of periodic repetition of melting point minima is unprecedented.[41]

It is of interest that the amides associate in the same manner as the fatty acids and may be used in place of the fatty acids for the determination of structures. Solidification point curves are shown in Fig. 8 for the amides of the fatty acids whose solidification point curves appear as the lower pair in Fig. 4.

Acknowledgment.—The writer is indebted to Dr. James Cason, Vanderbilt University, for generously supplying samples of *dl*-16- and 17-methyloctadecanoic acids and derivatives, and to Dr. W. E. Militzer, University of Nebraska, for determining optical rotations.

Summary

Thirty-two of the acidic constituents of degras have been isolated and identified. These include: (1) nine normal fatty acids, C_{10} to C_{26}; (2) two optically active 2-hydroxy acids, C_{14} and C_{16}; (3) ten iso acids, C_{10} to C_{28}; (4) eleven dextrorotatory *anteiso* acids, C_9 to C_{27} and C_{31}.

Dark field photomicrographs of representative members of each of the four series have been prepared.

A new method of structure elucidation applicable to acids or amides with simple branched chains is based on the number of transitions appearing in the solidification point curves of binary mixtures of the branched acid or amide with normal fatty acids or amides.

WHITING, INDIANA RECEIVED OCTOBER 19, 1944

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[41] Gilman, "Organic Chemistry," 2d ed., John Wiley & Sons, Inc., New York, N. Y., 1943, Vol. II, p. 1730.

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

A Spectrophotometric Study of the Anhydro Base of Viridine Green

BY TERRELL L. HILL,[1] GERALD E. K. BRANCH AND MORRIS PATAPOFF

Introduction

In a solution of N,N′-diphenyl-*p*,*p*′-diaminotriphenylmethyl chloride in methyl alcohol the following triphenylmethane derivatives can exist

I $(C_6H_5NHC_6H_4)(C_6H_5)C{=}C_6H_4{=}N^+HC_6H_5$
II $(C_6H_5NHC_6H_4)(C_6H_5)C{=}C_6H_4{=}NC_6H_5$
III $(C_6H_5N^+H_2C_6H_4)(C_6H_5NHC_6H_4)(C_6H_5)COCH_3$
IV $(C_6H_5NHC_6H_4)_2(C_6H_5)COCH_3$

II is the conjugate base of I. It is called the Homolka base, or better the anhydro base, since it is the anhydride of the color base. IV is the pseudo base of I in the methanol system, just as the carbinol is the pseudo base in the water system. It is a methyl ether. III is the conjugate acid of IV.

Equilibria between I and II, and between III and IV are very rapid, since the reactions are simple neutralizations. But the reversible reactions of I or II to III or IV are slower. I is stable with respect to III, and IV is stable with respect to II. Hence II and III are metastable compounds, and they can exist in appreciable concentrations only because they are formed by reactions that are faster than those by which equilibria are achieved.

I is green, II is red, and III and IV are colorless. Hence many of the reactions between these compounds can be studied colorimetrically.

In our work we started with a solid preparation of the bases. This solid contained a much larger proportion of the anhydro base than corresponds to equilibrium. This material we shall call the red solid in the rest of this article. Since we had a method of analyzing the red solid for anhydro base the colorless pseudo bases present were not objectionable.

The anhydro base polymerizes or resinifies slowly when dissolved in a solvent with which it cannot combine to form an ether. It is much more stable as the red solid, though even in this form it gradually deteriorates.

The anhydro base was first prepared by Baeyer and Villiger[2] by evaporating a brown ethereal solution obtained by shaking a salt of the dye with a mixture of aqueous sodium hydroxide and ether. Prepared in this way it is contaminated with colored polymers or resins. These impurities are to a great extent avoided when the anhydro base is formed in a methanol solution of the dye, transferred by extraction methods to an inert solvent from which it can be precipitated without concentrating the solution. Such methods allow the formation of pseudo bases much more than the method of Baeyer and Villiger does.

Preparation and Analysis

The chloride of the dye was prepared in a way that is essentially that first used by Meldola.[3]

Diphenylamine and aluminum chloride in the ratio of 17 to 13 by weight were mixed in a large container. An amount of benzotrichloride equal to half of the diphenylamine in moles was added. When this mixture was warmed the reaction started and proceeded to completion with some violence. The reaction product was washed with warm dilute aqueous hydrochloric acid, and then dried with hot toluene. The residue was dissolved in methyl alcohol, and aqueous sodium hydroxide, carbon tetrachloride and water were added in the order given. The red carbon tetrachloride layer was repeatedly washed with water and dried with sodium sulfate. From this solution the chloride was precipitated with a little less hydrochloric

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[1] This paper has been constructed from portions of a Thesis presented by T. L. Hill, in partial fulfillment of the requirements for the Ph.D. degree at the University of California.

[2] Baeyer and Villiger, *Ber.*, **37**, 2866 (1904).

[3] Meldola, *J. Chem. Soc.*, **41**, 189 (1882).

acid gas than would completely remove the dye from the solution. The chloride was filtered off and dried *in vacuo*. The product at this stage was a coarse crystalline powder with a strong copper colored metallic lustre. It contained carbon tetrachloride. It was dissolved in methyl alcohol and the above process was repeated, except that benzene was used in the place of carbon tetrachloride.

The chloride was dissolved in methyl alcohol, and neutralized with aqueous sodium hydroxide. Benzene was added, and then excess of water. The benzene layer was washed several times with water, and dried over sodium sulfate. It was then added to four volumes of hexane. A bright red finely divided powder was precipitated. On standing overnight, the precipitate agglutinated to a coarse crystalline looking powder, with a green metallic luster. It was filtered and dried *in vacuo*. When triturated the product loses its metallic luster, and reverts to a red powder. The melting point was 84° with decomposition. The yield was 50% calculated from the diphenylamine used to prepare the chloride. This product is a mixture of the anhydro base and the methyl ether and carbinol.

Analysis and molecular weight determinations gave C, 85.4, 85.4; H, 6.04, 5.98; N, 6.7, 6.6; mol. wt., 433, 438. Calculated for 37% $C_{31}H_{24}N_2$ and 63% $C_{32}H_{28}ON_2$: C, 85.4; H, 6.0; N, 6.3; mol. wt., 444. The value chosen for the percentage of anhydro base was that found by a method that is described later. The analysis by itself could mean anywhere between 20 and 60% anhydro base. Analysis cannot distinguish between the carbinol and the methyl ether as the other product. Presumably both are present, but the method of preparation is such that the anhydro base had a better chance of reacting with methyl alcohol than with water.

Spectrophotometry

Experimental.—The spectrophotometric measurements were made with a Beckman quartz photoelectric spectrophotometer, model D, made by the National Technical Laboratories. The instrument has been described by Cary and Beckman.[4] Using this spectrophotometer the absorption of the solvent is corrected for automatically. The apparatus reads $\log_{10} I_0/I$ directly. One obtains the extinction of the solute in the cell without further calculation. Since the length of our cell was 1 cm., division of the reading by the molarity of the solution gives ϵ, the molecular extinction coefficient.

The solvent used was a mixture of 60 cc. of methyl alcohol, 42 cc. of benzene, and 0.5 cc. of water. Benzene was added because in methyl alcohol alone the reaction was a little too fast for accurate measurements at room temperature, and because the red solid could be dissolved in benzene before it was added to the solvent. Otherwise there would have been a time lag while the solute was dissolving. Water was used so that sodium hydroxide and hydrochloric acid could be added as aqueous standard solutions. The amount of water used was in large molecular excess over the dye, so that no appreciable changes in the proportions of the solvent could have resulted from the reaction.

Many of the experiments were done at room temperatures without the use of a thermostat. In these experiments the temperature was constant to within 0.2°. The entire experiment was done with a single filling of the spectrophotometer cell. Where more accurate temperature control was thought to be needed the reacting solution was in a thermostat, and samples of the solution were withdrawn from time to time for measurement. In these experiments the temperature of each sample was the same to within 0.05°.

Assumptions and Symbols.—Some approximations and assumptions have been made in the interpretation of our experiments.

In the preparation of the red solid and in its reactions both methyl alcohol and water were involved. Both the methyl ether and the carbinol were present in the red solid and were formed during reaction with the solvent. We have treated the mixtures of the methyl ether and the carbinol as a single substance, which we have called the methyl ether. The justification is that neither component absorbs much visible light, and so differences in extinction due to differences in the proportions are negligible.

Since the solvent contained both methyl alcohol and water, both hydroxide ion and methoxide ion in unknown proportions were present. However, the trace of water present is in great molecular excess over the anhydro base, and in consequence the proportions of water to methyl alcohol and of hydroxide ion to methylate ion are always the same. We have, therefore, treated this mixture of the two ions as a single species, called the negative ion of the solvent.

We have assumed all the positive ions of the dye to be $C_{31}H_{25}N_2^+$. Actually this ion is in equilibrium with the colorless ion of the methyl ether whenever it has existed in the solution for some time, and immediately after formation the proportion of the ions depends on the history of the solution. However, the methyl ether acting as a simple base giving the colorless ion, $C_{32}H_{29}ON_2^+$, should be about as strong as diphenylamine. It is about a hundred times as strong as this when it is given time to reach equilibrium with both ions, so that at equilibrium only about 1% of the ion can be $C_{32}H_{29}ON_2^+$. In all our experiments the anhydro base was the chief source of ions, so that in our experiments the colorless ion varied between zero and 1% of the total ion. Such amounts could not have been detected in our measurements. A red doubly charged positive ion can also be obtained. For this it is necessary to add large quantities of concentrated sulfuric acid to the solution. Our experiments did not extend into the acid range further than was necessary to prevent appreciable hydrolysis of the first ion. No error could have resulted from the presence of the doubly charged positive ion.

The molecular extinction coefficient of the positive ion in the mixed solvent was found to be invariant to changes of concentration. We wish to thank Mr. Bert Tolbert for these experiments. However, the molecular extinction coefficient of the anhydro base was never directly measured. The molecular weight determinations showed that the anhydro base is not associated in benzene, and it may be presumed that it is not associated in still more dilute solutions in the benzene–methyl alcohol mixture. We have therefore assumed the extinction of the anhydro base to be proportional to its concentration.

In describing and interpreting our measurements, it has been desirable to break up the extinctions of the solute into those due to various forms of the dye, and to consider the times, the wave lengths and other conditions of measurement. To distinguish between these extinctions

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(4) Cary and Beckman, *J. Optical Soc. Am.*, **31**, 682 (1941).

we have used subscripts and superscripts to the letter E, which we have used as the basic symbol for all extinctions.

When an extinction has been obtained by extrapolation to zero time, a zero sign has been added as a superscript to E. When the extinction has been measured after the quinoidal and benzoidal forms of the dye have reached equilibrium an infinity sign has been superscripted.

A letter subscript has been used to show that only that part of the extinction due to the particular species or combination of species represented by the letter is to be considered. A letter superscript has been used when the extinction considered is that which would be found were all the dye present as the species represented by the letter. For instance, "i" has been used to indicate the positive ion of the dye, E_i has therefore been used for the extinction due to the positive ion, and E^i for the extinction that would be obtained were the dye completely ionized.

We have shown the wave lengths by subscripting numbers that give the wave lengths in units of 100 Å. Thus E_{64} is the extinction at 6400 Å.

Combinations of subscripts and superscripts have been used. Thus E^0_{i64} means the extinction due to the ionized part of the dye at 6400 Å., extrapolated back to the time of mixing.

In order to obtain linear functions of time, for extrapolations and interpolations, we have used an empirical combination of measured extinctions. This combination we have denoted by E'. It is defined by the equation

$$E' = E - E_{64}\cdot E^i/E^i_{64}$$

Values of E^i are obtainable by turning all the dye to the ion with excess hydrochloric acid and then measuring the extinction. Superscript zero and infinity signs and subscript numbers can be used with E'.

This system of subscripts and superscripts is in part applicable to the molecular extinction coefficient, ϵ, the fraction of the dye present in some form, α, and the molarity, M. Thus M^0_i means the molarity of the positive ion of the dye at zero time.

The following table shows the various molecular species or combinations of species indicated by subscripted or superscripted letters.

TABLE I

MEANING OF LETTERS USED AS SUBSCRIPTS OR SUPERSCRIPTS

Letter	Meaning
i	Positive ion of dye
a	Anhydro base of dye
e	Methyl ether of dye
u	Un-ionized forms of dye
q	Quinoidal forms of dye
o	Negative ion of solvent
H	Hydrogen ion
N	Na^+ from NaOH added

Extrapolation.—It was found that, for wave lengths near to 6400 Å., log $(E - E^\infty)$ is a linear function of time. After extrapolating this function to zero time, E^0_{64} can be obtained. The first measurements of E_{64} are slightly smaller than would be expected from the above relationship. They were neglected in the extrapolations. The low initial values of E_{64} can be attributed to failure to obtain complete equilibrium between the anhydro base and the positive ion in one or two minutes, probably on account of the presence of traces of carbon dioxide.

In general E^∞_{64} is negligible with respect to E_{64}, and in most cases E^0_{64} was obtained by extrapolating log E_{64} to zero time.

At shorter wave lengths log $(E - E^\infty)$ is not a linear function of time, but log $(E' - E'^\infty)$ is. E^0 values were obtained after extrapolating log $(E' - E'^\infty)$ to zero time. To obtain E' it is necessary to know E_{64}. The values of E_{64} were obtained from measurements of E_{64} at other times and using the linear relationship between log E_{64} and time for interpolation.

Fraction of Anhydro Base.—For any solution $E^0_i/E^i_{64} = \alpha^0_i\cdot\epsilon_i/\epsilon_{i64}$, and for two solutions $\Delta(E^0_i/E^i_{64}) = \Delta\alpha^0_i\cdot\epsilon_i/\epsilon_{i64}$. Similarly $\Delta(E^0_u/E^i_{64}) = \Delta\alpha^0_e\cdot\epsilon_e/\epsilon_{i64} + \Delta\alpha^0_a\cdot\epsilon_a/\epsilon_{i64}$. But α^0_q is the same for all solutions, being α_a for the red solid, so $\Delta\alpha^0_e = 0$, and $\Delta\alpha^0_i = -\Delta\alpha^0_a$. Hence $\Delta(E^0_i/E^i_{64})/\Delta(E^0_u/E^i_{64}) = -\epsilon_i/\epsilon_a$. At 6400 Å. only the ion absorbs strongly, and at 5000 Å. only the anhydro base. Then approximately $E^0_{64} = E^0_{i64}$ and $E'^0_{50} = E^0_{u50} = E^0_{a50}$. So that if measurements are made at 6400 and 5000 Å., $\Delta(E^0_{64}/E^i_{64})/\Delta(E'^0_{50}/E^i_{64}) = -\epsilon_{i64}/\epsilon_{a50}$, and for either solution α_a for the red solid $= \alpha^0_q = (E^0_{64} + E'^0\cdot\epsilon_{i64}/\epsilon_{a50})/E^i_{64}$.

The extinctions of an alkaline solution of the red solid were measured alternately at 6400 and 5000 Å. until no further change was observed. The solution was acidified and E^i_{64} measured. From the data E^0_{64} and E'^0_{50} were calculated. The experiment was repeated with a slightly acidified solution. The results are shown in Table II.

TABLE II

DATA FOR CALCULATION OF α_a FOR RED SOLID, $T = 23.5 \pm 0.05°$

Acid or alkali	E^i_{64}	E^0_{64}	E'^0_{50}	E^0_{64}/E^i_{64}	E'^0_{50}/E^i_{64}
HCl	17.6	3.21	1.12	0.182	0.0636
NaOH	22.8	0.10	2.69	0.004	.118
			Difference	0.178	0.054

The ratio of the two differences was 3.3. A value of 5.0×10^4 was found for ϵ_{i64}. Hence $\epsilon_{a50} = 1.52 \times 10^4$. For the red solid $\alpha_a = \alpha^0_q = 0.182 + 3.3 \times 0.0636 = 0.39$. For a solution to which no acid or alkali had been added we found $\alpha^0_q = 0.35$. We have taken the mean 0.37 as the value for the fraction of anhydro base in the red solid. The experimental error was probably less than 10%. The approximations used would not lead to errors of this magnitude.

Degree of Ionization.—Values of E^0_{64}/E^i_{64} were obtained for solutions containing varying amounts of sodium hydroxide. This quantity is related to the fractions present as the ion, the anhydro base and the methyl ether by the equation

$$E^0_{64}/E^i_{64} = \alpha^0_i + \alpha^0_a E^a_{64}/E^i_{64} + \alpha^0_e E^e_{64}/E^i_{64}$$

At 6400 Å., $E^e_{64} = 0$. When the ionization is entirely repressed by alkali, E^0_{64} divided by 0.37, which is the fraction of anhydro base in the red solid, is equal to E^a_{64}, and a value of 0.0036 was found for E^0_{64}/E^i_{64}. Hence

$$E^0_{64}/E^i_{64} = \alpha^0_i + \alpha^0_a \times 0.0036/0.37$$

But $\alpha^0_i + \alpha^0_a = 0.37$; hence

$$\alpha^0_i = (E^0_{64}/E^i_{64} - 0.0036)/0.99$$

When the molarities of the red solid and the added sodium hydroxide are known, the molarities of the anhydro base, the positive ion, and the negative ion, and the equilibrium constant can be calculated from α^0_i. The equations are

$$M^0_a = (0.37 - \alpha^0_i)M,\ M^0_i = \alpha^0_i M,\ M^0_o = \alpha^0_i M + M_N,$$
$$\text{and } K_b = M^0_i \cdot M^0_o/M^0_a$$

Table III shows the results of an experiment.

TABLE III

THE DEGREE OF IONIZATION AND THE EQUILIBRIUM CONSTANT OF THE ANHYDRO BASE

$T = 22.5 \pm 0.2$ $M = 3.56 \times 10^{-4}$

$M_N \times 10^4$	E^0_{64}/E^i_{64}	α^0	$M^0 \times 10^6$	$M^0_a \times 10^6$	$M^0_o \times 10^6$	$K_b \times 10^6$
0.0	0.0691	0.0661	23.5	108.4	23.5	5.1
2.46	.0419	.0387	13.8	118.1	38.4	4.5
4.92	.027	.0236	8.4	123.5	57.6	3.9
460	.0036	....	..	...	..	...
						Mean 4.5

The trend in K_b can be attributed to traces of an acidic impurity in the solvent. In that case the error in K_b may be very great; but this error does not affect the values of α^0_i, M^0_i and M^0_a.

Spectra.—In a single solution E_{64} and E at seven other wave lengths were measured repeatedly at noted times until no further change was observed. The values of E^i at the same wave lengths were also obtained. From the data the values of E^0 for the eight wave lengths were obtained by extrapolation to zero time. The curve obtained by plotting E^0/M against the wave length is shown in the figure as the spectrum of the red solid. It is the spectrum of a mixture of the ion, the anhydro base, and the methyl ether of the dye. Since the spectrum of the ion is known, and that of the anhydro base in the visible can be expected to consist of a single nearly symmetrical band, this spectrum should be fairly accurate, although extinctions were measured at only a few wave lengths.

Now $E^0_a = E^0 - \alpha^0_i E^i - \alpha^0_e E^e$. The above measurements include the data from which α^0_i can be calculated, E^i was measured, $\alpha^0_e = 0.63$, and E^e is approximately E^∞. However, the spectrum of the faded solution (E^∞) has a shoulder in the region of maximum values of E^0_a. We attributed this shoulder to traces of the anhydro base left at equilibrium. We corrected for these traces by drawing a smooth curve for E^∞, and taking the values obtained from the corrected spectrum equal to E^e.[5] On this basis the values of E^0_a were calculated. The molecular extinction coefficients were obtained from the equation $\epsilon_a = E^0_a/M^0_a = E^0_a/M\ (0.37 - \alpha^0_i)$.

This experiment was repeated on a solution containing excess sodium hydroxide ($M_N = 2.5 \times 10^{-4}$). The results of both experiments are shown in Table IV. The plot of ϵ_a against the wave length is shown in the figure. Points obtained from the neutral solution are shown as circles, those from the alkaline solution as crosses. Except at 5800 Å. the agreement between the two experiments is excellent. This plot should be a fairly accurate representation of the spectrum of the anhydro base in a sixty to forty mixture of methyl alcohol and benzene.

TABLE IV

MOLECULAR EXTINCTION COEFFICIENTS OF THE ANHYDRO BASE

Ionization repressed by NaOH

$\alpha^0_i = 0$, $M = 4.16 \times 10^{-4}$, $E^0_{64}/E^i_{64} = 0.0036$, $T = 24° \pm 0.2°$

λ in Å.	E^0	E^0	E_u	E^0_e	E_a	$\epsilon_a \times 10^{-4}$
4000	1.410	0.0	1.410	0.430	0.98	0.64
4400	1.574	.0	1.574	.200	1.374	.89
4600	2.040	.0	2.040	.131	1.909	1.42
4800	2.416	.0	2.416	.077	2.339	1.52
5000	2.336	.0	2.336	.039	2.297	1.49
5300	1.737	.0	1.737	.013	1.724	1.12
5800	0.508	.0	0.508	.002	0.506	0.33
6400	0.075	.0	0.075	.000	0.075	0.049

No NaOH added

$\alpha^0_i = 0.0746$, $M = 4.16 \times 10^{-4}$, $E^0_{64}/E^i_{64} = 0.0775$, $T = 26° \pm 0.2°$

4000	1.347	0.147	1.200	0.430	0.770	0.63
4400	1.574	.354	1.220	.200	1.020	.83
4600	1.931	.303	1.628	.131	1.497	1.22
4800	2.121	.176	1.945	.077	1.868	1.52
5000	1.952	.084	1.868	.039	1.829	1.49
5200	1.573	.069	1.504	.017	1.487	1.21
5800	0.841	.550	0.291	.002	0.289	0.24
6400	1.614	1.550	0.064	.000	0.064	0.052

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(5) In the figure the corrected curve is shown as a dotted line. At 5000 Å. the correction is 0.25 of E^∞_{50}, and 4×10^{-8} of E^a_{50}. The latter fraction is the equilibrium ratio of the anhydro base to the methyl ether. The small value shows that the correction is not important.

By combining the results of these two experiments a check can be obtained on the previously determined value of α_a for the red solid (0.37). In the calculation of E_a^0 the value 0.37 has been used only as a second order correction. It affects the value of α_i^0 only to a small extent, and it determines the fraction of E^∞ used in correcting for extinction due to the methyl ether in the red solid. But this correction is in general small. If E_a^0 for the alkaline solution is divided by x, and equated to E_a^0 for the neutral solution divided by $x - 0.0746$, the solution of the equation for x gives a value of α_a for the red solid. The values so obtained are at 6400 Å., 0.51; at 5800, 0.17; at 5000, 0.37; at 4800, 0.37; at 4600, 0.45; at 4400, 0.29; at 4000, 0.35. Only at 5000, 4800 and 4600 could this method give fairly accurate values, and at these wave lengths the agreement with 0.37 is good. The close agreement at 4000 Å. should be considered fortuitous, while the large error at 5800 Å. is evidently experimental.

The spectrum of the red solid dissolved in benzene was obtained by direct measurement at 50 to 100 Å. intervals. The extinctions were divided by 0.37 M to reduce them to molecular extinction coefficients of the anhydro base, but there has been no correction for the extinction of the methyl ether.

The spectra obtained are shown in Fig. 1 with the exception of those of the red solid in an alkaline solution and the positive ion in the methanol-benzene mixture. The former is a miniature of the spectrum of the anhydro base with a little extra extinction on the short wave length side. The latter is almost the same as the spectrum of the chloride in methyl alcohol. This spectrum is shown in Fig. 2. The spectra shown in Fig. 1 are not all on the same scale. The extinction coefficients of the faded solution have been multiplied by ten, and those of the anhydro base in benzene by two.

Inspection of Fig. 1 shows the large effect of the solvent on the spectrum of the anhydro base. In the methanol-benzene mixture the wave length of the peak of the band is about 500 Å. longer than it is in benzene, and the maximum extinction coefficient is about twice as great. In the methanol-benzene mixture $\lambda_{\text{max.}} = 4890$ Å. and $\epsilon_{\text{max.}} = 1.55 \times 10^4$, in benzene $\lambda_{\text{max.}} = 4420$ and $\epsilon_{\text{max.}} = 8.3 \times 10^3$.

This effect of the methyl alcohol is not surprising. It is generally observed when a molecule is a resonance hybrid of a structure in which no atoms have formal charges and one that is internally

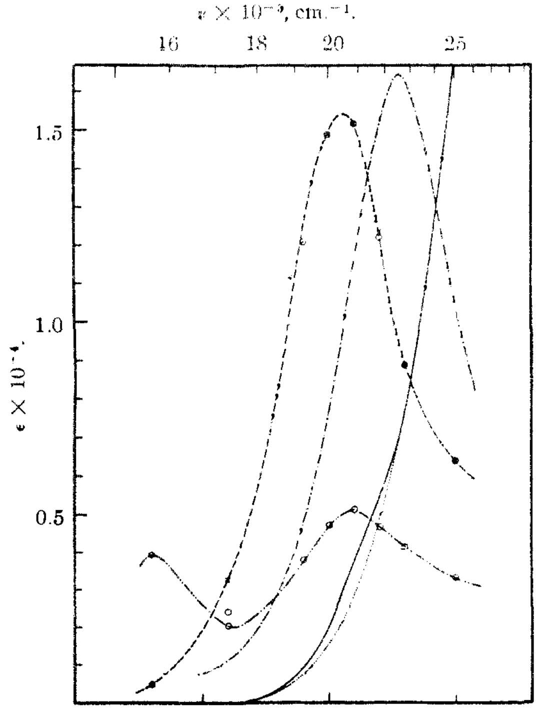

Fig. 1.—Spectra of the bases: ----, the anhydro base in the methyl alcohol-benzene mixture; -·--·-, 2 × ε for anhydro base in benzene; -··-··-, the red solid in the methanol-benzene mixture; ———, 10 × ε for faded solution in the methanol-benzene mixture; ·······, above corrected for anhydro base left at equilibrium.

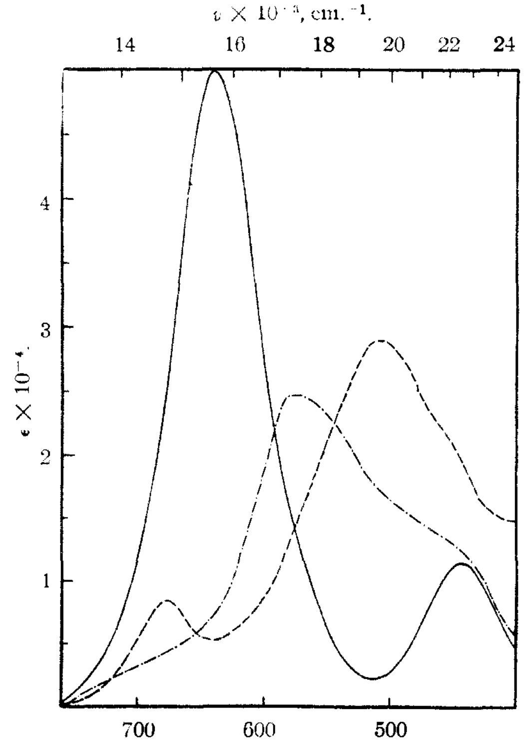

Fig. 2.— ———, ε for the chloride in methanol; ----, ε for the chloride in 95% sulfuric acid; -·-·-·, ε for the chloride in 95% sulfuric acid, after standing for two weeks.

ionized. The chief internally ionized structure of the anhydro base is $(C_6H_5N^-C_6H_4)(C_6H_5)C{=}C_6H_4{=}N^+HC_6H_5$, in which there is a very large separation of the electric charges.

Changing from the singly charged quinoidal ion to the second quinoidal ion ($C_{31}H_{26}N_2^{++}$) is opposed by the resonance resulting from the two equivalent structures of the singly charged ion, and that from the high degree of phenylation of the amino groups. In consequence it is necessary to have very acid conditions to obtain the spectrum of the second ion. We found that in a mixture of two volumes of methanol and one of concentrated sulfuric acid, a mixed spectrum of the two ions was obtained, and the position of the absorption band of the second ion could not be located. We then tried to obtain the spectrum of a solution of the dye in 95% sulfuric acid. The spectrum obtained was unexpected. There was a strong absorption band at 5100 Å., which was probably the absorption band of the second ion, but there was also a weaker band at 6780 Å. Since in the mixture containing one volume of sulfuric acid to two volumes of methanol there was no sign of any shift of the absorption band of the first ion to a longer wave length, we do not think that this band is due to the first ion.

When the solution in sulfuric acid was allowed to stand the color changed from red to violet. After standing at room temperature for two weeks the spectrum was measured again. By then the band at 6780 Å. had almost disappeared, and there was a maximum at 5800 Å. It is possible that the band at 6780 Å. was due to an intermediate in the reaction of the dye with concentrated sulfuric acid, and that at 5800 Å. to the product of this reaction. These spectra are shown in Fig. 2.

The spectrum obtained for the chloride of the dye in methyl alcohol containing enough hydrochloric acid to prevent the hydrolysis of the ion is shown in Fig. 2. It was obtained from measurements at 50 and 100 Å. intervals. This spectrum has the same form as that of malachite green, consisting of a strong band and a weaker one at a shorter wave length. The peaks of both these bands come at longer wave lengths than those of the corresponding bands of malachite green. The wave lengths of these peaks are 6390 and 4440 Å. for the viridine green, and 6180 and 4260 Å. for malachite green. The ratios of the wave lengths are about the same for the two dyes, being 1.44 and 1.45, respectively.

Kinetics.—The rate of the reaction was studied as a function of the actual and relative concentrations of the ion, the anhydro base and the methyl ether, but not as a function of the concentration of methyl alcohol. The experimental method was to observe the extinctions at 6400 and 5000 Å. from time to time until equilibrium was reached, using solutions containing hydrochloric acid, sodium hydroxide, or no extraneous acid or base other than the traces present as impurities in the solvent. The results of these measurements are given later as E_{64} and E'_{50} at alternate times. Simultaneous values are obtained readily by interpolation.

Usually one does not change extinctions to concentrations in a kinetic study; but, since this reaction was somewhat complicated by the presence of two colored reactants, and since all the molecular extinction coefficients had been measured, it was thought better to calculate the concentrations of the components. The method used was a second approximation, the first approximation being $M_i = E_{64}/\epsilon_{i64}$ and $M_a = E'_{50}/\epsilon_{a50}$.

Taking E'_{50} as an approximate measure of E_{a50}, $E_{i64} = E_{64} - E_{a64} = E_{64} - E_{a50}\epsilon_{a64}/\epsilon_{a50} = E_{64} - E'_{50}\epsilon_{a64}/\epsilon_{a50}$, and $M_i = E_{i64}/\epsilon_{i64}$. The spectra show $\epsilon_{a64}/\epsilon_{a50} = 0.033$ and $\epsilon_{i64} = 5 \times 10^4$. So M_i was taken as equal to $(E_{i64} - 0.033\,E'_{50})/5 \times 10^4$.

$E_{u50} = E'_{50} + E_{a50}\epsilon_{a64}\epsilon_{i50}/(\epsilon_{a50}\epsilon_{i64})$. The spectra show $\epsilon_{a64}\epsilon_{i50}/(\epsilon_{a50}\epsilon_{i64}) = 0.002$. Hence taking $E'_{50} = E_{a50}$, $E_{u50} = 1.002\,E'_{50}$. $E_{64} + 3.3\,E'_{50}$ is approximately proportional to M_q. The quinoidal forms diminish by an approximately first order reaction, whose rate constant we have called k_q. At zero time 0.37 of the solute is quinoidal. From a comparison of E_{50}^{∞} with the corrected spectrum of the methyl ether we estimated that 0.75 of E_{50}^{∞} is due to the methyl ether. Hence $E_{e50} = 0.75\,(1 - 0.37e^{-k_qt})\,E_{50}^{\infty}$, and $E_{a50} = 1.002\,E'_{50} - 0.75\,(1 - 0.37e^{-k_qt})E_{50}^{\infty}$. In each experiment k_q was estimated from the time needed for $E_{64} + 3.3\,E'_{50}$ to fall to half its value. A rough estimate of k_q is all that is necessary, for at the beginning E_{a50} is nearly equal to E_{u50}, and as the reaction proceeds e^{-k_qt} soon becomes negligible. M_a was calculated from the equation $M_a = E_{a50}/\epsilon_{a50}$, using 1.5×10^4 as the value of ϵ_{a50}.

In general the constants used in the above calculations were fairly accurately determined, but $E_{e50}^{\infty}/E_{50}^{\infty} = 0.75$ was only a rough estimate. Since $M_a - M_a^{\infty}$ was used to derive the rate laws and constants, the value chosen had only a very minor effect on our results. $E_u - E_u^{\infty} = (\epsilon_a - \epsilon_e)(M_a - M_a^{\infty})$. The left-hand side of this equation does not depend on $E_{e50}^{\infty}/E_{50}^{\infty}$. The value of ϵ_e does, but ϵ_a is very much larger than ϵ_e, so that the values calculated for $M_a - M_a^{\infty}$ depend very little on the value chosen for $E_{e50}^{\infty}/E_{50}^{\infty}$, and the relative values do not depend on it at all.

The results of our experiments have been shown in Table V, which includes columns for the time, E_{64}, E'_{50}, M_i, M_a and various rate constants. Some of the values given for M_i and M_a were obtained by interpolation. These have been enclosed in parentheses. The values of M_i and the derived rate constant for alkaline solutions are not given in the table. If the values of M_i in the alkaline solutions are calculated by the method described, they are in general less than 1×10^{-7},

TABLE V

KINETICS

Time, min.	E_{64}	E'_{50}	$M_i \times 10^5$	$M_a \times 10^5$	k_i, min.$^{-1}$	k_a, min.$^{-1}$	k_q, min.$^{-1}$	k_l, min.$^{-1}$
Neither hydrochloric acid nor sodium hydroxide added; $T = 23.5 \pm 0.02°$								
2.17	...	1.083	...	6.960				
4.25	0.72	...	1.392	...				
5.00	...	0.697	(1.281)	4.353	0.127 (4.25 to 6.83)	0.176 (2.17 to 7.5)		
6.83	0.534	...	1.034	...				
7.50	...	0.467	(0.946)	2.793		0.178 (5 to 12.67)	0.172 (5 to 10)	0.150 (5 to 10)
9.58	0.371	...	0.720	...				
10.00	...	...	(0.676)	(1.790)				
10.25	...	0.308	...	1.713	0.137 (6.83 to 14.42)			
12.00	0.264	...	0.512	...				
12.67	...	0.234	...	1.207				
14.42	0.197	...	0.382	...	0.155 (9.58 to 17.33)	0.161 (10.25 to 18)		
15.00	...	...	(0.346)	(0.863)			0.163 (10 to 20)	0.132 (10 to 20)
15.08	...	0.181	...	0.853				
17.33	0.122	...	0.234	...	0.153 (6.83 to 21)			
18.00	...	0.141	...	0.580				
20.00	...	...	(0.164)	(0.440)		0.173 (18.08 to 21.75)		
21.00	0.075	...	0.144	...	0.157 (12 to 21)			
21.75	...	0.108	...	0.353				
∞	0.015	0.0735	0.026	0.123				
					0.147 (graph)	0.173 (graph)	0.168 (Mean)	0.141 (Mean)
1.33	...	1.563	...	10.11				
4.67	...	0.886	...	5.520		0.184 (1.33 to 7.08)		
5.00	...	...	(1.688)	(5.203)				
5.58	0.810	...	1.570	...				
7.08	...	0.602	...	3.607				
7.50	...	...	(1.211)	(3.352)				
8.00	0.589	...	1.144	...	0.129 (5.58 to 10.33)	0.193 (4.67 to 12)	0.177 (5 to 10)	0.154 (5 to 10)
9.50	...	0.404	...	2.260				
10.00	...	...	(0.879)	(2.069)				
10.33	0.437	...	0.850	...				
12.00	...	0.286	...	1.460	0.151 (8 to 15.42)	0.197 (7.08 to 16.17)		
13.08	0.287	...	0.558	...				
15.00	...	...	(0.407)	(0.876)				
15.42	0.203	...	0.392	...	0.161 (10.33 to 18.5)	0.174 (9.5 to 20)	0.169 (10 to 20)	0.136 (10 to 20)
16.17	...	0.177	...	0.727				
18.50	0.129	...	0.248	...	0.166 (13.08 to 21)			
20.00	...	0.136	(0.197)	0.493				
21.00	0.089	...	0.170	...				
∞	0.017	0.093	0.028	0.153				
					0.154 (graph)	0.184 (graph)	0.173 (Mean)	0.145 (Mean)
A trace of hydrochloric acid added. $T = 23.5 \pm 0.02°$								
0.91	...	1.040	...	6.687				
3.33	...	0.539	...	3.293				
4.33	1.215	...	2.404	...		0.283 (0.91 to 5.75)		

TABLE V (*Concluded*)

Time, min.	E_{64}	E'_{60}	$M_i \times 10^5$	$M_a \times 10^5$	k_i, min.$^{-1}$	k_a, min.$^{-1}$	k_q, min.$^{-1}$	k_1, min.$^{-1}$
5.00	...	...	(2.250)	(2.128)				
5.75	...	0.319	...	1.793				
6.75	0.957	...	1.898	...	0.186 (4.33 to 8.91)			
7.50	...	...	(1.689)	(1.127)		0.276 (3.33 to 8.08)	0.200 (5 to 10)	0.136 (5 to 10)
8.08	...	0.199	...	0.973				
8.91	0.686	...	1.360	...		0.272 (5.75 to 10.50)		
10.00	...	...	(1.137)	(0.649)	0.183 (6.75 to 13.75)			
10.50	...	0.142	...	0.587				
11.25	0.470	...	0.932	...				
12.91	...	0.112	...	0.380		0.251 (8.08 to 12.91)		
13.75	0.320	...	0.634	...				
15.00	...	...	(0.535)	(0.307)	0.187 (11.25 to 18.75)		0.200 (10 to 20)	0.129 (10 to 20)
15.33	...	0.101	...	0.300				
16.00	0.238	...	0.470	...				
18.75	0.173	...	0.340	...	0.182 (16 to 21.83)			
20.00	...	...	(0.301)	(0.176)				
21.83	0.132	...	0.258	...				
∞	0.075	0.075	0.146	0.127				
					0.182 (graph)	0.260 (graph)	0.200 (Mean)	0.133 (Mean)

Time, min.	E_{64}	E'_{60}	$M_a \times 10^5$, min.$^{-1}$	k_a, k_q or k_1, min.$^{-1}$
Sodium hydroxide added, $M_N = 2.5 \times 10^{-4}$, $T = 23.5° \pm 0.05°$				
1.08	0.068	...	....	
1.91	...	1.794	11.61	
4.00	0.050	...	....	
4.75	...	1.309	8.33	0.139 (1.91 to 7.42)
6.75	0.037	...	....	
7.42	...	0.888	5.49	0.138 (1.91 to 15.58)
10.08	0.026	...	....	
10.91	...	0.589	3.47	
12.67	0.023	...	....	0.142 (4.75 to 13.42)
13.42	...	0.454	2.56	
15.50	0.016	...	....	
16.58	...	0.327	1.69	0.133 (10.91 to 18.91)
18.25	0.013	...	....	
18.91	...	0.271	1.31	
∞	0.008	0.102	0.173	0.138 (Graph)
Sodium hydroxide added, $M_N = 2.5 \times 10^{-4}$, $T = 0° \pm 0.05°$				
26.25	...	0.888	5.46	
28.08	0.029	...	....	
31.00	...	0.749	4.52	0.0448 (26.25 to 36.17)
33.25	0.020	...	....	
36.17	...	0.620	3.64	0.0412 (31.0 to 50.2)
41.42	...	0.520	2.97	
50.50	...	0.397	2.13	
51.50	0.014	...	....	
61.00	...	0.297	1.45	0.0387 (41.42 to 90.83)
61.67	0.011	...	....	
74.75	...	0.222	0.93	0.0387 (61.0 to 74.75)
90.83	...	0.172	0.60	
∞	0.006	0.112	0.19	0.0405 (Graph)

in one case the value is negative, and they do not decrease with time. There were therefore no measurable concentrations of the ion in the alkaline solutions.

One should add to the results shown in the table the observation that the rate of the reaction was not appreciably different with sodium hydroxide at 2.5×10^{-4} M and at 2.5×10^{-3} M.

In any single experiment plots of ln $(M_i - M_i^\infty)$ and ln $(M_a - M_a^\infty)$ are nearly straight lines. The slopes of these lines are given at the bottom of the columns, k_i and k_a. The values given in the columns were obtained from the equations $\Delta \ln (M_i - M_i^\infty)/\Delta t = k_i$ and $\Delta \ln (M_a - M_a^\infty)/\Delta t = k_a$, taking Δt between the times indicated in parentheses. The values of k_i and k_a depend on the acidity of the solution, but for any single experiment they are fairly constant over ten to forty fold changes of $M_i - M_i^\infty$ and $M_a - M_a^\infty$. For any single run, $k_a > k_i$, and the trend is such as to equalize the constants as the reaction proceeds. The constant k_a can be considered as the sum of a first order rate constant for the disappearance of the anhydro base and that for the reverse process. Similarly k_i can be considered as the sum of first order rate constants for the disappearance of the positive ion and the reverse process. In all runs, these reactions are almost complete, and k_i and k_a are approximately the rate constants of the forward reactions. In the earlier stages of the reactions $k_i = \mathrm{d} \ln M_i/\mathrm{d}t$ and $k_a = \mathrm{d} \ln M_a/\mathrm{d}t$ approximately.

The over-all reaction for the production of one mole of the methyl ether can be expressed by the equation

$$(1 - y)C_{31}H_{28}N_2 + yC_{31}H_{29}N_2^+ + (1 - y + x)CH_4O + (y - x)CH_3O^- = xH^+ + C_{32}H_{32}ON_2$$

The product of the concentrations of the ions of the solvent does not change during the reaction. So $M_H M_o = (VM_H + x)(VM_o - y + x)/V^2$, where V is the volume. Since V can be made as large as desired, the above equation reduces to $xM_H - yM_H + xM_o = 0$, and $x = \mathrm{d}M_H/\mathrm{d}M_e$ and $y = -\mathrm{d}M_i/\mathrm{d}M_e$. Assuming that during the reaction an equilibrium or steady state is maintained between the ion and the anhydro base, one can put $M_i = kM_aM_H$ and $\mathrm{d}M_i = k(M_H\mathrm{d}M_a + M_a\mathrm{d}M_H)$. By combining these equations one obtains $(\mathrm{d} \ln M_a/M_e)/(\mathrm{d} \ln M_i/\mathrm{d}M_e) = 1 + M_i/(M_H + M_o)$, or the approximate equation $k_a/k_i = (\mathrm{d} \ln M_a/\mathrm{d}t)/(\mathrm{d} \ln M_i/\mathrm{d}t) = (\mathrm{d} \ln M_a/\mathrm{d}M_e)/(\mathrm{d} \ln M_i/\mathrm{d}M_e) = 1 + M_i/(M_H + M_o)$. Hence $k_a > k_i$, and k_a and k_i approach equality as the reaction proceeds.

However, the agreement between the above theory and the data is not quantitative. In the experiments in neutral solution, M_i varied between 1×10^{-5} and 1×10^{-6}, but if the solutions contained no impurity, M_H would have been less than 1×10^{-7}, and M_i and M_o would have been equal. Under these conditions, k_a/k_i should have been nearly equal to two, but it was not. This discrepancy is readily explained by assuming that a trace of an acidic or basic impurity was present. Such an impurity acts as a buffer, and tends to make $k_a = k_i$. That a trace of impurity can have a noticeable effect is due to the extreme dilutions of the solution.

The method used to obtain the ratio between d ln $M_a/\mathrm{d}t$ and d ln $M_i/\mathrm{d}t$ when the solvent is pure can also be used when a buffer is present, by introducing the equilibrium reaction between the acidic and basic forms of the buffer. The equation obtained in this way is

$$(\mathrm{d} \ln M_a/\mathrm{d}t)/(\mathrm{d} \ln M_i/\mathrm{d}t) = 1 + M_i/[M_H + M_o + M_Q M_p/(M_Q + M_p)]$$

when M_Q and M_p are the molarities of the acidic and basic forms of the buffer.

If one assumes the mechanism of the reaction to be

$$CH_3OH + C_{31}H_{24}N_2 \rightleftharpoons C_{31}H_{25}N_2^+ + CH_3O^- \qquad \text{(fast)}$$

$$C_{31}H_{25}N_2^+ + CH_3OH \rightleftharpoons C_{32}H_{28}ON_2 + H^+ \qquad \text{(slow)}$$

$$C_{31}H_{25}N_2^+ + CH_3O^- \rightleftharpoons C_{32}H_{28}ON_2 \qquad \text{(slow)}$$

the rate of the reaction can be expressed by the equation

$$-\mathrm{d}M_a/\mathrm{d}t - \mathrm{d}M_i/\mathrm{d}t = -\mathrm{d}M_q/\mathrm{d}t = k_1M_a + k_2M_i - k_1'M_e - k_2'M_eM_H$$

where k is the product of the equilibrium constant of the first reaction and the rate constant of the last, and the primes indicate constants for reverse reactions. Owing to the presence of traces of a buffer the concentrations of hydrogen ion cannot be calculated from the composition of the original solutions and the extent of the reaction. However, the reactant is an indicator, and M_i/M_a is proportional to M_H, and can be obtained from the data at any stage of the reaction. The above rate law reduces to

$$-\mathrm{d}M_q/\mathrm{d}t = M_q[k_1(1 - M_i/M_q) + k_2M_i/M_q] - M_e(k_1' + k_2''M_i/M_a)$$

In our experiments considerable changes in M_q were accompanied by comparatively small changes in M_i/M_a and M_i/M_q). For long periods in a single experiment these ratios can be taken as constants having the values observed for them at the middle of the period. With these ratios constant the equation becomes that for a reversible unimolecular reaction, and can be put in the form

$$\mathrm{d} \ln (M_q - M_q^\infty)/\mathrm{d}t = k_q = k_1(1 - M_i/M_q) + k_2M_i/M_q + k_1' + k_2''M_i/M_a$$

where k_q is only constant for a period in a single experiment. Within the range of the conditions of our experiments the equilibrium greatly favors the methyl ether, so approximately

$$k_q = k_1(1 - M_i/M_q) + k_2M_i/M_q$$

Values of k_q between any interval can be calculated from the data shown in Table V, and the value of M_i/M_q in the middle of the interval can be similarly obtained. The calculations have been carried out for the intervals five minutes to ten minutes, and ten minutes to twenty minutes for the experiments carried out in neutral or acid solutions, and the values are given in the table. For alkaline solutions $M_q = M_a$, and hence the values obtained for k_a are also the values of k_q. From these values of k_q the values of k_1 and k_2 have been calculated. The values obtained are $k_1 = 0.139$ min.$^{-1}$ and $k_2 = 0.232$ min.$^{-1}$.

Using $k_2 = 0.232$ min.$^{-1}$ we have calculated k_1 for each determination of k_q. The values are shown in the table. Considering the probable experimental errors the agreement is good. The values vary between 0.154 min.$^{-1}$ and 0.129 min.$^{-1}$. The values of $M_q - M_q^\infty$ at mid-times vary from 7×10^{-6} to 8×10^{-5}, and those of M_i/M_q at mid-times from 0 to 1.7. There is no consistent trend in k_1 with change of M_i/M_q. But k_1 tends to decrease as the reactions proceed. The average of the first determinations is 0.145 min.$^{-1}$, that of the last 0.132 min.$^{-1}$. This trend is not surprising. It would occur if the anhydro base acted to a small extent as the base that changes quinoidal to benzenoidal forms, or if any other anhydro base were present as an impurity. Theoretically such an impurity was present, because the anhydro base can be the *cis* or the *trans* compound.

There are other mechanisms that are kinetically equivalent to the one suggested. For instance k_2 can be the rate constant for the reactions $C_{31}H_{24}N_2 + CH_3OH_2^+ \rightarrow C_{31}H_{28}ON_2 + H^+$, or $C_{31}H_{26}N_2^{++} + CH_3O^- \rightarrow C_{32}H_{28}ON_2 + H^+$, and k_1 can be the rate constant for the reaction $C_{31}H_{24}N_2 + CH_3OH \rightarrow C_{32}H_{28}ON_2$. The mechanism suggested is part of a more general one in which benzenoidal compounds are formed by the combination of various bases present with the various quinoidal forms. Our measurements show that only those reactions in which the base is not a derivative of the dye, and the net sum of the charges of the reactants is one or zero, are sufficiently rapid to be important in the range of conditions covered by our experiments.

The value of k_1 was obtained also at 0°, by measuring the change of E'_{50} in an alkaline solution. The value obtained was 0.0405 min.$^{-1}$. The heat of activation was calculated as 8400 cal. This heat of activation is for the mechanism $CH_3OH + C_{31}H_{24}N_2 \rightarrow C_{31}H_{25}N_2^+ + CH_3O^- \rightarrow C_{32}H_{28}ON_2$. It does not include the heat of activation of the alcoholysis of the ion. If we accept the above mechanism for the reaction in alkaline solution, the heat of activation measured is the sum of the heat of reaction of the preliminary rapid reaction and the heat of activation of the follow reaction. This follow reaction does not require a very violent collision, but a very special configuration of the reacting molecules.

Photo-ionization.—When a solution that has faded is exposed to sunlight the color returns in part. The tint obtained in this way is that of the solution before it had faded. Apparently the light shifts the equilibrium between the methyl ether and the positive ion in favor of the latter. The positive ion rapidly achieves equilibrium with the anhydro base, and the tint depends on the proportion of positive ion and anhydro base. The photo-ionization is increased by using ultraviolet light, but it can be quite easily observed with light that has passed through window glass.

To confirm that except for ionization the dye is not changed by the light we measured the extinctions at two wave lengths while the solution faded, irradiated the faded solution, and then measured the extinctions at the same two wave lengths while the solution faded in the dark. By interpolation it was possible to compare the extinctions of the original and the faded solutions at one of the wave lengths when they had the same extinction at the other. Their comparison is an exacting criterion of identity. It was found that the relative extinctions of the original and the irradiated solutions were identical. The results are shown in Table VI.

TABLE VI

EXTINCTIONS BEFORE AND AFTER EXPOSURE TO LIGHT

Before exposure		After exposure	
E_{64}	E_{44}	E_{64}	E_{44}
0.312	0.235	0.312	0.237
.234	.198	.234	.198
.153	.164	.153	.162
.096	.142	.096	.142

Summary

A mixture of the anhydro base and the methyl ether of viridine green was prepared.

The extinctions of rapidly fading solutions of this product in a mixture of methyl alcohol and benzene were measured at various wave lengths at noted times. By interpolation and extrapolation of these measurements the extinctions of the solutions at any time, including that of mixing, could be obtained.

From the values of the extinctions at zero time the fraction of anhydro base in the original preparation, the fraction of this base converted to the ion on solution, and the molecular extinction coefficients of the anhydro base were calculated.

The spectra of the anhydro base in the mixture of methyl alcohol and benzene, and in benzene alone were obtained and compared. Methyl alcohol was found to produce a large shift of the absorption maximum toward the red end of the spectrum.

The rates of change of extinctions at 6400 and 5000 Å., in alkaline, neutral, and slightly acid solutions were measured. The rate of conversion of the anhydro base to the methyl ether was found to be the sum of two reaction rates, both first order with respect to the anhydro base, but one independent of the acid and alkali, and the other first order with respect to acid. A fast reversible conversion of the anhydro base to the ion, followed by slower reactions of the ion with methylate ion and methyl alcohol has been suggested for the mechanism of the reaction.

BERKELEY, CALIFORNIA RECEIVED NOVEMBER 21, 1944