

Solvolyse of Ferrocenylmethyl and α -Ferrocenylethyl Acetates: A Y_{OAc} Solvent Ionizing Power Scale

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Received July 28, 1992

The solvolysis of ferrocenylmethyl acetate has been studied in 2,2,2-trifluoroethanol (TFE)-ethanol mixtures and in aqueous ethanol, acetone, and TFE; a Y_{OAc} solvent ionizing power scale is developed. For 19 solvents, a fair correlation with Y_{OTs} values is obtained (slope of 0.88 ± 0.08 , correlation coefficient of 0.930); lateral dispersion is observed between excellent acetone-water, ethanol-water, and TFE-ethanol plots. In aqueous ethanol, the product partitioning is almost identical to that previously observed for benzhydryl derivatives. The developed Y_{OAc} scale is used to correlate the specific rates of solvolysis of triphenylmethyl and α -ferrocenylethyl acetates. Previous studies of acetolyses and formolyses of acetate and benzoate esters are discussed.

Acetate esters (CH_3COOR) tend to react via bimolecular reaction at the acyl carbon ($B_{AC}2$ or $A_{AC}2$ mechanism).^{2,3} However, when the R group gives a very stable carbocation, it is possible to observe alkyl-oxygen fission ($B_{AL}1$ or $A_{AL}1$ mechanism). The $B_{AL}1$ mechanism can be considered as one type of S_N1 mechanism, with a carboxylate leaving group.

Solvolyse of carboxylic acid esters are subject to an extremely powerful catalysis by added mineral acids. Indeed, Stimson has shown that, for hydrochloric acid catalyzed solvolyses of carboxylic acid esters of *tert*-butyl alcohol⁴ and benzhydryl,⁵ plots of specific rates of solvolysis in aqueous acetone against $[HCl]$ give negligible intercepts. Even in the presence of alkyl groups which form relatively stable carbocations (*tert*-butyl or benzhydryl), alkyl-oxygen fission was not assured and, for acid-catalyzed solvolyses in aqueous acetone, it was proposed that benzoate esters solvolyse by the $A_{AL}1$ mechanism, formate esters by the $A_{AC}2$ mechanism, and acetate esters by a combination of these two pathways.^{4c,5} These suggestions, based on kinetic studies, are strongly supported for acetate esters by product studies using ^{18}O -labeled water. It was found⁶ that *tert*-butyl acetate solvolyse under acid conditions in 70% aqueous dioxane at 25 °C with only about 36% alkyl-oxygen bond fission and predominantly with acyl-oxygen bond fission.

Insertion of a third carbocation-stabilizing α -phenyl group into benzhydryl acetate leads to the triphenylmethyl (trityl) acetate, and this has been shown⁷ to solvolyse in either aqueous dioxane or methanol almost entirely by alkyl-oxygen bond fission. In aqueous dioxane, under neutral conditions, ^{18}O tracer studies indicated 94-96% alkyl-oxygen bond fission. In methanol, an 82% yield of ether was isolated, giving a minimum value for alkyl-oxygen bond fission. In 80% dioxane at 65 °C, a strong catalysis by sulfuric acid was observed, but initially added

0.03 M acetic acid had a negligible kinetic effect. Studies of solvent variation in the neutral solvolysis of trityl acetate^{8,9} indicated a general tendency for faster solvolyses in solvents of higher ionizing power, consistent with an S_N1 ($B_{AL}1$) mechanism.

The high tendencies for acid catalysis in the alkyl-oxygen bond fission and for competition from acyl-oxygen bond fission (even with the possibility of the formation of a relatively stable carbocation) are, in part, a reflection of the very poor leaving group ability of an acetate anion.¹⁰ The trifluoroacetate is a much better leaving group,¹¹⁻¹³ but even so, the benzhydryl ester was shown by tracer and kinetic studies to solvolyse in neutral solution by a combination of $B_{AC}2$ and $B_{AL}1$ mechanisms.¹¹

To establish a scale of solvent ionizing power for an acetate leaving group (Y_{OAc}), for use within the Grunwald-Winstein equation (eq 1),¹⁴ it is necessary to study an

$$\log(k/k_0) = mY_{OAc} \quad (1)$$

ester which will lead to a very stable carbocation, so as to give the required $B_{AL}1(S_N1)$ reaction. In eq 1, k and k_0 are the specific rates of solvolysis of a given substrate (preferably an acetate or closely related ester) in a given solvent and in 80% ethanol, respectively, and m in the sensitivity of the specific rates of solvolysis toward changes in solvent ionizing power.

One possible standard system is afforded by solvolyses of trityl acetate.⁷⁻⁹ However, it has been claimed^{15,16} that the presence of even one α -aryl group leads to effects due

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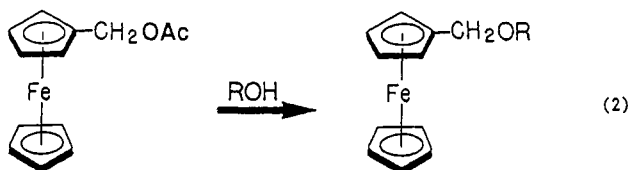
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to differential solvation of the aromatic ring at the ground and transition states of the S_N1 reaction. It has been suggested¹⁷ that, when the Grunwald-Winstein equation is being used to aid in assigning mechanism, these effects are usually small enough to be ignored. However, the presence of three aromatic rings should probably, if possible, be avoided.

An alternative is to use esters which, upon operation of the $B_{AL}1$ mechanism for solvolysis, will lead to a very stable α -metallocenylcarbenium ion.¹⁸ For example, the relatively high stability of ferrocenylcarbinyl cations^{18,19} is reflected in their isolation as stable salts,^{20,21} the ease of solvolysis of neutral precursors in solvents of reasonably high ionizing power,²²⁻²⁵ and the observation of appreciable secondary kinetic deuterium isotope effects in solvolysis reactions of ferrocenylmethyl carboxylates.²⁵⁻²⁷ An ionization-dissociation pathway for the solvolysis is supported by detailed studies of common-ion rate depressions for α -ferrocenylethyl acetate²⁴ and the observation of both common-ion rate depressions and special salt effects for ferrocenylmethyl carboxylates.²⁵⁻²⁷

The precise mechanism by which the ferrocenyl group releases electrons is controversial. Both direct participation by iron electrons^{18,22,28} and conjugation with the π electrons of the pentadienyl ring systems²⁹ have been proposed;³⁰ indeed, it has been suggested that, dependent on the nature of the leaving group and the solvent, either type of pathway can operate during solvolysis.^{26,27}

In the present investigation, the detailed mode of carbocation stabilization is not addressed; we have chosen to study the solvolysis of ferrocenylmethyl acetate (eq 2)



because the high stability of the incipient carbocation leads to a solvolysis mechanism involving predominantly, if not entirely, the $B_{AL}1$ pathway,^{3,24,26} thus allowing the use of the specific rates of solvolysis within eq 1 (with the m value set at unity) to establish a Y_{OAc} scale of solvent ionizing power. The scale developed is then used to correlate previously reported^{8,9} data for trityl acetate solvolysis (trityl acetate solvolyzes in 80.7% acetone at 30 °C about 1.6 times faster than ferrocenylmethyl acetate^{22,24}) and to correlate primarily^{22,24} new data reported for α -ferrocenylethyl acetate solvolysis.

The product distribution obtained in aqueous ethanol

Table I. Specific Rates of Solvolysis of Ferrocenylmethyl Acetate (k), at 25.0 °C, and Derived Solvent Ionizing Power (Y_{OAc}) Values

solvent ^a	$10^6 k, ^b s^{-1}$	Y_{OAc}^c	Y_{OTs}^d
100% EtOH	0.635 ± 0.049	-1.33	-1.75
96% EtOH	1.95 ± 0.01 ^e	-0.84	
90% EtOH	4.82 ± 0.21	-0.45	-0.58
80% EtOH	13.6 ± 0.5	0.00	0.00
70% EtOH	29.4 ± 1.1	0.33	0.47
60% EtOH	60.6 ± 2.3	0.65	0.92
90% acetone	0.118 ± 0.007	-2.06	-1.70
80% acetone	0.863 ± 0.048 ^f	-1.20	-0.79
70% acetone	3.77 ± 0.23	-0.56	0.07
60% acetone	12.7 ± 0.8	-0.03	0.66
50% acetone	37.3 ± 1.7	0.44	1.26
100% TFE	642 ± 51	1.67	1.77
97% TFE	965 ± 47 ^g	1.85	1.83
90% TFE	806 ± 58 ^h	1.77	1.90
80% TFE	451 ± 15 ^h	1.52	1.96
70% TFE	493 ± 26	1.56	2.00
80T-20E	518 ± 25	1.58	0.98
60T-40E	85.5 ± 2.4	0.80	0.21
40T-60E	17.0 ± 1.0	0.10	-0.44
20T-80E	3.20 ± 0.07	-0.63	-1.18

^a Mixed solvents are prepared on a volume-volume basis, except for the aqueous TFE solvents, which are on a weight-weight basis. ^b With associated standard deviation; $FcCH_2OAc$ concentration of ca. 0.006 M. ^c Calculated according to eq 2. ^d From ref 14, some values adjusted as indicated in ref 36. ^e From ref 26. ^f A value of $1.60 \times 10^{-5} s^{-1}$ has been reported at 30 °C in 80.7% acetone (refs 22 and 24).^g In the presence of 0.0060 M AcOH, a value of $738 (\pm 33) \times 10^{-5} s^{-1}$ was obtained. ^h Substrate was dissolved in 0.5 mL of acetone and 20 mL of the indicated solvent added (solvent contains 2.4% acetone).

is found to be similar to that previously reported for corresponding solvolyses of benzhydryl derivatives.³¹⁻³³

Results

Solvolysis of Ferrocenylmethyl Acetate ($FcCH_2OAc$). The specific rates of solvolysis of ferrocenylmethyl acetate have been obtained, at 25.0 °C, in 100–60% aqueous ethanol (five compositions), 90–50% aqueous acetone (five compositions), 100–70% (by weight) aqueous 2,2,2-trifluoroethanol (TFE) (five compositions), and in TFE-ethanol mixtures (four compositions). These values, together with a literature value²⁶ for 96% aqueous ethanol, are reported in Table I. Also in Table I are reported the derived values for a solvent ionizing power scale^{14,34} for an acetate leaving group, based on ferrocenylmethyl acetate solvolysis (Y_{OAc}). For comparison, Y_{OTs} values previously obtained in a similar manner but based on the specific rates of solvolysis of 2-adamantyl *p*-toluenesulfonate^{14,35,36} are also listed in Table I.

In 80% ethanol and 97% TFE, measurements were also made at three other temperatures and the specific rates of solvolysis and the enthalpies and entropies of activation (calculated using these data plus data from Table I) are presented in Table II.

Solvolysis of α -Ferrocenylethyl Acetate ($FcCH_2CH_2OAc$). The specific rates of solvolysis of α -ferrocenylethyl acetate, at 25.0 °C, have been measured in ethanol, 80% ethanol, and three TFE-ethanol composi-

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Table II. Specific Rates of Solvolysis of Ferrocenylmethyl Acetate at Temperatures Other than 25.0 °C and Enthalpies (ΔH^\ddagger) and Entropies (ΔS^\ddagger) of Activation

solvent	temp, °C	$10^5 k, \text{ s}^{-1}$	$\Delta H_{298}^{\ddagger}, \text{ kcal/mol}$	$\Delta S_{298}^{\ddagger}, \text{ cal/mol}^\circ\text{K}$
80% EtOH ^e	34.3	27.5 ± 1.5		
80% EtOH ^e	50.2	87.5 ± 4.1		
80% EtOH ^e	62.9	285 ± 9	15.2 ± 0.2	-25.3 ± 0.8
97% TFE/ ^f	-6.8	48.8 ± 2.5		
97% TFE/ ^f	3.5	170 ± 4		
97% TFE/ ^f	13.6	372 ± 14	14.0 ± 0.2	-20.8 ± 0.7

^a With associated standard deviation; FcCH₂OAc concentration of ca. 0.006 M. ^b Calculated using also the specific rates at 25.0 °C (from Table I). ^c Units of kcal/mol. ^d Units of cal mol⁻¹ K⁻¹. ^e Volume to volume at 25.0 °C. ^f Weight to weight.

Table III. Specific Rates of Solvolysis (k) of α -Ferrocenylethyl Acetate

solvent ^a	temp, °C	$10^5 k, \text{ s}^{-1}$	$\log(k/k_0)^c$
100% EtOH	25.0	9.73 ± 0.70	-1.18
80% EtOH	25.0	148 ± 5	0.00
20T-80E	25.0	44.3 ± 3.2	-0.52
40T-60E	25.0	193 ± 10	0.12
60T-40E	25.0	1180 ± 58	0.90
80.7% acetone	25.0	9.93^d	-1.17 ^e
80% EtOH	-2.2	9.9 ± 0.5	0.00
60T-40E	-1.7	55.0 ± 3.7	0.72 ^f
80T-20E	-1.7	436 ± 23	1.62 ^f

^a Mixed solvents are prepared on a volume-volume basis at 25.0 °C. ^b With associated standard deviation; FcCH₂CH₂OAc concentration of ca. 0.006 M. ^c Where k_0 is the specific rate of solvolysis in 80% ethanol. ^d Obtained by interpolation (Arrhenius equation) within literature data (ref 24) for four other temperatures. ^e Interpolation within data of Table I leads to a corresponding Y_{OAc} value of -1.27. ^f Based on interpolated specific rate of solvolysis in 80% ethanol at -1.7 °C of $10.5 \times 10^{-5} \text{ s}^{-1}$.

tions. These values, together with an interpolated value (using the Arrhenius equation) from a study²² of the solvolysis in 80.7% acetone at four other temperatures, are presented in Table III. Values at ca. -2 °C for the specific rates of solvolysis in 80% ethanol and two TFE-ethanol compositions are also presented.

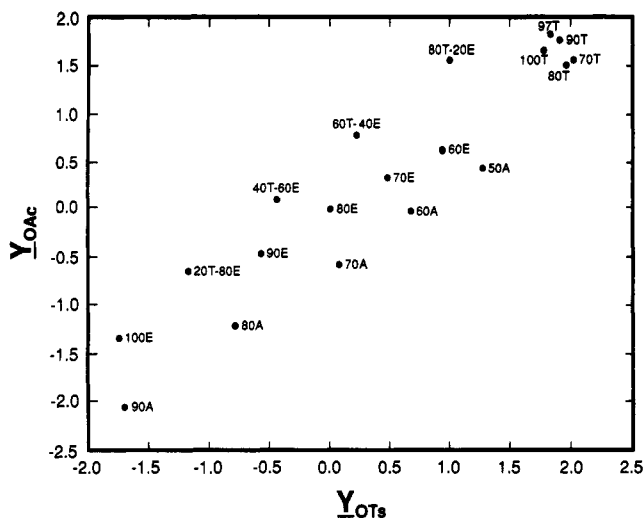
Product Study in Aqueous Ethanol. The reaction of 0.0031 M FcCH₂OAc in 60% ethanol-40% water (by volume) at 25.0 °C was allowed to proceed for in excess of 10 half-lives. Analysis by GC-MS indicated the formation of two products, which were identified as FcCH₂OH (47%) and FcCH₂OCH₂CH₃ (53%). This corresponds to a selectivity (S), defined by eq 3, of 0.36.

$$S = \frac{[\text{FcCH}_2\text{OH}][\text{EtOH}]}{[\text{FcCH}_2\text{OEt}][\text{H}_2\text{O}]} \quad (3)$$

Discussion

Consideration of the Y_{OAc} Scale. Several neutral solvolyses of acetate esters R'COOR, involving R groups which give highly stable carbocations, have been shown to proceed, at least primarily, via the B_{AL}1 (S_N1) mechanism.^{7-9,22-24,26} In aqueous-organic solvents, these solvolyses are subject to a powerful catalysis by added mineral acid but, highly relevant to the present study, autocatalysis by formed acetic acid has not been observed.⁷ In the present study, we similarly find no evidence for autocatalysis in solvolyses of ferrocenylmethyl and α -ferrocenylethyl acetates and no rate increase upon addition of acetic acid to a solvolysis of ferrocenylmethyl acetate in 97% TFE (Table I).

The Y_{OAc} values based on ferrocenylmethyl acetate give only a fair correlation ($r = 0.930$) against the Y_{OTs} values^{14,35,36} also reported in Table I. Inspection of Figure

**Figure 1.** Plot of Y_{OAc} against Y_{OTs} for solvolyses in aqueous ethanol (E), aqueous acetone (A), aqueous 2,2,2-trifluoroethanol (T), and T-E mixtures.**Table IV. Correlation^a of the Specific Rates of Solvolysis of Ferrocenylmethyl Acetate, at 25.0 °C, Against Y_{OTs} or Y_{BnOTs} Values**

solvents	scale	n^b	m	c	r^c
All ^d	Y _{OTs}	19	0.88 ± 0.08	-0.03 ± 0.44	0.930
TFE-EtOH ^e	Y _{OTs}	5	1.06 ± 0.02	0.56 ± 0.04	0.9995
EtOH-H ₂ O ^{d,f}	Y _{OTs}	5	0.74 ± 0.01	-0.02 ± 0.02	0.9998
acetone-H ₂ O	Y _{OTs}	5	0.84 ± 0.02	-0.60 ± 0.05	0.9992
All ^d	Y _{BnOTs}	19	0.91 ± 0.04	-0.15 ± 0.24	0.980
TFE-EtOH ^e	Y _{BnOTs}	5	1.10 ± 0.03	0.10 ± 0.06	0.9991
EtOH-H ₂ O ^{d,f}	Y _{BnOTs}	5	0.94 ± 0.06	-0.08 ± 0.09	0.9946
acetone-H ₂ O	Y _{BnOTs}	5	0.88 ± 0.03	-0.38 ± 0.06	0.9987

^a Using eq 1 with Y_{OTs} values from Table I and Y_{BnOTs} values from ref 16c (plus interpolated Y_{BnOTs} values of 2.11 for 90% TFE and -0.70 for 20TFE-80EtOH). The m and c values are reported with associated standard errors. ^b Number of solvents (data from Table I). ^c Correlation coefficient. ^d Excluding 96% ethanol (no Y_{OTs} value). ^e The four TFE-EtOH mixtures and 100% EtOH. ^f The four aqueous ethanol mixtures and 100% EtOH.

1 shows a dispersion into separate plots for aqueous acetone, aqueous ethanol, and TFE-ethanol mixtures, together with (as expected) a bunching together of the aqueous-TFE points. The overall Grunwald-Winstein correlation and three subcorrelations are reported in Table IV. For all 19 solvents, the slope (m value) of 0.88 is consistent with an ionization mechanism. Excellent correlations ($r > 0.999$) are obtained for the three separate plots mentioned above, again with the magnitude of the slopes being consistent with an ionization mechanism. The detailed nature of the dispersions is not consistent with them arising from a sensitivity toward solvent nucleophilicity. For example, the points corresponding to solvolyses in aqueous acetone mixtures of moderate nucleophilicity lie below those for solvolyses in TFE-ethanol mixtures of similar Y value but lower solvent nucleophilicity. Indeed, a treatment in terms of the extended Grunwald-Winstein equation^{33,37} (eq 4) gives

$$\log(k/k_0) = lN_T + mY_{OTs} + c \quad (4)$$

essentially no improvement in correlation, with values for l of -0.17 ± 0.13 , for m of 0.74 ± 0.14 , and for c of -0.15 ± 0.43 , and with the correlation coefficient improved only to a value of 0.937 from the value of 0.930 obtained using

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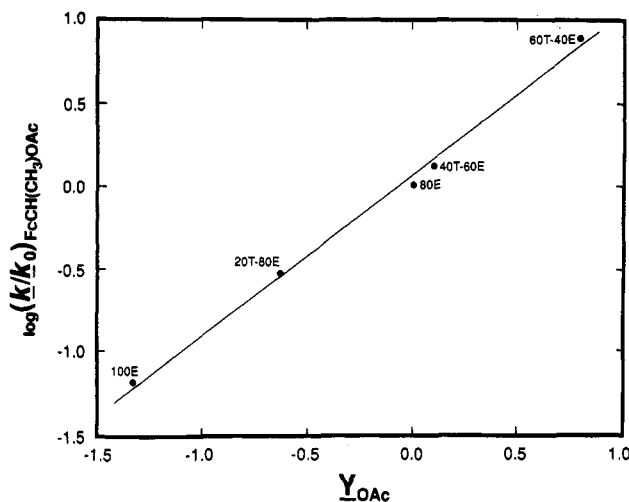


Figure 2. Plot of $\log(k/k_0)$ for α -ferrocenylethyl acetate solvolysis, at 25.0 °C, against Y_{OAc} values.

the simple (one-term) equation (eq 1). In eq 4, the symbols are defined as in eq 1, plus l is the sensitivity of the specific rates of solvolysis to changes in solvent nucleophilicity (using the N_T scale³⁸). If the influence of the ferrocenyl group does involve participation by electrons associated with the iron atom, then these will interact at the rear of the α -carbon³⁹ (internal S_N2 -type reaction) and the most favorable route for nucleophilic assistance by the solvent, either by covalent attachment or solvation, will be blocked.

Within Table I, a Y_{OAc} value is also included for solvolysis in 96% ethanol.²⁶ No corresponding Y_{OTs} value is available, but the value is reasonable with respect to Y_{OAc} values for 100 and 90% ethanol.

Recently, Y_{BnX} scales have been developed¹⁶ for the correlation of the specific rates of solvolysis of benzylic derivatives, based on the use as the standard substrate of 2-adamantyl derivatives which also carry a 2-aryl substituent. A Y_{BnOTs} scale is available^{16c} for use when a *p*-toluenesulfonate, or a similar leaving group, is in a benzylic position. Since the solvolyses of ferrocenylmethyl acetate (eq 2) can be considered to be related to benzylic solvolyses, we have investigated the extent to which correlations are improved by substitution of Y_{BnOTs} for Y_{OTs} . A plot of Y_{OAc} against Y_{BnOTs} (equivalent to Figure 1) shows an identical dispersion pattern but with the extent of dispersion reduced. This is illustrated by a comparison of the entries within Table IV for use of either Y_{OTs} or Y_{BnOTs} . For all 19 solvents, the slopes (m values) are identical but the reduced dispersion leads to a better correlation coefficient with use of Y_{BnOTs} . Similarly, the intercepts (c values) for the individual TFE-ethanol and aqueous acetone plots are reduced when Y_{BnOTs} values are used; however, the correlation coefficients are now marginally better with Y_{OTs} values.

When Y_{BnOTs} values replace Y_{OTs} values within the two-term equation (eq 4), values are obtained for l of 0.04 ± 0.08 , for m of 0.94 ± 0.08 , and for c of -0.12 ± 0.24 , and the correlation coefficient of 0.981 is essentially unchanged from the value obtained when the $\log(k/k_0)$ values are correlated against only Y_{BnOTs} . One can conclude that Y_{BnOTs} does give somewhat improved correlations but, consistent with the opinions expressed in a recent review,¹⁷ no additional mechanistic insight is gained over that obtained by use of the more generally applicable Y_{OTs} scale.

The study of the effect of temperature variation on the specific rates (Table II) leads to quite large negative entropies of activation; appreciably negative values have been observed previously in neutral solvolyses of ferrocenylmethyl acetate,²⁶ α -ferrocenylethyl acetate,²⁴ and trityl acetate²⁴ in aqueous solvents.

Correlation of the Rates of Solvolysis of Trityl and α -Ferrocenylethyl Acetates. The $\log(k/k_0)$ values for neutral solvolysis of trityl acetate in 80 and 60% ethanol and 80 and 50% acetone have been reported.⁸ A correlation against Y_{OTs} values^{14,35,36} leads to a slope of 0.86 ± 0.35 and an intercept of -0.52 ± 0.58 ($r = 0.862$); the correlation is much improved when Y_{OAc} values (Table I) are substituted for the Y_{OTs} values: slope of 1.11 ± 0.12 and intercept of -0.18 ± 0.18 ($r = 0.988$). The good correlation with a slope of close to unity supports the S_N1 assignment for ferrocenylmethyl acetate solvolyses.

An excellent correlation against Y_{OAc} values is obtained using our data for α -ferrocenylethyl acetate solvolysis. It has previously been shown²² that the introduction of an α -methyl group into ferrocenylmethyl acetate leads to only a 10-fold increase in the rate of solvolysis (in 80% acetone). Presumably, most of the dispersion of positive charge is into the ferrocenyl system, and introduction of the α -methyl group provides only a minor route for further charge dispersion. Consistent with this viewpoint, a correlation of $\log(k/k_0)$ for five solvolyses of α -ferrocenylethyl acetate at 25.0 °C (Table III) leads to a slope (m value) of essentially unity: slope of 0.96 ± 0.04 and intercept of 0.07 ± 0.06 ($r = 0.998$). A value at 25.0 °C, obtained by interpolation within data at other temperatures for solvolysis in 80.7% acetone,²⁴ can be used in conjunction with a Y_{OAc} value obtained by interpolation within data for other solvent compositions. This additional point lies on the correlation line for the five solvent systems of the present investigation. A new correlation with all six solvent compositions leads to essentially unchanged values for the slope and intercept: slope of 0.96 ± 0.03 and intercept of 0.07 ± 0.05 ($r = 0.998$).

Also in Table III are presented three specific rates at -1.7 °C. Consistent with the excellent correlation against Y_{OAc} values at 25 °C, with a slope of essentially unity and a very small intercept, the $\log(k/k_0)$ value for solvolysis in 60% TFE-40% ethanol of 0.72 is in good agreement with the Y_{OAc} value of 0.80 (Table I). Similarly, the $\log(k/k_0)$ value for solvolysis in 80% TFE-20% ethanol (not studied at 25 °C) of 1.62 is virtually identical to the Y_{OAc} value of 1.58.

The S_N1 Solvolyses of Carboxylate Esters in Acetic and Formic Acids. A kinetic study of an achiral acetate ester in acetic acid requires isotopic labeling, and such a study has been carried out previously for the acetolysis of trityl acetate. The acetolysis was found⁹ to give a $\log(k/k_0)$ value of +1.18, which can be compared to a Y_{OTs} value of -0.9. Earlier, we demonstrated that a Grunwald-Winstein plot of the specific rates of solvolysis of trityl acetate⁹ in four aqueous-organic solvents against Y_{OTs} values gave a slope of 0.86 and intercept of -0.52; on this basis a $\log(k/k_0)$ value of -1.29 would be predicted for solvolysis in acetic acid, such that the measured specific rate is about 300 times higher than the predicted value. One possible explanation, consistent with the powerful catalysis by mineral acid to solvolyses in aqueous-organic solvents,⁷ is that the actual reactant in acetic acid is not the neutral trityl acetate but an equilibrium concentration of the faster reacting protonated species. Promotion of

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the ionization of *p*-chlorobenzhydryl acetate in acetic acid by electrophilic involvement of a specific solvent molecule has been suggested previously.⁴⁰

Available data for the solvolyses of benzoate esters can be used to arrive at secondary Y_{OAc} values. Due to the close similarity between the leaving groups, values based on benzoate would be expected to be a reliable substitute; support comes from the observation that the solvent ionizing power scale based on methanesulfonate as leaving group is virtually identical to the *p*-toluenesulfonate scale.^{14,41,42} In 96% ethanol at 25 °C, the ferrocenylmethyl benzoate reacts about twice as fast as the acetate ester.²⁶

The acetolysis of ferrocenylmethyl benzoate proceeds 15 times faster than the solvolysis in 96% ethanol,²⁷ a solvent with a Y_{OAc} value of -0.84 (Table I), allowing one to estimate a Y_{OAc} value of +0.35 for acetic acid. Similarly, one can estimate a Y_{OAc} value of +0.17 for formic acid.²⁵ The Y_{OAc} value for acetic acid is considerably higher than other Y_x values, which range from -0.8 for a methanesulfonate leaving group to -2.2 for an iodide leaving group.¹⁴ It is, however, also appreciably less than the value of 1.18 obtained⁹ as log (*k*/*k*₀) for trityl acetate acetolysis. It has been suggested⁴³ that *k*₀^{ext} values (return from solvent-separated ion pairs prevented) are better suited for use as acetolysis values within the Grunwald-Winstein equation. Recently, the *k*₀^{ext} value for acetolysis was found to better fit the correlation line based on other solvents than the regular titrimetric rate coefficient (*k*_t) in a study of the solvolysis of cholesteryl *p*-toluenesulfonate.⁴⁴ A special salt effect is also found^{25,27} in the acetolysis (*k*₀^{ext}/*k*_t value of 5.1) and formolysis (*k*₀^{ext}/*k*_t value of 2.4) of ferrocenylmethyl benzoate, leading to alternative Y_{OAc} values of 1.06 for acetolysis and 0.55 for formolysis. The revised value for acetic acid is now in excellent agreement with the log (*k*/*k*₀) value for acetolysis of trityl acetate.

The report²⁵ of the study of both acetolysis and formolysis of ferrocenylmethyl benzoate mentions several unusual features, including a smaller kinetic isotope effect in the more ionizing formic acid, surprisingly low preexponential ratios (*A*_H/*A*_D), and unusual variation of some of the kinetic isotope effects upon addition of lithium perchlorate. However, the most unusual feature is, in our opinion, the observation of lower solvolysis rates in formic acid than in acetic acid, reflected in turn in the calculated secondary Y_{OAc} values. The Y_x values for acetic and formic acids listed in a recent review¹⁴ show Y_x values for formic acid to be uniformly considerably greater than those for acetic acid, with differences ranging from 3.2 units for a trifluoromethanesulfonate leaving group to 4.8 units for a chloride leaving group; these differences are very far removed from the value of -0.2 (or adjusted value of -0.5) which we have estimated based on the recent report.

The close similarity in reaction rates could be nicely rationalized by reaction being of the protonated ester. It has been shown that the rates of S_N1 solvolyses with a neutral leaving group are virtually insensitive to changes in solvent ionizing power.⁴⁵ Unfortunately, a new problem arises on this basis in that the formolysis rates are actually lower than one would anticipate based on the other

available Y_x values for this solvent, and it is difficult to visualize that the protonated species would react in S_N1 reactions at a lower rate than the original substrate.

Product Study. The selectivity of 0.36 in 60% ethanol indicates a modest preference for product formation involving attack by ethanol rather than water. This is consistent with capture of an unencumbered highly reactive carbocation. The kinetic similarity to the solvolyses of benzhydryl derivatives, especially with regard to common ion rate depression, is consistent with both ferrocenylmethyl and benzhydryl carbocations being captured at the free-ion stage. The similarity extends also to selectivities, with essentially identical values to that obtained for ferrocenylmethyl acetate being reported for solvolysis of benzhydryl derivatives in 60% ethanol at 25 °C: benzhydryl chloride (0.31 and 0.33),^{31,32} the benzhydryldimethylsulfonium ion (0.40),³³ and benzhydryl *p*-nitrobenzoate (0.30, at 100 °C).³²

Experimental Section

Materials. Ferrocenylmethyl acetate^{22,26} was prepared by treatment of the alcohol with acetyl chloride and triethylamine in methylene chloride. The alcohol was prepared from (*N,N*-dimethylamino)methylferrocene (Tokyo Kasei) or (ferrocenylmethyl)trimethylammonium iodide (Tokyo Kasei), following the procedure of Lindsay and Hauser.⁴⁶ To allow the materials used in the kinetic and product studies to be of fairly recent origin, several small-scale preparations were performed.

The α -ferrocenylethyl acetate^{22,24,47} was prepared similarly from the alcohol, which was obtained by lithium aluminum hydride reduction of acetylferrocene (Tokyo Kasei).⁴⁷

The purification of 2,2,2-trifluoroethanol was using a previously reported procedure.⁴⁸ Other solvents were purified as described previously.⁴⁹

Kinetic Procedures.²⁴ A substrate concentration of ca. 6 × 10⁻³ M was used. The required amount of acetate ester was transferred to 25 mL of the solvent under investigation, maintained in a constant temperature water bath. After a brief period for temperature reequilibration, 2-mL portions were removed at suitable time intervals. Infinity titers were taken after at least 10 half-lives. The portions were added to 10 mL of ice-cold 85% acetone, containing phenol red as indicator, and titrated against a standardized (ca. 0.0025 M) sodium hydroxide solution. Prior to its use, nitrogen was bubbled through the 85% acetone for about 10 min. Calculation of the first-order rate coefficients was as previously described.⁵⁰

Product Study. A 3 × 10⁻³ M solution of ferrocenylmethyl acetate in 60% ethanol was allowed to react at 25.0 °C for 4 h, and the products were analyzed by a GC-MS technique. A Hewlett-Packard Model 5995 instrument with a 0.25-mm × 15-m fused silica capillary SPB-1 column, with temperature programming, was used for the analysis.

Acknowledgment. The authors wish to thank Dr. Malcolm J. D'Souza for technical assistance and valuable suggestions. D.N.K. thanks Professor R. Gompper, Institut für Organische Chemie der Universität München, for hospitality during the time that this paper was being prepared. In addition, A.R.P. would like to thank the National Science Foundation for, in part, making his sabbatical leave at Northern Illinois University possible.

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