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Quaternization Kinetics. V. Di-tertiary Amines with Butyl Bromide in Propylene Carbonate[1]

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I. Rate constants at 25 and 50° for the quaternization by *n*-butyl bromide in propylene carbonate (dielectric constant 65) of the following amines were determined: $Me_2N \cdot C_6H_5$, *p*-$Me_2N \cdot C_6H_4Me$, *p,p'*-$Me_2N \cdot C_6H_4 \cdot CH_2 \cdot C_6H_4 \cdot NMe_2$, 4,4'-$C_5H_4N(CH_2)_3C_5H_4N$, 4,4'-$C_5H_4N(CH_2)_2C_5H_4N$ and $C_5H_4NCH{=}CHC_5H_4N$. The rate of quaternization of the second nitrogen in the diamines is always less (about 0.5–0.7) than that of the first. The decrease is ascribed primarily to an electrostatic field effect rather than to an intramolecular shift of electron density. II. The main reaction product of dimethylaniline and butyl bromide in solvents of low dielectric constant is trimethylphenylammonium bromide. Molecular decomposition of the expected primary addition product into methyl bromide and methylbutylaniline accounts for the result. III. The deceleration of the rate of quaternization of poly-4-vinylpyridine as the reaction proceeds is a consequence of electrostatic effects and not of the polymer structure *per se*.

Introduction

The rate of quaternization of pyridine and 4-picoline[4–6] in a variety of solvents has been studied as a preliminary to attacking the problem of the peculiar behavior of poly-4-vinylpyridine on quaternization.[7] The latter begins to quaternize at a normal rate, but the rate begins to decrease markedly after about half of the pyridine nitrogens have been quaternized. This behavior might be ascribed to one of (at least) three causes: (a) intramolecular electronic effects of quaternized neighbors located on the polymer chain; (b) extramolecular electrostatic field effects of quaternized neighbors; or (c) high local concentration of pyridine groups in the centers of polymer coils. The experiments presented in this paper were designed to test these hypotheses: our conclusion is that hypothesis (c) is excluded and that hypothesis (b) is probably correct.

The poly-4-vinylpyridine chain has the repeated structure

$$-CH_2 \cdot CHPy \cdot CH_2 \cdot CHPy \cdot CH_2-$$

Obviously 1,3-di-(4-pyridyl)-propane is the simplest model substance which can represent a segment of the chain, as far as effects of neighboring groups are concerned. We have found that the rate of quaternization of the second nitrogen in 4,4'-$Py(CH_2)_3Py$ is only about 70% of that of the first; consequently, the deceleration observed in the polymer does not depend primarily on the fact that the 4-pyridyl groups are attached to a polymer chain. Furthermore, the rate constants for the second quaternization of 1,3-dipyridylpropane and 1,2-dipyridylethane are so nearly alike (3.3×10^{-4} and 2.8×10^{-4}) that an intramolecular inductive effect can hardly be considered as the cause of the decrease from the rate constant for the first quaternization (4 to 5×10^{-4}, practically equal to that for 4-picoline). Comparison of these rates with those for two other model substances $PyCH{=}CHPy$ and *p,p'*-$Me_2N \cdot C_6H_4 \cdot CH_2 \cdot C_6H_4 \cdot NMe_2$ suggests that the decrease probably is due to an extramolecular electrostatic field effect produced by the positive charge on the first nitrogen.

Experimental

Materials.—Propylene carbonate (Jefferson Chemical Co.) was redistilled; the middle cut (111–114° at 12 mm.) was used. Butyl bromide was redistilled. *p,p'*-Methylene-bis-(N,N-dimethyaniline) was recrystallized twice from 95% ethanol after decolorizing with charcoal; approx. solubility in boiling ethanol, 8 g./100 cc., m.p. 89.5°. *p,p'*-Bis-(dimethylamino)-benzophenone was recrystallized from 95% ethanol; solubility, 4 g./100 cc.; m.p. 175°. Dimethylaniline was first purified by two fractional freezings, decanting and discarding about one-half each time. The final crystals were allowed to melt; the liquid was dried overnight with anhydrous calcium sulfate and then distilled under reduced pressure using nitrogen.

1,3-Di-(4-pyridyl)-propane was prepared by the Aldrich Chemical Company, by reaction between dimethoxymethane and 4-picoline.[8] It was recrystallized from 5:1 *n*-hexane–benzene: 6.5 g. as first crop were recovered from 10 g. in 150 cc. of mixed solvent; m.p. 60.5–61.5°. 1,2-Di-(4-pyridyl)-ethane also was prepared by Aldrich; it was recrystallized from 3:1 cyclohexane–benzene (approx. solubility, 7.5 g./100 cc.). The spectrum[9] showed negligible absorption at 299 and at 289 mμ, indicating absence of the corresponding ethylene from which it was prepared by hydrogenation, using charcoal supported palladium as catalyst. Aldrich 1,2-di-(4-pyridyl)-ethylene was recrystallized from water; solubility, 1.6 g./100 cc. at 100°; m.p. 153–154°. We take this opportunity to thank Dr. Alfred Bader of the Aldrich Chemical Company, Inc. (Milwaukee, Wisconsin), for his helpful coöperation in the synthesis of the above compounds and for the information that the ethylene is the *trans*-derivative.

Method.—Solutions were prepared by weight and sealed into ampoules which were then placed in thermostats at 25° (or 50°). At appropriate intervals, bromide ion content was determined potentiometrically, using 0.005 *N* silver nitrate solution. Details of procedure already have been described.[7]

An interesting side problem arose from plans to check the rate of quaternization by conductimetric methods; we started by attempting to synthesize dimethylbutylphenylammonium bromide from butyl bromide and dimethylaniline, both by heating the two reagents together undiluted and in acetone solution. The yield was poor, in contrast to the usual nearly quantitative course of quaternization reactions. The recrystallized products (m.p. 216–217°) analyzed to 37.04% Br, *vs.* 30.95% expected! Elementary

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[1] Technical Report No. 55 submitted to the Office of Naval Research. Reproduction of this paper in whole or in part is permitted for any purpose of the United States Government.

[2] ONR Research Assistantship, Frank M. Shu Scientific Fellowship (China Institute in America) and American Cyanamid Scholarship are gratefully acknowledged.

[3] Results presented in this paper are based on a dissertation presented by Miss Lue-Yung Chow to the Graduate School of Yale University in partial fulfillment of the requirements for the Degree of Doctor of Philosophy, June, 1957.

[4] P. L. Kronick and R. M. Fuoss, THIS JOURNAL, **77**, 6114 (1955).

[5] E. Hirsch and R. M. Fuoss, *ibid.*, **77**, 6115 (1955).

[6] M. Watanabe and R. M. Fuoss, *ibid.*, **78**, 527 (1956).

[7] B. Coleman and R. M. Fuoss, *ibid.*, **77**, 5472 (1955).

[8] A. Ladenburg, *Ber.*, **21**, 3099 (1888).

[9] M. Yamin and R. M. Fuoss, THIS JOURNAL, **75**, 4860 (1953); E. D. Bergmann, F. E. Crane, Jr., and R. M. Fuoss, *ibid.*, **74**, 5979 (1952).

analysis (Schwarzkopf) gave the following results: C, 50.32, 50.49; H, 6.75, 6.60; N, 7.01, 7.20. Freshman chemistry applied to these figures suggested that our product was trimethylphenylammonium bromide. Vorländer and Siebert[10] report 214° as the melting point of Me_3NPh-Br and 110–115° for the corresponding nitrate. We accordingly converted a sample of our bromide to nitrate by metathesis in aqueous solution with silver nitrate. The product on purification melted at 123–127°; considering the 5° spread on the earlier melting point, we felt reasonably certain that our product was indeed Me_3NPhBr. We therefore prepared the latter salt by addition of methyl bromide to dimethylaniline in acetone solution. The product was recrystallized from *sec*-butyl alcohol; its infrared spectrum was then taken in chloroform solution. The fingerprint region is shown in Fig. 1B. Curve C of the same figure is the spectrum of the product obtained from BuBr and Me_2NPh; there can be no doubt that these reagents produce the trimethylphenyl salt.

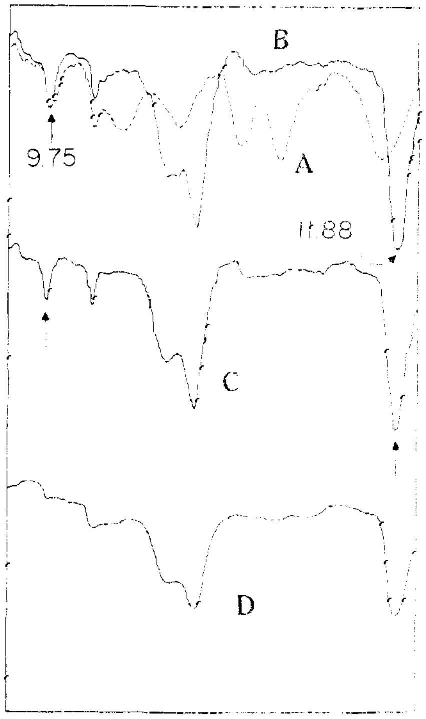

Fig. 1.—Infrared spectra of salts.

We next investigated the addition of methyl bromide to methylbutylaniline; the latter was prepared by the method of Reilly and Hickinbottom.[11] (Since the expected impurity in the MeBuNPh would be methylaniline, the product was treated with phenyl isocyanate to remove it.) The purified amine was treated with methyl bromide in acetone solution; the solid which separated (85% yield) analyzed to 31.07, 31.04% Br, in excellent agreement with the value calculated for $Me_2BuNPhBr$. The infrared spectrum is shown in Fig. 1A; it is, of course, markedly different from that of Me_3NPhBr. These experiments thus show that MeBr adds normally to MeBuNPh but that BuBr gives an abnormal *final* product with Me_2NPh. Since several of our kinetic studies on the addition of BuBr to aryl amines had already been completed, it obviously became necessary to learn whether the *initial* product of BuBr addition was normal and whether this reaction controlled the rate of production of bromine ion. Incidentally, dimethyltoluidine and butyl bromide also give the trimethyl salt: the addition product analyzed to 34.82% Br; calculated for $BuMe_2NTlBr$, 29.34%; calculated for Me_3NTl-Br, 34.72%.

If $BuMe_2NPhBr$ is the initial product of the reaction, it should be possible to obtain Me_3NPhBr from this salt by treatment with Me_2NPh. The butyldimethyl salt is much more soluble in acetone than the trimethyl salt. We therefore mixed the butyldimethyl salt and dimethylaniline (0.0058 mole each) in 20 cc. of acetone: no precipitate appeared in one day at room temperature but after 4 days at 50° (sealed tube), crystals appeared. Their spectrum is shown in Fig. 1D, which identifies them as Me_3NPhBr. The filtrate gave on evaporation a high boiling liquid whose spectrum is shown in Fig. 2C. Comparison with the spectra of Me_2NPh (Fig. 2B) and of BuMeNPh (Fig. 2A) shows that the product is a mixture of the two amines. These experiments show that the trimethyl salt can be produced from the butyldimethyl salt in the presence of dimethylaniline, if the reaction is rapid and bimolecular

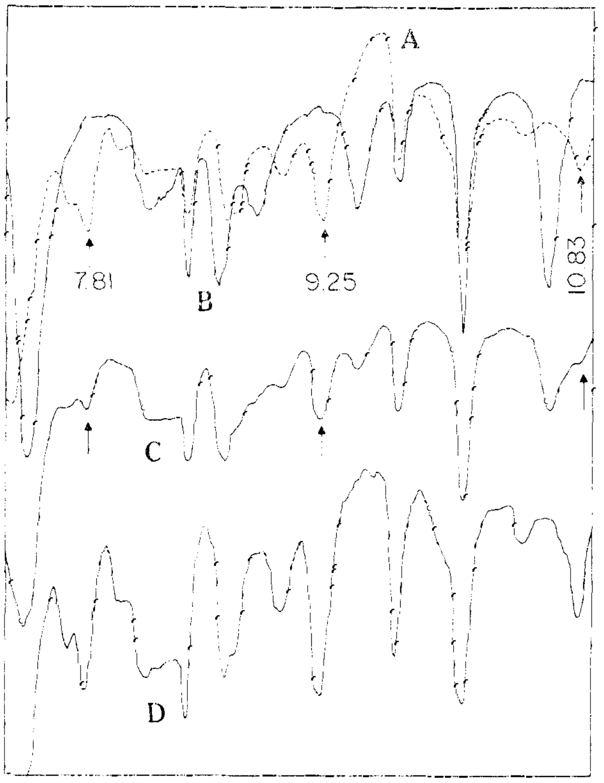

Fig. 2.—Infrared spectra of amines.

$$BuMe_2NPhBr + Me_2NPh \longrightarrow Me_3NPhBr + BuMeNPh \quad (1)$$

it would consume dimethylaniline (without changing bromide ion concentration) and replace it by an equivalent amount of BuMeNPh which probably has a somewhat different rate of reaction with butyl bromide.

Another possibility exists: molecular dissociation of the butyldimethyl salt

$$BuMe_2NPh{\cdot}Br \longrightarrow BuMeNPh + MeBr \quad (2)$$

could release methyl bromide, which would then add to dimethylaniline to give the trimethyl salt observed in the attempted synthesis. We therefore refluxed a sample of $BuMe_2NPhBr$ in acetone solution for 18 hr. On subsequent evaporation of the acetone, two liquid layers remained. The spectrum of the top layer is shown in Fig. 2D; it obviously is that of BuMeNPh and is evidence for reaction 2 as the primary source of the trimethyl salt in the synthesis. Granting this, we have confidence in our kinetic data, because (2) requires the presence of ion pairs in order to occur, and in propylene carbonate ($D = 65.1$) the concentration of ion pairs would be lower by several orders of magnitude than in acetone whose dielectric constant is only 20.7. The strong dependence of the quaternization rate on dielectric constant of the solvent[6] demonstrates the existence of a partially ionized transition state, which can then either go to an ion pair and dissociate into free ions or revert to an un-

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[10] D. Vorländer and E. Siebert, *Ber.*, **52**, 283 (1919).

[11] J. Reilly and W. J. Hickinbottom, *J. Chem. Soc.*, **117**, 130 (1920).

charged system which can dissociate into amine and alkyl halide; evidently, when the latter occurs, methyl bromide splits off in preference to butyl bromide. Reaction 2 also accounts for the good yield in the preparation of $BuMe_2NPhBr$ from BuMeNPh and MeBr; any decomposition by (2) simply regenerates reagent. The reaction is similar to the von Braun bromocyanogen reaction[12a] Hughes[12b] has also pointed out that addition of alkyl iodide to dimethyl sulfide frequently gives trimethylsulfonium iodide instead of the expected product.

Trimethylphenylammonium Bromide.—I. 116 g. (0.96 mole) of dimethylaniline and 131 g. (0.96 mole) of butyl bromide were mixed and heated at 100° for 24 hr. under an air condenser. The solution turned blue and crystals (49 g.) separated. On two recrystallizations from *sec*-butyl alcohol, the product melting at 218° and analyzing to 37.04% Br was obtained. II. 49.7 g. (0.36 mole) of butyl bromide and 27.0 g. (0.20 mole) of dimethylaniline were refluxed in 120 g. of acetone for 48 hr. Only 4.6 g. of salt separated; m.p. 216–217°; 36.70% Br. III. 41.7 g. (0.44 mole) of methyl bromide was absorbed in 98 g. of cold acetone. Then 26.3 g. (0.22 mole) of dimethylaniline was added, using a Dry Ice reflux. Salt crystallized out within 2 hr., in nearly quantitative yield; after recrystallization from *sec*-butyl alcohol, the product melted at 212–213°. This material gave the spectrum of Fig. 1B (0.082 molal in chloroform solution).

Dimethylbutylphenylammonium Bromide.—26.8 (0.25 mole) of methylaniline and 35.8 g. (0.26 mole) of butyl bromide were heated on the steam-bath for 1 hr.; then 88 cc. of water was added and any unreacted material was extracted with petroleum ether. Butylmethylaniline was released by addition of sodium carbonate and chloride; it was dried with sodium hydroxide; yield 33 g. This product was heated for 3 hr. with 65 g. of phenyl isocyanate, and then 100 cc. of water was added to destroy the excess isocyanate. Steam distillation gave 18 g. of methylaniline-free BuMeNPh. This was dried over potassium hydroxide and distilled; 79–80° at about 1.5 mm. Picrate: m.p. 86°; Reilly[11] gives 90°. Next, 38 g. of methyl bromide was absorbed in 39 g. of acetone and 11.2 g. of BuMeNPh was added under Dry Ice reflux. Within 5 hr., solid separated; yield, after washing with acetone and drying over phosphorus pentoxide, 14.0 g. The salt is extremely hygroscopic, in contrast to Me_3NPhBr, which is only slightly hygroscopic. This product analyzed to 31.07, 31.04% Br and gave the spectrum of Fig. 1A (0.083 molal in chloroform).

Reaction 1.—1.501 g. (0.0058 mole) of $Me_2BuNPhBr$ and 0.698 g. (0.0058 mole) of Me_2NPh were dissolved in 16.7 g. of acetone and sealed in ampoules. Nothing was observed after one day, but after 4 days at 50°, crystals collected on the walls. From an ampoule containing 3.15 g. of solution, 94 mg. of crystals was obtained; m.p. 215–216°, spectrum Fig. 1D. The yield of 94 mg. corresponds to conversion of at least 44% of the butyldimethyl salt to trimethyl salt. The liquid in the tube was evaporated to give a blue gel plus a yellow oil; the latter gave the spectrum of Fig. 2C.

Reaction 2.—A solution of 0.775 g. of $BuMe_2NPhBr$ in 36 g. of acetone was refluxed for 18 hr., and then the acetone was pumped off by water aspirator. Two liquid layers (oil and aqueous salt solution) remained; the upper layer (weight, 0.15 g., corresponding to 30% decomposition) gave the spectrum of Fig. 2D.

Results and Discussion

The data and results for the reference monoamines, dimethylaniline and dimethyltoluidine are summarized in Table I, where a and b are initial concentrations in *moles per liter*[13] of butyl bromide and amine, respectively, and k is the rate constant (l./mole min.). The values of k were obtained as the slopes of the straight lines obtained by plotting $[1/(b - a)] \ln[a(b - x)/b\cdot(a - x)]$ against time, where x is observed concentration of bromide ion at time t. The scatter of individual chord slopes from the mean slope corresponds to about 1% in k at 25° and 2% at 50°. The reactions were followed to the conversions (x/a or x/b, depending on which reagent was present in excess) shown as "%" in Table I which were reached at the final times (hr.) given under t_f. Using the Arrhenius equation, the values of ΔE calculated from the chord slope between 25 and 50° are 15.0 for dimethylaniline and 14.0 for dimethyltoluidine. As expected, the *p*-methyl group of the latter lowers the energy of activation and increases the rate constant.

TABLE I

QUATERNIZATION OF MONOBASIC AMINES

t, °C.	a	b	%	t_f	10^4k
		Dimethylaniline			
25	0.2344	0.0921	37.8	1079.7	0.350
25	.0746	.2396	28.4	691.0	0.353
50	.1625	.1506	31.9	187.9	2.50
50	.1943	.1513	36.5	187.5	2.48
		Dimethyltoluidine			
25	0.1701	.4271	57.7	408.3	0.93
25	.4659	.1713	56.0	361.6	0.90
50	.1948	.3774	85.0	198.8	6.07
50	.4792	.2058	55.0	54.6	5.82

When we come to the diamines, there are of course two rate constants to be considered

$$\mathrm{N\ldots N + BuBr \longrightarrow N\ldots N^+ + Br'}\ (k_1') \qquad (3)$$

$$\mathrm{N\ldots N^+ + BuBr \longrightarrow N^+\ldots N^+ + Br'}\ (k_2) \qquad (4)$$

where (3) and (4) are consecutive reactions which compete for butyl bromide. If concentrations (moles/liter) are represented by these symbols

$$A = [\mathrm{BuBr}],\ x = [\mathrm{Br'}]. \qquad (5)$$
$$B = [\mathrm{N - N}],\ y = [\mathrm{N - N^+}],\ z = [\mathrm{N^+ - N^+}]$$

the following stoichiometric relations obtain

$$\begin{aligned} b &= B + y + z \\ a &= A + x \\ x &= y + 2z \end{aligned} \qquad (6)$$

where a and b are initial concentrations of alkyl halide and base, respectively. The reactions are described by the differential equations

$$\mathrm{d}B/\mathrm{d}t = -\ k_1'BA \qquad (7)$$

$$\mathrm{d}y/\mathrm{d}t = -k_2yA + k_1'BA \qquad (8)$$

$$\mathrm{d}A/\mathrm{d}t = -\ k_1'BA - k_2yA \qquad (9)$$

$$\mathrm{d}x/\mathrm{d}t = k_1'BA + k_2yA \qquad (10)$$

Explicit solution in the form $x = (k_1', k_2, a, b, t)$ cannot be obtained, but elimination of time followed by integration gives[14] the following relationships between instantaneous concentrations

$$y = (B\alpha b^{1-\alpha} - B)/(1 - \alpha) \qquad (11)$$

$$z = b - (B\alpha b^{1-\alpha} - \alpha B)/(1 - \alpha) \qquad (12)$$

and

$$x = 2b - (B\alpha b^{1-\alpha})/(1 - \alpha) - B(1 - 2\alpha)/(1 - \alpha) \qquad (13)$$

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[12] (a) J. von Braun, *Ber.*, **33**, 1438 (1900); (b) E. D. Hughes C. K. Ingold and G. A. Maw, *J. Chem. Soc.*, 2072 (1948).

[13] In the preceding papers of this series, we used a and b to designate initial concentrations of reagents in *moles per gram* of reaction mixture.

[14] E. Abel, *Z. physik. Chem.*, **56**, 558 (1906): C. K. Ingold, *J. Chem. Soc.*, 2170 (1931): F. H. Westheimer. W. A. Jones and R. A. Lad, *J. Chem. Phys.*, **10**, 478 (1942); W. C. Schwemer and A. A. Frost. THIS JOURNAL, **73**, 4541 (1951): A. A. Frost and W. C. Schwemer. *ibid.*, **74**, 1268 (1952).

Equations 11, 12 and 13 express x, y and z as functions of B and the ratio $\alpha = k_2'/k_1'$; integration of (7) gives

$$\ln b/B = k_1' \int_0^t (a - x)\mathrm{d}t \qquad (14)$$

In principle, we can eliminate B between (13) and (14), but due to the (unknown) fractional exponents in (11–13), this operation cannot be carried out in closed form, and hence the graphical or numerical methods of previous authors must be used in general. By using a large excess of either one of the reagents, however, it is possible to reduce the reactions to pseudo-first order and obtain the rate constants from the corresponding equations in a fairly direct way.

In comparing diamines with the corresponding mono-amine, a stoichiometric factor of two appears because one mole of diamine naturally contains two equivalents of quaternizable nitrogen. If we designate by k_1 the rate constant for the bimolecular reaction between a mono-amine and an alkyl halide, it is numerically the same in units (l./mole min.) or (l./equiv. min.). When a diamine is considered, the k_1' of the above equation then becomes $2k_1$ where k_1 is the rate constant for the corresponding mono-amine. This easily can be shown by kinetic argument. Suppose k_1 is the rate constant for the reaction RN + BuBr, and let k and k' be the constants (l./mole min.) for the quaternizations of a diamine whose nitrogens are at first different (*e.g.*, one aryl, one alkyl): $\mathrm{RN-NAr} \rightarrow \mathrm{RN^+-NAr}(k)$; $\mathrm{ArN-NR} \rightarrow \mathrm{ArN^+-NR}(k')$. Then for the first quaternization, the total rate of production of bromide ion is $\mathrm{d}x/\mathrm{d}t = kAB + k'AB$. Now let R = ϕ; then $k = k'$ and $\mathrm{d}x/\mathrm{d}t = 2kAB$. We shall therefore use $2k_1$ to replace k_1' of (7) – (10) in all subsequent equations. The analysis which follows requires, for rapid convergence, that $k_2 < 2k_1$. We tested several sets of our data by Swain's graphical method[15] for consecutive first-order reactions and found that this condition was fulfilled.

When excess base is present ($2b >> a$), then $z = [\mathrm{N^+{-}N^+}]$ can be neglected in eq. 6, with $x \approx y$. Then (10) becomes

$$\mathrm{d}x/\mathrm{d}t = 2k_1(a - x)(b - Kx) \qquad (15)$$

where

$$K = 1 - k_2/2k_1 \qquad (16)$$

Integration and use of the initial condition $x = 0$ at $t = 0$ immediately gives

$$F_1(x) = \frac{1}{b - Ka} \ln \frac{a(b - Kx)}{b(a - x)} = 2k_1t \qquad (17)$$

Since $b >> Ka$ by hypothesis, (17) becomes, to first approximation

$$F_1'(x) = (1/b) \ln [a/(a - x)] \approx 2k_1t \qquad (18)$$

and k_1 is determined by the initial slope of the function given in (18). Then from the other limiting case ($a >> 2b$), a first approximation to k_2 is obtained; these two values give K for insertion in (17), and a second approximation to k_1 is obtained.

When excess alkyl halide is present, $a >> x$, $a - x \approx a$ and (7) becomes

$$\mathrm{d}B/\mathrm{d}t \approx -2k_1aB$$

which immediately integrates to

$$B = b \exp(-2k_1at) \qquad (19)$$

To the same approximation, (10) becomes after substitution of (19)

$$\mathrm{d}x/\mathrm{d}t = 2ab(k_1 - k_2) \exp(-2k_1at) + ak_2(2b - x) \qquad (20)$$

which on integration subject to the boundary condition at $t = 0$ gives

$$1 - (x/2b) = [(k_1 - k_2)/(2k_1 - k_2)] \exp(-2k_1at) + [k_1/(2k_1 - k_2)] \exp(-k_2at) \qquad (21)$$

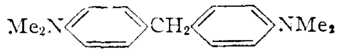
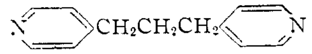
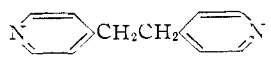
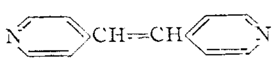
By hypothesis, $2k_1 > k_2$, so if we wait long enough (*i.e.*, until substantially all diamine molecules have been once-quaternized; $x/2b \geqslant 0.5$), the first term on the right of (21) becomes negligible compared to the second, and a plot of $F_2'(x) = \ln [1 - (x/2b)]$ against time gives a first approximation to k_2. This value, together with the first approximation to k_1 from the previous case allows us to compute the correction term in (21), and then a plot of

$$F_2(x) = \ln\{1 - x/2b - [(k_1 - k_2)/(2k_1 - k_2)] \exp(-2k_1at)\}$$

against time gives a second approximation to k_2.

TABLE II

QUATERNIZATION OF DIBASIC AMINES

t, °C.	a	b	%	t_t	10^4k_1	10^4k_2
						
25	0.03080	0.3185	37.2	476.9	0.77	...
25	.03273	.3135	36.0	454.2	0.77	...
25	.4423	.04229	93.9	2852.0	...	0.30
25	.3652	.03441	85.4	1989.0	...	0.35
50	.03592	.3464	46.9	148.3	5.10	...
50	.02907	.2388	45.4	168.3	5.25	...
50	.5236	.04949	87.3	273.3	...	2.1
50	.5064	.04006	88.5	299.8	...	2.2
						
25	0.01321	0.1622	38.4	168.7	4.65	...
25	.01373	.1557	40.5	194.0	4.70	...
25	.1808	.01583	90.5	604.0	...	3.22
25	.1710	.01165	95.0	790.7	...	3.40
50	.02717	.2332	49.3	47.8	37.0	...
50	.01675	.1810	48.9	47.6	37.3	...
50	.2032	.01762	96.8	99.2	...	27.0
50	.2093	.01418	93.8	75.7	...	27.3
						
25	0.01860	0.2130	43.7	217.2	3.88	...
25	.01774	.2241	45.8	213.5	4.15	...
25	.5163	.01522	98.8	523.1	...	2.65
25	.5647	.01569	90.7	217.3	...	2.95
50	.02005	.2843	41.6	16.53	32.5	...
50	.01961	.1991	41.5	24.82	32.3	...
50	.4686	.01495	99.4	77.90	...	22.2
50	.4458	.01370	96.2	51.28	...	22.2
						
25	0.02029	0.2027	39.7	241.1	2.76	...
25	.01442	.1365	37.9	326.8	2.73	...
25	.3252	.01219	90.5	787.0	...	1.32
25	.5115	.01746	96.8	764.6	...	1.33
50	.01787	.1904	41.1	31.92	23.9	...
50	.01870	.1920	31.1	18.27	23.5	...
50	.5101	.01225	98.3	99.30	...	11.7
50	.4509	.01524	99.4	129.42	...	11.9

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[15] C. G. Swain, THIS JOURNAL, **66**, 1696 (1944).

The results for the diamines[16] are summarized in Table II, where the symbols (except k, of course) have the same meaning as in Table I. The values of k_1 and k_2 are the final values obtained by the method of successive approximations described above.

An example of the determination of k_1 is shown in Fig. 3, for 1,2-di-(4-pyridyl)-ethylene at 50° where $b/a = 10.66$. At the beginning of the reaction, $F_1'(x)$ defined by (17) and (18), are indistinguishable, but after about half of the butyl bromide has reacted, $F_1'(x)$ becomes visibly concave-down (dashed curve). However, using $k_2/2k_1 \approx 0.26$ from the preliminary values of these constants to evaluate K, we obtain $F_1(x)$ which is linear up to 41% reaction, where the experiment was terminated. In Fig. 4 is shown the determination of k_2 for 1,2-di-(4-pyridyl)-ethylene at 50° where $a/b = 41.6$. After somewhat more than one-half of the nitrogens have been quaternized, $F_2'(x) = \ln[1 - (x/2b)]$ becomes practically linear, and a preliminary value of k_2 is given by the slope of the line; in the earlier stages of the reaction, $F_2'(x)$ is curved as expected (dashed curve). But again, with the preliminary value of k_2, and k_1 from the other run, the exponential correction term in $F_2(x)$ can be evaluated and the result is the linear plot shown.

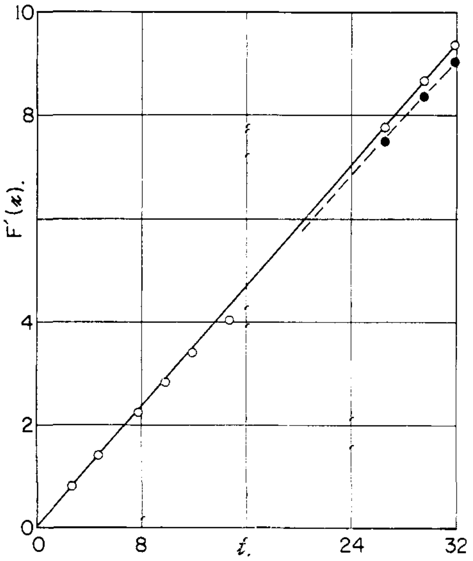

Fig. 3.—Evaluation of k_1.

The average values of the rate constants for the diamines are summarized in Table III and the activation energies ΔE in Table IV, where Ar denotes the p-$Me_2N{\cdot}C_6H_4$ group and Py the 4-pyridyl group. For comparison, we recall the following values for the reference monobasic amines: dimethylaniline, $10^4k(25°) = 0.35$, $10^4k(50°) = 2.49$ and $\Delta E = 15.0$; dimethyltoluidine, 0.92, 6.0 and 14.0; pyridine,[4] 2.58, 22.3 and 16.4; 4-picoline,[4] 4.7, 39.0 and 16.2.

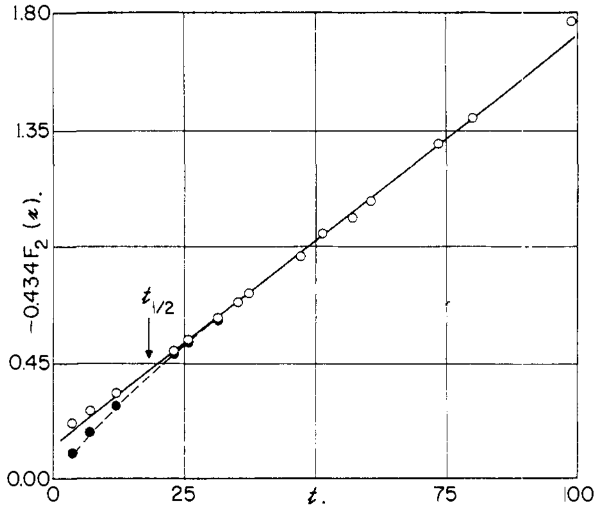

Fig. 4.—Evaluation of k_2.

It will be seen that k_1 for $ArCH_2Ar$ is somewhat smaller than the constant for dimethyltoluidine but considerably larger than that for dimethylaniline: the medial methylene group naturally can increase the electron density in the two adjacent rings less than the single methyl group in the toluidine can influence its one ring. The result shows, however, that the methylene group is electron-repelling, as expected. Next, we note that the rate constant for the second quaternization is less than half that of the first. One might argue that the fully charged nitrogen at one end of the molecule transmits an inductive effect through the single methylene linking the two aryl groups; this effect is certainly present, but consideration of the pyridyl derivatives suggests that an additional effect must be present. The rate of the first quaternization of $Py(CH_2)_3Py$ is identical with that of 4-picoline but that of the second is only 70% as large. After transmission through three methylene groups, an inductive effect

TABLE III

RATE CONSTANTS OF DIAMINE QUATERNIZATIONS

	25°			50°		
Diamine	10^4k_1	10^4k_2	$k_2/2k_1$	10^4k_1	10^4k_2	$k_2/2k_1$
$ArCH_2Ar$	0.77	0.32	0.21	5.1	2.2	0.21
$Py(CH_2)_3Py$	4.7	3.3	.36	37.2	27.0	.37
$Py(CH_2)_2Py$	4.0	2.8	.35	32.3	22.2	.34
$PyCH{=}CHPy$	2.75	1.33	.24	23.7	11.8	.25

TABLE IV

ACTIVATION ENERGIES OF QUATERNIZATION WITH BUTYL BROMIDE

Reaction	ΔE
$ArCH_2Ar \longrightarrow (ArCH_2Ar)^+$	14.6
$(ArCH_2Ar)^+ \longrightarrow (ArCH_2Ar)^{++}$	14.0
$Py(CH_2)_3Py \longrightarrow [Py(CH_2)_3Py]^+$	15.9
$[Py(CH_2)_3Py]^+ \longrightarrow [Py(CH_2)_3Py]^{++}$	16.3
$Py(CH_2)_2Py \longrightarrow [Py(CH_2)_2Py]^+$	15.8
$[Py(CH_2)_2Py]^+ \longrightarrow [Py(CH_2)_2Py]^{++}$	16.2
$PyCH{=}CHPy \longrightarrow [PyCH{=}CHPy]^+$	16.5
$[PyCH{=}CHPy]^+ \longrightarrow [PyCH{=}CHPy]^{++}$	16.7

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[16] One other diamine, p,p'-N,N-dimethylaminobenzophenone was investigated only in a preliminary way; its solubility was very low (about 0.04 M) and its rate of reaction was extremely slow. Even with a very great excess of butyl bromide, the reaction was only 50% complete after 11 days at 50°. Evidently the central carbonyl reduces the electron density at the nitrogens so far that quaternization becomes extremely sluggish.

is strongly reduced,[17] but let us concede for the moment that the reduction here is due to an inductive effect. This hypothesis is immediately contradicted by the results for $Py(CH_2)_2Py$: here, k_2 is again 70% of k_1 and the change from three to two methylenes would call for a much greater reduction in k_2 if the reduction were due solely to an effect transmitted intramolecularly along the methylene chain. Furthermore the effect of the first quaternization in $ArCH_2Ar$ seems too large when compared with the (almost identical) observed effect in PyCH=CHPy, where the charge is *in* the ring which is conjugated with the second ring *via* the ethylene linkage. Structural models show that the N–N distance in $Py(CH_2)_3Py$ is only slightly greater than in $Py(CH_2)_2Py$ and that this distance is less for $ArCH_2Ar$. Taken together, these results argue that an electrostatic field effect is operating: the positive charge on the nitrogen first quaternized would attract an approaching BuBr molecule (dipole) and thereby decrease its probability of reaching the uncharged nitrogen and hence decrease the probability of forming the intermediate complex necessary for SN2 reaction at that site. The activation energy for the second quaternization is slightly higher than that for the first; this could well correspond to the extra energy needed for the BuBr molecule to make a successful contact with the uncharged nitrogen in the field of the first charged one. An alternative electrostatic effect cannot be excluded; indeed both may be active. The reaction medium is highly polar; therefore electrostriction on a molecular scale might so increase the local density around a once quaternized diamine that the diffusion rate of the BuBr molecules to the reaction site would be decreased.

Comparison of the results for $PyCH_2CH_2Py$ and PyCH=CHPy also argues against an intramolecular effect as the sole cause of the decrease in k_2 with respect to k_1: in the ethane, the two rings are joined by the essentially insulating methylene groups, while in the ethylene, they are joined by an excellent electronic conductor; hence any intramolecular effect due to the first quaternization should be enormously enhanced in the ethylene. Experiment shows only a slightly greater effect. The absolute magnitude of k_1 for the ethylene is about the same as the rate constant for pyridine; this may well be a consequence of the conjugative coupling which leads to the same electron density in PyCH=CHPy as in pyridine: push and pull just balance.

NEW HAVEN, CONNECTICUT

(17) C. K. Ingold. "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, New York, N. Y., 1953, p. 737, Table 46-6.

[CONTRIBUTION FROM THE AVERY LABORATORY OF THE UNIVERSITY OF NEBRASKA]

Syntheses and Infrared Spectra of α,β-Unsaturated-β-ketoamines and their Copper Chelates[1]

BY HENRY F. HOLTZCLAW, JR., JAMES P. COLLMAN AND RICHARD M. ALIRE

RECEIVED AUGUST 14, 1957

Syntheses and infrared spectra are described for several α,β-unsaturated-β-ketoamines and their copper chelates. The spectra are discussed and comparisons are made with spectra for other compounds with which analogies can logically be expected.

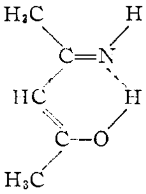
Introduction

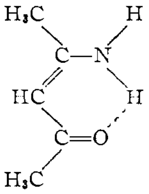
In a previous paper from this Laboratory,[2] the infrared spectra for various 1,3-diketones and their metal chelates were discussed. The present paper discusses syntheses and infrared spectra of several α,β-unsaturated-β-ketoamines and their copper chelates.

Although a few α,β-unsaturated-β-ketoamines have been prepared previously, the literature reveals very little work with metal chelates of these compounds. Combes and Combes[3] reported the formation of a crystalline material in an alcoholic solution of 4-amino-3-pentene-2-one and copper-(II) acetate. No attempt to characterize the substance was reported. Ueno and Martell[4] have recently reported the preparation and spectra of the ligand molecules and several corresponding metal chelates for bisacetylacetoneethylenediimine and related compounds.

Results and Discussion

Three forms, A, B and C, are possible for the α,β-unsaturated-β-ketoamines.


A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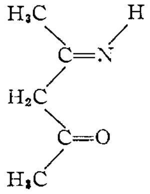
C

Ueno and Martell[4] concluded that a tautomeric equilibrium exists between the forms corresponding to A and B for bisacetylacetoneethylenediimine and related substances. Inasmuch as no absorption was obtained in the region around 1700 cm.$^{-1}$, the free carbonyl group, and hence structure C, was ruled out for that type of compound. Cromwell, *et al.*,[5] in an infrared study of various amino-sub-

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(1) Abstracted from the M.S. Theses of James P. Collman, June, 1956, and Richard M. Alire, June, 1956, University of Nebraska.

(2) H. F. Holtzclaw, Jr., and J. P. Collman, THIS JOURNAL, **79**, 3318 (1957).

(3) A. Combes and C. Combes, *Bull. soc. chim. France*, [3] **7**, 778 (1892).

(4) K. Ueno and A. E. Martell, *J. Phys. Chem.*, **59**, 998 (1955); **61**, 257 (1957).

(5) N. H. Cromwell, F. A. Miller, A. R. Johnson, R. L. Frank and D. J. Wallace, THIS JOURNAL, **71**, 3337 (1949).