

摘要

本年度完成之工作包括：

第一部分：

- (一) 補充及修訂上年度苯甲醯溴之溶離反應研究結果，已正式發表（附件一）。
- (二) 補充及修訂上年度苯甲醯氯之氧 17 和碳 13 核磁共振研究結果，已正式發表（附件二）。
- (三) 完成四種萘甲醯氯之溶離反應研究。

第二部分：

- (一) 合成十種含多個氧為側鏈之 β -雙酮配位基，並製出十種銅錯鹽與十種鈮錯鹽，研究其液晶性質。
- (二) 合成八種苯環含不同取代基之 β -雙酮配位基，並製出八種銅錯鹽與八種鈮錯鹽，研究其液晶性質。
- (三) 其他如席富鹽之液晶研究仍在繼續進行中。

關鍵詞

溶離反應，苯甲醯溴，萘甲醯氯，氧 17 核磁共振，碳 13 核磁共振， β -雙酮銅錯鹽液晶， β -雙酮鈮錯鹽液晶，液晶

Abstract

The work done with completion in this year including:

Part 1.

- (1) Additional work and revision on the solvolysis of benzoyl bromides reported last year. It was published in *Tetrahedron* **2001**, *57*, 3343-3347 (Appendix 1)
- (2) Additional work and revision on the DFT calculation of oxygen-17 and carbon 13 NMR chemical shifts reported last year. It was published in *Journal of Physical Organic Chemistry* **2001**, *14*, 591-596. (Appendix 2)
- (3) Solvolytic study on four naphthoyl chlorides was complete.

Part 2.

- (1) Ten β -diketone ligands containing side-chain with more than one oxygen atoms were prepared. Their copper (II) complexes and palladium (II) complexes were made, and liquid crystal properties of these complexes were examined.
- (2) Eight β -diketone ligands containing different substituents on phenyl ring were prepared. Their copper (II) complexes and palladium (II) complexes were made, and liquid crystal properties of these complexes were examined.
- (3) The study on Schiff base complexes is in progress.

Keywords

Solvolysis, benzoyl bromides, naphthoyl chlorides. O-17 NMR, C-13 NMR, liquid crystals, β -diketone complex of copper (II), β -diketone complex of palladium (II)

ANNUAL REPORT (2000-2001)

Part 1.

The following results were published :

1. Application of Grunwald-Winstein correlation analyses with Y_{BnBr} scales to the solvolysis of benzoyl bromides, published in *Tetrahedron* **2001**, *57*, 3343-3347 (Appendix 1).
2. Density functional theory calculations of ^{17}O and ^{13}C NMR chemical shifts for aromatic acyl chlorides, published in *Journal of Physical Organic Chemistry* **2001**, *14*, 591-596 (Appendix 2).

The following naphthoyl chlorides (1-4). Scheme 1. were prepared and were solvolyzed in a variety of solvents. First order rate constants are shown in Table 1-1.

Table 1-1. Solvolytic rate constants at 25°C

solvent	1	2	3	4
100E	2.05×10^{-3}	7.50×10^{-4}	7.00×10^{-3}	7.45×10^{-4}
90E	6.70×10^{-3}	2.08×10^{-3}	2.37×10^{-2}	2.08×10^{-3}
80E	1.69×10^{-2}	3.37×10^{-3}	6.56×10^{-2}	5.46×10^{-3}
70E	4.03×10^{-2}	5.58×10^{-3}	—	1.07×10^{-2}
60E	9.08×10^{-2}	9.33×10^{-3}	—	2.44×10^{-2}
100M	1.51×10^{-2}	4.55×10^{-3}	4.35×10^{-2}	5.40×10^{-3}
90M	2.69×10^{-2}	8.54×10^{-3}	1.52×10^{-1}	1.29×10^{-2}
80M	9.34×10^{-2}	1.49×10^{-2}	5.13×10^{-1}	2.60×10^{-3}
70M	3.12×10^{-1}	2.13×10^{-2}	—	5.97×10^{-2}
90A	5.14×10^{-4}	3.37×10^{-4}	1.10×10^{-3}	9.15×10^{-4}
80A	1.96×10^{-3}	7.58×10^{-4}	5.30×10^{-3}	1.05×10^{-3}
70A	7.21×10^{-3}	1.43×10^{-3}	1.96×10^{-2}	3.16×10^{-3}
60A	2.68×10^{-2}	3.28×10^{-3}	7.81×10^{-2}	9.94×10^{-3}
50A	—	8.96×10^{-3}	—	3.44×10^{-2}
100T	5.36×10^{-1}	3.29×10^{-3}	—	3.33×10^{-2}
80T20E	1.26×10^{-1}	1.13×10^{-3}	1.02×10^0	1.59×10^{-2}
60T40E	2.88×10^{-2}	7.38×10^{-4}	1.59×10^{-1}	4.74×10^{-3}
40T60E	9.63×10^{-3}	2.05×10^{-3}	5.00×10^{-2}	2.24×10^{-3}

Correlation analyses using single-parameter and dual-parameter Grunwald-Winstein equations (Eqn 1 and 2) were carried out. The results are listed in Table 2 and Table 3..

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

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

Table 2. Correlation analyses using single parameter equation (1)

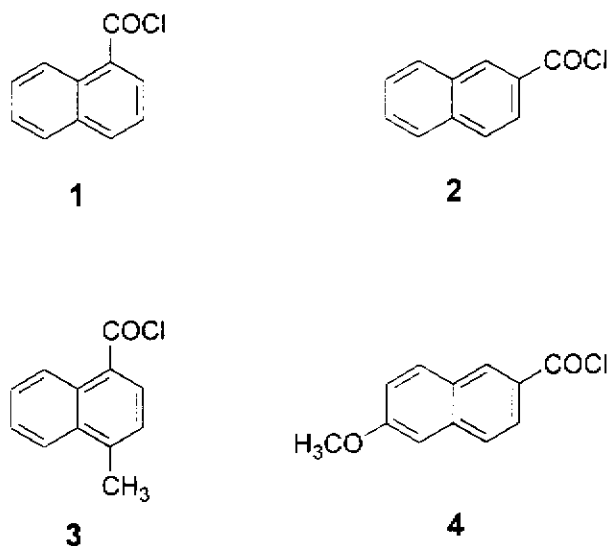
Substrate	Parameters	n^a (solvent)	R	m (s.d.) ^b
1	Y_{BnCl}	17 (All)	0.968	0.533 (0.037)
		13 (AEM)	0.987	0.666 (0.033)
		5 (TE)	0.996	0.470 (0.024)
	$Y_{\text{N-BnCl}}$	17 (All)	0.968	0.533 (0.036)
		13 (AEM)	0.993	0.657 (0.024)
		5 (TE)	0.997	0.530 (0.025)
2	Y_{BnCl}	18 (All)	0.708	0.260 (0.065)
		14(AEM)	0.962	0.445 (0.037)
		5 (TE)	0.910	0.215 (0.057)
	$Y_{\text{N-BnCl}}$	18 (All)	0.737	0.278 (0.064)
		14(AEM)	0.982	0.448 (0.025)
		5 (TE)	0.912	0.243 (0.030)
3	Y_{BnCl}	13 (All)	0.970	0.633 (0.048)
		10(AEM)	0.973	0.720 (0.061)
		4 (TE)	0.999	0.583 (0.016)
	$Y_{\text{N-BnCl}}$	13 (All)	0.989	0.650 (0.029)
		10(AEM)	0.996	0.715 (0.022)
		4 (TE)	0.999	0.663 (0.016)
4	Y_{BnCl}	18 (All)	0.874	0.409 (0.057)
		14(AEM)	0.996	0.609 (0.017)
		5 (TE)	0.996	0.328 (0.017)
	$Y_{\text{N-BnCl}}$	18 (All)	0.889	0.428 (0.055)
		14(AEM)	0.994	0.600 (0.018)
		5 (TE)	0.996	0.370 (0.066)

^a Numbers of data points. ^b Standard deviation.

Table 3. Correlation analyses using dual-parameter equation (2)

Substrate	Parameters	n^a	R	m (s.d.) ^b	l (s.d.) ^b
1	$Y_{\text{BnCl}} \cdot N_{\text{OTs}}$	14	0.986	0.656 (0.044)	0.335 (0.069)
	$Y_{\text{N-BnCl}} \cdot N_{\text{OTs}}$	14	0.984	0.648 (0.046)	0.241 (0.068)
2	$Y_{\text{BnCl}} \cdot N_{\text{OTs}}$	15	0.850	0.454 (0.082)	0.505 (0.131)
	$Y_{\text{N-BnCl}} \cdot N_{\text{OTs}}$	15	0.755	0.308 (0.078)	0.261 (0.130)
3	$Y_{\text{BnCl}} \cdot N_{\text{OTs}}$	11	0.985	0.745 (0.055)	0.432 (0.117)
	$Y_{\text{N-BnCl}} \cdot N_{\text{OTs}}$	11	0.995	0.733 (0.031)	0.269 (0.062)
4	$Y_{\text{BnCl}} \cdot N_{\text{OTs}}$	16	0.970	0.625 (0.062)	0.448 (0.093)
	$Y_{\text{N-BnCl}} \cdot N_{\text{OTs}}$	16	0.952	0.563 (0.072)	0.312 (0.105)

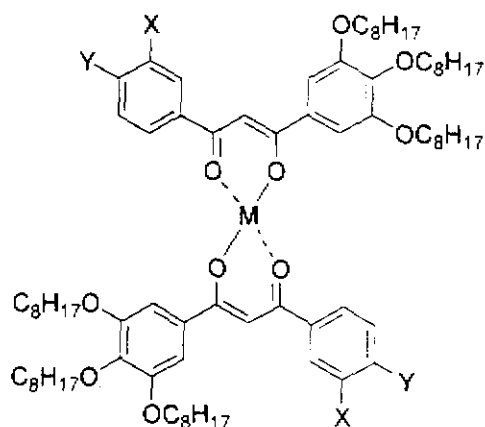
^a Numbers of data points. ^b Standard deviation.



(Scheme 1)

Part 2.

- (1) Ten β -diketone ligands containing side-chain with more than one oxygen atoms were prepared, and their copper (II) complexes and palladium (II) complexes (Scheme 2-1) were made. The results of DSC studies and, in some cases, PM studies are listed in Table 2-1 to Table 2-4.
- (2) Eight β -diketone ligands containing different substituents on phenyl ring were prepared, and their copper (II) complexes(Scheme 2-2)and palladium (II) complexes(Scheme 2-3) were made. The results of DSC studies and, in some cases, PM studies are listed in Tables 2-5 and 2-6.
- (3) A few Schiff bases and their Cu (II) complexes were prepared. This work is still in progress.



1: M = Cu, Pd X = H, Y = OR

C₂OC₄-M : R = C₂H₄OC₄H₉

C₄OC₄-M : R = C₄H₈OC₄H₉

C₂OC₂OC₂-M : R = C₂H₄OC₂H₄OC₂H₅

C₂OC₂OC₄-M : R = C₂H₄OC₂H₄OC₄H₉

2: M = Cu, Pd X = Y = OR

Di-C₂OC₂-M : R = C₂H₄OC₂H₅

Di-C₂OC₄-M : R = C₂H₄OC₄H₉

Di-C₂OC₆-M : R = C₂H₄OC₆H₁₃

Di-C₂OC₈-M : R = C₂H₄OC₈H₁₇

Di-C₄OC₄-M : R = C₄H₈OC₄H₉

Di-C₂OC₂OC₄-M : R = C₂H₄OC₂H₄OC₄H₉

(Scheme 2-1)

Table 2-1. DSC data for Cu(II) complexes of β -diketone (R-Cu), °C (J/g)

C2OC4-Cu	K	$\frac{86.67 (47.94)}{37.17 (37.79)}$	D _{hd}	$\frac{130.82 (2.26)}{128.58 (2.23)}$	I
C4OC4-Cu	K	$\frac{70.81 (35.54)}{25.73 (28.95)}$	D _{hd}	$\frac{121.78 (2.27)}{117.36 (2.28)}$	I
C2OC2OC2-Cu	K	$\frac{79.47 (80.24)}{52.40 (75.04)}$	D _{hd}	$\frac{103.74 (1.93)}{101.70 (1.88)}$	I
C2OC2OC4-Cu	K	$\frac{74.12 (21.22)}{23.47 (9.59)}$	D _{hd}	$\frac{107.00 (0.54)}{102.55 (0.56)}$	I

K, crystal phase); D_{hd}, disordered hexagonal columnar phase; I, isotropic phase;
Temperature gradient, 10.0°C min⁻¹.

Table 2-2. DSC data for Pd(II) complexes of β -diketone (R-Pd). °C (J/g)

C2OC4-Pd	K	$\frac{88.16 (52.60)}{< 25^a}$	D_{hd}	$\frac{122.51 (1.54)}{113.82 (1.21)}$	I
C4OC4-Pd	K	$\frac{67.83 (10.20)}{< 25^a}$	D_{hd}	$\frac{103.87 (1.42)}{98.73 (0.84)}$	I
C2OC2OC2-Pd	K	$\frac{79.75 (23.31)}{72.97 (0.58)}$	D_{rd}	$\frac{122.44 (0.18)}{118.40 (0.14)}$	I
C2OC2OC4-Pd	K	$\frac{46.48 (21.99)}{< 25^a}$	D_{hd}	$\frac{90^a}{71.74 (0.36)}$	I

K, crystal phase); D_{hd} , disordered hexagonal columnar phase; I, isotropic phase; Temperature gradient, $10.0^\circ\text{C min}^{-1}$. ^a Observed from polarized microscope.

Table 2-3. DSC data for Cu(II) complexes of β -diketone (Di-R-Cu). °C (J/g)

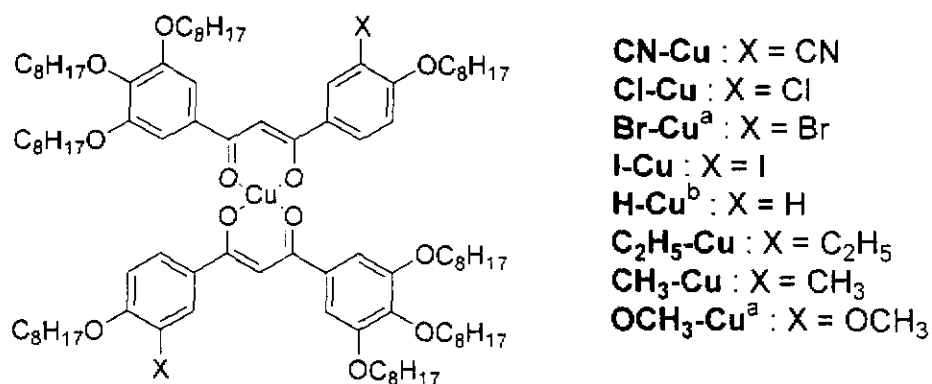
Di-C2OC2-Cu	K	$\frac{53.22 (4.67)}{< 25^a}$	D_{rd}	$\frac{114.83 (3.83)}{109.70 (3.93)}$	I
Di-C2OC4-Cu	K	$\frac{42.26 (0.16)}{38.58 (0.14)}$	D_{rd}	$\frac{130.29 (4.56)}{126.62 (4.58)}$	I
Di-C2OC6-Cu	K	$\frac{51.98 (26.55)}{< 30^a}$	D_{hd}	$\frac{120^a}{114^a}$	I
Di-C2OC8-Cu	K	$\frac{25.44 (3.93)}{< 30^a}$	D_{hd}	$\frac{106^a}{99^a}$	I
Di-C4OC4-Cu	K	$\frac{36.06 (1.88)}{27.92 (0.20)}$	D_{rd}	$\frac{125.01 (4.17)}{122.11 (3.98)}$	I
Di-C2OC2OC4-Cu	K_1	$\frac{87.22 (11.83)}{< 25^a}$	K_2	$\frac{118.21 (0.34)}{118.08 (12.50)}$	I

K, crystal phase); D_{hd} , disordered hexagonal columnar phase; I, isotropic phase; Temperature gradient, $10.0^\circ\text{C min}^{-1}$. ^a Observed from polarized microscope.

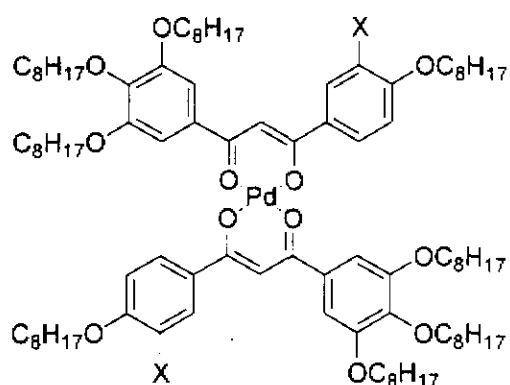
Table 2-4. DSC data for Pd(II) complexes of β -diketone (Di-R-Pd), °C (J/g)

Di-C2OC2-Pd	K $\frac{44.71 (4.82)}{26.27 (4.55)}$	D_{rd}	$\frac{110^a}{107^a}$	I
Di-C2OC4-Pd	K $\frac{58.06 (26.60)}{< 30}$	D_{rd}	$\frac{130.16 (2.15)}{121.30 (2.00)}$	I
Di-C2OC6-Pd	K $\frac{58.45 (20.82)}{< 30}$	D_{rd}	$\frac{111.55 (1.00)}{102.41 (1.06)}$	I
Di-C2OC8-Pd	K $\frac{24.23 (1.26)}{14.55 (1.77)}$	D_{hd}	$\frac{112.12 (1.36)}{104.58 (1.28)}$	I
Di-C4OC4-Pd	K $\frac{16.60 (5.92)}{14.86 (3.66)}$	D_{rd}	$\frac{124^a}{122^a}$	I
Di-C2OC2OC4-Pd	K $\frac{53.53 (23.76)}{< 30}$	D_{rd}	$\frac{114^a}{110^a}$	I

K, crystal phase); D_{hd} , disordered hexagonal columnar phase; I, isotropic phase; Temperature gradient, $10.0^\circ\text{C min}^{-1}$. ^a Observed from polarized microscope.



(Scheme 2-2)



CN-Pd : X = CN
Cl-Pd : X = Cl
Br-Pd^a : X = Br
I-Pd : X = I
H-Pd : X = H
C₂H₅-Pd : X = C₂H₅
CH₃-Pd : X = CH₃
OCH₃-Pd^a : X = OCH₃

(Scheme 2-3)

Table 2-5. DSC data for Cu(II) complexes of β -diketone (X-Cu), °C (J/g)

CN-Cu :		Col _{hd}	<u>235.0^a</u>	
			233.9 ^a	
Cl-Cu :		Col _{hd}	<u>181.09(2.68)</u>	
			174.32(2.48)	
Br-Cu :		Col _{hd}	<u>160.5^a</u>	
			150.0 ^a	
I-Cu :		Col _{hd}	<u>165.37(2.17)</u>	
			156.96(2.34)	
H-Cu⁽¹⁰⁾ :	K		<u>82.7(31.07)</u>	
			<u>43.9(19.84)</u>	
OCH₃-Cu :	K	Col _{hd}	<u>98.4^a</u>	
			74.8 ^a	
C₂H₅-Cu :	K	Col _{rd}	<u>106.18(2.65)</u>	
			97.30(2.88)	
CH₃-Cu :	K	Col _{rd}	<u>125.24(0.69)</u>	
			118.39(0.64)	

Col_{hd}, disordered hexagonal columnar phase; Col_{rd}, disordered rectangular columnar phase) ,
 K, crystal phase); D_{hd}, disordered hexagonal columnar phase; I, isotropic phase;
 Temperature gradient, 10.0°C min⁻¹. ^a Observed from polarized microscope.

Table 2-6. DSC data for Pd (II) complexes of β -diketone (X-Pd), °C (J/g)

CN-Pd :		Col _{hd}	$\frac{203.8^a}{201.4^a}$	I
Cl-Pd :		Col _{hd}	$\frac{161.3^a}{160.7^a}$	I
Br-Pd :		Col _{hd}	$\frac{139.8^a}{138.4^a}$	I
I-Pd :		Col _{hd}	$\frac{150.2^a}{148.5^a}$	I
H-Pd :	K		$\frac{73.06(33.88)}{17.40(20.62)}$	Col _{hd}
				$\frac{124.41(0.91)}{111.42(0.72)}$
OCH₃-Pd :	K		$\frac{>25^a}{>25^a}$	Col _{hd}
				$\frac{146.0^a}{134.2^a}$
C₂H₅-Pd :	K		$\frac{>25^a}{>25^a}$	Col _{rd}
				$\frac{105.13(1.24)}{88.65(1.31)}$
CH₃-Pd :	K		$\frac{46.23(6.40)}{29.17(10.37)}$	Col _{rd}
				$\frac{142.34(1.73)}{123.06(1.12)}$

Col_{hd}, disordered hexagonal columnar phase; Col_{rd}, disordered rectangular columnar phase; K, crystal phase; D_{hd}, disordered hexagonal columnar phase; I, isotropic phase; Temperature gradient, 10.0°C min⁻¹. ^a Observed from polarized microscope.



Pergamon

Tetrahedron 57 (2001) 3343–3347

TETRAHEDRON

Application of Grunwald–Winstein correlation analyses with Y_{BnBr} scales to the solvolysis of benzoyl bromides

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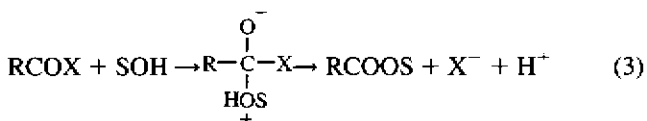
Received 26 December 2000; accepted 19 February 2001

Abstract—The solvolysis of 4-methoxy-(1), 4-methyl-(2), unsubstituted (3) and 4-chloro-(4) benzoyl bromide in a variety of solvents was studied. The linear $\log k - Y_{\text{BnBr}}$ plots for 1 indicates limiting $S_{\text{N}}1$ mechanism, whereas the splitting of lines for nucleophilic solvents and poorly nucleophilic solvents in the case of 2 suggests significant nucleophilic solvent participation. The mechanism for the solvolysis of 3 and 4 probably varies with solvents, similar to that of the corresponding chlorides. Good linear Hammett $\log k - \sigma^+$ plot could be found in a few solvents. A comparison of the solvolytic behavior for aromatic acyl bromides and chlorides will be discussed. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

Acyl halides are fundamental organic substrates with very high reactivity. Although acyl chlorides were continuously studied from mechanistic¹ and synthetic² points of view, much less attention was paid to the corresponding bromides. Nucleophilic substitution of substituted aromatic acyl bromides with methanol in acetonitrile solution was examined and the mechanism was found substituent-dependent.³ To our knowledge, little work on the solvent effect for the solvolysis of acyl bromides has been performed.

Early mechanistic studies led to a conclusion of three possible pathways for the solvolysis of acyl halides,⁴ namely, the unimolecular dissociation (Eq. (1)), the bimolecular synchronous $S_{\text{N}}2$ -type (Eq. (2)) and the addition–elimination (Eq. (3)) mechanisms.



Previously, based on the observation of linear correlation between logarithms of rate constants in a number of solvents for 4-methoxybenzoyl chloride, which was proposed to

solvolysed via limiting $S_{\text{N}}1$ mechanism from linear Grunwald–Winstein plots with Y_{Cl} scales,⁵ 2,6-dimethylbenzoyl chloride and 4-methoxybenzoyl chloride were both considered to solvolyze with $S_{\text{N}}1$ mechanism similar to the 1-adamantyl system.⁶ Non-linear $\log k - mY_{\text{Cl}}$ plots suggested different mechanisms of solvolysis for other aromatic acyl chlorides.⁷ However, by employing the single⁸ and the dual-parameter⁹ Grunwald–Winstein (Eqs. (4)⁸ and (5)⁹) with Y_{BnCl} ¹⁰ and N_{OTs} ¹¹ scales to examine solvolytic mechanisms for a series of benzoyl chlorides, and in association with the results of Hammett-type correlation analyses and of ab initio calculations, we concluded^{1a} that 2,6-dimethylbenzoyl chloride solvolyzed with limiting $S_{\text{N}}1$ mechanism (Eq. (1)), while 2-methyl-, 4-methoxy- and 4-methylbenzoyl chloride proceeded with nucleophilic solvent participation.

$$\log(k/k_0) = mY \quad (4)$$

$$\log(k/k_0) = mY + lN \quad (5)$$

More complicated mechanisms were involved for other benzoyl chlorides.

Obviously, correlation analysis using Y_{BnCl} scales will provide a better understanding to the solvolytic mechanism for benzoyl chlorides. We therefore undertook to explore the applicability of using Y_{BnBr} ¹² in a similar approach for studying the solvolysis of benzoyl bromides. The results are reported in the present paper.

2. Results

4-Methoxybenzoyl bromide (1), 4-methylbenzoyl bromide (2), benzoyl bromide (3), and 4-chlorobenzoyl bromide (4),

Keywords: solvolysis; Y_{BnBr} ; Grunwald–Winstein correlation.

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Table 1. Solvolysis rate constants ($\times 10^2$) for aromatic acyl bromides (1–4) at 25°C

Solvent ^a	1	2	3	4
100E	9.53	3.16	5.90	9.22
90E	50.2 ^b	8.87	7.12	20.4 ^b
80E	130 ^b	19.5 ^b	8.44	
90A	4.09	1.96	3.26	2.52
80A	34.3 ^b	6.94	5.77	6.10
70A	113 ^b	16.6 ^b	8.38	
100M	84.5 ^b	18.3 ^b	12.8 ^b	43.8 ^b
90M		32.7 ^b	18.9 ^b	
80M			35.5 ^b	
100T			8.12	2.03
80T20E		33.8 ^b	6.07	2.78
60T40E	327 ^b	19.2 ^b	5.51	3.54
40T60E	117 ^b	9.88	4.71	4.73

^a For abbreviation of solvents: A=acetone, E=ethanol, M=methanol, T=2,2,2-trifluoroethanol. Figures shown are percentages of volume in water; 80T20E indicates T-E of 80:20 v/v and likewise for 60T40E and 40T60E.

^b From data at other temperatures.

Table 2. Correlation analyses using single parameter Eq. (1)

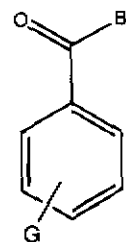
Substrate	Parameters	n^a (solvent)	R	m (S.D.) ^b
1	Y_{BnBr}	9 (All)	0.993	0.702 (0.031)
		7 (AEM)	0.995	0.745 (0.032)
2	Y_{BnBr}	11 (All)	0.926	0.359 (0.049)
		8 (AEM)	0.995	0.509 (0.020)
3	Y_{BnBr}	13 (All)	0.397	0.086 (0.060)
		9 (AEM)	0.923	0.299 (0.047)
4	Y_{BnBr}	9 (All)	0.383	-0.115 (0.105)
		5 (AEM)	0.882	0.597 (0.184)

^a Number of data points.

^b Standard deviation.

were solvolysed in a variety of solvents, and the rate constants were measured by conductimetric method as described.^{10a} Because of the high reactivity and the low solubility at temperature below -10°C , the rate of

solvolysis in solvents of relatively large solvent ionizing power could not be measured accurately. Pertinent data at 25°C are given in Table 1.



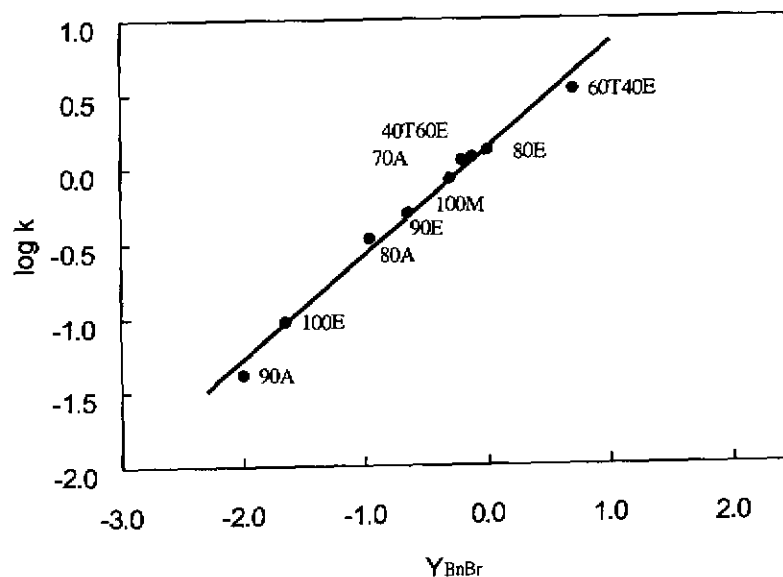
- 1 G = 4-OCH₃
- 2 G = 4-CH₃
- 3 G = H
- 4 G = 4-Cl

Correlation analyses of $\log k$ values against Y_{Br} ¹³ using Eq. (4) or against Y_{Br} and N_{OTs} using Eq. (5) showed poor correlation with scattered data points in every case. The results of the analysis against Y_{BnBr} are shown in Table 2. An excellent linear relationship¹⁴ ($R=0.993$) was found in $\log k$ - Y_{BnBr} plots for acyl bromide 1 in all solvents where k could be measured (Fig. 1). In the case of compound 2, two lines, one in nucleophilic solvents ($R=0.995$ in aqueous acetone, ethanol and methanol) and the other in poorly nucleophilic ethanol-trifluoroethanol, were observed against Y_{BnBr} (Fig. 2). Only dispersed $\log k$ - Y_{BnBr} plots were found for 3 and 4, even if only nucleophilic solvents were considered. The analysis for $\log k$ against Y_{BnBr} and N_{OTs} or N_{T} ¹⁵ by using Eq. (5) revealed no good linear relationship for acyl bromides 2, 3 and 4 either.

Hammett-type correlation analyses of $\log k$ values against σ^+ constants¹⁶ (Eq. (6)) were carried out for substrates if three or four rate constants in same solvent were available (Table 3).

$$\log(k/k_0) = \sigma^+ \rho \quad (6)$$

Among the limited number of solvent systems under examination, excellent linear correlation ($R=0.994$) was observed for all four substrates in 60T40E with ρ of -2.20 (Fig. 3).

**Figure 1.** Plots of $\log k$ for 1 against Y_{BnBr}

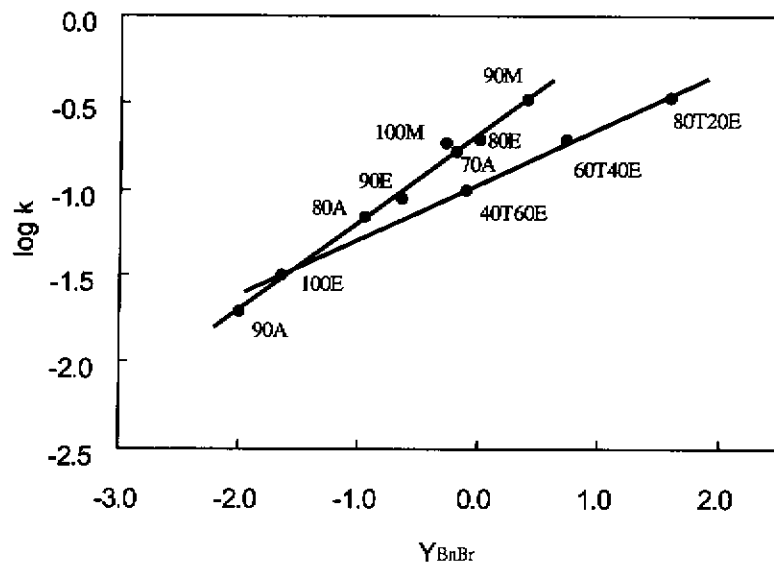


Figure 2. Plots of $\log k$ for 2 against Y_{BnBr} .

Table 3. Hammett plots of selective $\log k$ values against σ^+ constants

Solvent	Substrate	n	ρ	R
90E	1–3	3	-1.13	0.954
80E	1–3	3	-2.03	0.995
80A	1–4	4	-0.859	0.927
80A	1–3	3	-1.03	0.951
70A	1–3	3	-1.48	0.988
100M	1–3	3	-1.08	0.974
80T20E	2–4	3	-2.52	0.999
60T40E	1–4	4	-2.20	0.994
40T60E	1–4	4	-1.60	0.968
40T60E	1–3	3	-1.83	0.983

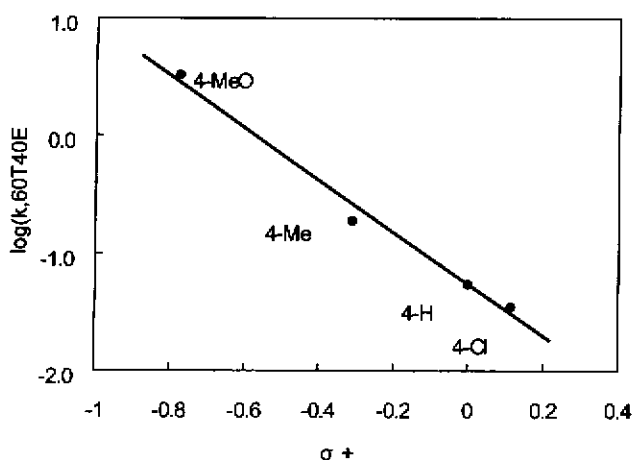


Figure 3. Plots of $\log k$ in 60T40E for 1–4 against σ^+ constants.

3. Discussion

Correlation of rates of solvolysis using Grunwald–Winstein Eqs. (4) and/or (5) with appropriate scales of solvent ionizing power (Y) and solvent nucleophilicity (N) has been generally applied to mechanistic studies for the solvolysis of substrates at saturated carbons.¹⁷ Recently, it was also employed in the elucidation of solvolytic

mechanisms for unsaturated systems, such as styryl-iodonium salt,¹⁸ N,N -diphenylcarbamoyl chloride¹⁹ and aromatic acyl chlorides.^{1a,c,d,6} The usefulness of Y_{BnCl} scale in studying the solvolysis of substituted benzoyl chlorides^{1a} suggested an extension to the study of the corresponding benzoyl bromides with Y_{BnBr} would be worthwhile. Indeed, valuable information about the solvolytic mechanism for benzoyl bromides was obtained.

Owing to the high reactivity, only limited number of aromatic acyl bromides were found suitable for the study of solvent effects. Although seven substituted benzoyl chlorides were examined in the previous work,^{1a} the reaction kinetics for only four bromides (1–4) could be monitored in reasonable varieties of solvent systems, including both highly nucleophilic and poorly nucleophilic ones, for correlation analyses. In spite of their low solubility in solvents of high water-content, 1–4 could still be solvolyzed in solvent systems with sufficiently large difference in solvent ionizing power ($\Delta Y_{\text{BnBr}}=2.7\text{--}4.6$) and made the interpretation meaningful. However, due to insufficient kinetic data in the non-nucleophilic trifluoroethanol (100T) available, which was found necessary in correlating experimental reactivity with the energy of isodesmic reaction,^{1a} ab initio calculation for the formation of acylium ion (ArCO^+) from benzoyl bromides (RCOBr) was not performed. Besides, the three-parameter Eq. (7) suggested by Kevill and coworkers²⁰ was not tested, as it would be meaningless to treat such regression with less than ten variables.

$$\log(k/k_0) = mY_{\text{Cl}} + lN_{\text{T}} + hI \quad (7)$$

In the previous study,^{1a} the solvolyses of 4-methoxy- and 4-methylbenzoyl chlorides were considered to proceed with non-limiting $S_{\text{N}}1$ mechanisms, while the unsubstituted benzoyl chloride was on the borderline of unimolecular dissociation (Eq. (1)) and the addition–elimination (Eq. (3)) mechanisms. Moreover, the solvolyses of 4-chloro- and 4-nitrobenzoyl chlorides were likely to involve an $S_{\text{N}}2$ mechanism (Eq. (2)) in nucleophilic solvents, and an addition–elimination (Eq. (3)) mechanism

in trifluoroethanol–ethanol.^{1a} Similar to the corresponding chlorides, no linear correlation with Y_{Br} (Eq. (5)), or Y_{Br} and N_{OTs} (Eq. (6)) was found for **1** to **4** in the present work. On the other hand, $\log k - Y_{\text{BnBr}}$ plots showed excellent linear correlation (Fig. 1; $R=0.993$, Table 2) for the solvolysis of 4-methoxybenzoyl bromide (**1**), and therefore, a limiting $S_{\text{N}}1$ mechanism could be deduced. The lack of significant nucleophilic solvent participation as compared with the analogous 4-methoxybenzoyl chloride^{1a} is likely due to the better leaving ability of bromide ion in **1**.

In the case of the 4-methyl derivative (**2**), two separate lines, one for nucleophilic solvents (AEM) and the other for poorly nucleophilic solvents (TE), were observed (Fig. 2). The use of isodielectric trifluoroethanol–ethanol mixture²¹ has been shown to be a diagnostic probe for nucleophilic solvent participation in solvolyses of various substrates.²² Therefore, the downward splitting of line for data points obtained in TE from that in AEM suggests the intervention of nucleophilic solvents in the solvolysis of **2**. The poor regression for **2** with respect to all solvents ($R=0.926$, $n=11$, Table 2) by using the single-parameter Eq. (4) could be improved ($R=0.964$, $n=9$) from the dual-parameter Eq. (5), $\log(k/k_0)=0.458Y_{\text{BnBr}}+0.301N_{\text{OTs}}$. Although no excellent linear correlation ($R\geq 0.99$)¹⁴ was obtained, the low m value and the high l value could also indicate significant nucleophilic solvent participation in the solvolysis of **2**. Unlike 4-methoxybenzoyl bromide **1** and the corresponding chloride (vide supra), but similar to 4-methoxybenzyl halides,^{22c} the reactivity of the bromide leaving group is still not good enough to yield an unassisted solvolysis.

The solvolysis of benzoyl bromides **3** and **4** gave nonlinear relationship for Eqs. (4) or (5). Scattered data points were resulted from $\log k - Y_{\text{BnBr}}$ plots. Poor correlation with Y_{BnBr} and N_{OTs} by using the dual-parameter Eq. (5), $R=0.7-0.8$, was found in both cases. The results show some similarities with those found for the corresponding benzoyl chlorides,^{1a} indicating a variation of mechanisms in different solvent. Logarithm plots of rate data for **3** and **4**, respectively, against those for the corresponding chlorides^{1a} showed fair linear relationships ($R=0.96$). Probably different types of non- $S_{\text{N}}1$ reactions were involved in the solvolysis of **3** and **4** in nucleophilic solvents, similar to the corresponding chlorides.^{1a}

The results of Hammett plots against σ^+ constants (Table 3) are also interesting. The solvolysis of **1** to **4** showed linear $\log k - \sigma^-$ relationship in 60T40E (Fig. 3), but not in other nucleophilic solvents. Bromide **1** was too reactive in 80T20E to yield a reliable rate constant. Nevertheless, linear plot was observed for **2-4** in 80T20E, and presumably for **1-4** as well. In 40T60E, linear regression for **1-3** was realized as a marginal case, but significant deviation was found for the 4-chloro derivative **4**. The rate constant for **4** in 70A or in 80E could not be measured conductimetrically due to the low solubility at the temperature below 0°C. But linear plots were obtained for **1-3** in these solvents. Pertinent data for $\log k - \sigma^-$ regression are listed in Table 3. For acyl chlorides corresponding to **1-4**, linear relationships were found only in solvents containing high percentage of water (50A, 50E and 60M) or high percentage of trifluoro-

ethanol (100T and 80T20E).^{1a} But for those corresponding to **1-3**, linear $\log k - \sigma^+$ plots were observed in solvents containing less water (60A, 60E and 70M) or less trifluoroethanol (60T40E).^{1a} Apparently, the more reactive acyl bromides **1-4** will display linear Hammett $\log k - \sigma^-$ plots in solvents of smaller ionizing power, such as 70A and 80E, as compared with corresponding chlorides. The small negative ρ values in 60T40E and 80T20E, and even smaller in nucleophilic solvents could also be attributed to the less extent of charge development at the transition state, similarly to that found in the solvolysis of acyl chlorides.^{1a}

4. Conclusions

In summary, solvolytic mechanisms for benzoyl bromides could be understood by means of Grunwald–Winstein type correlation analysis using Y_{BnBr} scales, in association with Hammett-type plots against σ^+ constants. 4-Methoxybenzoyl bromide (**1**) solvolyzes with limiting $S_{\text{N}}1$ mechanism (Eq. (1)), whereas 4-methylbenzoyl bromide (**2**) proceeds with nucleophilic solvent participation. Different types of $S_{\text{N}}1$ and non- $S_{\text{N}}1$ reactions are probably involved in the solvolysis of benzoyl bromide (**3**) and 4-chlorobenzoyl bromide (**4**). The presence of the better leaving group, bromide as compared with chloride, could make benzoyl halides more likely to solvolyze via limiting or non-limiting $S_{\text{N}}1$ mechanism and to exhibit linear Hammett-type plots, $\log k - \sigma^+$ in solvents of smaller ionizing power.

5. Experimental

5.1. Materials

Spectral-grade or reagent-grade solvents (E. Merck) were purified following conventional methods²³ for kinetic studies. Doubly deionized water was used to prepare aqueous solvent mixtures for solvolytic studies. Benzoyl bromide (**3**) was commercially available (across) and other acid bromides **1**, **2** and **4** were prepared from corresponding acids and thionyl bromide,²⁴ respectively. The IR and NMR spectra were found to agree with the assigned structure. All of the acid bromides were freshly distilled for kinetic studies.

5.2. Kinetic measurements

Rate constants were measured by conductimetric method at least in duplicate. The conductivity cells containing about 1.8 mL of 1×10^{-4} – 1×10^{-5} M solution of substrate and 1 μL of 2,6-lutidine were placed in a thermostat with a temperature variation of $\pm 0.02^\circ\text{C}$. The maximum error for the measurement of k is $\pm 2\%$.

Rate constants (in s^{-1}) were monitored at 25°C or at appropriate temperatures. The rate constants (in s^{-1}) measured at low temperatures are listed as follows:

For **1** in 90E, $k(-10^\circ\text{C})=1.79 \times 10^{-2}$, $k(-5^\circ\text{C})=3.04 \times 10^{-2}$ and $k(0^\circ\text{C})=5.10 \times 10^{-2}$; in 80E, $k(-10^\circ\text{C})=2.77 \times 10^{-2}$, $k(-5^\circ\text{C})=5.10 \times 10^{-2}$ and $k(0^\circ\text{C})=9.19 \times 10^{-2}$; in 80A, k

(-10°C)= 1.62×10^{-2} , $k(-5^{\circ}\text{C})=2.63\times 10^{-2}$ and $k(0^{\circ}\text{C})=4.20\times 10^{-2}$; in 70A, $k(-10^{\circ}\text{C})=2.54\times 10^{-2}$, $k(-5^{\circ}\text{C})=4.46\times 10^{-2}$ and $k(0^{\circ}\text{C})=8.30\times 10^{-2}$; in 100M, $k(-10^{\circ}\text{C})=3.15\times 10^{-2}$, $k(-5^{\circ}\text{C})=5.31\times 10^{-2}$ and $k(0^{\circ}\text{C})=8.79\times 10^{-2}$; in 60T40E, $k(-10^{\circ}\text{C})=4.02\times 10^{-2}$ and $k(-5^{\circ}\text{C})=8.08\times 10^{-2}$; in 40T60E, $k(-10^{\circ}\text{C})=2.92\times 10^{-2}$, $k(-5^{\circ}\text{C})=5.24\times 10^{-2}$ and $k(0^{\circ}\text{C})=9.22\times 10^{-2}$.

For 2, in 80E, $k(-10^{\circ}\text{C})=5.03\times 10^{-3}$, $k(-5^{\circ}\text{C})=8.99\times 10^{-3}$ and $k(0^{\circ}\text{C})=1.57\times 10^{-2}$; in 70A, $k(-10^{\circ}\text{C})=4.83\times 10^{-3}$, $k(-5^{\circ}\text{C})=8.47\times 10^{-3}$ and $k(0^{\circ}\text{C})=1.46\times 10^{-2}$; in 100M, $k(-10^{\circ}\text{C})=4.48\times 10^{-3}$, $k(-5^{\circ}\text{C})=8.07\times 10^{-3}$ and $k(0^{\circ}\text{C})=1.42\times 10^{-2}$; in 90M, $k(-10^{\circ}\text{C})=6.05\times 10^{-3}$, $k(-5^{\circ}\text{C})=1.14\times 10^{-2}$ and $k(0^{\circ}\text{C})=2.10\times 10^{-2}$; in 80T20E, $k(-10^{\circ}\text{C})=5.64\times 10^{-3}$, $k(-5^{\circ}\text{C})=1.08\times 10^{-2}$ and $k(0^{\circ}\text{C})=2.10\times 10^{-2}$; in 60T40E, $k(-10^{\circ}\text{C})=4.47\times 10^{-3}$, $k(-5^{\circ}\text{C})=8.03\times 10^{-3}$ and $k(0^{\circ}\text{C})=1.43\times 10^{-2}$.

For 3, in 100M, $k(-10^{\circ}\text{C})=4.67\times 10^{-3}$, $k(-5^{\circ}\text{C})=7.90\times 10^{-3}$ and $k(0^{\circ}\text{C})=1.31\times 10^{-2}$; in 90M, $k(-10^{\circ}\text{C})=5.54\times 10^{-3}$, $k(-5^{\circ}\text{C})=9.71\times 10^{-3}$ and $k(0^{\circ}\text{C})=1.67\times 10^{-2}$; in 80M, $k(-10^{\circ}\text{C})=7.03\times 10^{-3}$, $k(-5^{\circ}\text{C})=1.31\times 10^{-2}$, $k(0^{\circ}\text{C})=2.39\times 10^{-2}$.

For 4, in 90E, $k(-10^{\circ}\text{C})=3.14\times 10^{-3}$, $k(-5^{\circ}\text{C})=6.09\times 10^{-3}$ and $k(0^{\circ}\text{C})=1.15\times 10^{-2}$; in 100M, $k(-10^{\circ}\text{C})=7.31\times 10^{-3}$, $k(-5^{\circ}\text{C})=1.40\times 10^{-2}$ and $k(0^{\circ}\text{C})=2.62\times 10^{-2}$.

The rate constants measured at 25°C and those from extrapolation to 25°C by using Arrhenius plot are given in Table 1.

Acknowledgements

The authors acknowledge the financial support from the National Science Council, Republic of China (Grants NSC88-2113-M-002-014 and NSC89-2113-M-002-012).

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Density functional theory calculations of ^{17}O and ^{13}C NMR chemical shifts for aromatic acyl chlorides

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Received 8 October 2000; revised 14 March 2001; accepted 6 April 2001

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ABSTRACT: Density functional theory (DFT) at the B3LYP/6-31 + G(d,p)//B3LYP/6-31G(d) level was used to calculate ^{17}O and ^{13}C NMR chemical shifts of the carbonyl group of aromatic acyl chlorides **1a–n**. The aryl groups included substituted phenyl, furyl, thienyl and naphthyl. The calculated ^{17}O chemical shifts correlated well with the experimental values and with Hammett-type σ^+ constants. Therefore, in many cases it is possible to deduce σ^+ constants of substituted aryl groups via gas-phase calculation of ^{17}O chemical shifts of the carbonyl groups. The σ^+ values obtained in the gas-phase calculation show the intrinsic property of substituents, so they provide a good reference set for systematic comparison to evaluate the effect of the environment. Furthermore, the concept of $n-\pi^*$ mixing can be used to understand the sensitivity of the O and Cl atoms and the insensitivity of the C atom towards substituent effects in aromatic acyl chlorides. Copyright © 2001 John Wiley & Sons, Ltd.

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KEYWORDS: ^{17}O chemical shift; theoretical calculation; substituent constant; $n-\pi^*$ mixing; solvolysis; solvent effect

INTRODUCTION

With the use of substituted acetophenones and benzaldehydes, it has been shown that the ^{17}O NMR chemical shift $\delta(^{17}\text{O})$ of a carbonyl group is sensitive to substituents of the neighboring phenyl group.^{1,2} Studies of acyl-containing compounds such as acids, amides, esters and other derivatives of carboxylic acids [YC(=O)X] have also confirmed the sensitivity of ^{17}O chemical shifts in reflecting the electronic nature of substituents X and Y.^{3–9} Owing to this sensitivity, ^{17}O chemical shifts have been studied from different viewpoints. Dahn and co-workers used them to establish a scale of electrophilicity of the carbonyl group.^{3–5} Others used them to study the effectiveness of transmission of the substituent effect.^{9–13}

It was found that an excellent linear correlation existed between σ^+ and ^{17}O chemical shifts measured in the non-polar solvent CCl_4 for 12 α,α,α -trifluoroacetophenones (correlation coefficient $R = 0.998$).⁷ Extending the study of benzene derivatives of trifluoroacetyl compounds to heteroaromatic derivatives such as furyl and thienyl, the same correlation between σ^+ and ^{17}O chemical shifts was also observed, except in the case of 3-furyl.¹⁴ More

recently, we demonstrated that density functional theory (DFT) calculations of ^{17}O chemical shifts at the B3LYP/6-31 + G(d,p)//B3LYP/6-31G(d) level of the above trifluoroacetyl compounds were compatible with the experimental values measured in CCl_4 .¹⁵ The small deviation (absolute values of <5 ppm in most cases) of the calculated values from the experimental values might be fortuitous, but the good correlation between the calculated and observed values is important. An excellent linear correlation ($R = 0.993$) between the calculated and observed ^{17}O chemical shifts of 15 trifluoroacetyl compounds was obtained when the data for the 3-furyl compound was excluded. Therefore, for functional groups the σ^+ values of which are difficult to deduce experimentally, theoretical calculation of ^{17}O chemical shifts of corresponding carbonyl compounds seems to be a potential substitute.

In contrast to the high sensitivity of the oxygen atom to the donor/acceptor ability of a neighboring group, the ^{13}C chemical shift of the carbonyl carbon atom is less dependent on the electronic nature of a neighboring group.^{11,12,16,17} Analysis of components of shielding tensors of HCOX with *ab initio* calculation has revealed that $n-\pi^*$ mixing contributes to the sensitivity of ^{17}O chemical shifts toward the nature of X.¹⁶ As the n -orbital is basically localized on the oxygen atom, the sensitivity observed on the oxygen atom does not occur on the carbon atom.

In order to establish whether the good correlations

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Contract/grant sponsor: National Science Council of ROC.

Published online 24 July 2001

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Table 1. Calculated and experimentally observed chemical shifts of aromatic acyl chlorides

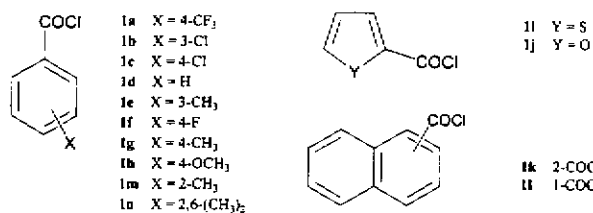
ArCOCl	Ar	σ^+	$\delta(^{17}\text{O})_{\text{calc}}$	$\delta(^{17}\text{O})_{\text{obs,CCl}_4}$	$\delta(^{17}\text{O})_{\text{obs,CH}_3\text{CN}}$	$\Delta\delta_{\text{CCl}_4}^a$	$\Delta\delta_{\text{CH}_3\text{CN}}^b$	$\delta(^{13}\text{C})_{\text{calc}}$	$\delta(^{13}\text{C})_{\text{obs}}$	$\Delta\delta^c$	$\sigma_{\text{iso}}(\text{Cl})_{\text{calc}}$
1a	4- $\text{CF}_3\text{C}_6\text{H}_4$	0.612	506.9	505.2	497.5	1.7	9.4	169.9	167.9	2.0	523.6
1b	3- ClC_6H_4	0.399	501.3	499.2		2.1		169.5	167.4	2.1	525.8
1c	4- ClC_6H_4	0.114	495.6	494.6	487.7	1.0	7.9	169.0	167.0	2.0	532.1
1d	C_6H_5	0	494.8	493.6	485.5	1.2	9.3	170.1	168.0	2.1	531.5
1e	3- $\text{CH}_3\text{C}_6\text{H}_4$	-0.066	493.4	492.3		1.1		170.1	167.8	2.3	533.5
1f	4- FC_6H_4	-0.073	492.1	490.6	483.6	1.5	8.4	168.6	166.9	1.7	530.6
1g	4- $\text{CH}_3\text{C}_6\text{H}_4$	-0.311	489.2	487.7	479.3	1.5	9.9	169.3	167.6	1.7	534.2
1h	4- $\text{CH}_3\text{OC}_6\text{H}_4$	-0.778	479.4	477.4	468.9	2.0	10.5	168.2	165.3	2.9	540.4
1i	2-Thienyl	-0.928	479.5	476.7		2.8		160.2	159.3	0.9	511.3
1j	2-Furyl	-1.030	479.9	470.6		9.3		156.1	154.6	1.5	512.2
1k	2-Naphthyl	-0.126	493.7	489.0	485.3	4.7	8.4	170.1	172.2	-2.1	534.5
1l	1-Naphthyl		508.2	508.3	505.8	-0.1	2.4	169.3	175.2	-5.9	510.4
1m	2- $\text{CH}_3\text{C}_6\text{H}_4$		514.7	511.6	505.5	3.1	9.2	169.7	167.3	2.4	514.1
1n	2,6- $(\text{CH}_3)_2\text{C}_6\text{H}_3$		546.4	536.3	523.3	10.1	23.1	175.3	177.0	-1.7	423.8

^a $\Delta\delta_{\text{CCl}_4} = \delta(^{17}\text{O})_{\text{calc}} - \delta(^{17}\text{O})_{\text{obs,CCl}_4}$

^b $\Delta\delta_{\text{CH}_3\text{CN}} = \delta(^{17}\text{O})_{\text{calc}} - \delta(^{17}\text{O})_{\text{obs,CH}_3\text{CN}}$

^c $\Delta\delta = \delta(^{13}\text{C})_{\text{calc}} - \delta(^{13}\text{C})_{\text{obs}}$

between calculated and observed ^{17}O chemical shifts and between σ^+ constants and calculated ^{17}O chemical shifts also exist in systems other than the trifluoroacetyl compounds, we have studied other carbonyl compounds. In this paper, we present results for aromatic acyl chlorides (compounds **1a–n**). The aryl groups also include furyl, thienyl and naphthyl, not just limited to substituted phenyl of which the σ^+ constants vs observed ^{17}O chemical shift correlation have been reported in the literature.⁸ In addition to the analysis of the ^{17}O chemical shifts of acyl chlorides, the ^{13}C chemical shifts of the acyl carbon atom were also analyzed to verify if the explanation deduced from the calculation of HCOX can be invoked to explain the sensitivity difference of ^{17}O and ^{13}C chemical shifts in ArCOCl.



EXPERIMENTAL AND COMPUTATIONAL DETAILS

^{17}O NMR spectra were recorded on a Bruker AM-300 WB spectrometer equipped with a 10 mm broadband probe operating at 40.670 MHz and values were reported relative to deuterium oxide. A 0.5 M solution in carbon tetrachloride was prepared in a dry-box. Perdeuterated benzene was used as the external lock. The recording temperature (51 °C) was corrected by using 80% ethylene glycol in DMSO- d_6 as the standard. A preliminary study of the unsubstituted benzoyl chloride indicated that 0.3 and 0.5 M solutions showed very close $\delta(^{17}\text{O})$ values ($\Delta\delta = 0.3$ ppm). Therefore, 0.5 M is probably an appropriate concentration to minimize the possible dipole interactions between solute molecules. ^{13}C NMR spectra were recorded on a Bruker AM-300 spectrometer using chloroform- d solutions at ambient temperature (uncertainty: 0.5 ppm). The observed chemical shifts at natural abundance are given in Table 1.

Stable conformers of aromatic acyl chlorides were searched and checked with frequency analysis at the AM1 level.¹⁸ The structures of the conformers found were further optimized and verified by frequency analysis at the B3LYP/6-31G(d) level. B3LYP means that Becke's three parameter functional^{19a} is used for the exchange energy and the Lee, Yang and Parr functional^{19b} for correlation energy. Single-point energy calculations and GIAO NMR chemical shift calculations²⁰ were carried out at the B3LYP/6-31 + G(d,p) level based on the B3LYP/6-31G(d) optimized struc-

tures. The energy differences at the B3LYP/6-31 + G(d,p) level between conformers were used to calculate the population of conformers according to the Boltzmann distribution ($T = 298$ K). The chemical shifts of conformers were all taken into account according to the population. All the semi-empirical calculations were carried out with the program SPARTAN 4.1.²¹ The *ab initio* calculations were carried out with Gaussian 94,^{22a} except for the orbital energies listed in the supplementary material, which were calculated with Gaussian 98.^{22b}

To calculate the shielding tensor components (σ_{xx} , σ_{yy} and σ_{zz}), the convention of Dahn and Carrupt was followed.²³ In brief, the direction of the C=O bond is defined as the z -axis and the direction perpendicular to the acyl chloride plane is defined as the x -axis. Because the σ^+ constants for the *ortho*-substituted **1l–n** are not available, we only calculate the tensor components for **1a–k** in their lowest energy conformations.

RESULTS AND DISCUSSION

The calculated chemical shifts are analyzed in two directions. The degree of similarity between gas-phase calculated values and chemical shifts observed in non-polar CCl_4 is examined by plotting δ_{calc} against δ_{obs} . The sensitivity of the calculated chemical shifts to substituent effects in solvolysis reactions is checked by plotting δ_{calc} against σ^+ . Table 1 shows the ^{17}O NMR chemical shifts of **1a–n**. The range of the ^{17}O NMR chemical shifts in CCl_4 is 470.6–536.3 ppm. The deviations between the calculated [$\delta(^{17}\text{O})_{\text{calc}}$] and observed [$\delta(^{17}\text{O})_{\text{obs}}$] chemical shifts are small (ca 2 ppm) for benzoyl chlorides **1a–h** and the calculated values are consistently downfield relative to the observed values. The $\delta(^{17}\text{O})_{\text{calc}} - \delta(^{17}\text{O})_{\text{obs}}$ correlation is excellent ($R = 0.999$) for **1a–h**. As the observed values correlate well with σ^+ constants ($R = 0.995$), the calculated values correlate equally well with σ^+ ($R = 0.996$). If *ortho*-substituted phenyl (**1m** and **n**), naphthyl (**1k** and **l**) and heteroaromatic (**1j** and **j**) acyl chlorides are all taken into account, the $\delta(^{17}\text{O})_{\text{calc}} - \delta(^{17}\text{O})_{\text{obs}}$ correlation (Fig. 1) is still reasonable ($R = 0.985$). Among the 14 compounds, the calculated chemical shifts of **1j** (2-furyl) and **1n** (2,6-dimethylphenyl) show the largest deviations (9–10 ppm) from the observed values. Basically, the magnitude of the deviations of $\delta(^{17}\text{O})_{\text{calc}}$ from $\delta(^{17}\text{O})_{\text{obs}}$ is similar to that in the trifluoroacetyl series.¹⁵ For compounds without *ortho* substituents to the carbonyl group, **1a–k**, the correlation coefficient for the $\delta(^{17}\text{O})_{\text{calc}} - \sigma^+$ correlation is 0.988 and for $\delta(^{17}\text{O})_{\text{obs}} - \sigma^+$ it is 0.993. The reason for the large deviations for **1j** and **1n** is not clear. With two *ortho*-methyl groups, **1n** (2,6-dimethylphenyl) possesses the greatest steric congestion among the 14 acyl chlorides. The dihedral angle between the phenyl ring and the acyl plane is 58.5° in the calculated geometry of **1n** whereas the corresponding angle is no more than 5° in other

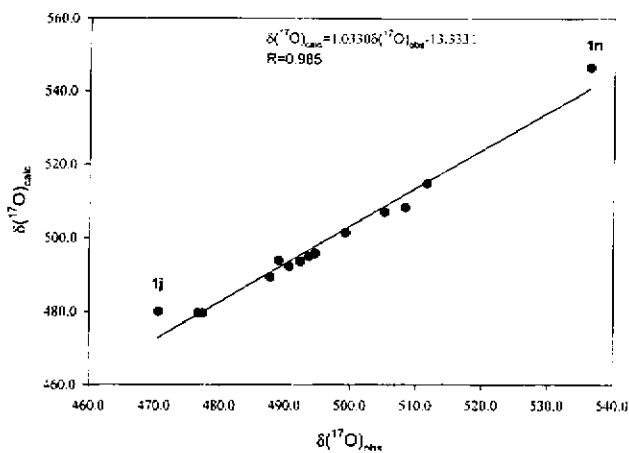


Figure 1. Correlation between $\delta(^{17}\text{O})_{\text{calc}}$ and $\delta(^{17}\text{O})_{\text{obs}}$ for compounds **1a–n**

compounds. Since proper treatment of electron correlation is important for NMR calculations as we have shown in Ref. 15 (p. 1002) that correlation between calculated and measured chemical shifts dropped if NMR calculations were carried out at the HF level, it is likely that better electron correlated theory levels are needed to handle sterically congestive systems such as **1n**.

In the literature, the ^{17}O chemical shifts measured in polar acetonitrile (CH_3CN) solvent^{8,10} have been reported for **1a, c, d, f–h** and **k–n**. They were more upfield than that in the non-polar CCl_4 by several ppm in most cases (Table 1). The sterically congested **1n** has a larger deviation [$\delta(^{17}\text{O})_{\text{obs,CCl}_4} - \delta(^{17}\text{O})_{\text{obs,CH}_3\text{CN}} = 13$ ppm]. The correlation between gas-phase calculated chemical shifts [$\delta(^{17}\text{O})_{\text{calc}}$] and those measured in CH_3CN [$\delta(^{17}\text{O})_{\text{obs,CH}_3\text{CN}}$] is fair ($R = 0.968$). With the exclusion of **1n**, the correlation improves ($R = 0.985$). The corresponding R value for the $\delta(^{17}\text{O})_{\text{calc}} - \delta(^{17}\text{O})_{\text{obs}}$ correlation in CCl_4 with the same set of compounds (also excluding **1n**) is 0.992. The better correlation between calculated values and chemical shifts in the non-polar solvent demonstrate that gas-phase calculated chemical shifts are reasonable and they may be used as a control group to contrast the influence of solvents on solutes.

The ^{13}C chemical shifts of the carbonyl carbon atom of **1a–n** in CDCl_3 are in the range 154.6–177.0 ppm [Table 1, $\delta(^{13}\text{C})_{\text{obs}}$]. Although the calculated chemical shifts deviate from the observed values by less than 5.9 ppm, the relatively small variation range of $\delta(^{13}\text{C})_{\text{obs}}$ (ca 23 ppm) makes the $\delta(^{13}\text{C})_{\text{calc}} - \delta(^{13}\text{C})_{\text{obs}}$ correlation ($R = 0.904$) much worse than that for ^{17}O chemical shifts. Scattered $\delta(^{13}\text{C})_{\text{obs}} - \sigma^+$ and $\delta(^{13}\text{C})_{\text{calc}} - \sigma^+$ plots were obtained ($R < 0.77$) even if the sterically congested compounds **1l–n** were not included.

A chemical shift is the difference in isotropic shieldings [σ_{iso} ; $\sigma_{\text{iso}} = (\sigma_{xx} + \sigma_{yy} + \sigma_{zz})/3$, where σ_{xx} , σ_{yy} , and σ_{zz} are the shielding tensor components in the x , y and z directions, respectively] between the reference

compound and the measured compound. In the study of HCOX ($X = \text{SiH}_3, \text{H, Me, SH, Cl, F, OMe, OH, NH}_2$ and O^-), Dahn and Carrupt found that σ_{zz} of ^{17}O is far more sensitive than σ_{xx} and σ_{yy} to the electronic nature of X .¹⁶ The range of σ_{zz} is -1649 ($X = \text{SiH}_3$) to -9 ppm ($X = \text{O}^-$), whereas the range of σ_{xx} is 414 – 215 ppm and that of σ_{yy} is -604 to -126 ppm. Shielding tensor component σ_{zz} is related to charge circulation in the x, y plane. Analyzing the mixing of unoccupied and occupied ground-state orbitals in the presence of a magnetic field from IGLO^{24,25} calculation results, Dahn and Carrupt¹⁶ found that the n (in the y direction)– π^* (in the x direction) mixing is the major cause of the large variation of σ_{zz} and is therefore responsible for the sensitivity of ^{17}O chemical shifts. On the other hand, the magnitudes of σ_{xx} , σ_{yy} and σ_{zz} of ^{13}C do not differ as much as in the case of ^{17}O . Furthermore, although some sensitivity towards X has been found for σ_{xx} and σ_{yy} of ^{13}C , the irregular variation of σ_{zz} results in a poor overall sensitivity of the carbonyl carbon atom towards X .¹⁶ In brief, the ^{17}O shift values are strongly influenced by the n – π^* mixing, whereas the ^{13}C shift values are determined by multiple factors. The n – π^* mixing does not affect the ^{13}C chemical shifts because the lone pair is located on the O atom.

In comparison with HCOX, the ArCOCl system, with the presence of an aryl group, is more complex in terms of mixing of orbitals under the influence of a magnetic field. Whether a specific shielding tensor component still dominates the sensitivity of an atom is unclear. Using the same definition of the x, y, z , directions as in Dahn and Carrupt's study, we calculated σ_{xx} , σ_{yy} and σ_{zz} of carbonyl oxygen and carbon atoms and plotted them against σ^+ constants to examine whether the tensor components are sensitive to the substituent effect. As shown in Fig. 2, the slopes for σ_{xx} , σ_{yy} and σ_{zz} of ^{17}O are 6.68, -23.18 and -33.50 , respectively; the correlation coefficients are 0.490, 0.992 and 0.920, respectively. Therefore, although σ_{zz} is inferior to σ_{yy} in correlating with σ^+ , it is the most sensitive component toward substituent effects as judged by the slopes. This result is similar to that of HCOX in that σ_{yy} correlates the best with Hammett–Taft σ_{R}° constants, but is less sensitive than σ_{zz} .¹⁶ Because the substituent effect is controlled by groups not directly bonded to the carbonyl group, unlike in the HCOX series, the variation ranges of the components are smaller in ArCOCl than in HCOX. When only the phenyl analogs **1a–h** ($\sigma^+ = 0.612$ to -0.188) are considered, all three components correlate well with σ^+ ($R = 0.988, 0.997$ and 0.996 for σ_{xx} , σ_{yy} and σ_{zz} , respectively). The slopes are 9.79, -24.25 and -42.30 for σ_{xx} , σ_{yy} and σ_{zz} , respectively, so σ_{zz} still contributes significantly to the variation of σ_{iso} .

Figure 3 shows the correlation between shielding tensor components of ^{13}C and σ^+ constants. All correlation coefficients are less satisfactory (< 0.9) than those for ^{17}O . The slopes do not differ much from each

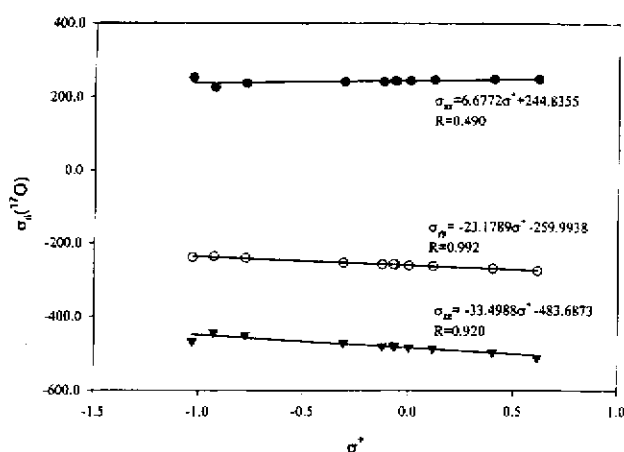


Figure 2. Plot of calculated σ_{ii} of ^{17}O against σ^+ constants for compounds **1a–k**

other, so the variation of σ_{iso} is not dominated by any specific component. Therefore, it will not be possible to describe the variation of ^{13}C chemical shifts qualitatively by a specific argument. Unlike for ^{17}O chemical shifts, the dominance of σ_{zz} makes the argument of $n-\pi^*$ mixing plausible.

Examination of frontier orbitals of the lowest energy conformer of **1a–h** shows that HOMO and HOMO-1 are π orbitals distributed basically on the phenyl ring. The HOMO-2 contains the oxygen lone pair along the y -axis (in the acyl chloride molecular plane and perpendicular to the C—O bond). The LUMO consists of π^* of C—O and the phenyl ring. Therefore, the HOMO-2 to LUMO transition has the smallest energy gap among transitions that are responsible to the magnitude of $\sigma_{zz}(^{17}\text{O})$. Plotting this $n-\pi^*$ energy gap against σ_{zz} and σ_{iso} of ^{17}O afforded a fair correlation (both $R \approx 0.96$) (only the lowest energy conformers of **1a–h** are used in finding the correlation; the values of orbital energies are reported in the supporting information at the epoc website at <http://www.wiley.com/epoc>). The HOMO–LUMO $\pi-\pi^*$ transition is irrelevant to the O atom, so it is not surprising that when the HOMO–LUMO gaps are plotted against σ (σ_{zz} or σ_{iso}), the correlation is very poor ($R < 0.4$).

Since HOMO-2 contains not only the lone pair of the oxygen atom, but also the lone pair of the chlorine atom in the y,z plane, we postulate that chlorine may also exhibit sensitivity towards substituent effects with a similar $n-\pi^*$ mixing mechanism. Plotting calculated σ_{zz} of the chlorine atom of sterically unhindered **1a–k** against σ^+ constants indeed shows a fair correlation ($R = 0.952$). Because the σ_{xx} of the two five-membered heteroaryl **1i** and **1j** deviate significantly from the trend for other aromatic acyl chlorides (Fig. 4), it makes the σ_{iso} of these two compounds much smaller than one would expect on the basis of the σ^+ value (Table I). To have a fair comparison between O, C and Cl, we use **1a–h** again to examine how well σ_{iso} of Cl reflects substituent effects. Plotting σ_{iso} of Cl against σ^+ gives a correlation

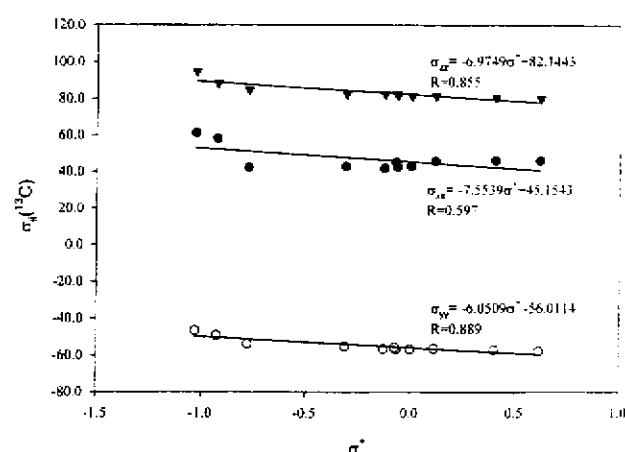


Figure 3. Plot of calculated σ_{ii} of ^{13}C against σ^- constants for compounds **1a–k**

coefficient of 0.972. This is worse than the $\delta(^{17}\text{O})_{\text{calc}}-\sigma^+$ correlation, but significantly better than the $\delta(^{13}\text{C})_{\text{calc}}-\sigma^+$ correlation.

CONCLUSION

We have shown that calculations of ^{17}O chemical shifts at the B3LYP/6-31 + G(d,p)//B3LYP/6-31G(d) level afford good results for ArCOCl , as found previously for ArCOCF_3 . In general, the correlation between calculated and observed ^{17}O chemical shifts is good, especially when unhindered phenyl analogs are considered. Therefore, the calculation of ^{17}O chemical shifts has the potential to determine the σ^- constant for a given group. It is known that σ^+ values (and also other substituent constants) for certain groups observed in different solvent systems are at significant variance.²⁶ The σ^- values obtained in gas-phase calculations show the intrinsic

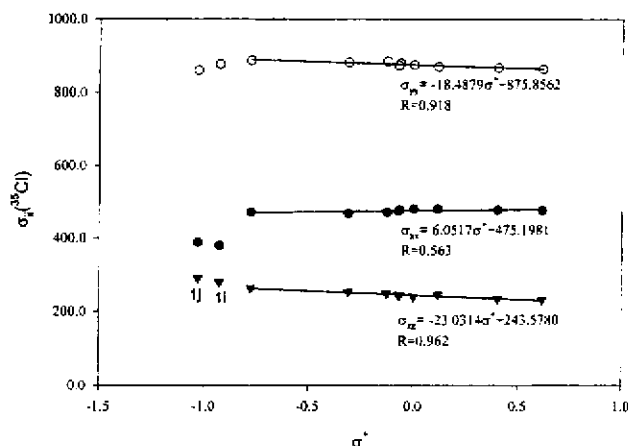


Figure 4. Plot of calculated σ_{ii} of Cl against σ^+ constants for compounds **1a–k**. The correlation is determined without the consideration of **1i** and **1j**. When σ_{zz} of **1i** and **1j** are included in the $\sigma_{zz}-\sigma^+$ correlation, $R = 0.952$.

property of substituents, so they provide a good reference set for systematic comparison to evaluate the effect of the environment.

The calculated absolute deviation of ^{13}C chemical shifts from the observed values is similar to that for ^{17}O . Nevertheless, the significantly smaller variation range of observed ^{13}C chemical shifts of the carbonyl carbon atom makes the analysis of $\delta(^{13}\text{C})$ not worthwhile in terms of detecting substituent effects. Our results demonstrate that for ArCOCl the sensitivity of $\delta(^{17}\text{O})$ and the insensitivity of $\delta(^{13}\text{C})$ could be understood in terms of $n-\pi^*$ mixing, in line with the conclusion obtained from HCOX by Dahn and co-workers. Furthermore, this concept leads us to analyze the σ_{iso} of Cl and we have found a correlation between $\sigma_{\text{iso}}(\text{Cl})$ and σ^+ for closely related compounds.

Supporting information

A table of calculated shielding tensors and a table of orbital energies of HOMO-2, HOMO and LUMO of lowest energy conformers of **1a-h** at the B3LYP/6-31+G(d,p) level are available at the epoc website at <http://www.wiley.com/epoc>.

Acknowledgements

This work is supported by the National Science Council of ROC (Taiwan). We also thank the National Center of High-Performance Computing and the Academia Sinica Computing Center for allocation of computing resources.

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