Correlation of the Rates of Solvolysis of Methyl Chloroformate with Solvent Properties†

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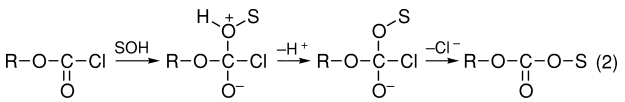
The specific rates of solvolyis of methyl chloroformate are very well correlated by the extended Grunwald–Winstein equation over a wide range of solvents; the pathway is believed to be predominantly addition–elimination, except that a positive deviation for solvolysis in 90% 1,1,1,3,3,3-hexafluoropropan-2-ol suggests an 80% contribution from an ionisation mechanism.

The extended Grunwald–Winstein equation [eqn. (1)] has been successfully applied to the solvolyses of several chloroformate[1,2] and chlorothioformate[2,3] esters. In eqn. (1), k and k_0 are the specific rates of solvolysis of a substrate in a given solvent and in 80% ethanol, respectively; l is the sensitivity towards changes in N_T, a scale of solvent nucleophilicity based on the specific rates of solvolysis of the *S*-methyldibenzothiophenium ion;[4,5] and m is the sensitivity towards changes in Y_{Cl}, a scale of solvent ionising power based on the specific rates of solvolysis of 1-adamantyl chloride.[6–8]

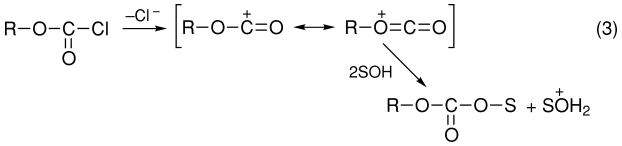
$$\log(k/k_0) = lN_T + mY_{Cl} + c \quad (1)$$

The solvolyses of phenyl chloroformate have been correlated using eqn. (1), with one correlation applying over the full range of solvent composition studied, including studies in solvents rich in the highly ionising and poorly nucleophilic 1,1,1,3,3,3-hexafluoropropan-2-ol (HFIP) or 2,2,2-trifluoroethanol (TFE). Appreciable sensitivities to changes in both solvent nucleophilicity ($l = 1.68 \pm 0.10$) and solvent ionising power ($m = 0.57 \pm 0.06$) were observed.[1] The solvolyses of ethyl chloroformate[2] could be successfully correlated using eqn. (1) with similar l and m values ($l = 1.56 \pm 0.09$; $m = 0.55 \pm 0.03$), but only in the less ionising and more nucleophilic solvents. In the more ionising and least nucleophilic solvents (HCO_2H, 100% and 97% TFE and 97%–50% HFIP), eqn. (1) could be applied, but only with very different sensitivity values ($l = 0.69 \pm 0.13$; $m = 0.82 \pm 0.16$).

Two competing reaction pathways have been proposed. There is strong independent evidence[9–12] that phenyl chloroformate solvolyzes by an addition–elimination pathway involving a tetrahedral intermediate [eqn. (2), or closely related variant]. Evidence that this addition–elimination pathway often operates for the solvolyses of haloformate esters includes F/Cl leaving-group effects of close to unity,[13–16] consistent with the addition step being rate-determining. The l values in the range 1.5–1.7 and m values in the range 0.5–0.6 were considered[1,2] to be typical values for the operation of this mechanism.



The competing mechanism operating for ethyl chloroformate is believed to involve ionisation [eqn. (3)], but incorporating, relative to 1-adamantyl chloride solvolysis, an appreciable solvation of the developing carbocation by the nucleophilic center of the solvent molecules. Incorporation of sulfur within the alkoxy (or phenoxy) group favors an increased participation by the ionisation mechanism in its competition with the addition–elimination pathway.[2,3]



In the present study, the solvolyses of methyl chloroformate[9,17,18] are investigated. First-order specific rates of solvolysis measured at, or extrapolated to, 40.0 °C are reported in Table 1 for a variety of pure and binary solvent mixtures. Analysis of the data using eqn. (1) leads to a fair linear correlation with values of 1.52 ± 0.11 for l, 0.55 ± 0.07 for m, and 0.11 ± 0.11 for c (correlation coefficient of 0.9584; $n = 21$). Inspection of the plot showed that there are serious deviations for 90% HFIP and formic acid, which lie above and below the plot, respectively. The deviation for 90% HFIP is consistent with a superimposed contribution to the log (k/k_0) values from an ionisation mechanism. A considerably improved correlation (Fig. 1) results when these two data points are omitted and values are obtained for 19 solvents of 1.59 ± 0.09 for l, 0.58 ± 0.05

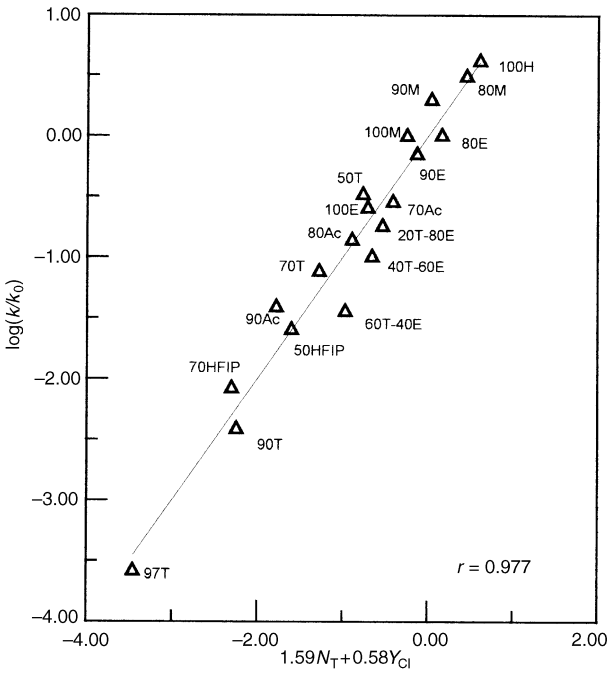


Fig. 1 Plot of log (k/k_0) for solvolyses of methyl chloroformate at 40.0 °C against ($1.59\,N_T + 0.58\,Y_{Cl}$)

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Table 1 Specific rates of solvolysis (with standard deviations) of methyl chloroformate at 40.0 °C together with the appropriate N_T and Y_{Cl} values

Solvent[a]	$10^5\ k/s^{-1}$	N_T[b]	Y_{Cl}[c]
100% EtOH	13.2 ± 0.1[d]	0.37	−2.52
90% EtOH	37.1 ± 0.1	0.16	−0.94
80% EtOH	52.7 ± 0.3	0.00	0.00
100% MeOH	52.1 ± 0.7[e]	0.17	−1.17
90% MeOH	103 ± 3	−0.01	−0.18
80% MeOH	162 ± 3	−0.06	0.67
90% Acetone	2.02 ± 0.02	−0.35	−2.39
80% Acetone	7.18 ± 0.08	−0.37	−0.80
70% Acetone	14.9 ± 0.1	−0.42	0.17
97% TFE	0.0136 ± 0.0002	−3.30	2.83
90% TFE	0.200 ± 0.005	−2.55	2.85
70% TFE	3.98 ± 0.06	−1.98	2.96
50% TFE	17.1 ± 0.1	−1.73	3.16
90% HFIP	0.106 ± 0.008	−3.84	4.31
70% HFIP	0.434 ± 0.021	−2.94	3.83
50% HFIP	1.31 ± 0.03	−2.49	3.80
100% HCO_2H	0.102 ± 0.002[f]	−2.44	3.20
100% H_2O	217 ± 1[g]	−1.38	4.57
60 T–40E[h]	1.86 ± 0.04	−0.94	0.63
40 T–60E[h]	5.24 ± 0.08	−0.34	−0.48
20 T–80E[h]	9.34 ± 0.02	0.08	−1.42

[a]Volume/volume basis at 25.0 °C, except for TFE–H_2O and HFIP–H_2O mixtures, which are on a weight/weight basis. [b]From ref. 5. [c]From refs. 7 and 8. [d]Interpolation within values of ref. 13 gives a value of 13.0×10^{-5} s^{-1}. [e]Extrapolation of values in the range 15–35 °C (ref. 17) leads to a value of 51.3×10^{-5} s^{-1}. [f]By extrapolation, using the Arrhenius equation, of values of 0.869 ($\pm$0.013) $\times 10^{-5}$ s^{-1} at 60.0 °C and 0.307 ($\pm$0.005) s^{-1} at 50.0 °C; in ref. 18, a value in 99% HCO_2H of 0.103×10^{-5} s^{-1} at 50 °C was reported. [g]From ref. 9. [h]T–E are TFE–ethanol mixtures.

for m and 0.16 ± 0.07 for c (correlation coefficient of 0.9774). The log (k/k_0) value calculated for the 90% HFIP solvent then lies 0.75 units below the experimental value, corresponding to an addition–elimination contribution to the overall solvolyis of 18%.

It is noteworthy that the specific rates of solvolysis in 97% TFE and in 70 and 50% HFIP lie nicely on the plot (Fig. 1) governed by l and m values which are within the range expected for an addition–elimination pathway. Further, as one might anticipate, the changeover from a dominant addition–elimination mechanism to a dominant ionisation mechanism is at solvents of considerably lower nucleophilicity and/or greater ionising power than what was the case for the solvolyses of ethyl chloroformate.

It is puzzling as to why the experimental log (k/k_0) value for solvolysis in HCO_2H should lie 0.85 units below the calculated line. In an attempt to shed light on this deviation, we have given further consideration to values previously reported,[18] at 50.0 °C, for solvolyses of MeOCOCl and EtOCOCl in 99% formic acid and in 35% acetone. Using interpolated values of −0.91 for N_T and 2.86 for Y_{Cl} for 35% acetone and the corresponding values for HCO_2H from Table 1, together with the appropriate l and m values, from Fig. 1 or the literature, one can estimate addition–elimination pathway ratios ($k_{HCO_2H}/k_{35\%A}$) of 5.4×10^{-3} for MeOCOCl solvolyses and 6.3×10^{-3} for EtOCOCl solvolyses. This corresponds to only a 9% contribution to the experimental value for the formolysis of EtOCOCl (assuming a negligible effect of a 1% water content). The corresponding estimated specific rate of formolysis of methyl chloroformate is 1.32×10^{-5} s^{-1}, 13 times the reported[18] experimental value. Indeed, the reported value is threefold lower than the value we report (Table 1) for 100% formic acid at the identical temperature, which is already lower than the value one would estimate for an addition–elimination pathway. The claim[18] that the solvolysis of methyl chloroformate proceeds by an ionisation process in formic acid, the plausibility of which is based on the approximately equal rate decreases reported as one moved from isopropyl chloroformate formolysis to ethyl chloroformate formolysis to methyl chloroformate formolysis, is rendered dubious based on the observation that these 70-fold decreases cause the MeOCOCl solvolysis to be considerably slower even than the estimate for the addition–elimination pathway. We propose that the formolysis of MeOCOCl is proceeding by the addition–elimination pathway, but do not have any good explanation for the low specific rate values observed both in the present study and previously.[18]

In conclusion, the solvolyses of methyl chloroformate are indicated to proceed by a bimolecular addition–elimination pathway in 20 of the 21 solvents considered. Only in the most ionising–lowest nucleophilicity combination (90% HFIP) is there evidence for a dominant ionisation pathway. This behaviour differs from the analyses of the specific rates of solvolysis of ethyl chloroformate, where the ionisation pathway was dominant in formic acid, in 97% TFE, and over the full range of HFIP–H_2O mixtures investigated.[2]

Experimental

Methyl chloroformate (Aldrich, 99%) was further purified by fractional distillation. Kinetic measurements were made conductometrically using a TOA Electronics Ltd. (Japan) Model CM-40 S instrument, with a cell constant of 0.915 cm^{-1}. All runs were performed in duplicate with at least 70 readings taken at appropriate intervals over three half-lives and infinity readings taken after ten half-lives.

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References

1 D. N. Kevill and M. J. D'Souza, *J. Chem. Soc., Perkin Trans. 2*, 1997, 1721.
2 D. N. Kevill and M. J. D'Souza, *J. Org. Chem.*, 1998, **63**, 2120.
3 D. N. Kevill, M. W. Bond and M. J. D'Souza, *J. Org. Chem.*, 1997, **62**, 7869.
4 D. N. Kevill and S. W. Anderson, *J. Org. Chem.*, 1991, **56**, 1845.
5 D. N. Kevill, in *Advances in Quantitative Structure–Property Relationships*, ed. M. Charton, JAI Press, Greenwich, Connecticut, 1996, vol. 1, pp. 81–115.
6 T. W. Bentley and G. E. Carter, *J. Am. Chem. Soc.*, 1982, **104**, 5741.
7 T. W. Bentley and G. Llewellyn, *Prog. Phys. Org. Chem.*, 1990, **17**, 121.
8 D. N. Kevill and M. J. D'Souza, *J. Chem. Res. (S)*, 1993, 174.
9 A. Queen, *Can. J. Chem.*, 1967, **45**, 1619.
10 C. Csunderlik, R. Bacaloglu and G. Ostrogovich, *J. Prakt. Chem.*, 1975, **317**, 81.
11 I. S. Koo, K. Yang, K. Kang, I. Lee and T. W. Bentley, *J. Chem. Soc., Perkin Trans. 2*, 1998, 1179.
12 I. S. Koo, K. Yang, K. Kang and I. Lee, *Bull. Korean Chem. Soc.*, 1998, **19**, 968.
13 S. I. Orlov, A. L. Chimishkyan and M. S. Grabarnik, *J. Org. Chem. USSR* (*Engl. Transl.*), 1983, **19**, 1981.
14 M. Green and R. F. Hudson, *J. Chem. Soc.*, 1962, 1055.
15 A. Queen and T. A. Nour, *J. Chem. Soc., Perkin Trans. 2*, 1976, 935.
16 D. N. Kevill and J. B. Kyong, *J. Org. Chem.*, 1992, **57**, 258.
17 R. Leimu, *Chem. Ber.*, 1937, **70**, 1040.
18 E. W. Crunden and R. F. Hudson, *J. Chem. Soc.*, 1961, 3748.