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Solvolysis of aromatic benzoyl chlorides: how is the π-electron stabilization of the aromatic acyl chlorides and acylium cations related to the π-electron delocalization?[†]

Tadeusz M. Krygowski,[1]* Michal K. Cyrański,[1] Dae D. Sung[2] and Beata T. Stepień[1]

[1]Department of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland
[2]Dong-A University, 840 Hadan 2-dong, Saha-gu, Busan, Korea

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ABSTRACT: Homodesmotic stabilization energies of XPhCOCl and $XPhCO^+$ estimated at the B3LYP/6–311G** level of theory for eight *para*-substituted derivatives (X = H, Cl, F, OH, OCH_3, NH_2, NO_2 and CH_3) are good descriptors for changes of the π-electron delocalization parameters of the ring, measured by NICS and HOMA, and also for geometry parameters of COCl and CO^+ groups. Good correlations are also found for atomic charges in these groups. Electron-donating substituents elongate the C—Cl bond dramatically and increase the negative charge at the Cl atom in the XPhCOCl molecule. Copyright © 2004 John Wiley & Sons, Ltd.
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KEYWORDS: aromaticity; *ab initio*; solvolysis; benzoyl chloride; acylium cation

INTRODUCTION

Acyl chlorides belong to the most reactive organic substrates, versatile in a great number of transformations, and hence they are very attractive for mechanistic studies.[1] Solvolysis of aromatic acyl chlorides differs from aliphatic cases at least in the possibility of a substantial effect due to the π-electron delocalization intervening during the reaction and hence affecting the reaction path.

Early mechanistic studies[2] have shown that there are three possible model reaction pathways for the solvolysis of acyl chlorides:

1. unimolecular dissociation (S_N1);
2. bimolecular (S_N2);
3. addition–elimination mechanisms.

These three mechanisms may be combined in practical situations, leading to very complex reaction paths. The strong dependence of the kinetics of solvolysis on the solvent is very well documented.[3] Analysis of the dependence of log$k$ of solvolysis on the solvent or, more generally, on medium parameters has often been employed to look for the correct mechanism for a given system. The S_N1 pathway is usually attributed to the solvolysed systems which follow the linear Grunwald–Winstein relationship.[4] Non-linear log$k$ vs $m_{Y_{Cl}}$ plots may suggest a different mechanism of solvolysis of aromatic acyl chlorides.[5] Solvolysis of benzoyl chlorides has also been studied by employing the Grunwald–Winstein equation[6] and by use of its more advanced modifications.[7] Extension of the Grunwald–Winstein equation into two-parameter[8] and three-parameter[9] equations has accounted for the complexity of interactions of the solvent and substrate molecules on the route from the initial to the final stage of the reaction. In order to simplify the situation, authors of recent work have often applied isodielectric binary mixtures.[10] In this way, the methanolysis of *para*-substituted benzoyl chloride[11] carried out in methanol binary mixtures with acetonitrile, nitrobenzene and nitromethane led to dramatic differences in the plots of log$k$ vs mole fraction of methanol. The irregular behaviour for differently *para*-substituted benzoyl chloride was interpreted as a complex pathway which may include a combined S_N1–S_N2 and carbonyl addition mechanisms. Solvolysis of 1- and 2-naphthoyl chlorides[12] is another example showing a substantial dispersion of the data points in the Grunwald–Winstein correlation.

In the case of aromatic systems, as both the acyl chloride and the acylium cation group are strongly electron accepting, they interact with the π-electron system of the aromatic moieties. Thus a strong intramolecular charge transfer from the ring to both groups may be expected. This in turn will lead not only to a decrease in the positive charge at COCl and CO^+ groups, but also to an increase in the positive charge in the ring. Certainly, the charge distribution depends significantly on the nature of the ring and also on the presence of another substituent(s) in the

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**Correspondence to:* T. M. Krygowski, Department of Chemistry, University of Warsaw, Pasteura 1, 02 093 Warsaw, Poland.
E-mail: tmkryg@chem.uw.edu.pl
Contract/grant sponsor: Dong-A University.
[†]Dedicated to Professor Alan R. Katritzky on the occasion of his 75th birthday.

ring. In this kind of situation, a very useful tool is the Yukawa–Tsuno equation,[13] allowing the prediction of the characteristics of a transition state whose reaction centre is attached to a substituted aromatic system. On the other hand, it was also found many years ago[14,15] that both the resonance and inductive effects in benzene-like systems depend on the solvent in different ways. A remarkable enhancement was found of the negative σ_p values for strong π-donor substituents in benzoic acids,[14] and a smaller attenuation of resonance compared with the inductive effect was observed with substituted phenols.[15] These problems were discussed again more recently.[16] Thus, the blend of the inductive–resonance effects from the group being the reaction site, both in the initial state [ArylCOCl] and during the reaction process, may vary owing to several factors, the most important of which seem to be

1. the change of COCl in direction to CO^+;
2. the solvent influence on the reaction site and the moiety to which the reaction site is attached;
3. the solvent effects on the attacking reagent.

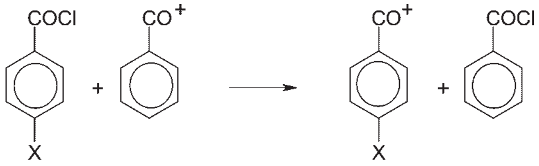
These factors work simultaneously during the reaction, but despite their substantial similarity, they will be discussed separately for simplicity.

The effectiveness of the reagent, e.g. of the methanol molecules in the case of methanolysis, also depends on other species that are components of the binary solution. The components of binary mixtures should be considered as Lewis acid–base amphoteric systems,[17] which rarely follow a linear relationship in a plot against the mole fraction.[18] The above-mentioned interactions are also present in the case of another substrate of the reaction, the aromatic acid chloride molecules.

The purpose of this work was to study the interrelations between the substituent effect on the relative stabilization energy of the benzoyl chloride and acylium cation pairs, and also the π-electron delocalization and changes in the structure and atomic charges of these systems. As model systems we have taken *para*-substituted benzoyl chlorides[11] for which substantial dispersions from the Grunwald–Winstein and similar relationships were observed.[12]

RESULTS AND DISCUSSION

Undoubtedly, the π-electron delocalization and in consequence stabilization of the transition and/or intermediate states due to interactions between the reaction site and the substituted aromatic moiety play an important role in determining the mechanism of solvolysis of aromatic acyl chlorides. In the simplest case, when the reaction is of the S_N1 type, the relative stabilization due to the substituent effect may be estimated by the homodesmotic reaction,[19] which takes into account only the *para*-substituted benzoyl chlorides and their acylium cations, while other species are added to fulfill the homodesmotic reaction requirements (Scheme 1).[19]



X = H, F, Cl, CH_3, OCH_3, OH, NH_2, NO_2

Scheme 1

The relative stabilization energy due to substituent effects (SE) is defined as the difference between the total energies of products and substrates:

$$SE = E(\mathrm{PhCOCl}) + E(\mathrm{XPhCO^+}) - E(\mathrm{PhCO^+}) - E(\mathrm{XPhCOCl}) \tag{1}$$

In this work, the calculations were carried out by the DFT method at the B3LYP/6–311G** level of theory[20] with C_s symmetry. All species correspond to minima with no imaginary frequencies. The atomic charges were calculated in the frame of the Mulliken population analysis.[21]

The optimized geometry of the rings of both the PhCOCl and $PhCO^+$ systems allowed us to estimate the *HOMA* index,[22] defined as

$$HOMA = 1 - \frac{\alpha}{n}\sum\left(R_{\mathrm{opt}} - R_i\right)^2 \tag{2}$$

where R_{opt} is a reference bond length assumed to be present in a fully delocalized system, R_i are the running bond lengths in the system under study, α is a normalization factor leading to $HOMA = 0$ for the Kekulé structure with alternate CC bond lengths as in 1,3-butadiene,[23] $HOMA = 1$ for the cases with $R_i = R_{\mathrm{opt}}$, and n is the number of bonds taken into account.

For a long time, *HOMA* has served effectively to account for π-electron delocalization, being one of the most effective[24] and frequently used geometry-based criteria of aromaticity.[25,26] At the same level of theory were computed Schleyer's *NICS*s,[27] which have often served to estimate the π-electron delocalization.[28] *NICS* is defined as the negative value of the absolute shielding and may be computed in two ways, in the centre of the ring (labelled *NICS*) and 1 Å above the centre [labelled *NICS(1)*]. The latter accounts better for the π-electron ring current.[29] For π-electron systems with a homogeneous variation of structure, as was found in substituent effects on aromaticity in 6-substituted fulvenes[30] and heptafulvenes,[31] *HOMA* and *NICS* work equivalently; if the variation in structure is more complex, then aromaticity parameters may give different pictures.[32]

Table 1. Calculated *SE* (kcal mol^{-1}), *NICS*, *NICS(1)* and *HOMA* for *p*-XPhCOCl and XPhCO$^+$ systems

		ArylCO$^+$			ArylCOCl		
X	*SE*	*HOMA*	*NICS*	*NICS(1)*	*HOMA*	*NICS*	*NICS(1)*
H	0.00	0.888	−9.00	−11.00	0.980	−10.54	−12.60
F	2.07	0.860	−9.91	−10.54	0.981	−12.00	−12.22
Cl	2.11	0.851	−8.88	−10.39	0.983	−11.05	−12.09
CH_3	−4.54	0.837	−8.29	−10.45	0.971	−10.24	−12.02
OCH_3	−9.54	0.732	−7.79	−9.10	0.959	−10.84	−11.66
OH	−6.27	0.768	−8.15	−9.27	0.964	−10.97	−11.57
NH_2	−15.31	0.631	−6.16	−7.61	0.928	−9.56	−10.57
NO_2	12.05	0.912	−11.13	−11.76	0.985	−11.96	−12.62
O^{-}[a]	—	—	—	—	0.377	−3.87	−6.30
Mean	−2.43	0.810	−8.66	−10.02	0.969	−10.90	−11.29
Range	27.36	0.281	4.97	4.15	0.057	2.40	2.05
Benzene		0.991[43]	−10.50[43]	−12.30[43]			

[a] The data for O^- substituent are given only for *p*-XPhCOCl to avoid confusion in the case of the XPhCO$^+$ derivative. See text. These data are not used for calculation of the mean value and the range.

Table 1 presents the *SE*, *HOMA* and *NICS* values for both series of system, XPhCOCl and XPhCO$^+$. For comparison are added the values of *HOMA* and *NICS* computed for benzene at the same level of theory, being references for situations without intramolecular interactions due to CO$^+$/COCl groups and substituents.

Consider first the energy of the homodesmotic reaction (1). The negative values of the stabilization energy, *SE*, indicate greater stability of the substituted cation, whereas positive values represent less stable species. The results in Table 1 are in line with this interpretation: the most negative *SE* values are for electron-donating substituents such as amino, methoxy, hydroxy and methyl, whereas *SE*>0 are observed for electron-attracting substituents such as nitro, fluoro and chloro. The variation in *SE* due to the substituent effects is substantial, around 27 kcal mol^{-1} (1 kcal = 4.184 kJ). Our approach is different from that employed by Liu and Chen[7e] who employed a comparison with the CH_3COCl/CH_3CO^+ system and therefore their data were represented by the isodesmic reaction,[33,34] with computation at the RHF/6–31G* level of theory. The advantage of our calculations is that the homodesmotic reaction is employed and the DFT method accounts for electron correlation, and the basis set is much more adequate (B3LYP/6–311G**) and thus leads to more reliable results, particularly for systems with strong intramolecular interactions. Interestingly, the energetics for both cases is alike: the ranges of *SE* values are nearly the same, 12.47 (Liu and Chen) and 11.65 kcal mol^{-1} (this work), if the same substituted systems are compared (MeO and Cl groups).

Additionally, for both COCl and CO$^+$ groups, interacting with the π-electron systems studied in this paper substituent constants σ^- were estimated, following the model published recently.[35] It relies on linear regression of the aromaticity index *HOMA*[22] on σ^- values for a set of exocyclically substituted heptafulvene derivatives. For these systems a very high correlation coefficient (*cc*) = 0.993 was found and therefore these model systems could well be used to estimate σ^- values.[35] The values are 1.26 for COCl and 2.96 for CO$^+$, estimated by computation at the same level of theory, i.e. DFT B3LYP/6–311 + G**.[35] Note that the estimated theoretical value for COCl is very close to the experimental estimate, 1.24.[36] Hence both of these groups induce a positive charge in the aryl moiety, the effect realized mostly by the π-electron system.

The π-electron delocalization, estimated by means of the *HOMA*, *NICS* and *NICS(1)* indices of aromaticity (Table 1), vary substantially, being stronger to a different extent in the case of acylium cations than in the case of acid chlorides. This is clearly shown by the ranges of variation of HOMA and both sets of NICS values. When we look at the ranges of variation, we find that they are substantial for ArylCO,$^+$ Δ*HOMA* = 0.281 and Δ*NICS(1)* = 4.15, whereas they are much smaller for ArylCOCl, 0.057 and 2.05, respectively.

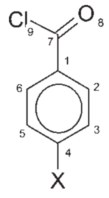
The regressions of the aromaticity indices *HOMA* and both *NICS* vs *SE* show good correlations for XPhCO$^+$ and slightly worse for XPhCOCl, as shown in Table 2. These findings are obviously due to a stronger electron-accepting power of the CO$^+$ group in comparison with the COCl group, as shown by the reported earlier values of σ^-.

Analysis of the changes in geometry (Table 1 in Supplementary Material), i.e. bond lengths and atomic charges, is more informative.

First, it is important to note that the bond lengths in the rings of both systems, XPhCOCl and XPhCO$^+$, only partly correlate with the *SE* values and mostly concerning

Table 2. Correlation coefficient for regression of indices of aromaticity plotted against *SE*

	ArylCO$^+$			ArylCOCl		
	HOMA	*NICS*	*NICS(1)*	*HOMA*	*NICS*	*NICS(1)*
SE	0.918	−0.974	−0.934	0.889	−0.807	−0.879



Scheme 2

the bonds in the vicinity of the substituent, C_3—C_4 and C_4—C_5, (for numbering of bonds, see Scheme 2).

In principle, correlations for the acylium cation are better than for the acylium chloride. Table 3 presents correlation coefficients for regressions defined as $R(\text{C—C}) = aSE + b$, where the subscripts for C–C in Table 3 label the kind of bond and those in bold are the correlation coefficients of which absolute value is >0.9. The differences in the correlation coefficient values for dependences between aromatic stabilization energy (ASE) and equivalent fragments of the benzene ring, e.g. C_1—C_2 and C_1—C_6 are due to the AGIBA (angular group induced bond alternation) effect.[37] It is well documented[38] that angular substituents, such as OCH_3 or OH, differentiate geometry in the *ipso–ortho* fragment of the benzene ring.

The best correlations are observed for geometry parameters in the reaction site groups (with the modulo of *cc*>0.92). A similar situation is observed for the changes in atomic charges: the well correlated data with *SE* values are the charges at C_1, C_7 and, in the case of PhCOCl, additionally at Cl_9 and O_8 atoms. Table 4 shows the *cc* values for regressions defined as $q(\text{atom}) = a'SE + b'$. Again, for better illustration, the bonds and atoms whose parameters correlate well (modulo of *cc*>0.9) are in bold.

When the C_1—C_7 bond lengths are plotted against *SE* values for XPhCOCl and $XPhCO^+$ species, then fairly good linear regressions are found with correlation coefficients of 0.967 and 0.963, respectively. The lowering of the stabilization energy is associated with a shortening of the C_1—C_7 bond being the result of a quinoid structure formation due to the intramolecular charge transfer when the substituent becomes more electron donating (X = D), Scheme 3.

Another significant pattern is that the decrease in SE is associated with a substantial increase in the C_7—Cl_9 bond length in XPhCOCl. Figure 1(a) presents this scatter plot for which $cc = -0.990$. Interestingly, in a similar manner the negative charge increases at the Cl_9 atom, $q(Cl_9)$, as shown in Fig. 1(b) ($cc = 0.992$).

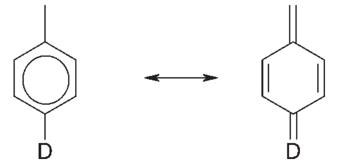
When the charges at C_7 and Cl_9 are subtracted, $\Delta q = q(C_7)$—$q(Cl_9)$, then the difference may be considered as an approximate measure of the iconicity of the bond. For a purely covalent bond $\Delta q = 0$, increasing to $\Delta q = 2$ for an ideally ionic bond (the case of an ideal pure cation and anion system). Figure 2(a) shows the scatter plot of Δq vs *SE* with $cc = -0.985$. The increase in ionic

Table 3. Modulo of the correlation coefficients for regression between bond length and *SE*

	ArylCO$^+$								ArylCOCl								
	C_1—C_2	C_2—C_3	C_3—C_4	C_4—C_5	C_5—C_6	C_6—C_1	C_1—C_7	C_7—O_8	C_1—C_2	C_2—C_3	C_3—C_4	C_4—C_5	C_5—C_6	C_6—C_1	C_1—C_7	C_7—O_8	C_7—Cl_9
SE	**0.902**	0.889	**0.965**	**0.966**	0.874	0.856	**0.963**	**0.955**	0.518	0.647	**0.918**	**0.932**	0.759	0.702	**0.967**	**0.923**	**0.990**

Table 4. Modulo of the correlation coefficients for regression between atomic charges and *SE*

	ArylCO$^+$								ArylCOCl								
	C_1	C_2	C_3	C_4	C_5	C_6	C_7	O_8	C_1	C_2	C_3	C_4	C_5	C_6	C_7	O_8	Cl_9
SE	**0.955**	0.520	0.527	0.300	0.475	0.283	**0.931**	0.432	**0.944**	0.697	0.632	0.309	0.600	0.669	0.894	**0.983**	**0.992**



Scheme 3

character measured by Δq is associated with an increase in the C_7—Cl_9 bond length, *cc* for this scatter plot [Fig. 2(b)] being equal to 0.990.

The other important parts of the reacting systems are the C_1 (in the ring) and C_7 atoms. The changes in atomic charges at C_1 and C_7 clearly depend on the *SE* values, as shown in Fig. 3 for acylium cation and its chloride derivatives.

Unfortunately, it is impossible to estimate *SE* for stronger electron-donating substituents, such as the negatively charged substituent O^-, since this would lead to a completely different electron arrangement in the case of the $XPhCO^+$ system, then applying the energy of such a system in Eqn (1) would lead to confusing results. Hence no analogous scatter plots against *SE* can be made for this kind of substituent. However, if the C_7—Cl_9 bond lengths, the atomic charge at Cl and the 'ionicity' parameter Δq correlate so well with *SE*, then these three parameters should correlate with each other, making it possible to use the data from optimization of XPhCOCl with $X = O^-$. For the purpose of this kind of scatter plot, the optimization of XPhCOCl with $X = O^-$ was done at the same level of theory and the point for this system is indicated by the most negative value in (a) and the most positive one in (b) in Fig. 4(a) and (b). The charge for the Cl_9 atom in this case is -0.35 and a very long C_7—Cl_9 bond, 2.004 Å, with ionicity parameter $\Delta q = 0.96$. From these plots it results that the C_7—Cl_9 bond becomes very long and more ionic than any of the others, and the charge at the Cl atom becomes very negative. This nicely illustrates that the chlorine atom is about to leave the system as a chloride anion as is known for solvolysis of benzoyl chlorides.

The *SE* values may also be interpreted by means of the recently published Yukawa–Tsuno equation formulated for the substituent-dependent stabilization energy $\delta_x \Delta E$[39]

$$\delta_X \Delta E = \rho\left\{\left(\sigma^0\right)_{ab} + r\left(\Delta\bar{\sigma}_R^+\right)_{ab}\right\} \qquad (3)$$

where ρ is the reaction constant, σ^0 is the normal substituent constant,[13c] $\Delta\bar{\sigma}_R^+ = \sigma^+ - \sigma^0$ is the resonance subsituent constant to measure the capability for π-delocalization of π-electron donor *para*-substituents, σ^+ is the electrophilic substituent constant[40] and r is the resonance demand, which is a measure of the degree of resonance interaction between the carbocation centre and the benzene π-system.[13] The subsript *ab* means that the parameters are obtained by use of *ab initio* modelling (at the MP2/6–31G*//RHF/6–31G* level of theory).[20] Application of this equation to *SE* values for the substituted benzylium cations (Table 1) leads to $\rho = -15.8$ and $r = 0.77$ with $cc = 0.999$. This correlation is very similar to that for protonated acetophenone derivatives, for which $\rho = -15.0$ and $r = 0.83$.[39] This is a substantial support for the electron-withdrawing efficiency of CO^+ being similar to that in COH^+ in the protonated acetophenone derivatives.

It should be added that the consequences of $CH_2{}^+$ substitution of benzene[41] and benzenoid hydrocarbons[42] on the π-electron delocalization and geometry parameters also showed great diversity, depending on the kind of counter substituent (benzene case) and the position of the substituent. These results are conceptually in line with the results presented in this paper.

The above results and their interpretation are presented for isolated molecules or cations. If we take it into account that these systems are immersed in reactive media, then we have to take into consideration the obvious fact that atoms in a molecule, particularly atoms with non-zero charge, may interact with the species of the medium, which in most cases are dipolar. Some of them are just reagent molecules of the reaction. We should be aware of the fact that molecules of the medium approaching the XPhCOCl moiety with a positive pole (charge) of the dipole interact with the substrate molecule, leading in consequence to a situation resembling qualitatively an action observed in a much stronger way when the electron-attracting substituent is attached to this position. An opposite view is found for molecules of medium approaching the substrate molecule with a negative charge. For example, the approach of the H atom of the hydroxyl group of MeOH to a carbon atom in *para* and *ortho* positions of PhCOCl acts similarly to (but much more weakly than) an electron-accepting substituent, e.g. the NO_2 group. In contrast, when the MeOH molecule

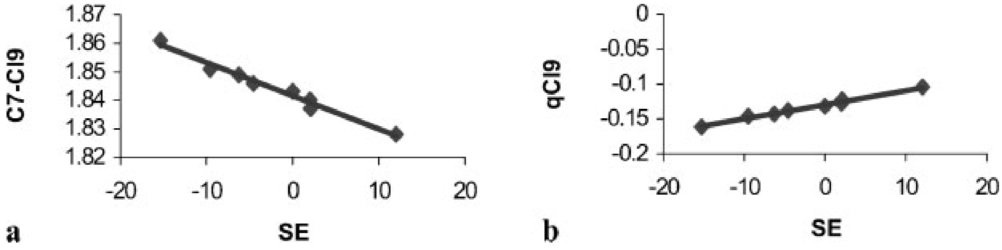


Figure 1. Dependence of (a) C_7—Cl_9 bond lengths on stabilization energy, *SE* ($cc = -0.990$) and (b) the atomic charge at the Cl_9 atom on *SE* ($cc = 0.992$)

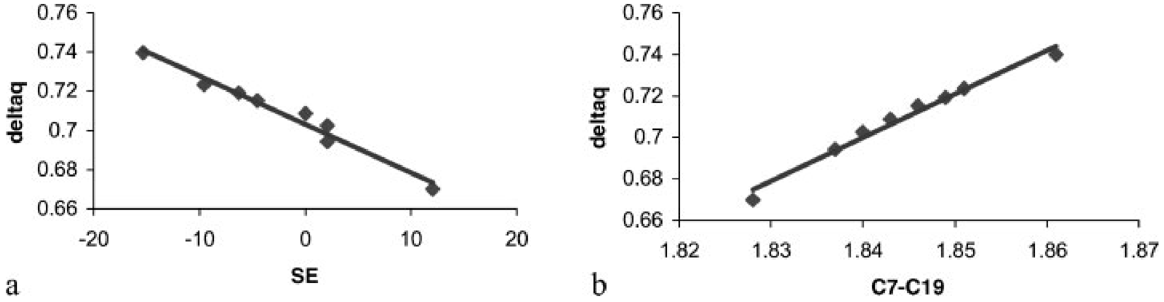
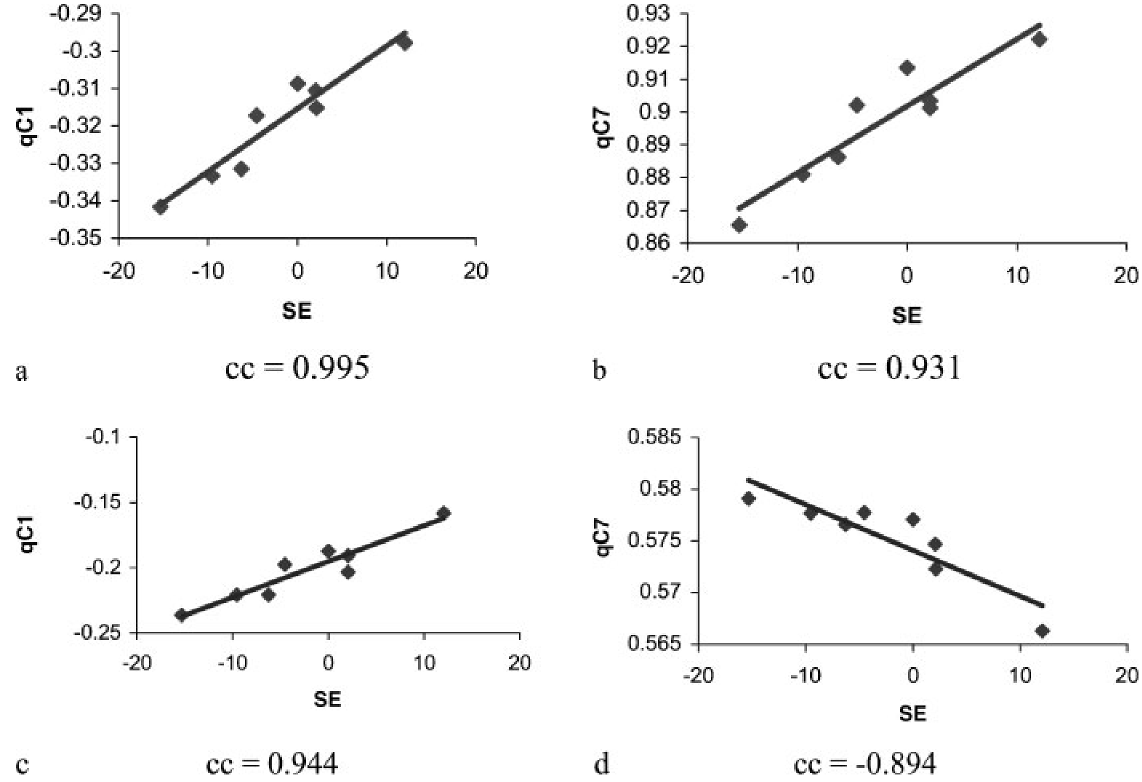


Figure 2. Dependence of $\Delta q = q(C_7) — q(Cl_9)$ on (a) stabilization energy, *SE* ($cc = -0.985$) and (b) $C_7—Cl_9$ bond length ($cc = 0.990$)



a cc = 0.995

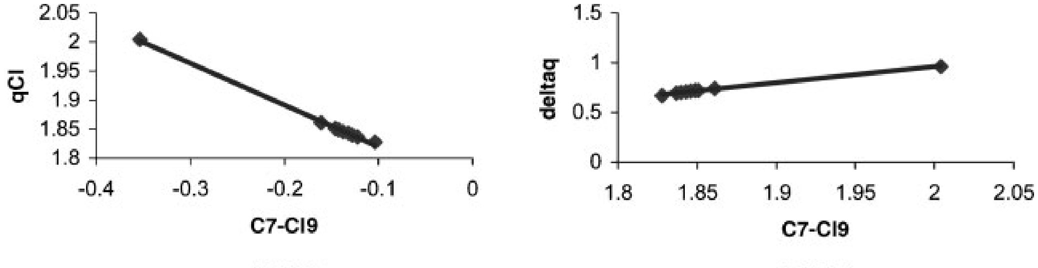
b cc = 0.931

c cc = 0.944

d cc = -0.894

Figure 3. Scatter plots of atomic charges at C_1 and C_7 vs *SE* for (a), (b) acylium cation and (c), (d) its chloride derivatives

approaches the *para* and *ortho* carbon atoms with an oxygen atom, then it induces a charge at C(*para*) and C(*ortho*), like the electron-donating substituent. This is a very qualitative view but it brings us closer to a better understanding of the medium effect on the electron structure of the substrate and its possible ways of further rearrangement as a result of interactions with the attacking reagent.



a cc = -0.999

b cc = 0.998

Figure 4. Scatter plots of atomic charges at Cl_9 and $\Delta q = q(C_7) — q(Cl_9)$ vs $C_7—Cl_9$ bond length for chloride derivatives for XPhCOCl with $X = O^-$

The above qualitative vision of potential interactions during the solvolysis of XPhCOCl is associated with the following assumptions, which as single properties are well known:

1. The variability of charge distribution and geometry (bond lengths) of the reaction site, i.e. COCl (and CO^+), is caused by electron-donating/accepting properties of the covalently bonded substituents as shown in this work.
2. The substituent effect, being a blend of resonance and inductive interactions with the reaction site (through the ring), depends not only on the nature of the substituent but also on the nature of the medium in which the system is immersed.[14–16] This in turn gives rise to some irregularities of the substituent effect itself on the reaction site observed in a real medium.
3. Molecules of the medium of the reaction, and also (often) of the attacking reagent, should be treated as Lewis acid–base amphoteric systems. Hence their molecules may act in both ways, e.g. activating the C—Cl bond if they approach the negative pole (qualitative analogy with an electron-donating substituent) to both *ortho* and *para* positions and the exocyclic carbon atom, or approach a positive pole to the Cl atom in the COCl group inducing an increase in the negative charge of Cl^-. If these actions coincide, the probability of leaving of the chloride anion increases.

Supplementary material

Optimized bond lengths, atomic charge, absolute electronic energies and zero-point vibrational energies (ZPE) at the B3LYP/6–311G** level for all analysed benzonyl chlorides and their acylium cations are summarized in the Supplementary Material, available in Wiley-Interscience.

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