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Stoichiometric Solvation Effects. Product-Rate Correlation for Solvolyses of Phenyl Chloroformate in Alcohol-Water Mixtures

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Solvolyses of phenyl chloroformate in water, D₂O, CH₃OD, 50% D₂O-CH₃OD, and in aqueous binary mixtures of acetone, ethanol and methanol are investigated at 25.0 °C. Product selectivities are reported at 25 °C for a wide range of ethanol-water and methanol-water solvent compositions. The Grunwald-Winstein plots of first-order rate constants for phenyl chloroformate with Y_{Cl} (based on 2-adamantyl chloride) show marked dispersions into three separate lines for the three aqueous mixtures with a small m value ($m < 0.2$) and a rate maximum for aqueous alcohol solvents. Third-order rate constants, k_{aw} , k_{aw} , k_{wa} and k_{aa} were calculated from the observed k_{ww} and k_{aa} values together with k_{aw} and k_{wa} calculated from the intercept and slope of the plot of $1/S$ vs. $[\text{alcohol}]/[\text{water}]$. The calculated rate constants, k_{calc} and mol % of ester agree satisfactorily with those of the observed rate constants, k_{obs} and mol % of ester, supporting the stoichiometric solvation effect analysis. The kinetic solvent isotope effects determined in water and methanol are consistent with the proposed mechanism of the general base catalyzed and/or carbonyl addition for phenyl chloroformate solvolyses based on mass law and stoichiometric solvation effect studies.

Introduction

Many acyl transfer reactions in protic solvents involving esters,¹ amide derivatives² and acid chlorides³ are third order overall, and it is thought that one molecule of solvent acts as a nucleophile and a second molecule acts as a general base.⁴ In the third order process, methanol probably acts as both nucleophile and general base, because large rate enhancements are observed when chloride ion (a base in acetonitrile) is added while only minor rate enhancements are observed when phenol is added.³

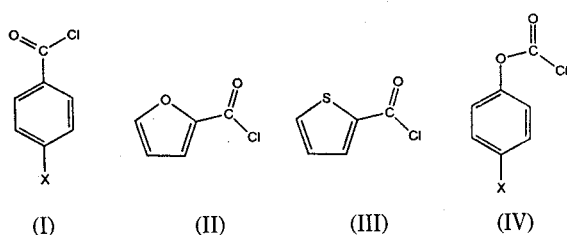
The other process may be pseudo second order, and may involve methanol as nucleophile with acetonitrile, present in large excess, acting as general base.^{3b} Similar results have been obtained for aminolyses involving primary and secondary amines.⁵ According to change of reaction condition as variation of substituent or solvent composition, nucleophilic reactions of acyl halides were reported as an addition-elimination, S_N1 or S_N2 reaction mechanism.^{6,7} Based on product-

rate study, benzoyl chloride (I) solvolyses by an S_N2 mechanism in high polarity solvents, whereas it favors general-base catalyzed or possible addition-elimination pathway ($S_A N$) in less polar media.^{8,9}

Nucleophilic substitution reactions of furoyl chloride (II) and thenoyl chloride (III) were reported to proceed via different reaction mechanisms, the former by an addition-elimination and the latter by an S_N2 mechanism based on a product-rate study.¹⁰ Though the only difference between two substrates is sulfur atom in thenoyl chloride which is replaced by an oxygen atom in furoyl, two substrates show a remarkable change in reaction mechanism.⁵

Therefore, it will be very interesting to test product-rate behaviors for solvolyses of IV, which has an oxygen atom adjacent to carbonyl group, in alcohol-water mixtures.

Competing nucleophilic substitution reactions in alcohol-water mixtures are interpreted in terms of product selectivities, S , defined from molar ratios of products and of solvents [equation (1)]. If these reactions simply involved competitive



attack upon the substrate by either water or alcohol, S values would be independent of solvent composition.¹¹ Contrary to trend expected from the reactivity-selectivity principles (RSP),¹³ S values often increase in more aqueous media with the increase in reactivity.^{9,12}

$$S = \frac{[\text{alcoholysis prod.}][\text{water solv.}]}{[\text{hydrolysis prod.}][\text{alcohol solv.}]} \quad (1)$$

$$1/S = (\text{slope})([\text{alcohol solv.}]/[\text{water solv.}]) + (\text{intercept}) \quad (2)$$

We recently reported a new equation (2), accounting for the solvent dependence of product selectivities in alcohol-water mixtures;¹⁴ this equation is successful for the product-forming step of reactions of free cation,¹⁵ for concerted nucleophilic substitution reactions,^{10,16} and also for the general-base or addition-elimination reactions.¹⁰

In this study, we determined rate constants and products selectivities for solvolyses of IV in alcohol-water mixtures at 25 °C, and we calculated third order rate constants, k_{ww} , k_{wa} , k_{aw} , and k_{aa} using observed first-order rate constants and selectivity values. We will discuss stoichiometric solvation effects of solvolytic reaction of phenyl chloroformate using third order rate constants.

Results and Discussion

The rate constants for solvolyses of IV in methanol-water, ethanol-water and acetone-water mixtures at 25.0 °C are summarized in Table 1.

Reference to Table 1 reveals that the rate increases in the order Acetonitrile-H₂O < Acetone-H₂O < EtOH-H₂O < MeOH-H₂O, and it shows maximum rate constants at near

Table 1. Solvolyses of phenyl chloroformate in aqueous alcohol and aqueous acetone binary mixtures at 25 °C

v/v %	MeOH	EtOH	Acetone
	$k \times 10^3$		
100	7.93	2.19	
90	12.9	4.13	
80	16.7	5.05	0.781
70	19.4	5.78	1.25
60	22.2	6.64	1.95
50	24.5	7.92	2.89
40	24.8	10.1	4.28
30	24.7	12.7	6.56
20	22.0	14.3	8.97
10	17.5	13.7	11.5
0	13.3	13.3	13.3

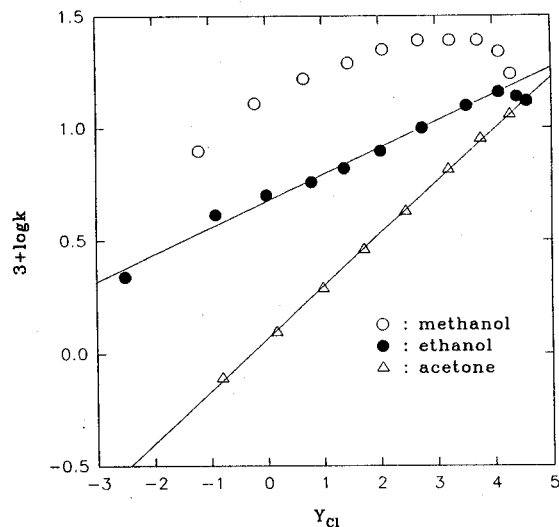


Figure 1. Logarithms of first-order rate constants for solvolyses of phenyl chloroformate at 25 °C vs Y_{Cl} . For acetone-water: slope=0.23, $r=0.999$; for ethanol-water: slope=0.12, $r=0.995$.

40% methanol in alcohol-water mixtures.

The rate increases slowly as the water content of the mixtures increases; this means that the rate is small accelerated by the solvent with higher ionizing power, Y , suggesting that bond breaking in the TS is little important. First-order rate constants for solvolysis of IV vary only over six-fold range in alcohol-water mixtures, whereas the observed first-order rate constants for thenoyl chloride vary over 7000-fold range¹⁰ which is known to react *via* an S_N2 reaction mechanism. This results indicate that the rate determining step is not the bond breaking step which was found in the reaction of thenoyl chloride but the addition step for the reaction of phenyl chloroformate where transition state is not sensitive to solvent ionizing power. These results are very similar to those of solvolytic reaction of *p*-nitrobenzoyl chloride,^{16,18} *p*-nitrobenzenesulfonyl chloride^{11,14} and furoyl chloride,¹⁰ but they are different from the results of solvolytic reaction of thenoyl chloride and *p*-methoxybenzoyl chloride.

The Grunwald-Winstein plots of the rates in Table 1 are presented in Figure 1 using solvent ionizing power scale Y_{Cl} based on 2-adamantyl chloride.¹⁷ Examination of Figure 1 shows that the plots for the three aqueous mixtures exhibit dispersions into three separate lines of different phenomenon, the maximum rate constant at near 40M in methanol aqueous mixtures and also maximum rate constant at near 20E in ethanol aqueous mixtures.

The plots for 20E-10E and acetone-water show very small m values, $m=0.12$ ($r=0.995$) and $m=0.23$ ($r=0.999$), respectively. Such a small m value implies that the solvolysis of phenyl chloroformate in the binary mixtures proceeds by the addition-elimination (S_{AN}) or S_N2 mechanism channel rather than by an S_N1 channel.

$$\log(k/k_o)_{RX} = m Y_{Cl} \quad (3)$$

The product selectivities, S , for the solvolysis of IV in aqueous alcohols are summarized in Table 2. Examination of Table 2 reveals that for the solvolysis of IV in aqueous methanol mixtures the selectivity increase with increasing

Table 2. Selectivities (*S*) for solvolyses of phenyl chloroformate in alcohol-water mixtures at 25 °C^{a,b}

v/v %	Methanol/Water		Ethanol/Water	
	[Ester]/[Acid]	<i>S</i>	[Ester]/[Acid]	<i>S</i>
90	9.085	2.28	3.813	1.37
80	6.598	3.71	2.540	2.06
70	5.418	5.23	1.938	2.69
60	3.997	6.00	1.526	3.30
50	3.042	7.70	1.156	3.75
40	2.175	7.80	0.827	4.02
30	1.482	7.80	0.534	4.04
20	0.861	7.76	0.301	3.88
10	0.402	8.12	0.122	3.56

^aDetermined (eq. 1) by duplicate HPLC analyses of each solvent composition; average deviation $< \pm 1\%$. ^bInjected 5 μL of a 10% solution of phenyl chloroformate in acetonitrile into 5 mL of solvent.

water contents, whereas the selectivity exhibits a maximum behavior in aqueous ethanol; thus the reactivity-selectivity principle (RSP)¹³ is not obeyed in methanol and partially obeyed (up to the 20E) in ethanol mixtures. Generally, *S* values decrease with increasing water content because the amount of alcoholysis product increases. However, the greater value of *S* in more aqueous media for IV is a strong indication that the role of alcohol as a nucleophile is important while the effect of ionizing power is insignificant in the product determining step of the reaction of IV. These types of selectivity changes with IV have been shown to be typical for a general-base catalyzed and/or a carbonyl addition-elimination channel in aqueous alcohol media.²⁰ Moreover the RSP is violated for the solvolysis of IV in aqueous alcohol, i.e., the selectivity is proportional to the reactivity; the same argument as to the importance of nucleophilicity and low sensitivity to the ionizing power of the solvent mixtures should apply to the rate determining step. Thus the favoured channel for IV in the aqueous alcohol mixtures is most likely to be a carbonyl addition-elimination pathway.

The Grunwald-Winstein plot (Figure 1) for IV shows a low response to solvent ionizing power, and shows a maximum reactivity at near 40M with a nonlinear line in methanol-water mixtures. In order to examine the nonlinear Grunwald-Winstein plot, it is necessary to take into account the stoichiometric solvation effects based on third order reaction mechanism. For corresponding solvolyses in alcohol-water mixtures, interpretations based on a third order mechanism are more complex, but significant new information is available because two products are formed. Thus there are four possible third order rate constants in the solvolysis reaction: (i) k_{aa} for a mechanism in which one molecule of alcohol acts as a nucleophile and second molecule acts as a general base; (ii) k_{aw} in which alcohol acts as a nucleophile and water acts as a general base; (iii) k_{wa} in which water acts as nucleophile and alcohol acts as general base; (iv) k_{ww} in which water acts as both nucleophile and general base.^{10,11,14,16} Therefore, observed first-order rate constants in alcohol-water mixtures are given by equation (4).

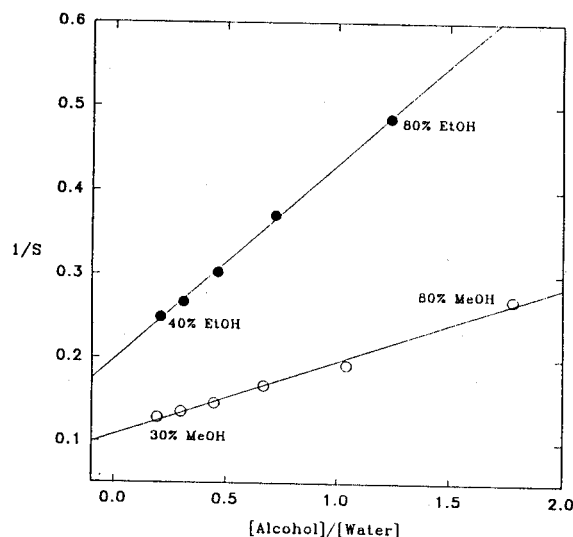
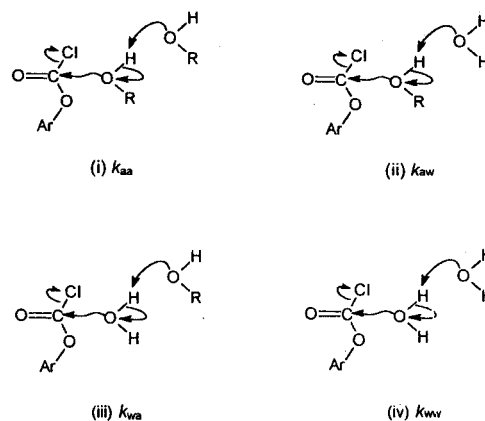


Figure 2. Correlation of $1/S$ and alcohol/water molar ratio for solvolyses of phenyl chloroformate. For methanol-water; slope = 0.088, intercept = 0.108, $r = 0.996$; for ethanol-water: slope = 0.233, intercept = 0.198, $r = 0.999$.

$$k_{obs} = k_{aa}[\text{alcohol}]^2 + (k_{aw} + k_{wa})[\text{alcohol}][\text{water}] + k_{ww}[\text{water}]^2 \quad (4)$$

The k_{aa} terms can be calculated from observed first order rate constants in pure alcohols ($k_{aa} = k_{obs}/[\text{ROH}]^2$); similarly k_{ww} can be obtained from the observed first order rate constant in water ($k_{ww} = k_{obs}/[\text{H}_2\text{O}]^2$).^{11,16} In order to determine k_{aw} and k_{wa} terms, it is necessary to have product selectivity data as well as kinetic data. Also, *S* [equation (1)] is then given by equation (5), and the reciprocal of equation (5) simplifies to equation (6).^{11,16}

$$S = \frac{(k_{aw}[\text{alcohol}][\text{water}]) / (k_{wa}[\text{alcohol}][\text{water}] + k_{ww}[\text{water}]^2)}{[\text{water}]/[\text{alcohol}]} \quad (5)$$

$$1/S = (k_{wa}/k_{aw})([\text{alcohol}]/[\text{water}] + k_{ww}/k_{aw}) \quad (6)$$

The above derivation of equation (6) implies that it may be possible to calculate the observed first-order rate constants if one of the three third-order rate constants is known. We calculated k_{ww} from the observed first-order rate constant in water divided by square of the molar concentration of water, and then k_{aw} and k_{wa} were obtained from the intercept

Table 3. The third-order rate constants, k_{ww} , k_{aw} , k_{wa} and k_{aa} for phenyl chloroformate solvolysis in alcohol-water mixtures

Solvent	$/10^{-5} \text{ M}^{-2}\text{s}^{-1}$			
	k_{ww}	k_{aw}	k_{wa}	k_{aa}
Methanol	0.432	3.97	0.349	1.30
Ethanol	0.432	2.18	0.508	0.745

and slope of Figure 2, respectively. The third-order rate constants are summarized in Table 3.

The third-order rate constants, k_{aw} and k_{aa} , in which alcohol acts as nucleophile are larger than k_{wa} and k_{ww} terms in which water acts as nucleophile (Table 3). In $(k_{wa} + k_{aw})$ [water][alcohol] terms of equation (4), k_{aw} is indeed greater than k_{wa} in the second term in equation (4), and third order rate constant for methanol is more than twice greater than the one for ethanol.

It appears therefore that the maximum rate behaviour of ten observed²⁰ in the solvolysis of methanol mixtures is due to exceptionally greater contribution of k_{aw} term, i.e., methanol is acting as a nucleophile and water is acting as general base catalysis (Figure 1).

Catalysis of nucleophilic attack by water is favoured in the decreasing order of water ($k_{ww} = 0.432 \times 10^{-5} \text{ dm}^6 \text{ mol}^{-1} \text{ s}^{-1}$) > ethanol ($k_{ww} = 0.363 \times 10^{-5} \text{ dm}^6 \text{ mol}^{-1} \text{ s}^{-1}$) > methanol ($k_{ww} = 0.310 \times 10^{-5} \text{ dm}^6 \text{ mol}^{-1} \text{ s}^{-1}$); as this is not accepted order of pK_a values for these weak acids,¹⁹ the second solvent molecule may act not only as general base but also as a hydrogen bond donor to the carbonyl oxygen. The large value of k_{ww} shows greater general base catalysis by water in spite of smaller pK_a values than that of ethanol.

The third-order rate constants observed, calculated third-order rate constants, k_{calc} , using Eq. (7), observed percent of ester, and calculated percent of ester using Eq. (8) are summarised in Table 5.

$$k_{calc} = k_{ww}[\text{water}]^2 + (k_{wa} + k_{aw})[\text{water}][\text{alcohol}] + k_{aa}[\text{alcohol}]^2 \quad (7)$$

$$\text{mol \% of ester} = (k_{aw}[\text{water}][\text{alcohol}] + k_{aa}[\text{alcohol}]^2) / k_{calc} \quad (8)$$

The maximum difference between calculated and observed rate constant is about 20%, but the one between calculated and observed mol % of ester is only 10% (Table 4). Agreement between calculated and observed results for methanol-water mixtures are reasonably good: in 70% methanol-water, the difference in the first order rate constant is only 6.7% and the difference in the mol % ester is only 3.1%. Such good agreements between calculated and experimental values (Table 4) implies that the use of equation (6) in the analysis of stoichiometric solvation effects and reaction mechanism is justified. It also means that the role of water as a general base is more important than as a nucleophile as water content is increased. These results are in a good agreement with the carbonyl addition-elimination (S_N) mechanism.

Finally we have determined the kinetic solvent isotope effects (KSIE), k_{SOH}/k_{SOD} , for the substrate using deuterated water (D_2O) and methanol (CH_3OD), and the results are presented in Table 5. Previous works indicated that the KSIE

Table 4. Calculated rate constants, k_{calc} , and contributions of third-order terms to k_{calc} , with calculated percentage ester product for 2-phenyl chloroformate solvolysis in aqueous methanol (M) and ethanol (E)

Alcohol % (v/v)	$/10^{-3}\text{s}^{-1}$		$/10^{-3}\text{s}^{-1}$			% Ester	
	k_{calc}	k_{aa}	k_{aw}	k_{wa}	k_{ww}	Obs	Calc
90M	11.6	6.42	4.68	0.382	0.133	90.1	95.7
80M	14.6	5.08	8.31	0.680	0.532	86.8	91.7
70M	16.9	3.89	10.9	0.892	1.20	84.4	87.5
60M	18.5	2.86	12.5	1.02	2.13	80.0	83.0
50M	19.4	1.98	13.0	1.06	3.33	75.3	77.2
40M	19.6	1.27	12.5	1.02	4.79	68.5	70.3
30M	19.0	0.714	10.9	0.892	6.52	59.7	61.1
20M	17.8	0.317	8.31	0.680	8.52	46.3	48.5
10M	15.9	0.0793	4.68	0.382	10.8	28.7	29.9
90E	3.87	1.77	1.66	0.311	0.133	79.0	88.6
80E	5.43	1.40	2.95	0.552	0.532	71.6	80.1
70E	6.87	1.07	3.87	0.725	1.20	66.6	71.9
60E	8.17	0.787	4.43	0.828	2.13	60.4	63.9
50E	9.35	0.547	4.61	0.863	3.33	53.6	55.2
40E	10.4	0.350	4.43	0.829	4.79	45.3	50.0
30E	11.9	0.197	4.43	0.725	6.52	34.8	37.0
20E	12.5	0.0876	3.32	0.553	8.52	23.1	27.3
10E	12.8	0.0218	1.44	0.310	10.8	10.9	11.4

Table 5. Kinetic solvent isotope effect of phenyl chloroformate at 25 °C

	k_{SOH}	k_{SOD}	KSIE
Methanol	7.93×10^{-3}	3.79×10^{-3}	2.09
50% Methanol	24.8×10^{-3}	11.7×10^{-3}	2.09
Water	13.3×10^{-3}	7.76×10^{-3}	1.71

value is relatively large, ≥ 1.7 , for a general base catalyzed reaction but is small, 1.2-1.5, for S_N2 reaction.²² For phenyl chloroformate, the KSIE is ≥ 1.7 in methanol, 50% aqueous methanol and water, and KSIE are identical values for methanol and 50% aqueous methanol. These results are again in good agreement with our proposed reaction channels: in aqueous alcohol and acetone phenyl chloroformate solvolyzes through a general base catalyzed and/or a carbonyl addition-elimination channel.

Experimental

Materials. Methanol, ethanol, and acetone were Merck GR grade (<0.1% H_2O), and D_2O and CH_3OD were from Aldrich (99.9% D). Distilled water was redistilled with Buchi Fontavapor 210 and treated using ELGA UHQ PS to obtain specific conductivity of less than 1×10^{-6} mhos/cm. Phenyl chloroformate was Aldrich Gr grade (99.8%).

Rate Measurement. The rates were measured conductometrically at 25 (± 0.03) °C at least in duplicate as described previously,⁸ with concentrations of substrate ca. 10^{-3} M.

Product Selectivity. The solvolysis products, ester and

acid, were determined by HPLC analysis described previously,¹⁰ and the product selectivity, S , were calculated from equation (1).

The S values calculated from the observed peak area ratios of ester and acid gave S_{raw} values, which were divided by a response factor to arrive at true S values. For HPLC response calibrations, area ratios from pure alcohol and 40% acetonitrile-water mixtures were used. Eluent solvent used was 70% methanol-water mixture and flow rate was adjusted to 1 mL/min. The HPLC system used was Hewlett-Packard 1050 Series with 250×4 mm Spherisorb ODS reversed phase column.

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