[CONTRIBUTION NO. 1313 FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

Quaternization Kinetics. I. Some Pyridine Derivatives in Tetramethylene Sulfone[*]

BY BERNARD D. COLEMAN AND RAYMOND M. FUOSS

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The quaternization at 25, 50 and 75° of pyridine, 4-picoline and 4-isopropylpyridine by *n*-butyl bromide in tetramethylene sulfone (dielectric constant 42 at 50°) quantitatively follows second-order kinetics; at 25°, $k_2 = 4.7 \times 10^{-4}$, 8.4×10^{-4} and 9.0×10^{-4} l./mole min. for these three bases, respectively. The corresponding values of ΔE are 16.0, 15.95, 15.6 kcal./mole; of $\Delta S^{\ddagger}$, −30.0, −29.3 and −30.3 e.u. The quaternization of poly-4-vinylpyridine starts with about the same rate as the other 4-alkylpyridines, but the rate decreases as the reaction proceeds. The concentration range was higher than that at which diffusion of alkyl halide to individual polymer coils would control the rate. Ultraviolet absorption spectra for 4-picoline, 4-ethylpyridine, 4-isopropylpyridine, 4-vinylpyridine, poly-4-vinylpyridine, 4-methyl-N-methylpyridinium bromide and 4-methyl-N-*n*-butylpyridinium bromide are reported.

Introduction

A considerable part of our research program on polyelectrolytes[1] has been based on quaternized poly-4-vinylpyridine; during the preparation of these materials, a number of puzzling incidental observations were made which suggested a systematic study of the quaternization of pyridine derivatives. Hinshelwood[2-6] and co-workers have studied the quaternization of pyridine itself by methyl iodide in a variety of solvents, and found second-order kinetics in most cases. We were, however, unable to locate any information on quaternization by *n*-butyl bromide, which offers certain advantages in the preparation of polyelectrolytes. The purpose of this paper is to present results of a study of the quaternization of pyridine, 4-picoline and 4-isopropylpyridine in tetramethylene sulfone at 25, 50 and 75° by *n*-butyl bromide. This solvent has a dielectric constant of 42 at 50° (sufficiently high to give useful rates) and does not involve side reactions such as appear with nitrobenzene and dimethylformamide. Second-order kinetics were found.

Preliminary experiments on the quaternization of poly-4-vinylpyridine under the same conditions indicate that the reaction begins at about the same rate as that of the simple 4-alkylpyridines; as the reaction proceeds, however, the rate begins to decrease. At extremely low concentrations, this effect might be explained on the assumption that the alkyl halide molecules were uniformly distributed, while the basic nitrogen atoms were concentrated locally in the individual polymer coils; hence diffusion of halide from the bulk of the solvent to the coils might control. But our experiments were made at concentrations sufficiently high to permit individual coils to overlap; therefore it must be the influence of charged nitrogens on neighboring as yet unquaternized atoms which decelerates the reaction. It is not likely that an inductive effect could be strongly transmitted through a methylene group; possibly the electrostatic field of a quaternized nitrogen can directly affect the transition state of a nearby nitrogen–butyl bromide complex. Work with simpler model substances (α,ω-dipyridyl alkanes) is in progress.

Experimental

Preliminary.—Both for quantitative work on kinetics and for the preparation of compounds, it is desirable to use a solvent in which the reaction is reasonably rapid, one in which reagents and product are soluble and above all, one which does not react with reagents or products. Menschutkin[7] and all subsequent workers[8] have found that the quaternization reaction goes faster the higher the dielectric constant of the solvent. Methanol has a dielectric constant[9] of 32.63 at 25° and is a good solvent; it proved to be unsuitable, however, because alcoholysis of the alkyl halide contaminated the product with hydrobromide. Nitrobenzene[9] ($\epsilon' = 34.82$) and dimethylformamide[10] ($\epsilon' = 109.5$) likewise proved to be unsatisfactory due to side reactions. We were unable to locate any previous comment on side reactions with nitrobenzene, although several previous studies of quaternization have been made in this solvent; some of our observations are therefore summarized below.

Nitrobenzene (7.3 ml.), *n*-butyl bromide (1.8 ml.) and 4-picoline (0.8 ml.) gave a practically colorless solution on mixing at room temperature. On standing, color developed as follows: 30 min., yellowish-green; 60 min., dark green; 3 hr., very dark green and fluorescent (blue-green to reflected light, red-brown to transmitted light). Potentiometric titration showed about 10% conversion to quaternary salt at this stage. Color did not develop on mixing any pairs of the above three reagents; furthermore, substitution of pyridine or 4-isopropylpyridine for 4-picoline eliminated the color; the 4-methyl group thus appears to be necessary for colored products. Different lots of C.P. nitrobenzene gave the same sequence of colors but at various rates; carefully purified nitrobenzene,[11] however, gave only a reddish-brown on standing with 4-picoline and butyl bromide. The blue-green product appears to be due to impurities normally present in C.P. nitrobenzene, because mere redistillation gives a solvent which does not show the above colors. With nitromethane as the solvent for *n*-butyl bromide and 4-picoline, the mixture became yellow in a few hours and deep orange in a week.

Dimethylformamide, used immediately after distillation, gives no color with a mixture of *n*-butyl bromide and 4-picoline or with N-butyl-4-picolinium bromide. But a sample which had been distilled 9 mo. previously gave a pink color within 5 min. after adding 0.167 g. of the above salt to 2.0 ml. of solvent; within an hour, the solution was deep orange (peak at 470 mμ). The picolinium concentration was unchanged, according to the ultraviolet spectrum; hence only trace quantities were involved in the colored products.

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[*] Office of Naval Research Project NR 051-002, Paper No. 48. Reproduction in whole or in part is permitted for any purpose of the United States Government. Results presented in this paper are abstracted from a dissertation presented by Bernard D. Coleman to the Graduate School of Yale University in partial fulfillment of the requirements for the Degree of Doctor of Philosophy, June, 1954.

(1) R. M. Fuoss, *Discs. Faraday Soc.*, **11**, 125 (1951).

(2) C. A. Winkler and C. N. Hinshelwood, *J. Chem. Soc.*, 1147 (1935).

(3) N. J. T. Pickles and C. N. Hinshelwood, *ibid.*, 1353 (1936).

(4) R. A. Fairclough and C. N. Hinshelwood, *ibid.*, 538, 1573 (1937).

(5) K. J. Laidler and C. N. Hinshelwood, *ibid.*, 858 (1938); K. J. Laidler, *ibid.*, 1786 (1938).

(6) H. C. Raine and C. N. Hinshelwood, *ibid.*, 1378 (1939).

(7) N. Menschutkin, *Z. physik. Chem.*, **6**, 41 (1890).

(8) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., New York, N. Y., 1941, pp. 414–423, 449–450, 457.

(9) A. A. Maryott and E. R. Smith, *Natl. Bureau Stand. Circular*, **514**, 1 (1951).

(10) G. R. Leader, THIS JOURNAL, **73**, 856 (1951).

(11) C. R. Witschonke and C. A. Kraus, *ibid.*, **69**, 2472 (1947).

After standing about a week, redistilled dimethylformamide again starts to give color with the salt. Possibly traces of water are absorbed and a little dimethylamine formate is produced, but we can offer no suggestion for the further steps in the reactions which produce the colored material.

Tetramethylene sulfone (TMS) gives no color with butyl bromide and pyridine or 4-isopropylpyridine. With 4-picoline, no color appears if butyl bromide is in excess, but with excess base, a yellow color appears at about 80% conversion, and the solution becomes deep red-brown on standing. A solution of 0.103 g. of N-*n*-butyl-4-picolinium bromide in 6.0 ml. of TMS was heated at 50° for 14 days; no color developed and the bromide titer was unchanged. But if picoline is added to the salt solution in TMS, the solution becomes yellow in 24 hr. at 50°. After 51 hr., however, the bromide concentration was still unchanged. These experiments showed that only traces of intensely colored products were formed in TMS and furthermore that they were products of reaction between the quaternary salt and the 4-methyl group of the free base. Possibly an analog of Cyanine Blue is produced.

Materials.—*n*-Butyl bromide (Matheson) was distilled from anhydrous calcium sulfate; the middle fraction (b.p. 41.5° at 95 mm.) was used. Pyridine (Merck) was distilled from anhydrous sodium sulfate; b.p. 115° at 760 mm. 4-Picoline (Matheson) was refluxed over sodium hydroxide flakes for 4 hr. and then fractionated; b.p. 145°. It was stored over activated alumina and redistilled before use. 4-Isopropylpyridine (Reilly Tar and Chemical) was twice fractionated, once under reduced pressure; b.p. 180°.

N-Methyl-4-picolinium bromide was prepared by condensing 14 ml. of methyl bromide in a flask cooled with Dry Ice, adding a precooled solution of 20 ml. of 4-picoline in 75 ml. of absolute methanol, and allowing the mixture to stand 24 hr. under a Dry Ice condenser. Chilling the reaction mixture caused part of the product to separate; the yield was increased by adding diethyl ether. The colorless crystals were recrystallized from a 1:1 ether–ethanol mixture; potentiometric bromide found: 42.37, 42.36%; calcd., 42.49%. N-*n*-Butyl-4-picolinium bromide was prepared by refluxing 9 ml. of 4-picoline and 17.5 ml. of *n*-butyl bromide in 10 ml. of 95% ethanol for 4 hr. Product separated on cooling in an ice-bath. It was recrystallized from dry acetone; m.p. 140°. Both salts are extremely hygroscopic.

Polyvinylpyridine was prepared and fractionated by Dr. M. Yamin[12]; we are most grateful for this material. The three samples used had reduced viscosities of 6.34, 0.64 and 0.48 dl./g. in 95% ethanol at a concentration of 0.2 g./100 ml., and cover the approximate range $2 \times 10^6 < M < 5 \times 10^4$.

Tetramethylene sulfone melts at 27°; solution of reagents (bromide and pyridine base) in it depressed the freezing point below 25°. It is quite hygroscopic, and was dried by distillation at 130° and 6.5 mm., a forerun of 20% being rejected. Densities (for conversion of weight concentrations to volume) are as follows: 25°, 1.27 (extrapolated); 50°, 1.24_5; 75°, 1.22. The dielectric constant was measured in a guarded cell[13] at 200 and 100 kc., using a guarded Schering bridge (General Radio Type 716 C). At 50°, the dielectric constant is 42.0; the specific conductance of this sample was 0.36×10^{-8}. We are indebted to the Polychemicals Department of E. I. du Pont de Nemours Company for the supply of tetramethylene sulfone which made this research possible.

Ultraviolet spectra of the compounds used in this investigation and of several related substances were measured, using 1 cm. quartz cuvettes and a Beckman DU spectrophotometer. The results are shown in Figs. 1–3, where the molar extinction $\epsilon = D/lc$, $D = \log_{10} I_0/I$ is the optical density and c is concentration in moles per liter. As expected, the spectra in 95% ethanol of 4-picoline, 4-ethylpyridine and 4-isopropylpyridine are quite similar (Fig. 1), all being characterized by a sharp major peak at 256 mμ. In this region, the compounds obeyed Beer's law over the approximate concentration range $1\text{–}10 \times 10^{-4}$. In absolute ethanol, the peak at 256 mμ for 4-picoline was somewhat reduced (Fig. 2), and became a little higher in absolute methanol. Polyvinylpyridine also has its peak at 256 mμ, but the secondary maximum at 262.5 shrinks to a shoulder; this is consistent with the trend with increasing length of alkyl chain shown in Fig. 1. On quaternization, the peak at 256 nearly doubles in height and becomes much broader; furthermore, a new maximum near 224 mμ appears. The height and location depend a little on the quaternizing alkyl group: for N-methylpicolinium bromide, $\epsilon_{\max.}$ 7600 at 223 mμ, and for N-*n*-butylpicolinium bromide, $\epsilon_{\max.}$ 8100 at 225 mμ. The working range of concentrations for the pyridinium salts was $0.5\text{–}2 \times 10^{-4}$; Beer's law was obeyed. Also shown in Fig. 3 are the spectra of vinylpyridine and γ-dipyridyl[14]; the resonance energy due to conju-

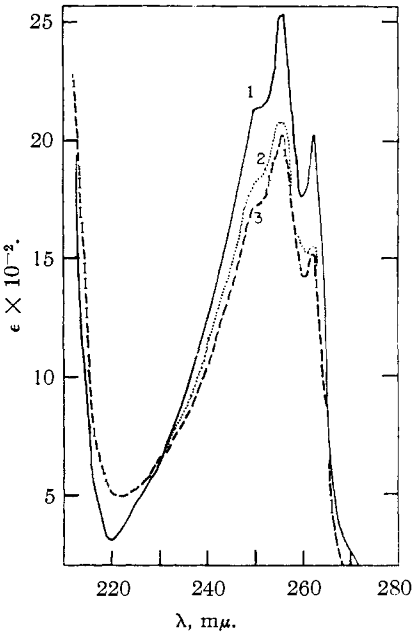

Fig. 1.—Ultraviolet absorption spectra for 4-picoline (solid), 4-isopropylpyridine (dotted) and 4-ethylpyridine (dashed) in 95% ethanol.

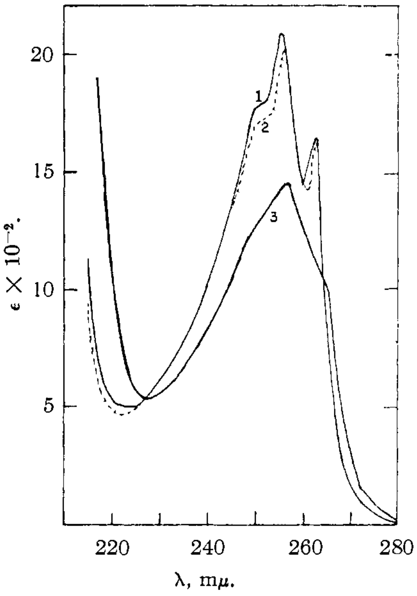

Fig. 2.—Ultraviolet absorption spectra for 4-picoline in absolute methanol (curve 1), 4-picoline in absolute ethanol (curve 2) and poly-4-vinylpyridine in absolute ethanol (curve 3).

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[12] Du Pont Postdoctoral Research Fellow, Yale University, 1952–1953.

[13] H. Sadek and R. M. Fuoss, This Journal, **76**, 5897 (1954).

[14] P. Krumholz, *ibid.*, **73**, 3487 (1951).

gation produces a marked hypsochromic shift with respect to the γ-alkylpyridines.

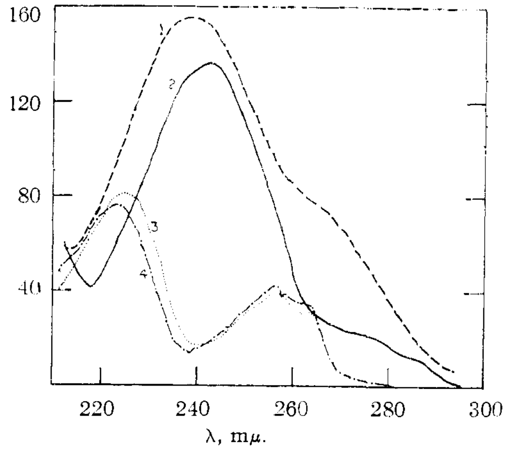

Fig. 3.—Ultraviolet absorption spectra for γ-dipyridyl[14] (curve 1), 4-vinylpyridine (curve 2), N-*n*-butyl-4-picolinium bromide (curve 3) and N-methyl-4-picolinium bromide (curve 4).

We had hoped to follow the kinetics of quaternization by means of absorption spectra; the situation seemed especially favorable, because the strong absorption maximum due to N^+ appears at the wave length where the unquaternized pyridines have a minimum in absorption. But precisely for this reason, the method was inapplicable: the slightest trace of acid impurities caused the amines to absorb around 225 mμ. This was shown experimentally by the fact that deviations from Beer's law for the amines in this region of the spectrum were completely erratic. The behavior in absolute ethanol was much better than in 95% ethanol, but due to the hazard of absorption of acid from the laboratory air, we decided to follow the reaction by determination of the bromide ion generated.

Method.—Solutions of base and of *n*-butyl bromide in TMS were made up by weight, and then known weights of these solutions were mixed. Samples of the mixture were injected into cylindrical ampoules (9 × 0.9 cm.) by means of a hypodermic syringe; the thin stem was then sealed by a microflame. Each tube contained 1.5–2.5 ml. of reaction mixture. About 30 min. were required to prepare the tubes for a run; after sealing, the tubes were placed in a rack of coarse mesh screen which was then immersed in a bath at the chosen temperature (25.0, 50.0, 75.0). For experiments at 25°, time was reckoned from the time of initial mixing at room temperature. At the higher temperatures, time was counted from the moment of immersion in the thermostat. Since our rate curves all extrapolated to zero bromide at zero time when time was so reckoned, the positive errors due to reaction at room temperature during the loading time closely compensated the negative errors due to too slow reaction during the warm-up time. At appropriate intervals, a tube was taken from the thermostat, and the stem was broken. A sample of the contents was withdrawn by a syringe and injected into a methanol-acid mixture for analysis. The weight of sample was obtained by difference in syringe weights.

Analysis.—Spectrophotometric analysis was tried and abandoned, as mentioned above. A potentiometric method was therefore used. A sample of reaction mixture (estimated to consume 5–10 ml. of 0.005 *N* silver nitrate solution) was weighed into 45 ml. of methanol and 6 ml. of 2 *N* sulfuric acid in a beaker containing a magnetic stirrer, a Beckman glass electrode and a pure silver wire. (The glass electrode is the reference electrode and is stabilized by the acid.) Then silver nitrate solution is added in the usual way; the break at the end-point is over 200 mv. Blank determinations showed that hydrolysis of unreacted butyl bromide was negligible under the conditions of analysis. Other checks included titration of known amounts of quaternary salts in the presence of amine, butyl bromide and TMS in various amounts and combinations: no interference was found. The dilution completely quenched the reaction; titrations of duplicates, one immediately after dilution and the other one hour later, agreed within 0.02 ml.

One competing side reaction must be considered: S_N1 reaction of butyl bromide to give butene and hydrogen bromide in the presence of pyridine. Noller and Dinsmore[15] found that this reaction proceeds only $^1/_{47}$ as fast as the quaternization at 150°, and from their data on *sec*-butyl bromide, we estimate that the energy of activation for the reaction of *n*-butyl bromide is at least 25 kcal. Since ΔE is about 16 for the quaternization, it appears safe to disregard production of bromide ion *via* hydrogen bromide. This conclusion was verified by checking the *p*H of an aqueous extract of the reaction mixtures when butyl bromide was in excess. For example, in a mixture where $10^4a = 2.272$, $10^4b = 1.070$, which was kept at 50° for 24 days, the *p*H of the extract (5.0 ml. of water, 0.663 g. of reaction mixture) was 4.87. From this, we calculate that the bromide ion from decomposition of butyl bromide was only 10^{-7} mole/g.; the corresponding error is less than 0.2% of the total titer. Bromide produced by pyrolysis of the product does not constitute a source of error, of course, because any hydrogen bromide from this source would count in the total titer, and the salt obviously had to be formed by the Menschutkin reaction before it could decompose.

Results and Discussion

The experimental data are summarized in Table I where b is initial moles of base per *gram* of reaction mixture, a is initial concentration of butyl bromide in the same units and k'_2 is the bimolecular rate constant defined by the familiar equation

$$dx/dt = k'_2(a - x)(b - x) \qquad (1)$$

The weight concentrations were converted to volume concentrations, using the approximation that solution density equals solvent density ρ; the dimensions of k_2 as given in Table I are (liters/mole min.). The values of k'_2 were obtained from

TABLE I

QUATERNIZATION BY *n*-BUTYL BROMIDE IN TETRAMETHYLENE SULFONE

t, °C.	10^4b	10^4a	10^3k_2
	Pyridine		
25	1.923	0.935	0.474
25	1.070	2.272	0.454
25	0.998	2.103	0.464
25	3.445	1.783	0.459
25	0.788	0.363	0.513
50	1.636	0.893	3.86
50	1.070	2.272	3.65
50	3.445	1.783	3.67
75	1.923	0.935	23.1
75	0.998	2.103	22.4
75	3.445	1.783	23.0
75	0.788	0.363	25.2
	4-Picoline		
25	1.928	0.938	0.825
25	0.805	1.885	0.849
50	1.928	0.938	6.59
50	0.805	1.885	6.58
75	1.831	0.902	40.1
75	0.882	1.752	40.1
	4-Isopropylpyridine		
25	1.695	0.871	0.904
50	1.695	0.871	6.95
75	1.685	0.858	39.7

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[15] C. R. Noller and R. Dinsmore, THIS JOURNAL, **54**, 1025 (1932).

the titration data (x = concentration of bromide ion) by plotting

$$F(x) = \frac{1}{a - b} \ln \left(\frac{1 - x/a}{1 - x/b}\right) \qquad (2)$$

against time; integration of (1) gives $F(x) = k'_2t$, where $k'_2 = 1000\ k_2\ p$ and k'_2 thus is the slope of the F–t plot. All of the F–t plots were linear over the entire working range; the latter covered 6–80% of theoretical conversion. Most of the experiments were actually carried further, but the analytical error naturally becomes quite large when x approaches (the smaller of) a or b, and these data were disregarded in determining the values of k_2.

Several runs were carried to completion; we found no indication whatsoever of reversibility of the quaternization reaction in TMS. This conclusion agrees with that drawn from work on tritium-labeled methyl iodide.[16] Laidler[5] and Hinshelwood[5] have explained their results on quaternizations in nitrobenzene on the hypothesis that the reaction proceeded to an equilibrium; they make no mention of colored by-products. Considering the strength of the C–N bond (66 kcal.), and recalling our observations on the quaternization of pyridine derivatives in nitrobenzene, it seems possible that side reactions rather than reversibility are the cause of the failure of simple second-order kinetics in these systems.

The values of slopes calculated as ($\Delta \log k_2 / \Delta T^{-1}$) from pairs of temperatures agreed very closely for a given system, showing that the data all conform to the Arrhenius equation

$$k_2 = Ae^{-\Delta E/RT} \qquad (3)$$

Some variation was found in the A values, depending on whether base or bromide was in excess and on initial concentrations; these differences amounted to only 0.08 maximum spread in log A and averages are therefore given in Table II. Entropies, calculated by the Eyring equation[17]

$$\begin{aligned}\Delta S^{\ddagger} &= 2.3\ R \log k_2 + \Delta E/T - 2.3\ R \log (eRT/Nh) \quad (4)\\ &= 2.3\ R (\log A - 15.01)\end{aligned}$$

are also given in Table II; for k_2 expressed in (liters/mole min.), the value of log (eRT/Nh) at 25° is 15.01.

TABLE II

Cpd.	log A	ΔE	$\Delta S^{\ddagger}$
C_5H_5N	8.46	16.04	−30.0
$CH_3 \cdot C_5H_4N$	8.61	15.95	−29.3
$C_3H_7 \cdot C_5H_4N$	8.39	15.60	−30.3

We next consider the quaternization of polyvinylpyridine (PVP). In Fig. 4, $F(x)$ as defined in eq. 2 is plotted against time for the reaction at 25° between butyl bromide and several samples of PVP of different molecular weights (concentrations in monomoles, etc., are given in the caption of Fig. 4). First, we note that the rate of reaction does not depend on the molecular weight of the polymer. Using for PVP the values given by Flory and Fox[18] for polystyrene, we estimate that the volume available per polymer molecule was less than the volume $(4\pi/3)(r_0^2)^{3/2}\alpha^3$ of an isolated PVP molecule in a good solvent. Therefore there must have been considerable interpenetration of the polymer coils under our experimental conditions, and diffusion of alkyl halide to individual polymer molecules cannot have influenced the reaction rate.

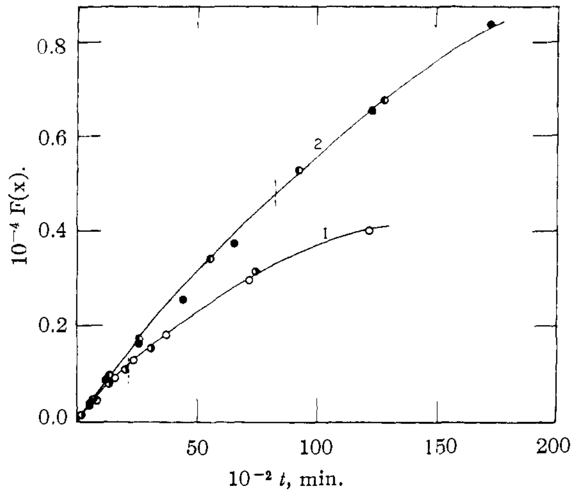

Fig. 4.—Quaternization of polyvinylpyridine at 25°: Curve 1, open circles, $10^4a = 6.12$, $10^4b = 1.242$, $M \approx 2 \times 10^6$; right-shaded circles, $10^4a = 5.70$, $10^4b = 1.198$, $M \approx 5 \times 10^4$. Curve 2, solid circles, $10^4a = 2.074$, $10^4b = 0.946$, M $\approx 2 \times 10^6$; left-shaded circles, $10^4a = 1.968$, $10^4b = 0.875$, $M \approx 1 \times 10^5$. Half completion shown by vertical dashes.

For the simple bases of Table I, the F–t plots were accurately linear over the entire course of the reaction. But for the polymer, the plots become concave-down, and since $k'_2 = dF/dt$, it is clear that the quaternization of the polymer proceeds less and less rapidly as the degree of quaternization increases. The deviation from linearity occurs sooner, the higher the concentration, for equivalent quantities of reagents. If a large excess of polymer nitrogen is present, linearity persists longer; for example, with a ratio $a/b = 1/10$, the F–t plots are linear up to about 50% of completion, but then start to deviate downwards.

It is evident that the quaternization of PVP begins like that of a simple 4-alkylpyridine, because the initial slopes of the curves gives the following values for 10^3k_2: 0.64 at 25°, 5.4 at 50° and 29.4 at 75°. From these results and eq. 3 and 4, we find $\Delta E = 15.7$ and $\Delta S^{\ddagger} = -30.4$. These values are completely consistent with those given in Table II for the monomeric bases. In the initial stages, the quaternization is undoubtedly a random process along a given polymer chain, and probability of quaternization of near neighbors is small. But as the reaction proceeds, unquaternized nitrogens inevitably must have quaternized neighbors; our results show that the effect of the latter is to slow down the reaction. This might be an inductive effect, wherein the positive charge on a quaternized pyridine nitrogen makes the lone pair of electrons on an adjacent pyridine group less available for reaction with alkyl halide, but inductive effects usu-

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[16] D. Harman, T. D. Stewart and S. Ruben, THIS JOURNAL, **64**, 2294 (1942).

[17] Ref. 8, p. 199.

[18] P. J. Flory and T. G. Fox, Jr., THIS JOURNAL, **73**, 1904 (1951).

ally are considerably weakened by the interposition of even a single methylene group between charged site and reaction site. The charge on an N^+ might orient an approaching dipolar molecule of butyl bromide into an unfavorable position for reaction with a neighbor, or possibly the field of a nearby N^+ can stabilize the $\geqslant N \cdot BrBu$ complex in its transition state, so that decomposition into $\geqslant N^+Bu$ and Br′ becomes less probable. Finally, the intense field (megavolts/cm.) of a quaternized nitrogen might increase the density of the highly polar solvent in its neighborhood by electrostriction, and thereby make access to the region by alkyl halide more difficult. One interesting consequence of the decelerating effect of partial quaternization should be mentioned. If there were no interaction, the distribution of quaternized sites among the chains would be a Bernouilli distribution around an average degree of quaternization. The interaction sharpens the distribution, because chains with more quaternized sites than the average will react more slowly with further alkyl halide, while those with less than the average will react more rapidly.

NEW HAVEN, CONN.

[CONTRIBUTION FROM THE NOYES LABORATORY OF CHEMISTRY, UNIVERSITY OF ILLINOIS]

The Stereochemistry of Metal Chelates with Polydentate Ligands. Part I

BY BASUDEB DAS SARMA AND JOHN C. BAILAR, JR.

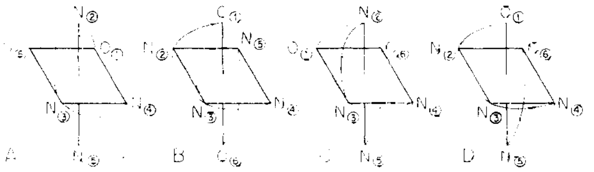
RECEIVED APRIL 25, 1955

This paper describes bis-salicylaldehyde–triethylenetetramine, the nitrogen analog of Dwyer and Lions' sexadentate 1,8-bis-(salicylideneamino)-3,6-dithioöctane, as a chelating agent. The Schiff base offers six points of attachment and gives well defined, stable compounds with Co^{+3}, Co^{+2}, Fe^{+3}, Fe^{+2}, Al^{+3}, Cu^{+2}, Ni^{+2}, Pd^{+2} and the ions of other transition metals. The octahedral complexes of Co^{+3}, Fe^{+3}, Al^{+3} have been obtained in their optically active forms, only two of the eight possible isomers being obtained. The copper compound, which is tetra-coördinated and planar, has been obtained in optically active forms through a method of asymmetric synthesis. The tentative structures of the complexes have been described from the steric point of view and their infrared spectra. The Fe^{+3} compound is covalent with d^2sp^3 bonding and this has been resolved directly into the optical isomers.

Since the work of Dwyer and Lions[1] there has been a number of publications on complexes with sexadentate chelating agents.[2] The sexadentate ligand (I)

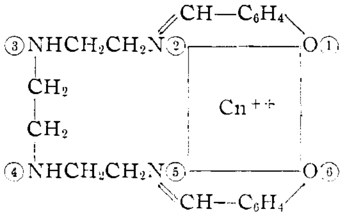
$$HOC_6H_4CH{=}NCH_2CH_2NHCH_2CH_2NHCH_2CH_2N{=}CHC_6H_4OH$$
(1) (2) (3) (4) (5) (6)

may span the octahedral positions around a metal ion in the following ways



together with the mirror images of each, as they are all asymmetric structures. But Fisher–Hirschfelder models show that the structures B, C and D are greatly strained and the models for them cannot be made. The angle N–N–O tends toward 90°, as is the case with A. In all probability, therefore, these compounds have the structure represented by A.

The picture is slightly changed when all of the six coördinating positions are not utilized. For example, the cupric ion is normally reluctant to extend its coördination number of four, and is generally planar. If we assume that the two protons are replaced from the hydroxyl groups by cupric ion (like those of other Schiff bases, the compounds formed with a bivalent metal are non-electrolytes), and two of the four remaining nitrogens are coördinated to it, the structure



is still not symmetrical as the two benzene rings cannot lie in the plane of the complex. This gives rise to two active forms and of course, a *meso*-form. The classical method of resolution cannot be applied here, the chelate being a non-electrolyte. But if the compound is made from an optically active copper complex, such as the *d*-tartrate, it is obtained in optically active form. We have not yet been able to prepare the *meso*-form.

There is an alternate structure for this compound, with copper coördinated to N_3 and N_4 instead of N_2 and N_5. This will require the stabilization of two nine-membered rings, instead of one large ring and two six-membered rings. This alternate structure is more difficult to make with a model. The infrared spectra of these compounds (Table I) show that when the secondary amine nitrogens, N_3 and N_4, are coördinated, there is a multiplicity of the NH stretching vibrations in the region 3100–3600

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[1] F. P. Dwyer and F. Lions, THIS JOURNAL, **69**, 2917 (1947).

[2] F. P. Dwyer, F. Lions and co-workers, *ibid.*, **72**, 1545 (1950); **72**, 5037 (1950); **74**, 4188 (1952); **75**, 2443 (1953). G. Schwarzenbach and H. Ackermann, *Helv. Chim. Acta*, **31**, 1029 (1948). D. H. Busch and J. C. Bailar, Jr., THIS JOURNAL, **75**, 4574 (1953). A. K. Mukherjee, *Science and Culture*, **19**, 107 (1953).