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INTERMOLECULAR INTERACTION OF BIS(ALKYLCYCLOPENTADIENYL)TUNGSTEN DIHALOGENIDES WITH TETRACYANOETHYLENE AND TETRACYANOQUINODIMETHANE STUDIED BY UV ABSORPTION SPECTROSCOPY

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Summary

Electron-donor ability of bis-cyclopentadienyl derivatives of tungsten (Alk-$C_5H_4)_2WX_2$ (Alk = Me, Et, n-Pr, n-Bu, i-Pr, t-Bu; X = Cl, Br, I), towards the strong π-acids tetracyanoethylene and 7,7,8,8-tetracyanoquinodimethane, has been studied using the method of UV absorption spectroscopy. It has been found that $(AlkC_5H_4)_2WX_2$ form 1 : 1 ion-radical salts with π-acceptors in the strongly polar solvent acetonitrile. The degree of transition into ion-radical salts is determined, mainly, by steric factors and it changes with the different Alk and X species in the series Cl > Br > I and CH_3 > Et ≈ n-Pr ≈ n-Bu > i-Pr > t-Bu.

Introduction

The majority of bis-cyclopentadienyl derivatives of the transition metals are characterized by relatively low ionization potentials [1–3]. Because of this, such compounds readily enter into donor–acceptor interaction with various acceptors. Hence, the following may be formed: (a) charge-transfer (CT) complexes, $D + A \rightarrow [D^{\delta+}A^{\delta-}]$, where there is a partial transfer of electron density from the highest occupied molecular orbital (HOMO) of donor D to the vacant orbital of acceptor A; (b) ion-radical salts (IRS), $D + A \rightarrow D^{+\cdot} + A^{-\cdot}$, where the transfer of one electron from the highest occupied molecular orbital of the donor is achieved without formation of a new chemical bond. The donor–acceptor interaction of organic and organometallic compounds in solution (formation of charge transfer complexes or ion-radical salts) is determined, as is known [4], by the relative strength of donor or acceptor, as well as by the polarity of the solvent. The same is also true for bis-cyclopentadienyl derivatives of the transition metals. Thus, for example, ferrocene produces CT complexes with the π-acceptor tetracyanoethylene (TCNE) in cyclohexane, but it forms ion-radical salts in acetonitrile [5]. In low polarity solvents, ferrocene is also inclined to form charge transfer complexes with other π-acceptors, both strong ((7,7,8,8-tetracyanoquinodimethane)(TCNQ)) and weak (chloranil, trinitrobenzene and others) [6,7]. On the other hand, the analogous CT complexes of Cp_2Co and Cp_2Ni are much less stable, and their reductive ability and, hence, the inclination to form ion-radical salts is substantially higher [8]. Formation of ion-radical salts is observed during interaction of Cp_2Ru and Cp_2Os with π-acceptors [9].

The aim of this work was to investigate, using UV absorption spectroscopy, the donor–acceptor interaction in solution of some bis-cyclopentadienyl derivatives of tungsten, $(AlkC_5H_4)_2WX_2$; Alk = Me (*a*), Et (*b*), n-Pr (*c*), n-Bu (*d*), i-Pr (*e*), t-Bu (*f*); X = Cl (I), Br (II), I (III), with the typical π-electron acceptors TCNE and TCNQ. We knew of only one work [10] which dwelt upon the study of intermolecular interactions of analogues of I–III, i.e. the compounds Cp_2WH_2 and Cp_2MoH_2 with various π-acceptors. In [10] it was shown that reactions with weak π-acceptors (maleic anhydride, trinitrobenzene), in toluene or methylene chloride, lead to the formation of CT complexes. On the contrary, under the action of strong acceptors (TCNE and TCNQ), these dihydrides were subjected to one-electron oxidation.

Another objective which was pursued during the investigation of the electron absorption spectra of the π-acceptor complexes of the compound systems I–III, and on the basis of the discovered spectral regularities, was to analyse the influence of substituents, both in the cyclopentadienyl ring and σ-bonded to the metal atom, on the electron–donor abilities of I–III. It is known [11], through investigation of a number of organic and some organometallic compounds with a large variety of substituents, that use of the method of UV spectroscopy on the CT complexes gives valuable information on intermolecular interactions in the donor compounds. Along with this, it seems that only in one work [12] has such an approach been applied to bis-cyclopentadienyl derivatives of the transition metals. The authors [12] have shown that for a series of (R-) substituted ferrocenes the strength of the CT complex with TCNE increases in the series, $R = CH_3COO < I < C_6H_5 < H < C_2H_5 < 1,1\text{-}(C_2H_5)_2 < 1,3\text{-}(C_2H_5)_2$. In the same sequence there was observed a bathochromic shift of the CT transition band, which indicates destabilization of the HOMO of the ferrocenes and, hence, an increase in electron-donor ability.

Results and discussion

The UV absorption spectra of mixtures of bis-cyclopentadienyl derivatives, I–III, with π-acceptors (TCNE, TCNQ) in weakly polar solvents (methylene chloride, dioxane, alkanes, tetrahydrofuran, toluene) do not undergo substantial changes as compared with the spectra of the individual components. Thus, the compounds under investigation do not form CT complexes with TCNE and TCNQ in the above-mentioned solvents. Neither are they subjected to noticeable oxidation under the action of these acceptors.

In the strongly polar solvent, acetonitrile, the interaction in the system under investigation is variable. Thus, during the interaction of compounds I–III with TCNE (E_a 2.75 eV [13]), there is a change in solution colour from green to red. This change is accompanied by the disappearance of the long wavelength band in the UV spectrum of the individual I–III compounds (λ_{max} 575, 630 and 660 nm, respectively). It is also accompanied by the appearance of a new structural band in the region of 360–500 nm. According to Webster et al. [14], this band can be attributed to the absorption of the $TCNE^{-\cdot}$ anion radical. Besides this, additional bands, with maxima at 560 and 510 nm, respectively, appear in the spectra of compounds I and II. They are attributed to the absorption of the cation radicals $(AlkC_5H_4)_2WCl_2{}^+$ and $(AlkC_5H_4)_2WBr_2{}^+$, as identical spectra are observed during oxidation of compounds I and II by the other oxidizing agents, such as mineral acids or copper(II) salts. For the compounds of series III, the band corresponding to the cation radical $(AlkC_5H_4)_2WI_2{}^{+\cdot}$ is not observed. Judging by the tendency of λ_{max} of cation radicals for the series I–III to shift to shorter wave regions, it is possible that for the diiodine cation of compounds III the band of the cation radical is being overlapped by the more intense band of $TCNE^-$ anion radicals.

The formation of ion radicals in the system containing the dihalides of tungsten and TCNE is also confirmed by the ESR data. In the ESR spectrum of compounds I and II with TCNE, two signals of equal intensity are observed: the high field signal, with $g = 1.997$, is due to the presence of $TCNE^{-\cdot}$ anion radicals [15], whereas the g-factor of 1.953 (for chlorides) and 2.014 (for bromides) is due to the presence of cation radicals $(AlkC_5H_4)_2WX_2{}^{+\cdot}$ (X = Cl, Br) in the solution. The features of the cation radical spectra are close to the values which are known for the non-substituted analogues $Cp_2WCl_2{}^+$ and $Cp_2WBr_2{}^{+\cdot}$ ($g = 1.955$ and 2.013, respectively [16]), and they coincide fully with the parameters of the ESR spectra obtained by us with the action of copper(II) salts on solutions of compounds I and II. For the compounds of series III, there was found only one signal in the ESR spectrum which was related to the $TCNE^{-\cdot}$ anion radical. The absence of the signal for $(AlkC_5H_4)_2WI_2{}^+$ is, it seems, related to the broadening of the peak, one of the reasons for which could be the high quadrupole moment of the iodine nucleus. But taking into consideration the similar interaction features of compounds with π-acceptors, it is possible to assume that formation of the ion radical $(AlkC_5H_4)WI_2{}^{+\cdot}$ occurs for the iodine as well.

The interaction of dihalides of the alkyl-substituted tungstenocenes I–III with stronger π-acceptors, say, TCNQ (E_a 2.80 eV [13]) in acetonitrile solution, judging by the UV and ESR spectra, proceeds in the same way as described for the case of TCNE. In the UV spectrum, along with the bands belonging to cation radicals, one can observe a band with λ_{max} 420 (TCNQ) and 842 nm (TCNE), which is attributed to the $TCNQ^{-\cdot}$ anion radical [17]. The signal in the ESR spectrum with $g = 2.000$ also indicates the presence of $TCNQ^-$ and this is in agreement with the data of other authors [18].

Thus, the intermolecular interaction of tungstenocene dihalides with TCNE and TCNQ in a strongly polar solvent is a one-electron oxidation, not the formation of the CT complex. A study of the intensities of the bands corresponding to anion and cation radicals in the UV and ESR spectra shows that this process is accompanied by the formation of 1 : 1 ion-radical salts. But the transformation into ion-radical salts is different for different compounds. It changes within a wide range with variation of the substituents in the Cp ring, as well as with the σ-bonded halogen, X. Quantitatively, the process of ion-radical salt formation can be characterized by an equilibrium constant K. But for the accurate definition of K it is necessary to study in detail the mechanism of ion-radical salt formation; in particular, one should know if the ion-radical salt is a close pair or if the ions of this pair are relatively free. The experimental data do not permit a definite answer to this question *. That is why, as the means of quantitative characterization of the donor–acceptor interaction under study, it is possible to assume the degree of transformation of compounds I–III into ion-radical salts which can be defined as: $\delta = [A^-]/[A]_0 \times 100$, where $[A^-]$ is the equilibrium concentration (mol/l) of anion radicals, and $[A]_0$ is the initial concentration (mol/l) of the acceptor.

It is evident that by using a fixed initial concentrations of donor and acceptor, and under the standard conditions for the experiment, the δ-value should depend only on the properties of the reactant molecules. For calculation of δ, the equilibrium concentration $[A^-]_0$ is defined spectrophotometrically at the moment of adding the solution of donor to the solution of acceptor at the (λ_{max} =) 842 nm band for $TCNQ^-$ and 420 nm for $TCNE^-$. The high values of the molar absorptivities of these bands, such as ($E_{TCNQ^-} = 43300$ [17], $E_{TCNE^-} = 7100$ [14]), make it possible to identify ion-radical salts at sufficiently low concentrations, i.e. of about 10^{-5}–10^{-7} mol/l. Thus, the degree of transformation into ion-radical salts de-

TABLE 1

DEGREE OF TRANSFORMATION OF THE COMPOUNDS STUDIED INTO ION-RADICALS WITH TCNE AND TCNQ, AND THE EQUILIBRIUM CONSTANTS OF THE IRS FORMATION PROCESS

Compound	Acceptor, TCNE		Acceptor, TCNQ		Q (rad)
	δ (%)	$10^3 K$	δ (%)	$10^3 K$	
Ia $(MeC_5H_4)_2WCl_2$	81	494.5	64	34.9	12.70
Ib $(EtC_5H_4)_2WCl_2$	81	494.5	63	32.9	12.78
Ic $(n\text{-}PrC_5H_4)_2WCl_2$	80	457.6	63	32.9	12.78
Id $(n\text{-}BuC_5H_4)_2WCl_2$	80	457.6	63	32.9	12.78
Ie $(i\text{-}PrC_5H_4)_2WCl_2$	58	111.0	45	11.2	13.18
If $(t\text{-}BuC_5H_4)_2WCl_2$	17	4.6	13	0.6	13.72
IIa $(MeC_5H_4)_2WBr_2$	45	50.1	33	4.9	13.06
IIb $(EtC_5H_4)_2WBr_2$	41	38.6	32	4.6	13.14
IIc $(n\text{-}PrC_5H_4)_2WBr_2$	41	38.6	30	3.9	13.14
IId $(n\text{-}BuC_5H_4)_2WBr_2$	41	38.6	30	3.9	13.14
IIe $(i\text{-}PrC_5H_4)_2WBr_2$	29	15.8	23	2.1	13.54
IIf $(t\text{-}BuC_5H_4)_2WBr_2$	11	1.8	9	0.3	14.08
IIIa $(MeC_5H_4)_2WI_2$	24	10.0	16	0.9	13.24
IIIb $(EtC_5H_4)_2WI_2$	24	10.0	15	0.8	13.32
IIIc $(n\text{-}PrC_5H_4)_2WI_2$	24	10.0	16	0.9	13.32
IIId $(n\text{-}BuC_5H_4)_2WI_2$	23	9.1	16	0.9	13.32
IIIe $(i\text{-}PrC_5H_4)_2WI_2$	19	5.9	12	0.5	13.72
IIIf $(t\text{-}BuC_5H_4)_2WI_2$	9	1.2	6	0.1	14.26

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* If, nevertheless, one can tentatively assume that the two ion radicals (D^+ and A^-) which are produced during the interaction of D and A are completely independent, it is possible to estimate the value of the apparent equilibrium constant, K, in the process of ion-radical salt formation (Table 1). The use of K-values does not lead to the principal change in the correlations obtained below when the δ-parameter is used instead of K, but it causes a slight decrease in the correlation coefficient.

termined in this way, can be used for a comparative study of their relative donor ability.

The measured δ-values are given in Table 1. From this Table it is seen that transformation into ion-radical salts of compounds I–III varies within a wide range: i.e. from about 80 to ~ 10% for TCNE, and from about 65 to ~ 5% for TCNQ.

Based on δ-values, let us analyse the change in donor ability of compounds I–III with the substituent in the Cp ring. For each separate series of compounds I–III, the δ-values with the same halogen substituent are approximately similar for the compounds with alkyl substituents of normal structure (Me, Et, n-Pr, n-Bu) and decrease in the course of transition to the compounds containing i-Pr and t-Bu radicals. Such a change in the compounds under study of the degree of transformation into ion-radical salts with branching of the alkyl group on the Cp ring is observed during the use of both acceptors and it is opposite to the increase of electron-donor ability of the Alk substituent in the series Me < Et ≈ n-Pr ≈ n-Bu < i-Pr < t-Bu. That is why it is more useful to compare the δ-values with the steric influence of the Alk substituent. The treatment of the results by least-squares methods shows that there is a satisfactory linear correlation of the measured δ-values with the steric Charton constants $v(X)$ [19] (see Table 2). Moreover, the data in Table 2 show that the sensitivity of the ion-radical salt formation process to variation of the substituents on the Cp ring, which is characterized by the slope of the corresponding straight lines, is to a great extent defined by the nature of the σ-bonded halogen. So, in the case of interaction of compounds I with TCNQ, the δ-value decreases by 50%, in the course of transition from the methyl to the t-butyl derivative. For the bromides, the same δ-change is 25%, and for the iodides it is only 10%. Qualitatively, the same change of δ-sensitivity to variation of the Alk substituents is true also for the interaction of I–III with TCNE. Simultaneously, with the decrease of sensitivity of the ion-radical salt formation process in the series Cl–Br–I to the insertion of substituents on the Cp ring, there is a considerable reduction in the electron-donor properties of the compounds under study as a whole, which is qualitatively characterized by the intercept of the correlations in Table 2. However, in accordance with the electronic influence of halogens on the energy of the HOMO in the compounds similar to I–III [2], the inverse dependence would have been expected. It can be assumed that the above series of electron-donor ability changes of I–III towards the π-acceptors depending on the type of σ-bonded X-substituents, is mainly caused by the steric effects of halogen atoms. In fact, from Fig. 1 it is seen, that the transformation into ion-radical salts of I–III with TCNE

TABLE 2

PARAMETERS OF CORRELATIONS ($\delta = av + b$) BETWEEN DEGREE OF TRANSFORMATION INTO IRS (δ) AND CHARTON STERIC CONSTANTS (v) OF SUBSTITUENTS

Reaction series	a	b	S_a	S_b	r
I+TCNE	−95.6	136.9	12.6	9.8	0.967
I+TCNQ	−75.6	107.8	10.3	8.0	0.965
II+TCNE	−47.6	69.9	6.2	4.8	0.968
II+TCNQ	−34.5	51.7	3.1	2.4	0.984
III+TCNE	−22.3	37.0	2.6	2.1	0.973
III+TCNQ	−14.5	24.2	2.5	2.0	0.945

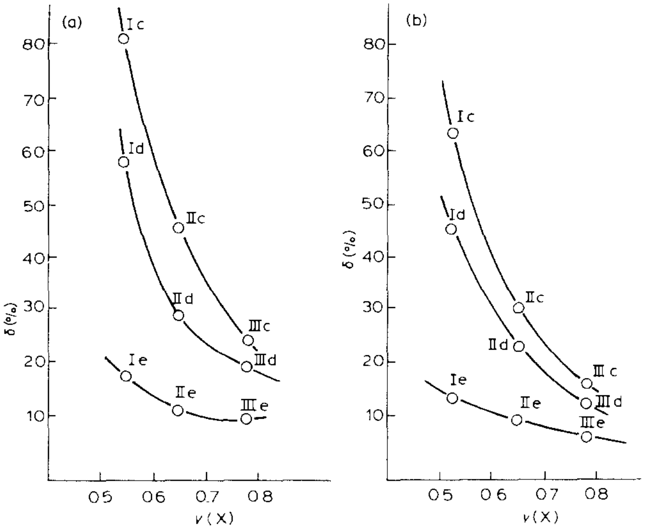

Fig. 1. Dependence of the transformation of compounds I–III into IRS on the steric constants of halogen X: (a) acceptor, TCNE; (b) acceptor, TCNQ. The identification of the points is given in Table 1.

and TCNQ decreases regularly with increase of the effective volume of ligand X, which is characterized by Charton constants.

Thus, it is possible to state that the ability of compounds $(AlkC_5H_4)_2WX_2$ to produce ion-radical salts with π-acceptors is controlled mainly by steric factors and is practically independent of the electronic influence of the Alk and X substituents. As, according to the data from quantum-chemical calculations and photoelectronic spectroscopy of compounds similar to I–III, the HOMO from which a transfer of electron to the molecule of π-acceptor takes place, is localized mainly on the metal atom [20], the steric influence of Alk and X is nothing but shielding of the reacting centre (in this particular case a tungsten atom). Obviously, shielding should increase with increase of the effective volume of ligands $AlkC_5H_4$ and X, and with the

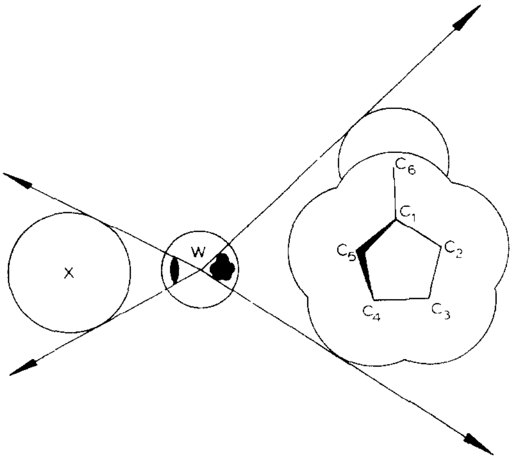

Fig. 2. Diagram showing plotting of the exocyclic angle of the MeC_5H_4 ligand, and that of halogen X.

decrease of the metal–ligand bond length. Due to this, there is a necessity to determine the nature of the steric hindrance from the Alk and X substituents to the processes of donor–acceptor interaction of compounds I–III with π-acceptors, because the scale of Charton substituent constants is based only on the Van der Waals radii of the substituents and does not take into consideration that substituent-reacting centre bond lengths change in the series of structurally-related compounds. A stricter evaluation of the degree of shielding of the central W-atom by substituents, with an account of the real geometry of molecules $(AlkC_5H_4)_2WX_2$, is possible with the help of values of the exocyclic angle (the apex on atom W), the angles which are filled with CpAlk and X ligands. This approach has been proposed [21]. The general idea for calculating the exocyclic angles (q) of substituents consists of plotting the molecular projection in the spheric coordinate system on the sphere of unit radius, the atoms being represented as rigid balls with the corresponding Van der Waals radii * (Fig. 2). The calculation of values of exocyclic angles of various substituents can be done using data from X-ray analysis, as well as using idealized models or experimental data from gas electron diffraction and microwave spectra [21].

Figure 3 illustrates the dependence of the exocyclic angle (q) of the ligands $AlkC_5H_4$ (Alk = Me, Et, n-Pr, n-Bu, i-Pr, t-Bu) and X (X = Cl, Br, I) on the metal–ligand distance calculated with the help of the programme described in ref. [21]. The calculation of exocyclic angles for MeC_5H_4 and EtC_5H_4 is done on the

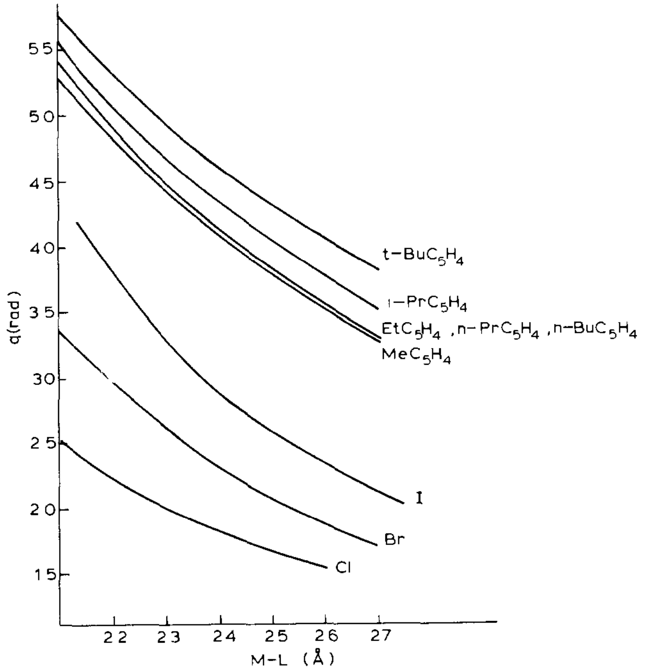

Fig. 3. Dependence of exocyclic angles (q) of ligands on M–L distances.

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* During the calculations, the following values of Van der Waal radii were used: r(C) 1.59 (half the value described in [22], as the boundary between "normally" and "severely" reduced intermolecular contacts C...C), r(Cl) 1.73, r(Br) 1.84, r(I) 2.01 Å [23].

TABLE 3

PARAMETERS OF CORRELATIONS ($\delta = aq(\mathrm{R}) + b$) BETWEEN THE DEGREE OF TRANSFORMATION INTO IRS (δ) AND THE EXOCYCLIC ANGLES ($q(\mathrm{R})$) OF LIGANDS

Reaction series	a	b	S_a	S_b	r
I+TCNE	−128.9	632.8	7.2	31.6	0.994
I+TCNQ	−102.3	501.5	5.0	22.0	0.996
II+TCNE	−64.5	318.1	1.7	7.6	0.999
II+TCNQ	−45.7	226.9	2.5	11.0	0.994
III+TCNE	−29.8	151.2	2.1	9.4	0.990
III+TCNQ	−20.0	101.3	1.2	5.2	0.993

corresponding fragments of the molecules $V(C_5H_4Me)_2Cl_2$ and $[Ru(CO)_2(C_5Me_4Et)]_2$ [24,25], the structures of which has been determined by X-ray analysis. Exocyclic angles for the remaining $AlkC_5H_4$ groups have been calculated using the models made from the above-mentioned C_5H_4Et fragment. It was assumed that alkyl group carbon atoms lie on the extension of C–H bonds of the ethyl group of the initial fragment, and that the length of the C–C bond is 1.54 Å [22]. The orientation of the Alk group in respect to the Cp ring plane was based on minimal steric interactions in the molecules I–III.

In order to determine the values of the exocyclic angles of $AlkC_5H_4$ and X ligands in the compounds under study, we tentatively assumed that the W–C(Cp) bond lengths are 2.36 Å and those of W–X (X = Cl, Br, I) are equal to the sum of the covalent radii according to Pauling [26], i.e. 2.29 (W–Cl), 2.41 (W–Br), 2.58 Å (W–I). The exocyclic angles corresponding to these values of the bond lengths are (see Fig. 3): $q(MeC_5H_4)$ 4.25, $q(EtC_5H_4$, n-PrC_5H_5, n-$BuC_5H_4)$ 4.29, q(i-PrC_5H_4) 4.49, q(t-BuC_5H_4) 4.76, q(Cl) 2.10, q(Br) 2.28, q(I) 2.37 radians (rad). Thus the calculated values of the q-exocyclic angles turn out to be better than the steric constants of Charton. The values depict the change in the reactivity of I–III towards π-acceptors under the effect of Alk substitutes on the Cp ring (compare the correlation coefficients of the corresponding equations in Tables 2 and 3). As is seen from Fig. 4, the increase in shielding of the central metal atom in the series Me < Et ≈ n-Pr ≈ n-Bu < i-Pr < t-Bu leads to a decrease in the ability of I–III to form ion-radical salts with TCNE and TCNQ, in the same order for both donors. When more bulky substituents than t-Bu are inserted into the Cp ring, it would be expected that a complete levelling out of the value in the compounds with different halides will take place.

The same regularity in the change of δ, depending on the value of the exocyclic angle is also observed for the shielding action of the halogen (Fig. 5). The increase in the shielding action on the tungsten atom in the course of transition from chlorides to iodides in all reacting series is accompanied by a decrease in the degree of transformation of I–III into ion-radical salts. Hence, δ and q-values are linked by a linear relationship (in contrast to curves for δ vs. $v(X)$ in Fig. 1). The change in slope and intercept values for $\delta = f(q(\mathrm{R}))$ from Table 3, characteristic of the sensitivity of donor-acceptor interaction of I–III compounds with π-acceptors to structural variations in $(AlkC_5H_4)_2WX_2$, remains the same as when using Charton constants.

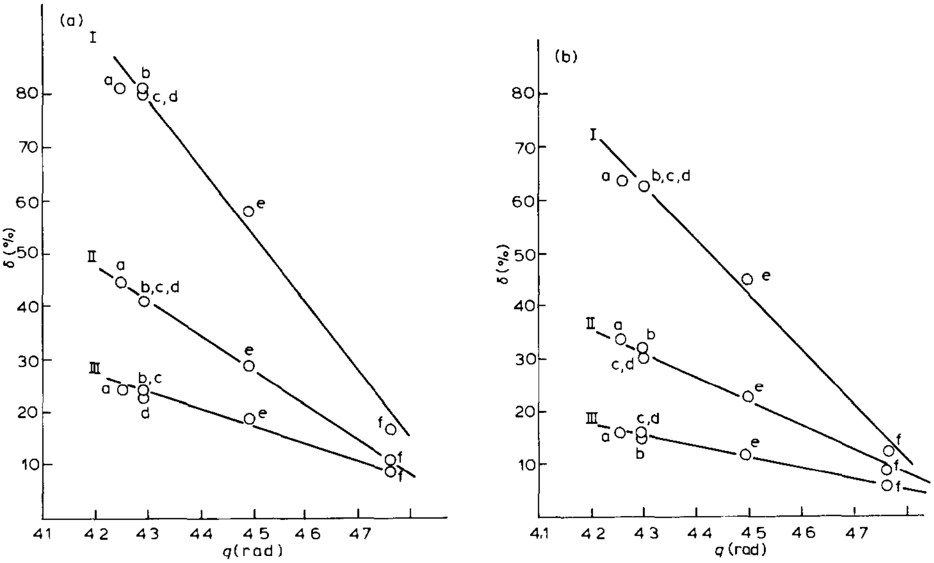

Fig. 4. Dependence of the transformation of the compounds I–III into IRS on exocyclic angles of the AlkC$_5$H$_4$ ligands: (a) Acceptor, TCNE; (b) Acceptor, TCNQ. Identification of the compounds is given in Table 1.

However, the conclusions mentioned above regarding the decrease in sensitivity and electron-donor ability of I–III with the change of X and Alk in the series Cl < Br < I and Me = Et = n-Pr = n-Bu > i-Pr > t-Bu seems at this point to be more substantiated.

While plotting the correlations shown in Figs. 5 and 6 to describe the degree of space shielding of the W atom in the molecules of the I–III compounds, we have

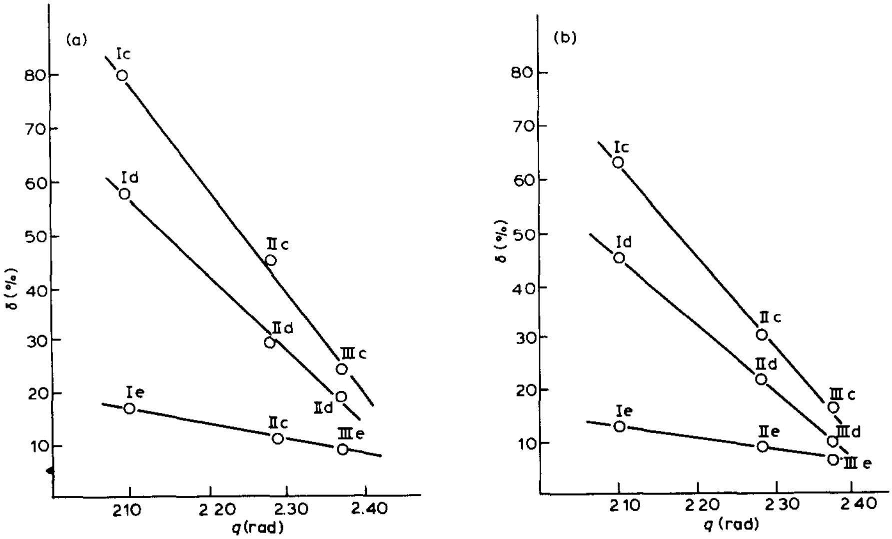

Fig. 5. Dependence of the transformation of compounds I–III into IRS on exocyclic angles of halogen X: (a) Acceptor, TCNE; (b) Acceptor, TCNQ. The labelling of the points is given in Table 1.

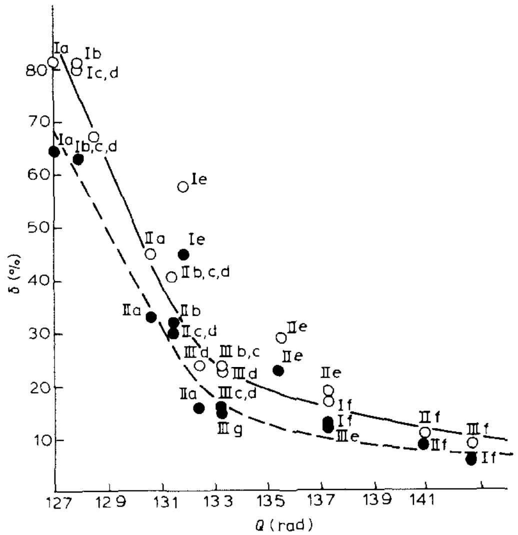

Fig. 6. Dependence of the transformation of compounds I–III into IRS on the sum of the exocyclic angles of the ligands, with TCNE (———) or TCNQ (— — —) as acceptor Identification of the points is given in Table 1.

restricted ourselves to the exocyclic angle value of only one AlkC$_5$H$_4$ or X ligand, which was sufficient to conduct the above comparison in the series of X and Alk. However, the nature of donor–acceptor interaction of the compounds I–III with TCNE and TCNQ depends, undoubtedly, on the space shielding of the W atom by all ligands. Obviously, the degree of such shielding is characterized by the sum Q, of the exocyclic angles of all the ligands in the molecule. As the Q-value is measured in absolute units (rad), it can be used for estimating the effect of space shielding of the W atom on the donor–acceptor interaction of TCNE and TCNQ with I–III compounds for all the compounds under study, and not only in the Alk and X series.

The dependence of the donor ability of I–III compounds in the course of their donor–acceptor interaction with TCNE and TCNQ on the Q-value, is shown in Fig. 6. It should be mentioned that the Q-values for all of the molecules under study exceed the value of the full exocyclic angle, i.e. $4\pi = 12.56$ rad. The reason for this could lie in a shortening of the metal–Cp ring and metal–X bond lengths, used for Q calculations (vide supra), and this, naturally, leads to higher Q-values (for example, an increase of the bond length W–C(Cp) and W–I during Q calculation by 0.05 Å, reduces the theoretical Q-value in the molecule (e.g. in t-BuC$_5$H$_4$)$_2$WI$_2$ to 13.70 rad). Besides, Q-values do not take into account the possible hiding of the substituents behind each other in the molecules under study. In spite of the approximation used, the theoretical Q-values adequately describe the density of the substituent ligands surrounding the tungsten atom in the molecules under study. As seen from Fig. 6, by increasing the general shielding of the tungsten atom, the donor ability of the compounds under investigation (in relation to π-acceptors) is decreased; in the region of higher Q-values (more than 13.1 rad.), the change in donor ability becomes negligible. The higher the Q-value, the more the atom is closed to access from the outside and the more considerable is the steric hindrance for ion-radical salt formation. When more bulky Alk and X substituents are inserted into the $(AlkC_5H_4)_2WX_2$ molecule, the distance to which TCNE and TCNQ molecules can approach it increases and this, it seems, reduces the interaction between the cation and anion radicals. Moreover, with the increase to steric saturation of molecules I–III, their rigidity is increasing and, hence, there is an increase in the prevention of possible deformation of the ligands surrounding the donor molecule at the moment of contact with the acceptor. The possibility for deformation of the $(AlkC_5H_4)_2WX_2$ molecule, which does not cause the disruption of bonds within it, is higher the closer can the centres of positive and negative charges in ion-radical pair become and, thus, the interaction between donor and acceptor becomes stronger. Taking this into consideration, the lower δ-values for the systems $(AlkC_5H_4)_2WX_2$–TCNQ, as compared to the corresponding δ-values for the interaction of I–III molecules with TCNE (a weaker acceptor), become understandable (see Fig. 6 and Table 1). As for the electron-donor molecule with a given Q, the one-electron transfer is easier when the less bulky tetracyanoethylene molecule approaches. It seems that the same ideas can be used to explain the higher sensitivity of donor–acceptor interaction processes of tungstenocenes with TCNE to structural changes in the molecule, as compared to those for TCNQ (higher values of the slopes for TCNE correlations in Tables 2 and 3).

Thus, an important peculiarity of donor–acceptor interaction of bis-cyclopentadienyl tungsten dihalides $(AlkC_5H_4)_2WX_2$ with the strong π-acceptors TCNE and TCNQ in a strongly polar solvent has been established using the method of UV absorption spectroscopy: the processes of one-electron oxidation of the organometallic compounds I–III is mainly controlled by steric factors. The observed regularities are, in our opinion, of practical interest, as the formation of ion-radical salts between $(AlkC_5H_4)_2WX_2$ and π-acceptors can be considered as a model for catalytic reactions with the participation of similar cyclopentadienyl compounds of Group VI metals [27].

It should be mentioned that the method of UV spectroscopy of ion-radical salts, used in the present work for the investigation the intermolecular interactions, is the logical extension of the UV spectroscopy method for charge-transfer complexes [11] of organometallic compounds with low ionization potentials.

Experimental

Compounds I–III have been synthesized using the methods described in ref. 28. The purity of the synthesized substances was checked by NMR spectroscopy and mass spectrometry. The UV absorption spectra of individual compounds and of ion-radical salts of compounds I–III with π-acceptors were recorded on a Perkin–Elmer 402 spectrophotometer. The measurements were performed in an argon medium at 20°C. Acetonitrile, used as the solvent, was purified using a known technique [29]. Ion-radical salts were prepared just before measurements, by mixing the solutions of donor and acceptor. The concentrations used were: donor, 1.66×10^{-3} mol/l, acceptor 2.13×10^{-4} (TCNE) or 0.50×10^{-4} mol/l (TCNQ). The acceptors used were purified by sublimation in vacuum.

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