Coordinative Role of Alkali Cations in Organic Reactions. V. The Perkin Reaction

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The Perkin condensation of benzaldehyde (PhCHO) and acetic anhydride (Ac_2O) in the presence of an alkali acetate (M^+OAc^-) involves extensive participation of M^+ and takes place best with K^+OAc^-. Employing an excess of meticulously dehydrated K^+OAc^-, a record high yield of cinnamic acid ($\approx 75\%$) can be obtained in a 60 min reaction. The product of the reaction before hydrolysis is not $PhCH=CHCOOCOCH_3$ as usually believed but potassium cinnamate plus $K^+(OAc, HOAc)^-$. Conductometric solution stability studies on M^+ –ligand ($M^+=Na^+$ and K^+; Ligand$=PhCHO$, o-$NO_2C_6H_4CHO$, o-HOC_6H_4CHO) systems in 2-propanol show that stability sequences for PhCHO and o-$NO_2C_6H_4CHO$ are NaOAc$<$KOAc and KOAc$<$NaOAc, respectively. These are in line with the catalytic efficiency these salts displayed during the condensation reaction. o-HOC_6H_4CHO, for which the Perkin condensation is extremely poor, is practically non-complexing with M^+OAc^- in 2-propanol.

It is a rather established belief[1] that in the organic reactions involving caustic alkalis (M^+OH^-) and alkali salts (M^+X^-) the anion of the inorganic reactant is the only or the main participant in the reaction. Because of our experience in the coordination chemistry of these cations,[2] we initiated work on some such reactions and found that M^+ is very important in determining the route[3,4] as well as the efficiency[3-7] of the reaction and discussed such features of alkali and alkaline earth cations as one of the main themes related to their coordination chemistry.[8] In the course of our work we noticed that participation of M^+ was discussed in the nineteen fifties and sixties with respect to reactions such as the aldol condensation of esters with ketones,[9] certain displacement reactions[10] and the benzil-benzilic acid rearrangement[11] but these reports do not appear to have stimulated other workers.

In this article we discuss the role of M^+ during the Perkin reaction, in particular with respect to the synthesis of cinnamic acid. The Perkin reaction is one of the most general organic reactions[12] and has also been reviewed repeatedly.[13-16] Of the various conflicting views about its mechanism the most accepted is that for a system such as $PhCHO-Ac_2O-M^+OAc^-$, the OAc^- works as a nucleophile and eliminates the α-proton of Ac_2O to produce the carbanion which condenses with PhCHO (Scheme 1).
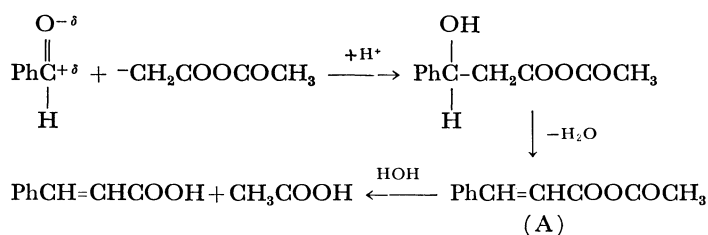
In the absence of an ionising medium, however, it is difficult to visualize how the chelating OAc^- can be charge-separated from the formally charged M^+ in preference for a feebly charged α-proton of Ac_2O unless M^+ is effectively stabilized through coordinative interactions with PhCHO and Ac_2O. Detailed studies on cinnamic acid synthesis employing K^+OAc^- reveal that K^+ is extensively involved in the reaction and

that the product of the reaction before hydrolysis is not A (Scheme 1) but potassium cinnamate plus K^+-$(OAc, HOAc)^-$. A record high yield of cinnamic acid ($\approx 75\%$ for a condensation period of 60 min as against 60% and 72% for condensation periods of five[17] and eight[18] hours, respectively) is obtained by using excess potassium acetate. The results of the Perkin reaction with respect to PhCHO, o-NO_2C_6-H_4CHO, and o-HOC_6H_4CHO are discussed in the light of their complexing ability toward M^+OAc^- in a medium of low polarity (2-propanol).

Results and Discussion

Synthetic Studies. For the synthesis of cinnamic acid it is known that the yield of the reaction product is drastically decreased when K^+OAc^- in the reaction is replaced by Na^+OAc^-.[19] We confirm this and show further (see Table 1) that the reaction almost fails when Li^+OAc^- is used. This is, obviously, because the M^+OAc^- ion pair is increasingly tight in the order $K^+<Na^+<Li^+$ so that the activity of OAc^-, the complexation of M^+ with PhCHO and Ac_2O, and hence the dissolution of M^+OAc^- in the latter reactants all become increasingly unfavored.

Detailed work with K^+OAc^- revealed that the primary products of the reaction are potassium cinnamate and the acid salt, $K^+(OAc, HOAc)^-$ as evident from the spectra of the reaction products (d to f) in comparison with those of the standard samples (a to c) in Fig. 1. Comparison of the spectra d to f with that of the 1:1 K^+Cin^-–$K^+(OAc, HOAc)^-$ (spectrum c) reveals that the K^+Cin^- contribution dominates when less K^+OAc^- is used in the reaction (spectrum d) and that the $K^+(OAc, HOAc)^-$ contribution dominates

$$O^{-\delta}$$
$$\|$$
$$PhC^{+\delta} + {}^-CH_2COOCOCH_3 \xrightarrow{+H^+} PhC-CH_2COOCOCH_3$$
$$| \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad |$$
$$H \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad H$$

with OH at top and $-H_2O$ below, leading to:

$$PhCH=CHCOOH + CH_3COOH \xleftarrow{\;HOH\;} PhCH=CHCOOCOCH_3$$
$$(A)$$

Scheme 1.

TABLE 1. ENLISTING SELECTED EXPERIMENTAL RESULTS;
REACTION TIME 5 h, REACTION TEMPERATURE, 180 ± 2 °C

PhCHO : Ac$_2$O : M$^+$OAc$^-$ [a]	Percentage yield[b] of cinnamic acid
Reaction mixture involving different M$^+$OAc$^-$	
1 : 1.5 : 0.63[c] (Li$^+$OAc$^-$)	nil
1 : 1.5 : 0.63[d] (Na$^+$OAc$^-$)	24
1 : 1.5 : 0.63[d,e] (K$^+$OAc$^-$)	56
Reaction mixture involving varying proportions of K$^+$OAc$^-$	
1 : 1.5 : 1.25	58
1 : 1.5 : 2.00	63
1 : 1.5 : 2.25	70
1 : 1.5 : 2.50	75
1 : 1.5 : 2.50 (1 h)[f]	75
1 : 1.5 : 2.75	65
Reaction mixture involving varying proportions of PhCHO and Ac$_2$O with K$^+$OAc$^-$	
1 : 1 : 1	63
1.5 : 1 : 1	51[g]
1 : 1.5 : 1	45[g]
2 : 1 : 1	49[h]
1 : 2 : 1	39[h]
2 : 2 : 1[i]	48

a) All experiments were carried out under nitrogen atmosphere. b) Average of three experimental results, the reaction yield of which varied within ±1%. c) This particular proportion of the reactants has usually been recommended.[17] d) The Perkin condensation is a typically time-dependent and a slow reaction; with this proportion of the reactants the yield is increased to 39% and 72% with Na$^+$OAc$^-$ and K$^+$OAc$^-$ respectively, when reaction time was increased to 8 h. e) On addition of the reation product to water, free cinnamic acid is insolubilized in low yield (2—5%) as observed earlier,[1] but this byproduct gradually disappears as K$^+$OAc$^-$ in the reaction is increased. This may be attributed to partial hydrolysis of potassium cinnamate with the residual amount of AcOH which can persist in reaction mixtures offering insufficient K$^+$OAc$^-$ for its conversion into K$^+$(OAc, HOAc)$^-$. f) The yield of cinnamic acid decreases if reaction time is decreased any further but is practically constant if the time is increased even to as long as 8 h. g) The yield of cinnamic acid decreased because of displacement of one reactant from K$^+$ by the other which is used in excess; the effect is pronounced when the bidentate and hence strongly complexable Ac$_2$O is used in excess. h) The benzene wash of the reaction product was found to contain potassium cinnamate which was, obviously, carried into this nonpolar phase through complexation with Ac$_2$O. i) The amount of potassium cinnamate in the benzene phase increased further which indicates that PhCHO acts as a co-ligand during complexation (and hence benzene solubilization) of potassium cinnamate with Ac$_2$O.

when excess K$^+$OAc$^-$ is used (spectrum f).

Direct production of potassium cinnamate may be attributed to an interactive organisation[8] of the reactants as shown in Scheme 2. This interactive mode helps (i) PhCHO to develop the required carbonium character, (ii) Ac$_2$O to have its α-proton
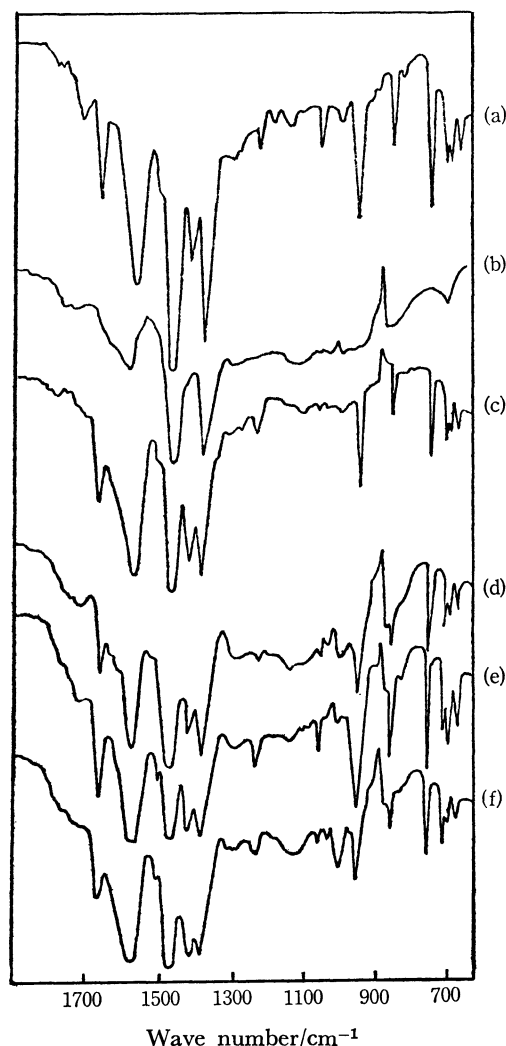

Wave number/cm^{-1}

Fig. 1. Showing infrared features (1700—700 cm^{-1}) of some authentic samples [a, potassium cinnamate, b, K$^+$(OAc,HOAc)$^-$, and c, a 1:1 physical mixture of potassium cinnamate and K$^+$(OAc,HOAc)$^-$ which was heated at ≈180 °C for 30 min] and products of the Perkin condensation employing different proportions of PhCHO, Ac$_2$O, and K$^+$OAc$^-$ [d, 1:1:1; e, 1:1.5:0.6 and f, 1:1.5:2.5].

cationized, and (iii) K$^+$OAc$^-$ to become the loose ion pair required to make OAc$^-$ an available nucleophile. Above all, the energy of coordinative interaction of PhCHO and Ac$_2$O with K$^+$OAc$^-$ should help the thermodynamically unfavorable processes, viz., charge separation of K$^+$OAc$^-$ and cleavage of the C–H$_\alpha$ covalent bond. That the alkali cation is required for such an interactive organisation is evidenced by the failure of the condensation when the cation in the reaction is concealed through sandwich encapsulation using benzo-15-crown-5.[20] Simultaneous interaction of PhCHO and Ac$_2$O with K$^+$OAc$^-$ is evidenced by the observation that the yield of the reaction is drastically lowered when either PhCHO or Ac$_2$O is displaced from K$^+$OAc$^-$ by using the other in excess (see Table 1).

Coordination of K$^+$OAc$^-$ with PhCHO and Ac$_2$O

Scheme 2.
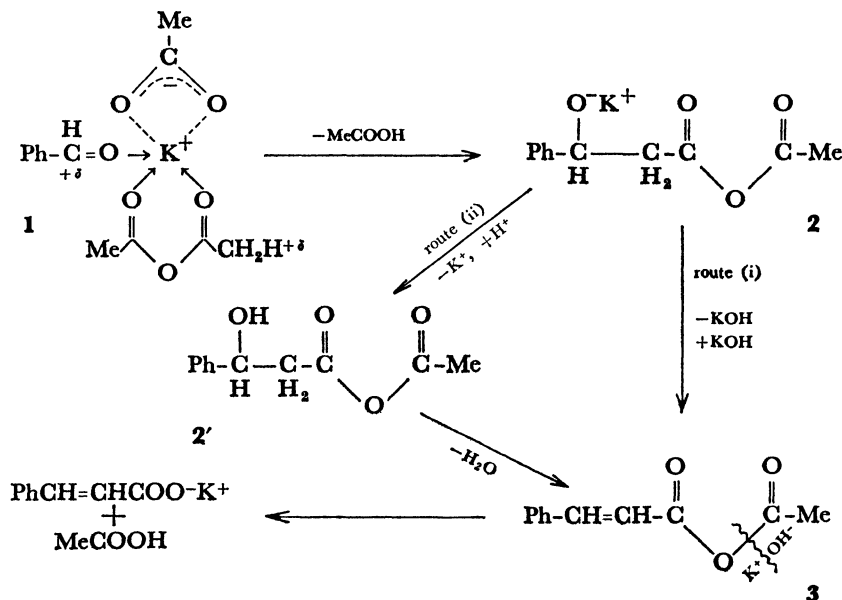
is also supported by the observation that the salt can be solubilised just in PhCHO and particularly when Ac_2O is also present. When PhCHO and Ac_2O are used in excess during condensation, even the reaction product, potassium cinnamate, gets complexed and rendered benzene-soluble (see Experimental). Stable solid solvates of alkali and alkaline earth salts involving coordinated PhCHO[21,22] acetone,[21,23] and other ketones[23] have long been characterised.

Accurate kinetic work on this reaction cannot be carried out because it is a high temperature reaction and each organic reactant is unstable with time. Synthesis of a stoichiometric $PhCHO-Ac_2O-K^+OAc^-$ complex is also not possible for it requires a coordinative ligation of a ligand with the cation to be of a particular minimum strength which is apparently not so with PhCHO and Ac_2O.

During the reaction, Ac_2O is susceptible to hydrolysis by moisture which can be incorporated in the system through the hygroscopic K^+OAc^-. AcOH produced by hydrolysis reduces also the effective concentration of K^+OAc^- through the formation of $K^+(OAc, HOAc)^-$. If, on the contrary, an excess of meticulously dehydrated K^+OAc^- is used (see Table 1) a record high yield of cinnamic acid ($\approx 75\%$) can be obtained by refluxing the reactants just for 60 min. This may in part be because excess K^+OAc^- serves to bind the deleterious byproduct of the reaction, AcOH, and partly because it may help shift the reaction equilibria toward the complexation required for "cationization" of PhCHO and carbanion formation of Ac_2O. In condensation reactions employing M_2CO_3, the favorable role of the alkali has been attributed to its neutralizing action toward HOAc.

Solution Studies.   Conductometric studies in the feebly polar 2-propanol reveal (Figs. 2 and 3, Table 2) that K^+OAc^- undergoes a 1:1 interaction with PhCHO (log $K=2.48$) and Ac_2O (log $K=3.23$). Na^+OAc^-, which is less favorable for Perkin condensa-
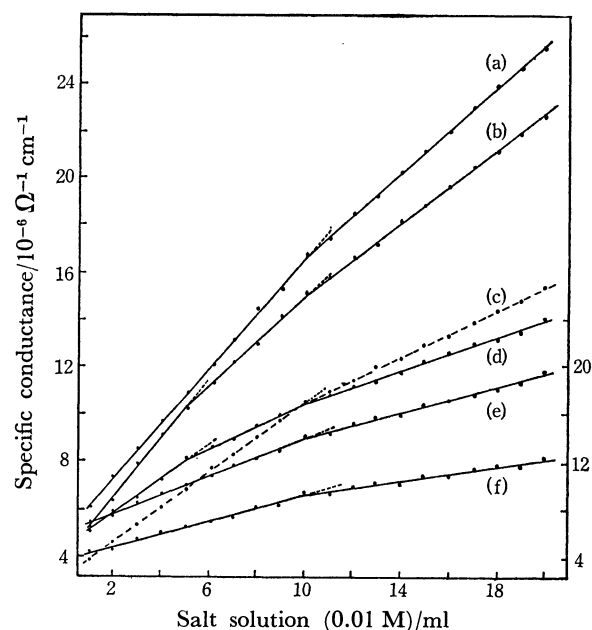

Fig. 2. Specific conductance *versus* salt concentration plots for K^+OAc^- in presence of (a) $NO_2C_6H_4CHO$, (b) Ac_2O, and (c) PhCHO, and for Na^+OAc^- in presence of (d) $NO_2C_6H_4CHO$, (e) Ac_2O and (f) PhCHO. Conductance scale on the right refers to Na^+-OAc^- systems.

tions, interacts relatively weakly with PhCHO (log $K=2.08$) as well as Ac_2O (log $K=2.35$). Li^+OAc^-, which does not aid the condensation, behaves insoluble and hence tightly ion-paired in 2-propanol. The most facilitated complexation of K^+ may be attributed to its large size (low charge density) because of which it is comparatively loosely paired with OAc^- (see K_d values in Table 2), and gets effectively polarized by the donor atoms of the neutral ligands. The fact that Ac_2O complexes K^+ more strongly than does PhCHO explains why, in reactions employing a dis-

TABLE 2. DISSOCIATION CONSTANTS (K_d) OF M^+OAc^- AND log OF FORMATION CONSTANTS (log K) OF THEIR COMPLEXES WITH AROMATIC ALDEHYDES AND ACETIC ANHYDRIDES; MEDIUM, 2-PROPANOL; TEMPERATURE 25 ± 1 °C

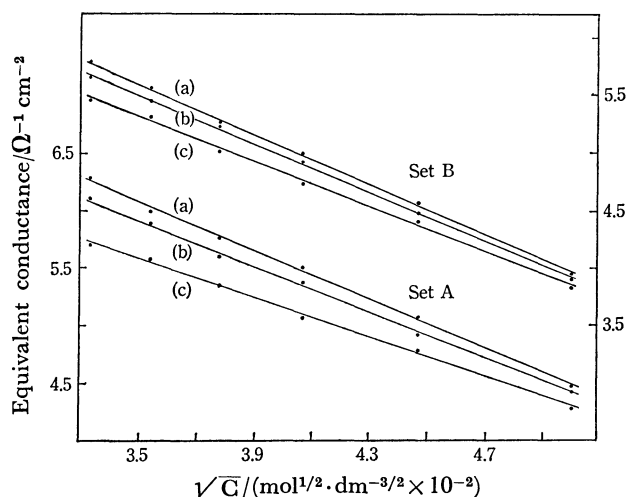| Salt	K_d mol l^{-1}	System	Stoichiometry	log K
KOAc	2.19×10^{-6}	KOAc-PhCHO	1 : 1	2.48
		KOAc-NO$_2$C$_6$H$_4$CHO	1 : 1	2.03
		KOAc-Ac$_2$O	1 : 1	3.23
			1 : 2	—
NaOAc	5.49×10^{-8}	NaOAc-PhCHO	1 : 1	2.08
		NaOAc-NO$_2$C$_6$H$_4$CHO	1 : 1	2.47
			1 : 2	—
		NaOAc-Ac$_2$O	1 : 1	2.35

Fig. 3. Equivalent conductance versus salt concentration plots which were used to determine the solution stability values. Set A (K$^+$OAc$^-$–PhCHO systems); (a) K$^+$OAc$^-$, (b) K$^+$OAc$^-$–PhCHO (1:1), and (c) K$^+$OAc$^-$–PhCHO (1:10). Set B (K$^+$OAc$^-$–Ac$_2$O systems); (a) K$^+$OAc$^-$, (b) K$^+$OAc$^-$–Ac$_2$O (1:1), and (c) K$^+$OAc$^-$–Ac$_2$O (1:10). Conductance scale on the right refers to Ac$_2$O systems.

proportionately high amount of either of these two, Ac$_2$O is more effective in reducing the efficiency of the condensation (through displacement of PhCHO from K$^+$). o-HOC$_6$H$_4$CHO, which yields only traces of o-hydroxycinnamic acid by Perkin reactions,[24] has been found to be practically non-interacting with Na$^+$-OAc$^-$ or K$^+$OAc$^-$.[25]

o-NO$_2$C$_6$H$_4$CHO shows a strong complexation with Na$^+$OAc$^-$ as well as K$^+$OAc$^-$ (Table 2) and synthesis of o-nitrocinnamic acid is also possible with both.[26] Contrary to what has been noted for PhCHO, however, the stability value is high for Na$^+$OAc$^-$ and, interestingly, yields of o-nitrocinnamic acid in Perkin reaction is also higher for Na$^+$OAc$^-$. One of the possible interacting sites of the nitroaldehyde with M$^+$ is the nitro oxygen which, being linked to the electronegative nitrogen, can be visualized as "reinforced"[8] or "anionic" and hence a more preferable site for the comparatively anionphilic Na$^+$.[27]

The Condensation Mechanism. Detailed studies on PhCHO–Ac$_2$O–M$^+$OAc$^-$ reveal that even before the

water treatment the product of the reaction is potassium cinnamate. Obviously, the reaction intermediate (*e.g.*, A in Scheme 1 or 3 in Scheme 2) undergoes molecular degradation right during condensation through some bond cleavage process. Understandably, therefore, 2 loses MOH (*cis*-elimination of M$^+$ and OH$^-$) to produce an unsaturated intermediate 3 and MOH molecule then causes bond cleavage of 3 as shown in Scheme 2. That MOH and not M$^+$OAc$^-$, is involved in bond cleavage, appears to be supported by the observation that the alkali cinnamate can be produced from a reaction mixture containing less than an equivalent amount of M$^+$OAc$^-$ such as from PhCHO:Ac$_2$O:M$^+$OAc$^-$ (1:1.5:0.6) (see Fig. 1).

There is a likelihood of K$^+$/H$^+$ exchange between 2 and MeCOOH so that 2′ is produced (Route (ii)). The water molecule which gets eliminated from the latter, however, has the only recourse of hydrolyzing MOAc and especially Ac$_2$O. The hydrolysis of the latter appears evidenced by the observation that for obtaining maximum efficiency of the reaction, use of some excess Ac$_2$O is a requirement (see Table 1).

The suggested mechanism involving simultaneous coordinative organization of the three reactants sorts out earlier conflicts wherein either AcO$^-$–Ac$_2$O[28,29] or AcO$^-$–PhCHO[28,30] interaction has been argued to be a possible triggering step for the condensation. Since alkali cinnamate is the product of the reaction the Perkin's original diacetate mechanism,[31] which has already been disputed[30,32] becomes even less acceptable.

During the o-NO$_2$C$_6$H$_4$CHO–Ac$_2$O condensation in the presence of PhCH$_2$COONa, ML, the acid salt Na$^+$(PhCH$_2$COO, PhCH$_2$COOH)$^-$, MLHL, has been detected and considered to be an intermediate of the reaction[33a] because reaction of this acid salt with a mixture of o-NO$_2$C$_6$H$_4$CHO and Ac$_2$O yielded the α,β-unsaturated acid. This view, however, does not present anything new and infact creates confusion because use of this MLHL (wherein L and HL are only hydrogen bonded) at a high reaction temperature amounts to the use of ML plus HL and ML as a participating species. We have failed to synthesize cinnamic acid by the reaction of K$^+$(AcO, AcOH)$^-$ and PhCHO. Detection of the acid salt as a product (infact byproduct), however, is understandable as we, too, detected in the present work.

The rather "modern view" involving the formation

and participation of alkali salt of enolic acetic anhydride[13] appears unlikely because we failed to synthesize an alkali enolate by the direct reaction of Ac_2O and Na^+OAc^- or K^+OAc^- at 180 °C.[33] Since the condensation temperature (180 °C) is well below the fusion temperature of Na^+OAc^- (324 °C) and K^+OAc^- (299 °C), possible reaction routes involving $^-CH_2COO^-$ (which is believed to exist in fused M^+OAc^-) are also ruled out.

Experimental

Synthesis Procedure.   Using 22.5 mmol (2.39 g) as a unit of weight for PhCHO, the $PhCHO-Ac_2O-K^+OAc^-$ mixtures were fused at 180±2 °C in different proportions for different time periods (see Table 1) under a nitrogen atmosphere. The fused solid product was cooled and divided into two equal parts. One part was subjected to the recovery of cinnamic acid to determine its yield following the conventional procedure. The other part was subjected to qualitative examination for which the residue was first scrubbed with benzene or acetone (50 ml) and filtered. The washed residue was subjected to hot stage microscopy and infrared spectroscopy which indicated it to be potassium cinnamate plus $K^+(OAc, HOAc)^-$ (see Fig. 1). The organic filtrate, which contains the polymeric material and the unused PhCHO and Ac_2O plus potassium cinnamate complex involving PhCHO and Ac_2O, was evaporated to dryness in the open to destroy the unused reactant and to decompose the complex. The organic matter from this residue was eliminated by washing with benzene or acetone. The clarified residue was found to be pure potassium cinnamate, the amount of which was found to be in accordance with the amount of PhCHO and Ac_2O used in the reaction.

Condensation in Absence of Alkali Cation.   Potassium acetate (1 mmol, 0.098 g) was scrubbed in the absence of moisture with benzo-15-crown-5 (2 mmol, 0.536 g). The solid mixture was treated with PhCHO (1 mmol, 0.106 g) and Ac_2O (1 mmol, 0.102 g). The reaction mixture was subjected to condensation at 180±2 °C for five hours and then processed for the recovery of cinnamic acid following the conventional procedure. A polymeric product instead of cinnamic acid was obtained.

Conductometric Solution State Studies.   Stock solutions of the salt (10 mmol) and the ligands (2.5 mmol) were prepared in anhydrous 2-propanol. Complexation and stoichiometry of the resultant complex was followed adopting the conductometric monovariation titration technique[34] while solution stability of each complex was determined following the Matsuura's conductometric dilution technique.[35] For the monovariation technique 40 ml of the ligand solution was titrated with the salt solution (1—25 ml) while applying volume correction.[36] Since for each system which indicated complexation, the initially formed biligand (1:2) complex was converted to a 1:1 complex on the addition of more salt, Matsuura's method was followed to determine the stability of the apparently more stable 1:1 species only. Figure 2 shows the stoichiometry of the selected complexes while Fig. 3 displays the exemplary sets of the phoreograms obtained for the systems $K^+OAc^--PhCHO$ and $K^+OAc^--Ac_2O$.

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