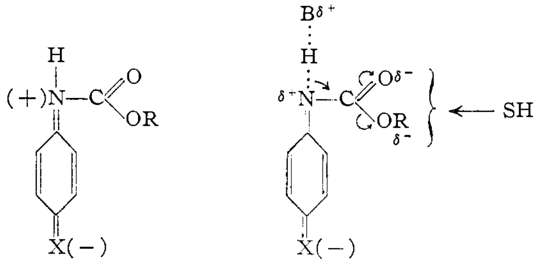
however, they solvate more with the transition state and less with the ground state. Consequently the lower activation energy and greater negative entropy of activation in the activation process is expected.



ground state transition state

A similar argument suggests that urethans with electron-donating substituents are slow to donate a proton; however, they solvate more with the ground state and solvation in the transition state is not so noticeable as in the former urethans. Therefore the higher activation energy and a lower negative entropy of activation is expected.

ortho Substituted urethans give a lower activation energy and a more negative entropy of activation than those of urethans correspondingly substituted in the *meta* and *para* positions. Because of the steric strain in *ortho* derivatives, the hydrogen atom of the urethan linkage becomes more acidic, and donates a proton to a base more readily and thus lowers the activation energy. However, solvation is less with the ground state by reason of steric hindrance of the *ortho* substituents. This may explain the more negative entropy in *ortho* derivatives.

Acknowledgment.—The authors wish to express their hearty thanks to Prof. Toshio Hoshino for his encouragement throughout the course of this experiment.

MEJIRO, TOSHIMA-KU, TOKYO, JAPAN

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE SPRAGUE ELECTRIC CO.]

Molecular Compounds. VIII. Evidence for the Existence of 2:1 and 1:2-Complexes in Chloroform Solutions of 1,3,5-Trinitrobenzene and N,N-Dimethylaniline

BY SIDNEY D. ROSS AND MORTIMER M. LABES

RECEIVED JULY 30, 1956

It is shown that 1,3,5-trinitrobenzene and N,N-dimethylaniline form 1:2- and 2:1-complexes as well as a 1:1-complex in chloroform solution. The effects of the presence of the 1:2- and 2:1-complexes on the determination of the equilibrium constant for formation of the 1:1-complex have been explored. The equilibrium constants and extinction coefficients have been determined for the 1:1-complex and 1:2-complex.

The equilibrium constant for formation of the 1:1 1,3,5-trinitrobenzene–N,N-dimethylaniline complex in chloroform solution at 17.5° has been measured by Ley and Grau[1] both by a solubility method and spectroscopically. The first method gave an average value of 1.45 l. mole^{-1}; the latter method resulted in an average value of 1.82 l. mole^{-1}, and the authors considered the first of these values the more reliable one. More recent spectroscopic measurements by Foster and Hammick[2] have resulted in a value of 1.3 l. mole^{1} for the equilibrium constant at 21°.

In connection with other studies, we have recently measured this equilibrium constant at 24.8 ± 0.1° by the spectroscopic method. Our initial values were strongly at variance with all three of the previous results and led to the more detailed study which is described below.

Experimental

Solvents and Reagents.—Baker and Adamson Reagent Grade chloroform, containing 0.75% ethanol as stabilizer, was used without further purification. Eastman Kodak Co. white label aniline and N,N-dimethylaniline were distilled *in vacuo* from calcium hydride immediately before use, and the middle fractions, b.p. 65° at 8 mm. and 70° at 10 mm., respectively, were used. 1,3,5-Trinitrobenzene, Eastman Kodak Co. white label, was crystallized once from glacial acetic acid and twice from absolute ethanol; m.p. 121°. Naphthalene, Eastman Kodak Co. white label, was crystallized twice from methanol as colorless plates, m.p. 80–81°.

The 1:1 1,3,5-trinitrobenzene–N,N-dimethylaniline complex was prepared by pouring a hot, concentrated solution of the trinitrobenzene in ethanol into a slight excess of hot N,N-dimethylaniline. On cooling, the complex separates as dark violet needles, m.p. 105–108°, m.p. 110–111° after crystallization from ethanol.[3]

The 1:1 1,3,5-trinitrobenzene–aniline complex was prepared in the same manner. It was obtained as orange-red crystals, m.p. 124–125.5° after crystallization from ethanol.[3]

The 1:1 1,3,5-trinitrobenzene–naphthalene complex was prepared by dissolving separately equimolar amounts of the two components in minimum amounts of hot ethanol and mixing the two solutions. On cooling, the 1:1-complex separates as pale yellow needles, m.p. 153–154°.[3]

The Absorption Spectra Measurements.—Stoppered 1-cm. absorption cells were used in a Beckman model DU spectrophotometer. The cell housing was maintained at constant temperature by means of two Beckman thermospacers through which water from a constant temperature bath was circulated. A detailed description of the experimental methods used in determining the equilibrium constant has been given previously.[4]

Results and Discussion

Table I presents the results of representative measurements of the equilibrium constant for formation of the 1:1 1,3,5-trinitrobenzene–N,N-dimethylaniline complex in chloroform at 24.8 ± 0.1°. These measurements result from thirteen different sets of amine and trinitrobenzene concentrations, with the former varied from 0.92

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(1) H. Ley and R. Grau, *Ber.*, **58**, 1765 (1925).

(2) R. Foster and D. Ll. Hammick, *J. Chem. Soc.*, 2685 (1954).

(3) P. Hepp, *Ann.*, **215**, 358, 377 (1882).

(4) S. D. Ross, M. Bassin, M. Finkelstein and W. A. Leach, THIS JOURNAL, **76**, 69 (1954).

to 0.26 *M*, and the latter from 0.0005 to 0.0027 *M*. The tabulated K's and ϵ's were determined by the usual method[4]; the method of least squares was used, in all cases, to define the best straight line through the experimental points.

TABLE I

EQUILIBRIUM CONSTANT AND EXTINCTION COEFFICIENTS OF THE 1,3,5-TRINITROBENZENE–N,N-DIMETHYLANILINE COMPLEX IN CHLOROFORM AT 24.8 ± 0.1°; TRINITROBENZENE-AMINE RATIOS FROM 5.8×10^{-4} to 7.0×10^{-3}

Wave length, mμ	K, l. mole^{-1}	ϵ
460	0.60	1760
470	.62	1800
490	.65	1800
510	.70	1630
520	.70	1530

Two features of these data stand out. The first is the striking difference between these results and the values previously reported.[1,2] The average value for K, based on the results in Table I, is 0.65 l. mole^{-1}, and the maximum deviation from this average value is less than 8%. Nevertheless, there is a definite tendency for the measured K to increase with increasing wave length.

Table II presents the data for another representative set of measurements of the equilibrium constant. In this case, the ratio of amine to trinitrobenzene was decreased by increasing the trinitrobenzene concentrations and decreasing the amine concentrations. Nine different sets of concentrations were used, and the amine concentrations were varied from 0.31 to 0.12 *M* and the trinitrobenzene concentrations from 0.0025 – 0.005 *M*.

TABLE II

EQUILIBRIUM CONSTANT AND EXTINCTION COEFFICIENTS OF THE 1,3,5-TRINITROBENZENE–N,N-DIMETHYLANILINE COMPLEX IN CHLOROFORM AT 24.8 ± 0.1°; TRINITROBENZENE-AMINE RATIOS FROM 8.0×10^{-3} TO 2.2×10^{-2}

Wave length, mμ	K, l. mole^{-1}	ϵ
440	0.83	1130
470	.79	1470
490	.85	1430
520	.92	1210
560	1.06	712

These values of K are appreciably higher, but still very much lower than the previously reported values. In this case, the variation of K with wave length is much more pronounced; the maximum deviation from the average value is 19%, yet in both sets of data the experimental points all fall satisfactorily on the least squares straight lines. The sizable differences in the determined K's, as between the two sets of data, make it apparent that the values of K are strongly concentration dependent. Nevertheless, for both sets of data, the product $K\epsilon$, at any given wave length, is very nearly constant. Thus, at 470 mμ, the $K\epsilon$'s equal 1120 and 1160; at 490 mμ, the values are 1170 and 1220; at 520 mμ the values are 1110 and 1070.

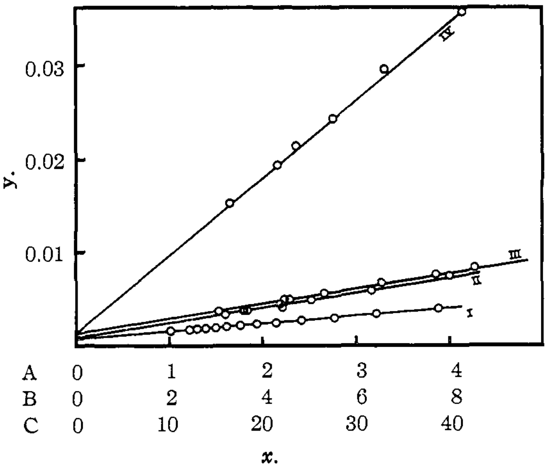

Fig. 1.—Plots of data at 490 mμ. For lines I, II and III, $x = 1/A_0 + T_0$ and $Y = A_0T_0/d_c(A_0 + T_0)$. For line IV, $x = 1/2(TA)_0$, $Y = (TA)_0/2d_c$. For the x-values, use scale A for line I, scale B for lines II and III, and scale C for line IV.

The foregoing is illustrated graphically in Fig. 1 for the data at 490 mμ. The straight lines are the least squares straight lines. Line I is for the data of Table I, and line II is for the data of Table II. These straight lines are obtained by plotting

$$y = \frac{A_0T_0}{d_c(A_0 + T_0)} \ vs.\ x = \frac{1}{A_0 + T_0}$$

where A_0 is the initial amine concentration, T_0 is the initial trinitrobenzene concentration, and $d_c = d_T - A_0\epsilon_A - T_0\epsilon_T$, where d_T is the total measured optical density. The intercepts for these lines are equal to $1/\epsilon$ and the slopes are equal to $1/K\epsilon$. The least squares values for the slope and intercept, respectively, for line I are 8.55×10^{-4} and 5.56×10^{-4}; for line II the values are 8.18×10^{-4} and 6.98×10^{-4}.[5]

Let us now consider what would be the consequences if the solutions which we have studied contained some 1:2 trinitrobenzene-N,N-dimethylaniline complex along with the 1:1 complex. The presence of 1:2-complex would not appreciably alter the x-values plotted in Fig. 1, but the y-values would be too small, since the measured d_c's would be too high. If 1:2 complex is present

$$d_c = d_T - \epsilon_A A_0 - \epsilon_T T_0 = \epsilon_{TA} TA + \epsilon_{TA_2} TA_2$$

and the correct value of d_c to use in determining K and ϵ for the 1:1 complex is $d_c - \epsilon_{TA_2} TA_2$. If ϵ_{TA_2} is comparable in magnitude to ϵ_{TA}, and if the concentration of TA is appreciably larger than the concentration of TA_2, we would qualitatively expect a lower intercept for the data of Table I, since the amine concentrations were higher in this case, and this would result in relatively higher TA_2 concentrations. Also, we might expect the differences in the slopes as between the two sets of experiments to be minor. This, in fact, is what we observe.

If the presence of a 1:2-complex is the only disturbing element, it should be possible to obtain

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(5) To be rigorously correct, we should plot $y = \frac{A_0T_0}{d_c(A_0 + T_0 - TA)}$ *vs.* $x = \frac{1}{A_0 + T_0 - TA}$, where TA is the equilibrium concentration of the complex. For the data of Table II, if we use the first value of K to calculate TA and then correct the data at 490 mμ accordingly, the value of K changes from 0.854 l. mole^{-1} to 0.856 l. mole^{-1}.

reliable values of K and ϵ for the 1:1-complex by making measurements in solutions in which the ratios of the trinitrobenzene concentrations to the amine concentrations are kept very large. The results of such an experiment are shown in Table III, and a plot of the data at 490 mμ is shown in Fig. 1 (straight line III). For these measurements, seven different sets of amine and trinitrobenzene concentrations were used; the former were varied from 0.005 to 0.01 M, the latter from 0.32 to 0.10 M.

TABLE III

EQUILIBRIUM CONSTANT AND EXTINCTION COEFFICIENTS OF THE 1,3,5-TRINITROBENZENE–N,N-DIMETHYLANILINE COMPLEX IN CHLOROFORM AT 24.8 ± 0.1°; TRINITROBENZENE–AMINE RATIOS FROM 11–64

Wave length, mμ	K, l. mole^{-1}	ϵ
460	1.14	926
470	1.18	954
490	1.23	959
510	1.18	954
520	1.14	926
560	1.12	623

For this set of measurements, the average K is 1.17 l. mole^{-1}. The maximum deviation from the average value is 5.1%, and the average deviation is only 3.2%. The values of the equilibrium constant show no trend with wave length, and, finally, the result is in excellent agreement with the value reported by Foster and Hammick.[2] Referring now to the data at 490 mμ (Fig. 1, line III), the slope, 8.48×10^{-3}, is again relatively unchanged from the slopes obtained in the previous experiments, but the intercept is appreciably higher (10.4×10^{-4} compared to the previous values of 5.56×10^{-4} and 6.98×10^{-4}). In this case, we have eliminated the disturbance due to the presence of TA_2, and the measured d_c's are more probably the correct d_c's for 1:1-complex formation.

However, by making the T_0/A_0 ratios large, we have introduced the possibility that a 2:1 complex, T_2A, may be present in these solutions. Complexes involving two acceptor molecules have been isolated as crystalline solids,[6] and in many instances the acceptor involved was 1,3,5-trinitrobenzene.[7]

Where both a TA_2 and a T_2A complex may be formed, the best conditions for obtaining reliable values for the equilibrium constant for formation of the 1:1-complex are to make measurements in relatively dilute solutions and to keep the trinitrobenzene amine ratios as near to one as possible. In this particular case, this last condition can be very handily met by starting with the 1:1 1,3,5-trinitrobenzene-N,N-dimethylaniline complex, which is a known, stable, crystalline solid.[3] This assures initial trinitrobenzene amine ratios of exactly one, and it may be shown, in a manner analogous to that used by Keefer and Andrews,[8] that for this condition

$$\frac{(TA)_0^2}{2d_c[(TA)_0 - TA]} = \frac{1}{K\epsilon_{TA}}\left(\frac{1}{2(TA)_0 - TA}\right) + \frac{1}{\epsilon_{TA}} \quad (1)$$

where $(TA)_0$ and TA are the initial and equilibrium 1:1-complex concentrations, respectively. In the usual case $(TA)_0 \gg TA$, and equation 1 simplifies to

$$\frac{(TA)_0}{2d_c} = \frac{1}{K\epsilon_{TA}}\left(\frac{1}{2(TA)_0}\right) + \frac{1}{\epsilon_{TA}} \quad (2)$$

and K and ϵ_{TA} are determined as before.[4]

Table IV summarizes the results obtained starting with the 1:1 complex. In this case, six different concentrations varying from 0.01 to 0.03 M, of the complex were used. The tabulated values were calculated using equation 2. The average value of K is 1.85 l. mole^{-1}; the maximum deviation from this average value is 3.3%. Taking the data at 490 mμ, if we use this first value of K to calculate TA and then use equation 1 to calculate a revised K, the value of K changes from 1.81 to 1.87 l. mole^{-1}, a change of 3.3%.

TABLE IV

EQUILIBRIUM CONSTANT AND EXTINCTION COEFFICIENTS OF THE 1,3,5-TRINITROBENZENE–N,N-DIMETHYLANILINE COMPLEX AT 24.8 ± 0.1°; TRINITROBENZENE–AMINE RATIOS EXACTLY 1

Wave length, mμ	K, l. mole^{-1}	ϵ
460	1.85	591
470	1.91	608
490	1.81	667
510	1.91	608
520	1.85	591
560	1.79	402

This value of the equilibrium constant is in agreement with the value obtained by Ley and Grau[1] from their spectroscopic measurements, and it is of interest that in their measurements, too, the trinitrobenzene–amine ratios were always 1. The data at 490 mμ are plotted in Fig. 1 (line IV). Once again, the slope (8.29×10^{-4}) is relatively unchanged from the previously obtained slopes, but the intercept (15.0×10^{-4}) is higher. It is our contention that this value, 1.85 l. mole^{-1}, is the most reliable value for the equilibrium constant for 1:1 complex formation and that the perturbing influence in the three other sets of measurements is the presence of either TA_2 or T_2A.

This hypothesis can be tested by using this value of K and the extinction coefficients in Table IV to calculate equilibrium constants and extinction coefficients for TA_2 and T_2A. Let us first consider the two sets of experiments with $A_0 \gg T_0$. In this case, the two complexes present are TA and TA_2, and the related equilibrium constants are

$$K = \frac{[TA]}{[T][A]} \text{ and } K_2 = \frac{[TA_2]}{[TA][A]}$$

The equilibrium concentrations of the species involved are given by the expressions

$$T = T_0 - TA - TA_2$$

$$A = A_0 - TA - 2TA_2 \cong A_0$$

$$TA = \frac{KT_0A_0}{1 + KA_0 + KK_2A_0^2}$$

$$TA_2 = K_2[A_0][AT]$$

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(6) R. v. Goedicke, *Ber.*, **26**, 3042 (1893); J. J. Sudborough and N. Picton, *J. Chem. Soc.*, **89**, 583 (1906); M. Orchin, L. Reggel and E. O. Woolfolk, THIS JOURNAL, **69**, 1225 (1947).

(7) K. A. Hofmann and H. Kirmreuther, *Ber.*, **43**, 1764 (1910); J. J. Sudborough and S. H. Beard, *J. Chem. Soc.*, **99**, 209 (1911); J. Weiss, *ibid.*, 462 (1943).

(8) R. M. Keefer and L. J. Andrews, THIS JOURNAL, **74**, 1891 (1952).

From the spectroscopic data, we obtain

$$d_c = \epsilon_{TA}TA + \epsilon_{TA_2}TA_2$$

Combining this expression with the previous equations, we obtain equation 3

$$\frac{d_c(1 + KA_0) - \epsilon_{TA}\,KA_0T_0}{A_0{}^2T_0K} = \epsilon_{TA_2}\,K_2 - \frac{d_c}{T_0}\,K_2 \qquad (3)$$

The only unknown quantities in this equation are ϵ_{TA_2} and K_2. A plot of the left-hand member of this equation *vs.* d_c/T_0 should be a straight line with the slope equal to $-K_2$ and the intercept equal to $\epsilon_{TA_2}K_2$.

We have applied this equation to all of the data (the 22 different sets of concentrations of A_0 and T_0 of Tables I and II) with $A_0 \gg T_0$ at five different wave lengths, using the method of least squares to define the best straight line through the experimental points. A typical plot is shown in Fig. 2, and the resulting values of ϵ_{TA_2} and K_2 are given in Table V. The data plotted in Fig. 2 are at 490 mμ and are fully representative of the data at the other wave lengths. The line shown in Fig. 2 is the least squares straight line. At this wave length, the maximum deviation of any point from the line is 14.9%, and the average deviation is less than 4%. Equation 3 does, therefore, fit the available data.

TABLE V

EQUILIBRIUM CONSTANT AND EXTINCTION COEFFICIENTS OF THE 1:2-1,3,5-TRINITROBENZENE-N,N-DIMETHYLANILINE COMPLEX IN CHLOROFORM AT 24.8 ± 0.1°

Wave length, mμ	K_2, l. mole^{-1}	$\epsilon \times 10^{-3}$
460	0.2	3
470	.4	2
490	.2	3
510	.5	2
520	.3	2

The best value that we can assign to K_2 is 0.3 ± 0.1 l. mole^{-1}. This is a reasonable order of magnitude for K_2, for, on a purely statistical basis, we might expect K to be approximately $4K_2$. More important, the fit of the data to equation 3 and the constancy of K_2 with wave length are all that can be expected, since the value of K_2 obtained is highly sensitive to the values of K and ϵ_{TA} used. For the data at 520 mμ, if we take K to be 1.75 l. mole^{-1}, a change of 5.4%, this will change the resultant K_2 by 119%. Similarly, if we take ϵ_{TA} to be 560, a change of 5.3%, K_2 will change by 116%. Finally, if we use a value of 2.0 l. mole^{-1} for K, equation 3 no longer fits the data, since the value of K_2 becomes negative.

The amount of data with $T_0 \gg A_0$ available is not sufficient to warrant an attempt to evaluate the equilibrium constant for T₂A formation. However, it may be shown qualitatively that the lower values for K in Table III are due to the presence of T₂A. In these solutions, the two complexes present are TA and T₂A, and the equilibrium constant for formation of the latter is

$$K_3 = \frac{[T_2A]}{[TA][T]}$$

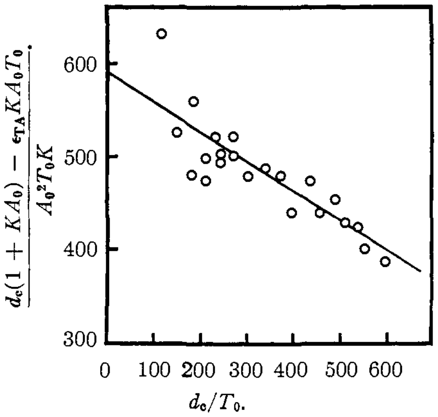

Fig. 2.—A plot of data at 520 mμ according to equation 3. The slope is equal to $-K_2$, and the intercept is equal to $\epsilon_{TA_2}K_2$.

The equilibrium concentrations of the species involved are given by the expressions

$$T = T_0 - TA - T_2A \cong T_0$$

$$A = A_0 - TA - T_2A \cong A_0 - TA$$

$$AT = \frac{KT_0A_0}{1 + KT_0}$$

In the above, we have assumed that $A_0 - TA \gg T_2A$. From the spectroscopic data, we obtain

$$d_c = \epsilon_{TA}TA + \epsilon_{T_2A}T_2A$$

Combining this expression with the previous ones, we obtain equation 4.

$$\frac{d_c(1 + KT_0)}{A_0T_0} = \epsilon_{TA}\,K + \epsilon_{T_2A}\,KK_3T_0 \qquad (4)$$

A plot of the left-hand member of this equation *vs* T_0 should be a straight line with the slope equal to $\epsilon_{T_2A}KK_3$ and the intercept equal to $\epsilon_{TA}K$, a quantity which we can obtain from Table IV. Using data at 470 mμ, seven different sets of amine and trinitrobenzene concentrations, the least squares value for the intercept, $\epsilon_{TA}K$, is 1139. This is to be compared with the value of 1126 from Table IV. More important, all of the experimental points fall on a straight line, and the maximum deviation of any point from the least squares straight line is less than 2.5%.

It seemed pertinent to demonstrate, at this point, that in a case where no 1:2 and 2:1 complexes are present, one obtains the same value for the equilibrium constant for complex formation by starting either with the individual components or the 1:1-complex. For this purpose, the 1,3,5-trinitrobenzene–naphthalene complex was convenient, since the crystalline 1:1-complex is known[3] and since we had previously determined the equilibrium constant by starting with the individual components.[9] Our previous value for the equilibrium constant was 1.30 ± 0.04 l. mole^{-1}, and the extinction coefficients for the complex were 87 at 450 mμ, 37 at 460 mμ, and 15 at 470 mμ. In the present determination, we used seven different concentrations of the 1:1 complex (0.2 to 0.08 M) in chloroform at 24.8 ± 0.1° and made measurements at the same

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[9] S. D. Ross and M. M. Labes, THIS JOURNAL, **77**, 4916 (1955).

three wave lengths. These measurements resulted in a value of 1.25 ± 0.08 l. mole^{-1} for the equilibrium constant, and the extinction coefficients were 78 at 450 mμ, 38 at 460 mμ, and 16 at 470 mμ.

This demonstration of the large uncertainties introduced in the values of the equilibrium constants by the presence in the solutions of small amounts of 2:1 or 1:2-complexes led us to question some of our previous results. In particular, there was an unexplained discrepancy between our value of 0.257 ± 0.005 l. mole^{-1} for the equilibrium constant for formation of the 1,3,5-trinitrobenzene–aniline complex[9] in chloroform and the value of 5.1 ± 0.7 mole fraction^{-1} (approximately 0.41 ± 0.06 l. mole^{-1}) reported by Landauer and McConnell.[10] We repeated our measurements starting with the crystalline complex, but this gave erratic results, which we attribute to an instability of the 1:1-complex. By mixing the two components in solution in exactly 1:1 molar ratios we obtained satisfactory measurements. These resulted in a value of 0.51 ± 0.03 l. mole^{-1} for the equilibrium constant. This suggests that all of our previously reported results on this complex may be in error because of the presence of 1:2-complex. We hope to be able to repeat some of these measurements in the future.

Acknowledgment.—We are indebted to Miss Kathryn Church and Mr. Kurt Schoeni for assistance with the calculations.

NORTH ADAMS, MASS.

[10] J. Landauer and H. McConnell, THIS JOURNAL, **74**, 1221 (1952).

[CONTRIBUTION NO. 2106 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

The Formation and Reactions of Certain Oxazolonium Ions

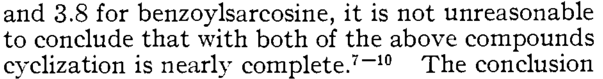
BY JOSEPH L. O'BRIEN[1] AND CARL NIEMANN[2]

RECEIVED JUNE 11, 1956

A cryoscopic investigation has shown that α-acylamino acids may undergo complex ionization in sulfuric acid to form the corresponding oxazolonium ions. The structural requirements for this acid-catalyzed cyclization have been considered and a mechanism consistent with the facts is presented. Auxiliary experiments have not only confirmed the cryoscopic evidence but also indicate that the azlactonization of α-acylamino acids in acetic anhydride is catalyzed by sulfuric acid. A sulfuric acid catalyzed Erlenmeyer synthesis is described which gives an excellent yield of 2-phenyl-4-benzal-5-oxazolone, obtained as a mixture of the geometrical isomers. The stereochemistry of this condensation is discussed and it is suggested that sulfuric acid inhibits the mutarotation of the intermediate addition product. An improved preparation of α-(N-methylbenzamido)-cinnamic acid from benzoylsarcosine by the new method provides further evidence for an oxazolonium ion intermediate.

It has been shown[3,4] that amino acids ionize normally in sulfuric acid, behaving to a varying extent as di-acid bases. For the simplest α-amino acid, glycine, the van't Hoff factor of 2.2 indicates that the second ionization is only about 20% complete. The lack of extensive protonation of the carboxyl group of the glycine cation in sulfuric acid may be attributed to the influence of the positively charged α-ammonium group.[3,4]

In the present investigation the cryoscopic behavior in sulfuric acid of several derivatives of glycine has been determined. Of particular interest are the results obtained for the α-acylamino acids, *cf.* Table I. While the data for acetylglycine are inconclusive, it is clear that the ionization of benzoylglycine and benzoylsarcosine to give *i* factors of nearly 4 cannot be explained on the basis of simple protonation. Rather, it appears that these latter α-acylamino acids undergo complex ionization[5] in sulfuric acid with the formation of the corresponding oxazolonium ions.[6] A possible mechanism for this dehydrative cyclization is presented in Fig. 1. Although the theoretical value of the *i* factor for the over-all reaction



$$C_6H_5CONRCH_2CO_2H + 2H_2SO_4 \rightleftarrows \left[C_6H_5\overbrace{C{=}NRCH_2C}^{O}O\right]^+ + H_3O^+ + 2HSO_4^-$$

is 4 and the observed value is 3.6 for benzoylglycine and 3.8 for benzoylsarcosine, it is not unreasonable to conclude that with both of the above compounds cyclization is nearly complete.[7–10] The conclusion that cyclization of the above benzoyl compounds is entirely consistent with the mechanism suggested in Fig. 1 but it is contrary to the notion that enoli-

TABLE I

i-FACTORS FOR SEVERAL α-ACYLAMINO ACIDS IN SULFURIC ACID

Compound	
Acetylglycine	2.5
Benzoylglycine	3.6
Benzoylsarcosine	3.8
Phthalylglycine	1.8
Benzenesulfonylglycine	2.2
Benzoylglycine ethyl ester	2.5

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[1] Rohm and Haas Co., Inc., Philadelphia, Pa.

[2] To whom inquiries regarding this article should be sent.

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[8] R. J. Gillespie, *ibid.*, 2493 (1950).

[9] R. J. Gillespie, J. Graham, E. D. Hughes, C. K. Ingold and E. R. A. Peeling, *ibid.*, 2504 (1950).

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