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A Kinetic Study of the Solvolyses of Methyl and Ethyl Chloroglyoxalates

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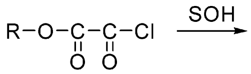
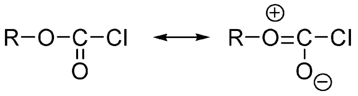


$$\mathrm{R = Me{:}}\ \log k = 1.45N_{\mathrm{T}} + 0.30Y_{\mathrm{Cl}} - 1.54$$
$$\mathrm{R = Et{:}}\ \log k = 1.57N_{\mathrm{T}} + 0.35Y_{\mathrm{Cl}} - 1.57$$
$$k_{\mathrm{ROCOCOCl}} / k_{\mathrm{ROCOCl}} \sim 10^{6}$$

Solvolyses of methyl and ethyl chloroglyoxylates proceed about 10^6 times faster than the identical solvolyses of the corresponding chloroformates. The correlation parameters obtained from application of the extended Grunwald−Winstein equation are consistent with an addition−elimination (association−dissociation) mechanism over the full range of solvents, with the addition step being rate determining.

There have been numerous measurements of the specific rates of solvolysis of chloroformate esters.[1] Recent studies have included solvent isotope effects,[2,3] Grunwald−Winstein equation correlations,[2,3] and product selectivity values in mixed solvents.[2,3] Other aspects have included Hammett equation correlations,[2] treatments in terms of third-order rate coefficients,[2] studies of accompanying decomposition with loss of CO_2,[3,4] the influence of sulfur-for-oxygen substitution,[5] studies of the corresponding fluoroformates,[6] and the influence of systematic variation of the alkyl group of alkyl chloroformates.[7−9] Chloroformate esters (ROCOCl) are frequently employed in kinetic studies of nucleophilic substitutions at an acyl carbon because they tend to react at convenient rates at temperatures close to ambient. This is in contrast to conventional acyl chlorides (RCOCl), which tend to undergo rather rapid nucleophilic substitution reactions.[10] The slower reaction is usually rationalized in terms of a resonance-based ground-state stabilization, which is possible for ROCOCl but not for RCOCl (eq 1).


$$\mathrm{R{-}O{-}C({=}O){-}Cl} \longleftrightarrow \mathrm{R{-}\overset{\oplus}{O}{=}C(O^{\ominus}){-}Cl} \qquad (1)$$

The mechanism of solvolysis is believed to involve an addition−elimination (association−dissociation) process for phenyl,[11] methyl,[8] and primary alkyl[7] chloroformates in all but the most ionizing solvents and those with the lowest nucleophilicity. For tertiary alkyl chloroformates, an ionization process, with loss of carbon dioxide, is favored.[4] Secondary alkyl chloroformates follow the ionization pathway in all but the more nucleophilic and less ionizing solvents (100% and 90% ethanol and methanol).[9]

Related compounds are chloroglyoxalate esters, with the naming of the parent acid as chloroglyoxalic acid being based on the replacement of the hydrogen of glyoxalic acid by chlorine. Alternatively, they can be named as chlorooxoacetate esters or as alkyl (or aryl) oxalyl chlorides. Hydrolysis leads to monosubstituted oxalic acid derivatives and, in contrast to the half-esters of carbonic acid,[12] this product is stable and can be isolated.[13] With alcohols or phenols, a disubstituted oxalate ester is formed.[14] Although there have been studies of the rates of decomposition of chloroglyoxalate esters in the gas phase[15] or in inert solvents,[14b,16] no quantitative studies appear to have been made of the kinetics of solvolysis in hydroxylic solvents. Conventional aliphatic acyl chlorides are already reactive species and further increases in the reactivity toward nucleophilic species are to be expected upon the incorporation of the powerfully electron-withdrawing alkoxycarbonyl (RCO_2−) group. It has previously been demonstrated, for example, that the introduction of electron-withdrawing chloro-

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TABLE 1. Specific Rates of Solvolysis (k) of Methyl and Ethyl Chloroglyoxalates and N_{T} and Y_{Cl} Values of the Solvents at Various Temperatures

solvent[a]	T, °C	$10^2 k_{\mathrm{Me}}$,[b] s^{-1}	$10^2 k_{\mathrm{Et}}$,[b] s^{-1}	N_{T}[c]	Y_{Cl}[d]
100% EtOH	−61.2	10.1 ± 0.5	6.79 ± 0.39		
	−69.2	5.05 ± 0.17	3.18 ± 0.11		
	−76.2	1.71 ± 0.08	1.26 ± 0.05	0.37	−2.52
	25.0[e]	$9.1(\pm 2.6) \times 10^3$	$4.2(\pm 0.6) \times 10^3$		
90% EtOH	−76.2	3.25 ± 0.22	3.22 ± 0.25	0.16	−0.94
100% MeOH	−61.2	18.7 ± 0.1	15.7 ± 1.0		
	−69.2	7.75 ± 0.31	6.58 ± 0.18		
	−76.2	3.02 ± 0.13	3.09 ± 0.09	0.17	−1.17
	25.0[e]	$19.1(\pm 1.5) \times 10^3$	$7.6(\pm 0.3) \times 10^3$		
90% MeOH	−76.2	3.60 ± 0.13	3.32 ± 0.12	−0.01	−0.18
60T-40E[f]	−76.2	0.178 ± 0.010	0.108 ± 0.004	−0.94	0.63
40T-60E[f]	−76.2	0.409 ± 0.013	0.333 ± 0.017	−0.34	−0.48
20T-80E[f]	−76.2	0.965 ± 0.043	0.769 ± 0.045	0.08	−1.42
100% TFE	25.0	0.0519 ± 0.0047	0.0359 ± 0.0016[g]		
97% TFE[h]	25.0	2.13 ± 0.08	1.72 ± 0.06		
	0.0	0.486 ± 0.011	0.374 ± 0.007		
	−21.2	0.109 ± 0.004	0.0756 ± 0.0012		
	−76.2[e]	$5.09\ (\pm 0.06) \times 10^{-4}$	$2.74\ (\pm 0.10) \times 10^{-4}$	−3.30	2.83
90% TFE[h]	−10.0	2.87 ± 0.10	2.04 ± 0.04		
	−21.2	1.15 ± 0.04	0.811 ± 0.011		
	−31.2	0.462 ± 0.018	0.313 ± 0.010		
	−76.2[e]	$26.0\ (\pm 0.6) \times 10^{-4}$	$15.5\ (\pm 0.7) \times 10^{-4}$	−2.55	2.85

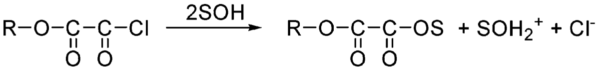
[a] On a volume−volume basis (at 25.0 °C), unless otherwise stated. [b] With associated standard deviations. [c] Values from refs 18 and 19. [d] Values from refs 20 and 21. [e] From an Arrhenius equation extrapolation of values at other temperatures. [f] Mixtures of 2,2,2-trifluoroethanol and ethanol in the proportions stated. [g] Titration of the production of acid as a function of time led to a specific rate of $3.40(\pm 0.23) \times 10^{-4}$ s^{-1}. [h] On a weight−weight basis.

TABLE 2. Enthalpies ($\Delta H^{\#}$, kcal mol^{-1}) and Entropies ($\Delta S^{\#}$, cal mol^{-1} K^{-1}) of Activation for the Solvolyses of Methyl and Ethyl Chloroglyoxalates[a]

	MeOCOCOCl		EtOCOCOCl	
solvent	$\Delta H^{\#}$	$\Delta S^{\#}$	$\Delta H^{\#}$	$\Delta S^{\#}$
100% EtOH[b]	9.41 ± 0.17	−18.0 ± 1.0	8.93 ± 0.09	−21.1 ± 0.5
100% MeOH[b]	9.68 ± 0.05	−15.5 ± 0.3	8.62 ± 0.03	−20.9 ± 0.2
97% TFE[c]	9.03 ± 0.02	−35.9 ± 0.1	9.51 ± 0.02	−34.7 ± 0.1
90% TFE[d]	10.38 ± 0.06	−25.9 ± 0.1	10.66 ± 0.03	−25.5 ± 0.1

[a] Each calculation uses the three experimental specific rate values from Table 1; errors quoted are standard errors. [b] Values calculated at −76.2 °C. [c] Values calculated at 25.0 °C. [d] Values calculated at −10.0 °C.

substituents greatly increases the rate of methanolysis of acetyl chloride.[17] In the present communication, we report upon the kinetics of the solvolysis reactions of methyl and ethyl chloroglyoxalates (eq 2) and compare the specific rates, activation parameters, and parameters from an extended Grunwald−Winstein treatment[18] with those previously obtained from studies of chloroformate esters, especially the methyl[8] and ethyl[7a] esters.



$$\mathrm{R{-}O{-}\underset{\underset{O}{\|}}{C}{-}\underset{\underset{O}{\|}}{C}{-}Cl} \xrightarrow{\mathrm{2SOH}} \mathrm{R{-}O{-}\underset{\underset{O}{\|}}{C}{-}\underset{\underset{O}{\|}}{C}{-}OS} + \mathrm{SOH_2^+} + \mathrm{Cl^-} \quad (2)$$

The specific rates of solvolysis of methyl and ethyl chloroglyoxalate were determined in several pure and binary hydroxylic solvents at temperatures below −60 °C. For ethanol and methanol, approximate values at 25.0 °C were obtained by extrapolation using the Arrhenius equation. Reactions in solvents rich in 2,2,2-trifluoroethanol (TFE) would be very slow at these low temperatures and values in 100% and 97% TFE were determined at higher temperatures. For both 97% TFE and 90% TFE, an extrapolated specific rate of solvolysis at −76.2 °C was calculated. Both the experimentally determined and the extrapolated values for the specific rates of solvolysis plus solvent nucleophilicity (N_{T}) values[18,19] and solvent ionizing power (Y_{Cl}) values[20−22] are reported in Table 1. The enthalpies and entropies of activation for the four solvolyses which were studied at three temperatures are reported in Table 2.

The range of solvents which could be studied was limited by the need to measure the specific rates of solvolysis in solvents without a fluoro alcohol component at low temperatures, below the freezing point of most of the commonly used alcohol−water or acetone−water combinations. The corresponding chloroformate esters were conveniently studied at or near ambient temperature.[7,8] The factors which reduce the rates of solvolysis of chloroformate esters relative to those of conventional acyl chlorides must be absent during the solvolyses of

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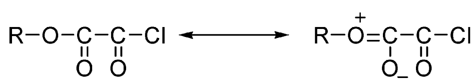
the chloroglyoxalate esters. The resonance stabilization of chloroformate esters (eq 1) will also be present in chloroglyoxalate esters (eq 3), but it is away from the



$$\mathrm{R{-}O{-}\underset{O}{\underset{\|}{C}}{-}\underset{O}{\underset{\|}{C}}{-}Cl \longleftrightarrow R{-}\overset{+}{O}{=}\underset{O^{-}}{\underset{|}{C}}{-}\underset{O}{\underset{\|}{C}}{-}Cl} \qquad (3)$$

reaction center and it will be maintained at the transition state of substitution reactions taking place at the carbonyl carbon bonded to the chlorine. The major influence of the additional carbonyl group will be one of electron withdrawal from the carbonyl carbon reaction center, intensifying the positive charge and, therefore, favoring nucleophilic attack and disfavoring ionization.

The methanolysis and ethanolysis of the two chloroglyoxalates were studied at three temperatures, and a long Arrhenius equation extrapolation allows the estimation of values at 25.0 °C (Table 1). These values can be compared to the corresponding values for methyl[6b,23] and ethyl[6b,7a,23,24] chloroformates. The $k_{\mathrm{MeOCOCOCl}}/k_{\mathrm{MeOCOCl}}$ ratios are $12(\pm 1) \times 10^5$ for methanolysis and $21(\pm 7) \times 10^5$ for ethanolysis. For the ethyl esters, the corresponding ratios are $8.5(\pm 0.4) \times 10^5$ and $17(\pm 3) \times 10^5$. The values are consistent with a mechanism involving a rate-determining nucleophilic attack at carbonyl carbon, assisted by the electron-withdrawing influence of the adjacent carbonyl group. Indeed, the specific rates are considerably faster than those of the corresponding acyl halides. Using a specific rate for ethanolysis of acetyl chloride at 25.0 °C ($147 \times 10^{-3}\ \mathrm{s}^{-1}$) from the literature,[25] we find the relative specific rates for MeCOCl:MeOCOCl:MeOCOCOCl to be $1.0{:}2.9 \times 10^{-4}{:}6.2 \times 10^2$.

Since TFE freezes at −23 °C, it is fortunate that the considerably slower solvolyses allow measurements to be made at higher temperatures, as high as 25.0 °C for 100% and 97% (w/w) TFE. For 97% and 90% TFE, the specific rates were determined at three temperatures and Arrhenius parameters (Table 2) and specific rates at −76.2 °C (Table 1) were calculated. The eight sets of Arrhenius parameters (Table 2) contain entropies of activation in the range of −15 to −36 cal $\mathrm{mol}^{-1}\ \mathrm{K}^{-1}$, consistent with the proposed bimolecular attack of solvent on the substrate. For comparison, values for the ethanolysis of methyl and ethyl chloroformates of −37.0 and −32.3 cal $\mathrm{mol}^{-1}\ \mathrm{K}^{-1}$, respectively, have been reported[6b] and the methanolysis of methyl chloroformate[23] has a value of −27.9 cal $\mathrm{mol}^{-1}\ \mathrm{K}^{-1}$.

While a bimolecular mechanism for the solvolyses is strongly indicated by the much slower reactions in TFE-rich solvents and by the appreciably negative entropies of activation, it is not established whether the process involves a stepwise addition−elimination (association−dissociation) or a concerted (S_N2) pathway. A powerful test in considering detailed mechanisms of solvolysis is to carry out a correlation analysis using the extended Grunwald−Winstein equation (eq 4).[26] In eq 4, k and k_0

$$\log(k/k_0) = lN_{\mathrm{T}} + mY_{\mathrm{X}} + c \qquad (4)$$

are the specific rates of solvolysis of a substrate RX in a given solvent and in 80% ethanol (arbitrarily chosen[27] as the standard solvent), l is the sensitivity to changes in solvent nucleophilicity (N_{T} values), m is the sensitivity to changes in solvent ionizing power (Y_{X} for a leaving group X), and c is a constant (residual) term.

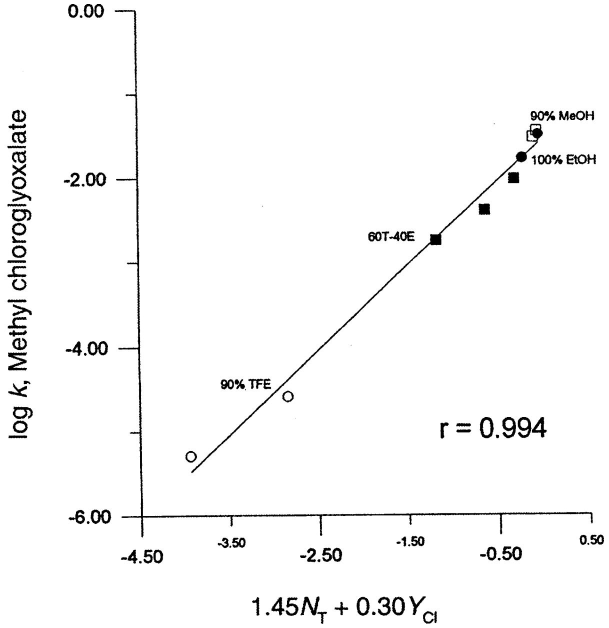


FIGURE 1. Plot of log k for solvolyses of methyl chloroglyoxalate at −76.2 °C against ($1.45N_{\mathrm{T}} + 0.30Y_{\mathrm{Cl}}$).

The specific rates directly measured or obtained by extrapolation to −76.2 °C (Table 1) have been analyzed by using eq 4. The nine data points are on the borderline of the minimum needed for a meaningful two-term correlation, but they do have the advantage of covering a good selection of solvent types. Since it was not possible to obtain a value for 80% ethanol, log k rather than log(k/k_0) was plotted. In this way, the log k_0 value is incorporated into the c value. The values obtained for the solvolyses of methyl chloroglyoxalate lead to values of 1.45 ± 0.16 for l, 0.30 ± 0.11 for m, and -1.54 ± 0.13 for c; the multiple correlation coefficient (R) was 0.994 and the F-test value was 237. The corresponding values for the ethyl chloroglyoxalate solvolyses were 1.57 ± 0.19 for l, 0.35 ± 0.14 for m, and -1.57 ± 0.16 for c; the R value was 0.992 and the F-test value was 192. The errors quoted are standard errors, and the errors associated with the m values were such that there are only low probabilities (0.038 and 0.043, respectively) that the contribution from the mY_{Cl} term is statistically insignificant. The two correlations are plotted in Figures 1 and 2.

One possible cause for concern is that the N_{T} and Y_{Cl} scales are being used at a temperature more than 100 °C lower than those at which they were experimentally determined. We have previously shown,[28] in a study of the solvolyses of cyclohexyl p-toluenesulfonate at a variety of temperatures, that the l and m values do not

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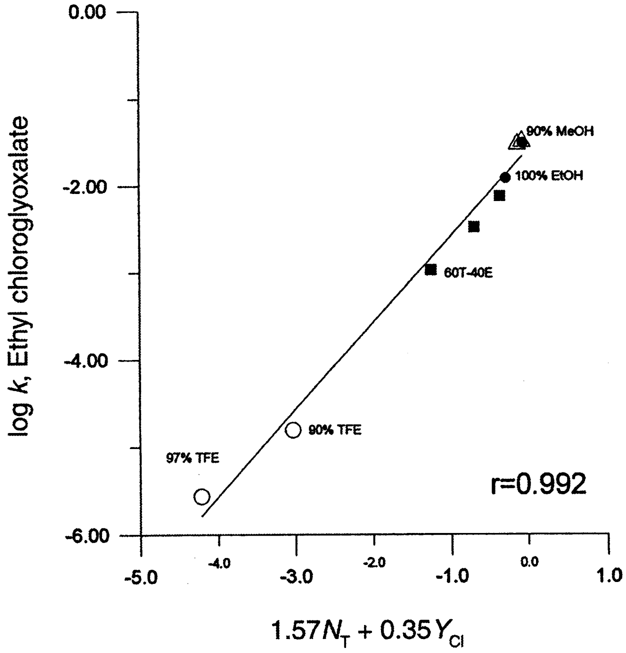

FIGURE 2. Plot of log *k* for solvolyses of ethyl chloroglyoxalate at −76.2 °C against ($1.57N_T + 0.35Y_{Cl}$).

vary appreciably when unchanged N_T and Y_{OTs} values are used over a 50 °C range, and this suggests that the influence on the correlation of working at a rather low temperature could well be small. Nonetheless one must be cautious, in any mechanistic assignment, of small differences between the sensitivity values of the present study and earlier studies of related systems at considerably higher temperatures.

It is of interest to compare the effect of introduction of a carbonyl group at the reaction center for solvolysis reactions taking place at sp^2- and sp^3-hybridized carbon. Studies[29,30] have shown that, for bimolecular solvolyses at sp^3-carbon, the carbonyl group has only a very minor effect upon the reaction rate, which is plausibly explained in terms of a balance of electronic effects between assistance to the nucleophilic attack and hindrance to the departure of the leaving group in a close to synchronous concerted process. For example,[30] the introduction of a benzoyl group into methyl tosylate *reduces* the rate of ethanolysis at 62.5 °C by a factor of 8.1, while changing the 2-methylene group of 2-phenylethyl bromide to a carbonyl group *increases* the rate of solvolysis in 80% ethanol by a factor of 7.0. These changes of less than 1 order of magnitude are indeed very small when compared to the change of approximately 6 orders of magnitude observed in the rates of solvolysis after inserting a carbonyl group into methyl or ethyl chloroformate to give the corresponding chloroglyoxalate. The observations are very plausibly explained by the operation of an S_N2 mechanism for the solvolyses at sp^3-carbon and of an addition−elimination mechanism, with the addition step being rate determining, for the solvolyses at sp^2-carbon.

In conclusion, the solvolyses of methyl and ethyl chloroglyoxalates proceed about 10^6 times faster than the corresponding solvolyses of the chloroformate esters. The extended Grunwald−Winstein equation (eq 4) was used to correlate the data and the rather large sensitivities to changes in solvent nucleophilicity (1.45 and 1.57) and the modest sensitivities to changes in solvent ionizing power (0.30 and 0.35) are consistent with an addition−elimination (association−dissociation) mechanism, with the addition step being rate determining.[7,8,11]

Experimental Section

The methyl and ethyl chloroglyoxalates (methyl chlorooxoacetate, Aldrich, 96%; and ethyl chlorooxoacetate Aldrich, 98%) were used as received. Runs were performed with ca. 5×10^{-3} M substrate. The titrimetric determination of specific rates and the purifications of the solvents were as previously described.[19] The low-temperature experiments were carried out by allowing a solid CO_2−acetone slush in a Dewar flask to slowly warm to room temperature. At just below the required temperature, the reaction vessel containing 25 mL of the solvent was immersed and stirring was started. After temperature equilibration and warming to the desired temperature, 12 μL of substrate was added and the conductivity changes measured as a function of time. Conductance measurements at appropriate time intervals were used, in conjunction with the infinity value, to obtain integrated rate coefficients and all values from duplicate runs for up to 80% reaction were used to obtain the reported averages (Table 1). Temperatures were monitored using a factory-calibrated alcohol thermometer. The runs were sufficiently fast (half-lives of 4 s to 6 min) for temperature variation during the runs to be negligible. Runs at temperatures above −22 °C were carried out with immersion of the conductivity cell in a conventional low-temperature constant-temperature bath, and temperatures were determined using a standardized mercury thermometer.

The apparatus for measurement of the conductance as a function of time consisted of an efficiently stirred conductivity cell (capacity 10−50 mL) connected to a TENMA multimeter (72-602 model with 72-6251 connector, linked to a PC through an RS232C port and with a Simpson 420 function generator). The multiple regression analyses were performed using commercially available statistical packages.

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