tion was not attained, the analyses were of more qualitative than quantitative significance. The derivative charred at 180–190° without melting

Preparation of the 2,4-Dinitrophenylhydrazine Derivative.—The 2,4-dinitrophenylhydrazine derivative was obtained by adding a saturated alcoholic solution of 2,4-dinitrophenylhydrazine to an alcohol solution of the fluorescent substance. The derivative precipitated immediately. The derivative was so insoluble in all common inert solvents that it was not possible to redissolve it for crystallization. It charred without melting at 200–215°.

Adsorption on Magnesium Oxide.—A portion of the fluorescent substance obtained by precipitating with ether as previously described was dissolved in absolute methanol and diluted with 9 volumes of dry ethyl ether. This solution was put through a column of powdered magnesium oxide (2642 Micron Brand obtained from Westvaco Chlorine Products Corp.). After development with methanol a blue-green fluorescent band was found at the top of the column and several centimeters lower a well-defined band which showed the characteristic bright blue fluorescence. The lower band was eluted with methanol and used to obtain absorption curve A, Fig. 1.

Adsorption on Charcoal.—The fluorescent substance in aqueous potato extract at *p*H 1.0 may be adsorbed on Nuchar W or on Norite A and partially eluted with acetone, methanol, or ethanol. However, poor elution yields and the strongly oxidizing character of activated charcoals led to the abandonment of this means of purification.

Absorption Spectra.—All absorption measurements were made with a Beckman model DU spectrophotometer. The spectral region isolated varied between 20 and 40 A.

Summary

1. A colorless precursor of the pigment which causes some white potatoes to turn grey or black when they are cooked has been isolated.

2. The fluorescent pigment precursor is unsaturated, and contains a carbohydrate group and a nitrogenous group. The latter is probably an amino acid or a peptide.

3. Tyrosine and trytophan are not contained in the fluorescent pigment precursor.

4. The absorption curve of the precursor shows a maximum at 2800 Å.

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

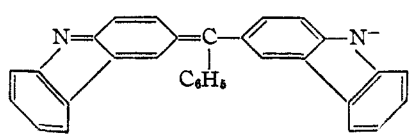
The Kinetics of the Reaction of Methanol with 3,3'-Dicarbazylphenylmethyl Ion in Alkaline Solution

BY GERALD E. K. BRANCH AND B. M. TOLBERT

The quinoidal derivatives of a diaminotriphenyl carbinol react with water or alcohols to form carbinols or ethers. Sidgwick and his co-workers,[1] working with very dilute aqueous solutions of *p,p'*-diaminotriphenylmethyl ion (Döbner's violet), and its tetramethyl and tetraethyl derivations (malachite green and brilliant green), found that in reactions at a fixed *p*H, the kinetics were those of reversible unimolecular reactions, but that the rate constants varied with the *p*H in ways that depended on the dye and the range of *p*H used. They satisfactorily explained these results by assuming rapid reversible reactions between the various quinoidal species possible, and similar reactions among benzenoidal species, and that each rate determining reaction was first order with respect to the quinoid or benzenoid involved. In such a setup, the distributions of the quinoid and benzenoid among their species depend on the *p*H and what species are possible for the particular dye.

In previous work on the kinetics of benzoidation of diaminotriphenylmethane dyes the quinoid has existed as Q^{++}, Q^+ or Q. The present investigation goes one step further to the case in which the quinoid is distributed between the anhydrobase and its negative ion. The kinetics of the corresponding reactions of the negative ions of the closely related dihydroxytriphenylmethane dyes have been studied over a long period of time, especially by La Mer and his co-workers,[2] who find the rate determining reaction to be one between the negative ions of the dye and of the bleaching agent.

To obtain significant concentrations of the negative ion of a diaminotriphenylmethane dye with the negative charge on the nitrogen atoms rather than on an acidic side group, it is necessary to have exceedingly basic conditions or a dye made from an exceptionally acidic amine. For that reason, 3,3'-dicarbazylphenylmethyl chloride was chosen as the dye. It was synthesized from carbazol, an exceptionally acidic amine.[3] The formula of the negative ion is given below.



The negative of this dye is green and has a strong band in the neighborhood of 730 $m\mu$[4]; while the anhydrobase has a violet red color with a strong band in the neighborhood of 500 $m\mu$. One can, therefore, easily regulate the amount of alkali to obtain significant concentrations of both anhydrobase and negative ion, and the decay of both of these quinoids can be followed separately

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[1] Sidgwick and Moore, *J. Chem. Soc.*, **95**, 889 (1909), and Sidgwick and Rivett, *ibid.*, 899 (1909).

[2] For a list of examples, see Hochberg and LaMer, THIS JOURNAL, **63**, 3110 (1941).

[3] Branch, Tolbert and Lowe, *ibid.*, **67**, 1693 (1945).

[4] Tolbert and Branch, *ibid.*, **68**, 315 (1946).

for neither quinoid absorbs much in the region in which the other absorbs strongly.

The anhydrobase is very insoluble in water and, when dissolved in an alcohol, the color fades too rapidly for measurements to be made at room temperature. However, solutions of the anhydrobase and the negative ion are moderately stable in mixtures of acetone and water. The speed of fading of such a solution is greatly enhanced by small quantities of methanol. It is thus possible by the use of these solutions to study the rate of fading as a function of the concentration of the bleaching agent as well as of the concentration of alkali.

It is advantageous to use a mixture of acetone and water rather than acetone alone, for with acetone alone only very small amounts of sodium hydroxide can be dissolved. In all experiments, the proportions of acetone and water were the same, so that though the bleaching action of the solvent was not negligible, it was a constant function of the concentration of sodium hydroxide. The fixed proportions of the acetone and water were seven volumes of acetone to three of water. The corresponding molarities are 9.84 *M* with respect to acetone and 17.3 *M* with respect to water.

Experimental Method.—The extinctions were measured with a Beckman quartz spectrophotometer, modified to allow the solutions to be kept at a constant temperature. A small bath was substituted for the cell compartment, and water from a thermostat was circulated through this bath. The optical cells were immersed in the bath. The cells were 1-cm. square glass tubing ground optically flat on two sides, and equipped with tapered joints and stopcocks, to permit evacuation and rapid introduction of the solution.

One of the cells was filled with a mixture of acetone, water, sodium hydroxide, and alcohol. The other cell contained the same proportions of these substances (the identity even including age), and a small amount of the anhydro base of the dye. The anhydro base was introduced as a solution made from the chloride of the dye and sodium hydroxide. The amount of sodium hydroxide necessary to form the dye was taken into account in making the solutions in the two cells equally alkaline. The concentrations of sodium hydroxide given in this paper are all corrected for that needed to neutralize the chloride of the dye. This correction was always small. It is equal to the amount of sodium chloride that was present in the reaction cell that is not present in the blank. The initial concentrations of the dye were between 10^{-5} and 10^{-4} *M*.

The two cells were put into the spectrophotometer, and after allowing a little time for temperature equilibrium to be reached, *E*, the extinction, was measured alternately at 730 and 500 mμ. At the former wave length, the negative ion absorbs light strongly, but the anhydrobase is practically transparent; while at 500 mμ the anhydrobase absorbs strongly, but the negative ion very feebly.

The measurements were continued until the extinctions were too small to obtain significant results. As a rule, this range corresponded to a twenty to fifty fold change in $E - E_\infty$. After further standing, the extinctions were again measured to obtain E_∞, at the two wave lengths. At lower temperatures, this standing was done at room temperatures and the cells were then cooled to the appropriate temperatures before the final extinctions were meausred.

The acetone and methanol used were standard C.P. chemicals which were redistilled. Distilled water was used. The sodium hydroxide contained only traces of carbonate. Carbon dioxide was not rigidly excluded. Its action would be to neutralize some of the sodium hydroxide, but the errors from this cause could hardly be significant. The pipet used to measure the methanol was such that no more than a five per cent. error would be expected in measuring 1 ml. In only one experiment was less than this amount of methanol measured.

The chloride of the dye was precipitated from a benzene solution of the methyl ether with hydrochloric acid dissolved in ether. The preparation of the methyl ether of the dye has been described by Branch, Tolbert and Lowe.[3]

Rate of Fading as a Function of Time and Wave Length.—In all experiments, it was found that when ln $(E - E_\infty)$ was plotted against time, a straight line was obtained, and within experimental error the slopes of the lines obtained for any experiment were the same whether the extinction was measured at 730 or 500 mμ. The data for a typical run are shown in Table I.

TABLE I

THE CHANGE OF EXTINCTION WITH TIME FOR A TYPICAL EXPERIMENT

NaOH = 2.03×10^{-2} *M*, CH_3OH = 0.25 *M*, *T* = 25°

λ = 730 mμ			λ = 500 mμ		
Time, min.	$E - E_\infty$	*k* min.$^{-1}$	Time, min.	$E - E_\infty$	*k* min.$^{-1}$
2.7	0.562	0.143	3.7	0.320	0.132
4.7	.423	.120	5.7	.246	.135
6.7	.333	.158	7.7	.188	.137
8.7	.243	.120	9.7	.143	.135
10.7	.191	.127	11.7	.109	.130
12.7	.148	.145	13.7	.084	.128
14.7	.111	.121	15.7	.065	.141
16.7	.087	.146	17.7	.049	.155
18.7	.065	.125	19.5	.036	.112
21.7	.045	.119	23.7	.023	.142
25.7	.028	.157	27.7	.013	
29.7	.015	.101			
33.7	.010				
	Mean	0.132		Mean	0.135
	k from slope	.130		*k* from slope	.135

This table is divided into two parts, one for measurements at 730 mμ and the other for those at 500 mμ in the same run. In each part $E - E_\infty$, the times in minutes, and the values of k calculated between successive times from the equation $k = \Delta \ln (E - E_\infty)/\Delta t$ are shown. At the bottom of each part, the average values of these k's are compared with the slope of a straight line, obtained by plotting $\ln(E - E_\infty)$ against time in minutes.

The constancy of $-\mathrm{d} \ln (E - E_\infty)/\mathrm{d}t$ shows that the reaction is first order with respect to the total concentration of quinoids. That is, that each rate determining reaction involves only one molecule of some quinoidal species. It is also evident that the quinoids as a whole must obey Beer's law in the range of concentrations over which the experiments extend. Since the reaction is almost irreversible the constancy of $-\mathrm{d} \ln (E - E_\infty)/\mathrm{d}t$, does not prove that the reverse reaction is first order with respect to the total benzenoids.

That $-\mathrm{d} \ln (E - E_\infty)/\mathrm{d}t$ is the same at 730 and 500 mμ, shows that the proportions of anhydrobase to quinoidal negative ion does not change during a run. It also confirms the previous finding that the reaction is first order with respect to the total concentration of quinoids. Were two quinoids to react, the product would be half benzenoid and half quinoid, but the anhydrobase would have no proton on the nitrogen atoms of the quinoidal half. In consequence it could not form a quinoidal negative ion, nor absorb strongly at 730 mμ. Such a reaction would give a larger value of $-\mathrm{d} \ln (E - E_\infty)/\mathrm{d}t$ at 730 than at 500 mμ.

In the rest of this paper we shall give the experimental results as k's in reciprocal minutes. The k given will be that determined from the slope of the line of the plot of $\ln (E - E_\infty)$ at 730 mμ against time. We have chosen the longer wave length values because at these E_∞ was always very small. However, the measurements at 500 mμ were just as consistent as those at 730 mμ.

The Rate Constant as a Function of the Concentration of Sodium Hydroxide.—A series of measurements were made at 25° using 0.25 *M* methanol in every case, but varying the concentration of sodium hydroxide from 1.25×10^{-3} to 3.10×10^{-2} *M*. The results are shown in Table II.

TABLE II

EFFECTS OF VARYING THE CONCENTRATION OF SODIUM HYDROXIDE

Methanol, 0.25 *M*; $T = 25°$

Molarity of NaOH	k(obs.) min.$^{-1}$	k(calcd.) min.$^{-1}$
1.25×10^{-3}	0.0243	0.0246
5.30×10^{-3}	.0586	.0585
1.03×10^{-2}	.0907	.090
1.03×10^{-2}	.0876	.090
1.03×10^{-2}	.0893	.090
1.10×10^{-2}	.0890	.094
2.03×10^{-2}	.130	.133
2.10×10^{-2}	.133	.135
3.10×10^{-2}	.155	.162

To the data given in Table I, one should add the observation that a solution of the anhydro base containing no excess of sodium hydroxide fades at a rate that is not much slower than that observed at the lowest concentration of sodium hydroxide used. If a point for this observation were included in a plot of the observed values of k against the logarithm of the molarity of sodium hydroxide, one obtains a nearly flat portion followed by a rising curve that tends to flatten out at the higher concentrations of sodium hydroxide. The experimental points fall in the rise between two flatter portions of the curve.

This is the type of curve that would be obtained if there are two rate determining reactions, in one of which the sum of the charges of the reactants is zero, and in the other this sum is minus one. Since the experiments included in Table II were all done with the same proportions of acetone, water and methanol, the bleaching agent can be treated as a single substance, and the concentration of sodium hydroxide added can be taken as equivalent to the concentration of the negative ion of the bleaching agent. The over-all rate constant, k, can then be expressed as a function of the sodium hydroxide concentration by the equation,

$$k = k_1 + k_2(\mathrm{NaOH})/\{1 + K(\mathrm{NaOH})\} \qquad (1)$$

where k_1 and k_2 are rate constants and K is the equilibrium constant for the conversion of the anhydro base to the quinoidal negative ion by sodium hydroxide. Terms for the back reaction have been omitted. They are negligible.

The values of k_1, k_2 and K were calculated from the measurements at the three lowest concentrations of sodium hydroxide. To two significant figures these values were $k_1 = 1.2 \times 10^{-2}$, $k_2 = 11$ and $K = 38$, when time is expressed in minutes, and concentrations in moles per liter. From these values, the values of k have been calculated for the other concentrations of sodium hydroxide. The calculated values of k are shown in the last column of Table II.

In equation (1) the contributions of reactions having the same sum of charges of reactants are not distinguished. In a case such as this one in which each of the two reactants, quinoid and bleaching agent, can exist as several species in rapid equilibrium, the way in which the rate varies with the sodium hydroxide concentration can show what the sum of the charges of the reactants of the rate determining reactions are, but not how this sum is obtained. The primary salt effect on k also would not distinguish between reactions with the same sum of charges of reactants, even though the individual rate determining steps could belong to different ionic types.

The Rate Constant as a Function of the Concentration of Methanol.—Two series of measurements of k were made in which only the concentration of methanol was varied. One of these series was made at 25° and the other at 2°. The results and details are given in Table III.

When k was plotted against the molarity of methanol a straight line was obtained. These lines intercepted the k axis at $k = 0.006$ at 0°, and $k = 0.022$ at 25°. The slopes of the lines were 0.0680 at 0°, and 0.275 at 25°. These are the values of k_0 and k_m in the linear equation

$$k = k_0 + k_m(CH_3OH) \qquad (2)$$

In Table II, the values $k_0 = 0.006$ at 0° and $k_0 = 0.022$ at 25° are assumed and the values of k_m in equation (4) calculated on the basis of these values are shown. With one exception the values agree with each other within experimental error, and their averages agree with the values obtained geometrically.

TABLE III

EFFECT OF VARYING THE CONCENTRATION OF METHANOL

$NaOH = 1.03 \times 10^{-2}\ M$

$T = 25°$, $k_1 = 0.022$ min.$^{-1}$			$T = 2°$, $k_1 = 0.006$ min.$^{-1}$		
k, min.$^{-1}$	CH_3OH, moles-liters^{-1}	k_m, liters-moles-min.$^{-1}$	k, min.$^{-1}$	CH_3OH, moles-liters^{-1}	k_m, liters-moles^{-1} min.$^{-1}$
0.0693	0.125	0.378	0.0228	0.250	0.0672
.0893	.250	.269	.0409	.500	.0698
.0907	.250	.275	.0563	.750	.0672
.0876	.250	.262	.0759	1.00	.0699
.122	.375	.267			
.170	.500	.269			
.159	.500	.274			
.206	.625	.294			
	Mean	.287		Mean	.0685
	From slope	.275		From slope	.0680

In equation (1) the contributions of the component rate determining reactions are divided into two classes, the zero reactions in which the sum of the charges of the reactants are zero, and the minus reactions in which the sum of the charges of the reactants are minus one. Each of these classes can be divided into sub classes according as the bleaching agent is the solvent or methanol. The resulting four types of reactions can be called the solvent-zero, the methanol-zero, the solvent-minus, and the methanol-minus reactions. When the rate is expressed as the sum of the rates of these reactions, k can be expressed as a function of the concentrations of the sodium hydroxide and of methanol by the equation.

$$k = [k_c + k_d\,(CH_3OH) + k_e\,(NaOH) + k_f\,(NaOH)(CH_3OH)]/[1 + K(S^-)] \qquad (3)$$

if no more than one unit of methanol (the undissociated molecule or its ion) is included in the reactants, and methanol is not associated with itself. This equation reduces to equation (2) when (NaOH) is kept constant. The validity of equation (2) for experiments in which a fixed concentration of sodium hydroxide was used but the concentration of methanol was varied shows that the methanol does not appreciably neutralize the ion of the solvent, that is, that methanol is a weaker acid than the solvent. The validity of equation (2) also shows that only one molecule of methanol takes part in any of the rate determining reactions, and that methanol is not associated with itself under the conditions of the experiment. The lack of association of methanol with itself is to be attributed to its small concentration and the dispersing power of the solvent.

The results given in Tables II and III show that the methanol-minus type of reaction is the most important in the range covered by the experiments. Were this reaction one in which methanol acts as an acidic reagent on the negative ion of the quinoid, it ought not to be as fast as the solvent-minus reaction, for methanol is the weakest acid present. If the reaction is one in which methanol acts as a base on the negative ion one has difficulty in accounting for its predominance over the reactions in which (a) the negative ion of the solvent reacts as an electron donor with the quinoidal negative ion, (b) the solvent reacts similarly with the quinoidal negative ion and (c) methanol reacts similarly with the anhydrobase. That (b) is specifically much slower than the methanol-minus reaction would indicate that the rate of reactions of bases with the quinoidal negative ion increases greatly with the strength of the base, but in that case, reaction (a) in which the base is very much stronger should be specifically much faster than the methanol-minus reaction, but this reaction is a minus-two reaction, and were it specifically much faster than the minus-one reactions, it should have been found at the higher concentrations of sodium hydroxide, whose concentration at the limit is one-tenth that of methanol. It does not appear that this paradox could be ascribed to the repulsion between similarly charged ions. The point of reaction is at the central carbon atom of the quinoid, and this is somewhat distant from the nitrogen atoms on which the negative charge is chiefly located. Indeed, it would be almost as near to the positively charged sodium ions that are attracted into the neighborhood of the negatively charged nitrogen atoms.

In the reaction of a base with the central atom of a quinoid, no base is removed from the central atom. In that case, the specific rate of the reaction of the anhydrobase with an electron donor should be greater than that of the quinoidal negative ion with the same base. Hence, the rate of reaction (c), which is a methanol-zero reaction, should be greater than that of methanol with the quinoidal negative ion, when the anhydrobase and its negative ion have the same concentrations. These concentrations are equal at 1/38 N sodium hydroxide, but at this concentration, the zero reactions are less than ten per cent. of the total reaction. These difficulties are removed if the reaction of methoxide ion with the anhydrobase is assumed to be the principal methanol-minus reaction.

The reactions of a variety of bases with the same substrate increase in rate with the strength of the base. Approximately, the logarithm of the specific rate constant is a linear function of the logarithm of the dissociation constant of the base. Hence, when the rates of the reactions of a substrate with the negative ions of two acids are compared

$$\frac{\gamma_A}{\gamma_B} = \frac{(HA)}{(HB)}\left(\frac{K_{HA}}{K_{HB}}\right)^{n-1} \tag{4}$$

where γ_A and γ_B are the rates with A^- and B^-, respectively, (HA) and (HB) are the concentrations of the two acids, K_{HA} and K_{HB} are the dissociation constants of these acids, and n is the slope of the line obtained by plotting the logarithm of the rate constant against the logarithm of the reciprocal of the dissociation constant of the acid. When the weaker of the two acids has the smaller concentration, the reaction of its negative ion can be faster than that of the other ion only if n is greater than one. In the present case, n must be assumed to be greater than one, for the reaction of the anhydrobase with methoxide ion was faster than that with the solvent ion, although methanol was at a low concentration, and the validity of equation (2) showed that methanol is a weaker acid than the solvent. The solvent-minus reaction should be attributed to the reaction of the anhydrobase with hydroxide ion rather than to the reaction with the negative ion of the hydrate of acetone, water being a weaker acid than the hydrate of acetone.

If it is correct to assume that n in equation (4) is greater than one, the reactions of the anhydrobase with the negative ions are specifically much faster than the reactions of water and methanol with the anhydrobase. The latter are zero reactions and the former are minus-one reactions. The specific rate constant of the zero reactions considered as a single reaction is k_1 (equation 1) divided by the molarity of water and methanol, and that of the minus-one reactions considered as a single reaction is k_2 (equation 1). The latter quantity is about 10^4 times the former. This 10^4 factor is much too small in view of the difference between the basicities of the undissociated bleaching agent and the negative ions even though the latter are chiefly the ions of the strongest acid present (acetone hydrate). Therefore, it is probable that the zero reactions are not those between the anhydrobase and the undissociated bleaching agents, but those of the positive ion of the quinoid and the negative ions of the bleaching agents. Therefore, the rate determining reactions are probably

$$Q^+ + OH^- \longrightarrow T_{H_2O}$$
$$Q^+ + CH_3O^- \longrightarrow T_{CH_3OH}$$
$$Q + OH^- \longrightarrow T^-_{H_2O}$$
$$Q + CH_3O^- \longrightarrow T^-_{CH_3OH}$$

where T_{H_2O}, etc., are transition states made up of the dye and the bleaching agent indicated by the subscript and carrying the electrical charge shown.

The Rate Constant as a Function of the Temperature.—Measurements of k were made at 25, 15 and 2° for three sets of concentrations of methanol and sodium hydroxide. For each set, the logarithm of k was plotted against the reciprocal of the absolute temperature. In each case the plot was a straight line, and the three lines were approximately parallel. From the slopes of these lines $-R\,d(\ln k)/d(1/T)$ was calculated for each set of experiments. The values obtained are shown in the last column of Table IV.

TABLE IV

CHANGE OF THE RATE CONSTANT WITH TEMPERATURE

Molarity of sodium hydroxide	Molarity of methanol	Temp., °C.	k, min.$^{-1}$	$-R\,d(\ln k)/d(1/T)$
1.03×10^{-2}	0.50	2	0.0409	10000 ± 400
1.03×10^{-2}	.50	15	.0938	
1.03×10^{-2}	.50	25	.160	
1.03×10^{-2}	.50	25	.170	
1.03×10^{-2}	.50	25	.159	
1.03×10^{-2}	.25	2	.0228	9800 ± 400
1.03×10^{-2}	.25	15	.0520	
1.03×10^{-2}	.25	25	.0876	
1.03×10^{-2}	.25	25	.0907	
1.03×10^{-2}	.25	25	.0893	
2.03×10^{-2}	.25	2	.0352	10070 ± 400
2.03×10^{-2}	.25	15	.0706	
2.03×10^{-2}	.25	25	.0130	
2.03×10^{-2}	.25	25	.0133	
			Mean	9970

The quantity $-R\,d(\ln k)/d(1/T)$ is not a simple heat of activation, even though it has the form of a heat of activation of a unimolecular reaction. That the change of the number of collisions per unit time with change of temperature has been neglected is not significant, for this effect is small compared to the probable errors. But k is not the rate constant of a single reaction, but a function of several rate constants and an equilibrium constant.

The equilibrium constant is for the neutralization of a very weak acid (the anhydro base) by the ion of an acid which is not much weaker. The heat of this reaction would be small. Further it would not contribute fully to the heat of activation, for K(NaOH) was always less than one, and is summed to one in the expression for k. The quantity $-R\,d(\ln k)/d(1/T)$ is therefore essentially a weighted mean of the heats of activation of the component reactions, the heats of preliminary fast reactions being included in the heats of activation. The principal reaction is the methanol-minus reaction, and the other reactions would probably not have contributed much if their heats of activation had been much greater than that of this reaction, consequently the value of 10000 calories is probably within 1000 calories of the heat of activation of the methanol-minus reaction.

One cannot assume a mechanism which involves a rapid preliminary step which absorbs more heat than the heat of activation of the over-all reaction. The value of 10000 calories found in this case does not preclude any of the suggested mechanisms. It would preclude any fanciful mechanism involving hydrogen ion as a reactant in the rate determining step. It would require the absorption of more than 10000 calories per mole to obtain hydrogen ion under the conditions of these experiments.

Summary

The fading of solutions of 3,3'-dicarbazylphenylmethyl chloride in mixtures of acetone, water, methanol and sodium hydroxide have been investigated. Fixed concentrations of acetone and water were used. The concentrations of methanol and sodium hydroxide and the temperature were varied.

When the concentrations of sodium hydroxide and methanol were constant, the rate of fading was found to be proportional to the total concentration of the quinoids. The proportionality constant obeyed the law, $k = \{k_1 + k_2(\text{NaOH})\}/\{1 + K(\text{NaOH})\}$ when the concentration of sodium hydroxide was varied, but that of methanol was fixed. When the concentration of sodium hydroxide was fixed and that of methanol was varied, the proportionality constant was a linear function of the concentration of methanol. The logarithm of the proportionality constant was found to be a linear function of the reciprocal of the absolute temperature.

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[CONTRIBUTION FROM THE METCALF RESEARCH LABORATORY OF BROWN UNIVERSITY]

Properties of Electrolytic Solutions. XXV. The Conductance of Choline and Related Picrates in Ethylene Chloride at 25°

BY D. J. MEAD, J. B. RAMSEY, D. A. ROTHROCK, JR., AND C. A. KRAUS

I. Introduction

It is well known that the strength of organic acids and bases is markedly influenced by the presence of electronegative substituents and by their position with respect to the charge on the ion. There is no clear evidence that such substituents have a similar effect in the case of salts, largely because such salts have been investigated in water, a solvent of high dielectric constant, in which salts are normally completely dissociated into their constituent ions.

In a later paper, some results will be presented showing what influence electronegative elements have on the dissociation constant of salts when introduced into the negative ion. In the present paper, we are concerned with the influence which electronegative atoms or groups have on the dissociation constant of salts of the onium type when introduced into the positive ion.

Among the simpler compounds in which negative atoms or groups occur in onium ions, are the cholines. The conductance of picrates of various ions of the choline type have been measured. The choline ion, itself, hydroxyethyltrimethylammonium, contains a hydroxyl group attached to the end carbon atom of the ethyl group. In place of the hydroxyl group, other groups or elements may be introduced. Of interest is the methoxymethyltrimethylammonium ion, which is isomeric with the choline ion. Other compounds studied are the picrates of ethyl-, bromoethyl-, acetylethyl-, bromomethyl and iodomethyltrimethylammonium. Investigated also, were arsenocholine and acetylarsenocholine picrates.

II. Experimental

Salts.—Choline, acetylcholine, arsenocholine and acetylarsenocholine picrates were kindly furnished by Professor Arnold DeM. Welch, now of Washington University, and Dr. M. H. Roepke, of the University of Toronto. Because of the limited quantities of the arseno derivatives available, these salts were recrystallized only once from pure ethanol. The choline and acetylcholine picrates were recrystallized twice from ethanol. The melting points were as follows: choline picrate, 242-245°; acetylcholine picrate, 109-110°; arsenocholine picrate, 251-253°; acetylarsenocholine picrate, 125.6°.

While the purity of the salts, as finally obtained, was not as high as might have been desired, the results are probably not in error by more than a few tenths of a per cent. for the nitrogen cholines and one per cent. in the case of the arseno derivatives.

Methoxymethyltrimethylammonium picrate was prepared by metathesis of the chloride with potassium picrate in pure ethanol. The resulting mixture was filtered while hot and the salt obtained from the filtrate was recrystallized from pure ethanol; m. p. 198°. The chloride had been prepared by the reaction of trimethylamine and chloromethyl methyl ether in cold, dry ether, as described by Litterscheid and Thimme.[1] A white solid was formed during the reaction. The ether was removed at room temperature, leaving the chloride as a viscous liquid which dissolved as such in pure ethanol and reacted with potassium picrate as mentioned above.

Ethyltrimethylammonium picrate was prepared by metathesis of the chloride with silver picrate. The salt was recrystallized from ethanol; m. p., 307-308° (dec.).

Chloroethyltrimethylammonium picrate was prepared by metathesis of the chloride with silver picrate. The salt was recrystallized from alcohol containing 10% water; m. p. 209°. The chloride was prepared by reaction of ethylene chloride with trimethylamine.

Bromoethyltrimethylammonium picrate was prepared by metathesis of the bromide with sodium picrate in aqueous solution. It was recrystallized from water; m. p. 160°. The bromide had been prepared according to the method of Kruger and Bergel[2] by the reaction of trimethylamine with ethylene bromide at 120°.

Bromomethyltrimethylammonium bromide was prepared by the interaction of methylene bromide with trimethylamine in alcoholic solution. This salt was metathesized with silver picrate to prepare the corresponding picrate; m. p. 155°.

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[1] Litterscheid and Thimme, *Ann. Chem.*, **334**, 50 (1904).

[2] Kruger and Bergel, *Ber.*, **36**, 2901 (1903).