{-5}	0.52×10^{-4}
Chloroacetic acid	......	1.6×10^{-3}	......	......
m-Toluidine	5.8×10^{-10}	......	1.7×10^{-5}	......
p-Toluidine	1.8×10^{-10}	......	0.56×10^{-5}	......

the meta-acid is thus slightly weaker than monochloroacetic acid, the ortho- and para-acids stronger, while as bases all three lie between *m*- and *p*-toluidine, the ortho-acid being twice as strong a base as aniline.

The strongly *negative* character of the NH_2 group may also be seen in the antagonistic action of neighboring NH_2 groups.

	$K_B = K_W/K'$.	K'.		$K_1 = K_W/K''$.	K''.
[1]NH_3	1.8×10^{-5}	$55. \times 10^{-11}$	N_2H_4	$3. \times 10^{-6}$	$300. \times 10^{-11}$
$C_2H_5NH_2$	5.6×10^{-4}	1.8×10^{-11}	[3]$(CH_2)_2(NH_2)_2$	0.85×10^{-4}	11.8×10^{-11}
$C_3H_7NH_2$	4.7×10^{-4}	2.1×10^{-11}	$(CH_2)_3(NH_2)_2$	3.5×10^{-4}	2.9×10^{-11}
[2]*iso*-$C_4H_9NH_2$	3.1×10^{-4}	3.2×10^{-11}	$(CH_2)_4(NH_2)_2$	5.1×10^{-4}	2.0×10^{-11}
[2]*iso*-$C_5H_{11}NH_2$	5.0×10^{-4}	2.0×10^{-11}	$(CH_2)_5(NH_2)_2$	7.3×10^{-4}	1.4×10^{-11}

Summary.

1. For polybasic acids the ionization constants K' and K'' as ordinarily defined are related to the constants, K_1, K_2, for the separate removal of the respective hydrogens, thus:

$$K' = K_1 + K_2 \qquad (1)$$

$$K'' < \frac{K_1K_2}{K_1 + K_2}, \qquad (6)$$

whence

$$\frac{K'}{K''} > 4. \qquad (7)$$

2. Phenolphthalein and crystal violet give values for this ratio very near the limiting value. (At high concentrations of dibasic organic acids, E. E. Chandler has shown that this same limit is approached.)

3. The acid esters of a symmetrical dibasic acid have constants equal to approximately one-half the first constant of the acid, while the sum of the constants of the isomeric esters of an unsymmetrical dibasic acid is approximately equal to the first constant of the acid. (This generalization is due to Wegscheider.)

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[1] Not given in Scudder.

[2] Normal amine not given.

[3] For ethylenediamine $K' = 1.0 \times 10^{-14}/6.0 \times 10^{-7} = 1.7 \times 10^{-8}$; for the others it is not given. It is to be remembered that a larger constant means a stronger acid or a weaker base.

4. The constants of aminoacetic acid and the aminobenzoic acids are explained by the strong *negative* character of the NH_2 group.

BERKELEY, CAL.

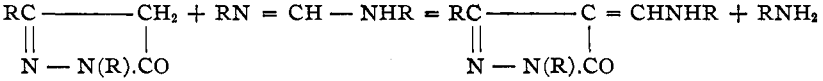
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF KANSAS.]

ON THE REACTIONS OF THE FORMAMIDINES. V. ON SOME PYRAZOLONE DERIVATIVES.

BY F. B. DAINS, H. R. O'BRIEN AND C. L. JOHNSON.

Received May 31, 1916.

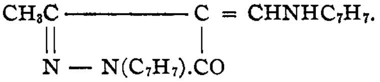
This is a continuation of a previous investigation on the pyrazolones,[1] where it was shown that the methylene group in this class of derivatives reacted with the formamidines, the hydrogen being replaced by the grouping >CHNHR. The general equation can be formulated as follows,



$$\begin{array}{lcl}\mathrm{RC{-}{-}{-}{-}CH_2} & & \mathrm{RC{-}{-}{-}{-}C = CHNHR + RNH_2}\\ \| \qquad | & + \mathrm{RN = CH - NHR} = & \| \qquad | \\ \mathrm{N - N(R).CO} & & \mathrm{N - N(R).CO}\end{array}$$

the reaction yielding a substituted 4-amino methylene pyrazolone and the free amine. The following paper includes further experimental evidence as to the general nature of this reaction and a partial study of the action of certain reagents upon the substituted pyrazolones.

4-*m*-Toluido-methylene-1-*p*-tolyl-3-methyl-5-pyrazolone,



$$\begin{array}{l}\mathrm{CH_3C{-}{-}{-}{-}C = CHNHC_7H_7.}\\ \quad \| \qquad\quad | \\ \mathrm{N - N(C_7H_7).CO}\end{array}$$

Molar quantities of the pyrazolone and di-*m*-tolyl formamidine were heated for twenty minutes in an oil bath at 150°. From the reaction product the new compound was isolated after treatment with dilute hydrochloric acid, which removed *m*-toluidine. This separated from alcohol in golden yellow crystals melting at 122°.

Calc. for $C_{19}H_{19}ON_3$: N, 13.78%. Found, 13.85%.

Under like conditions the pyrazolone and di-*o*-tolyl formamidine gave 4-*o*-toluido-methylene-1-*p*-tolyl-3-methyl-5-pyrazolone, yellow needles from alcohol which melt at 176.5°.

Calc. for $C_{19}H_{19}ON_3$: N, 13.78%. Found: 13.86%, 13.69%.

The ease of reaction of different formamidines seems to vary greatly. While many require heating at 120–150° in order to ensure condensation, others unite at much lower temperature. Thus *p*-tolyl methyl pyrazolone and di-*o*-phenetidyl formamidine at water-bath temperature gave the amine and 1-*p*-tolyl-3-methyl-4-*o*-ethoxyanilido-5-pyrazolone. It crystallizes from alcohol in canary-yellow needles with a melting point of 133°. The same reaction occurs slowly when the components are ground together in a mortar and allowed to stand.

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[1] Dains and Brown, THIS JOURNAL, 31, 1153 (1909).