Correlation of the rates of solvolysis of phenyl chloroformate†

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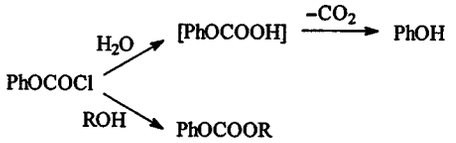
The specific rates of solvolysis of phenyl chloroformate in 21 solvents can be very well correlated using the extended Grunwald–Winstein equation, with incorporation of the N_T solvent nucleophilicity scale and the Y_{Cl} solvent ionizing scale, with sensitivities towards changes in the scale having values of 1.68 ± 0.10 and 0.57 ± 0.06, respectively. This is a solvolysis which, on the basis of several other types of evidence, is believed to follow an addition–elimination pathway with addition being rate-determining (or possibly an enforced concerted variant), and these sensitivities can be considered to be representative values for chloroformate esters following such a pathway.

Phenyl chloroformate hydrolyzes in water to give phenol, and it undergoes alcoholysis to give the alkyl phenyl carbonate[1–3] [eqn. (1)]. The kinetics of these processes can be conveniently

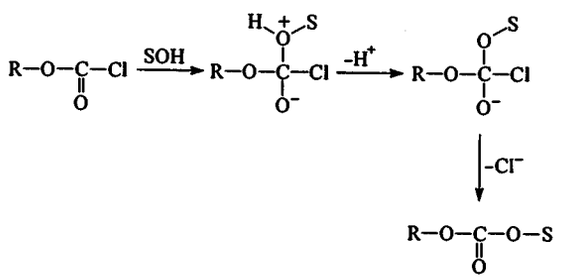


(1)

followed in terms of the hydrochloric acid which is produced in both pathways, in the present study using a titration technique and previously using conductivity measurements.[3–7] Spectroscopic determination of the phenol product has also been employed.[8]

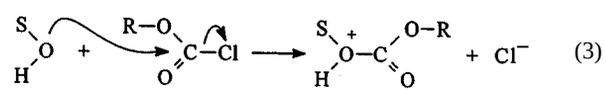
Because of the ground-state stabilization present in chloroformate esters,[1,2,6,7,9] the solvolyses of the chloroformates are considerably slower than those of simple acyl chlorides (RCOCl). Within the solvolyses of chloroformates, those of phenyl chloroformate are faster than those of primary alkyl chloroformates,[7] because the electron-withdrawing influence of the phenyl group counteracts the ground-state resonance stabilization. This effect is also reflected in a lower dipole moment for the phenyl chloroformate.[10]

For alkyl chloroformate esters (ROCOCl) both unimolecular and bimolecular pathways have been observed. The tertiary 1-adamantyl chloroformate solvolyzes by a unimolecular pathway, which also involves loss of carbon dioxide.[11] Stereochemical and kinetic evidence exists for carboxylium ion ($ROCO^+$) formation in the hydrolyses of secondary alkyl chloroformates.[7,12,13] Methyl and ethyl chloroformates are believed to solvolyze by the unimolecular pathway in moist formic acid but by a bimolecular pathway in a range of less ionizing solvents.[7,12,14–16] The bimolecular pathway has usually been considered to proceed *via* a tetrahedral intermediate [eqn. (2) or a



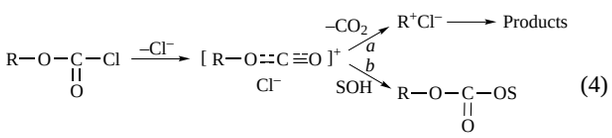
(2)

closely related variant] within an addition–elimination mechanism, but a direct displacement (S_N2) mechanism[17] has also been proposed [eqn. (3)].[9a,15]



(3)

The unimolecular pathway involves an intermediate carboxylium ion which, when R^+ is a relatively stable carbenium ion, can lose carbon dioxide [eqn. (4)] prior to product formation.



(4)

Queen[7] considered the hydrolysis of phenyl chloroformate to proceed by the addition–elimination bimolecular pathway, and this viewpoint was subsequently supported for solvolyses in both aqueous acetone[6] and ethanol.[18] Recently, a direct displacement bimolecular pathway has been suggested for solvolyses in methanol–acetonitrile mixtures;[3] this pathway differs, however, from the Kivinen concept of an S_N2-type mechanism[2,9a,15] in that the initial attack is believed to resemble that leading to the addition–elimination mechanism. However, the reaction was considered to be concerted, due to the belief that the tetrahedral intermediate had an insignificant lifetime.[19] A direct pathway of this type would be expected to show in kinetic investigations most of the characteristics of an addition–elimination process, including general-base catalysis by a second molecule of solvent.[20]

That the mechanism for phenyl chloroformate solvolysis, despite several studies, is not firmly established is suggested by the observation that a study involving solvolyses in aqueous dioxane and aqueous tetrahydrofuran was considered to give support to a unimolecular mechanism (pathway 4*b*, followed by loss of carbon dioxide to give phenol).[4]

In the present study, the extended Grunwald–Winstein equation [eqn. (5)][21] is applied to the solvolyses of phenyl chloroformate in a wide range of solvent types. This is the first time that this equation has been used as a tool in studies of chloroformate ester solvolysis. In eqn. (5), k and k_0 are the specific rates of solvolysis of the substrate in a given solvent and in 80%

$$\log (k/k_0) = lN_T + mY_{Cl} + c \qquad (5)$$

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Table 1 First-order rate coefficients for the solvolysis of phenyl chloroformate[a] at 25.0 °C

Solvent[b]	$k/10^{-5}$ s^{-1}[c]	N_T[d]	Y_{Cl}[e]
100% EtOH	260 ± 3[f]	+0.37	−2.52
90% EtOH	389 ± 6	+0.16	−0.94
80% EtOH	503 ± 11	0.00	0.00
70% EtOH	546 ± 9	−0.20	0.78
60% EtOH	658 ± 10	−0.38	1.38
100% H_2O	1338[g]	−1.38	4.57
100% MeOH	695 ± 9[h]	+0.17	−1.17
100% TFE[i]	0.001 32 ± 0.000 30	−3.93	2.79
97% TFE[i]	0.0570 ± 0.0030	−3.30	2.83
90% TFE[i]	1.15 ± 0.08	−2.55	2.85
80T–20E[j]	2.43 ± 0.21	−1.76	1.89
60T–40E	17.5 ± 0.5	−0.94	0.63
90% HFIP[i]	0.166 ± 0.004	−3.84	4.31
70% HFIP[i]	10.5 ± 0.3	−2.94	3.83
50% HFIP[i]	31.6 ± 0.6	−2.49	3.80
80% Acetone	68.8 ± 0.8	−0.37	−0.80
65% Acetone	168 ± 1[k]	−0.48[l]	0.60[l]
10% Acetone	1198 ± 9[k]	−1.23	4.28
30% Dioxane	780[m]	−0.98[l]	2.97
20% Dioxane	910[m]	−1.12	3.71
10% Dioxane	1090[m]	−1.25[l]	4.23

[a] Substrate concentration of 0.008–0.012 mol dm^{-3}. [b] Unless otherwise stated, binary solvents are on a volume–volume basis at 25.0 °C. [c] With associated standard deviation. [d] From ref. 22. [e] From ref. 23. [f] From ref. 18; also value of 320 (± 30) × 10^{-5} s^{-1} (ref. 5). [g] Interpolated from data at other temperatures (ref. 7). [h] A value of 694 × 10^{-5} s^{-1} has been reported (ref. 3). [i] On weight–weight basis. [j] T–E are TFE–ethanol mixtures. [k] Value from ref. 6. [l] Interpolated values. [m] Values from ref. 8.

Table 2 First-order rate coefficients for the solvolysis of *p*-methoxyphenyl chloroformate[a] at 25.0 °C and comparison with the values for the corresponding solvolyses of phenyl chloroformate

Solvent	$k/10^{-5}$ s^{-1}	$k_{p\text{-MeO}}/k_H$
100% EtOH	153 ± 4[b]	0.59
100% MeOH	414[c]	0.60
90% HFIP[d]	0.172 ± 0.007	1.04
50% HFIP[d]	24.9 ± 0.5	0.79
65% Acetone[e]	103 ± 1[f]	0.61
10% Acetone[e]	999 ± 9[f]	0.83

[a] Substrate concentration of 0.008–0.010 mol dm^{-3}. [b] From ref. 18. [c] From ref. 3. [d] On weight–weight basis. [e] On volume–volume basis at 25.0 °C. [f] From ref. 6.

ethanol, respectively; *l* is the sensitivity towards changes in solvent nucleophilicity (the N_T scale based on *S*-methyldibenzothiophenium ion solvolyses[22] being used); *m* is the sensitivity towards changes in solvent ionizing power (Y_{Cl} values based on 1-chloroadamantane solvolyses[23] being used) and *c* is a constant (residual) term.

Results

The specific rates of solvolysis of phenyl chloroformate, at 25.0 °C, were determined in methanol, 2,2,2-trifluoroethanol (TFE) and in binary aqueous solvents with the other component being ethanol, acetone, TFE, or 1,1,1,3,3,3-hexafluoropropan-2-ol (HFIP). Determinations were also made in TFE–ethanol mixtures. Values for 100% ethanol[18] and water[7] (interpolated from studies at other temperatures), 65 and 10% acetone,[6] and several aqueous dioxane compositions[8] were available from the literature. In Table 1 are presented the 21 data points used in correlations involving both simple and extended [eqn. (5)] forms of the Grunwald–Winstein equation. A more limited set of data was obtained either by experiment or from the literature for corresponding solvolyses of the *p*-methoxy derivative (Table 2).

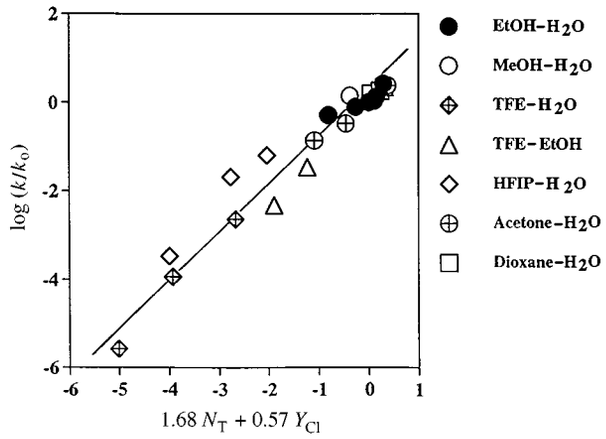

Fig. 1 Plot of log (k/k_0) for solvolyses of phenyl chloroformate at 25.0 °C against ($1.68N_T + 0.57Y_{Cl}$)

Discussion

The data presented in Table 1 are sufficient in and of themselves to refute the claim[4] that the solvolyses of phenyl chloroformate in aqueous dioxane and aqueous tetrahydrofuran are S_N1 in character. The 100% TFE and 90% TFE solvents have higher and essentially identical ionizing powers but differ in solvent nucleophilicity by 1.4 N_T units. The specific rate of solvolysis in the more nucleophilic 90% TFE is higher by a factor of 870, corresponding to an approximate (two point) sensitivity to changes in solvent nucleophilicity [*l* value of eqn. (5)] of 2.1. Such a very large value is clearly incompatible with an S_N1 process.

A comprehensive analysis, giving also the sensitivity to changes in solvent ionizing power (*m* value), has been carried out using all of the 21 specific rates of solvolysis listed in Table 1. An analysis in terms of the simple (original)[24] Grunwald–Winstein equation [eqn. (5) without the lN_T term] leads to an extremely poor correlation with a negative *m* value of −0.17 ± 0.18, *c* value of −0.73 ± 1.67, *F*-test value of only 0.96 and a correlation coefficient of 0.219. The correlation is enormously improved by the use of the full eqn. (5), with an *l* value of 1.68 ± 0.10, *m* value of 0.57 ± 0.06, *c* value of 0.12 ± 0.41, *F*-test value of 159, and a correlation coefficient of 0.973.

The very large sensitivity (*l* value) to changes in solvent nucleophilicity suggests a very pronounced involvement of the solvent as a nucleophile in the rate-determining step, consistent with the first step of an addition–elimination mechanism being rate-determining.

If eqn. (2), or a closely related variant, represents the mechanism, the nucleophilic attack by the solvent will be accompanied not by heterolysis of the carbon–chlorine bond (which will merely elongate slightly, due to the rehybridization of the carbon) but by the π electrons of the carbonyl group migrating to the oxygen, which formally now carries a full negative charge. The relatively large *m* value (0.57 ± 0.06) can be rationalized in terms of the stabilization (dispersion) by the solvent of the appreciable increase in negative charge on the oxygen at the transition state.

One very compelling type of evidence for a rate-determining addition, within an addition–elimination pathway, involves a study of chlorine *versus* fluorine leaving-group effects. This approach has been used very successfully in studies of the addition–elimination pathway involved in nucleophilic aromatic substitution.[25] When the carbon–halogen bond is broken in a nucleophilic displacement reaction, the chloro-derivative reacts appreciably faster than the fluoro-derivative, as much as 10^5 to 10^7 times faster for a unimolecular ionization[26,27] and some 10^1 to 10^3 times faster in concerted bimolecular displacements at a saturated carbon.[28] The previous observations[5,29–31]

that, when a bimolecular attack at an acyl carbon is operative, fluoroformate and chloroformate esters solvolyze at very similar rates, frequently with the fluoroformate ester the faster, have been uniformly rationalized in terms of the addition step of an addition–elimination mechanism being rate-determining. In particular, at 25.0 °C, the specific rates of ethanolysis of phenyl chloroformate and phenyl fluoroformate are identical.[5] Swain and Scott[26] rationalized the wide range of RCl : RF rate ratios in substitution reactions in terms of the replacement of chlorine by fluorine making both the heterolysis of the C–Hal bond more difficult and, by increasing the positive charge on the α-carbon, the formation of Nu–C bonds easier.

A recent study[3] of the solvolyses of the parent phenyl chloroformate and four ring-substituted derivatives in methanol and six methanol–acetonitrile mixtures led in each solvent to Hammett plots with a discontinuity. In the analyses, two lines were drawn, intersecting at the central (unsubstituted) data point, with slopes (ρ values) of *ca.* 0.8 and *ca.* 1.6. It was concluded that an associative S_N2-type mechanism was operative, with a transition state similar to a tetrahedral intermediate. However, to account for the discontinuity, a transition-state structure which varied with the identity of the substituent was proposed. A previous study[8] in aqueous dioxane was interpreted in terms of a linear plot. However, inspection of the plot shows that the point for the solvolysis of the *p*-methoxy derivative lies some distance above the best fit line.

The most thorough study is presented in two papers by Bacaloglu and co-workers.[6,18] For the parent phenyl chloroformate and eleven ring-substituted derivatives, they obtained a good linear plot against the traditional Hammett σ values for solvolyses in 10% aqueous acetone,[6] except that the data points for the *p*-methoxy and, especially, the *p*-benzyloxy substituents lay above the plot. Noting that similar behaviour in related solvolyses of diaryl carbonates had been corrected[32] by use of the 'normal' σ^0 values of Taft[33] (established using substrates with isolated substituted phenyl groups, with no resonance interaction[33–35]), they also substituted σ^0 values for the original σ values and found that a good linear relationship ($\rho = 1.03$) then resulted. Parallel behaviour was found in 65% acetone[6] ($\rho = 1.59$) and ethanol[18] ($\rho = 1.73$). Therefore, it appears that, with use of the appropriate substituent constants, one good linear relationship is obtained for solvolyses over the full range of substituted phenyl chloroformates (substituents ranging from *p*-benzyloxy to *p*-nitro), consistent with an essentially constant reaction mechanism not only over a wide range of solvents but also over a wide range of ring substituents.

A reinspection of the figure presented by Lee and co-workers[3] shows good linear plots for four of the five data points, with, as in the earlier studies,[6,8,18] the *p*-methoxy substituent lying above the plot. We believe, therefore, that these results are also best explained by the need to use 'normal' σ^0 values[33] (or σ^n values[34]), and there is no convincing evidence for appreciable variations in transition state structure[3] for these solvolyses. In support of this view, we have tabulated in Table 2 the $k_{p\text{-MeO}}/k_H$ ratios for solvolyses in six solvents and find a fairly constant ratio which is not far removed from unity, consistent with the small negative, somewhat solvent dependent,[6,33] 'normal' substituent constants for the *p*-methoxy group.[33,34]

Solvent isotope effects (k_{H_2O}/k_{D_2O}), which have been measured, include values for aryl chloroformates of 2.19 to 2.24 in 10% acetone[6] and 1.79 for phenyl chloroformate in 100% water.[7] Similar values have also been obtained for solvolyses of chloroformate esters containing a primary alkyl group.[7,9] These values are within the range predicted for a bimolecular solvolysis which is accompanied by general-base catalysis.[27,36] The solvent isotope effect of 2.3–2.5 for methanolysis (k_{MeOH}/k_{MeOD}) of a series of substituted phenyl chloroformates was also considered[3] to represent evidence for a bimolecular attack involving general-base catalysis.[17] The small activation energies and, especially, the negative entropies of activation which have been observed[3,6,7] for the solvolyses of phenyl chloroformate and ring-substituted derivatives are also indicative[37] of a bimolecular mechanism.

Conclusions

A very good correlation of the specific rates of solvolysis of phenyl chloroformate has been observed in a wide variety of solvent types. The extended Grunwald–Winstein equation was used, with incorporation of the N_T scale of solvent nucleophilicity and the Y_{Cl} scale of solvent ionizing power [eqn. (5)].

The very large sensitivity to changes in the N_T value (*l* value) of 1.68 ± 0.10 is clearly inconsistent with a recent discussion[4] of the mechanism of solvolysis of phenyl chloroformate in aqueous dioxane or tetrahydrofuran in terms of a rate-determining unimolecular ionization. It is consistent with the high degree of participation by the solvent which is to be expected if the addition step of an addition–elimination pathway is rate-determining. Such a mechanism has been given strong support based on an F/Cl leaving group effect of unity in the ethanolysis of phenyl haloformate, Hammett treatments of substituent effects, solvent isotope effects, and large negative values for the entropies of activation. Very recently, it has been suggested[3] that the tetrahedral intermediate involved may be so unstable that an enforced concerted variant pathway is followed. However, the F/Cl leaving-group effect suggests that, if followed, such a pathway must closely resemble the traditional addition–elimination pathway.

Accordingly, the *l* value and the *m* value of 0.57 ± 0.06 can be considered to be representative values for a mechanism involving rate-determining addition within an addition–elimination pathway, which will be very useful as reference values in extended Grunwald–Winstein treatments of the solvolyses of other chloroformate esters.

Experimental

Phenyl chloroformate (Aldrich, 99%) and *p*-methoxyphenyl chloroformate (Aldrich, 98%) were used without further purification. Solvents were purified and the kinetic runs carried out as previously described.[22a] The simple and multiple regression analyses were performed using the ABSTAT statistical package (Anderson–Bell, Arvada, Colorado, USA).

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