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Solvatochromism of carbenium–arene EDA (electron donor–acceptor) complexes and their behaviour on silica

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ABSTRACT: Spectral characteristics of two different types of electron donor–acceptor (EDA) complexes with charged components (arene–carbenium and anion–π acceptor) are presented. The UV–Vis absorption maxima of the charge-transfer (CT) band ($\nu_{max,CT}$) of the EDA complexes were measured in various solvents and after adsorption on silica. Tropylium, triarylmethylium and diarylmethylium ions in combination with aromatic π donors, e.g. pyrene, acenaphthene and methoxy-substituted benzene derivatives and also the tetraethylammonium iodide–1,3,5-trinitrobenzene complex have been investigated by means of a special UV–Vis technique in transparent slurries of silica nanoparticles in 1,2-dichloroethane. Multiple linear regression analyses of the $\nu_{max,CT}$ values of the EDA complexes in various solvents and on silica with the Kamlet–Taft solvent parameters and structure–reactivity terms of the complex components, e.g. the oxidation potential of the arene component or the Hammett substituent constant, $\sigma_p{}^+$, of the arylmethyl component, show their related properties to the solution complexes. The influence of the electron-pair donating capacity of a solvent on $\nu_{max,CT}$ of carbenium/arene complexes was compared with the property of the silica surface in order to link EDA complexes. For the diarylmethyl carbenium ion–pyrene complexes on silica, the presence of a σ-like structure is discussed. Copyright © 2001 John Wiley & Sons, Ltd.

KEYWORDS: solvatochromism; carbenium–arene EDA complexes; silica; adsorption

INTRODUCTION

The formation of weak electron donor–acceptor (EDA) complexes between various kinds of organic and inorganic components in solution has been studied by numerous workers and reported in more than 1000 original papers, review articles and books. A selection of important reviews and recent original contributions in this field are cited in the references.[1–6]

EDA complex formation on surfaces of inorganic materials has not been extensively studied. In earlier work by Kortüm and co-workers[7] it was shown that the nature of the inorganic material plays an important role in the stability of the adsorbed EDA complex. A higher polarity of the support (silica) competes with the components of the molecular complex, e.g. pyrene–1,3,5-trinitrobenzene, and its stability decreases. According to the influence of polar solvent on the stability constant of EDA complexes,[2c,d] a high polarity of the inorganic material (e.g. silica)[7c] also decreases the concentration of the complex whereas a neutral inorganic support, e.g. NaCl, has no influence. Kochi and co-workers[8a] reported that it is possible to use inorganic particles (silica or alumina) as a support for tropylium–arene complexes. Then, the UV–Vis charge-transfer (CT) absorption bands were measured by means of the reflectance technique. However, specific effects of the polarity of the inorganic solid on the position of the maxima of the CT absorption bands were not discussed by the authors. In two other papers,[8b,c] Kochi and co-workers showed that acceptor cations (e.g. tropylium or viologens) with iodide or complex manganate as donor anions can be used to measure distinct geometric effects when a component is located within the cavities of zeolite supercages. UV–Vis spectroscopic properties of viologen–arene complexes on silica and their photochemical behaviour in zeolites were reported by Dabestani *et al.*[9a] and Park *et al.*,[9b] respectively. Furthermore, CT complexes of 1,2,4,5-tetracyanobenzene with arenes serve as a probe for surveying chemical properties inside zeolites.[9c]

In this paper, we report on EDA complex formation of silica surface-linked carbenium ions with arenes in organic solvent suspension.

Surface-coordinated arylmethylium ion pairs can be obtained by adsorption of the corresponding haloarylmethane on various moderately strong solid acids and

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also supports with basic sites, e.g. silica, alumina, aluminosilicates and magnesia:[10]

$$\text{silica}-\text{OH} + \text{X}-\text{CR}^1\text{R}^2\text{R}^3 \rightleftharpoons$$
$$\text{silica}-\text{OH}\cdots\text{X}^-\cdots\text{C}^+\text{R}^1\text{R}^2\text{R}^3 \qquad (1)$$

The interaction of $\text{X—CR}^1\text{R}^2\text{R}^3$ with various kinds of silica particles in non-polar or weakly polar solvents (e.g. cyclohexane, toluene or 1,2-dichloroethane) usually gives a coloured slurry because the corresponding UV–Vis absorption band of the $\text{R}^1\text{R}^2\text{R}^3\text{C}^+$ carbenium ion can be monitored on the particle surface.[11] The primary step of the heterolytic dissociation process of $\text{X—CR}^1\text{R}^2\text{R}^3$ on the silica surface is the electrophilic attack of the silanol groups upon the negatively polarized halide atom X. Thus, the degree of heterolytic dissociation of the carbon–halide bond depends on both the electrophilicity of $\text{C}^+\text{R}^1\text{R}^2\text{R}^3$ and the basicity of X^-.[11b]

For the generation of arylmethylium ions on silica, we used mainly the corresponding halides because the corresponding carbinols do not ionize sufficiently for this purpose. In Eqn (1) it is shown that a silanol–halide bridge seems to be responsible for the linking of the carbenium ion at the silanol group. This mechanism was suggested based upon results from model reactions and UV–Vis spectroscopy of triarylmethyl model compounds.[11a,b] However, several criticisms regarding this adsorption mechanism can be mentioned.[11] It is still not clear whether a proton transfer from silanol groups to the coordinated halide takes place and a silanolate carbenium ion pair is also present. Hence the donor strength of the counter ion, either a halide coordinated by silanols or silanolate, is probably influenced by both the carbenium and the silica surface groups.

Arylmethylium–silica adsorbates are well suited as initiators for cationic surface polymerizations of vinyl ethers,[11d] 4-methoxystyrene[11a] or cyclopentadiene.[11e]

In the course of further studies on the utility of surface-coordinated carbenium ion pairs on silica Eqn (1),[11d] we have also investigated their interaction with several arenes in order to produce the corresponding Friedel–Crafts alkylation products by a heterogeneous catalysis reaction. As expected, triarylmethylium– and diarylmethylium–silica adsorbates do not react with arenes of low Friedel–Crafts reactivity such as benzene, toluene or mesitylene. Arenes with higher nucleophilicity,[12] e.g. 1,3-dimethoxybenzene or 1,3,5-trimethoxybenzene, give the expected extractable Friedel–Crafts products in good yield (see later). Surprisingly, many electron-rich arenes did not yield the Friedel–Crafts product, only a fairly strongly coloured silica sample was sometimes obtained. The bis(4-methoxyphenyl)methylium (**1**$^+$) chloride Aerosil adsorbate (red suspension, $\lambda_{\text{max}} = 510$ nm) interacts with 1,4-dimethoxybenzene and pyrene and a green or violet suspension, respectively, is obtained. This observation was unexpected and does not relate to the behaviour in solution where only the Friedel–Crafts reaction occurs. It is also well known that arylmethylium salts are convenient π-acceptors which undergo CT complex formation with arenes in homogeneous solution.[13] EDA complex formation of positively charged acceptors, e.g. tropylium and triarylmethylium, with arenes have been investigated by several workers.[13] However, diarylmethylium compounds, e.g. the bis(4-methoxyphenyl)methylium (**1**$^+$), which possess a similar electrophilicity to triphenylmethylium (**2**$^+$), react about three to four orders of magnitude faster with several arenes and, therefore, yield rapidly the Friedel–Crafts product in solution.[12] The reason for the higher reactivity of diarylmethylium ions, as compared with triarylmethylium ions, with π nucleophils in solution is due to the smaller steric hindrance of the former.

The objective of this paper is to show that various carbenium ion pairs on silica form EDA complexes with arenes in special cases.

The appearance of the characteristic CT absorption band in the visible region of the spectrum is attributed to the rapidly reversible electron transfer from the neutral π donor (D) to the positively charged carbenium (Cat^+) according to the equation.

$$\text{Cat}^+\text{X}^-\text{HO}-\text{silica} + \text{D} \overset{K}{\rightleftharpoons}$$
$$\text{Cat}^+\text{DX}^-\text{HO}-\text{silica} \xrightarrow{h\nu_{\text{CT}}} \text{Cat}^{\cdot}\text{D}^{\cdot+}\ \text{X}^-\text{HO}-\text{silica} \qquad (2)$$

This is consistent with the Mulliken theory.[1a,b]

A specific objective of this work was to investigate the influences of the structure of the π-donor (D) and electron acceptor ($\text{EA} \mathrel{\hat{=}} \text{Cat}^+$) component and also of the counter ion X^- on the position of the CT band ($h\nu_{\text{CT}}$) of the $\text{Cat}^+\text{D X}^-\text{HO—silica}$ complexes. The CT transition energies of the complexes were tested for correlation with the oxidation potential of the π-donor ($E_{\frac{1}{2}\text{ox.}}$) and the reduction potential of the carbenium ($E_{\frac{1}{2}\text{red.}}$) according to the well established relationship[2b,13d]

$$h\nu_{\text{CT}} = E_{\frac{1}{2}\text{ox.}}(\text{D}) + E_{\frac{1}{2}\text{red.}}(\text{EA}) + E_{\text{c}} \qquad (3)$$

where E_{c} is the coulombic energy of the excited state of the complex that is proportional to e^2/r_{AD}; r_{Ad} is the distance of the components EA and D in the excited state of the EDA complex.

The maximum of the CT energy ($\nu_{\text{max,CT}}$) of tropylium–arene and triphenylmethylium–arene EDA complexes in solution shows also a significant dependence on the donor strength of the solvent used.[13f] This is documented by linear correlations of $\nu_{\text{max,CT}}$ with the donor number (DN)[14] of the solvent. Therefore, the capacity of the relevant surface group for donating an electron pair towards the electrophilic carbenium ion centre during the EDA complex formation is expected to be measured by a shift of $\nu_{\text{max,CT}}$.

Table 1. Data for correlation analyses for the solvatochromism of seven carbenium–arene EDA complexes using the Kamlet–Taft solvent parameters β and π^{*a}

EDA complex	$(\nu_{\max,CT})_0$ $\times 10^{-3}$ (cm^{-1})	b	s	n	r	Ref. for the $\nu_{\max,CT}$ data
$C_7H_7{}^+$–pyrene	18.30	5.40	–	8	0.951	13a,b
	19.90	4.70	−1.83	6	0.968	
$C_7H_7{}^+$–anthracene	20.80	3.96	–	11	0.832	13c
	20.80	3.96	−2.33	11	0.857	
$C_7H_7{}^+$–hexamethylbenzene	22.96	2.14	–	11	0.614	13c
	27.30	2.69	−5.6	10	0.914	
$C_7H_7{}^+$–acenaphthene	20.30	3.20	–	10	0.596	13f
N-Methylacridinium–anthracene	18.82	2.90	–	9	0.813	13c
	17.85	2.90	1.2	9	0.827	
$(C_6H_5)_3C^+$–acenaphthene	15.20	5.40	–	7	0.89	13f
$(C_6H_5)_3C^+$–pyrene	14.07	5.08	–	9	0.820	This work
	17.20	6.06	−4.16	9	0.995	(Experimental)

[a] b and s are the coefficients according to Eqn (4), n is the set of solvents used and r the correlation coefficient.

Unprecedented solvatochromic shifts of $\nu_{\max,CT}$ of weak EDA complexes and of other solvatochromic compounds can often be quantitatively interpreted in terms of the Kamlet–Taft solvent parameters.[15] The simplified Kamlet–Taft linear solvation energy (LSE) relationship applied to solvatochromic shifts is[15]

$$\nu_{\max,CT} = [\nu_{\max,CT}]_0 + a\alpha + b\beta + s(\pi^* + d\delta) \qquad (4)$$

where α describes the HBD (hydrogen-bond donating) ability and β the HBA (hydrogen-bond accepting) ability (several workers[16] have shown that the initially defined solvent HBA ability correlates well with the basicity of solvents; therefore, it makes no difference which of the two is used), and π^* is the dipolarity/polarizability of the solvents; δ is a polarizability correction term that is 1.0 for aromatic, 0.5 for polyhalogenated and zero for aliphatic solvents; a, b, s and d are solvent-independent coefficients.

The three empirical polarity terms α, β and π^* can also be used for characterizing the manifold properties of the silica surface.[17] The silica surface exhibits a fairly strong dipolarity/polarizability ($\pi^* \approx 1$), an evident hydrogen-bond donating capacity ($\alpha > 1$) and a very weak HBA property ($\beta < 0.1$).[17a]

It is conceivable that the nature of the counter ion X^- influences the CT mechanism and consequently $\nu_{\max,CT}$. Accordingly, a second objective of this work was the investigation of the property of the relevant surface site on the shift of $\nu_{\max,CT}$ of adsorbed EDA complexes by means of corresponding LSE relationships of the solvatochromism of the EDA complexes in well-behaved regular solvents which serve as the reference system. For the measurements we selected tropylium, triphenylmethylium and diarylmethylium halide–silica adsorbates in conjunction with arenes and also the iodide–1,3,5-trinitrobenzene (TNB) complex when adsorbed on silica. The latter EDA complex was chosen to see how relevant the surface coordination of anions can really be measured by a shift of $\nu_{\max,CT}$. As the silica component we used Aerosil 300, because it forms transparent suspensions in 1,2-dichloroethane or dichloromethane as solvents, which allows one to take UV–Vis transmission spectra of good quality. However, it is not of importance whether Aerosil or neutral silica gels are used for this purpose.

In homogeneous solutions, EDA complex formation is usually weak for carbenium–arene complexes; K_c is of the order of 0.5–5 l mol^{-1}.[13f] As a consequence, one of the two components must be present in a large excess in order to measure the CT absorption band. This makes a quantitative interpretation of adsorbed EDA complexes difficult. Therefore, in this work we preferentially report qualitative results on the EDA complex formation on silica, because $\nu_{\max,CT}$ is independent of the concentration of the EDA complex. The choice of the arene components was determined from two different points of view; a low ionization potential should favour the π- and σ-complex formation[18] and a high nucleophilicity the Friedel–Crafts product formation.[12]

RESULTS AND DISCUSSION

General remarks on solvatochromism of EDA complexes with charged components

Despite the knowledge from many papers reporting on the solvatochromism of EDA complexes with charged components,[19–21] the Kamlet–Taft solvents parameter set has been rarely used for quantitatively describing this behaviour.[6a,14b] Therefore, we have calculated the LSE equations according to Eqn (4) for seven tropylium– and triphenylmethylium–arene complexes using the $\nu_{\max,CT}$ values and corresponding solvent parameters from the literature (Table 1).[12,14] The $\nu_{\max,CT}$ data for the triphenylmethylium–pyrene EDA complex in various

Table 2. Data for correlation analyses for the solvatochromism of halide–π acceptor complexes using the Kamlet–Taft solvent parameter α, β and π^* [a]

EDA complex	r	$\nu_0 \times 10^{-3}$ (cm^{-1})	a	b	s	Ref. for the $\nu_{\text{max,CT}}$ data
I^-–TNB	0.939	20.29 ± 0.50	5.66 ± 0.39	–	1.93 ± 0.96	20c,d
	0.921	21.62 ± 0.17	5.48 ± 0.43	–		
Br^-–TCQ	0.959	21.23 ± 0.45	3.48 ± 0.27	–	0.53 ± 0.61	20c
	0.957	21.60 ± 0.11	3.38 ± 0.25	–		
$I^-C_7H_7^+$	0.976	15.56 ± 1.52	7.67 ± 0.86	–	2.63 ± 1.79	21c
	0.963	17.61 ± 0.69	7.51 ± 0.95	–		
	0.969	17.90 ± 0.86	7.51 ± 0.49	–	6.06 ± 1.11	13a,b
	0.910	22.36 ± 0.44	7.16 ± 0.79	–		
Li^+Br^-–TCQ	0.501	22.31 ± 0.42	10.47 ± 0.01	–	–	20c,d
	0.521	23.78 ± 0.76	–	2.57 ± 1.33	–	
	0.568	23.33 ± 1.28	3.83 ± 7.92	-4.24 ± 2.70	2.03 ± 2.77	

[a] *a*, *b* and *s* are the coefficients according to Eqn (4), *n* is the set of solvents and *r* the correlation coefficient.

solvents were specially measured for this paper (see Experimental section).

As expected, the basicity of the solvent causes a hypsochromic shift of $\nu_{\text{max,CT}}$ of the carbenium–arene EDA complexes due to the moderate interaction of the lone electron pairs of the solvent with their electrophilic carbenium component.[22] According to the CT transition mechanism for cation–arene complexes as shown by the equation

$$\begin{aligned}&(\underline{\text{Cat}}^+\underline{\text{D}} \longleftrightarrow \text{Cat}^{\cdot}\text{D}^{\cdot+})\text{X}^-\\ &\xrightarrow{h\nu_{\text{CT}}} (\text{Cat}^+\text{D} \longleftrightarrow (\underline{\text{Cat}}^{\cdot}\underline{\text{D}}^{\cdot+})\text{X}^- \qquad (5)\end{aligned}$$

there is no remarkable difference expected between the dipolarity of the ground and excited states. In Eqn (5), the mainly contributing resonance structure of each electronic state is underlined [see also Eqns (6) and (7)].

Despite this argument, for the triphenylmethylium–pyrene and tropylium–hexamethylbenzene EDA complexes, a significant bathochromic effect on the CT absorption energy, caused by the dipolarity/polarizability term of the solvent, is observed, also for some of the other tropylium and triphenylmethylium complexes. The contribution of the $\underline{\text{Cat}}^{\cdot}\underline{\text{D}}^{\cdot+}$ species causes a larger dipole moment of the excited state than does the $\underline{\text{Cat}}^+\underline{\text{D}}$ in the ground state of the EDA complex. This is also consistent with the result that the coefficient *s* in Eqn (4) for the solvent influence on $h\nu_{\text{CT}}$ is also dependent on the nature of the arene component D. However, a systematic influence of the nature of D on *b* and *s* is still not detectable on the basis of available data.

It should be noted that the solvatochromism of carbenium–arene complexes occurs very similarly to those of EDA complexes with non-charged components (A–D), i.e. of the Michler's ketone–TCNE complex or others.[6a,19] For both types of complexes, Cat^+D and A–D, the influences of the β term (hypsochromic effect) and π^* term (bathochromic effect) of the solvent upon $h\nu_{\text{CT}}$ are opposite. However, only the solvatochromism of the *N*-methylacridinium–anthracene complex approaches the theoretically expected behaviour for cation–arene CT complexes.[13d]

The influence of the dipolarity/polarizability term on the shifts of $h\nu_{\text{CT}}$ of adsorbed EDA complexes cannot be neglected for carbenium–arene complexes. As already mentioned, silica as environment shows a large value of the π^* term. Therefore, the single correlation equations $1/\lambda = f(\text{DN})$ from Ref. 13f are not sufficient for the quantitative description of the solvatochromism of EDA complexes when considering silica as environment for EDA complex adsorption.

The CT energy of halide (bromide, iodide)–acceptor [1,3,5-trinitrobenzene (TNB), tetrachloro-*p*-quinone (TCQ), tropylium] EDA complexes is also significantly dependent on the nature of the solvent.[20,21] For halide–π acceptor complexes, the corresponding CT transition mechanism is shown by[20a,b]

$$\begin{aligned}&\text{Cat}^+[(\underline{\text{X}}^-\underline{\text{EA}}) \longleftrightarrow (\text{X}^{\cdot}\text{EA}^-)]\\ &\xrightarrow{h\nu_{\text{CT}}} \text{Cat}^+[(\text{EA}^-\text{X}^- \longleftrightarrow \underline{\text{EA}}^{\cdot}\underline{\text{X}}^{\cdot})] \qquad (6)\end{aligned}$$

For an intermolecular anion → cation CT transition, the established mechanism is shown by[21a,b]

$$(\underline{\text{Cat}}^+\underline{\text{X}}^- \longleftrightarrow \text{Cat}^{\cdot}\text{X}^{\cdot}) \xrightarrow{h\nu_{\text{CT}}} (\text{Cat}^+\text{X}^- \longleftrightarrow \underline{\text{Cat}}^{\cdot}\underline{\text{X}}^{\cdot}) \quad (7)$$

The Kamlet–Taft LSE correlations for the solvatochromism of several halide–acceptor and halide–cation CT complexes are shown in Table 2. The LSE equations were calculated using $h\nu_{\text{CT}}$ data from the literature and some additional data specially measured in this work. The measured data are given in the Experimental section.

For the tetraalkylammonium iodide–TNB and the tetraalkylammonium bromide–TCQ EDA complexes fairly good LSE equations, $h\nu_{\text{CT}} = f(\alpha,\pi)$, are obtained. $h\nu_{\text{CT}}$ increases with increasing HBD capacity of the

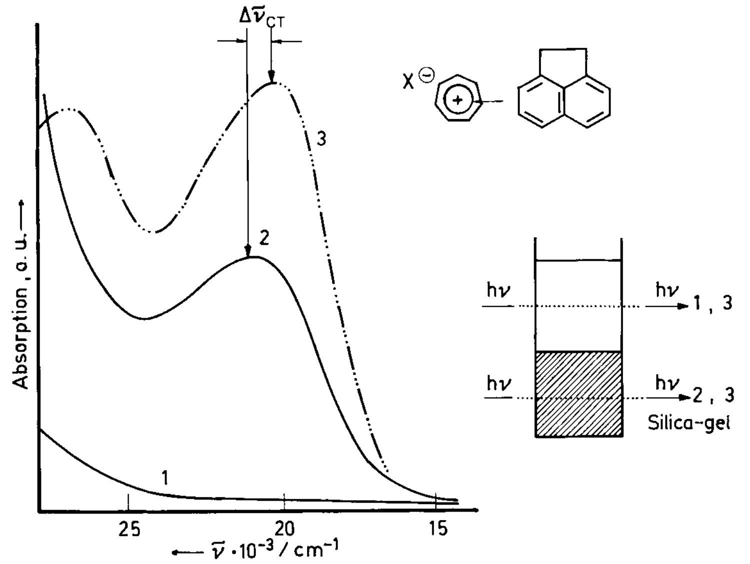


Figure 1. Qualitative UV–Vis spectra of the tropylium–acenaphthene complex in a slurry of silica in 1,2-dichloroethane. The sections measured by the transmission technique are indicated in the inset. 1 denotes $C_7H_7{}^+BF_4{}^-$ with acenaphthene measured in the supernatant solution and 2 denotes $C_7H_7{}^+BF_4{}^-$ with acenaphthene measured on the surface of the silica particles; 3 denotes $C_7H_7{}^+SbCl_6{}^-$ with acenaphthene measured either in the slurry *or* in the supernatant solution

solvent, because the anion component of the complex is strongly specifically solvated by these solvents. The dipolarity/polarizability strength of the solvent (value of the π^* term) also has a significant hypsochromic effect on $h\nu_{CT}$. For the lithium bromide–tetrachloro-*p*-quinone EDA complex, no significant contribution of any solvent term is detectable. However, the β term causes a bathochromic shift of $h\nu_{CT}$ because the lithium cation is evidently complexated by the donor site of the solvent.[14] Unfortunately, the influence of the solvent on $h\nu_{CT}$ of $Li^+X^- \rightarrow$ EA is manifold.[20] Hence lithium halide–acceptor complexes are not suitable as polarity indicators for parameterizing.

It is also striking that the Kamlet–Taft correlation analyses for the solvatochromism of Cat^+X^- complexes give qualitatively similar results as for the EA-X^- complexes rather than those for the Cat^+D complexes. This result points out that the influence of the β term of the solvent upon $h\nu_{CT}$ of the latter seems to be unimportant. This result was unexpected for the tropylium ion as acceptor because the basicity of the solvent causes a significant hypsochromic effect on the CT maxima of tropylium–arene complexes (see Table 1). For pyridinium ions as acceptor, the solvatochromism has been extensively discussed in the literature, e.g. the *Z* and $E_T(30)$ scales of solvent polarity,[15d] and will not be treated in this paper.

EDA complexes on silica

Iodide–TNB. For the tetraethylammonium iodide–TNB complex adsorbed on undried Aerosil 300 ($\alpha = 1.17$ and $\pi^* = 0.94$), $\nu_{max,CT}$ is expected at about $\nu = 28\,500\ cm^{-1}$. This is also observed when the $(C_2H_5)_4N^+$ iodide–TNB complex is adsorbed on Aerosil 300 from a 1,2-dichloroethane solution ($\nu_{max,CT} = 20\,000\ cm^{-1}$). Then, the CT absorption appears strongly hypsochromically shifted at $\nu_{max,CT} = 28\,500\ cm^{-1}$ as a shoulder in the UV–Vis spectrum. Unfortunately, the CT absorption intensity of the iodide–TNB complex on silica is rather weak and, therefore, its detection is not easy to achieve. A similar effect is observed for *N*-methylacridinium iodide (NMI), which shows $\nu_{max,CT}$ at $\nu = 20\,000\ cm^{-1}$ in 1,2-dichlorethane.[13c] After adsorption of NMI on silica, the former CT absorption band in the UV–Vis spectrum is completely disappeared. However, the iodide–TNB EDA complex is not very suitable as a surface polarity indicator, but the results clearly show that the Kamlet–Taft polarity parameters for the silica particles surface can be well used for the interpretation the electronic behaviour of adsorbed anions.

Tropylium Aerosil–arene complexes. In order to demonstrate the importance of the role of the counter ion for the adsorption of tropylium–arene complexes on silica particles, a very simple experiment is recommended that can be easily carried out with commercially available chemicals in any laboratory.

Two separate solutions of the tropylium $BF_4{}^-$-acenaphthene and tropylium $SbCl_6{}^-$–acenaphthene ($\nu_{max,CT} = 20\,000\ cm^{-1}$) EDA complexes should be prepared in 1,2-dichloroethane or dichloromethane as solvent (see Experimental). Then, either of the red EDA

Table 3. UV–Vis CT absorption maxima for four $C_7H_7^+BF_4^-$–arene EDA complexes in 1,2-dichloroethane (DCE) and after adsorption on dried Aerosil 300, measured in the same solvent

	$\nu_{max,CT} \times 10^{-3}$ (cm^{-1})	
Arene component	In DCE	On Aerosil in DCE
Pyrene	18.3	18.9
Anthracene	18.4	19.0
Acenaphthene	20.0	20.6
Naphthalene	23.0	23.1

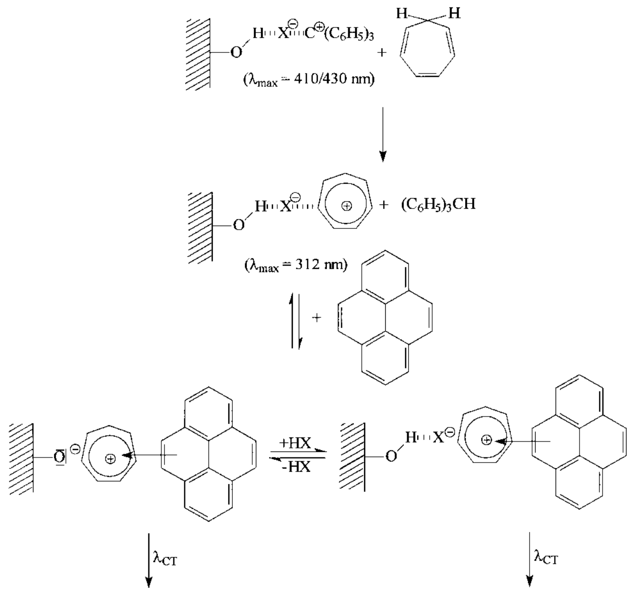
complex solutions is stirred with an amount of silica in a glass vessel. One observes that in the case of the tetrafluoroborate salt, the silica becomes orange–red and the supernatant solution remains colourless. It makes no difference for these measurements whether silica (KG 60, Merck) or Aerosil 300 (Degussa) is used.[11f]

In contrast, the EDA complex with hexachloroantimonate as the counter ion remains quantitatively in the surrounding solution and the silica is still colourless. Both the intensity and the position of the CT band in the UV–Vis spectrum of the tropylium $SbCl_6^-$–acenaphthene EDA complex are unchanged on treating the solution with silica. The corresponding UV–Vis spectra are shown in Fig. 1.

Of course, both anions are weak hydrogen-bonding acceptors[23], (basicity parameters of weakly co-ordinating anions are not well established; for a discussion to this topic, see. Ref. 23a) but BF_4^- is slightly more basic towards OH groups than $SbCl_6^-$ when using the corresponding stability constants with phenol (K_C in l mol^{-1}) in CH_2Cl_2 as the reference value.[23b] Thus, $SbCl_6^-$ ($K_C < 0.1$ l mol^{-1})[23b] is non-nucleophilic and BF_4^- ($K_C = 10$ l mol^{-1}) is a very weak basic anion. For comparison, the Cl^- ion is a fairly strong base ($K_C = 400$ l mol^{-1}).[23b] This reflection shows the importance of the role of the basicity of the counter ion for adsorption processes of carbenium ions on silica surfaces. UV–Vis spectroscopic results for four different tropylium BF_4^-–arene complexes when adsorbed on silica are shown in Table 3.

The adsorption of tropylium tetrafluoroborate–arene EDA complexes on silica in dichloromethane is always associated with a small hypsochromic shift of the CT absorption band. The difference between the CT energy of the tropylium–pyrene complex on silica and that of the solution complex in CH_2Cl_2 is about $\Delta\nu = 600$ cm^{-1}. This corresponds to a β value of the silica surface-coordinated BF_4^- ion of about 0.12 when using the LSE equation for the tropylium–pyrene complex from Table 1 and the π^* value for bare silica.

Tropylium salts with various counter ions can be conveniently synthesized by the hydride transfer reaction of cycloheptatriene with the corresponding triphenylmethylium salts.[24] For producing silica surface-linked tropyliums, we used triphenylmethyl halides when adsorbed on silica as hydride-acceptor component according to scheme 1.



Scheme 1. Surface-mediated hydride transfer reaction from cycloheptatriene to triphenylmethylium ions adsorbed on silica and CT complex formation with pyrene

The reaction shown in Scheme 1 occurs quantitatively. The bare tropylium UV–Vis absorption is expected at about $\nu = 40000$ cm^{-1},[24b] but a new UV–Vis absorption is observed at $\nu = 32000 \pm 500$ cm^{-1} on silica. This UV–Vis absorption band is independent of the nature of the halotriphenylmethane used, either the chloride or bromide. The characteristic UV–Vis CT absorption bands of $C_7H_7^+Br^-$ and $C_7H_7^+Cl^-$, which occur in dichloromethane at $\nu_{max,CT} = 24900$ and 30000 cm^{-1}, respectively,[24b] are not observed on silica. Whether the bromide ion is strongly coordinated by silanol groups or bonded in the form of HBr_2^- through an excess of HBr. Both options would correspond to a strong hypsochromic shift of the intramolecular halide or HX_2^- tropylium CT transition. For instance, the $HBr_2^- \rightarrow$ tropylium CT transition occurs in dichloromethane at $\nu_{max,CT} = 28600$ cm^{-1}.[24c] Owing to the large α value of undried Aerosil, a hypsochromic shift of about $\Delta\nu = 9000 \pm 1000$ cm^{-1} is theoretically expected for $C_7H_7^+I^-$ on silica (according to the results from Table 2).

Both of these tropylium silica adsorbates, the chloride and also the bromide form give the typical EDA complex with pyrene on silica. For these experiments, the pyrene is added to the freshly prepared tropylium–Aerosil adsorbate in the slurry.

The position of the UV–Vis absorption maxima of the tropylium–pyrene complexes on silica is $\nu_{max,CT} = 18800$ cm^{-1} for X = Cl and 19200 cm^{-1} for X = Br, similar to that for BF_4^-. Therefore, we conclude that the halide ions adsorbed are very strongly bonded on

Table 4. Calculated β values for anions on silica derived from the LSE equations in Table 1

Anion	β (in DCE)[a]	β (in DCE)[c]	β (on silica)[c] for Cu(tmen)(acac)$^+$	β (on silica) for $(C_6H_5)_3C^+$	β (on silica) for $C_7H_7^+$
F^-	2.95	–	–	–	–
Cl^-	1.00	1.63	1.13	0.37	0.12
Br^-	0.67	1.51	0.95	0.20	0.20
BF_4^-	0.55[b]	–	–	–	0.12

[a] From Ref. 23e.

[b] Estimated value via correlation of data from Refs. 23b and 23e.

[c] Data from Ref. 17b.

the silica surface, because of the weak shift of $\nu_{\max,CT}$ observed.

Triarylmethylium halide Aerosil-arene complexes. Despite the fact that the arene component was used in a large excess [$D \geq 0.1$ mol l^{-1}), an evident charge-transfer UV–Vis absorption of substituted triphenylmethylium halide Aerosil adsorbates with acenaphthene or other π donors at the solid–liquid interface in 1,2-dichloroethane can be observed only in a few cases. With unsubstituted triphenylmethylium halide Aerosil adsorbates, very weak EDA complex formation with acenaphthene is observed. Unfortunately, with pyrene as arene component, a CT band cannot be detected. The EDA complex formation can be easely detected visually. The colour of the silica particles surface changes from yellow (the triphenylmethylium UV–Vis absorption appears at $\lambda = 410/430$ nm) to green (CT absorption at about $\lambda = 600$ nm) after addition of acenaphthene. The formation of the EDA complex is time dependent. The equilibrium state of complex formation is usually accomplished after a 12 h reaction time. For methoxy-substituted triarylmethylium ions as acceptor component, the less intense CT absorption of the EDA complex, which is expected at about $\lambda = 500$ nm, cannot be observed because it is covered by the fairly intense UV–Vis absorption of the carbenium ion. 4-Nitro- or trichloro-substituted chlorotriarylmethanes do not ionize sufficiently on silica. Thus, the carbenium ion concentration derived from these compounds on the surface is too low for measuring UV–

Table 5. CT absorption maxima for the bis(4-methoxyphenyl)methylium chloride Aerosil complex with arenes and Friedel–Crafts product formation observed, and the corresponding CT maxima of the arenes with TCNE in 1,2-dichloroethane

Arene	$\nu_{\max,CT} \times 10^{-3}$ (cm^{-1}) ($\mathbf{1}^+$ on Aerosil)	Yield of the extracted Friedel–Crafts product (%)	$\nu_{\max,CT} \times 10^{-3}$ (cm^{-1}) (with TCNE)
Benzene	(25.62)[a]	0	26.04
Toluene	(24.36)[a]	0	24.63
Mesitylene	(21.80)[a]	0	21.69
Methoxybenzene	(20.40)[b]	30[c]	19.56
1,2-Dimethoxybenzene	20.70	0	16.86
1,3-Dimethoxybenzene	18.40[b]	75[d]	18.18
1,4-Dimethoxybenzene	16.00	0	15.77
1,4-Diethoxybenzene	16.20	0	–
1,2,4-Trimethoxybenzene	16.80	90[g]	14.50
1,2,3-Trimethoxybenzene	19.80	82[h]	19.42
1,3,5-Trimethoxybenzene	(20.62)[a]	95[e]	18.15
Naphthalene	(18.64)[a]	0	18.18
Acenaphthene	16.70	0	15.30
2-Methoxynaphthalene	16.10	0	16.32
Pyrene	14.60	2–3	13.80
Anthracene	13.00[f]	2–3	–
Stilbene	(17.41)[a]	0	16.80
4,4′-Dimethoxystilbene	(15.03)[a]	0	14.12

[a] The EDA complex concentration on the surface is too low to detect the UV–Vis CT absorption band. The values in parentheses are the theoretically expected UV–Vis absorption maxima calculated by means of Eqn (8a) or (8b).

[b] The UV–Vis CT absorption appears as a shoulder.

[c] Tris(4-methoxyphenyl)methane and (2,6-dimethoxyphenyl)bis(4-methoxyphenyl)methane are obtained in a product ratio of 2:1.

[d] (2,4-Dimethoxyphenyl)bis(4-methoxyphenyl)methane.

[e] (2,3,5-Trimethoxyphenyl)bis(4-methoxyphenyl)methane.

[f] Weak absorption intensity.

[g] The reactions proceed highly regioselectively: (2,3,5-trimethoxyphenyl)bis(4-methoxyphenyl)methane is exclusively obtained.

[h] (2,3,4-Trimethoxyphenyl)bis(4-methoxyphenyl)methane and (4,3,5-trimethoxyphenyl)bis(4-methoxyphenyl)methane are obtained in a product ratio of 6:1.

Vis spectroscopically the EDA complex of triarylmethylium ions (see later for diarylmethylium ions). Hence only halotriphenylmethanes where the corresponding carbenium ions possess pK_{R^+} values[25] between −7 and −4 are suitable as acceptor components on silica in order to form a detectable EDA complex with a π donor component.

The CT band of the triphenylmethylium Aerosil–acenaphthene EDA complexes can only be observed as a broad shoulder in the UV–Vis spectrum. Their absorption maxima are shifted hypsochromically as compared with the corresponding EDA complex of $(C_6H_5)_3C^+\ SbCl_6^-$ in 1,2-dichloroethane. The extent of the hypsochromic shift of the CT band corresponds to the basicity of the counter ion: $F^- \gg Cl^- > Br^-$.[23] For adsorbed $(C_6H_5)_3CF$, the UV–Vis CT absorption band with acenaphthene or pyrene was not detectable.

For an estimate of the basicity of the surface-coordinated anions we have used the LSE relationships for the charge-transfer energies of the $C_7H_7^+$–π donor and $(C_6H_5)_3C^+$–π donor EDA complexes from Table 1. Calculated β values for the surface-coordinated anions are shown in Table 4. They are apparent values. However, the difference between these values and the values for anions in solution is evident.

It seems that the β value of the adsorbed anion depends also on the electrophilicity of the cation. However, the results clearly show that anions on surfaces are significantly reduced in their basicity.

According to the shift of $\nu_{max,CT}$, three methyl groups in the 4-position of the triphenylmethylium ion cause a similar decrease in its acceptor strength as when a surface-linked chloride ion is coordinated to it.

The hypsochromic shift of the CT absorption of the ion-pair complexes, compared with analogous species in 1,2-dichloroethane solution, is attributed to a stronger interaction of the electronic ground state of the complex with the surface-coordinated counter ion. Hence the electron affinity of the carbenium ion-pair intermediate on the surface is slightly decreased as compared with the same EDA complex in solution.

Diarylmethylium halide Aerosil–arene complexes.

Amongst the triphenylmethylium ions ($\mathbf{2}^+$) as acceptor component on silica we used bis(4-methoxyphenyl)-methylium ($\mathbf{1}^+$) on Aerosil. Both carbenium ions possess similar electrophilicity. This can be shown in terms of their pK_{R^+} values ($\mathbf{2}^+$, $pK_{R^+} = -6.3$; $\mathbf{1}^+$, $pK_{R^+} = -5.9$)[25] and reduction potentials ($\mathbf{2}^+$, $E_{\frac{1}{2}red.} = -0.635V$; $\mathbf{1}^+$, $E_{\frac{1}{2}red.} = -0.62V$).[26]

The typical UV–Vis CT absorption band of the EDA complex can be observed for the $\mathbf{1}^+$ chloride with some π donors on silica in a 1,2-dichloroethane suspension. For the measurements we used typical concentrations suitable for synthetic procedures (see Experimental). The experimental results regarding the yield of Friedel–Crafts product and qualitative indications of EDA complex formation are compiled in Table 5.

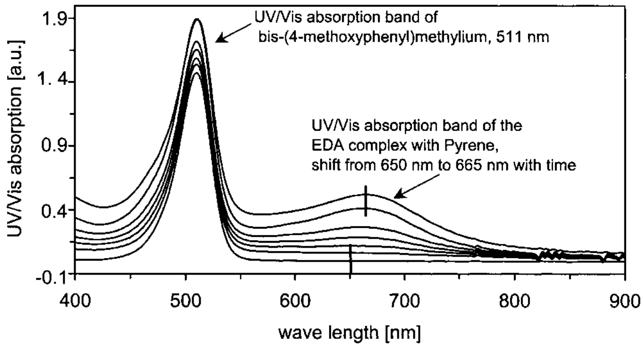


Figure 2. Time-dependent measured UV–Vis transmission spectra of the EDA complex formation of 0.0197 g of (4-$CH_3OC_6H_4)_2CHCl$ with 0.0152 g of pyrene on 1.04 g of Aerosil 300 in 25 ml of dichloromethane. Optical path-length = 0.5 cm. From the bottom to the top, the UV–Vis spectra were measured 1, 2, 3, 4, 6 and 24 h after mixing the components)

The CT complex formation can be clearly observed by the characteristic change of colour of the silica gel phase in the suspension. In the supernatant liquid phase, no CT band was observed. For instance, with 1,4-dimethoxybenzene as π donor component the colour of the silica particles changes from red to violet. Despite the characteristic change of colour in the slurry, the detection of the CT band was not easy to achieve because the UV–Vis absorption bands of the diarylmethylium ion and that of the corresponding CT absorption of this EDA complex interfere.

EDA complex formation between $\mathbf{1}^+\ SbCl_6^-$ and arenes in dichloromethane solution cannot be observed, because the tendency of $\mathbf{1}^+SbCl_6^-$ to undergo Friedel–Crafts and other electrophilic reactions with arenes prevents the possibility of detecting UV–Vis CT absorption bands. Quantitative determination of the true EDA complex concentration on the surface is very difficult to achieve. The main restricting factor for these experiments is that the EDA complex formation on the silica particles takes place in a time-dependent manner. Usually, for $\mathbf{1}^+$ on Aerosil with pyrene after 12 h the EDA complex formation is complete as indicated by the invariably remaining intensity of the new UV–Vis CT absorption band at $\lambda_{max} = 656$–683 nm. Figure 2 shows characteristic UV–Vis spectra for the interaction of **1**-Cl with pyrene on Aerosil 300 in dichloromethane.

Two notable experimental results are found. Immediately after mixing the components $(4\text{-}CH_3OC_6H_4)_2CHCl$, Aerosil 300 and pyrene, only the UV–Vis absorption band of the $\mathbf{1}^+$ carbenium ion at $\lambda_{max} = 511$ nm is observable.

After 3 h, a broad CT band slowly appears at $\lambda_{max} = 650$ nm. This UV–Vis band shifts to longer wavelength up to $\lambda_{max} = 680$ nm with increasing reaction time. Using

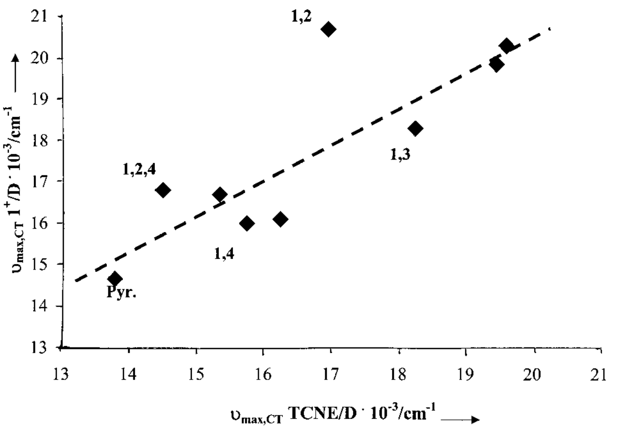


Figure 3. Correlation between the UV–Vis CT maxima of EDA complexes for $\mathbf{1}^+$ Aerosil π donors with those of TCNE π donors in 1,2-dichloroethane; 1,2, 1,2,4, 1,4 and 1,3 denote the positions of the methoxy substituents at the benzene ring for some π donors and Pyr is pyrene

a 10 fold amount of both $(4\text{-}CH_3OC_6H_4)_2CHCl$ and pyrene, the CT band appears much faster. As the intensity of the CT band increases, an increase in the carbenium ion UV–Vis absorption at $\lambda_{max} = 511$ nm also occurs.

After separation (filtration) of the solid complex from the suspending liquid and careful extraction with dichloromethane, the intense coloured EDA complex remains strongly fixed on the silica particles surface. With pyrene as π donor component, the CT absorption of $\mathbf{1}^+$Py can be observed in the UV–Vis spectrum at about $\lambda = 660$–680 nm. This allows well-defined monitoring of the UV–Vis CT absorption band because interference with that of the precursor carbenium band is not a disturbing factor. Radical-cation formation can be excluded, as shown by EPR spectroscopy of the solid samples: no evident signal is observed. The definitive structure of the solid EDA complexes on silica is still not clear in detail. The solid-state cross-polarization magic angle spinning (CP/MAS) ^{13}C $\{^1$H$\}$ NMR spectrum clearly reflects the sum of all carbon atoms derived from pyrene and **1**-Cl (see Experimental). An ionic intermediate is not detectable in the solid-state ^{13}C NMR spectrum.[27,28] Quantitative elemental analysis (C, H, Cl) indicates a too low chlorine content, only 10% of the theoretically expected value when a 1:1 complex is presumed. This result also shows that diarylmethylium is probably adsorbed directly on the silanolate oxygen atoms instead on an adsorbed halide ion. This is consistent with the result that $\mathbf{1}^+$Cl$^-$ and $\mathbf{1}^+$Br$^-$ give the same CT absorption maximum with pyrene on silica.

It must be mentioned that the EDA complexes are formed in low quantity. They are, however, by-products for some of the π donor–carbenium pairs studied. To decide whether the new UV–Vis absorption band is attributable to a CT transition from the arene to the carbenium component or a new monomolecular species, correlations of $\nu_{max,CT}$ and the ionization potential or $E_{\frac{1}{2}ox.}$ [Eqn (3)] of D have been proved.[5,29]

The CT energies of the absorption maxima of bis(4-methoxyphenyl)methylium ion Aerosil–arene complexes correlate well with that of well established TCNE–arene complexes.[5,6b] However, 1,2-dimethoxy-substituted benzene gives an outlying point from the straight line, as shown in Fig. 3.

$$\nu_{max,CT} \times 10^{-3}(\text{silica}-\text{OHCl}^- 1^+ - \text{arene}) = 1.045\nu_{max,CT} \times 10^{-3}(\text{TCNE}-\text{arene}) + 0.3172 \quad (8a)$$

$r = 0.931$, $n = 8$ (the data for 1,2-dimethoxybenzene were not included in the correlation)

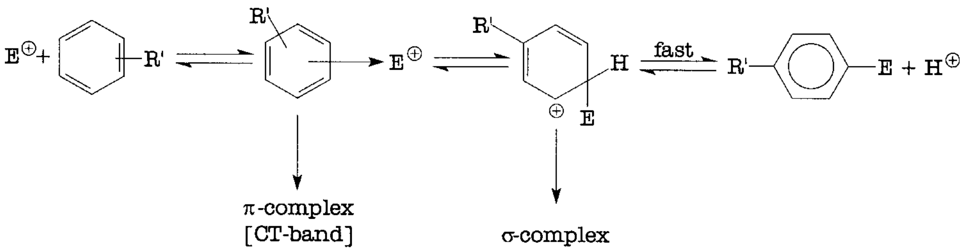
As expected, the slope from Eqn (8a) approaches unity, which shows an adequate influence of each arene compound on $\nu_{max,CT}$. Equation (8a) also shows that $\mathbf{1}^+$ and TCNE have similar electron affinities, because the intercept value is of the order of $\Delta\nu \approx 300\ \text{cm}^{-1}$, which is of the order of the error for detecting the $\nu_{max,CT}$ value. In an earlier paper we have already discussed that TCNE and $(C_6H_5)_3C^+$ have similar electron affinities.[13e]

Disappearance of the CT absorption band of the complex is observed when a competing π donor is added which reacts irreversibly with the carbenium component, i.e. trimethylethylene. According to Eqn. (3), for $\mathbf{1}^+$–arene complexes on silica the $E_{\frac{1}{2}ox.}$ values of the π donor[29] correlates with the CT energies of the EDA complex:

$$\nu_{max,CT} \times 10^{-3}[\text{cm}^{-1}](\text{silica}-\text{OHCl}^- 1^+ - \text{arene}) - 1.727\, E_{\frac{1}{2}ox.}(\text{arene})[\text{V}] + 10.676 \quad (8b)$$

$$r = 0.983, \quad n = 6$$

This result confirms the presumption that the new UV–Vis absorption band can probably be attributed to a CT transition from the arene component to the carbenium ion and is not derived from a new carbocationic species.[27]



(9)

However, Hubig and Kochi[18] showed that also the σ complex formation of cations with arenes is associated with strong colour formation. The wavelength position of the UV–Vis band derived from the σ complex is also dependent on the electron affinity and ionization potential of the components E^+ (electrophile) and D [Eqn (9)]. This makes the qualitative interpretation of the UV–Vis complex absorption on silica very difficult.

Analogous to the $(4\text{-}CH_3OC_6H_4)_2CH^+$–pyrene Aerosil complex, we measured various substituted diarylmethylium–pyrene halide Aerosil complexes in suspensions of 1,2-dichloroethane and cyclohexane.

Some chlorodiarylmethanes, for which the difference between the pK_{R^+} and pK_s of the corresponding carbocation and anion, respectively, is smaller than -1, i.e. $(4\text{-}CH_3C_6H_4)_2CHCl$, $(C_6H_5)_2CHCl$ or $(4\text{-}ClC_6H_4)_2CHCl$, do not ionize sufficiently on Aerosil to measure the corresponding UV–Vis absorption of the carbenium ion. For these halodiarylmethanes we found that CT complex formation with pyrene takes place very slowly on silica. The UV–Vis absorption bands of both the single diarylmethylium and corresponding CT complex absorption appear simultaneously after addition of the arene component pyrene. Characteristic time-dependent UV–Vis spectra are shown in Fig. 4 for the $(4\text{-}CH_3C_6H_4)_2CHCl$–pyrene Aerosil complex.

A catalytic influence of HCl via elimination from the solvent 1,2-dichloroethane can be excluded because the same result is found in cyclohexane suspension. In principle, two different mechanisms are possible to explain this experimental result, as follows

First option. The concentration of the former carbenium ion pair (before adding the arene component) on silica is very low ($[R^+] < 10^{-8}$ mol g^{-1}). Therefore, the intensity of the UV–Vis absorption band of the carbenium is too low to be monitored by UV–Vis spectroscopy. Since the rate-determining step (R_{EDA}) in forming a carbenium–arene EDA complex is the formation of the carbenium intermediate, then the rate for the formation of the EDA complex is given by

$$R_{EDA}(\text{on silica}) = k_{EDA}[R^+Cl^-]_{silica}[D] \qquad (10)$$

Assuming $k_{EDA} \approx 10^8\ l\ mol^{-1}\ s^{-1}$,[3b] $[D] = 0.01\ mol\ l^{-1}$ and $[R^+Cl^-]_{silica} < 10^{-9}$, this would obviously explain why the rate for the formation of EDA complex is low. R_{EDA} (on silica) is probably lower than $10^{-4}\ l^{-1}\ mol\ s^{-1}$. However, the EDA complex is evidently more stable than the bare carbenium on silica. Probably the cation–anion recombination and consequently the desorption process [Eqn (1)] occur more slowly between the π-complexed carbenium and the anion than with the non-complexated one. It should be noted that the diarylmethylium UV–Vis absorption also occurs on Aerosil when using the pure-halodiarylmethane after 2 days. However, in the presence of the arene component, the carbenium UV–Vis absorption appears faster.

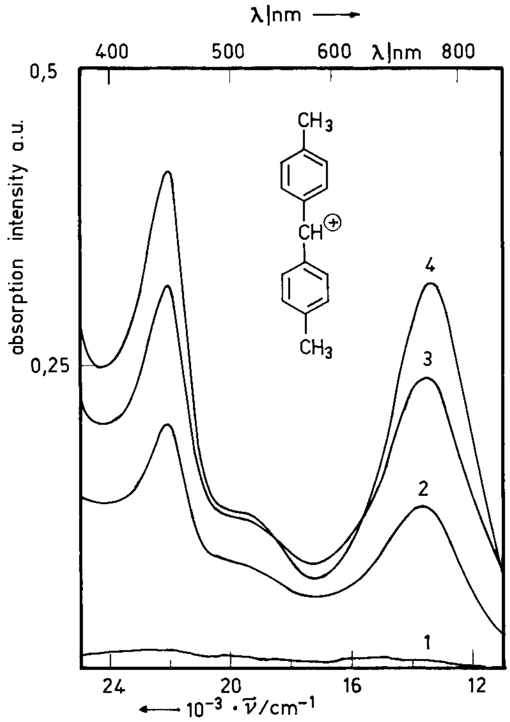


Figure 4. Time-dependent measured EDA complex formation for $(4\text{-}CH_3C_6H_4)_2CHCl$ with pyrene on Aerosil 300. 1, After 20 h; 2, after 3 days; 3, after 10 days; 4, after 24 days. For conditions, see Experimental section. The left UV–Vis absorption band is caused by the carbenium ion (shown as inset)

Second option. The nucleophilic attack of the π donor on the adsorbed haloarylmethane component causes a heterolytic dissociation (ionization) of the polarized carbon–halide bond and, consequently, carbenium ion UV–Vis absorption and CT band occur. It is established that chloromethyl-substituted aromatics interact more strongly with polar surfaces than do non-substituted aromatics.[30] The second option is also supported by the fact that the EDA complex formation occurs even in cyclohexane as solvent, which is non-polar in comparison with 1,2-dichlorethane.

However, the experimental results are not sufficient to decide which mechanism is the relevant one. Maybe both mechanisms can occur in turn. The stability of the EDA complex is probably attributable to the specific role of the silica and the bonded counter ion and to the stabilizing effect of the π donor. It seems that the presence of two stabilizing components for the carbenium ion, the negatively charged silica-surface group and the π donor, are the reason why Friedel–Crafts product formation occurs with very low yields and no cation–anion recombination takes place.

Quantitative elemental analysis of the coloured solid

Table 6. UV–Vis absorption maxima for ($R^1C_6H_4CHClC_6H_4R^2$) on Aerosil and in the presence of pyrene and the CT maxima of the corresponding EDA complex on Aerosil 300, measured in 1,2-dichloroethane (DCE) and cyclohexane at 293 K (the CT complex was measured after 24 h)

R^1	R^2	$\Sigma\sigma_p^+$	$\nu_{max}\times10^{-3}$ (cm^{-1}) (carbenium)		$\nu_{max}\times10^{-3}$ (cm^{-1}) (CT complex)	
			Without pyrene	With pyrene	In DCE	In cyclohexane
4-CH_3	4-CH_3O	−1.56	19.53	19.50	14.65	15.25
4-C_6H_4O	4-CH_3O	−1.31	19.53	19.50	14.65	15.00
4-C_6H_4O	4-C_6H_4O	−1.06	20.20	20.00	14.55	14.70
4-CH_3O	4-CH_3	−1.09	20.66	20.50	14.50	14.45
4-CH_3O	4-H	−0.78	21.83	21.80	14.20	14.25
4-CH_3O	4-Cl	−0.67	21.28	21.20	13.95	14.20
4-CH_3O	4-NO_2	0.01	19.19	19.00	13.80	13.90[c]
4-CH_3	4-CH_3	−0.62	21.1–21.6[a]	21.98	13.80	13.80
4-CH_3	4-H	−0.31	21.9–22.3[a]	22.83	13.75	13.80
4-H	4-H	±0	22.7–22.9[a]	23.26[b]	13.40	13.60
4-F	4-F	−0.14	22.1–22.6[a]	23.26[b]	14.10	14.10[c]
4-Cl	4-Cl	+0.23	20.6[a]	22.22[b]	Not observed	Not observed

[a] In the pure chlorodiarylmethane Aerosil suspension, the corresponding UV–Vis absorption band of the $R^1C_6H_4CH^+C_6H_4R_2$ ion is not observed after mixing the components, because the concentration of the carbenium ion is too low to be detectable. The data given are expected from the literature.[25]

[b] The UV–Vis absorption of the carbenium ion appears as a shoulder.

[c] The concentration of the EDA complex is rather low; only a shoulder of the CT band appears between 700 and 800 nm.

Aerosil–$\mathbf{1}^+$–pyrene complexes show that only 10–15% of chlorine remains in the whole EDA complex. Therefore, we conclude that different types of counter ions—silanolate versus adsorbed chloride—are present.

Qualitative UV–Vis spectroscopic results are summarized in the Table 6. For some of the combinations, the EDA complex absorption CT band is very weak (see footnotes to the table).

As expected, substituents with electron-donating capacity decrease the electron affinity of the diarylmethylium ion and the CT absorption of the corresponding EDA complex shifts hypsochromically (Fig. 5).

However, the effect of the substituent ($\sum'\sigma_p^+$) on the shift of ν_{CT} is much lower than expected theoretically when using Eqn (3) and the $E_{\frac{1}{2}red.}$ and $E_{\frac{1}{2}ox.}$ values from the literature.[26b,28] This hints at strong complexation of the pyrene component or/and strong coordination of the diarylmethylium on silica. Consequently, the coulomb term plays an important role in $\nu_{max,CT}$.

The weak influence of the electron affinity on $\nu_{max,CT}$

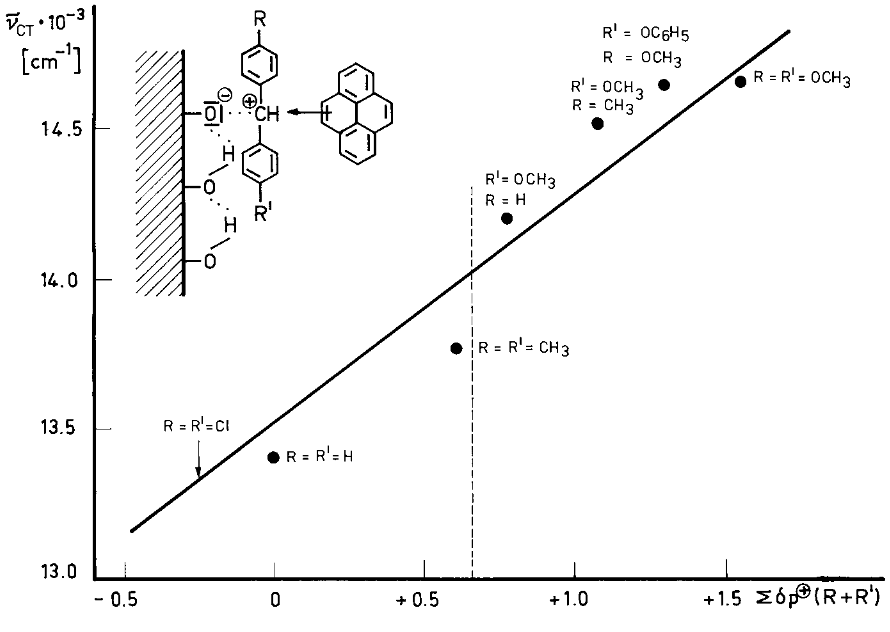


Figure 5. UV–Vis CT maxima of 4,4′-disubstituted diarylmethylium ions with pyrene on silica in 1,2-dichloroethane as a function of the sum of the Hammett σ_p^+ substituent constants

is also in accord with the second interpretation concerning the nature of the new UV–Vis absorption, i.e. it is probably attributable to a σ-like complex as suggested in Eqn (9).

CONCLUSIONS

The results presented indicate that tropylium and diarylmethylium ions form stable CT complexes with arenes on silica. For the sterically demanding triphenylmethylium ions, the EDA complex formation is very weak and the detection of the CT band is possible only for special cases.

The basicity of the silica surface, when linking a carbenium ion, is evidently larger than that for the solvent 1,2-dichloroethane, but lower than that for acetonitrile as solvent. Thus, the β values, according to the Kamlet–Taft solvent parameters, for silica-linked anions (Cl^-, BF_4^-, Br^-) are about $\beta = 0.1$–0.3.

Owing to the rigidity of the adsorbed EDA complexes, for diarylmethylium–arene complexes the coulomb term contributes strongly to $\nu_{max,CT}$, which is in accord with a σ complex-related structure.

EXPERIMENTAL

Chemicals. Triphenylmethylium hexachloroantimonate was synthesized from chlorotriphenylmethane and antimony pentachloride in tetrachloromethane as solvent. The crude product was recrystallized from 1,2-dichloroethane.

Chlorotriphenylmethane and bromotriphenylmethane were obtained from Merck. They were recrystallized from a benzene–hexane mixture containing 2–3% of acetyl chloride and bromide, respectively. Fluorotriphenylmethane was synthesized from triphenylmethylcarbinol and acetyl fluoride.

Tropylium hexachloroantimonate was synthesized from cycloheptatriene and triphenylmethylium hexachloroantimonate according to the literature.[24a] Tropylium tetrafluoroborate, was obtained from Aldrich and used without further purification.

The chlorodiarylmethane compounds were synthesized from the corresponding carbinols in dichloromethane as solvent with HCl gas and $CaCl_2$ powder as drying agent. The procedure and NMR data for some of these compounds are given elsewhere.[10] Data for chloro(4-methoxyphenyl) (4′-nitrophenyl)methane and chloro(4-methoxyphenyl)(4′-chlorophenyl)methane were not reported in the literature.[31]

The π donors pyrene, acenaphthene, anthracene, hexamethylbenzene, 4-methoxybenzene, 2,4-dimethoxybenzene, 1,2-dimethoxybenzene, 1,3-dimethoxybenzene, 1,2,3-trimethoxybenzene, 1,2,4-trimethoxybenzene, 1,3,5-trimethoxybenzene, stilbene, and 4,4′-dimethoxystilbene were commercially available products and were recrystallized. All compounds were carefully dried over CaH_2 before use. The solvents employed were commercially available products (UV grade) from Merck and Aldrich. They were dried over CaH_2 (excluding the nitroalkanes, danger!) and freshly distilled before use. Nitromethane and nitroethane were purified by fractional distillation and used immediately.

UV–Vis spectroscopy. The UV–Vis spectra of the EDA complexes in solution were recorded with a Specord M 40 instrument (Carl Zeiss Jena) in closed cuvettes. The concentration of the carbenium salts was about 5×10^{-2} mol l^{-1} and that of the arene component was about 0.1–0.5 mol l^{-1}.

The following CT transition energies (in parentheses as $\nu_{max,CT}$) of the triphenylmethylium–pyrene hexachloroantimonate complex in various solvents were measured for the correlation analyses in Table 1: nitromethane ($\nu_{max,CT} = 15\,500$ cm^{-1}), nitroethane ($\nu_{max,CT} = 15\,600$ cm^{-1}), nitrobenzene ($\nu_{max,CT} = 14\,800$ cm^{-1}), acetic anhydride ($\nu_{max,CT} = 15\,100$ cm^{-1}), acetonitrile ($\nu_{max,CT} = 16\,400$ cm^{-1}), benzonitrile ($\nu_{max,CT} = 16\,000$ cm^{-1}), 1,1-dichloroethane ($\nu_{max,CT} = 14\,200$ cm^{-1}), dichloromethane ($\nu_{max,CT} = 14\,300$ cm^{-1}), trichloromethane ($\nu_{max,CT} = 14\,800$ cm^{-1}), 1,1,2-trichloroethane ($\nu_{max,CT} = 14\,100$ cm^{-1}) and 1,1,2,2-tetrachloroethane ($\nu_{max,CT} = 13\,900$ cm^{-1}).

The following CT maxima of the $(C_2H_5)_4N^+I^-$–TNB EDA complex were additionally measured: 1,1,2,2-tetrachloroethane ($\nu_{max,CT} = 23\,000$ cm^{-1}), 1,1,1-trichloroethane ($\nu_{max,CT} = 20\,500$ cm^{-1}), trichloroethene ($\nu_{max,CT} = 22\,500$ cm^{-1}), and 1,1-dichloroethane, ($\nu_{max,CT} = 21\,960$ cm^{-1}). The EDA complexes on silica were prepared according to the following procedure.

A 1.000 g amount of Aerosil 300 (Degussa) was heated for at least 12 hours at 400 °C, and finally under vacuum, and was then allowed to cool to room temperature under argon. Then 0.75 mmol of the arene component and a solution of 0.75 mmol (0.197 g) of chlorobis(4-methoxyphenyl)methane in 25 ml of dried CH_2Cl_2 were added. The suspension was shaken gently for several hours. Usually, about after 5 h a new absorption appeared which was monitored using the transmission technique by UV–Vis spectroscopy. The UV–Vis spectra of the complexes on silica were recorded using an MC-41 diode-array spectrometer, (Carl Zeiss Jena) with glass-fibre optics. The transparent silica–1,2-dichloroethane suspensions were measured by means of a TSM 5 immersion cell.[11a]

For preparing the surface-linked tropylium ions, the same procedure was used. Solid-state CP/MAS CP ^{13}C {1H} NMR spectra of the $(4\text{-}CH_3OC_6H_4)_2CHCl$–pyrene Aerosil EDA complex were measured by means of a Bruker AMX 400 instruments. Chemical shifts were determined by reference to adamantane for ^{13}C.

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