ELSEVIER

Journal of Organometallic Chemistry 552 (1998) 1–8

Journal of Organometallic Chemistry

Spectral properties and kinetics of the alkaline hydrolysis of chromium, tricarbonyl[3-[(η^6-aryl)methylene]-Z-1(3H)-isobenzofuranones]

Alexander Perjéssy [a,*], Pavol Hrnčiar [a], Zora Šusteková [a], Keith Bowden [b,1], Richard J. Ranson [b], Olga Hritzová [c], Nad'a Prónayová [d]

[a] *Department of Organic Chemistry and Institute of Organic Chemistry, Faculty of Natural Sciences, Comenius University, Mlynská dolina CH-2, 842 15 Bratislava, Slovak Republic*
[b] *Department of Biological and Chemical Sciences, University of Essex, Central Campus, Wivenhoe Park, Colchester Essex CO4 3SQ, UK*
[c] *Department of Organic Chemistry, Faculty of Natural Sciences, P.J. Šafárik University, 041 67 Košice, Slovak Republic*
[d] *Central Laboratories, Faculty of Chemical Technology, Slovak Technical University, 812 37 Bratislava, Slovak Republic*

Received 3 April 1997

Abstract

The infrared and ^{13}C NMR spectra and the kinetics of alkaline hydrolysis of chromium, tricarbonyl[3-[(η^6-aryl)methylene]-Z-1(3H)-isobenzofuranones] have been studied in comparison with those of 3-arylmethylene-Z-1(3H)-isobenzofuranones. The ^{13}C NMR spectroscopy has been found to be the most suitable tool for recognition of the site of complexation in the 3-arylmethylene-Z-1(3H)-isobenzofuranone system. A statistically significant correlation has been found between the arithmetic means of the wave numbers of symmetric and asymmetric stretching vibrations of $Cr(CO)_3$ group and σ_p constants of the substituents. The large slope of this linear dependence suggests an important role of the mesomeric mechanism in the transmission of electronic effects to the $Cr(CO)_3$ moiety. The strong electron-withdrawing effect of the $Cr(CO)_3$ group causes a significant decrease of the polarity of the phthalide C=O bond. The reaction rates of the alkaline hydrolytic ring-opening reaction dramatically increase due to the effect of $Cr(CO)_3$ group. The absorption bands of the carbonyl stretching vibrations are markedly split due to Fermi resonance effect. After mathematical correction for Fermi resonance the wave numbers of the unperturbed fundamental C=O stretching vibration and the log k values of alkaline hydrolysis exhibit significant linear correlations mutually, as well as with Hammett σ substituent constants. Charton's transmissive factors $\gamma(PhCr(CO)_3)$ have been determined for tricarbonylchromiumphenyl system using the parameters of the linear correlations. The efficiency of the substituent effect transmission is high in CCl_4, because a back-donation effect of the carbonyl ligands and decreases in $CHCl_3$ due to the hydrogen bonding between carbonyl groups and solvent molecules. The preparation of some novel chromium, tricarbonyl[3-[(η^6-aryl)methylene]-Z-1(3H)-isobenzofuranones] is described. © 1998 Elsevier Science S.A.

Keywords: Chromium; Phthalide; Carbonyl; Alkaline hydrolysis; Kinetics; Nuclear magnetic resonance; Infrared spectroscopy; Fermi resonance; Transmission of substituent effects

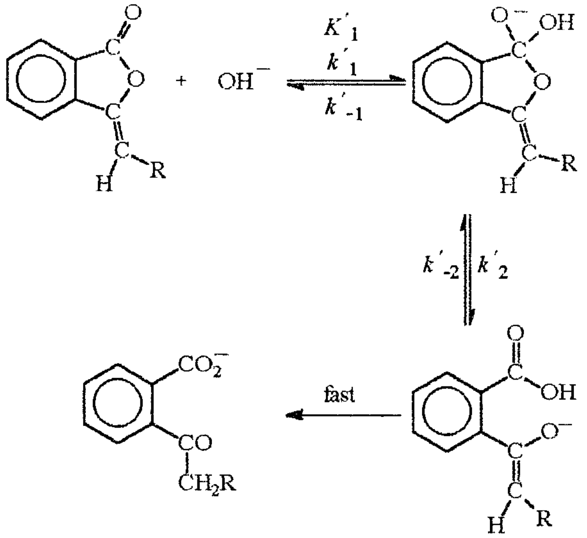
1. Introduction

The preparation and ^1H NMR spectra of some $Cr(CO)_3$ complexes of isobenzofuranone derivatives have been reported recently [1]. Our earlier studies of several 3-(substituted methylene)-Z-1(3H)-isobenzofuranones [2–5] showed that the their infrared spectra are strongly influenced by the occurrence of Fermi resonance interaction. Therefore the absorption bands of the C=O stretching vibration were recently carefully analysed, for a number of 3-(substituted methylene)-Z-1(3H)-isobenzofuranones and the unperturbed values of ν(C=O) wave numbers were obtained [6].

The alkaline hydrolysis of relatively small ring unsaturated lactones has been investigated [7]. The latter lactones are much more reactive than comparative acyclic esters or relatively large ring lactones. The latter have their ester group in *trans/Z* conformation, whereas the former in a *cis/E* conformation. Scheme 1 shows the mechanistic pathway for the alkaline hydrolysis of the lactones, with the rate determining step being the addition of hydroxide to carbonyl group, i.e., k_1' in scheme [7]. Reactivity-structure correlations for 3-(aryl

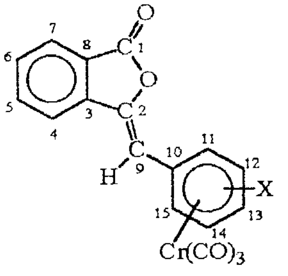
---

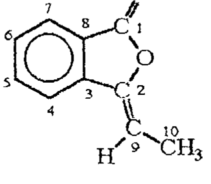
[*] Corresponding author.
[1] Also corresponding author.



Scheme 1.

and alkyl methylene)-*Z*-1(3H)-isobenzofuranones have been studied very recently [8]. There are good correlations of the rate coefficients of alkaline hydrolysis of 3- or 4-substituted phenyl series with the wave numbers of carbonyl stretching vibration and Hammett σ constants to give values of ca. 1.49 in 70% aqueous dioxane at 30°C and ca. 14.0 in $CHCl_3$, respectively. However, the spectral properties and the reactivity of $Cr(CO)_3$ complexes of isobenzofuranone derivatives have not been investigated systematically. Our recent studies [8] showed that a combination of the kinetic study with the IR investigation of electronic structure of the carbonyl group involved in the hydrolytic reaction can serve as a powerful way for better understanding of the reaction mechanism. Therefore, the aim of the present work is to study the ^{13}C NMR and infrared spectra and the kinetics of alkaline hydrolysis of a series of chromium, tricarbonyl[3-[(η^6-substituted phenyl)methylene]-*Z*-1(3H)-isobenzofuranones] (**I**–**XII**) and chromium, tricarbonyl[3-(η^6-ethylidene)-*Z*-1(3H)-isobenzofuranone] (**XIII**).





XIII

I X = 4-OCH_3
II X = 2-OCH_3
III X = 4-CH_3
IV X = 2-CH_3
V X = 3,4-$(OCH_3)_2$
VI X = H
VII X = 4-F
VIII X = 3-OCH_3
IX X = 4-Cl
X X = 3-F
XI X = 3-CF_3
XII X = 3,5-F_2

2. Results and discussion

2.1. ^{13}C NMR spectra

The ^{13}C NMR chemical shifts for most of the chromium, tricarbonyl[3-[(η^6-substituted)methylene]-*Z*-1(3H)-isobenzofuranones] are listed in Table 1. For assignment of the signals of the aromatic rings the reported empirical substitution rules [9] were employed. The comparison of the ^{13}C NMR data with those for a model compound bis(η^6-chromiumtricarbonylphenyl)methane [10] and for a series of 3-arylmethylene-*Z*-1(3H)-isobenzofuranones [11] suggests that the complexation of the $Cr(CO)_3$ group takes place with the benzene ring of the arylmethylene moiety in the compounds **I**–**XII**. The strong electron-withdrawing effect of the $Cr(CO)_3$ group causes a significant deshielding of all carbon atoms of the complexed benzene ring, resulting in a considerable increase of their chemical shifts by 30–40 ppm. This phenomenon makes the recognition of the site of complexation in 3-arylmethylene-*Z*-1(3H)-isobenzofuranones more reliable when using ^{13}C NMR spectroscopy compared to the analysis of ^{1}H NMR spectra [1].

2.2. Infrared spectra

The two most intense and very sharp absorption bands in the infrared spectra of compounds **I**–**XII** are observed in the region of 2000–1900 cm^{-1} (see Table 2) and can be assigned to the symmetric and asymmetric stretching modes of the tricarbonylchromium moiety [12–14]. The wave number of the $\nu_{as}(C{=}O)$ vibration is always more sensitive to both the substituent and the solvent effects than that of the $\nu_s(C{=}O)$ vibration. A similar behaviour is common and can be observed also with other systems showing vibrational interactions [15].

The patterns of the absorption bands of the C=O stretching vibration of the lactone ring carbonyl group of compounds **I**–**XII**, in the region of 1803–1771 cm^{-1}, are similar to those of the corresponding uncomplexed 3-(substituted methylene)-*Z*-1(3H)-isobenzofuranones [6]. All compounds in CCl_4 solutions exhibit more or less single $\nu(C{=}O)$ absorption bands, whereas in $CHCl_3$ a significant splitting caused by Fermi resonance interaction occurs (see Table 3). The absence of the $\nu(C{=}O)$

Table 1

^{13}C NMR chemical shifts δ (ppm) for $Cr(CO)_3$ complexes of 3-(substituted methylene)-*Z*-1(3H)-isobenzofuranone[a]

Compound	C^1	C^2	C^3	C^4	C^5	C^6	C^7	C^8	C^9	C^{10}	C^{11}	C^{12}	C^{13}	C^{14}	C^{15}	$Cr(CO)_3$
I	165.68	144.83	139.10	120.86	135.36	130.77	125.36	122.37	103.07	95.20	97.53	80.19	143.28	80.19	97.53	233.11
III	165.59	145.48	139.03	120.93	135.33	130.87	125.31	122.38	103.26	99.23	96.84	94.52	110.63	94.52	96.84	233.75
IV	165.96	146.70	139.30	121.87	135.47	131.27	125.45	122.90	101.35	101.14	111.08	97.21	95.61	92.10	95.99	234.14
V	165.62	145.36	139.02	120.79	135.50	130.97	125.46	122.39	103.30	96.29	N.R.	N.R.	N.R.	N.R.	N.R.	234.35
VI	165.91	146.30	139.21	121.28	135.70	131.36	125.62	122.64	103.66	102.41	95.94	94.95	94.37	94.95	95.94	233.89
VII	165.90	145.52	138.90	120.80	135.20	130.99	125.20	122.43	102.12	97.26	95.85	81.30	105.65	81.60	95.85	232.60
VIII	165.75	143.74	139.01	121.17	135.68	131.62	125.60	122.63	103.68	104.68	81.50	146.94	78.71	97.01	88.62	234.38
X	165.64	147.48	138.74	121.21	135.64	131.53	125.13	122.64	102.46	103.43	82.02	103.55	80.78	95.56	90.36	232.94
XI	165.41	146.75	138.82	121.05	135.55	131.32	125.57	122.57	101.98	99.27	91.44	96.26	91.03	91.60	96.80	231.07
XII	165.48	146.03	139.01	121.03	135.43	131.20	125.41	122.46	102.34	96.29	81.61	133.27	132.68	79.95	90.15	232.38

[a] The chemical shifts were measured in d_6-dimethylsuphoxide.

Table 2
Wave numbers (cm^{-1}) of C=O stretching vibration of chromiumtricarbonyl groups for $Cr(CO)_3$ complexes of 3-(substituted methylene)-*Z*-1(3H)-isobenzofuranones

Compound	$CHCl_3$		CCl_4	
	ν_{as}(C=O)	ν_s(C=O)	ν_{as}(C=O)	ν_s(C=O)
I	1899.2	1969.6	1909.2	1974.4
II	1900.8	1969.6	1909.2	1974.4
III	1902.2	1969.2	1908.8	1974.4
IV	1900.8	1969.6	1909.2	1974.4
V	1936.0	1993.0	1936.5	1976.8
VI	1905.2	1973.2	1918.8	1984.4
VII	1912.0	1976.0	1926.4	1986.8
VIII	1908.0	1968.4	1905.6	1971.6
IX	1913.6	1980.4	1924.0	1988.0
X	1915.2	1980.8	1923.4	1984.8
XI	1928.4	1989.2	1936.0	1993.2
XII	1939.2	1996.0	1940.2	1997.5
XIII	1934.0	1993.2	1944.9	1994.2

Table 4
Rate coefficients (k_2) for the alkaline hydrolysis of $Cr(CO)_3$ complexes of 3-(substituted methylene)-*Z*-1(3H)-isobenzofuranones in 70% (v/v) aqueous dioxane at 30.0°C[a]

Compound	k_2 (dm^3 $mol^{-1}s$)	(nm)[b]
I	3.06	445
II	3.09	445
III	4.05	445
IV	4.41	445
V	6.64	450
VI	4.54(10.1, 24.1)[c,d]	450
VII	5.92	440
VIII	7.69	445
IX	6.91	445
X	10.0	440
XI	8.89	440
XII	10.6[e]	440
XIII	45.5[f]	440

[a] Rate coefficients were reproducible to ±3%.
[b] Wavelength used to monitor alkaline hydrolysis.
[c] At 45.0 and 60.0°C, respectively.
[d] For uncomplexed 3-phenylmethylene-*Z*-1(3H)-isobenzofuranone [8] k_2: 1.02 (30.0°C), 2.22 (40.0°C) and 7.70 (60.0°C).
[e] For uncomplexed 3-(3,5-difluorophenyl)methylene-*Z*-1(3H)-isobenzofuranone [8] k_2: 4.41 (30.0°C)
[f] For uncomplexed 3-ethylidene-*Z*-1(3H)-isobenzofuranone [8] k_2: 0.400 (30.0°C).

band splitting in the compound **XIII** and the similarity with the spectra of 3-(substituted methylene)-*Z*-1(3H)-isobenzofuranones [6] suggests that the first overtone $\omega_{02}(CH) \approx 2\ \ \omega_{01}(CH)$ of an out-of-plane deformation vibration ω_{01}(CH) belonging to the benzene ring of the arylmethylene moiety is involved in the Fermi resonance interaction. It is known that Fermi resonance has a major influence on the dependence of the ν(C=O) values on the substituent effects in several series of aromatic compounds [16,17]. This implies that if the correlation between the spectral data and substituent effects are to be assessed, the wave numbers of the absorption bands free from effect of Fermi resonance must be obtained. This is because only such wave numbers will be dependent on the C=O band force constants alone [18]. For this reason the relations based on the method of Langseth and Lord and improved by Nyquist et al. [19] have been applied for the case involving a two-level interaction to enable the calculation of the wave numbers of the bands corrected for Fermi resonance. The extent of this effect depends on that of the interaction between the wave numbers of bands with states that are involved in the resonance [19,20]. It has been found that on the basis of a detailed investigation, similar to the case of 3-arylmethylene-*Z*-

Table 3
Wave numbers (cm^{-1}) of the C=O stretching vibration of lactone ring carbonyl group for $Cr(CO)_3$ complexes of 3-(substituted methylene)-*Z*-1(3H)-isobenzofuranones

Compound	Perturbed data[a] ($CHCl_3$)		ω (CH) ($CHCl_3$)	Unperturbed data[b] ($CHCl_3$)		W_{AB}	ν_{01}(C=O) (CCl_4)
	Branch A	Branch B		ν_{01} (C=O)	ω_{02} (CH)		
I	1791.4 (3.36)	1772.3 (2.89)	870.4	1782.6	1781.1	9.5	1796.8
II	1792.0 (3.38)	1773.4 (3.09)	870.4	1783.1	1782.3	9.3	1795.2
III	1791.3 (3.76)	1771.8 (2.20)	870.6	1784.1	1779.0	9.4	1797.2
IV	1792.1 (3.77)	1774.0 (2.34)	873.6	1785.2	1780.9	8.8	1797.6
V	1791.4 (3.94)	1770.7 (2.25)	873.6	1783.9	1778.2	10.0	1798.2
VI	1794.6 (3.39)	1775.9 (2.89)	870.4	1786.0	1784.5	9.3	1798.4
VII	1791.5 (3.71)	1772.2 (2.10)	870.2	1785.5	1779.2	9.3	1797.2
VIII	1794.1 (3.59)	1774.6 (1.80)	870.8	1787.6	1781.1	9.2	1800.1
IX	1795.5 (2.63)	1778.9 (2.80)	870.0	1786.9	1787.5	8.3	1800.2
X	1794.5 (4.28)	1773.3 (1.34)	869.6	1789.4	1778.4	9.0	1802.5
XI	1795.3 (3.96)	1776.0 (2.22)	867.2	1788.4	1782.9	9.3	1802.4
XII	1792.8 (2.52)	1780.8 (3.12)	870.4	1786.2	1787.4	6.0	1802.8
XIII	–	–	–	1779.2	–	–	1795.3

[a] After deconvolution and band separation.
Integrated intensities (dm^3 mol^{-1} cm^{-2}) are given in parentheses.
[b] Corrected for Fermi resonance.

Table 5
Activation parameters for the alkaline hydrolysis of derivatives of 3-phenylmethylene-*Z*-1(3H)-isobenzofuranone in 70% (v/v) aqueous dioxane at 30.0°C[a]

Compound	$\Delta H^{\ddagger}$ (kcal mol^{-1})[b]	$\Delta S^{\ddagger}$ (kcal mol^{-1} K^{-1})[b]
VI	10.6	-21
Uncomplexed[c]	12.7	-17

[a] Values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are considered accurate to ± 500 kcal mol^{-1} and ± 2 kcal mol^{-1} K^{-1}, respectively.
[b] 1 cal = 4.184 J.
[c] For uncomplexed 3-phenylmethylene-*Z*-1(3H)-isobenzofuranone [8].

1(3H)-isobenzofuranones [6], for compounds **I**–**XII** the more intense band in the Fermi doublet is associated with the branch, that after elimination of the resonance, belongs to the fundamental ν_{01}(C=O) stretching vibration. Furthermore, the less intense branch can be assigned to the first overtone (ω_{02}(CH)) of an out-of-plan C–H deformation vibration. The measure of the vibrational interaction between the fundamental vibration and the first overtone is expressed by the Fermi resonance coefficient W_{AB}. This is for compounds **I**–**XII** generally a little higher than in the case of parent 3-arylmethylene-*Z*-1(3H)-isobenzofuranones. The infrared spectral data for the lactone ring carbonyl group of compounds **I**–**XII** are listed in Table 3.

2.3. Kinetics of the alkaline hydrolysis

The rate coefficients for the alkaline hydrolysis of the lactones **I**–**XIII** in 70% (v/v) aqueous dioxane at 30.0°C, as well as for the parent compound of Cr(CO)$_3$ complex VI at several temperatures, are shown in Table 4. The reaction is first order both in substrate and in hydroxide. The activation parameters for the parent lactone of compound VI is shown in Table 5.

2.4. Spectral data correlations

The influence of the substituents X on the ^{13}C NMR chemical shifts of C^1 (i.e., the carbonyl group carbon atoms) is much smaller than for the parent 3-arylmethylene-*Z*-1(3H)-isobenzofuranones [6]. This is evidently caused by the strong deactivation of the arylmethylene benzene ring by the Cr(CO)$_3$ group. The change in the chemical shifts of the Cr(CO)$_3$ group carbon atoms, induced by substitution in the benzene ring, exhibits a maximal value of 3.3 ppm and is rather irregular and independent on any empirical substituent constants.

The wave numbers of both the symmetric and asymmetric C=O stretching vibrational modes of the Cr(CO)$_3$ group in the series of chromium, tricarbonyl[3-[(η^6-substituted phenyl)-methylene]-*Z*-1(3H)-isobenzofuranones] are strongly influenced by the electronic properties of the substituents X attached to the complexed phenylmethylene moiety. Since the maximal change in the ν(C=O) values of the Cr(CO)$_3$ group is 40 cm^{-1} a dependence of these vibrational characteristics upon the electronic properties of substituents X was investigated. A statistically significant relationship with a large slope ($\varrho = 30$–32 cm^{-1}) exists if the arithmetic means ($\overline{\nu(\mathrm{C=O})}$) of the ν_s(C=O) and ν_{as}(C=O) values are correlated with σ_p constants of substituents [21] attached to the complexed benzene ring (see Table 6). From these correlations the data of disubstituted compounds **V** and **XII** were excluded as outliers. In all cases for *ortho*-, *meta*- and *para*-substituents Hammett σ_p values were employed, which is in a good agreement with the assumption about a perfect conjugation between the substituted benzene ring and the Cr(CO)$_3$ moiety. The use of the arithmetic means of the ν_s(C=O) and ν_{as}(C=O) wave numbers is similar to that in the case of other systems which exhibit vibrational interactions [22]. The high sensitivity of the carbonyl stretching vibration to substituent effects suggests a significant contribution of the mesomeric mechanism to the transmission of electronic effects from the substituted benzene ring to the Cr(CO)$_3$ moiety.

The ν_{01}(C=O) wave numbers of the lactone ring for chromium, tricarbonyl[3-[(η^6-substituted phenyl)methylene]-*Z*-1(3H)-isobenzofuranones] measured in CHCl$_3$

Table 6
The correlation of infrared spectral data for Cr(CO)$_3$ complexes of 3-(substituted methylene)-*Z*-1(3H)-isobenzofuranones[a]

$y = \varrho x + q$

y	x[b]	Solvent	n[c]	r	s	F	ϱ	q
$\overline{\nu(\mathrm{C=O})}$	σ_p	CHCl$_3$	10	0.969	2.20	121	30.73 ± 2.79	1941.8
$\overline{\nu(\mathrm{C=O})}$	σ_p	CCl$_4$	10	0.955	2.77	83	32.08 ± 3.52	1949.8
ν_{01}(C=O)	σ_p, σ_m	CHCl$_3$	10	0.942	0.80	63	8.40 ± 1.06	1785.6
ν_{01}(C=O)	σ_p, σ_m	CCl$_4$	10	0.942	0.82	63	8.62 ± 1.09	1798.4
ν_{01}(C=O)	ν_{01}(C=O)^{IBF}	CHCl$_3$	10	0.927	0.89	49	0.64 ± 0.09	644.2
ν_{01}(C=O)	ν_{01}(C=O)^{IBF}	CCl$_4$	10	0.858	1.25	22	0.78 ± 0.17	390.1

[a] n is the number of compounds involved in correlations.
r is the correlation coefficient and s the standard deviation.
[b] ν(C=O)^{IBF} are the wave numbers of corresponding uncomplexed 3-(substituted methylene)-*Z*-1(3H)-isobenzofuranones taken from Ref. [6].
[c] Compounds **V** and **XII** are omitted.

Table 7
The correlation of the alkaline hydrolysis of the $Cr(CO)_3$ complexes of 3-(substituted methylene)-*Z*-1(3H)-isobenzofuranones and corresponding parent compounds[a]

$y = \varrho x + q$							
Series	y	x	n	r	s	ϱ	q
$Cr(CO)_3$ complexes	$\log k_2$	σ	8[b]	0.950	0.095	0.709	0.710
Parent compounds[c]	$\log k_2$	σ	15	0.980	0.085	1.485	−0.013
$Cr(CO)_3$ complexes	$\log k_2$	$\nu_{01}(C{=}O)$[d]	10[e]	0.974	0.007	0.0801	−142.2
Parent compounds[c]	$\log k_2$	$\nu_{01}(C{=}O)$[d]	33	0.959	0.005	0.0975	−173.2

[a] n is the number of compounds involved in correlations.
r is the correlation coefficient and s the standard deviation.
[b] Compounds **II**, **IV**, **V** and **XII** are omitted.
[c] Series of uncomplexed 3-(substituted methylene)-*Z*-1(3H)-isobenzofuranones taken from [8].
[d] Unperturbed values (free of Fermi resonance) in $CHCl_3$ taken from [7].
[e] Compounds **V** and **XII** are omitted.

and CCl_4 are in most cases by 3–9 cm^{-1} higher than those of 3-(substituted phenylmethylene)-*Z*-1(3H)-isobenzofuranones [6] and show a significant decrease in the polarity of the phthalide C=O bond due to the strong electron-withdrawing effect of the $Cr(CO)_3$ group. These $\nu_{01}(C{=}O)$ wave numbers measured in CCl_4 and the unperturbed $\nu_{01}(C{=}O)$ wave numbers in $CHCl_3$, i.e., corrected for Fermi resonance, were correlated with Hammett substituent σ (i.e., σ_p and σ_m) constants [20]. In the case of substituents attached to the benzene ring in the position 2 (*ortho*) the corresponding σ_p values were employed. The statistical results for above correlations are given in Table 6 and are more significant than the results of similar correlations for perturbed data, which is in good accordance with the results and conclusions obtained previously [6]. There are also satisfactory direct correlations between the $\nu_{01}(C{=}O)$ wave numbers measured in both $CHCl_3$ and CCl_4 with corresponding $\nu_{01}(C{=}O)^{IBF}$ values for uncomplexed 3-(substituted phenylmethylene)-*Z*-1(3H)-isobenzofuranones reported previously [6]. The ρ constants of above correlations directly express the transmissive factors (according to Charton's definition) γ $(PhCr(CO)_3)$ for the tricarbonylchromiumphenyl system:

$$\text{in}\,CCl_4{:}\quad \gamma(PhCr(CO)_3) = 0.78 \pm 0.17$$

$$\text{and in}\,CHCl_3{:}\quad \gamma(PhCr(CO)_3) = 0.64 \pm 0.09$$

These values are quite comparable with analogous transmissive factors determined indirectly as the rations of ϱ constants for $\nu_{01}(C{=}O)$ vs. σ correlations for $Cr(CO)_3$ complexes and uncomplexed isobenzofuranones [6]:

$$\text{in}\,CCl_4{:}\quad \gamma(PhCr(CO)_3) = 0.92 \pm 0.19$$

$$\text{and in}\,CHCl_3{:}\quad \gamma(PhCr(CO)_3) = 0.60 \pm 0.05$$

It is evident that the efficiency of the transmission of substituent effects trough the $PhCr(CO)_3$ system in CCl_4 is rather large. This is probably connected with a mesomeric interaction of the π-electrons of both the C≡O and the phenyl groups with d-electrons of the chromium atom resulting in a so-called back-donation effect. On the other hand, in $CHCl_3$ the transmission ability of the $PhCr(CO)_3$ system significantly decreases due to the formation of intramolecular hydrogen bonds between the $CHCl_3$ molecules and the $Cr(CO)_3$ moiety.

2.5. Reactivity correlations

The reactivity of the $Cr(CO)_3$ complexes is significantly greater than that of the corresponding uncomplexed lactones in their alkaline hydrolysis reactions. Thus, the presence of $Cr(CO)_3$ at the phenylmethylene ring accelerates the reaction by a factor of ca. 4.5, whereas at the isobenzofuranone ring accelerates the reaction by a factor of ca. 110. The $Cr(CO)_3$ group is powerfully electron-withdrawing.

Table 8
Novel chromium, tricarbonyl[3-[(η^6-substituted phenyl)methylene]-Z-1(3H)-isobenzofuranones]

Compound	Formula	MW	M.p.	(°C)	Reaction time (h)	Yield (%)
II	$C_{19}H_{12}CrO_6$	383.30	190	(dec.)	5.5	64
III	$C_{19}H_{12}CrO_5$	372.31	190	(dec.)	5.5	49
IV	$C_{19}H_{12}CrO_5$	372.31	200	(dec.)	5.5	61
V	$C_{20}H_{14}CrO_7$	418.16	155	(dec.)	3.5	25
VII	$C_{18}H_9FCrO_5$	376.31	260	(dec.)	6.5	40
IX	$C_{18}H_9ClCrO_5$	392.79	140	(dec.)	2.0	70

The combination of greater proximity and decreased dielectric constant (relative permittivity) of the transmissive cavity for the isobenzofuranone ring complex causes the greater effect. As shown in Table 5, the effect of the complexation decreases the enthalpy of activation, $\Delta H^{\ddagger}$, for the hydrolysis as reported, while the entropy of activation, $\Delta S^{\ddagger}$, is relatively unaffected.

The rates of alkaline hydrolysis of the complexed lactones have been correlated using the Hammett equation and the results are shown in Table 7. The correlation is satisfactory but somewhat poorer than that of corresponding uncomplexed lactones [8]. The poorer correlation and the significant decrease in the value observed probably arises from the strong direct interaction between tricarbonylchromium moiety and the substituents (Table 8). However, a very good correlation is also shown in Table 7 between the rates of alkaline hydrolysis and the carbonyl stretching vibration wave numbers. This confirms that the factors governing reactivity and the vibrational energy are the same.

3. Experimental details

3.1. Synthesis

The preparation and properties of compounds **I**, **VI**, **VII**, **X**–**XIII** have been described previously [1]. Substances **II**–**V**, **VII** and **VIII** were new compounds prepared using the general procedure given in [1] and their properties are listed in Table 6. The composition of compounds was determined by elemental analysis. The substances were purified by recrystallization prior to use for kinetics and spectroscopy.

3.2. Spectroscopy

The IR spectra of trichloromethane and tetrachloromethane solutions were recorded using a Zeiss Specord M-80 spectrometer at room temperature using NaCl cells of 0.1, 0.5 and 1.0 cm thicknesses. The concentrations of the solutions studied were 8.10^{-3} and 8.10^{-4} mol dm^{-3}. Peak positions were determined with and accuracy of ± 0.2 cm^{-1} against polystyrene standard spectra. The absorption intensities of the Fermi doublet components were determined after mathematical deconvolution and separation of overlapping bands. Curve analysis was carried out using a digital curve-fitting routine. The solvents employed were of spectroscopic purity (Uvasol, Merck).

The ^{13}C NMR spectra were measured at 25°C using a Varian VXR-300 instrument operating at 75.429 MHz. Solutions in d_6-dimethylsuphoxide were used. In order to assign the signals of ^{13}C atoms the experimental techniques COM, DEPT and SINEPT were employed.

3.3. Measurements of alkaline hydrolysis

Rate coefficients for the alkaline hydrolysis of the $Cr(CO)_3$ complexes of 3-(substituted methylene)-*Z*-1(3H)-*iso*-benzofuranones were determined spectrophotometrically by use of a Perkin-Elmer λ5 or 16 spectrometer. The reactions were followed at the wavelengths shown in Table 4. The detailed procedure used was that described previously [23]. It was found important to prepare fresh solutions of the $Cr(CO)_3$ complexed lactones immediately before study and use freshly purified dioxane [24] in these kinetic studies. The products of the hydrolysis reaction were found to be the anions of the corresponding carboxylic acids, i.e., the substituted 2-acetylbenzoic acids, in quantitative yield and were further confirmed spectrophotometrically by comparison of the spectrum of the acid in base with that of the reaction product [7,8,24].

Acknowledgements

The authors appreciate the financial support granted by the British Council in Bratislava for this project in the framework of 'Academic Link' between Colchester and Bratislava in 1994–1996. The authors wish also to thank Mrs. Eva Švanygová (Department of Organic Chemistry, Faculty of Natural Sciences, Comenius University, Bratislava) for assistance in preparation and purification of compounds studied.

References

[1] P. Hrnčiar, P. Ertl, P. Hrnčiar, Š. Toma, J. Organomet. Chem. 464 (1994) 65.
[2] A. Perrjéssy, P. Hrnčiar, Collect. Czech. Chem. Commun. 35 (1970) 112.
[3] A. Perjéssy, M. Lácová, P. Hrnčiar, Collect. Czech. Chem. Commun. 36 (1971) 2775.
[4] A. Perjéssy, M. Lácová, Collect. Czech. Chem. Commun. 36 (1971) 2944.
[5] A. Perjéssy, G. Melikian, P. Hrnčiar, M. Lácová, Collect. Czech. Chem. Commun. 39 (1974) 1862.
[6] A. Perjéssy, O. Hritzová, Z. Šusteková, P. Hrnčiar, K. Bowden, Monatsh. Chem. 128 (1997) 235.
[7] K. Bowden, K. Aghnihotri, J. Chem. Res., (1997), in press.
[8] K. Bowden, K. Agnihotri, R.J. Ranson, A. Perjéssy, P. Hrnčiar, I. Prokeš, W. Fabian, J. Phys. Org., Chem., in press.
[9] D.F. Ewing, Org. Magn. Res. 16 (1979) 499.
[10] W. Bramser, L. Ernst, W. Fachinger, R. Gerhards, A. Hardt, P.M.E. Lewis, Carbon-13 NMR Spectral Data, VCCH Verlagsgesellschaft, Weinheim, 1987.
[11] E. Solčániová, P. Hrnčiar, T. Liptaj, Collect. Czech. Chem. Commun. 45 (1980) 2772.
[12] P.S. Brateman, Metal Carbonyl Spectra, Academic Press, London, 1975.
[13] M. Salmain, A. Vessieres, G. Jauen, I.S. Butler, Anal. Chem. 63 (1991) 2323.

[14] C.E. Anson, C.S. Creaser, G.R. Stephenson, J. Chem. Soc., Chem. Commun., (1994) 2175.
[15] A. Perjéssy, P. Hrnčiar, Tetrahedron 27 (1971) 6159.
[16] M. Berthelot, M. Chabanel, C. Laurence, Spectrochim. Acta A32 (1976) 1771.
[17] C. Laurence, M. Berthelot, M. Lucon, Spectrochim. Acta A33 (1977) 353.
[18] T. Miyazawa, J. Mol. Spectrosc. 4 (1960) 168.
[19] R.A. Nyquist, H.A. Fauchea, G.A. Hoffman, D.L. Hasha, Appl. Spectrosc. 45 (1991) 860.
[20] H. Wolf, D. Horn, Bunsenges. Phys. Chem. 72 (1968) 419.
[21] C. Hansch, A. Leo, Substituent Constants for Correlation Analysis in Chemistry and Biology, Wiley, New York, 1979.
[22] A. Perjéssy, P. Hrnčiar, A. Krutošíková, Tetrahedron 28 (1972) 1025.
[23] K. Bowden, A.M. Last, J. Chem. Soc., Perkin Trans. 2 (1973) 345.
[24] D.D. Perrin, W.L.F. Armarego, Purification of Laboratory Chemicals, 3rd. edn., Pergamon, Oxford, 1988.