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Solvolysis of Alkyl *p*-Hydroxybenzoates in Fused Lithium–Sodium–Potassium Acetate

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Abstract: The Li^+,Na^+,K^+OAc^- eutectic (32, 30, 38 mol %), a molten salt in which phenolic compounds are soluble, is sufficiently basic to ionize aromatic amine indicators of pK_a = 15. Solutions of methyl *p*-hydroxybenzoate (**1**) react to form methyl acetate, carbon dioxide, methanol, phenol, and anisole. The kinetics of this $B_{Al}2$ displacement by acetate ion, at 181–220 °C in the presence of 1.3% acetic acid, shows k (s^{-1}) = $1.49 \times 10^5 e^{-19900/RT}$ for **1** and successively decreasing rates for the ethyl, propyl, isopropyl, and 2-butyl esters. 2-Butyl *p*-hydroxybenzoate (**2**) undergoes both elimination and displacement; optically active **2** yields 58% inverted, 42% racemized 2-butyl acetate. Thiocyanate ion, added to the molten salt, is a nucleophile which competes with acetate ion in the displacement, accelerating the solvolysis.

Molten salts have been used as solvents for kinetic studies of a very few homogeneous organic substitution and elimination reactions.[2-10] Having reported displacements on the alkyl group of esters by thiocyanate ion, the solvent nucleophile in fused sodium–potassium thiocyanate, Na^+,K^+SCN^-,[11] we now describe solvolysis in an acetate melt, Li^+,Na^+,K^+OAc^-. We used a ternary eutectic of lithium, sodium, and potassium acetates (32, 30, 38 mol %, mp 162 °C).[12] Other lower melting but more expensive eutectics such as Na^+,Rb^+,Cs^+OAc^- (30.5, 14.0, 55.5 mol %, mp 95 °C) have been characterized.[13]

Results

Solutions in the Fused Salt. Hydroxyl groups in organic compounds cause them to be quite soluble in the fused acetate at 200 °C, just as in ammonium nitrate[14] and potassium thiocyanate[15] melts. In contrast to thiocyanate, however, we find that molten acetate is sufficiently basic to ionize the phenolic hydroxyl groups in *p*-nitrophenol, *m*-nitrophenol, and alizarin as well as the amino group in 2,4-dinitroaniline (pK_a = 15.00 in water, 25 °C)[16] but not *p*-nitroaniline (pK_a = 18.37). The medium can be made less basic by adding acetic acid, giving rise to a protic solvent system containing a preponderance of lyate ion. If the fused salt contains 0.074 M acetic acid, the ionization of 2,4-dinitroaniline is repressed so that only about 50% of it is in the anionic form, $ArNH^-$. Addition of 11 mol % acetic acid to the melt raises its acidity sufficiently to protonate the alizarin dianion to the red monoanion while a medium 62 mol % acetic acid and 38 mol % Li^+,Na^+,K^+OAc^- favors the yellow, neutral form observed in slightly acidic aqueous solution.

Of the variety of polyhydroxy compounds soluble in the acetate melt, some, such as ethylene glycol, are probably not completely ionized and dissolve by hydrogen bonding to the acetate ion.[2] Others, as demonstrated by the indicator studies, go into solution as anions. However, sodium salts such as sodium methoxide, sodium benzoate, and sodium phenoxide, unlike their conjugate acids, do not dissolve immediately in the melt. For example, sodium benzoate (2 wt %) requires at least 20 min and in some experiments several hours, to dissolve at 200 °C. Decarboxylation does not occur; the salt can be recovered as benzoic acid.[17] Immediate solution of these sodium salts can be effected by adding small quantities of acetic acid with a syringe. While this observation supports the assumption that the anions are solvated by acids in the melt,[2] we were prevented from finding a relationship between concentrations and solubility by the slow dissolution mentioned above. Solubility of the salts of oxy anions is also increased by traces of water.

Although the acetate melt is ostensibly aprotic, it is really not strictly so. Even if acetic acid is neither added directly, as in most of the kinetic studies described below, nor indirectly through the ionization of dissolved acids, traces of acetic acid as well as water are present which are difficult to remove by heating or pumping. The melt is also protic in the sense that the hydrogen atoms in the methyl group of CH_3COO^- exchange with CD_3COO^- (40% in 10 h at 250 °C).[18]

The affinity of molten acetate for acetic acid is seen in the negative deviation from ideality of the partial pressure of acetic acid vapor over solutions of it in the melt. The dotted line in Figure 1 shows the observed pressure, p, as a function of the mole fraction x of acetic acid, up to its vapor pressure, 5260 Torr at $x = 1$. The line A, drawn through the points for low x (without regard for their apparent curvature), may be expressed as $p = 0.20p_0x$ where 0.20 is a Henry's law constant. Curve B is $p = p_0x$. The solubility of CH_3COOD is the same as that of CH_3COOH, within 1%, up to $x = 0.043$.

Water vapor is much less soluble in the acetate melt. It shows a positive deviation from ideality, $p = (9.5 \pm 0.1)p_0x$, at mole fractions of water near 10^{-4}. This fact, together with

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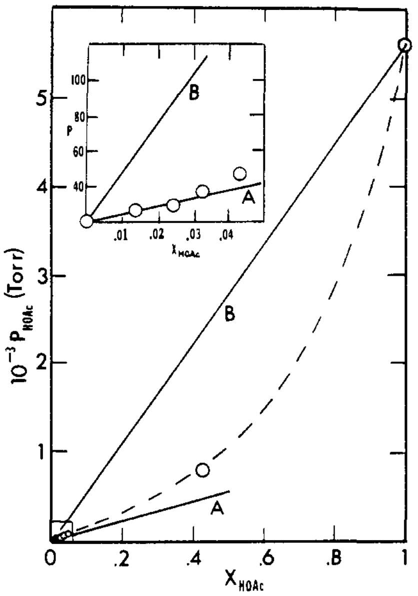


Figure 1. Partial pressure of acetic acid vapor over Li^+,Na^+,K^+OAc^- melt at 200 °C as a function of mole fraction X of acetic acid in solution. The inset is a conformal enlargement of square at the origin.

Table I. Volatile Product Analysis[a] for Reaction of 2-Butyl *p*-Hydroxybenzoate with Fused Acetate[b]

product	yield,[c] mmol	yield, mol %
carbon dioxide	9.3	90
2-butyl acetate	3.9	38
2-butanol	1.3	13
trans-2-butene	0.9	9
cis-2-butene	0.7	7
1-butene	0.7	7

[a] Incompletely volatile products remaining in reaction vessel were phenol and phenyl acetate. [b] At 246 °C, under nitrogen saturated with acetic acid at 25 °C. [c] From 10.3 mmol of ester in 19.8 g of molten salt.

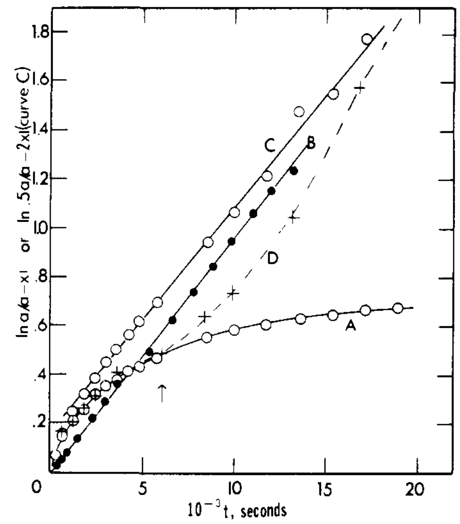


Figure 2. First-order plots of rate of carbon dioxide evolution from methyl *p*-hydroxybenzoate in molten acetate: (A) without acetic acid, 200 °C; (B) acetic acid in nitrogen stream, 199 °C; (C) same experiment as A, plotted as 0.5 ln $a/(a - 2x)$; (D) acetic acid added at time indicated by arrow (6000 s).

Table II. Effect of Acids in the Melt on Solvolysis Rate of *p*-HOC_6H_4COOR

R	melt temp, °C	acid	temp of N_2 saturation,[a] °C	10^5k, s^{-1}
Me	195.5	none		7.2
Me	195.4	HOAc	24	7.1
Me	195.2	$HOAc-H_2O$[b]	24	6.0
Me	199.1	HOAc	23	9.5
Me	199.6	DOAc	23	9.1
Me	200.1	H_2O	24	8.8
Me	199.6	H_2O	0	8.4
sec-Bu	246.6	none		9.7
sec-Bu	246.8	HOAc	23	12.0

[a] Temperature of the liquid acetic acid used to saturate the nitrogen stream. [b] 50:50 wt %.

its higher vapor pressure, allows water to be more easily removed from the melt by evacuation than acetic acid.

Solvolysis Products. Nucleophilic displacements on alkyl halides were noted by Packham and Rackley when the vapor was passed through molten sodium acetate.[19] Desiring a homogeneous reaction, we chose methyl *p*-hydroxybenzoate (**1**) as the substrate; the hydroxyl group renders it soluble in the melt and reaction occurs at the ester group. The ester was dissolved in the molten salt, the system was closed, and a stream of nitrogen containing acetic acid (see section on kinetics) was passed through the hot solution, sweeping volatile products into a cold trap. Carbon dioxide, methyl acetate, methanol, and phenol are formed. If acetic acid is omitted from the nitrogen stream, anisole is also produced (eq 1, R = CH_3).

$$CH_3COO^- + ROCOC_6H_4O^- + CH_3COOH \rightarrow CH_3COOR + CO_2 + C_6H_5O^- + CH_3COO^- \quad (1)$$

$$C_6H_5O^- + ROCOC_6H_4O^- + CH_3COOH \rightarrow C_6H_5OR + CO_2 + C_6H_5O^- + CH_3COO^-$$

Ethyl, propyl, and isopropyl *p*-hydroxybenzoate give products analogous to the methyl ester. Because 2-butyl *p*-hydroxybenzoate (**2**) reacts more slowly, the reaction was run at 246 °C for quantitative product estimation. The results are shown in Table I. Although 2-butyl acetate is the chief product (38%), evidently elimination (23% butenes) and alcohol formation (13%) also occur. At 200 °C, butenes were detected but no ethylene was produced in 24 h from ethyl *p*-hydroxybenzoate.

(+)-2-Butyl *p*-hydroxybenzoate (**2a**) (85.4% optically pure), at 246 °C, yielded (−)-2-butyl acetate of 50.0% optical purity. This corresponds to 58% inversion of configuration, and 42% racemization, of the 2-butyl group in the substitution of acetate for *p*-hydroxybenzoate. Unreacted **2a**, isolated after 37% reaction, showed no racemization.

Kinetics. The solvolysis of alkyl *p*-hydroxybenzoates was followed by determining the moles, x, of carbon dioxide evolved. A plot of ln $a/(a - x)$ vs. time for the methyl ester **1** shows a short induction period attributable to the response time of the absorption train, then is linear for 15–30% of the reaction, after which it tapers off as in curve A, Figure 2. This decrease in rate constant apparently is due to a lack of proton donors in the solution, for, if the nitrogen stream used to sweep products into the absorption train is passed through liquid acetic acid at 24 °C (resulting in p_{HOAc} = 14 Torr in the gas and 1.3 mol % acetic acid in the melt), the first-order plot is then linear to 90% reaction (curve B). Table II shows that, at the acid concentrations employed, the rate is not very sensitive to the nature of the acid nor to its concentration. In most of the kinetic runs, a 14 Torr partial pressure of acetic acid vapor was maintained to ensure first-order kinetics, and the rate constant k is defined as the slope of the long, linear portion of graphs

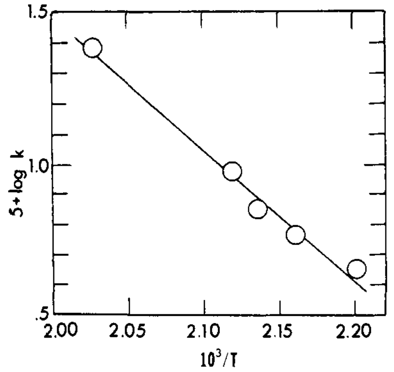


Figure 3. Arrhenius plot (eq 2) for solvolysis of methyl *p*-hydroxybenzoate in the melt, 181–220 °C.

Table III. Rate Constants for Reaction of p-HOC_6H_4COOR with Molten M^+OAc^- [a]

R	t, °C	k, s^{-1}	no. of runs	av dev, %
CH_3	181.5	4.46×10^{-5}	2	1.9
	190.3	5.85×10^{-5}	2	1.9
	195.4	7.08×10^{-5}	1	
	199.1	9.52×10^{-5}	3	0.8
	199.6	9.10×10^{-5}	1[b]	
	220.3	2.40×10^{-4}	2	2.4
CH_3CH_2	199.6	1.65×10^{-5}	2	0.6
$CH_3CH_2CH_2$	199.6	8.05×10^{-6}	2	1.8
$(CH_3)_2CH$	199.5	4.77×10^{-6}	2	3.3
$CH_3CH_2(CH_3)CH$	200.0	2.63×10^{-6}	2	
	246.8	1.20×10^{-4}	1	

[a] Containing CH_3COOH from nitrogen stream saturated at 25 °C. [b] Nitrogen stream saturated with CH_3COOD.

such as Figure 2B.

The acetolysis rate constants of the five esters studied are given in Table III. The Arrhenius plot (Figure 3) of the rate constants for the methyl ester **1** is $\log k = 5.174 - 4345/T$, leading to the rate equation

$$k(s^{-1}) = 1.49 \times 10^5 e^{-19900/RT} \qquad (2)$$

Thiocyanate ion was found to be a nucleophile suitable for addition to the melt. Potassium thiocyanate is very soluble in the fused acetate and is stable for a least 2 h at 200 °C. To minimize the formation of HNCS, acetic acid was not added when thiocyanate was present; more linear plots were obtained using a slightly different rate equation. On the grounds, considered more fully in the Discussion section, that 1 mol of acetic acid is removed from solution for every mol of carbon dioxide produced by decarboxylation after displacement (but not elimination), eq 3 was used.

$$\frac{1}{2}\ln\frac{a}{a-2x} = k't \qquad (3)$$

Figure 2C shows the data of curve A analyzed by eq 3, resulting in linearity to 80% reaction. At 5400–7200 s, the mol % carbon dioxide produced is 47.5–50.3, too close to 100% reaction, according to eq 3, to plot accurately. In the final stages of the reaction, above 10^4 s, the carbon dioxide produced (53–56.5 mol %) exceeds the limit of 50% assumed in deriving eq 3.

The effect of potassium thiocyanate is to accelerate the solvolysis of **1** and to produce methyl thiocyanate and methyl isothiocyanate in addition to all the products formed in the absence of the extra nucleophile. The rate constant k' is shown in Table IV as a function of the molarity of potassium thiocyanate dissolved in Li^+,Na^+,K^+OAc^-. It is linear in the thiocyanate ion concentration up to 2.88 M (eq 4). Alternatively, a rate constant k_{A^-} may be assigned to the acetate ion as in eq 5. By either equation, the k' calculated for the highest thiocyanate concentration, 3.97 M, is 17% higher than the observed k'.

Table IV. Products and Rate Constants for Methyl *p*-Hydroxybenzoate in Molten Acetate Containing Potassium Thiocyanate, 195 °C

[KSCN] M	$[OAc^-]$[a] M	mmol substrate	SCN^- reacted[b]	$10^4k'$, s^{-1}	$10^4k'$(calcd),[c] s^{-1}
0	16.7	4.80		0.92	(0.92)
0.86	15.9	6.65	0.53	1.5	1.53
1.98	14.8	6.59	1.0	2.4	2.32
2.88	13.8	9.74	1.5	2.9	2.95
3.97	12.7	14.01	3.4	3.1	3.72

[a] Acetate ion concentration in the melt is reduced by addition of potassium thiocyanate. Volume of solution about 10 mL. [b] By titration at completion, mmol. [c] Calculated by eq 5.

$$10^4k' = 0.92 + k_N[SCN^-] \quad k_N = 0.70\ M^{-1}\,s^{-1} \qquad (4)$$

$$10^4k' = k_{A^-}[OAc^-] + k_N[SCN^-] \quad k_N = 0.76\ M^{-1}\,s^{-1}$$
$$k_{A^-} = 0.055\ M^{-1}\,s^{-1} \qquad (5)$$

Discussion

Inversion of configuration of the 2-butyl group of **2** implies cleavage of the O-alkyl bond during solvolysis, since the substrate itself is not racemized in the fused salt. Formation of methyl thiocyanate[20] proves O-methyl cleavage when thiocyanate ion is present. No indications of free radicals, such as methane or ethane, in the reaction products were observed. Although the pure esters are stable at 200 °C, it might be argued that a four-center thermal decomposition could be taking place in the solvent, except for the fact that the methyl ester **1**, for which the mechanism is impossible, is the most reactive substrate. Moreover, 2-butene, though it might have formed by pyrolysis of **2**, was shown not to add acetic acid in the melt, precluding the formation of 2-butyl acetate by that route.

In the basic medium, the elimination reaction producing butene from **2**, concurrently with displacement, is certainly not unexpected, though we failed to detect ethylene when ethyl *p*-hydroxybenzoate reacted with the fused salt.

Acceleration with increasing thiocyanate concentration (Table IV) suggests that C–S bond formation contributes to the driving force of the reaction as in an S_N2 reaction. If we assume that the two nucleophiles, acetate and thiocyanate, compete in independent bimolecular reactions with **1**, we can conclude from the ratio k_N/k_{A^-} that thiocyanate ion is about 14 times as reactive as acetate under these conditions. Thiocyanate is also a stronger nucleophile toward saturated carbon[21] in aqueous solution at 25 °C, though not toward the carbonyl group of an ester.[22]

All these results are consistent with attack of acetate ion upon the alkyl group of the ester, forming alkyl acetate in a displacement reaction analogous to the $B_{Al}2$ ester hydrolysis mechanism.[23] The effect of alkyl substitution in the methyl group of **1** is to decrease the reaction rate at 200 °C (Table III). This is typical of S_N2 reactions. A closer comparison with the known effect of structure on the rates of displacement reactions can be made by extrapolating the observed rates down to 25 °C, using the activation enthalpy, $\Delta H^{\ddagger}$, of 19.9 kcal/mol observed for **1** and adding to it increments $\Delta\Delta H^{\ddagger}$ averaged for a number of displacements.[24] The resulting relative k values are compared with a composite set of rates[24] for substitution at saturated carbon in Table V.

The rates indicate solvent-assisted displacement rather than

Table V. Calculated Relative Solvolysis Rates of $p\text{-}HOC_6H_4COOR$ at 25 °C

R	$\Delta\Delta H^{\ddagger a}$	k_{200}	k_{25}(calcd)^b	$k_{25}(S_N2)^c$
Me	(0)	5.76	16.6	30
Et	1.66	(1)	(1)	(1)
Pr	1.65	0.48	0.49	0.4
i-Pr	3.91	0.28	0.07	0.025

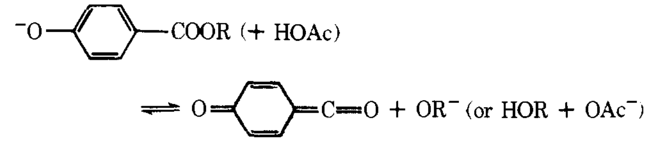
^{a} Average increments (kcal/mol) in enthalpy of activation for related S_N2 reactions (ref 24). ^{b} Calculated from k_{200} using $\Delta H^{\ddagger} = 19\,900 + \Delta\Delta H^{\ddagger}$. ^{c} Reference 24.

an S_N1 mechanism for the compounds studied. This is normal for simple primary and secondary alkyl chlorides and tosylates in aqueous-alcoholic solvents;[25] the nucleophilicity of the molten acetate appears sufficient to cause the much less reactive *p*-hydroxybenzoates to behave similarly.

The observation of incomplete inversion, or partial racemization, is common in the history of displacement reactions. Our molten salt solvolysis may be one more case in which racemization appears to occur as part of the displacement process. Several control experiments provide evidence against racemization by side reactions. 2-Butanol, bubbled into the melt as vapor together with acetic acid in the nitrogen stream, yielded no 2-butyl acetate. This surprising observation, the more so in view of the presence of ketene and acetic anhydride in equilibrium with acetic acid vapor above 268 °C,[26] may be due to the short time the alcohol is in contact with the melt. *trans*-2-Butene gave the same negative result. These potential sources of racemic product are therefore eliminated. Both the substrate **2** and the product, 2-butyl acetate, are optically stable under the reaction conditions.

Formation of a 2-butyl cation *p*-hydroxybenzoate ion pair is a possible racemization mechanism but this postulate should be supported by the relationships of products and rates to the thiocyanate concentration. From the data of Table IV, it can be shown that the observed consumption of thiocyanate ion is much less than would be predicted from its accelerating effect on the solvolyis, $k_N[SCN^-]$. This could be interpreted in terms of an ion-pair mechanism.[27] It would, however, be premature to do so, especially for a methyl substrate, until the product ratio, ROAc/RSCN, is known as a function of substrate structure as well as thiocyanate concentration. The increased potassium ion concentration in the ternary eutectic, due to additional potassium thiocyanate, was shown to have a minimal effect on the rates.

The considerable amount of 2-butanol from **2** and methanol from **1** may be the result of hydrolysis by the 0.11% water present in the solvent which would be equivalent to 12 mol % of the substrate in the results cited in Table I. Since the configuration of the 2-butanol was not determined, it could have been formed either by alkyl- or acyl-oxygen cleavage. The latter type of hydrolysis normally proceeds via a tetrahedral intermediate. But there are two other mechanisms for which we may have predisposing conditions. One, favored by the structure of the substrate, involves a quinone-ketene intermediate (eq 6). This mechanism, including the compounds in



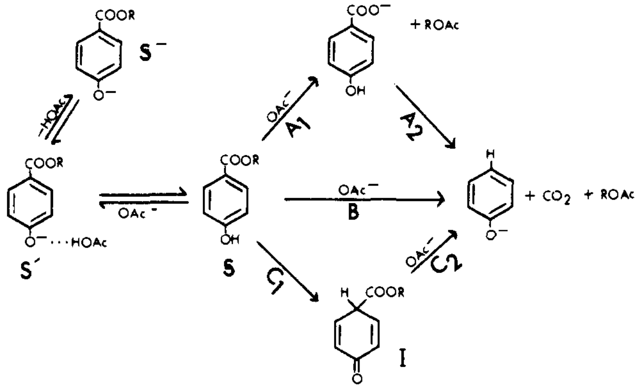
$$^{-}O-C_6H_4-COOR\ (+\ HOAc) \rightleftharpoons O{=}C_6H_4{=}C{=}O + OR^-\ (\text{or } HOR + OAc^-)$$

3

$$3 + H_2O \longrightarrow C_6H_5OH + CO_2 \qquad (6)$$

parentheses, would be acid-catalyzed acylium ion formation $(A_{Ac}2)$[28] except that the negatively charged para substituent gives rise to the neutral ketene **3**. Except for the presence of acetic acid, and the poor solvation of the anion OR^- in the melt, the species in parentheses could be omitted, leaving an E1cB ketene mechanism which is established for some β-keto esters[28] though apparently not for *p*-hydroxybenzoates.[29]

Scheme I

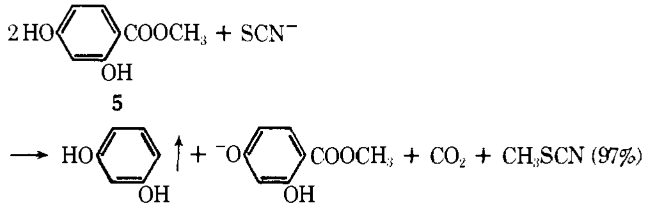


The other acyl-cleavage mechanism, nucleophilic catalysis via the anhydride **4**, would be favored by the high acetate ion and low water concentrations:

$$^{-}OC_6H_4COOR + CH_3COO^- \rightarrow {}^{-}OC_6H_4COOCOCH_3\ (\mathbf{4}) + OR^- \qquad (7)$$

Nucleophilic catalysis by acetate ion has been detected in aqueous solution and anhydrides have been proposed as intermediates and trapped in some hydrolyses.[30] The bimolecular reaction (7) between the two anions would, like the displacement (1), be accelerated by the high ionic strength. Separation of the poor leaving group OR^- might be facilitated by the acetic acid present.

The effect of acid on the reaction rate has some bearing on the mechanism of decarboxylation. In Scheme I, the reactive form of the substrate is assumed to be the un-ionized molecule **S** or the kinetically equivalent complex **S′**, suggested by the solubility and indicator experiments. If the acid content of the solution is depleted by the ring protonation inherent in decarboxylation, a portion of the substrate must be converted to the species S^-, which if unreactive will give rise to the rate equation (3). In our previous study of displacements on methyl 2,4-dihydroxybenzoate in molten Na^+,K^+SCN^-,[11] the sublimation of resorcinol from the reaction mixture (eq 8) together



$$2HO-C_6H_3(OH)-COOCH_3 + SCN^- \ (\mathbf{5}) \longrightarrow HO-C_6H_4-OH\uparrow + {}^{-}O-C_6H_3(OH)-COOCH_3\ (\mathbf{6}) + CO_2 + CH_3SCN\ (97\%) + CH_3NCS\ (3\%) \qquad (8)$$

with the observation that the reaction approached 50% completion with first-order kinetics (eq 3) led to the postulate that the conjugate base **6** of the substrate accumulated, possibly as a precipitate. (Methyl 3,5-dihydroxybenzoate, which does not decarboxylate, approached 100% yield of methyl thiocyanates. The sodium salt of **6** was prepared and proved unreactive.) Provided, however, that acetic acid is not removed after introduction of the substrate as the phenol **S**, no further catalysis is observed with higher acid concentrations (Table II).

The absence of acid catalysis implies that the decarboxylation step A_2, for example, cannot be rate controlling if it includes ring protonation as shown; in path A, therefore, the displacement A_1 is the slow step, and indeed must be since *p*-hydroxybenzoic acid is observed to undergo immediate decarboxylation in the fused salt.

Concerted displacement-decarboxylation-protonation (path B) seems to be ruled out on the same grounds. The reaction is first order in substrate. Only if the proton associated with the para oxygen atom of S or S′ effected the ring protonation could the reaction appear uncatalyzed. Or, if path B were modified to yield the carbanion, $HOC_6H_4^-$, as a transient intermediate which protonated faster than the preceding displacement-decarboxylation, the mechanism would be consistent with the kinetics. In the analogous reaction 8, the absence of any kinetic isotope effect of OD groups in **5**, as well as the nearly equal reactivity of the 2,4- and the 3,5-dihydroxy isomers of **5**, showed that the coupling between the displacement and the decarboxylation, which might be expected for a concerted process, was not detected.

Rate-controlling protonation (path C) is inconsistent with the observed S_N2-type rates. A preequilibrium, $\mathbf{S} \rightleftharpoons \mathbf{I}$, is of course admissible if it is so rapidly established that acid catalysis is superfluous and unobservable. Path A, however, is a more reasonable alternative.

A single experiment (Figure 2, curve D) confirms the assumption that the decrease in rate constant with time in curve A is due to proton depletion. If acetic acid is not introduced with the nitrogen stream until **1** is 35% reacted, the rate of carbon dioxide evolution decreases as the residual acid in the melt is consumed, but then increases when the acid is supplied at the time indicated by the arrow in Figure 1D. The last points in curve D (16 800 and 20 400 s) show an interesting complication: the reaction has produced as much carbon dioxide as though the acetic acid had been continuously present. The respective rate constants, calculated from zero time, are 9.3×10^{-5} and $1.1 \times 10^{-4}\ s^{-1}$. This evidence suggests that, in the absence of acid, an intermediate is being produced which is incapable of forming carbon dioxide in an aprotic medium but evolves the gas more rapidly than the original substrate **1** when an acid is supplied. The displacement product, $^-OC_6H_4COO^-$, would have these properties except that much faster decarboxylation would be expected upon introduction of the acetic acid, even if the anion accumulated as an insoluble salt. Additional work is needed to elucidate the effect of acid and the reason for the success of eq 3.

Experimental Section

General. Infrared spectra were recorded on a Perkin-Elmer 337 grating infrared spectrophotometer. The IR spectra of gas samples were determined after collecting the gas in an evacuated gas cell (10 cm) with NaCl windows. Mass spectra were obtained using a Hitachi Perkin-Elmer RMU-6E spectrometer. NMR spectra at 60 MHz were recorded on a Perkin-Elmer Hitachi R-20 spectrometer. Gas-liquid chromatography analyses and separations were performed on a Varian Aerograph Model A90-P3 instrument utilizing a thermal conductivity detector and one of two columns: 10-ft, 20% SE-30 on 60/80 Chromosorb W or 10-ft 20% Carbowax 20M on 60/80 Chromosorb W. Quantitative GLC analyses were done by the internal standard method, estimating peak areas using a disk integrator and/or cutting and weighing. Thin layer chromatography (TLC) was carried out on 0.25-mm precoated plates of silica gel, F-254 (EM Laboratories, Inc.).

The specific rotations of compounds were determined on a Perkin-Elmer 141 polarimeter with sodium and/or mercury lamps and a 10-cm sample cell. Reported specific rotations are the average of a least three readings of each sample and were reproducible to ±1.0%. Partially racemic compounds are reported in terms of their optical purity (observed rotation/rotation of optically pure compounds).

Kinetic measurements were made using a Colora Ultra-Thermostat HT13-0199 temperature bath filled with Dow Corning 210 H fluid (heat resistant silicone oil, 100 cS). The thermometer was standardized against a NBS-calibrated 99-201 °C total immersion thermometer.

Molten Salt. Anhydrous potassium and sodium acetates were oven dried for 16 h at 120 °C. Weighed quantities of these salts were mixed with lithium acetate dihydrate (Fisher) in mole ratio Li:Na:K: = 32:30:38 and melted at 200 °C and the pressure was gradually reduced to 0.5 Torr in a vacuum oven. Water and acetic acid were evolved. After 30 h, when the rate of acetic acid evolution was less than 0.002 wt %/h, the fused, anhydrous eutectic was cooled and stored in a desiccator. The vacuum drying was repeated immediately before each kinetic run.

The fused acetate showed a water content of 0.10 ± 0.01% (Karl Fisher determination); mp 162 °C; stable (differential thermal analysis) at 180–240 °C; pH of 0.12 M aqueous solution of fused salt 8.0.

The partial pressure of acetic acid as a function of its concentration in the melt was determined by passing dry nitrogen through glacial acetic acid at $t + 5$ °C, then upward through a condenser jacketed with water at a known temperature, t °C. The nitrogen, now saturated with acetic acid at t °C, was led through warmed glass tubing and into the 200 °C melt for 6 h. The resulting solution of acetic acid in Li^+,Na^+,K^+OAc^- was cooled, dissolved in water, and titrated with standard sodium hydroxide solution and phenolphthalein indicator to give the concentrations for Figure 1. The solubility of acetic acid at 760 Torr was determined by adding excess acetic acid to the 200 °C melt, allowing it to distill out until the solution attained constant weight (12 h), and analyzing the residual solution.

The qualitative solubilities given in the results usually refer to solutions of 2% (wt) of solute and 0.1% (wt) of indicators.

Preparation of Methyl (1), Ethyl, Propyl, and Isopropyl *p*-Hydroxybenzoates. The esters were made by Fisher esterification of 0.23 mol of *p*-hydroxybenzoic acid with 1.25 mol of the alcohol, catalyzed by 0.04 mol of concentrated sulfuric acid, and refluxed for 24 h. Excess alcohol and water were removed by distillation, the residual liquid was neutralized using 10% sodium carbonate solution, the precipitate formed was extracted with ether, and the ether was evaporated on a steam bath. The methyl ester **1** was recrystallized from 95% ethanol: mp 128.0 °C (lit. 128,[31] 127.2–129.2 °C);[32] yield 92%. Ethyl ester: 95% yield (water-methanol); mp 115 °C (lit.[31] 115 °C). Propyl ester (benzene): mp 95.5 °C (lit.[31] 96 °C). Isopropyl: 70% yield (benzene-hexane); mp 86.0 °C (lit.[31] 86.1 °C). All esters were homogeneous by TLC and gave rational NMR, IR, and mass spectra.

Preparation of 2-Butyl *p*-Hydroxybenzoate (2). *p*-Hydroxybenzoic acid (30 g, 0.217 mol), 92.5 g (1.25 mol) of 2-butanol (Matheson Coleman and Bell, distilled from type 3A molecular sieve, bp 99.5 °C), and 4 g of concentrated sulfuric acid were refluxed for 24 h in a Dean-Stark apparatus. After removal of excess alcohol and water by distillation, the residual liquid was neutralized with 10% sodium carbonate solution and the organic phase extracted several times with ether. Evaporation left a viscous, yellow oil which was redissolved in ether, dried over anhydrous magnesium sulfate, and again evaporated at 75 °C, and finally under vacuum (0.1 Torr) for 24 h. A light yellow, waxy solid formed which was dissolved in boiling hexane and cooled in ice, precipitating a yellow oil which solidified when seeded, yield 32.8 g (78%), mp 55–58 °C. The ester was further purified by sublimation at 90 °C (0.5 Torr) (white crystals, mp 55–57 °C, TLC two spots) and finally by dry column chromatography[33] on a 2.5-cm diameter Nylon column packed with 56 cm of F-254 absorbent (silica gel Woelm, activity 111/30 mm, 0.5% fluorescent indicator) using 20% (vol) ether in benzene. After developing, the product band was located under a UV lamp, cut out, and eluted with ether. The ester **2** was isolated in 56% overall yield, mp 58–59 °C (lit. 56–58,[34] 55–57 °C,[35] homogeneous by TLC) and gave rational NMR, IR, and mass spectra.

A more efficient esterification was desirable for (+)-2-butanol. Failing to prepare *p*-hydroxybenzoyl chloride,[36] we resorted to protection of the hydroxyl with a benzyl group.[37,38] The detailed synthetic procedure follows.

Preparation of 4-Benzyloxybenzoic Acid. To 69 g (0.5 mol) of *p*-hydroxybenzoic acid (Eastman) dissolved in 500 mL of 95% ethyl alcohol and 500 mL of 2 M sodium hydroxide in a 3000-mL round-bottom flask was added 173 mL (1.5 mol) of benzyl chloride (Mallinckrodt, AR) and the mixture was refluxed. Over a period of 2 h 400 mL of 5 M sodium hydroxide was added dropwise. After heating for an additional 1 h the mixture was distilled until about half the original volume remained. To this was added 1 L of water and the warm aqueous solution was acidified with 3 M hydrochloric acid to precipitate a white, solid product. Recrystallization from 95% ethyl alcohol yielded white, fluffy needles, yield 85.0 g (0.373 mol, 75%), mp

188–190 °C (reported[37] 188 °C).

Preparation of 4-Benzyloxybenzoyl Chloride. To 42.9 g (0.188 mol) of 4-benzyloxybenzoic acid placed in a 500-mL round-bottom flask, fitted with a condenser and protected from the atmosphere with a drying tube filled with Drierite, was added 100 mL (1.38 mol) of thionyl chloride (Matheson Coleman and Bell). With magnetic stirring, this solution was heated slightly until no more gas was given off. Excess thionyl chloride was removed by distillation under reduced pressure. The solid product was recrystallized from high-boiling petroleum ether to give white needles: yield 43.0 g (0.174 mol, 93%); mp 105–106.5 °C (reported[37] 110 °C); TLC (5% by volume ether in benzene) two spots, R_f 0.05 (major) and 0.75 (minor).

Preparation of (+)-2-Butyl 4-Benzyloxybenzoate. 4-Benzyloxybenzoyl chloride (20.8 g, 0.0844 mol, mp 105–106.5 °C) was placed in a two-neck, 100-mL round-bottom flask, fitted with condenser and dropping funnel, and heated to about 145 °C with magnetic stirring. To this was added over a period of 30 min 5.02 g (0.0678 mol) of (+)-2-butanol (Norse Laboratories, Inc.), $[\alpha]^{21}_{D}$ +11.85° (neat) and $[\alpha]^{23}_{D}$ +13.6° (*c* 6.07, ethanol), calculated to be 85.44% optically pure based on[39] $[\alpha]^{20}_{D}$ 13.87° (neat). The temperature was then reduced to 110 °C, and the mixture heated for an additional 2 h. After cooling to room temperature the contents of the flask was mixed with high-boiling petroleum ether and a solid material filtered off (mp 185–190 °C, indicating 4-benzyloxybenzoic acid). The filtrate was placed on a rotary evaporator (bath temperature 75 °C) and the solvent stripped off leaving a dark brown liquid in the flask. This liquid was used without further purification: yield 22.42 g (0.0790 mol, 116%); TLC (5% by volume ether in benzene) four spots, R_f 0.032, 0.17, 0.63 (major), 0.75.

Preparation of (+)-2-Butyl *p*-Hydroxybenzoate (2a). A mixture of 22.42 g (0.0790 mol) of (+)-2-butyl 4-benzyloxybenzoate, 2.0 g of 10% palladium on charcoal (Pfaltz and Bauer, Inc.), and 150 mL of ethanol (absolute) was subjected to a hydrogen pressure of 45 psi for 24 h on a low-pressure reaction apparatus (Parr Instruments Co., Inc.). After this time the theoretical pressure decrease was observed. The palladium-on-charcoal catalyst was filtered and saved. Ethanol and toluene were removed on the rotary evaporator at 60 °C. The remaining liquid was dissolved in ether, dried with anhydrous magnesium sulfate, and filtered with Celite. The pure product was isolated from this ether solution by the same procedure used for racemic 2-butyl *p*-hydroxybenzoate: yield 9.47 g (0.0488 mol, 72% from alcohol); mp 50–56 °C; $[\alpha]^{22}_{D}$ +27.5° (*c* 5, chloroform), from 85.4% optically pure 2-butanol; TLC (20% and 5% by volume ether in benzene) homogeneous.

Preparation of (+)-2-Butyl Acetate. To 5.14 g (0.0655 mol) of acetyl chloride in a 50-mL flask was added dropwise 3.23 g (0.0436 mol) of (+)-2-butanol, 85.1% optically pure. The mixture was then refluxed for 1 h at 119 °C, cooled to room temperature, and neutralized with 10% $NaHCO_3$. The organic layer was separated from the aqueous layer and the 2-butyl acetate distilled: yield 1.73 g (0.0149 mol, 34%); $[\alpha]^{22}_{D}$ +22° (*c* 4.39, ethanol); calculated to be 85% optically pure, based on[39] $[\alpha]^{20}_{D}$ +25.87° (*c* 5.02, ethanol).

Preparation of Dibromobutanes. *meso*-2,3-Dibromobutane was prepared as follows. *trans*-2-Butene (Phillips Pure Grade) was bubbled through 25 mL of 3 M bromine in CCl_4 solution until it turned clear. The CCl_4 was evaporated, leaving a clear liquid, yield 9.5 g, 59%. *dl*-2,3-Dibromobutane was prepared by a similar procedure from *cis*-2-butene, yield 9.9 g, 61%. 1,2-Dibromobutane was prepared from 1-butene, yield 9.8 g, 60%.

Reactions of Alkyl *p*-Hydroxybenzoates with Fused Acetate Melt. About 15 g of the dried fused acetate was melted and poured into the reaction vessel, a Pyrex tube 20 × 370 mm, which was heated to 200 °C, slowly evacuated to 0.1 Torr, and dried for 20 h. The weighed substrate ester (5–10 mmol) was added to the fused salt through a long funnel and stirred with a glass rod until dissolved (120 s required for **1**, 200 s for **2**). The reaction vessel was then connected to the nitrogen train. Ultrapure nitrogen passed through columns containing 3A and 4A molecular sieves and into the reaction vessel, under the surface of the fused salt solution. The gas, now containing volatile reaction products, was led through two U-tubes immersed in dry ice-trichloroethylene and one filled with Drierite. This treatment removed from the nitrogen stream all compounds except carbon dioxide, which was absorbed and weighed in a U-tube filled with Ascarite followed by Drierite. A two-way stopcock diverted the gases to a second U-tube while the first was weighed. Preceding each kinetic run, nitrogen gas was passed through each Ascarite U-tube until they attained constant weight. After the ester substrate was added the Ascarite U-tubes, weighed alternately, measured the amount of carbon dioxide evolved per unit time. The reaction could be followed in the presence of acetic acid by bubbling the nitrogen gas through glacial acetic acid at 24 °C immediately before the reaction vessel. Control experiments demonstrated that the eluent nitrogen gas contained neither carbon dioxide nor acetic acid.

Reaction Product Analysis. Qualitative identification of the liquid products isolated in the U-tube cold traps was accomplished by preparative GLC using the SE-30 and/or the Carbowax columns. These products had IR, NMR, and mass spectra identical with those of authentic samples.

The quantitative analysis of 2-butyl acetate and 2-butanol from **2** was accomplished by GLC using the internal standard (2-ethyl-1-butanol) method.

The gaseous products not condensed in a −77 °C cold trap were identified by comparing their IR spectra to those of authentic samples.

The quantitative analysis of butenes from the reaction of **2** involved the addition of bromine to the alkenes, forming the dibromo addition products which were analyzed by GLC. A typical run was made using liquid nitrogen in the cold trap and helium as the flow gas. After the reaction was completed the helium flow was directed through the U-tube, still in liquid nitrogen, and bubbled through 6 mL of a 3 M bromine in CCl_4 solution (at 50 °C) via a fritted glass disk bubbling tube. The butenes were slowly and quantitatively transferred to the bromine solution by successively placing the U-tube, with reaction products, into cold baths of −77, 0, and 24 °C. Ethylene was passed through the bromine solution to destroy unreacted bromine and the dibromobutanes produced were quantitatively analyzed by GLC on the SE-30 column using ethyl benzoate as internal standard. Control experiments demonstrated that at least 96% of a known amount of *cis*- or *trans*-2-butene could be recovered as the 2,3-dibromobutane products.

Products not sufficiently volatile to be flushed out of the reaction vessel into the cold trap during a run were identified by extracting an aqueous solution of the cooled reaction mixture with ether and analyzing by TLC and preparative GLC. All fractions were identified by comparing their IR, NMR, and mass spectra with those of authenic samples.

Reaction of Butene with Acetic Acid in Fused Acetate Melt. A gas mixture of 2-butene and nitrogen saturated with acetic acid was bubbled through 10 g of dried fused acetate melt at 246 °C for 4 h. Analysis of the volatile products collected in the cold traps by GC gave negative results for 2-butyl acetate.

Reaction of 2-Butanol with Fused Acetate Melt. Nitrogen bubbled through a 50% (vol) mixture of acetic acid and 2-butanol was passed through 10 g of dried fused acetate melt for 5.5 h. Analysis of the volatile products collected in the cold trap by GC gave negative results for 2-butyl acetate.

Stereoselectivity of Synthesis of 2a. A mixture of 1.016 g (5.23 mmol) of (+)-2-butyl *p*-hydroxybenzoate ($[\alpha]^{22}_{D}$ +27.5° (*c* 5, $CHCl_3$)) and 20 mL (40 mmol) of 2 M sodium hydroxide was refluxed for 4 h. The mixture was extracted four times with ether (5 mL) and the ethereal extract was dried ($MgSO_4$), concentrated, and purified by preparative GLC giving 0.152 g (2.05 mmol) of (+)-2-butanol, $[\alpha]^{23}_{D}$ +13.7° (*c* 5.33, C_2H_5OH). 2-Butanol originally used to synthesize **2a:** $[\alpha]^{23}_{D}$ +13.6° (*c* 6.07, C_2H_5OH).

Optical Stability of 2a and 2-Butyl Acetate in Fused Acetate Melt. **2a** (0.679 g, 3.50 mmol) was added to 11.5 g of dried fused acetate in the reaction vessel at 246 °C and nitrogen saturated with acetic acid (24 °C) was passed through for 1.25 h representing 37% reaction completion (CO_2 adsorption). The reaction mixture was cooled, dissolved in water, and extracted eight times with ether (5 mL). The ethereal extract was dried ($MgSO_4$) and concentrated. **2a** was isolated as in its synthesis: $[\alpha]^{23}_{D}$ +30.6° (*c* 4.33, $CHCl_3$), average of duplicate runs.

(+)-2-Butyl acetate, 1.02 g (0.008 80 mol), $[\alpha]^{22}_{D}$ +22° (*c* 4.39, ethanol), 85% optically pure, was carried as vapor in the nitrogen stream into 17.7 g of dried fused acetate melt at 200 °C. The volatile products were collected in a cold trap and the 2-butyl acetate was isolated by GC: yield 0.545 g (0.004 69 mol); $[\alpha]^{22}_{D}$ +22° (c 3.84, ethanol); 85% optically pure.

Reaction of 2 with Fused Acetate and KSCN Melt. The reaction procedure was the same with KSCN added as without it. KSCN (Mallinckrodt, AR) was oven dried at 110 °C for 1 h and stored in a desiccator. For each run the KSCN was weighed, added to the dried fused acetate melt in the reaction vessel, stirred until dissolved, and vacuum dried at 200 °C for 1 h. **1** was added to the reaction vessel and the reaction followed in the normal way.

Stability of KSCN in Fused Acetate Melt. KSCN (0.321 g, 3.31 mmol) and 4.03 g (48.6 mmol) of fused acetate melt were mixed in a test tube and heated for 2.5 h at 200 °C. The physical appearance changed from clear to very light yellow. The mixture was dissolved in water and the amount of KSCN was found to be 0.320 g (3.29 mmol) by the Volhard method. This represents only a 0.5% loss of KSCN.

Density of Melts at 200 °C. A 25-mL volumetric flask was weighed, filled with dried molten KSCN at 200 °C, and reweighed. The density of KSCN at 200 °C is 1.59 g/mL; of the acetate eutectic, 1.39 g/mL.

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Patterns of Carbon-13 Chemical Shift Response to Substituent Effects in Arylcarbenium Ions. The 2-Furyl, 2-Thienyl, 2-Benzofuryl, and 2-Benzothienyl Systems[1]

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Abstract: The response of ^{13}C chemical shifts at the ring positions in arylcarbenium ions to changes in substituents at the carbenium center is examined by plotting the chemical shifts vs. the chemical shifts at the para position in phenylcarbenium ions. In a previous study of hydrocarbon arylcarbenium ions, the slope of the response for a particular position was shown to be related to the amount of positive charge developed at that position. For heteroarylcarbenium ions, linear responses are also found, and these appear to at least qualitatively reflect the charge distribution patterns in the cations. However, the correlation of response slopes with calculated charge densities exhibits some obviously deviant points. The unusually high sensitivity of the C_5 position in thiophene is discussed in relation to calculated charges, nonadditivity of substituent chemical shifts in para-disubstituted benzenes, and other experimental probes of charge distribution.

Introduction

In an earlier paper, we demonstrated that there is a systematic dependence of arene carbon chemical shifts on the electronic effects of carbenium-type substituents.[3] The systematic dependence is demonstrated for each position in an aryl group by determining the carbon chemical shift response, which is defined by plotting the ^{13}C chemical shifts in arylcarbenium ions vs. the ^{13}C chemical shifts at the para position in the analogous phenylcarbenium ions. For the hydrocarbon systems studied previously, the slope of the response was shown to be related to the charge distribution in the arylcarbenium

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