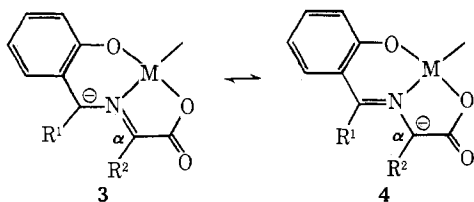


(2, CH<sub>3</sub>), ~7.1 ppm (4, phenyl); Zn(sal-L-ala)·H<sub>2</sub>O (methanol-d<sub>4</sub>) 1.35 (3, doublet (*J* = 7 Hz), CH<sub>3</sub>), 3.97 (1, quartet, CH), ~7.1 (4, phenyl), 8.33 ppm (1, azomethine).

The tautomerization kinetics of Cu(hba-prop)·H<sub>2</sub>O and Cu(hba-ival) were determined in 95% ethanol solutions containing equimolar sodium hydroxide under conditions closely similar to those employed in the study of the racemization kinetics of Cu(II) Schiff base complexes.<sup>13</sup> No reaction was observed in water, ethanol, or methanol solutions at 50° for 24 hr unless base was present. Tautomerization rate constants *k<sub>t</sub>*, which are averages of at least three kinetic runs, were found to be 2.29 ± 0.21 (30°) and 7.16 ± 0.64 M<sup>-1</sup> min<sup>-1</sup> (50°) for Cu(hba-prop)·H<sub>2</sub>O and 0.87 ± 0.11 (30°) and 3.70 ± 0.30 M<sup>-1</sup> min<sup>-1</sup> (50°) for Cu(hba-ival). The lower rates for the latter presumably reflect the greater degree of steric hindrance of the isopropyl group with regard to base attack on the methylene protons. The value of *k<sub>t</sub>* (50°) for the latter complex is directly comparable with the rate of racemization of its tautomer Cu(sal-L-val)·<sup>3</sup>/<sub>2</sub>H<sub>2</sub>O at the same temperature. The ratio *k<sub>t</sub>*/*k<sub>r</sub>*, ~150 provides a quantitative demonstration that ketimine → aldimine tautomerization (transamination), presumably preceding through the anion 3 ↔ 4 which preferentially protonates at the



α-carbon, is a faster process than racemization of the aldimine when determined under similar experimental conditions. The rate of aldimine → ketimine tautomerization, although not yet measured for the complexes 2, is clearly much less than that of aldimine racemization since no spectral features now known to be associated with M(hba-ka) were observed at any point during the racemization reactions of M(sal-aa).<sup>13</sup> Consequently, the scheme proposed for α-deuteration of amino acids by heating with Cu(II) and salicylaldehyde in D<sub>2</sub>O,<sup>21</sup> which involves the rapid interconversion of 1 and 2 and hydrolysis of the latter, is considered less likely than racemization and concomitant H-D exchange *via* the anion 4 followed by hydrolysis. It is also observed that the tautomerization rates of Cu(hba-ka) are qualitatively slower than those of M(pym-ival) (M = Cu(II), Zn(II)) in neutral methanol solution.<sup>8</sup> As discussed previously,<sup>5,6,13</sup> this situation arises at least in part from resonance stabilization of the anionic intermediate similar to 4 which is effected by an electron-withdrawing group ortho or para to the R<sub>1</sub>CNCR<sub>2</sub> unit.

Lastly, two complexes of structure 1 (R<sub>1</sub> = CH<sub>3</sub>), Cu(mhba-prop)·H<sub>2</sub>O and Cu(mhba-ival)·<sup>1</sup>/<sub>2</sub>H<sub>2</sub>O, were prepared from the potentially resolvable α-methyl-*o*-hydroxybenzylamine with the eventual goal of ascertaining if base-assisted proton transfer from an asymmetric center to the α-carbon necessarily resulted in a racemic product 2. Unexpectedly, these complexes

did not tautomerize when heated in methanol or 95% ethanol with equimolar base at 50–60° for 24 hr or in a pH 10 aqueous solution at 50° for several hours. Therefore, no attempt was made to obtain them in an optically active form.

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### Ion-Pair Dissociation of Periodic Group Ia Acetates in Anhydrous Acetic Acid

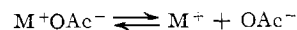
By ORLAND W. KOLLING\* AND HOWARD E. GRACEY

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Trends in the ion-pair association constants for alkali metal salts with variation of the cation have been established in water and in a number of aqueous-organic binary solvents. Conductometric methods for the measurement of these constants have been applied to mixed solvents in the dielectric constant (*D*) range of 9–30 (at 25°). In aqueous and other hydrogen-bonding media the order of increasing association for salts with an anion in common parallels that of increasing cationic radius.<sup>1</sup>

It is important to test this conclusion with non-aqueous solvents having still lower dielectric constants, and we are reporting new results for periodic group Ia acetates in anhydrous acetic acid (*D* = 6.2). Although values for the ion-pair dissociation constants of several acetates (as concentration constants) have been published, the data derived from different techniques are conflicting and the sequence for increasing association is unclear.<sup>2–4</sup>

Our potentiometric method for the determination of the ion-pair dissociation constant (*K<sub>B</sub>*) of the defined equilibrium



is based upon eq 1 and 2 which were derived earlier.<sup>5</sup>

$$E_B = (E^{\circ}_{GC} + E_i) + \frac{RT}{F} \ln K_s - \frac{RT}{2F} \ln K_B - \frac{RT}{2F} \ln C_B \quad (1)$$

$$pK_{B1} = pK_{B2} + \frac{2F}{RT}(E_{B1} - E_{B2}) \quad (2)$$

The cell potential (*E<sub>B</sub>*) developed by the glass-saturated calomel electrode pair when immersed in a solution of MOAc in anhydrous acetic acid is dependent upon the constant terms: standard cell potential, *E<sup>o</sup><sub>GC</sub>*; the liquid junction potential, *E<sub>i</sub>*; and the solvent

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TABLE I  
 EMF DATA FOR ACETATES IN ANHYDROUS ACETIC ACID (AT 25°)<sup>a</sup>

LiOAc		NaOAc		KOAc		RbOAc		CsOAc	
C <sub>B</sub>	E <sub>B</sub>	C <sub>B</sub>	E <sub>B</sub>	C <sub>B</sub>	E <sub>B</sub>	C <sub>B</sub>	E <sub>B</sub>	C <sub>B</sub>	E <sub>B</sub>
0.0228	397	0.0199	395	0.0210	383	0.0214	378	0.0174	378
0.0182	401	0.0159	398	0.0168	386	0.0171	381	0.0139	382
0.0136	404	0.0119	403	0.0126	390	0.0128	385	0.0104	385
0.00912	410	0.00796	408	0.00840	396	0.00856	391	0.00696	392
0.00456	420	0.00398	417	0.00420	405	0.00428	401	0.00348	401
0.00319	425	0.00278	423	0.00294	411	0.00300	405	0.00244	406
0.00228	430	0.00199	427	0.00210	415	0.00214	410	0.00174	411
0.000912	443	0.000796	440	0.00084	427	0.00086	422	0.00070	422

<sup>a</sup> C<sub>B</sub> values in moles per liter; E<sub>B</sub> values in millivolts. Mean slope of E<sub>B</sub> vs. -log C<sub>B</sub> is 0.0308 ± 0.0006 V.

autoionization constant,  $K_s$ . Under a condition of fixed concentration of base (C<sub>B</sub>), eq 2 permits the evaluation of the dissociation constant of base 1 by comparison with a reference base 2 having a known  $K_B$ . Two ionic reference bases having reliable  $K_B$  values in pure acetic acid were used in this investigation, *i.e.*, lithium acetate and sodium acetate.

The fundamental relationship between the ion-pair association constant ( $K_A$ ) and the ion size ( $a$ ) was derived by Fuoss and Onsager from a sphere-in-continuum model.<sup>6,7</sup> In applying eq 3 to real systems the

$$K_A = \left( \frac{4\pi N}{3000} \right) a^3 e^{-b} \quad (3)$$

theoretical ion-size parameter ( $a$ ) is usually replaced by a suitable ionic radius function. For the present study, cationic radii computed by different methods were correlated with the experimental ion-pair constants.

#### Experimental Section

Anhydrous acetic acid was made by dehydration of glacial acetic acid, following the method of Tappmeyer and Davidson.<sup>8</sup> The boiling range for the distilled solvent was 117.5–118°.

The samples of the ionic acetates were reagent grade and were dried at 110° for 1 hr before preparing stock solutions (~0.1 M) in anhydrous acetic acid. Because of the very hygroscopic character of cesium acetate, all manipulations of the solid were made in a drybag in a nitrogen atmosphere. All base solutions were standardized to three significant figures by titration with a standard 0.0998 M perchloric acid solution in anhydrous acetic acid.

Potentiometric measurements were made with a Leeds and Northrup Model 7401 pH meter, equipped with the Leeds and Northrup 117169 glass electrode and a standard fiber junction saturated (aqueous KCl) calomel electrode. Procedures for electrode storage and use have been reported.<sup>9,10</sup>

TriPLICATE measurements were made on a minimum of three separate solutions at each concentration level on each of the metal acetates. Representative mean emf data are listed in Table I. Stable potential readings were obtained within 30 min. The experimental precision in the potential values is ±1 mV for solutions of lithium, sodium, and potassium acetates, whereas the maximum uncertainty in E<sub>B</sub> for the acetates of rubidium and cesium is ±2 mV at the temperature of 24–25°.

Slopes were computed by the method of least squares, using the Monroe 1865 electronic calculator program No. 4003P (Monroe Calculator Co., Orange, N. J., 1970).

#### Results and Discussion

For all five of the metal acetates, plots of E<sub>B</sub> vs. log C<sub>B</sub> were linear over the concentration range from 0.001 to 0.02 M. The variation in the slope among the set was random and the mean value given in Table I was derived from the least-squares treatment of all of the

emf-concentration data. This experimental slope exceeds the theoretical one of 0.0295 in eq 1 by 4%.

Values for the ion-pair dissociation constants (as pK<sub>B</sub>) were obtained graphically from empirical E<sub>B</sub> vs. pK<sub>B</sub> plots, using lithium and sodium acetates as standards. The results in Table II are based upon a series

 TABLE II  
 ION-PAIR DISSOCIATION CONSTANTS (AS pK<sub>B</sub>) FOR GROUP Ia ACETATES IN ANHYDROUS ACETIC ACID (AT 25°)

Base	pK <sub>B</sub>	
	Exptl	Lit.
LiOAc	6.79 <sup>a</sup>	6.78 <sup>b</sup> 6.80 <sup>c</sup> 6.22 <sup>d</sup>
NaOAc	6.58 <sup>a</sup>	6.58 <sup>b</sup> 6.68 <sup>d</sup>
KOAc	6.13 ± 0.04	6.10 <sup>a</sup> 6.11 <sup>b</sup> 6.92 <sup>c</sup> 6.44 <sup>d</sup>
RbOAc	5.93 ± 0.10	6.04 <sup>b</sup> 6.89 <sup>c</sup>
CsOAc	5.84 ± 0.10	6.78 <sup>c</sup>

<sup>a</sup> Standard values obtained by S. Bruckenstein and I. M. Kolthoff, *J. Amer. Chem. Soc.*, **78**, 2974 (1956). <sup>b</sup> Previous results of Kolling and Lambert.<sup>4</sup> <sup>c</sup> Values of Proll and Sutcliffe.<sup>3</sup> <sup>d</sup> Calculated from data of Jones and Griswold.<sup>2</sup>

of 16 such graphs for fixed and identical concentrations of the five acetates within the range 0.032–0.0010 M. Statistical analysis of the pK<sub>B</sub> values for KOAc, RbOAc, and CsOAc gave no evidence for a concentration dependent drift; therefore, the measured cell potential appears to conform to the simple ion-pair equilibrium without complicating influences from triplet ions and higher aggregates.

Upon comparison of the ion-pair constants from the published literature with the new results in Table II, it is clear that all of the potentiometrically measured values form a single consistent sequence of increasing dissociation: LiOAc < NaOAc < KOAc < RbOAc < CsOAc. Although the experimental uncertainties in the rubidium and cesium constants are overlapping, we are convinced that their small difference is real. Additional support for the validity of this conclusion was obtained from the emf data for the same glass-calomel electrode pair dipped into acetate solutions in the mixed solvent acetic acid-chlorobenzene.

The acetic acid-chlorobenzene solvent system is nonleveling toward both strong and weak bases, and the apparent strengths of uncharged bases exhibit only a slight systematic increase in the mixed solvent without any alteration in the order of decreasing basicity from that in pure acetic acid.<sup>11</sup> The plot of E<sub>B</sub> as a function

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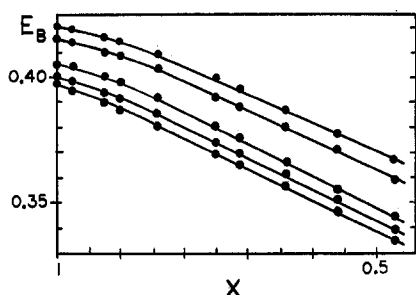


Figure 1.—Cell potential ( $E_B$ ) in V for 0.0040  $M$  solutions of bases in the solvent acetic acid–chlorobenzene. Mole fraction ( $X$ ) refers to HOAc. Curves in descending order are for LiOAc, NaOAc, KOAc, RbOAc, and CsOAc.

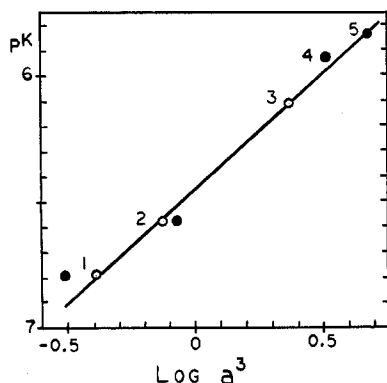


Figure 2.—The relationship of the MOAc ion-pair dissociation constant ( $pK_B$ ) to the radius ( $a$ ) of the cation: 1,  $\text{Li}^+$ ; 2,  $\text{Na}^+$ ; 3,  $\text{K}^+$ ; 4,  $\text{Rb}^+$ ; 5,  $\text{Cs}^+$ . Points  $\bullet$  are Goldschmidt radii and points  $\circ$  are radii reported by Waddington (radii in  $\text{\AA}$ ).

of the mole fraction of acetic acid in the mixed solvent (for constant  $C_B$ ) shown in Figure 1 verifies the sequence of increasing degree of dissociation for the group Ia acetates found in acetic acid as the solvent. From a quantitative point of view, the difference between the  $E_B$  values of the weakest and strongest bases expressed as  $\Delta = (E_B)_{\text{Li}} - (E_B)_{\text{Cs}}$  gradually increases from 23 mV in pure acetic acid to 32 mV in the mixed solvent having a mole fraction of 0.47 ( $D = 5.87$ ). The comparable values for the differences  $\Delta = (E_B)_{\text{Li}} - (E_B)_{\text{M}}$  for each metal acetate (MOAc) in the sequence were determined in acetic acid ( $X = 1.00$ ) and in the mixed solvent ( $X = 0.47$ ); and the equivalent  $E_B$  change (caused by the addition of chlorobenzene) expressed as a  $\Delta pK_B$  amounts to no more than 0.11 for NaOAc, 0.34 for KOAc and RbOAc, and 0.41 unit for CsOAc.

It follows from eq 3 that the ion-pair dissociation constant when expressed as  $pK_B$  is a linear function of  $\log a^3$  with a slope of unity. If the dissociative equilibrium for the acetates involves contact ion pairs in acetic acid media, then one can make the initial assumption justified by Benson and Copeland,<sup>12</sup> namely, that the solution radii are nearly the same as crystal radii for singly charged metallic cations. Various procedures for calculating crystal radii have been reviewed recently by Masterton, Bolocofsky, and Lee,<sup>13</sup> however, for the alkali metal cations, the most important differences among the computed radii are found in the  $\text{Li}^+$  and  $\text{Na}^+$  values. In constructing Figure 2 the radii

obtained by Goldschmidt (as summarized by Pauling<sup>14</sup>) and by Waddington<sup>15</sup> were used, and the empirical slope is 0.96 for the linear plot. When the Stokes radii for the gaseous cations<sup>16</sup> were substituted for crystal radii, the points in the  $pK_B$  vs.  $\log a^3$  graph were more scattered and linearity was uncertain.

In hydrogen-bonding solvents, including water, the order of increasing association of alkali metal salts with increasing cationic radius has been interpreted in terms of a systematic decrease in the extent of solvation of the cation with increasing ionic size.<sup>1</sup> This explanation is supported in part by the fact that the free energies of solvation of these cations<sup>17</sup> and their enthalpies of transfer<sup>18</sup> in both protonic solvents (including HOAc) and polar aprotic solvents follow a decreasing trend with increasing atomic number. By contrast, the reversed association sequence for group Ia acetates in anhydrous acetic acid (*i.e.*,  $\text{Li} > \text{Na} > \text{K} > \text{Rb} > \text{Cs}$ ) suggests that the thermodynamic influence from variation in cationic solvation is not the decisive factor determining the order. Here, the dominant structural effect upon the degree of association appears to be the role of variation of cationic radius upon the strength of the coulombic interaction within the ion pair. A comparable condition exists with a change of the anion radius for the rubidium halides in dioxane–water mixtures over a wide dielectric constant interval.<sup>19</sup>

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## Hydride and Carbonyl Complexes of Rhodium-Containing Di(tertiary phosphines and arsines)<sup>1</sup>

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Previously we have reported briefly on oxidative addition to  $[\text{Rh}(\text{cis}-(\text{C}_6\text{H}_5)_2\text{AsCH}=\text{CHAs}(\text{C}_6\text{H}_5)_2)]\text{Cl}$ .<sup>2</sup> We now report the details of a more convenient synthesis of this and related complexes and present complete spectroscopic data on a number of hydrido and carbonyl complexes derived from them.

### Experimental Section

All preparations were carried out under an atmosphere of dry nitrogen or Matheson CP grade carbon monoxide, and all solvents were appropriately dried and distilled before use. Hydrated rhodium(III) chloride was obtained from A. D. MacKay, Inc., and the published procedures were used to prepare *cis*-1,2-bis-

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