

## Transition-State Variation in the Solvolyses of *para*-Substituted Phenyl Chloroformates in Alcohol-Water Mixtures

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Solvolyses of *para*-substituted phenyl chloroformates in water, D<sub>2</sub>O, CH<sub>3</sub>OD, 50% D<sub>2</sub>O-CH<sub>3</sub>OD, and in aqueous binary mixtures of acetone, ethanol, methanol are investigated at 25.0 °C. Product selectivities are reported for a wide range of ethanol-water and methanol-water solvent compositions. These data are interpreted using the Grunwald-Winstein relationship, Hammett equation, and quantum mechanical model. Grunwald-Winstein plots of the first-order rate constants for phenyl chloroformates 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. To account for these results, third-order rate constants,  $k_{ww}$ ,  $k_{ow}$ ,  $k_{ow}$  and  $k_{aa}$  were calculated from the observed  $k_{ww}$  and  $k_{aa}$  values together with  $k_{aw}$  and  $k_{wa}$  calculated from the computer fit. The kinetic solvent isotope effects determined in water and methanol are consistent with the proposed mechanism of the general base catalyzed carbonyl addition-elimination for *para*-substituted phenyl chloroformates solvolyses based on mass law and stoichiometric solvation effect studies. This study has shown that the quantum mechanical model predicts transition state variation correctly for  $S_N2$  like  $S_A N$  reaction mechanism of *para*-substituted phenyl chloroformates.

### Introduction

The mechanism of acyl-transfer reactions has been investigated intensively for many years both experimentally<sup>1</sup> and theoretically.<sup>2</sup> The mechanism of most of these reactions are, 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.<sup>3</sup> Recent mechanistic work on the solvolysis of acyl chlorides in alcohol-water mixtures indicated that the reactions proceed by competing mechanisms involving two broad channels:<sup>4,5</sup> electron donation by an aryl group favors a carbocation or an  $S_N2$ - $S_N$  1 process whereas electron withdrawal favours a general base catalyzed process having a lower sensitivity to changes in solvent ionizing power. The aminolysis of substituted benzoyl halides has been extensively studied: Litvinenko and co-workers<sup>6</sup> reported on the reaction of benzoyl chlorides and bromides with anilines in organic solvents. Rogne<sup>7</sup> studied the reaction of benzoyl chlorides with anilines in water. Lee *et al.*<sup>8</sup> investigated the mechanism of the reactions of benzoyl fluorides and chlorides with anilines in methanol and acetonitrile. The results of all these works are reported to be consistent with a concerted displacement mechanism.

In contrast, Song and Jencks<sup>9</sup> reported that the results of the reaction of benzoyl fluorides with primary amines in aqueous solution can be accommodated by an  $S_N2$ -like mechanism but a stepwise addition-elimination mechanism cannot be rigorously excluded. Satchell and co-workers<sup>5</sup> have studied the aminolysis of benzoyl fluorides in non-hydroxylic solvents and found different kinetic behaviour from that found for aqueous solutions. They interpreted their results in terms of a stepwise addition-elimination

mechanism involving rate limiting breakdown of a tetrahedral intermediate.

Nucleophilic substitution reactions of furoyl chloride and thenoyl chloride 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.<sup>10</sup> 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.<sup>11</sup>

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 (eq. 1). If these reactions simply involved competitive attack upon the substrate by either water or alcohol,  $S$  values would be independent of solvent composition.<sup>12</sup> Contrary to trend expected from the reactivity-selectivity principles (RSP),<sup>13</sup>  $S$  values often increase in more aqueous media with the increase in reactivity.<sup>14,15</sup>

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

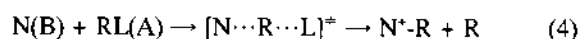
$$1/S = (\text{slope})([\text{alcohol}]/[\text{water}]) + (\text{intercept}) \quad (2)$$

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

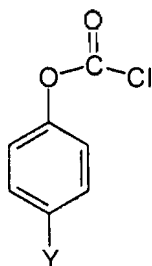
We reported new Eqs. (2) and (3), to account for the solvent dependence of product selectivities in alcohol-water mixtures;<sup>16</sup> these two equations have been successfully applied to the product-forming step of reactions of free cation,<sup>17</sup> to concerted nucleophilic substitution reactions,<sup>10,3a</sup> and also to the general-base catalyzed addition-elimination reactions.<sup>10</sup>

Pross<sup>18</sup> *et al.* and Lee *et al.*,<sup>19</sup> however, solved this difficulty by analyzing the effect of leaving groups on transition-state structure using a simplified quantum

mechanical (QM) model. In the method of Pross *et al.*,<sup>18</sup> transition states are defined in terms of linear combinations of reactant configurations. This model has been shown to predict correctly the effects of nucleophiles (N) and substrates (RL) as well as of leaving groups when applied to a limited family of reactions such as the  $S_N2$  reaction of benzyl derivatives.

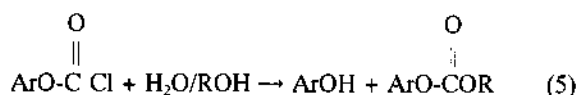


In this work, transition state variation in the solvolysis of phenyl chloroformates (I) in EtOH-H<sub>2</sub>O, MeOH-H<sub>2</sub>O and Acetone-H<sub>2</sub>O mixtures is investigated by applying the Hammett equation, quantum mechanical model and stoichiometric solvation effects.



## Results and Discussion

Solvolyses of aryl chloroformates (eq. 4) in alcohol-water mixtures lead to a phenol (ArOH) and ester an (ArOCOOR).<sup>20</sup> The rate constants for solvolyses of I in methanol-water, ethanol-water and acetone-water mixtures at 25 °C are summarized in Table 1. Products selectivities (S, eqn. 1) are given in Table 2, and solvent kinetic isotope effects are shown in Table 3.



Rate constants (Table 1) increase in the order Acetone-H<sub>2</sub>O < EtOH-H<sub>2</sub>O < MeOH-H<sub>2</sub>O, and show a maximum rate near 30% methanol-water (*p*-OCH<sub>3</sub>), 40% methanol-water (*p*-CH<sub>3</sub>, H), 50% methanol-water (*p*-Cl) and 70% methanol-water (*p*-NO<sub>2</sub>) in aqueous methanol 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 only over twenty-fold range in alcohol-water mixtures, whereas the observed first-order rate constants for thenoyl chloride vary over 7000-fold range<sup>10</sup> which is known to react *via* an  $S_N2$  reaction mechanism. 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 phenyl chloroformates where transition state is not sensitive to solvent ionizing power. These results are very similar to those of solvolytic reactions of *p*-nitrobenzoyl chloride,<sup>3a,21</sup> *p*-nitrobenzenesulfonyl chloride<sup>12,16,22</sup> and furoyl chloride,<sup>10</sup> but they are different from the results of solvolytic reactions of thenoyl chloride and *p*-methoxybenzoyl chloride.

**Table 1.** Rate constants ( $k \times 10^3 \text{ sec}^{-1}$ ) for solvolyses of *para*-substituted phenyl chloroformates in aqueous alcohol and acetone mixtures at 25 °C

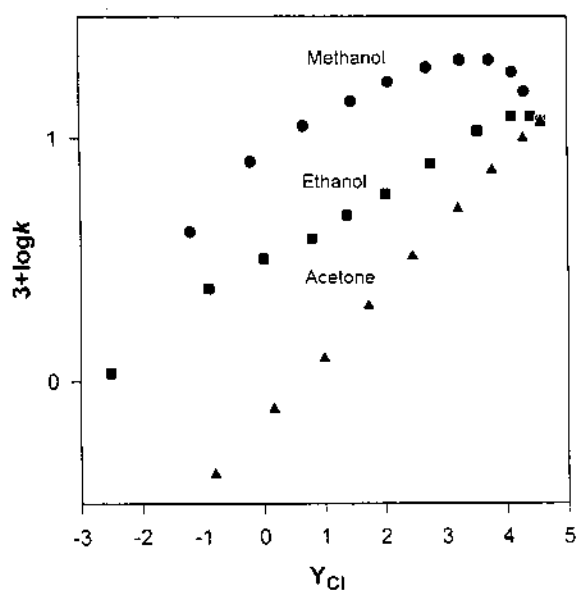
Solvent	v/v%	$k \times 10^3 \text{ sec}^{-1}$				
		<i>p</i> -OCH <sub>3</sub>	<i>p</i> -CH <sub>3</sub>	H	<i>p</i> -Cl	<i>p</i> -NO <sub>2</sub>
MeOH	100	4.10	4.79	7.93	18.1	135
	90	8.00	8.68	12.9	35.2	227
	80	11.3	11.8	16.7	41.7	277
	70	14.2	14.3	19.4	48.1	298
	60	17.0	16.1	22.2	51.7	294
	50	19.6	18.0	24.5	53.1	275
	40	20.7	19.3	24.8	50.8	239
	30	21.0	19.1	24.7	46.7	191
	20	18.8	16.7	22.0	39.1	148
	10	15.6	14.3	17.5	23.6	108
0	8.76	10.7	13.3	22.5	76.6	
EtOH	100	1.08	1.33	2.10	5.39	55.7
	90	2.39	2.71	4.13	12.5	118
	80	3.18	3.40	5.05	15.1	139
	70	3.85	3.94	5.78	16.8	148
	60	4.82	4.57	6.64	18.3	149
	50	5.89	5.43	7.92	20.1	149
	40	7.58	7.05	10.1	23.1	142
	30	10.6	9.47	12.7	26.1	128
	20	12.3	11.2	14.3	26.9	109
	10	12.2	11.3	13.7	24.5	89.2
Acetone	80	0.415	0.453	0.781	2.26	20.5
	70	0.774	0.792	1.25	3.76	31.9
	60	1.24	1.26	1.95	5.59	42.5
	50	2.03	1.98	2.89	7.83	51.7
	40	3.25	3.05	4.28	10.6	61.1
	30	5.10	4.69	6.56	13.9	68.7
	20	7.38	6.77	8.97	17.2	69.6
10	10.1	8.80	11.5	20.1	72.7	

The Grunwald-Winstein plots (equation 6) of the rates in Table 1 for solvolyses of *p*-methoxyphenyl chloroformate are presented in Figure 1 using the solvent ionizing power scale  $Y_{Cl}$ , based on 1-adamantyl chloride.<sup>24</sup> Examination of the figure shows that the plots for the three aqueous mixtures exhibit dispersions into three separate curves with maximum rate constants at near 30M in methanol aqueous mixtures and near 20E in ethanol aqueous mixtures. The other substituents show same trend with maximum rate constants at different solvent compositions, *i.e.*, near 40M (*p*-CH<sub>3</sub>, H), 50M (*p*-Cl) and 60M (*p*-NO<sub>2</sub>) in methanol aqueous mixtures and near 20E (*p*-CH<sub>3</sub>, H), 30E (*p*-Cl) and 40E (*p*-NO<sub>2</sub>) in ethanol aqueous mixtures.

The plot for acetone-water shows a very small  $m$  value,  $m=0.12-0.23$  ( $\geq 0.994$ ). Such a small  $m$  value implies that the solvolysis of phenyl chloroformates in the binary mixtures proceeds by the addition-elimination ( $S_N$ ) or associative  $S_N2$  mechanism channel rather than by an  $S_N1$  channel.

$$\log(k/k_{RX}) = m Y_{Cl} \quad (6)$$

The product selectivities,  $S$  summarized in Table 2, for the solvolysis of I in aqueous alcohols reveal that the selectivity increases with increasing water contents in



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

aqueous methanol mixtures, whereas the selectivity exhibits a maximum behavior in aqueous ethanol; thus the reactivity-selectivity principle (RSP)<sup>13</sup> is not obeyed in alcohol and partially obeyed (up to near 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 I 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 I. These types of selectivity changes with I have been shown to be typical for a general-base catalyzed addition-elimination channel in aqueous alcohol media.<sup>3a,10,12</sup> Moreover the RSP is violated for the solvolysis of I 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 I in the aqueous alcohol mixtures is most likely to be a carbonyl addition-elimination pathway.

**Solvent kinetic isotope effects.** We have determined the kinetic solvent isotope effect (KSIE),  $k_{SOH}/k_{SOD}$ , for the substrate using deuterated water ( $D_2O$ ), 50%  $D_2O$ -

**Table 2.** Products selectivities [*S*, eq(1)] for solvolyses of *para*-substituted phenyl chloroformates in alcohol-water at 25 °C<sup>a</sup>

Solvents % (v/v)	Substrate					
	<i>p</i> -OCH <sub>3</sub>		H		<i>p</i> -NO <sub>2</sub>	
	EtOH/ H <sub>2</sub> O	MeOH/ H <sub>2</sub> O	EtOH/ H <sub>2</sub> O	MeOH/ H <sub>2</sub> O	EtOH/ H <sub>2</sub> O	MeOH/ H <sub>2</sub> O
90	2.18	2.55	1.37	2.28	1.98	3.63
80	2.99	4.07	2.06	3.71	2.57	4.53
70	3.51	4.67	2.69	5.23	3.46	5.38
60	3.97	5.08	3.30	6.00	4.21	6.52
50	4.40	5.54	3.75	7.70	4.79	7.38
40	4.58	5.71	4.02	7.80	5.20	8.24
30	4.04	5.48	4.04	7.80	5.21	8.82
20	3.18	5.28	3.88	7.76	4.86	9.09
10	2.92	5.25	3.56	8.12	4.67	9.89

<sup>a</sup> Determined by at least duplicate HPLC analysis of two independent solutions.

$CH_3OD$ , and methanol-*d* ( $CH_3OD$ ), and the results are presented in Table 3. Previous works indicated that the KSIE values are relatively large,  $\geq 1.7$ , for a general base catalyzed reaction but are small, 1.2-1.5, for a  $S_N2$  reaction.<sup>25</sup> For phenyl chloroformates, the KSIE are  $\geq 1.7$  in methanol, 50% aqueous methanol and water, and KSIEs are similar for methanol and 50% aqueous methanol. These results are again in good agreement with our proposed reaction channel: in aqueous alcohol phenyl chloroformates solvolyse through a general base catalyzed addition-elimination channel. However, the KSIE values ( $\approx 1.7$ ) for water is smaller than those ( $\geq 2.1$ ) for 50% aqueous methanol and methanol. This results indicate that the solvolyses of phenyl chloroformates proceed by a predominantly  $S_N2$  like  $S_N$  pathway with a relatively tight transition state, where bond formation is more progressed in methanol than in water.

**Product-Rate Correlation.** The Grunwald-Winstein plot (Figure 1) for I shows a low response to solvent ionizing power, and shows a maximum reactivity at near 30M-60M 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

**Table 3.** Rate constants ( $s^{-1}$ ) and kinetic solvents isotope effects for solvolyses of *para*-substituted phenyl chloroformates at 25 °C<sup>a</sup>

Z	$k \times 10^3 \text{ sec}^{-1}$								
	Water			50% methanol			methanol		
	H <sub>2</sub> O	D <sub>2</sub> O	KSIE	50MeOH <sup>b</sup>	50MeOD <sup>c</sup>	KSIE	CH <sub>3</sub> OH	CH <sub>3</sub> OD	KSIE
<i>p</i> -OCH <sub>3</sub>	8.76	5.24	1.67	19.6	8.88	2.21	4.14	1.73	2.39
<i>p</i> -CH <sub>3</sub>	10.7	6.41	1.67	18.0	8.22	2.19	4.79	2.04	2.35
H	13.3	7.76	1.71	24.8	11.0	2.25	7.93	2.95	2.35
<i>p</i> -Cl	22.5	13.1	1.72	53.1	22.5	2.36	18.1	8.13	2.34
<i>p</i> -NO <sub>2</sub>	76.6	43.8	1.75	275	134	2.05	135	64.3	2.10

<sup>a</sup> Determined conductometrically in duplicate; average deviation is typically  $\pm 3\%$ . <sup>b</sup> 50% aqueous methanol (v/v). <sup>c</sup> 50% methyl alcohol-D<sub>2</sub> deuterated water (v/v).

information is available because two products are formed. Thus there are four possible third order rate constants in the solvolysis reaction: (i)  $k_{aw}$  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.<sup>3a,10,12,16</sup> Therefore, observed first-order rate constants in alcohol-water mixtures are given by Eq. (7).

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

The  $k_{aa}$  and  $k_{ww}$  terms can be calculated from observed first order rate constants in pure alcohol and water.<sup>3a,12</sup> Bentley *et al.* was determined  $k_{aw}$  and  $k_{wa}$  terms using Eq. (2) and (3).<sup>3a,12</sup> Also,  $S$  can be then given by Eq. (8) from Eqs. (1) and (7).

$$S = \frac{\{(k_{aa}[\text{alcohol}]^2 + k_{aw}[\text{alcohol}][\text{water}]) / k_{ww}[\text{alcohol}][\text{water}]\} \times \{[\text{water}]/[\text{alcohol}]\}}{1 + \frac{k_{wa}}{k_{ww}} \times \frac{[\text{alcohol}]}{[\text{water}]}} \quad (8)$$

$S$  is also given by Eq. (9) which can be rearranged to Eq. (8).

$$S = \frac{k_{aa}[\text{alcohol}]^2 + k_{aw}[\text{alcohol}][\text{water}]}{k_{ww}[\text{water}][\text{alcohol}] + [\text{water}]^2} \times \frac{[\text{water}]}{[\text{alcohol}]} = \frac{\frac{k_{aa}}{k_{ww}} \times \frac{[\text{alcohol}]}{[\text{water}]} + \frac{k_{aw}}{k_{ww}}}{1 + \frac{k_{wa}}{k_{ww}} \times \frac{[\text{alcohol}]}{[\text{water}]}} \quad (9)$$

A computer fit using Eq. (9) without any approximations, gives very similar results to those based on  $1/S$  Eq. (2) for solvolysis of *p*-methoxyphenyl chloroformate and phenyl chloroformate (see Table 4).<sup>26</sup> However, computer fit, without approximations, due to neglected terms, gives very similar results to those based on  $S$  Eq. (3) for solvolysis of *p*-nitrophenyl chloroformate<sup>27</sup> (see Table 4).

The third-order rate constants,  $k_{aw}$  and  $k_{wa}$ , in which alcohol acts as nucleophile are larger than  $k_{wa}$  and  $k_{ww}$  terms in which water acts as nucleophile (Table 4). In  $(k_{aw}+k_{wa})[\text{water}][\text{alcohol}]$  terms of Eq. (7),  $k_{aw}$  is indeed greater than  $k_{wa}$  in the second term in Eq. (7), and third order rate constant for methanol is greater than that for ethanol.

We note that the largest catalytic rate constant is  $k_{aw}$  which is followed by  $k_{aa}$ , i.e., alcohol is a stronger nucleophile than water, in contrast water is a better catalyst than alcohol. For methanol-water system,  $k_{aw}/k_{ww} \cong 6-10$  and  $k_{aa}/k_{ww} \cong 2-9$ , and the ratios increase as the *para*-substituent (Z) becomes a stronger electron acceptor. Interestingly, parallel changes are found with the KSIEs,  $k_{SOH}/k_{SOD}$ , which are greater for the reactions in 50% MeOH and MeOH than in water, and increase slightly for a stronger acceptor Y. These trends are in accord with a greater degree of bond formation with alcohol as a nucleophile and with a stronger acceptor (Y) substituent.

It appears therefore that the maximum rate behaviour often observed<sup>21,22</sup> in the solvolysis of methanol mixtures is due to exceptionally greater contribution of  $k_{aw}$  term (Figure 1).

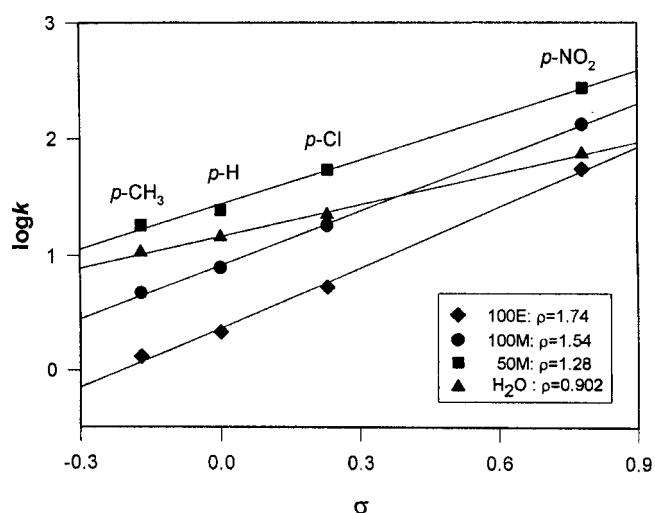
**Substituent Effects.** The Hammett plots for the variation of substituents Y on the benzene ring show good

**Table 4.** The third-order rate constants,  $k_{ww}$ ,  $k_{aw}$ ,  $k_{wa}$  and  $k_{aa}$  for *para*-substituted phenyl chloroformates solvolyses in alcohol-water mixtures

		$k/10^{-5} \text{ M}^{-2} \text{ s}^{-1}$				
Solvents	Plot	$k_{ww}$	$k_{aw}$	$k_{wa}$	$k_{aa}$	
<i>p</i> -OCH <sub>3</sub>	MeOH	1/S <sup>a</sup>	0.383	2.36	0.116	0.672
		Computer <sup>c</sup>	0.383	3.97	0.349	0.672
	EtOH	1/S <sup>a</sup>	0.383	1.95	0.222	0.367
		Computer <sup>c</sup>	0.383	2.04	0.437	0.367
H	MeOH	1/S <sup>a</sup>	0.432	3.97	0.343	1.30
		Computer <sup>c</sup>	0.432	4.77	0.808	1.30
	EtOH	1/S <sup>a</sup>	0.432	2.18	0.508	0.745
		Computer <sup>c</sup>	0.432	2.04	0.368	0.745
<i>p</i> -NO <sub>2</sub>		1/S <sup>b</sup>	2.49	24.9	1.94	22.1
	MeOH	S <sup>b</sup>	2.49	37.0	8.67	22.1
		Computer <sup>c</sup>	2.49	44.1	8.59	22.1
		1/S <sup>b</sup>	2.49	16.5	3.17	18.9
	EtOH	S <sup>b</sup>	2.49	35.5	15.9	18.9
		Computer <sup>c</sup>	2.49	44.0	16.4	18.9

<sup>a</sup> Reference 26 (a), (b). <sup>b</sup> Reference 27. <sup>c</sup> Computer fitting (using the program Sigma Plot) of data for 80-97% methanol-water and 83-97% ethanol-water to show similarity with results from S Plots.

linearities ( $r \geq 0.998$ ) with large positive slopes,  $\rho_Y = 0.90-1.7$  in various alcohol-water solvents at 25 °C (Figure 2). Relatively large  $\rho_Y$  values compared to  $\rho_Y$  of 0.4-1.5 for benzoyl chloride<sup>28</sup> suggest that bond formation tends to be advanced in the transition state of the solvolysis of phenyl chloroformates. If we assume virtually separate  $\rho$  values for bond formation ( $\rho_Y > 0$ ) and bond breaking ( $\rho_Y < 0$ ),<sup>29</sup> positive  $\rho_Y$  values obtained suggest predominance of the bond-formation in transition state. However, an increase of  $\rho_Y$  from pure water to methanol (0.90→1.50) implies a slightly increase in bond formation in the transition state. The transition state is therefore more product-like (asymmetric TS,  $[\text{N}^{\delta+} \cdots \text{C} \cdots \text{L}^{\delta-}]^\ddagger$ ), where bond formation and bond breaking are more progressed in the transition state. This is



**Figure 2.** Hammett plots for the solvolysis of *p*-substituted phenyl chloroformates in alcohol-water at 25 °C.

again in line with a relatively constant transition state tightness, i.e.,  $r_{\text{NL}}^{\ddagger} \cong \text{constant}$ , since a stronger nucleophile (EtOH) should lead to smaller  $r_{\text{NC}}^{\ddagger}$  with a larger  $r_{\text{CL}}^{\ddagger}$ , whereas a weaker nucleophile (H<sub>2</sub>O) lead to a larger  $r_{\text{NC}}^{\ddagger}$  with smaller  $r_{\text{CL}}^{\ddagger}$ , with approximately constant total tightness, i.e.,  $r_{\text{NL}}^{\ddagger} = r_{\text{NC}}^{\ddagger} + r_{\text{CL}}^{\ddagger} \cong \text{constant}$ .<sup>30</sup>

**Application of the QM model.** In general four types of interactions are involved in the perturbation of a system, A, by another B: electrostatic, polarization, exchange repulsion, and charge transfer interactions.<sup>31</sup> The former two are long range whereas the latter two are short range components of inter-system interactions. Pross and Shaik<sup>18</sup> considered only the two, polarization and charge transfer, in their quantum mechanical description of transition state structure. They expressed the various states of the reaction complex as a linear combination of the three configurations; ground BA, polarized BA\* and charge transferred B\*A configurations. In a nucleophilic substitution reaction, B may be a nucleophile N and A a substrate RX with a leaving group X. Analyses of bonding characteristics and the relative contribution to the structure of the transition state of the three key configurations allow us to predict how the transition state will change as a result of a given perturbation. Examination of the structural implications associated with each configuration using molecular orbital (MO) and valence bond (VB) description has led Pross and Shaik to a set of simple rules for prediction the structural effects of the three configurations on the reaction complex as presented in Table 5. Let us now apply the QM model based on these rules of structural effects. Application of the model to the predictions of effects of the nucleophile and substrate is entirely analogous to that for the benzyl and sulfonyl system.<sup>28,23</sup> An increase in the nucleophilic strength (ethanol) will increase electron donating ability of the nucleophile and hence increase the contribution of the B\*A<sup>-</sup> configuration to the transition state. Reference to Table 5 suggests that as a consequence both nucleophile-substrate (N-C) bond formation and substrate-leaving group (C-L) bond should increase. Our experimental results are consistent with this prediction since larger  $\rho_{\text{Y}}$  values clearly indicated a shorter N-C bond together with a longer C-L bond (keeping approximately constant  $r_{\text{NL}}^{\ddagger}$ ) as the nucleophilicity of solvents is increased in ethanol. Thus we conclude that the QM model predicts transition state variation correctly for S<sub>N</sub>2 like S<sub>N</sub>N reaction mechanism of phenyl chloroformates.

### Experimental

**Materials.** Methanol, ethanol, and acetone were Merck GR grade (<0.1% H<sub>2</sub>O), and D<sub>2</sub>O and CH<sub>3</sub>OD were from Aldrich (99.9% D). Distilled water was redistilled with

**Table 5.** The structural effects of the key configurations on the reaction complex, [N...R...X]

Configuration	Structural effect	
	N-R	R-X
BA	loose	tight
B*A	tight	loose
BA*	loose	loose

Buchi Fontavapor 210 and treated using ELGA UHQ PS to obtain specific conductivity of less than  $1 \times 10^{-6}$  mhos/cm. Phenyl chloroformate was Aldrich GR grade (>99.8%).

**Rate Measurement.** The rates were measured conductometrically at 25 ( $\pm 0.03$ ) °C at least in duplicate as described previously,<sup>14</sup> with substrate concentrations of substrate ca.  $10^{-3}$  M.

**Product Selectivity.** The solvolysis products, ester and acid, were determined by HPLC analysis described previously,<sup>16</sup> and the product selectivity, *S*, were calculated from Eq. (1).

The *S* values calculated from the observed peak area ratios of ester and acid gave *S*<sub>obs</sub> 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 60-70% methanol-water mixture and flow rate was adjusted to 1ml/min. The HPLC system used was Hewlett-Packard 1050 Series with 250×4 mm Spherisorb ODS reversed phase column.

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## Unusual Fluorescence Spectroscopic Properties of 9-Anthrylethylene Derivatives: Photoisomerization

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The fluorescence spectroscopic properties of both *trans* and *cis* forms of 9-anthrylethylene derivatives such as 9-AnthCH=CHCO<sub>2</sub>CH<sub>3</sub> [I] and 9-AnthCH=CHCN [II] as well as 9-AnthCH=CHCH<sub>2</sub>O<sub>2</sub>CCH<sub>3</sub> [III] and 9-AnthCH=CHCH<sub>2</sub>OH [IV] have been measured in various solvents. In nonpolar solvent, the *trans*-I and *trans*-II show dual emission spectral bands at 340 nm and 460 nm when exciting with 270 nm while the other *trans* derivatives show single emission band at 430 or 460 nm. The dual emissions exhibit different excitation spectra, indicating that two emissive states are different from each other. It is interesting to note that the 340 nm emission of both *trans*-I and *trans*-II is enhanced at the expense of the drastic quenching of the 460 nm emission as the solvent polarity increases. The dual emissions are also observed for both *cis*-I and *cis*-II. The solvent dependence of the fluorescence decay times and quantum yields can be correlated with the solvent and excitation wavelength dependences of the *trans*→*cis* photoisomerization quantum yields. These results indicate that the 340 nm emission is originated from the S<sub>2</sub> state of the *cis*-form, and the S<sub>1</sub> state is the only singlet excited state presenting a large CT (charge transfer) character to facilitate the photoisomerization.

### Introduction

The mechanism and the potential energy surfaces of *cis*-

*trans* isomerization of olefines have been actively investigated since the extensive works for the sensitized isomerization of stilbenes by Hammond, Saltiel, and co-workers in 1960s.<sup>1-6</sup> As a result it was revealed that stilbene undergoes mutual isomerization between *cis* and *trans*

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