Journal of Organometallic Chemistry, 128 (1977) 213—218
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

ELECTRONIC ABSORPTION SPECTRA OF SOME BENZENECHROMIUMTRICARBONYL DERIVATIVES

G.A. RAZUVAEV *, V.A. KUZNETSOV, A.N. EGOROCHKIN, A.A. KLIMOV,
Institute of Chemistry, Academy of Sciences, Gorky (U.S.S.R.)
A.N. ARTEMOV and N.I. SIROTKIN
Gorky State University, Institute of Chemistry, Gorky (U.S.S.R.)

(Received August 20th, 1976)

Summary

Absorption spectra of some arenechromiumtricarbonyl derivatives have been studied. The linear dependence of the extinction coefficient of the longer wavelength absorption band on σ_p^+ constants of substituents in a benzene ring has been established and it has been shown that a longer wavelength band is a band of intramolecular charge transfer from the central chromium atom to π-bonded arene.

Introduction

Some studies of the electronic spectra of arenechromiumtricarbonyls have already been reported [1—6]. They have described the main features and given a partial interpretation of the UV spectra [1—3] of these compounds. Certain peculiarities of the electronic structure of benzenechromiumtricarbonyl substituted derivatives have been found by the spectroscopic study of their photodecomposition [4—6].

The spectra of the compounds studied consist of three absorption bands; two shorter wavelength bands ($\lambda \sim 220$ and 250 nm) have been associated with electronic transitions in the π-bonded arene ligand, and the longer wavelength band ($\lambda \sim 320$ nm) is a band of intramolecular charge transfer, characterizing an electronic transition in the metal—aromatic ring. However the authors suggest that the band ($\lambda \sim 250$ nm) is also a band of intramolecular charge transfer. These conclusions have been drawn after the investigation of a small number of substituted arenechromiumtricarbonyls. Therefore it was of interest to study the effect of substituents in the aromatic ring of these compounds upon the frequency of the absorption bands in the electronic spectra as well as to try to give a simple explanation of the assignment made by other authors.

The formation of a ligand—metal bond is accompanied by an electron density transfer from the occupied ligand onto vacant orbitals of the metal and by a back donation from occupied orbitals of the metal onto antibonding π-orbitals of benzene [7—9]. As a result a partial transfer of electron density from bonding orbitals of the benzene ligand onto antibonding orbitals takes place, i.e. the process is analogous to transitions in benzene derivatives (to the excited state) [7—11]. The extent of the back donation (metal—ligand) of electron density depends on both the nature of other ligands bonded to the chromium atom and on the substituents in the benzene ring [9]. Since a longer wavelength absorption band in the electronic spectra of arenechromiumtricarbonyls has been assigned to the electronic transition of central chromium atom—arene, i.e. intramolecular charge transfer, we set out to obtain additional evidence for the assignment of this band by investigation of a sufficient number of benzenechromiumtricarbonyl substituted derivatives.

Results and discussion

The bands of intramolecular charge transfer (ICT) are distinguished by a number of special features. For some benzene derivatives it has been shown [8,9] that the oscillator strength of a longer wavelength absorption band, which is an ICT band, correlates with σ constants of Hammett substituents in a benzene ring. Also [12—13], a shift of electronic transition frequency $\Delta\nu_e^a$ is related to the molecule dipole moments in the ground (μ_g) and excited (μ_e) states by the relationship:

$$hc\Delta\nu_e^a = \frac{2\,\mu_g(\mu_g - \mu_e \cos\phi)}{r^3}F = C_1^a F \qquad (1)$$

where F is a function, characterizing the solvent properties; C_1^a is a value, expressing the dependence of the substituent effect on the difference of the ground and excited state energies from the nature of distribution of the electron density in a molecule; ϕ is the angle between the direction of the dipole moments of a molecule in its ground and excited states. For ICT bands the difference of the dipole moments in the ground and excited states approximately equals the value of the transition dipole moment, i.e.

$$|\vec{\mu}_g - \mu_e| \approx |\vec{D}| \qquad (2)$$

From eqn. 1 as well as on the basis of the spectroscopic data for the compounds with intramolecular charge transfer [11,12] it follows that

$$|\vec{\mu}_g| \approx |\vec{D}| \qquad (3)$$

Dipole moments of arenechromiumtricarbonyls [14—17] in the ground state are chiefly determined by a charge transfer in the direction perpendicular to the benzene ring plane. Change of the dipole moments of these compounds occurs probably via "back donation" from the central chromium atom to the arene [3,6,7], i.e. in the same (or opposite) direction as in the ground state. On the basis of this it may be supposed that $|\cos\phi| \simeq 1$. Eqns. 1—3 give:

$$C_1^a \simeq \frac{2}{r^3}|\vec{D}|^2 \qquad (4)$$

It is known [18] that the oscillator strength (f) is connected with the value $\vec{D}$ by the relation

$$f = \frac{8\,me}{hc}\,\nu|\vec{D}|^2 \qquad (5)$$

When comparing (4) and (5), taking into consideration that σ constants express the substituents' effect on the value of the electron density in a molecule, linear correlation between σ constants of substituents and the oscillator strength should be expected. The relationships (2) and (3) should also be met, i.e. the absorption band should be an ICT band, and also the same solvent should be used. For the bands of equal half-band-width the oscillator strength is related to the extinction coefficient (ϵ) [18], that is, only linear correlation between ϵ and σ may also be expected.

Earlier it has been shown [19] that on formation of intermolecular charge transfer complexes by benzene derivatives as well as by other aromatic compounds the influence of substituents in the aromatic ring is described by Brown-Okamoto σ_p^+ constants of these substituents. It is known [20] that ICT may be considered as a transition between two local states inside a molecule. Formally the same features as for intermolecular charge transfer are typical for this transition [21]. Therefore on the basis of the above, linear correlation between the extinction coefficients (ϵ) of a longer wavelength band in the spectra of benzenechromiumtricarbonyl derivatives and σ_p^+ constants of substituents in a benzene ring may be expected.

Fig. 1 shows typical absorption spectra of arenetricarbonyl complexes of chromium.

The spectra of all compounds studied have three absorption bands.

The position of the maximum of the two shorter wavelength absorption bands in arenechromiumtricarbonyls spectra and their mercury-containing analogs does

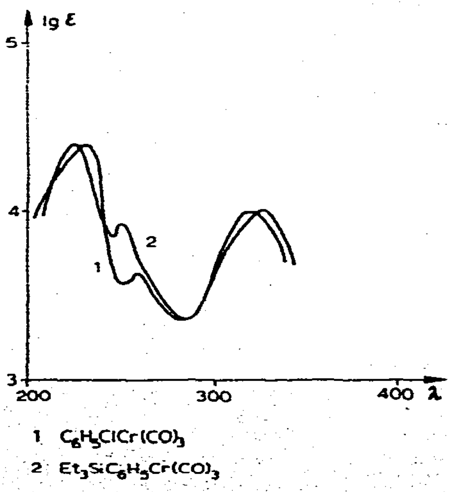

Fig. 1. Typical electronic absorption spectra of some benzenechromiumtricarbonyl derivatives.

not reveal clearly pronounced dependence upon donor—acceptor properties of substituents in a benzene ring. The extinction coefficients of these absorption bands also change irregularly on varying the substituents and in free ligands [22,23].

TABLE 1

WAVE LENGTHS, EXTINCTION COEFFICIENTS OF ABSORPTION BANDS AND σ_p^*-CONSTANTS OF SUBSTITUENTS FOR THE COMPOUNDS STUDIED

No.	Compound	λ(nm)	ϵ l mol^{-1} cm^{-1}	lg ϵ	$\Sigma\sigma_p^*$
1	$C_6(CH_3)_6Cr(CO)_3$	222	23200	4.37	—1.80
		317	7180	3.86	
2	$(CH_3)_2NC_6H_5Cr(CO)_3$	224	30000	4.48	—1.70
		256	15900	4.20	
		323	7100	3.85	
3	$1,2,4,5\text{-}(CH_3)_4C_6H_2Cr(CO)_3$	222	23600	4.37	—1.20
		322	8680	3.94	
4	$1,3,5\text{-}(CH_3)_3C_6H_3Cr(CO)_3$	222	19800	4.30	—0.90
		316	8470	3.93	
5	$CH_3OC_6H_5Cr(CO)_3$	221	25000	4.40	—0.80
		314	9060	3.96	
6	$1,4\text{-}(CH_3)_2C_6H_4Cr(CO)_3$	220	20400	4.31	—0.60
		253	6940	3.84	
		317	9060	3.96	
7	$CH_3C_6H_5Cr(CO)_3$	220	17400	4.24	—0.30
		253	7580	3.88	
		317	9470	3.98	
8	$FC_6H_5Cr(CO)_3$	222	22900	4.36	—0.10
		254	10300	4.01	
		314	10300	4.01	
9	$C_6H_6Cr(CO)_3$	213	30000	4.48	0.00
		256	7450	3.87	
		317	10600	4.03	
10	$(C_2H_5)_3SiC_6H_5Cr(CO)_3$	222	21700	4.34	—0.04
		256	7120	3.85	
		317	10300	4.01	
11	$ClC_6H_5Cr(CO)_3$	222	21200	4.33	0.10
		266	8210	3.91	
		323	10200	4.01	
12	$C_2H_5OOCC_6H_5Cr(CO)_3$	223	22300	4.35	0.50
		255	8230	3.92	
		323	10600	4.03	
		400	20400	4.31	
13	$[CH_3OC_6H_4Cr(CO)_3]_2Hg$	221	53100	4.73	—0.31
		326	18900	4.28	
14	$[C_2H_5COOC_6H_4Cr(CO)_3]_2Hg$	221	44400	4.65	
		326	16500	4.22	
		374	20300	4.31	
15	$[CH_3C_6H_4Cr(CO)_3]_2Hg$	223	45900	4.66	—0.17
		263	15800	4.20	
		325	20100	4.30	
16	$[C_6H_5Cr(CO)_3]_2Hg$	222	50200	4.70	—0.08
		266	15300	4.18	
		323	19700	4.29	
17	$[FC_6H_4Cr(CO)_3]_2Hg$	222	40800	4.61	—0.08
		270	17500	4.24	
		323	18900	4.28	

Similar features of arenechromiumtricarbonyl spectra are noted in [4]. Increasing of the extinction coefficients in the spectra of the compounds XIII—XVII to approximately double is caused by the presence of two aromatic rings in these compounds.

On considering the dependence of the wavelength and extinction coefficients of absorption bands upon the nature of the substituents in the compounds studied it is seen that on increasing electron-attracting properties of the substituents the absorption maximum of the longer wavelength band reveals the tendency to a bathochromic shift but there is no sharp dependence upon the electronic effects of the substituents. From the above-mentioned (eqn. 5 and its discussion) it may be concluded that variation of the extinction coefficient of a longer wavelength absorption band is related to variation of the transition dipole moment. It was also shown that for the ICT band a correlation between the extinction coefficient of this band and σ_p^+ constants of the substituents in a benzene ring may be expected. The data of Table 1 show that in a series of the compounds I—XII and XIII—XVII the ϵ value increases regularly. Electron-attracting properties of substituents in an aromatic ligand increase in the same sequence, which is characterized by an increase in the sum ($\Sigma\sigma_p^+$) of the substituents, σ_p^+ constants. Analysing the results by the least squares method shows that values ϵ and $\Sigma\sigma_p^+$ are linearly dependent.

$$\epsilon = 1400\ \Sigma\sigma_p^+ + 10100 \qquad (r = 0.92) \qquad (6)$$

The values of substituent σ_p^+ constants in the compounds X, XIII—XVII have been calculated by the method of [19] on the basis of the data on electronic absorption spectra of the charge transfer complexes of the free ligands. An insufficiently high coefficient of correlation for VI is probably connected with both the inaccuracy of the substituent σ_p^+ constants values and the approximate char-

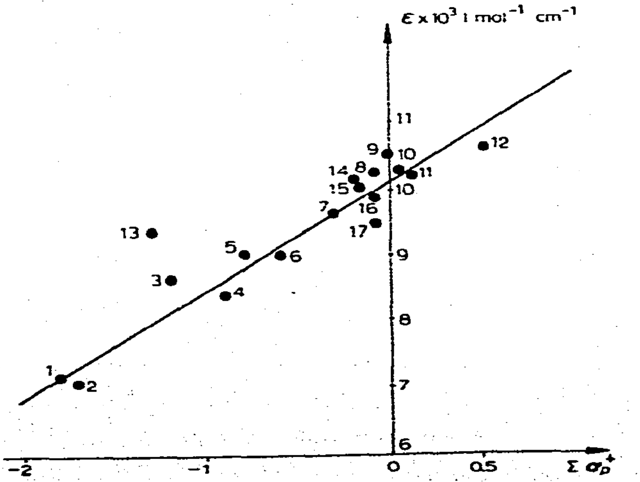

Fig. 2. The interdependenc of ϵ and $\Sigma\sigma_p^+$. The numbering of the points refer to the numbering of the compounds in Table 1.

acter of eqns. 1—4. The fact that there is a linear dependence for VI testifies, firstly, to the fact that a longer-wavelength absorption band in the spectra of benzenechromiumtricarbonyl derivatives is a band of intramolecular charge transfer, and secondly, that positive gradient of the straight line for VI confirms the conclusions [8] that ICT occurs from a central chromium atom to a π-bonded aromatic ligand. Actually, on increasing the electron-attracting properties of the substituents, the dipole moment of the transition for chromium atom—ring also increases. It leads to the increase of electron density on a π-bonded ligand. According to the literature [6—11] it may be concluded that back donation occurs from occupied chromium orbitals onto lowest antibonding arene orbitals. That is, only on increasing the electron-attracting properties of the substituents in a benzene ring should the probability of back donation increase. It is observed experimentally as an increase in the extinction coefficient of the ICT band. Since the electronic structure of free arene at the π-complex formation process varies greatly we have not apparently observed luminescence of benzenechromiumcarbonyl derivatives I—XVII.

Experimental

The absorption spectra were measured at 20°C in dichloromethane (concentration 10^{-4} mol l^{-1}) using a Specord UV-VIS spectrophotometer. The purity of the solvent was controlled by the UV spectroscopy method. The compounds investigated were prepared using methods previously described [24,25].

References

1 E.O. Fischer, H. Kriebitzch and R.D. Fischer, Chem. Ber., 92 (1959) 3214.
2 Sh. Jamada, H. Jamasaki, H. Nishikava and R. Tsuchida, Bull. Chem. Soc. Japan, 33 (1960) 481.
3 K. Ofele, Chem. Ber., 99 (1966) 1732.
4 B.M. Javorski, V.N. Trembovler, N.K. Baranetskaya and V.N. Setkina, Dokl. Akad. Nauk SSSR, 207 (1972) 1147.
5 V.N. Trembovler, B.M. Javorski, V.N. Setkina, N.K. Baranetskaya, G.B. Zaslavskaya and M.G. Evdokimova, Zh. Fiz.-Khim., 48 (1974) 2082.
6 V.N. Trembovler, B.M. Javorski, V.N. Setkina, N.V. Fok, N.K. Baranetskaya and G.B. Zaslavskaya, Dokl. Akad. Nauk SSSR, 218 (1974) 1153.
7 B.V. Lokshin, E.B. Rusach, V.S. Kaganovich, V.V. Krivih, A.N. Artemov and N.L. Sirotkin, Zh. Strukt. Khim., 16 (1975) 592.
8 S.P. Gubin, Doctorate Thesis, M., 1971.
9 D.M. Adams and A.S. Quire, J. Chem. Soc., Dalton (1974) 558.
10 R. Mason, Nature, 217 (1968) 543.
11 R. McWellny, R. Mason and A.D.C. Gonl., Diss. Faraday Soc., 47 (1969) 20.
12 N.G. Bahshiev and V.G. Saidov, Dokl. Akad. Nauk SSSR, 168 (1966) 120.
13 V.G. Saidov and N.G. Bahshiev, Dokl. Akad. Nauk SSSR, 175 (1967) 1090.
14 E.M. Randall and L.E. Lutton, Proc. Chem. Soc., (1959) 93.
15 W. Strohmeier and W. Langhauser, Z.-Phys. Chem., 28 (1961) 268.
16 W. Strohmeier and H. Hellman, Ber. Bunsenges. Phys. Chem., 67 (1963) 190.
17 H. Lumbroso, C. Segard and B. Rogues, J. Organometal. Chem., 61 (1973) 249.
18 R.N. Nurmuhametov, Absorption and luminescence of aromatic compounds, Chimeja, Moscow, 1971.
19 V.A. Kuznetsov, A.N. Egorochkin and G.A. Razuvaev, Zh. Prikl. Spektrosk., 22 (1975) 952.
20 R. Coorson and N. Wariyav, J. Chem. Soc., (1956) 2302.
21 N.G. Bahshiev, Spectroscopy of Intermolecular Interactions, Nauka, Leningrad, 1972.
22 N.K. Rao, Electron Spectra in Chemistry, Mir, Moscow, 1964.
23 J. Iter and A. Casodevoll, Bull. Soc. Chim., France (1969) 2355.
24 G.A. Razuvaev, A.N. Artemov, G.G. Petuhov, N.L. Sirotkin and N.A. Puhnarevich, Izv. Acad. Nauk SSSR, Ser. Chim., 5 (1973) 1172.
25 B. Nicholls and M.P. Whiting, J. Chem. Soc., (1959) 551.