Gas-phase Reactions of F^- with Phenyl Acetates. Translational Energy and Substituent Effects on Product Distribution

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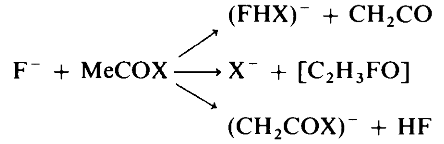
The gas-phase ion/molecule reactions of F^- with $MeCO_2C_6H_4Y$ (Y = H, *o*-, *m*-, *p*-Me, *p*-MeO, *p*-F, *p*-Cl) has been studied by Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry and is shown to yield two main products, $YC_6H_4O^-(HF)$ and $YC_6H_4O^-$. The solvated ion is the most abundant product except for the *p*-Cl compound which reacts to give almost equal abundances of the two ions. The contribution of the free phenoxide ion increases significantly with increasing translational energy of the reactant F^- ion. The strong translational energy dependence of the product distribution, and its invariance upon deuterium substitution in the methyl group, suggest that both products originate primarily from a common elimination mechanism. The trend in the product-ion distribution is consistent with the observation that formation of the free $YC_6H_4O^-$ ions from the intermediate complex is favoured by dynamical reasons when the internal energy is sufficient to overcome the endothermicity of the process. The product distributions also show a correlation with the overall free energy changes.

The elucidation of the intrinsic reactivity of simple chemical systems has been an underlying motivation in the study of gas-phase ion/molecule reactions that bear formal resemblance to solution processes. Remarkable differences may arise in the gas phase as a consequence of two primary reasons: (*i*) the absence of a solvent and solvation effects leads to pronounced changes in the energetic [illegible] *i*) the attractive potential generated by the ion-dipole and ion-induced dipole interaction can be sufficient to overcome local energy barriers of reactions resulting in very large rate constants. The gas phase ion/molecule reactions of simple anions such as OH^-, MeO^-, F^-, with organic substrates represent an eloquent illustration of the diversity between solution and gas-phase reactivity.[1,2]

It is now well accepted that ionic gas phase reactions are characterized by energy hypersurfaces that can feature several minima lying below the energy of the reactants. These minima correspond either to ion–dipole complexes or to species more akin to true chemical intermediates.[3,4] Reactions in these systems are often envisioned to proceed initially through these long-lived complexes by a process modelled from the classical dynamics of ion/neutral collisions averaged over the rotationally modulated orientation of the molecule.[5,6] The evolution of these collision complexes, or intermediates, towards the final products is then considered to be the result of a delicate interplay between three main components: (*a*) the energy content of the intermediates; (*b*) the energy barriers for the different channels; and (*c*) the geometry of the transition state through which these species must traverse along the reaction coordinate.[7] This latter factor associated with the entropy of activation of this step has been recognized to determine the reaction efficiency of some S_N2 reactions,[8] and slow proton transfer reactions.[9]

Present experimental methods are still limited to studying ionic reactions that proceed with efficiencies ($k_{reaction}/k_{collision}$) higher than 10^{-3}. Thus, reactions to occur under thermal or near thermal conditions are required to be exothermic or nearly thermoneutral. Thermochemistry has been frequently used, therefore, as a strong and definitive criterion to establish and rationalize reaction pathways in the gas phase. Few cases have been observed where endothermic reactions (8–12 kJ mol^{-1}) are rendered exoergic at 298 K by sizeable positive entropy changes for the overall process.[10]

A general scheme to account for the main ion/molecule reactions involving F^- and several derivatives of acetic acid, MeCOX [X = halogen, OAr, SR, OC(O)Me] has recently been proposed.[11]



$$F^- + MeCOX \longrightarrow (FHX)^- + CH_2CO \quad (1)$$
$$F^- + MeCOX \longrightarrow X^- + [C_2H_3FO] \quad (2)$$
$$F^- + MeCOX \longrightarrow (CH_2COX)^- + HF \quad (3)$$

The main reaction channel for most cases, reaction (1), provides an efficient and convenient way of generating gas-phase solvated fluoride ions for kinetic and thermodynamic studies. The proposed model emphasized the likelihood of a common mechanism for these reactions mediated by the F^- partial abstraction of an α-proton in the ester. The ensuing process could then yield the ions $(FHX)^-$, $(CH_2COX)^-$, X^- or even CH_2CFO^- (observed for the alkyl esters of acetic acid),[12] with the outcome dictated by the relative stability of these species. By comparison, products (X^- and neutral) resulting from a formal nucleophilic displacement at the carbonyl centre, or at the saturated carbon centre, were argued to correspond to minor channels. This approach is in line with the available experimental data that suggests that gas-phase elimination reactions in simple esters can be more facile than displacement reactions due to a favourable entropy of activation.[13,14]

The present paper reports a detailed study of the reactions between F^- and substituted phenyl acetates ($MeCO_2Ar$) under the low-pressure conditions characteristic of the FT-ICR method. The product-ion distribution in these systems is shown to be highly sensitive to substituents in the aromatic ring and to the translational energy of the reactant F^- ion. While the nature of the neutral product(s) of reaction (2) cannot be established unequivocally in these experiments, the above behaviour coupled to the absence of an isotope effect in the relative rate constants suggests that reaction (2) proceeds primarily by an elimination mechanism. The trend for these reactions typifies the strong influence of the translational energy of the reactant ion on the outcome of endothermic ion/molecule reactions. Furthermore, the results reveal a correlation between the product distributions and the changes in the overall free energy

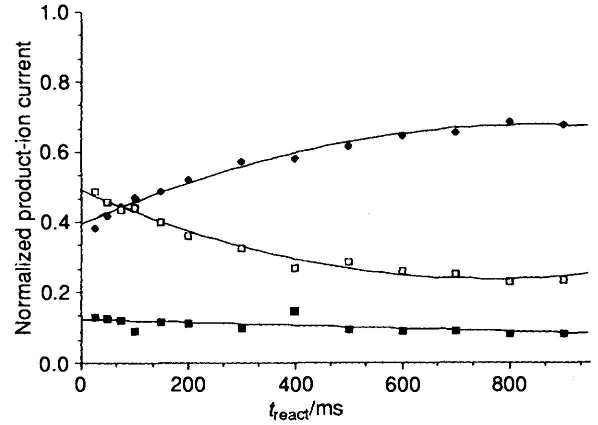


Fig. 1 Normalized product-ion distribution for the reaction of F^- with phenyl acetate as a function of time. The F^- ions were isolated immediately after ion formation: □, PhO^-; ◆, $PhO^-(HF)$; ■, $(CH_2CO_2Ph)^-$.

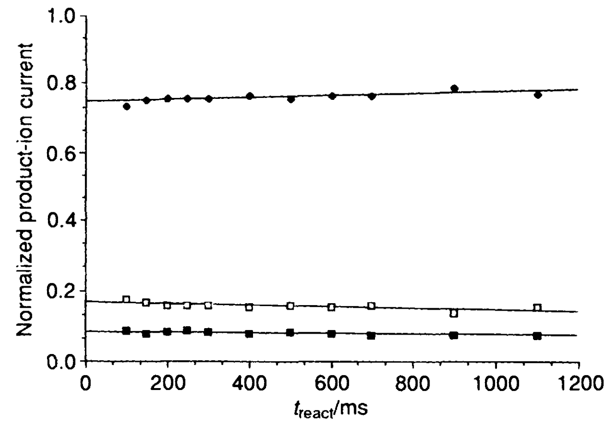


Fig. 2 Normalized product-ion distribution for the reaction of F^- with phenyl acetate as a function of time. The F^- ions were selected 800 ms after ion formation: □, PhO^-; ◆, $PhO^-(HF)$; ■, $(CH_2CO_2Ph)^-$.

of the processes that bears resemblance to the arguments invoked in discussions of systems under thermal equilibrium.

Experimental

Experiments were carried out with an FT-ICR mass spectrometer designed and constructed at the University of Amsterdam.[15] The instrument was operated at a fixed magnetic field strength of 1.23 T. Fluoride ions were generated from CF_4 by dissociative electron attachment[16] at 6 eV. Ion selection was achieved either by using the notch-ejection technique,[17] or by using sweep-out radio frequency, rf, pulses to remove all other unwanted ions.[18] This latter method was considered to be more reliable to avoid any additional translational excitation of the F^- ions.

The CF_4 compound was used in excess as an ion buffer gas, since the product ion distributions proved to be sensitive to the translational energy of the reactant F^- ion. Typical experiments were carried out at ester partial pressures of 2×10^{-5} Pa (uncorrected ionization gauge reading) and adding CF_4 to a total pressure of 8×10^{-5} Pa. Considerable difficulty was experienced in maintaining a constant pressure for the esters owing to their low volatility and their possible condensation on the metal walls. Thus, the effective pressures of the esters are considered to be poorly defined in most of the experiments precluding determinations of absolute reaction rate constants. A constant product-ion distribution was observed only in experiments where the reacting F^- ions were isolated 800 ms after ion formation. The chosen partial pressures and delay time were considered to yield data representative of translationally relaxed F^- ions. The temperature of the trapping plate of the cell on the filament side was measured to be 343 K. The filament current was kept at the lowest possible value compatible with a reasonable signal strength of the F^- ion to avoid pyrolysis of the acetates. A small amount of $(HC_2O)^-$ ions (less than 5% of the total product-ion current) was observed in most of the experiments indicating a minor extent of pyrolysis at the filament.

Relative rate constants were determined from relative abundances obtained by deconvolution of the measured mass spectra against the excitation spectrum. The translational energy dependence of the relative rate constants was determined by using an 0.08 V single rf pulse of variable length of time and measuring the relative intensities at reaction times between 200 and 400 ms.

The phenyl acetates were prepared from the corresponding phenol and acetic anhydride and purified according to standard procedures. Analysis by GC–MS showed no detectable impurities. The phenyl $[^2H_3]$acetate and the *p*-F-phenyl $[^2H_3]$-acetate were prepared in a similar fashion from 99% $[^2H_6]$acetic anhydride and purified by preparative GC prior to use.

Results and Discussion

The gas-phase reaction of F^- with the different phenyl acetates, $MeCO_2Ar$, (Ar = C_6H_4Y, and Y = H, *p*-CH_3, *o*-CH_3, *m*-CH_3, *p*-OCH_3, *p*-F, *p*-Cl) gives rise to three product ions, eqns. (4)–(6). The proton abstraction reaction (6) is always a minor channel amounting to less than 10% of the final product distribution.

$$\longrightarrow (FHOAr)^- + CH_2CO \qquad (4)$$

$$F^- + MeCO_2Ar \longrightarrow ArO^- + \text{neutral product(s)} \qquad (5)$$

$$\longrightarrow (CH_2CO_2Ar)^- + HF \qquad (6)$$

The time evolution of the product ion distribution in $MeCO_2Ph$ is shown in Fig. 1 for the case where selection of F^- occurs immediately after ionization. These trapped-ion plots reveal an unusual variation in branching ratio for the products that has also been observed in previous experiments carried out at much higher pressures in a drift-cell ICR mass spectrometer.[19] It is known that the dissociative electron attachment to CF_4 yields F^- ions with different amounts of translational excitation.[16] Since the PhO^- ion is unreactive towards the ester, the results in Fig. 1 suggest that excess translational energy of the reactant F^- ions significantly affects the product distribution of reactions (4)–(6).

A completely different situation is observed when the same experiment is carried out with the F^- ions selected 800 ms after ion formation (Fig. 2). The invariable product distribution now observed is indicative that this delay time is sufficient for collisions translationally to relax the F^- ions to a constant kinetic-energy distribution without complete depletion of these

Table 1 Product-ion distribution in the reaction of F^- with $MeCO_2Ar$[a]

	$ArO^-[H(^2H)F]$	ArO^-	$[CH_2(^2H_2)CO_2Ar]^-$
$MeCO_2Ph$	0.76	0.16	0.08
$C^2H_3CO_2Ph$	0.76	0.17	0.07
$MeCO_2$-*p*-FC_6H_4	0.67	0.27	0.06
$C^2H_3CO_2$-*p*-FC_6H_4	0.68	0.26	0.06
$MeCO_2$-*p*-ClC_6H_4	0.49	0.49	0.02

[a] The F^- ions were isolated with a delay of 800 ms: see the text.

Table 2 Relative rate constants, k_4/k_5, for the different substrates[a]

$MeCO_2Ph$	4.7 ± 0.35	$C^2H_3CO_2Ph$	4.5 ± 0.35
$MeCO_2$-*p*-MeC_6H_4	5.0 ± 0.35	$MeCO_2$-*o*-MeC_6H_4	3.8 ± 0.30
$MeCO_2$-*m*-MeC_6H_4	3.9 ± 0.30	$MeCO_2$-*p*-$MeOC_6H_4$	3.3 ± 0.25
$MeCO_2$-*p*-FC_6H_4	$2.5_0 \pm 0.14$	$C^2H_3CO_2$-*p*-FC_6H_4	$2.6_5 \pm 0.15$
$MeCO_2$-*p*-ClC_6H_4	0.94 ± 0.05		

[a] Isolation of the F^- ions with a delay of 800 ms. The quoted uncertainties refer to the standard deviation of 3-5 experiments performed over a period of several months.

Table 3 Dependence of k_4/k_5 on the translational energy of the F^- ions[a]

Duration of the rf pulse (t_{irr}/ms)	$MeCO_2Ph$	$C^2H_3CO_2Ph$	$MeCO_2$-*p*-FC_6H_4	$C^2H_3CO_2$-*p*-FC_6H_4
0	4.5	4.5	2.5	2.9
0.25	2.8	2.6	1.4	1.9
0.35	2.0	2.3	1.3	1.5
0.50	1.6	2.1	1.1	1.3

[a] The F^- ions were isolated with a delay of 800 ms. The approximate kinetic energy of the F^- ions is estimated to be 1.6 eV (t_{irr} = 0.5 ms), 0.8 eV (t_{irr} = 0.35 ms), and 0.4 eV (t_{irr} = 0.25 ms). The relative rate constants given for 0 ms refer to the specific experiment and not to an average value as listed in Table 2. The apparent variation of isotope effect with translational energy is not statistically significant as these results are based on a limited number of experiments.

ions by reaction with the ester. Measurements of the product distribution obtained under the second set of conditions (800 ms delay time) are listed in Table 1 for a few selected cases. Since the proton abstraction (6) is a minor channel, only relative rate constants are listed in Table 2 for reactions (4) and (5).

The effect of the translational energy of the F^- ions can be further demonstrated by monitoring the relative rate constant ratio as the relaxed F^- ions are accelerated to higher translational energies by short rf pulses at their cyclotron frequency. The results listed in Table 3 establish that reaction (5) can be driven by translational energy either directly or *via* fragmentation of the solvated ion.

The trend observed for the relative rate constants of reactions (4) and (5) as a function of substituent in the aromatic ring (Table 2) requires examination of the thermochemistry, the possible neutral products of reaction (5), and the likely mechanisms. For phenyl acetate the following alternatives can be considered.*

(1) Solvation-mediated elimination

$$F^- + MeCO_2Ph \longrightarrow PhO^-(HF) + CH_2CO \quad (7)$$
$$\Delta H^\circ = -(37 \pm 16\ \text{kJ mol}^{-1})$$

(2) Three alternatives can be postulated for the equivalent of reaction (5)

Elimination

$$F^- + MeCO_2Ph \longrightarrow PhO^- + CH_2CO + HF \quad (8)$$
$$\Delta H^\circ = (43 \pm 16\ \text{kJ mol}^{-1})$$

Addition–elimination at the carbonyl group

$$F^- + MeCO_2Ph \longrightarrow PhO^- + MeCFO \quad (9)$$
$$\Delta H^\circ = -(80 \pm 16\ \text{kJ mol}^{-1})$$

S_N2 Displacement

$$F^- + MeCO_2Ph \longrightarrow PhO^- + MeF + CO \quad (10)$$
$$\Delta H^\circ \approx 6\ \text{kJ mol}^{-1}$$

Substitution in the phenyl ring may be expected to modify the exothermicity of reaction (4). While the heats of formation of the $ArO^-(HF)$ species have not been measured, rough estimates can be obtained from the acidity of the ArOH compounds[20,24,25] and the known dissociation energy of F^-(HOPh) according to the approximate correlation suggested by McMahon[21] for fluoride binding energies in alcohols, and more recently by Kebarle[22] for the other halide ions with a large number of phenols. These estimates place the exothermicity of reaction (4) at 66 kJ mol^{-1} for Y = *p*-F and 80 kJ mol^{-1} for Y = *p*-Cl. Thus, formation of the solvated ion [reaction (4)] becomes more exothermic as the free phenoxide ion [reaction (5)] becomes more pronounced in the product-ion distribution (see Table 2).

The enthalpy changes of the possible reactions leading to the free phenoxide ions for the methyl substituted compounds are close to the values for phenyl acetate.* The elimination reaction and the S_N2 substitution are more endothermic with 13 kJ mol^{-1} for Y = *p*-OCH_3 than for Y = H while the addition reaction is estimated to be less exothermic with 13 kJ mol^{-1} for the methoxy-substituted compound than for phenyl acetate. The formation of the free phenoxide ion becomes more favourable from a thermochemical point of view for Y = *p*-F and *p*-Cl as can be seen by a comparison between the ΔH° values for reactions (8)–(10) (Y = H) and for reactions (11)–(13) (Y = *p*-F and *p*-Cl).

Elimination

$$F^- + MeCO_2Ar \longrightarrow ArO^- + CH_2CO + HF \quad (11)$$
$$Ar = p\text{-}FC_6H_4\ \Delta H^\circ \approx 29\ \text{kJ mol}^{-1}$$
$$Ar = p\text{-}ClC_6H_4\ \Delta H^\circ \approx -12\ \text{kJ mol}^{-1}$$

Addition–elimination at the carbonyl

$$F^- + MeCO_2Ar \longrightarrow ArO^- + MeCFO \quad (12)$$
$$Ar = p\text{-}FC_6H_4\ \Delta H^\circ \approx -94\ \text{kJ mol}^{-1}$$
$$Ar = p\text{-}ClC_6H_4\ \Delta H^\circ \approx -136\ \text{kJ mol}^{-1}$$

S_N2 Displacement

$$F^- + MeCO_2Ar \longrightarrow ArO^- + MeF + CO \quad (13)$$
$$Ar = p\text{-}FC_6H_4\ \Delta H^\circ \approx -8\ \text{kJ mol}^{-1}$$
$$Ar = p\text{-}ClC_6H_4\ \Delta H^\circ \approx -49\ \text{kJ mol}^{-1}$$

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* The enthalpy changes of the reactions are estimated on the basis of data in refs. 20–23.

The estimates of the reaction enthalpies indicate that the large variation in the product-ion distribution (Table 2) cannot easily be explained on thermochemical grounds if the competition is between reaction (4) and addition–elimination at the carbonyl leading to free phenoxide ions since both of these processes are more exothermic for the *p*-F and *p*-Cl compounds than for Y = H.

The kinetic isotope effects on these reactions also help to elucidate the possible mechanism and dynamics of these processes. The results shown in Table 2 reveal that for phenyl acetate the product distribution is essentially invariant to deuterium substitution at the α-position, $[(k_4/k_5)_H]/[(k_4/k_5)_D] = (1.06 \pm 1.14)$, similar to the observation for Y = F, where this ratio amounts to (0.94 ± 0.11). Given the experimental error associated with the reproducibility of the measurements of these ratios, it can be concluded that reactions (4) and (5) display essentially the same isotope effect. It can then be inferred that similar mechanisms are likely to account for reactions (4) and (5), or at least that the transition state responsible for determining the outcome of the two reactions must be similar with regard to the abstraction of the α-proton in the collision complex. Earlier examples of base promoted solvation reactions in esters[13,26] have shown that these reactions are subject to a significant isotope effect. By comparison, addition–elimination at carbonyl functions as well as S_N2 displacement reactions in the gas phase are expected to display very feeble secondary isotope effects, if any at all. Thus, in the case of competing elimination and addition–elimination/S_N2, introduction of deuterium atoms at the methyl group would lower the rate of the former reaction and increase the importance of the other possible channels and as a result lead to an increase in the relative abundance of the free phenoxide ion, in contrast with observation. In conclusion, the isotopic results are inconsistent with any significant contribution from addition–elimination and S_N2 substitution in the formation of the ArO^- ions for Y = H and F and possibly also for the other phenyl acetates studied.

The mechanism, energetics and isotope effect of gas-phase elimination type reactions in ethers,[27–29] sulfides,[30] and alkyl halides[31] have been the subject of some recent discussions. In the case of Et_2O, reactions promoted by a strong base such as OH^- result in the formation of the solvated ion, $EtO^-(H_2O)$, and free EtO^-, exclusively by elimination mechanisms that nevertheless display different isotope effects. The isotope effect for these reactions has been used to model these processes along the transition-state spectrum proposed for elimination reactions in solution.[32] Likewise, the difference in magnitude of the isotope effect encountered for the two channels has been interpreted as a result of stereoelectronic effects due to *syn*- and *anti*-processes, respectively. The present results for phenyl acetates and in particular the absence of an isotope effect on the product-ion distributions preclude any conclusions as to the geometry of the transition state(s) for the rate-determining step(s) in the process leading to the solvated and unsolvated phenoxide ions.

Aside from isolated thermochemical arguments that favour the addition–elimination at the carbonyl position for the formation of phenoxide ions [reaction (9)], the overall evidence strongly argues that this is not the case. Short of identifying the actual neutral products of reaction (5), a formidable and challenging task in gas-phase ion chemistry,[33] the growth of the channel leading to $YC_6H_4O^-$ as a function of substituent, the dependence of the product-ion distribution on the translational energy of the F^- ion and the absence of an isotope effect point to reactions (4) and (5) proceeding by a common elimination mechanism. Owing to the inherent limitations on the actual identification of the neutral products, it is of course not possible to rule out completely minor participation from addition–elimination at the carbonyl group or even an S_N2 displacement in the reaction leading to the free phenoxide ions.

The above arguments are consistent with the mechanism previously proposed[11] in which the efficiency of these reactions is determined by the initial α-proton abstraction leading to a $[HF + CH_2CO + ArO^-]$ complex (Scheme 1). The product distribution will then be determined (*i*) by the internal energy content of the $[HF + CH_2CO + ArO^-]$ complex if the free phenoxide is generated by decomposition of the $ArO^-(HF)$ ion, and (*ii*) by the geometry of the transition states for the exit channels if the complex reacts by competing pathways (see Scheme 1).

$$\begin{aligned} F^- + MeCO_2Ar &\longrightarrow [HF + CH_2CO + ArO^-]^* \\ &\xrightarrow{-CH_2CO} ArO^-(HF) \longrightarrow ArO^- + HF \\ &\longrightarrow ArO^-(HF) + CH_2CO \end{aligned}$$

$$\begin{aligned} F^- + MeCO_2Ar &\longrightarrow [HF + CH_2CO + ArO^-]^* \\ &\longrightarrow ArO^- + HF + CH_2CO \end{aligned}$$

Scheme 1 Proposed pathways leading to the formation of the $ArO^-(HF)$ and ArO^- ions

A rigorous description of the dynamics of these reactions is not possible because of their chemical complexity, the inability to determine rate constants and the approximate values of the quoted thermochemistry. The increasing contribution of the ArO^- ion as a function of the substituent and the translational energy of the F^- ions, however, can be qualitatively accommodated by Scheme 1. For Y = H, the fraction of F^- ions with a kinetic energy above 43 kJ mol^{-1} can cause free phenoxide ions to be formed by the elimination reaction. Under these conditions, the $PhO^-(HF)$ product ion can have sufficient internal energy to promote dissociation provided that the reaction proceeds through the first pathway in Scheme 1. On the other hand, partition of the products along the second pathway in Scheme 1 would be expected to favour formation of $PhO^- + HF$ over formation of the $PhO^-(HF)$ ion, as the internal energy of the $[FH + CH_2CO + PhO^-]$ complex rises above the threshold. This is a result of the larger density of rotational and translational energy states in the transition state for the reaction leading directly to the free phenoxide ion compared with the transition state for the formation of the $PhO^-(HF)$ ion.

The effect of the F^- ion translational energy on the product-ion distribution is particularly pronounced for phenyl acetate. With this substrate, unrelaxed F^- ions react to generate approximately equal amounts of the solvated and the unsolvated ions (see Fig. 1, reaction time *ca.* 100 ms), whereas the F^- ions isolated after a delay of 800 ms react to form nearly five times as much of the solvated ion than of the free phenoxide ion (Table 2). By comparison, the F^- ions react initially with the *p*-Cl compound to give a ratio of the abundances of the solvated and unsolvated ions of about 0.6 at 200 ms which becomes 0.94 after the F^- ions are isolated with a delay of 800 ms (Table 2). In the latter case the formation of the free phenoxide by elimination is associated with a favourable enthalpy change [reaction (11)] and the sampling of F^- ions with a higher translational energy does not significantly alter the product distribution.

While the product distributions can be rationalized on a microscopic scale, it is notable that the results also correlate with the trends which would be expected for systems studied under thermal equilibrium and on the basis of linear free-energy relationships. The free-energy changes for these systems can be calculated from the entropy changes obtained from tabulated values[20,23] and an estimate for the entropy of $MeCO_2Ph$ based on the group-additivity methods.[23] The calculated value amounts to 136 ± 12 J mol^{-1} K^{-1} for the ΔS° of reaction (8) at 298 K. This entropy change should be roughly constant for the same type of reaction within the series involving the different phenyl acetates. The resulting free-energy changes, ΔG° at 298 K, for reaction (14) can then be readily calculated for a few cases of interest.

$$\mathrm{F^- + MeCO_2Ar \longrightarrow ArO^- + CH_2CO + HF} \quad (14)$$

$$\begin{array}{ll} \mathrm{Ar = Ph} & \Delta G^\circ(298\ \mathrm{K}) = 2\ \mathrm{kJ\ mol^{-1}} \\ \mathrm{Ar} = p\text{-}\mathrm{FC_6H_4} & \Delta G^\circ(298\ \mathrm{K}) = -12\ \mathrm{kJ\ mol^{-1}} \\ \mathrm{Ar} = p\text{-}\mathrm{ClC_6H_4} & \Delta G^\circ(298\ \mathrm{K}) = -53\ \mathrm{kJ\ mol^{-1}} \end{array}$$

The main emphasis of this paper has been to show the preference of a base-induced elimination reaction over addition–elimination at the carbonyl or displacement at the Me group regardless of the energetically preferred pathway. The present data is unable to establish to what extent these other channels do contribute to the overall reactivity of the system, but they must be of minor importance. The slow displacement at the carbonyl position is particularly intriguing and one that deserves further investigation in light of the extensive studies dedicated to these systems in recent years.[14,34–40]

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