

bond. This would then give two bonds which are similar to the metal atom-olefin bonds of the platinum (or palladium) chloride complexes with ethylene, as suggested by Chatt and Duncanson,¹⁰ and subsequently confirmed by the X-ray analysis of Dempsey and Baenziger¹¹ and that of Holden and Baenziger.¹²

The bond angles between the carbonyl groups and those from the acetylene to the benzene rings differ appreciably from the ideal values of either of the *approximate* models given above. Undoubtedly some of the distortion is due to steric interaction involving the benzene rings and also other molecules but on the other hand no attempt has been made to evaluate the contribution of the partial double bond character of the cobalt-carbonyl bonds to the configuration of the molecule. A knowledge of the molecular dimensions of the dimethylacetylene derivatives and of the acetylene derivative would be valuable for comparison since they would have considerable less structural hin-

(10) J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2939 (1953).

(11) J. N. Dempsey and N. C. Baenziger, *THIS JOURNAL*, **77**, 4984 (1955).

(12) J. R. Holden and N. C. Baenziger, *ibid.*, **77**, 4987 (1955).

drance. A discussion of the relative merits of the two alternative systems of bonding for DHDPA, both of which lead to a closed krypton shell for the cobalt atoms, will be deferred until the structure is completely refined.

The structure which has been found for DHDPA is consistent with the absence of bridging carbonyl stretching frequencies in the infrared, the observed diamagnetism and the large observed dipole moment.^{2,3}

Acknowledgments.—I wish to thank Dr. Heinz W. Sternberg for supplying the material used in this investigation and for valuable discussion. I am indebted to Dr. J. D. Britton for carrying out the preliminary X-ray investigation and the density measurements and to Prof. David P. Shoemaker for helpful criticism. The calculations reported here were carried out in part at the MIT Computation Center. This work was supported in part by the George Ellery Hale Fund of the California Institute of Technology, by the National Institutes of Health and by a National Science Foundation Fellowship.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE POLYMER RESEARCH INSTITUTE, POLYTECHNIC INSTITUTE OF BROOKLYN]

Reactions of Polymers with Reagents Carrying Two Interacting Groups. I. The Quaternization of Poly-(4-vinylpyridine) with Bromoacetic Acid^{1,2}

BY H. LADENHEIM, E. M. LOEBL AND H. MORAWETZ

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Initial rates of quaternization of poly-(4-vinylpyridine) and 4-methylpyridine with bromoacetate ion and α -bromoacetamide were measured in water solution at 50°. The quaternizations of 4-methylpyridine are subject to a small positive salt effect. The reaction rate of the cationic polymer with bromoacetate increases sharply with an increase in the degree of ionization of the polymer and a decrease in the ionic strength of the solution due to the electrostatic attraction of the polycation with the anionic reagent. However, these variables have a smaller effect on the second-order rate constant for this reaction than on the apparent ionization constant of the pyridinium residues. It is concluded that in the transition state of the quaternization reaction the carboxylate group of the bromoacetate is at a lower electrostatic potential than the charges of the pyridinium residues.

Introduction

The generally accepted theories of enzyme action assume that a number of distinct sites of the enzyme cooperate in attaching themselves to different portions of the substrate molecule. A typical example of this principle is provided by the action of acetylcholine esterase, where an "esteratic site" of the enzyme is involved in the attack on the ester function, while an "anionic site" serves to stabilize the transition state by partly electrostatic interaction of a negatively charged site on the enzyme with the cationic end of the substrate molecule.³ In this and a following investigation, we shall explore the possibilities of producing similar cooperative effects in reactions of high polymers with bifunctional small molecules. In this study we selected the quaternization of partially ionized

poly-(4-vinylpyridine) with bromoacetate ions, since it might have been expected that the displacement of the bromine by an un-ionized pyridine residue would be aided by the interaction of the carboxylate with a neighboring cationic pyridinium group. The reaction of the anionic bromoacetate was compared with that of the uncharged bromoacetamide both in the quaternization of poly-(4-vinylpyridine) and its monofunctional analog 4-methylpyridine.

Experimental

Materials.—Bromoacetic acid of highest purity was melted, distilled under nitrogen, b.p. 118° (15 mm.) and kept frozen in a desiccator over sulfuric acid. The α -bromoacetamide was prepared by the procedure of Papendieck⁴ (m.p. 91°). Highest purity 4-methylpyridine was distilled under dry nitrogen from barium oxide, b.p. 64° (30 mm.), n_D^{25} 1.5034. Poly-(4-vinylpyridine) (PVPy) was prepared from freshly distilled 4-vinylpyridine by emulsion polymerization,⁵ with Tergitol P-28 (Carbide and Carbon Chem. Co.) as the emulsifier. The intrinsic viscosity of the polymer

(4) A. Papendieck, *Ber.*, **25**, 1160 (1892).

(5) E. B. Fitzgerald and R. M. Fuoss, *Ind. Eng. Chem.*, **42**, 1603 (1950).

(1) Taken in part from a thesis submitted by H. Ladenheim in partial fulfillment of the requirements for a Ph.D. degree, June, 1958.

(2) Financial assistance of this study by the Office of Ordnance Research, U. S. Army, and by a grant of the Monsanto Chemical Company are gratefully acknowledged.

(3) I. B. Wilson, D. Bergmann and D. Nachmansohn, *J. Biol. Chem.*, **186**, 761 (1950).

$[\eta] = 0.78$ in 92% ethanol) corresponded to a molecular weight of 168,000.⁶

Silver nitrate was standardized potentiometrically against highest purity potassium bromide.

Spectrophotometric Titration of Poly-(4-vinylpyridine).—The variation of the state of ionization of PVPy with pH at various ionic strengths was determined by spectrophotometric titration using a stirred 10 cm. cell thermostated at 50° and a Beckman DU spectrophotometer. For titrations at ionic strengths 0.0375 and 0.1515 the solutions contained initially 0.0375 *M* monosodium citrate, 0.0005 *M* citric acid and about 1.7×10^{-5} base molar PVPy in a 50-ml. volume; for the higher ionic strength the requisite amount of sodium chloride was added. At the lowest ionic strength (0.0065) no buffer was used. The solutions were titrated with 1.325 *N* HCl, observing changes in the optical density $D = \log(I_0/I)$ at 254 m μ . The exact base molar polymer concentration C_p was obtained from the optical density observed when 0.44 ml. of 12 *N* HCl were added at the end of the titration to ensure complete conversion of the polymer to the cationic form with an extinction coefficient of 3588 l.-base mole⁻¹.cm⁻¹. The extinction coefficient of PVPy in its basic form was determined by measurements in absolute methanol as 1403 l.-base mole⁻¹.cm⁻¹, and these two extinction coefficients were used to calculate α_{py} , the fraction of the pyridine residues present in their basic form. All the titrations were duplicated to correlate HCl addition with pH .

Potentiometric Measurements.—Measurements of pH were made at 50° on a Cambridge Research Model pH meter using external shielded electrodes and applying corrections for errors of the glass electrode at that temperature from information supplied by the pH meter manufacturer. In titrations involving PVPy a stream of nitrogen was used to stir the solution and protect it from atmospheric carbon dioxide and 3–4 minutes were allowed after each titrant addition for attainment of equilibrium. For bromide determinations, the acidified test solution was titrated potentiometrically with standardized silver nitrate using either a pure silver or a silver-silver bromide electrode⁷ with a reference glass electrode.

Kinetic Runs.—Kinetic runs were performed at $50 \pm 0.05^\circ$ in three neck flasks to allow the insertion of electrodes for pH measurement. The pH remained constant within 0.1 unit in any one run. A 50-ml. solution containing 9.6×10^{-3} base molar PVPy or 4-methylpyridine partially neutralized with nitric acid and sodium nitrate to produce the desired ionic strength was allowed to come to temperature equilibrium and 0.5 ml. of a freshly prepared about 0.2 *M* solution of bromoacetic acid or α -bromoacetamide was injected. The progress of the reaction was followed by quenching the reaction in 5-ml. aliquots with 15 ml. of cooled 0.08 *N* nitric acid and determining bromide potentiometrically as described above. Since a previous investigation of the quaternization of poly-(vinylpyridine) demonstrated kinetic complications at high polymer conversions,⁸ only initial rates at less than 10% quaternization were determined.

Treatment of Experimental Data

The State of Ionization of the Reagents.—Before the experimental results can be interpreted, the state of ionization of the reagents has to be known. For bromoacetic acid and 4-methylpyridine

$$pH = pK_{BAA} + \log [(A^-)/(HA)] + \log \gamma_{\pm} \quad (1)$$

$$pH = pK_{MP} + \log [(B)/(BH^+)] - \log \gamma_{\pm} \quad (2)$$

where (A^-) , (HA) , (B) and (BH^+) stand for concentrations of bromoacetate, un-ionized bromoacetic acid, 4-methylpyridine and 4-methylpyridinium ion, respectively. The value of $pK_{BAA} = 2.95$ at 50° was chosen since this is the pK of chloroacetic acid at 50°⁹ and since the two acids have been shown to have identical dissociation

(8) A. G. Boyes and U. P. Strauss, *J. Polymer Sci.*, **22**, 463 (1956).

(7) F. Halla, *Z. Elektrochem.*, **17**, 179 (1911).

(8) B. D. Coleman and R. M. Fuoss, *THIS JOURNAL*, **77**, 5472 (1955).

(9) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd Ed., Reinhold Publ. Corp., New York, N. Y., 1950, p. 580, 583.

constants over a range of temperatures.¹⁰ Potentiometric titration of 4-methylpyridine at 50° gave $pK_{MP} = 5.23$. The mean ionic activity coefficients γ_{\pm} were calculated from the Debye-Hückel equation assuming an effective ionic radius of 4 Å.

The state of ionization of PVPy was determined by spectrophotometric titration as described in the experimental section. The results are shown in Fig. 1. For any given degree of neutralization,

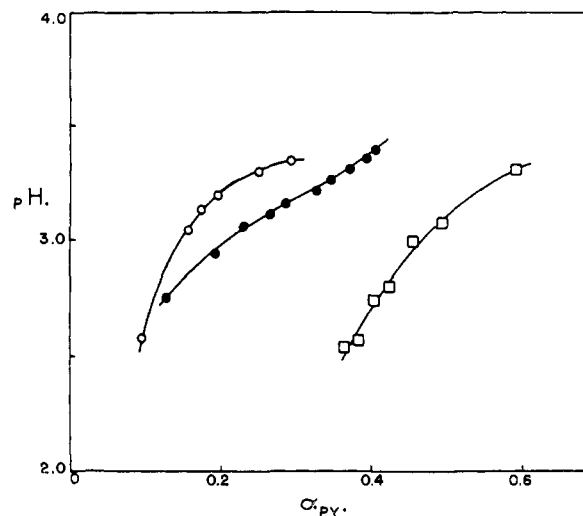


Fig. 1.—Spectrophotometric titration of poly-(4-vinylpyridine), ionic strength: □, 0.0065; ●, 0.0375; ○, 0.1515.

the ionization of the pyridine residues is strongly dependent on the concentration of simple electrolytes as would be expected, since the electrostatic free energy of ionization is very sensitive to the ionic atmosphere.^{11,12} A complication was introduced by the fact that the spectrophotometric titrations had to be carried out, because of the high extinction coefficient of PVPy, at a polymer concentration two orders of magnitude below that used in the kinetic runs. To compensate for this difference, 0.5 mole of NaCl was substituted for each base mole of ionized polymer, following the suggestion of Katchalsky and Lifson,¹² that in polyelectrolyte solutions only the small ions contribute to the "effective ionic strength."

Correction for Side Reactions.—Under the experimental conditions used (pH 2.52–7.34) the hydrolysis of the amide linkage of α -bromoacetamide was not significant. For the hydroxyl ion displacement of bromine in α -bromoacetamide and α -bromoacetate at 50°, rate constants of 0.0274 and 0.0245 l. mole⁻¹ min⁻¹, respectively, were determined; both of these rate constants are too low to contribute significantly to the observed rates of bromide formation. The only side reaction which had to be corrected for was the uncatalyzed hydrolysis of the C–Br bond; this reaction was characterized by rate constants of 3.7×10^{-5} , 4.1×10^{-5} and 9.7×10^{-5} min⁻¹ for α -bromoacetamide, un-ionized bromoacetic acid and bromo-

(10) F. L. Kortright, *Am. Chem. J.*, **18**, 365 (1896); W. Ostwald, *Z. physik. Chem.*, **3**, 170 (1889); K. Drucker, *ibid.*, **40**, 563 (1904).

(11) J. T. G. Overbeek, *Bull. soc. chim. Belges.*, **57**, 252 (1948).

(12) A. Katchalsky and S. Lifson, *J. Polymer Sci.*, **11**, 409 (1953).

acetate ion, respectively. None of these rates was significantly affected by electrolyte concentrations up to an ionic strength of 0.15.

Calculation of Rate Constants.—For quaternization by α -bromoacetamide, second-order rate constants were calculated by deducting from the observed initial rate of bromide evolution the expected rate of α -bromoacetamide hydrolysis and dividing by the concentration of α -bromoacetamide and the concentration of un-ionized pyridine residues. With reactions involving bromoacetic acid, the correction for hydrolysis contained two terms, corresponding to the hydrolysis of the ionized and the un-ionized acid. The corrected quaternization rate was again the sum of rates due to un-ionized bromoacetic acid and to bromoacetate ion, respectively. It was assumed that the quaternization rate constant for un-ionized bromoacetic acid was equal to that determined for bromoacetamide¹³ and after allowing for this reaction, the residual rate was divided by the concentrations of bromoacetate and the un-ionized pyridine residues to obtain the second-order rate constant of the bromoacetate reaction. All second-order rate constants are given in l. mole⁻¹·min⁻¹.

Results and Discussion

The second-order rate constant for the quaternization of 4-methylpyridine with α -bromoacetamide at 50° was found to be 0.39, 0.48 and 0.57 l. mole⁻¹ min⁻¹ at ionic strengths of 0.003, 0.034 and 0.148, respectively. Under the same conditions, the quaternization with bromoacetate ion was characterized by rate constants of 0.40, 0.41 and 0.43, respectively. It may be concluded that the reactivity of the two species is very similar and subject to a positive salt effect which is significantly larger for the α -bromoacetamide.

The results obtained with PVPy are listed in Table I. Here μ is the ionic strength, α_A the degree of ionization of bromoacetic acid, α_{Py} the fraction of pyridine residues in the basic form, k_2 the second-order rate constant for the quaternization reaction and $K_a = (H^+) \alpha_{Py} / (1 - \alpha_{Py})$ the apparent dissociation constant of the pyridinium groups. The rate constant for the quaternization of the polymer with α -bromoacetamide is about 40% lower than for its analog 4-methylpyridine, but it will be noted that the effect of variations in the ionic strength is quite similar in the two cases. Also, changes in the degree of ionization of the polymer at the ionic strength of 0.003 leads to no significant changes in the quaternization rate.

The situation is quite different when the negatively charged bromoacetate ion is the species reacting with the cationic polymer. Except for the data obtained at the highest ionic strength, the rate constants for the reaction of PVPy with bromoacetate ion increase sharply with increasing charge density of the polymer (decreasing α_{Py}). For a comparable polymer charge, the rate is strongly accelerated by a reduction in the concentration of simple electrolytes, although the reaction of bromoacetate with the analog 4-methylpyridine

(13) This assumption could not be checked since the dissociation constant of bromoacetic acid is 200 times as high as that of the 4-methylpyridinium ion.

TABLE I
QUATERNIZATION OF PVPy WITH BROMOACETATE AND WITH
 α -BROMOACETAMIDE

μ	pH	α_A	α_{Py}	k_2	$10^4 K_a$
Bromoacetate					
0.148	3.54	0.84	0.244	1.01	1.0
.148	3.34	.77	.193	1.0	1.1
.148	3.28	.75	.172	1.0	1.1
.148	2.68	.43	.092	1.3	1.8
.034	3.31	.73	.280	2.3	1.8
.034	3.07	.61	.225	2.7	2.5
.034	2.64	.37	.145	4.4	3.9
.034	2.52	.31	.125	4.5	4.5
.003	3.26	.68	.512	4.5	5.8
.003	2.86	.47	.426	5.1	10
.003	2.76	.41	.404	5.8	12
.003	2.55	.30	.364	6.7	16
Bromoacetamide					
.146	3.60		.246	.37	
.034	3.32		.284	.34	
.003	3.22		.506	.23	
.003	3.01		.455	.23	
.003	2.60		.373	.21	

has previously been shown to be subject to a positive salt effect. Both these phenomena may be explained qualitatively by the mutual electrostatic attraction of PVPy and bromoacetate. This attraction increases with increasing polymer charge and decreases with the concentration of counterions, which shield the electrical field of the polycation. Unfortunately, only a comparatively narrow range of α_{Py} could be investigated, since PVPy is insoluble in aqueous media at low degrees of ionization, while at high acidities the side reactions account for a large fraction of the bromide evolution, introducing a prohibitive uncertainty in the calculations of k_2 .

The first kinetic investigation of a reaction involving a polyion and a small charged species was carried out¹⁴ on the hydroxyl ion catalyzed hydrolysis of ester groups carried by the anionic chains of partially hydrolyzed pectin molecules. Since the polyion and the attacking hydroxyl carried charges of the same sign, the effect of variations in the polymer charge density and the ion atmosphere were, of course, qualitatively the reverse of those observed in the present study.

The apparent second-order rate constant k_2 for the ester hydrolysis was found to change with increasing charge density of the polymer chain by the same factor as K_a , the apparent ionization constant of the carboxyl groups.¹⁵ The results may be expressed as

$$K_a = K_a^0 \exp(-\Delta F_{a1}^{\text{ion}}/RT) \quad (3)$$

$$k_2 = k_2^0 \exp(-\Delta F_{a1}^{\pm}/RT) \quad (4)$$

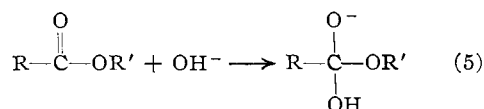
where $\Delta F_{a1}^{\text{ion}}$ is the "electrical free energy" due to the removal of the proton from the field of the polyion^{11,12} while ΔF_{a1}^{\pm} takes account of the free energy associated with the approach of the hydroxyl against the repulsion of the polyion in

(14) H. Denel, K. Hutschnecker and J. Solms, *Z. Elektrochem.*, **57**, 172 (1953).

(15) A. Katchalsky and J. Feitelson, *J. Polymer Sci.*, **13**, 385 (1954).

forming the transition state of the hydrolytic reaction.

Since the rate-determining step of this reaction is



and the transition state carries a negative charge in the same position as the ionized carboxyl groups, the identity of $\Delta F_{\text{st}}^{\text{ion}}$ and $\Delta F_{\text{st}}^{\ddagger}$ is not unexpected in this case.

In the case of the quaternization of PVPy by bromoacetate, a comparison of the last two columns of Table I shows that the dissociation constant of the pyridinium residues K_a is considerably more sensitive than the quaternization rate constant k_2 to the charge density of the polymer and the counterion atmosphere. This means that the anionic charge of the bromoacetate is, in the tran-

sition state of the quaternization reaction, in a region of lower electrostatic potential than the charge of a pyridinium residue. Only if the transition state involved an attack of an un-ionized pyridine residue on the C-Br bond with simultaneous ion-pair formation of the carboxylate with a second ionized pyridine group, would variations in k_2 be expected to be proportional to variations in K_a . Such a simultaneous attack of two polymer groups on two distinct sites of the low molecular weight reagent, analogous to the postulated action of enzymes, may not be realizable with polymers consisting of fairly flexible chains. It seems much more probable with polymers which maintain in solution a tightly coiled helical configuration,¹⁶ so that the spacing between their functional groups is closely defined.

(16) P. Doty and J. T. Yang, *THIS JOURNAL*, **78**, 498 (1956).

BROOKLYN, N. Y.

[CONTRIBUTION NO. 591 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

Heats of Dilution and Related Thermodynamic Properties of Aqueous Rare Earth Salt Solutions at 25°; Integral Heats of Solution of $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$ ¹

BY F. H. SPEDDING, A. W. NAUMANN AND R. E. EBERTS

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The heats of dilution at 25° of LaCl_3 , NdCl_3 , ErCl_3 , YbCl_3 , $\text{La}(\text{NO}_3)_3$ and $\text{Yb}(\text{NO}_3)_3$ solutions have been measured for concentrations up to about 0.2 molal. Relative apparent molal heat contents of the solute, ϕ_L , have been calculated for the solutions used and empirical expressions have been derived for the concentration dependence of ϕ_L . The integral heats of solution of $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$ have been measured and the relative apparent molal heat content of NdCl_3 derived from these quantities. The results are compared to theoretical predictions and to previous measurements. A tentative explanation has been given for the anomalous behavior of the erbium and ytterbium salts at very low concentrations.

Introduction

Ion-exchange separation techniques have made kilogram quantities of all the rare earth elements available in high purity.² This has made possible, and created a need for, the measurement of the properties of aqueous solutions of soluble rare earth salts.

The chemical similarity of the rare earth elements, their ability to form what may be considered strong electrolytes and the regular decrease in ionic radius through the rare earth series make the lanthanide elements attractive for theoretical studies of solution phenomena. A program was undertaken in this Laboratory to determine the properties of aqueous rare earth solutions, with the general aim of obtaining a consistent set of precise data with which to check and develop theories of aqueous solutions.³ The determination of the heats of

dilution of solutions of rare earth salts of the 3-1 type was an extension of this program.

Measurements of heats of dilution of 3-1 salts have been published by Nathan, Wallace and Robinson⁴ on lanthanum chloride and by Lange and Miederer⁵ on lanthanum nitrate. Both of these salts have been measured here, as a check on the data obtained in this Laboratory and to extend the data to higher concentrations. Spedding and Miller^{6a} have reported ϕ_L 's for neodymium and cerium chlorides from measurements of the heats of solution of the anhydrous salts. The measurements on the heat of solution of hydrated neodymium chloride were made in an attempt to explain the discrepancy in the neodymium chloride data of Spedding and Miller and those reported here from heats of dilution.

Experimental. Heats of Dilution

Apparatus.—The apparatus was patterned after one developed by Gucker, Pickard and Planck.⁷ Aside from several minor changes, the apparatus differed from the one

(1) Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission. This paper is based on theses by A. W. Naumann and R. E. Eberts, which were submitted to Iowa State College in partial fulfillment for degrees of Doctor of Philosophy.

(2) (a) F. H. Spedding, A. F. Voigt, E. M. Gladrow and N. R. Sleight, *THIS JOURNAL*, **69**, 2777 (1947); (b) F. H. Spedding, J. E. Powell and E. J. Wheelwright, *ibid.*, **76**, 612, 2557 (1954).

(3) (a) F. H. Spedding, P. E. Porter and J. M. Wright, *ibid.*, **74**, 2055, 2778, 2781 (1952); (b) F. H. Spedding and I. S. Yaffe, *ibid.*, **74**, 4751 (1952); (c) F. H. Spedding and J. L. Dye, *ibid.*, **76**, 879 (1954); (d) F. H. Spedding and S. Jaffe, *ibid.*, **76**, 882, 884 (1954).

(4) C. C. Nathan, W. E. Wallace and A. L. Robinson, *ibid.*, **65**, 790 (1943).

(5) E. Lange and W. Miederer, *Z. Elektrochem.*, **60**, 362 (1956).

(6) (a) F. H. Spedding and C. F. Miller, *THIS JOURNAL*, **74**, 3158 (1952); (b) **74**, 4195 (1952).

(7) F. T. Gucker, Jr., H. B. Pickard and R. W. Planck, *ibid.*, **61**, 459 (1939).