

# Solvolysis of *N,N*-diphenylcarbamoyl chloride revisited. Extended positive charge delocalization on phenyl rings in the transition state and possible contribution of non-canonical resonance structure

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**ABSTRACT:** Extended charge delocalization to phenyl rings in the cationic transition state in the solvolysis of *N,N*-diphenylcarbamoyl chloride (**2**) was suggested from the observation of an excellent linear correlation for the dual-parameter Grunwald–Winstein equation,  $\log(k/k_0) = mY_{\text{xBnCl}} + lN_{\text{OTs}}$ , and also the splitting of  $\log k - Y_{\text{xBnCl}}$  plots into two lines, one for nucleophilic solvents (aqueous acetone, ethanol and methanol) and the other for poorly nucleophilic solvents (trifluoroethanol–ethanol). Quantum chemical calculations of the charge distributions in **2** and in the acylium ion **3** were performed by using a basis set (RHF/6–31G\*) for a Hartree–Fock approximation on Mulliken population analysis, electrostatic potential analysis and natural population analysis, and using basis sets (SVWN, BP and pBP) for density functional models. Similar results were obtained with different approaches to indicate the partial positive charge developed on both phenyl rings in **3**. A possible contribution of a non-canonical resonance structure was proposed. Copyright © 2000 John Wiley & Sons, Ltd.

**KEYWORDS:** solvolysis; *N,N*-diphenylcarbamoyl chloride; correlation analysis; *ab initio* calculation; atomic charges; non-canonical resonance

## INTRODUCTION

The original Grunwald–Winstein equation [Eqn. (1)]<sup>1</sup> and the extended form [Eqn. (2)]<sup>2</sup> have long been considered useful tools for the mechanistic study of solvolytic reactions in a large variety of systems. A number of scales of solvent ionizing power  $Y_x$  have been developed to accommodate different aliphatic and alicyclic substrates containing a distinct leaving group X.<sup>3</sup> On the other hand, we have demonstrated the necessity of establishing  $Y_{\text{BnX}}$  scales for benzylic solvolyses.<sup>4</sup> More recently, new  $Y_{\text{xBnX}}$ <sup>5</sup> scales (for bromides,<sup>5a</sup> chlorides<sup>5b</sup> and *p*-nitrobenzoates<sup>5c</sup>) were found to be necessary in correlating solvolytic reactivity for substrates with extended charge delocalization in the cationic transition state. For examples, the behavior of both 9-fluorenyl and benzhydryl chlorides<sup>5b</sup> in solvolysis could be satisfactorily rationalized only from the use of  $Y_{\text{xBnCl}}$ .<sup>5b</sup> A non-limiting  $S_{\text{N}}1$  mechanism with significant nucleophilic solvent intervention was realized

in the solvolysis of 9-fluorenyl chloride (**1**) from an excellent linear relationship (correlation coefficient  $R = 0.995$ ) using the dual-parameter Eqn. (3).<sup>5b</sup> An exploration of extending the application of  $Y_{\text{xBnCl}}$  scale to other system would then be desirable.

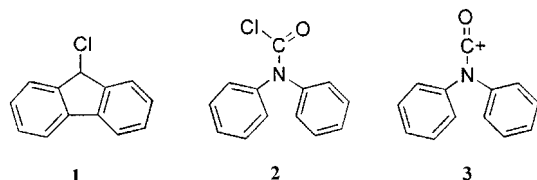
$$\log(k/k_0) = mY \quad (1)$$

$$\log(k/k_0) = mY + lN \quad (2)$$

$$\log(k/k_0) = mY_{\text{xBnCl}} + lN_{\text{OTs}} \quad (3)$$

Recently, the solvolysis of *N,N*-diphenylcarbamoyl chlorides (**2**) in a variety of solvents was reported.<sup>7</sup> The analysis using Eqn. (2) against  $Y_{\text{Cl}}$  and  $N_{\text{T}}$  and a three-term equation [Eqn. (4)]<sup>8</sup> suggested that nucleophilic solvent participation accompanied solvolysis, based on the observation of moderate correlation with  $R \approx 0.97$ .<sup>7</sup> Therefore, a confirmation seems to be needed. We report here our findings on the solvolysis of **2**, in which not only was the intervention of nucleophilic solvents confirmed but also a delocalized cationic transition state could be deduced from the correlation with the dual-parameter Eqn. (3). Moreover, *ab initio* calculations of the positive charge distribution in the corresponding acylium ion (**3**)

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indicated a spreading of charge over both phenyl rings, and therefore implied the possible contribution of certain kind of non-canonical resonance.

$$\log(k/k_0) = mY_{\text{Cl}} + lN_{\text{T}} + hI \quad (4)$$

## RESULTS

Hydrolysis of **2** in buffer solutions was first examined by Johnson and Giron.<sup>9</sup> A recent kinetic study by D'souza, *et al.*<sup>7</sup> was performed on a 98% pure sample in various solvents with concentrations of 0.003–0.007 M at 62.5 °C. However, we found that the carbamoyl chloride **2** was actually not completely soluble in binary solvents containing more than 40–50% (v/v) of water, even at a concentration of about  $10^{-4}$  M. Moreover, the colorless solution of a commercial sample of **2** (Aldrich)<sup>7</sup> in a conductivity cell or in a sealed ampoule turned pink to light purple during the course of solvolysis at 60 °C or at higher temperature if air had not been carefully removed from the solvent. Consequently, the commercial chemical was recrystallized (m.p. 82.5–84 °C; lit.<sup>10</sup> 82–84 °C), and the purified **1** was dissolved in solvents containing degassed water and/or organic solvents freshly distilled under nitrogen. Kinetic measurements were performed by using a conductimetric (50–85 °C) or potentiometric (90–110 °C) method. Even if precautions were taken, the reproducibility was poor at temperatures higher than 110 °C. Reliable rate constants, measured or extrapolated, are listed in Table 1. The data for 50E, 40A, 60M and 80T20E at 62.5 °C are in line with the literature values<sup>7</sup> within a 5–15% deviation. In the case of 100T, our result ( $4.50 \times 10^{-5} \text{ s}^{-1}$ ) is close to that in the literature for 97% trifluoroethanol ( $4.79 \times 10^{-5} \text{ s}^{-1}$ ) but not for trifluoroethanol ( $1.81 \times 10^{-5} \text{ s}^{-1}$ ).<sup>7</sup> The products, amine and ester, were known to retain the original skeleton.<sup>7</sup>

Regression analyses of  $\log k$  values at the temperature of 50 °C was used for regression analyses because at this temperature at least one rate constant (60M) could be measured directly against  $Y_{\text{Cl}}$ ,<sup>3</sup>  $Y_{\text{BnCl}}$ <sup>11</sup> or  $Y_{\text{xBnCl}}$ <sup>5b</sup> ( $Y_{\text{xBnCl}}$  for 70M was determined as 1.57 in this work) using the single-parameter Eqn. (1) and against a combination of  $Y$  and  $N$  ( $N_{\text{T}}$ <sup>12</sup> or  $N_{\text{OTs}}$ <sup>13</sup>) using the dual-parameter Eqn. (2) were carried out. The results are shown in Table 2. No analysis with Eqn. (4) was performed, as it would be meaningless to treat a three-parameter regression with less than 10 variables.

**Table 1.** Rate constants for the solvolysis of *N,N*-diphenylcarbamoyl chloride (**2**)

Solvent <sup>a</sup>	Temperature (°C)	$k$ (s <sup>-1</sup> )
80E	110	$4.32 \times 10^{-4}$
	95	$1.12 \times 10^{-4}$
	85	$4.24 \times 10^{-5}$
	50	$9.02 \times 10^{-7b}$
60E	85	$2.09 \times 10^{-4}$
	75	$8.64 \times 10^{-5}$
	62.5	$1.79 \times 10^{-5}$
	50	$4.10 \times 10^{-6b}$
50E	85	$4.26 \times 10^{-4}$
	75	$1.92 \times 10^{-4}$
	62.5	$3.85 \times 10^{-5}$
	50	$9.24 \times 10^{-6b}$
60A	105	$4.34 \times 10^{-4}$
	90	$1.03 \times 10^{-4}$
	80	$3.63 \times 10^{-5}$
	50	$1.12 \times 10^{-6b}$
50A	75	$7.02 \times 10^{-5}$
	62.5	$1.51 \times 10^{-5}$
	50	$2.88 \times 10^{-6b}$
40A	75	$1.53 \times 10^{-4}$
	70	$8.88 \times 10^{-5}$
	62.5	$3.95 \times 10^{-5}$
	50	$9.18 \times 10^{-6b}$
70M	75	$1.21 \times 10^{-4}$
	62.5	$3.10 \times 10^{-5}$
	50	$7.15 \times 10^{-6}$
60M	62.5	$5.26 \times 10^{-5}$
	50	$1.25 \times 10^{-5}$
	100T	75
62.5		$4.50 \times 10^{-5}$
50		$9.59 \times 10^{-6b}$
80T20E	75	$7.06 \times 10^{-5}$
	62.5	$1.81 \times 10^{-5}$
	50	$4.18 \times 10^{-6b}$

<sup>a</sup> E = ethanol; M = methanol; A = acetone; T = 2,2,2-trifluoroethanol. Numbers denote percentage of volume.

<sup>b</sup> From extrapolations of data at higher temperatures.

**Table 2.** Correlation analyses of  $\log k$  for **2** against  $Y$  and  $N$  at 50 °C

Parameter <sup>a</sup>	$n$	$R$	$m$ (s.d.)	$l$ (s.d.)
$Y_{\text{Cl}}$	10	0.864	0.430 (0.089)	
	8 <sup>b</sup>	0.879	0.493 (0.109)	
$Y_{\text{BnCl}}$	10	0.858	0.326 (0.069)	
	8 <sup>b</sup>	0.976	0.492 (0.045)	
$Y_{\text{xBnCl}}$	9	0.868	0.350 (0.076)	
	7 <sup>b</sup>	0.995	0.562 (0.025)	
$Y_{\text{Cl}}, N_{\text{OTs}}$	9	0.932	0.522 (0.088)	0.115 (0.073)
$Y_{\text{BnCl}}, N_{\text{OTs}}$	9	0.987	0.506 (0.035)	0.272 (0.038)
$Y_{\text{BnCl}}, N_{\text{T}}$	8	0.973	0.505 (0.062)	0.216 (0.058)
$Y_{\text{xBnCl}}, N_{\text{OTs}}$	8	0.992	0.555 (0.035)	0.275 (0.034)
$Y_{\text{xBnCl}}, N_{\text{T}}$	7	0.972	0.544 (0.082)	0.211 (0.069)

<sup>a</sup>  $Y_{\text{xBnCl}}$  value for 40A,  $N_{\text{OTs}}$  value for 70M, or  $N_{\text{T}}$  value for 70M or 50A is not available.

<sup>b</sup> Nucleophilic solvents only.

**Table 3.** Charge distribution by Hartree–Fock approximations at the 6–31G\* level

		Ph <sub>2</sub> NCOCI	Ph <sub>2</sub> NCO <sup>+</sup>	ΔCharge
N	Mulliken population	−0.786	−0.720	0.066
	Electrostatic potential	−0.070	−0.117	−0.047
	Natural population	−0.607	−0.560	0.047
Carbonyl C	Mulliken population	0.636	0.983	0.347
	Electrostatic potential	0.491	0.636	0.245
	Natural population	0.868	1.228	0.360
Carbonyl O	Mulliken population	−0.518	−0.299	0.219
	Electrostatic potential	−0.484	−0.194	0.290
	Natural population	−0.660	−0.421	0.239
Ring-1	Mulliken population	0.362	0.519	0.157
	Electrostatic potential	0.066	0.336	0.270
	Natural population	0.252	0.376	0.124
Ring-2	Mulliken population	0.363	0.517	0.154
	Electrostatic potential	0.155	0.339	0.184
	Natural population	0.259	0.377	0.118

*Ab initio* calculations on the charge distribution in **2** and **3** were performed both by a Hartree–Fock approximation<sup>14</sup> with the 6–31G\* basis set and by density functional models<sup>15</sup> with SVWN, BP and pBP functionals including three basis sets, DN, DN\* and DN\*\* (for definitions of these terms, see ref. 16), both using the Spartan version 5.1.2 program. The two phenyl rings are non-equivalent. Neither **2** nor **3** has any symmetry element. The charge distributions from Hartree–Fock approximations are summarized in Table 3. The results of Mulliken population analysis<sup>17</sup> and of electrostatic potential analysis<sup>18</sup> from DFT methods are given in Tables 4 and 5, respectively.

Representative results of Mulliken population analysis<sup>17</sup> for **2** and **3** are given in Scheme 1 and those of electrostatic potential analysis<sup>18</sup> are given in Scheme 2.

In both cases the charges on hydrogen have been summed into attached carbons.

## DISCUSSION

The solvent ionizing power *Y* is the most often used solvent polarity scale developed empirically for studying solvolytic reactivity and mechanisms.<sup>19</sup> It is generally considered to take account of effects due to specific solvation of the leaving group X.<sup>3</sup> Recently, the Brønsted base-type solvation toward the cationic moiety was suggested to play an important role,<sup>20</sup> although later work failed to evaluate the importance of such an interaction with the tertiary cumyl cation<sup>21</sup> as was stated.<sup>22</sup> On the other hand, the inapplicability of *Y*<sub>Cl</sub> to

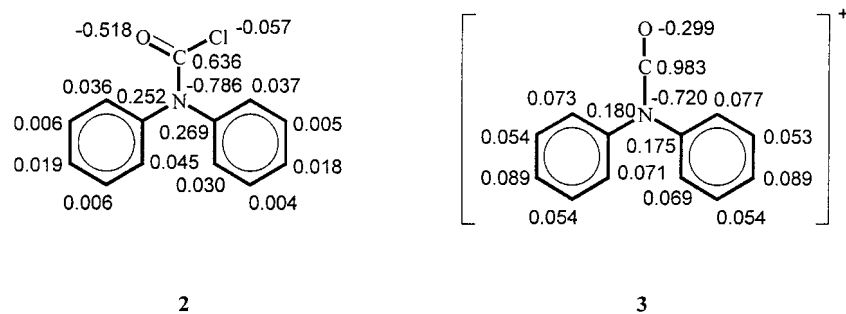
**Table 4.** Mulliken population analysis of charge distribution by density functional methods

		Ph <sub>2</sub> NCOCI	Ph <sub>2</sub> NCO <sup>+</sup>	ΔCharge
N	(SVWN/DN**)	−0.356	−0.348	0.008
	(BP/DN**)	−0.412	−0.388	0.024
	(pBP/DN*)	−0.398	−0.383	0.015
	(pBP/DN**)	−0.382	−0.368	0.014
Carbonyl C	(SVWN/DN**)	0.250	0.515	0.265
	(BP/DN**)	0.311	0.546	0.235
	(pBP/DN*)	0.266	0.527	0.261
	(pBP/DN**)	0.266	0.526	0.260
Carbonyl O	(SVWN/DN**)	−0.295	−0.059	0.236
	(BP/DN**)	−0.302	−0.073	0.229
	(pBP/DN*)	−0.290	−0.065	0.225
	(pBP/DN**)	−0.289	−0.066	0.223
Ring-1	(SVWN/DN**)	0.235	0.455	0.220
	(BP/DN**)	0.260	0.461	0.201
	(pBP/DN*)	0.257	0.454	0.193
	(pBP/DN**)	0.246	0.463	0.217
Ring-2	(SVWN/DN**)	0.251	0.445	0.194
	(BP/DN**)	0.267	0.457	0.190
	(pBP/DN*)	0.268	0.461	0.193
	(pBP/DN**)	0.257	0.453	0.196

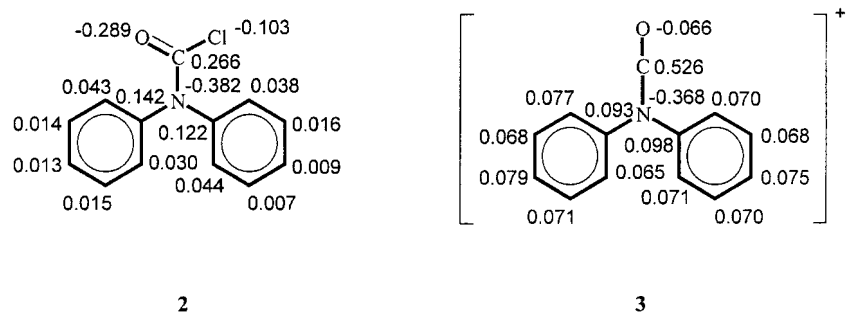
**Table 5.** Electrostatic potential analysis of charge distribution by density functional methods

		Ph <sub>2</sub> NCOCl	Ph <sub>2</sub> NCO <sup>+</sup>	ΔCharge
N	(SVWN/DN**)	-0.022	-0.222	-0.200
	(BP/DN**)	-0.046	-0.199	-0.153
	(pBP/DN*)	-0.090	-0.250	-0.160
	(pBP/DN**)	-0.054	-0.221	-0.167
Carbonyl C	(SVWN/DN**)	0.339	0.511	0.172
	(BP/DN**)	0.352	0.509	0.157
	(pBP/DN*)	0.350	0.515	0.165
	(pBP/DN**)	0.334	0.511	0.177
Carbonyl O	(SVWN/DN**)	-0.408	-0.112	0.296
	(BP/DN**)	-0.397	-0.115	0.282
	(pBP/DN*)	-0.396	-0.112	0.284
	(pBP/DN**)	-0.391	-0.114	0.277
Ring-1	(SVWN/DN**)	0.047	0.412	0.335
	(BP/DN**)	0.066	0.410	0.344
	(pBP/DN*)	0.084	0.423	0.339
	(pBP/DN**)	0.070	0.415	0.345
Ring-2	(SVWN/DN**)	0.168	0.410	0.242
	(BP/DN**)	0.173	0.410	0.237
	(pBP/DN*)	0.190	0.423	0.233
	(pBP/DN**)	0.179	0.412	0.233

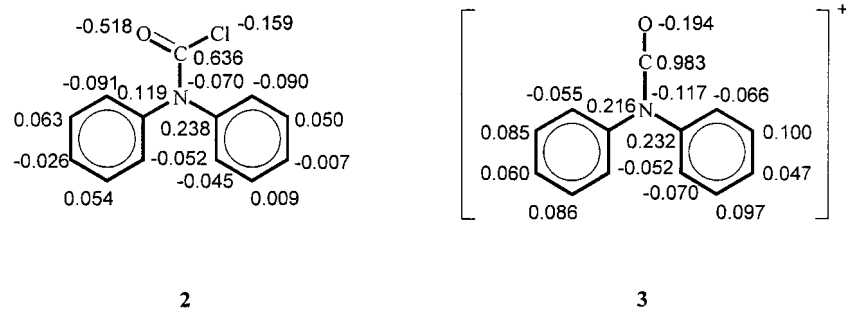
Mulliken population analysis (RHF/6-31G\*)



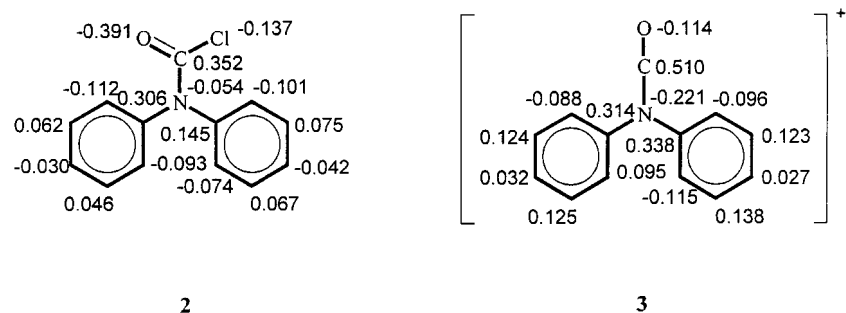
Mulliken population analysis (pBP/DN\*\*)

**Scheme 1**

## Electrostatic potential analysis (RHF/6-31G\*)



## Electrostatic potential analysis (pBP/DN\*\*)



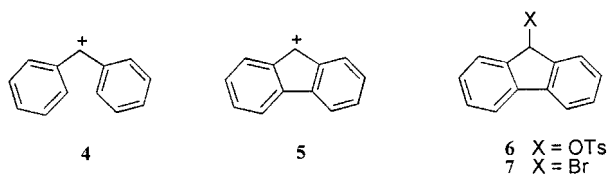
## Scheme 2

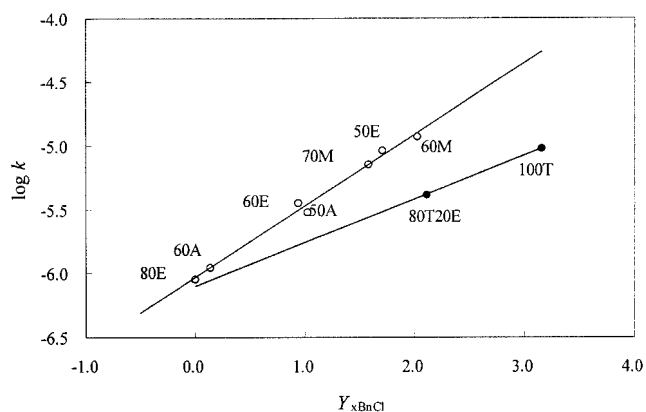
the solvolysis of tertiary benzylic chlorides owing to variable interaction of the solvent with localized and delocalized cationic transition states was not recognized until 1990.<sup>23</sup> New  $Y_{\text{BnX}}$  scales were then established.<sup>4</sup> However, the solvolysis of naphthylmethyl and benzhydryl substrates were found to act differently from the benzylic analogues,<sup>24</sup> and consequently, the necessity for developing  $Y_{\text{xBnX}}$  scales for solvolysis transition states with extended charge delocalization was realized.<sup>5</sup> Its advantage has been demonstrated by pointing out the resemblance of charge distribution between benzhydryl (**4**) and 9-fluorenyl (**5**) cations.<sup>6,25</sup> Moreover, the anti-aromatic character in the solvolytic transition state for **5** (for recent work, see Allen *et al.*<sup>26</sup>) was questioned based on the observation of a linear  $\log k - Y_{\text{xBnOTs}}$  plot for 9-fluorenyl tosylate (**6**) and  $\log k - (Y_{\text{xBnBr}}$  and  $N_{\text{OTs}})$  plot for

9-fluorenyl bromide (**7**). (An excellent linear relationship ( $R = 0.993$ ) was obtained for **7** from Eqn. (3) using  $Y_{\text{xBnBr}}$  and  $N_{\text{OTs}}$ .<sup>27</sup>)

To explore the application of correlation analysis using  $Y_{\text{xBnX}}$  parameters, *N,N*-diphenylcarbamoyl chloride (**2**) was the choice because an  $S_{\text{N}}1$  process for solvolysis had been proposed.<sup>28</sup> A preliminary analysis of the rate data at 62.5 °C in the literature<sup>7</sup> using Eqn. (3) yielded a fairly good linear correlation with  $R \approx 0.98$ . However, the unusual large difference between  $k_{100\text{T}}$  ( $1.81 \times 10^{-5} \text{ s}^{-1}$ ) and  $k_{97\text{T}}$  ( $4.79 \times 10^{-5} \text{ s}^{-1}$ ) cast a doubt on the accuracy of measurement. Indeed, in an independent study we observed that a colorless solution of a commercial sample of **2** (98% pure) became colored during the course of kinetic measurements at 60 °C. A purified sample and degassed solvents should therefore be used to avoid coloring. Furthermore, **2** was found to be not completely soluble in an aqueous solvent mixture containing high percentage of water. Therefore, a purified sample and degassed solvents were employed for the re-determination of rate constants. Owing to the experimental difficulty (see Results), reliable rate constants in only 10 different solvents were obtained.

From Table 2, it is obvious that only the use of a dual-





**Figure 1.** Correlation of  $\log k$  for **2** against  $Y_{x\text{BnCl}}$  at 50.0°C

parameter equation with  $Y_{x\text{BnCl}}$  and  $N_{\text{OTs}}$  gives a good linear relationship ( $R = 0.992$ ). Single-parameter regression [Eqn. (1)] with  $Y_{\text{Cl}}$ ,  $Y_{\text{BnCl}}$  or  $Y_{x\text{BnCl}}$  resulted in poor correlations ( $R < 0.9$ ) with dispersed points for all solvents, whereas separated lines were given for nucleophilic solvents (aqueous acetone, ethanol and methanol) and for poorly nucleophilic trifluoroethanol-ethanol solvents only if the  $Y_{x\text{BnCl}}$  scale was employed (Fig. 1). Downward deviations of the points for poorly nucleophilic solvents have long been considered an indication of nucleophilic solvent intervention in solvolysis.<sup>29</sup> The combination of an excellent linear correlation for  $\log k$  vs  $Y_{x\text{BnCl}}$  and  $N_{\text{OTs}}$  [Eqn. (3)] and the splitting of  $\log k$ - $Y_{x\text{BnCl}}$  plots into two lines clearly indicated a non-limiting mechanism with nucleophilic solvent assistance for the solvolysis of **2**, as has already been found in many cases, such as the recent example of 4-methoxybenzyl bromide and chloride.<sup>30</sup> The low  $m$  value (0.55) and significant  $l$  value (0.27) are in harmony with the unhindered reaction center, carbonyl carbon, being susceptible to nucleophilic solvent attack. Besides, it had already been found in many cases (for a recent example, see Liu *et al.*<sup>5b</sup>) that the use of  $N_{\text{OTs}}$ , rather than  $N_{\text{T}}$ , gave a better correlation for substrates with an anionic leaving group (in an analogous system containing a neutral leaving group, *N,N*-diphenylcarbamoylpyridium chloride,<sup>31</sup> however, no good correlation with  $N_{\text{T}}$  or  $N_{\text{OTs}}$  was found). The present work provides an additional example in this respect.

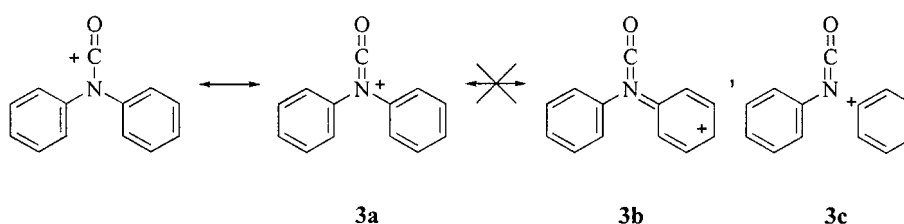
Although a good linear correlation ( $R = 0.987$ ) for

$\log k$  vs  $Y_{\text{BnCl}}$  and  $N_{\text{OTs}}$  was also realized (Table 2), less satisfactory linearity ( $R = 0.976$ ) for  $\log k$  vs  $Y_{\text{BnCl}}$  plots with eight data points in nucleophilic solvents was observed. Hence the preference of employing  $Y_{x\text{BnCl}}$ , the scale of solvent ionizing power for a substrate giving an extended charge-delocalized transition state, in the dual-parameter Eqn. (3) should be noted. In addition to the nucleophilic solvent attack at the solvolysis center, the positive charge developed in the transition state is likely to delocalize throughout both phenyl rings, like those found for 9-fluorenyl and benzhydryl systems,<sup>5,25</sup> albeit no delocalization from the nitrogen (**3a**) to the phenyl ring (**3b**) is possible according to the canonical resonance theory<sup>32</sup> (Scheme 3).

To judge whether or not the chemical evidence for such a delocalization is conceivable, *ab initio* calculations on the charge distribution in both **2** and **3** were carried out. Table 3 suggests that similar results were obtained from Mulliken population analysis, electrostatic potential analysis and natural population analysis.<sup>33</sup> Although slightly different results could be found by employing different approximations, the variation of charge at the same location between **2** and **3** ( $\Delta\text{charge}$ ) would be less profound. Moreover, the outcomes from Mulliken population and natural population analyses are very close. Similarly, all three density functional methods also yield results in harmony with one another, so only one (pBP/DN\*\*) has been depicted in Schemes 2 and 3.

From Mulliken population analysis (Tables 3 and 4), both phenyl rings are found to be similar and each phenyl ring carries 0.24–0.36 positive charge in the carbamoyl chloride **2** and 0.45–0.52 positive charge in the acylium ion **3**. In the former case (**2**), the inductive effect of nitrogen may account for the partial positive charge on the phenyl ring. The enhanced positive charge (0.16–0.22) on the phenyl ring in **3**, however, is unlikely owing to the more negative inductive effect by the partial positive nitrogen as predicted in a canonical resonance form (**3a**), since the nitrogen carries almost the same charge in **2** and **3**. On the other hand, the electrostatic potential analysis (Tables 3 and 5) indicates that the two phenyl rings are different in **2**: one has 0.05–0.09 and the other 0.16–0.19 positive charge. The enhanced positive charge (0.18–0.35) on the phenyl ring in **3** is unlikely owing to the compensation from the small increase (0.1–0.2 unit) of the negative charge on nitrogen.

The agreement between charge distributions computa-



**Scheme 3**

tion and of the correlation analysis for  $\log k$  against  $Y_{\text{XBnCl}}$  in the present study seems to suggest a promising combination to the understanding of solvolysis mechanisms. Our previous work<sup>5b</sup> also indicated that the result of correlation analysis from  $\log k$  against  $Y_{\text{BnCl}}$  was in line with the charge distribution from computations. It is therefore plausible that both  $Y_{\text{XBnCl}}$  and  $Y_{\text{BnCl}}$  scales could be applied to many systems with an appropriate extent of positive charge delocalization in the solvolytic transition state, regardless of the structural similarity. (The applicability of the  $Y_{\text{BnX}}$  scale was recently argued by using a similarity model.<sup>34</sup> However, there were misinterpretations and ignorance of literature data<sup>5a,5b,12</sup> in that paper, which made their conclusion unconvincing.)

In conclusion, the contribution of a certain kind of non-canonical resonance,<sup>35</sup> e.g. **3c** (Scheme 3), might be significant in accounting for the positive charge delocalization in the solvolysis transition state for *N,N*-diphenylcarbamoyl chloride (**2**). Further studies on kinetic measurements and quantum chemical calculations for evaluating the eligibility of applying the  $Y_{\text{XBnX}}$  scale to elucidate the transition-state structure involving extended positive charge delocalization with the contribution of non-canonical resonance are in progress.

## EXPERIMENTAL

**Materials.** *N,N*-Diphenylcarbamoyl chloride (Aldrich) was recrystallized to give colorless prisms of m.p. 82.5–84 °C (lit.<sup>10</sup> 82–84 °C). Solvents for kinetic studies were purified according to standard methods,<sup>36</sup> and were freshly distilled under nitrogen. Doubly de-ionized water was degassed prior to the preparation of aqueous solvent systems for solvolysis.

**Kinetic measurements.** Conductimetric or potentiometric rate constants ( $\pm 2\%$ ) were measured at least in duplicate as described.<sup>37</sup> The conductivity cells containing solution of  $1 \times 10^{-4}$ – $1 \times 10^{-5}$  M were placed in a thermostat with a temperature variation of  $\pm 0.02$  °C. For potentiometric measurement a solution of about  $5 \times 10^{-3}$  M was sealed in ampoules. Rate constants monitored at other temperatures were extrapolated to those at 50 °C by using an Arrhenius plot.

**Calculations.** All calculations were carried out by using the Spartan 5.1.2 program package.<sup>38</sup> The initial equilibrium geometries of **2** and **3** were first optimized using the AM1 semi-empirical method. The complete structure optimizations were then performed by four different models: the Hartree–Fock SCF method and density functional theory with SVWN, BP and pBP functionals. The default option for the geometry optimization was adopted in this study. The convergence criterion for the geometry optimization was also chosen

from default option. Three basis sets DN, DN\* and DN\*\*, were used to check their effects on the charge distribution.

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