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Stoichiometric Solvation Effects. Part 4. Product-Rate Correlations for Solvolyses of *p*-Methoxyphenyl Chloroformate in Alcohol-Water Mixtures

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Received July 12, 1997

Solvolyses of *p*-methoxyphenyl 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 *p*-methoxyphenyl chloroformate with Y_{Cl} (based on 1-adamantyl chloride) show marked dispersions into three separate curves for the three aqueous mixtures with a small *m* value and a rate maximum for aqueous alcohol solvents. Third-order rate constants, k_{wv} , k_{av} , k_{va} and k_{aa} were calculated from the observed k_{wv} and k_{aa} values together with k_{av} and k_{va} 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 carbonyl addition-elimination.

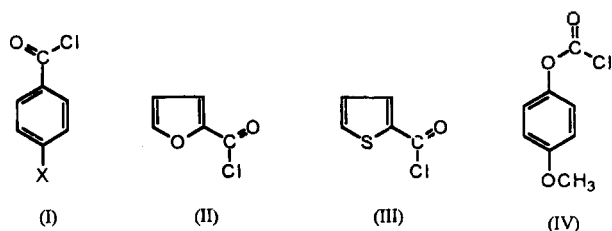
Introduction

The mechanism of acyl-transfer reactions has been investigated intensively for many years both experimentally¹ and theoretically.² The mechanism of most of these reactions is, however, still not well established. The solvolysis of acyl halides, RCOX, is believed to proceed either through a direct displacement mechanism (S_N2) or through an associative addition-elimination mechanism involving a tetrahedral intermediate.³ Many acyl-transfer reactions in protic solvents involving esters,⁴ amide derivatives⁵ and acid chlorides⁶ 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.⁷ 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.⁶

The other process may be pseudo second order, and may

involve methanol as nucleophile with acetonitrile, present in large excess, acting as general base.^{6a} Similar results have been obtained for aminolyses involving primary and secondary amines.⁸ Depending on reaction conditions, as substrates, and solvent compositions, nucleophilic reactions of acyl halides were reported as an addition-elimination, S_N1 or S_N2 reaction mechanism.^{9,10} Based on the 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_N1) in less polar media.^{11,12}

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 the product-rate study.¹³ 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.⁸



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.¹⁴ Contrary to trend expected from the reactivity-selectivity principles (RSP),¹⁵ S values often increase in more aqueous media with the increase in reactivity.^{11,16}

$$S = \frac{[\text{ester}][\text{water}]}{[\text{hydrolysis}][\text{alcohol}]} \quad (1)$$

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

$$S = (\text{slope})([\text{water}]/[\text{alcohol}]) + (\text{intercept}) \quad (3)$$

We recently reported new equations (2) and (3), accounting for the solvent dependence of product selectivities in alcohol-water mixtures¹⁷; these two equations are successful for the product-forming step of reactions of free cation,¹⁸ for concerted nucleophilic substitution reactions,^{13,19} and also for the general-base or addition-elimination reactions.¹³

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, $k_{\text{w}}, k_{\text{a}}, k_{\text{aw}},$ and k_{aa} using observed first-order rate constants and selectivity values. We will discuss stoichiometric solvation effects of solvolytic reaction of *p*-methoxyphenyl chloroformate using third order rate constants.

Results and Discussion

The rate constants for solvolyses of IV in methanol-water, ethanol-water, acetone-water mixtures at 25.0 °C are summarized in Table 1. Reference to Table 1 reveals that the rate increases in the order Acetone-H₂O < EtOH-H₂O < MeOH-H₂O, and it shows maximum rate constants at near 30M in methanol aqueous mixtures and near 20E in ethanol aqueous mixtures. The rate increases slowly as the water content of the mixtures increases; this means that the rate is slightly accelerated by the solvent with higher ionizing power, Y , suggesting that bond breaking in the transition state is of little importance. First-order rate constants for solvolysis of I vary over only a three-fold range in alcohol-water mixtures, whereas the observed first-order rate constants for III which is known to react via an S_N2 reaction mechanism vary over 7000-fold range.¹³ These 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 *p*-methoxyphenyl chloroformate where transition state is not sensitive to solvent ionizing power. These results are very similar to those of solvolytic reactions of *p*-nitrobenzoyl chloride,^{19,20} *p*-nitro-

Table 1. Rate constants (k) for solvolyses of *p*-methoxyphenyl chloroformate in aqueous binary mixtures at 25 °C

v/v %	MeOH	EtOH	Acetone
	$k \times 10^3$		
100	4.10	1.08	-
90	8.00	2.39	-
80	11.3	3.18	0.415
70	14.2	3.85	0.774
60	17.0	4.82	1.24
50	19.6	5.89	2.03
40	20.7	7.58	3.25
30	21.0	10.6	5.10
20	18.8	12.3	7.38
10	15.6	12.2	10.1
H ₂ O	11.8	11.8	11.8

benzenesulfonyl chloride^{14,17} and furoyl chloride,¹³ but they are different from the results of solvolytic reactions of thenoyl chloride and *p*-methoxybenzoyl chloride.

The Grunwald-Winstein plots (equation 4) of the rates in Table 1 are presented in Figure 1 using the solvent ionizing power scale Y_{Cl} , based on 1-adamantyl chloride.²¹ Examination of Figure 1 shows that the plots for the three aqueous mixtures exhibit dispersions into three separate curves with maximum rate constants at near 30 M in methanol aqueous mixtures and near 20E in ethanol aqueous mixtures.

The plot for 100E-20E and acetone-water show a very small m value, $m=0.15$ ($r=0.994$) and $m=0.27$ ($r=1.00$), respectively, implying that the solvolysis of *p*-methoxyphenyl chloroformate in the binary mixtures proceeds by the addition-elimination ($S_{\text{A}}\text{N}$) or associative $S_{\text{N}}2$ mechanism channel rather than by an $S_{\text{N}}1$ channel.

$$\log(k/k_{\text{RX}}) = m Y_{\text{Cl}} \quad (4)$$

The product selectivities, S , for the solvolysis of IV in aqueous alcohols (Table 2) reveal that aqueous methanol mixtures the selectivity increases with increasing water con-

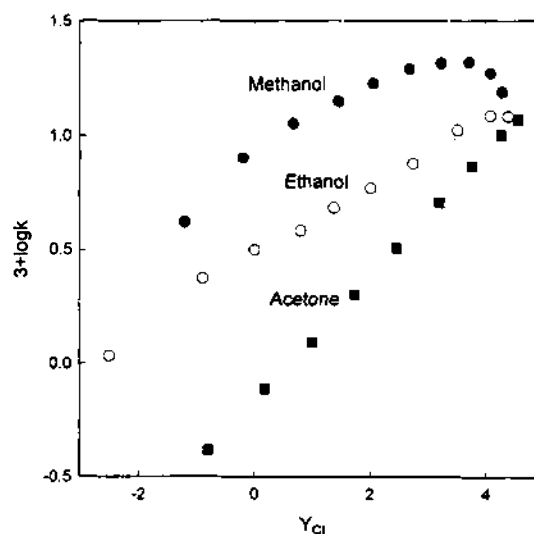


Figure 1. Logarithms of first-order rate constants for solvolyses of *p*-methoxyphenyl chloroformate at 25 °C vs. Y_{Cl} .

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

Vol %	Methanol/Water		Ethanol/Water	
	[Ester]/[Acid]	<i>S</i>	[Ester]/[Acid]	<i>S</i>
90	10.21	2.55	5.803	2.18
80	7.244	4.07	3.687	2.99
70	4.470	4.61	2.526	3.51
60	3.381	5.08	1.873	3.97
50	2.459	5.54	1.675	4.40
40	1.692	5.71	0.944	4.58
30	1.045	5.48	0.535	4.04
20	0.594	5.28	0.246	3.18
10	0.269	5.25	0.100	2.92

^a Determined (eq. 1) by duplicate HPLC analyses of each solvent composition; average deviation $\pm 1\%$. ^b Injected 5 L of a 10% solution of *p*-methoxyphenyl chloroformate in acetonitrile into 5 mL of solvent.

tents, whereas the selectivity exhibits a maximum behavior in aqueous ethanol; thus the reactivity-selectivity principle (RSP)¹⁵ is not obeyed in alcohol and partially obeyed (up to the 40% alcohol solvent) in alcohol-water 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 carbonyl addition-elimination channel in aqueous alcohol media.²² 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 favored 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 30M with a non-linear plot in methanol-water mixtures. In order to examine the non-linear Grunwald-Winstein plot, it is necessary to take into account the stoichiometric solvation effects based on a 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.^{13,14,17,19} Therefore, observed first-order rate constants in alcohol-water mixtures are given by equation (5).

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

Solvent	$\times 10^{-5} \text{ M}^{-2} \text{ s}^{-1}$			
	k_{ww}	k_{aw}	k_{wa}	k_{aa}
Methanol	0.383	2.36	0.116	0.672
Ethanol	0.383	1.95	0.222	0.367

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

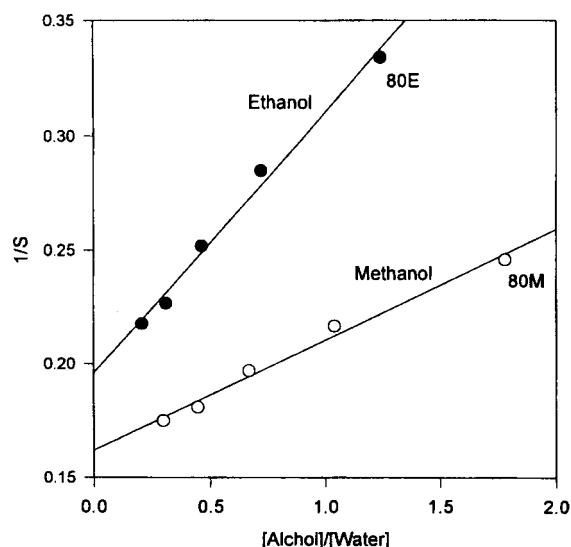
The k_{aa} terms can be calculated from observed first order rate constants in pure alcohol ($k_{aa} = k_{obs}/[\text{ROH}]^2$); similarly k_{ww} can be obtained from the observed first order rate constant in water ($k_{ww} = k_{obs}/[\text{H}_2\text{O}]^2$).^{14,19} In order to determine k_{aw} and 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 (6), and the reciprocal of equation (5) simplifies to equation (7).^{14,19}

$$S = \left(\frac{k_{aw}[\text{alcohol}][\text{water}]}{k_{ww}[\text{water}]^2} \right) \times \frac{[\text{water}]}{[\text{alcohol}]} \quad (6)$$

$$1/S = (k_{ww}/k_{aw})([\text{alcohol}/[\text{water}]] + k_{wa}/k_{aw}) \quad (7)$$

The above derivation of equation (7) 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 the square of the molar concentration of water, and then k_{aw} and k_{wa} were obtained from the intercept 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 $(k_{wa} + k_{aw})[\text{water}][\text{alcohol}]$ terms of equation (5), k_{aw} is indeed greater than k_{wa} in the second term in equation (5), and third-order

**Figure 2.** Correlation of $1/S$ and alcohol/water molar ratio for solvolyses of *p*-methoxyphenyl chloroformate. For methanol-water slope=0.05, intercept=0.16, $r=0.994$. For ethanol-water slope=0.11, intercept=0.19, $r=0.995$.

rate constant for methanol is greater than the one for ethanol.

It appears therefore that the maximum rate behaviour often 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 ($k_{ww}=0.383 \times 10^{-5} \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$) > ethanol ($k_{ww}=0.222 \times 10^{-5} \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$) > methanol ($k_{ww}=0.116 \times 10^{-5} \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$); as this is not accepted order of pK_a value 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 4.

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

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

The maximum difference between calculated and observed rate constant is about 22%, but the one between calculated and observed mol % of ester is only 11% (Table 4). Agreement between calculated and observed results for methanol-water mixtures are reasonably good: in 40% ethanol-water, the difference in the first-order rate constant is only 10% and the difference in the mol % ester is only 1.3%. Such good agreements between calculated and experimental values (Table 4) imply that the use of equation

Table 4. Calculated rate constants, k_{calc} , and contributions of third-order terms to k_{calc} , with calculated percentage ester product for *p*-methoxyphenyl 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	6.49	3.32	2.91	0.143	0.118	91.1	96.0
80M	8.17	2.62	5.18	0.254	0.472	87.9	95.5
70M	10.2	2.01	6.79	0.334	1.06	81.7	86.3
60M	11.5	1.48	7.76	0.382	1.89	77.2	80.3
50M	12.5	1.02	8.09	0.398	2.95	71.1	72.9
40M	13.1	0.660	7.77	0.382	4.25	62.9	64.4
30M	13.3	0.370	6.79	0.334	5.78	51.1	53.8
20M	12.9	0.164	4.71	0.255	7.75	37.3	37.8
10M	12.6	0.0410	2.91	0.144	9.55	21.2	23.4
90E	2.85	0.873	1.67	0.190	0.118	85.3	89.2
80E	4.47	0.690	2.97	0.338	0.472	78.7	81.9
70E	5.92	0.528	3.89	0.443	1.06	71.6	74.6
60E	7.24	0.388	4.45	0.507	1.89	65.2	66.8
50E	8.39	0.270	4.64	0.528	2.95	62.6	58.5
40E	9.38	0.172	4.45	0.507	4.25	48.6	49.3
30E	10.2	0.0970	3.89	0.443	5.78	34.9	39.1
20E	11.1	0.0432	2.97	0.338	7.75	19.7	27.1
10E	11.4	0.0107	1.66	0.190	9.95	9.09	14.6

Table 5. Kinetic solvent isotope effect for solvolyses of *p*-methoxyphenyl chloroformate at 25 °C

Solvent	$k_{SOH} (\text{s}^{-1})$	$k_{SOD} (\text{s}^{-1})$	KSIE
Methanol	4.14×10^{-3}	1.73×10^{-3}	2.29
50% Methanol	1.96×10^{-2}	8.88×10^{-3}	2.21
Water	8.76×10^{-3}	5.24×10^{-3}	1.67

(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_{AN}) 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 value is relatively large, ≥ 1.7 , for a general base catalyzed reaction but is small, 1.2-1.5, for S_N2 reaction.²⁴ For *p*-methoxyphenyl chloroformate, the KSIE is larger than 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 *p*-methoxyphenyl chloroformate solvolyses through a general base catalyzed carbonyl addition-elimination channel in aqueous alcohol solvents mixtures.

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 Büchi Fontavapor 210 and treated using ELGA UHQ PS to obtain specific conductivity of less than 1×10^{-6} mhos/cm. *p*-Methoxyphenyl 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,¹¹ with concentrations of substrate *ca.* 10^{-3} M.

Product Selectivity. The solvolysis products, ester and *p*-nitrophenol, were determined by HPLC analysis described previously,¹³ and the product selectivity, *S*, were calculated from equation (1).

The *S* values calculated from the observed peak area ratios of ester and phenol 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.

Acknowledgment. This work was supported by Korea Science and Engineering Foundation (961-0302-007-2).

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