

Solvent Influence on the Catalytic Activity and Surface Polarity of Inorganic Solid Acids

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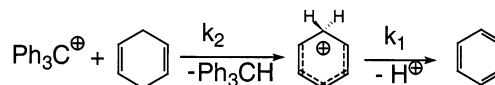
The surface-mediated hydride-transfer reaction of 1,4-cyclohexadiene with triphenylmethyl cation induced by two silicas, an alumina, and an aluminosilicate as solid acid catalyst, respectively, has been kinetically studied as a function of the polarity of the surrounding solvent. The specific rate constants k' have been determined in 10 different solvents. Generally, k' decreases with increasing polarity of the solvent. Kamlet–Taft's α (hydrogen-bond acidity) and π^* (dipolarity/polarizability) parameters of the solid acid/solvent interface have been determined for alumina and aluminosilicate in various solvents. $\text{Fe}(\text{phen})_2(\text{CN})_2$ [*cis*-dicyanobis(1,10-phenanthroline)iron(II), (**1**)] and Michler's ketone [4,4'-bis(*N,N*-dimethylamino)benzophenone, (**2**)] were used as solvatochromic surface polarity indicators. The UV/vis spectra of the two surface polarity indicators **1** and **2** adsorbed on solid acid catalysts from the solvents were measured by the reflection mode and the UV/vis absorption maxima were used to calculate the α and π^* values of the catalysts. α of the solid acid catalyst/solvent interface decreases with increasing β term (hydrogen-bond accepting) ability of the solvent, whereas the π^* term of the solvent marginally modifies the interfacial polarity. k' increases for each individual solvent with increasing β of the catalyst solvent interface in the order series silica < alumina < aluminosilicate. It can be shown that α of the solid acid catalyst/solvent interface decreases with increasing β term (hydrogen-bond accepting) ability of the solvent, whereas the π^* term of the solvent marginally modifies the interfacial polarity.

Introduction

The catalytic activity of common solid acids, e.g., various silicas, aluminas, titanium dioxides, and aluminosilicates, often specifically depends on the pretreatment and environment used for the process to be catalyzed.^{1–5} Chemical composition, residual amounts of water, pretreatment temperature, and the nature of the solvent influence diversely the surface polarity and catalytic activity of solid acids.^{6–16}

Especially, solvent influence on the catalytic activity of solid acids is of a complex nature. Solvents affect product, educt, reactive intermediate, and transition state, as well as the activity of the surface of the catalyst. Dissolving the products and educts as well as a successful occurrence of the reaction must be accomplished. Often polar solvents are required to dissolve the educts and products. Their dipolar natures often suppress the catalytic activity of strong acidic and basic sites of a catalyst, because polar groups of solvents compete with the reactants on the active sites of a catalyst's surface.^{12,13} Otherwise, polar solvents accelerate those reactions proceeding via a dipolar transition state. Drago reported on the outstanding large catalytic activity of AlCl_3 functionalized silicas in carbon tetrachloride compared to carbon–hydrogen bond containing solvents.⁸ Solvents can also mediate the proton-transfer reaction from Brønsted acidic surface groups to organic substrates.^{9b} Lewis sites on surfaces can interact with polar molecules such as acetone to generate a proton from the latter.⁹ Systematic studies on catalytic activity as the function of solvent property in terms of kinetic parameters are not established because many factors influence a reaction induced by a solid acid. Classification of

SCHEME 1: Hydride-Transfer Reaction of 1,4-Cyclohexadiene with Triphenylmethyl Cation Which Has Been Used as the Model Reaction for the Kinetic Study



solid acids in terms of “solid solvents” has been discussed,¹⁰ which suggests their application of concepts derived from solution chemistry.⁶

The objective of this work is to study the influence of solvent properties on catalytic activity and surface polarity in terms of the Kamlet–Taft parameters α [HBD (hydrogen-bond donating) acidity], β [HBA (hydrogen-bond accepting) ability], and π^* (dipolarity/polarizability) of different solid acids, two silicas, an alumina, and an aluminosilicate with similar morphology.

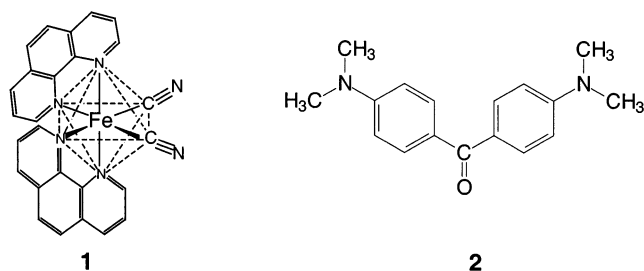
Catalytic activity of solid acid catalysts, expressed as $\log k'$ of the reaction of triphenylmethyl cation with 1,4-cyclohexadiene (Scheme 1),^{16a} is significantly a function of the surface acidity α .¹⁷ This reaction and related processes have been established to study kinetically the catalytic activity of solid acids.^{16b,c}

The surface-mediated hydride-transfer reaction of 1,4-cyclohexadiene (CHD), as the reagent, with $(\text{C}_6\text{H}_5)_3\text{C}^+$, which can be generated by chemisorption of chlorotriphenylmethane on silicas,¹⁸ aluminas, titanium dioxides, or aluminosilicates,¹⁹ yields quantitatively $(\text{C}_6\text{H}_5)_3\text{CH}$ and benzene.²⁰

Generally, for the polar reaction of a nucleophile (N) with an electrophile (carbenium ion) (R^+), the rate law in eq 1 is valid.²¹ For each kinetic plot and, therefore, for each solid acid

$$-\text{d}[\text{R}^+]/\text{d}t = -\text{d}[\text{N}]/\text{d}t = \text{RG} = k_2[\text{R}^+][\text{N}] = k'[\text{N}] \quad (1)$$

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CHART 1: Solvatochromic Probes *cis*-Dicyanobis(1,10-phenanthroline)iron(II) (1) and Michler's Ketone (2)

catalyst and surface-mediated reaction, a specific rate constant k' ($\text{s}^{-1} \text{m}^{-2}$) has been calculated with respect to the surface area (A) (eq 2).¹⁶ Consequently, k' is a complex quantity that involves

$$dk/dA = k' \quad (2)$$

the second-order-rate constant (k_2) of the elementary step and the concentration of triphenylmethylum per square meter of the solid acid catalyst. The quantitative treatment of the catalytic process has been reported in detail in a previous paper.¹⁶ It is expected that a solvent influences both k_2 and $[R^+]$ by specific and nonspecific interactions. $\log k'$ of this reaction will be determined as a function of solvent property to achieve information whether a solvent has an effect on k_2 or $[R^+]$.

Kamlet–Taft's solvent parameters α , β , and π^* are recommended by several authors as useful quantities for describing processes at the solid/liquid as well as solid/gaseous interfaces.^{22–27} The simplified Kamlet–Taft LSE (linear solvation energy) relationship applied to solvatochromic shifts $[XYZ = \nu_{\max}(\text{indicator})]$ is given in eq 3.^{28,29} (XYZ)₀ is the solute property

$$XYZ = (XYZ)_0 + a\alpha + b\beta + s(\pi^* + d\delta) \quad (3)$$

of a reference system, either a nonpolar medium or the gas phase. α , β , and π^* characterize the overall solvent polarity. δ is a polarizability correction term, which is 1.0 for aromatic, 0.5 for polyhalogenated, and zero for aliphatic solvents; a , b , s , and d are solvent-independent correlation coefficients.²⁸

α and π^* of functionalized silicas¹⁷ and solid acids²⁷ have been determined by means of $\text{Fe}(\text{phen})_2(\text{CN})_2$ [*cis*-dicyanobis-(1,10-phenanthroline)iron(II), **1**] and Michler's ketone [4,4'-bis-(*N,N*-dimethylamino)benzophenone, **2**]^{30,31} (Chart 1) as solvatochromic probes.

The transition metal complex $\text{Fe}(\text{phen})_2(\text{CN})_2$ has been used as a surface polarity indicator for acidic surfaces, because its solvatochromic band shift in the UV/vis spectrum is significantly dependent on the acidity of the environment.^{30,32}

Michler's ketone is a solvatochromic compound that mainly responds to the dipolarity/polarizability of the environment,^{30,31} because the coefficient ratio s/a in eq 3 is greater than 1.

1 and **2** have also been also successfully used to study the solvent effects on various silicas.²⁶ These results have shown that the morphology of the solid acid must taken into account.^{26b} Therefore, the solid acid catalysts chosen in this work are those similar in pore size distribution and BET surface area. Thus, **1** and **2** are also used to study the influence of solvent property on interfacial polarity of alumina and aluminosilicate in different solvents in this work.

It is obvious that with increasing acid–base interaction strength of the solid with a HBA solvent the HBD capacity of the surface site environment decreases.^{8,9,12,15,26,32}

The influence of the solvent on the dipolarity/polarizability (π^* term) of a catalyst's surface is quite ambiguous to interpret,

TABLE 1: Physical Properties and Source of the Solid Acid Catalysts Used

solid acid	BET surface ($\text{m}^2 \text{g}^{-1}$)	specific pore vol ($\text{cm}^3 \text{g}^{-1}$)	pore diam (nm)	producer
KG 60	423	0.63	9.0	Merck
SG 432	289	1.09	8.5	Grace
Al_2O_3 , Tonerdekugeln	160	0.40	5.2	Condea
Siral 40 S 713	460	0.81	3.5	Condea

TABLE 2: Kamlet–Taft Polarity Parameters and $E_T(30)$ Values of the Solvents Used

no.	solvent	α	β	π^*	$E_T(30)$ (kcal/mol)
1	<i>n</i> -hexane	0	0	−0.04	31
2	cyclohexane	0	0	0	30.9
3	CCl_4^a	0	0.1	0.28	32.4
4	diethyl ether	0	0.47	0.27	34.5
5	toluene	0	0.11	0.54	33.9
6	THF ^b	0	0.55	0.58	37.4
7	chloroform	0.2	0.1	0.58	39.1
8	anisole	0	0.32	0.73	37.1
9	DCM ^c	0.13	0.1	0.82	40.7
10	acetone	0.08	0.43	0.71	42.2
11	DCE ^d	0	0.1	0.81	41.3
12	ethanol	0.86	0.75	0.54	51.9
13	methanol	0.98	0.66	0.6	55.4
14	TFE ^e	1.51	0	0.73	59.8
15	nitromethane	0.22	0.06	0.85	46.3
16	HFI ^f	1.96	0	0.65	65.3
17	acetonitrile	0.19	0.40	0.75	45.6

^a Tetrachloromethane. ^b Tetrahydrofuran. ^c Dichloromethane. ^d 1,2-Dichloroethane. ^e 2,2,2-Trifluoroethanol. ^f 1,1,1,3,3,3-Hexafluoro-2-propanol.

because specific acid–base and nonspecific van der Waals interactions cause a modification of the dipolarity of the former surface in a complex manner.²⁴ Thus, a systematic study of solute properties of a solvent³³ on both catalytic activity and surface polarity is of importance to choose a suitable solvent for a heterogeneous catalysis from a LSE correlation analysis.

Experimental Section

Materials. The physical properties and sources of the solid acid catalysts used are compiled in Table 1. The solids were heated at 400 °C for 12 h and stored under dried argon after cooling to room temperature.

$\text{Fe}(\text{phen})_2(\text{CN})_2$ was prepared according to Schilt.³⁴ Michler's ketone was purchased from Merck, re-crystallized twice from ethanol, and carefully dried over CaH_2 before use.

All solvents were dried and freshly distilled before use. Their empirical polarity parameters α , β , and π^* are given in Table 2.

Chlorotriphenylmethane (Merck) was recrystallized from toluene that contains 2% of acetyl chloride.

1,4-Cyclohexadiene (CHD) was purchased from Merck and dried over CaH_2 , and the purity was checked by GC (gas chromatography) before use.

BET Measurements. The BET surface area was measured with N_2 at 77 K using a Sorptomatik 1900 (Fiscon).

Kinetic Measurements. A measured amount of the solid acid catalyst was put in a glass flask and immediately suspended in 25 mL of the appropriate solvent. Chlorotriphenylmethane (0.0020 mol) and 100 μL of toluene, as internal standard for the GC, were added. In the case of toluene as the solvent, chlorobenzene was used as an internal standard for the GC measurements. By pouring 100 μL of CHD ($n_{\text{CHD}} = 0.0011 \text{ mol}$) into the slurry, the reaction was started. During the reaction, the slurry was continually shaken and kept at 293 K in a

thermostat. The reaction was followed by analyzing the surrounding organic phase using a gas chromatograph (GC-14B, Shimadzu) provided with a 25 m capillary column of 5% phenylmethylsilicone.

UV/Vis Spectroscopic Measurements. The UV/vis absorption maxima of the dyes **1** and **2** when adsorbed on the solids were recorded using a diode array spectrometer with glass fiber optics. An amount of the catalyst was filled in the measurement cell and immediately suspended in the solvent (15 mL for transmission mode, 5 mL for reflectance technique). Then, a solution of the probe dye in the same solvent (usually 10^{-3} mol L $^{-1}$) was added to this slurry.

The equipment employed was a UV/vis spectrometer MCS 400 connected to an immersion cuvette TSM 5A (Zeiss) to measure the spectra of transparent slurries.

The UV/vis spectra of nontransparent particle suspensions of the alumina and the aluminosilicate were recorded by a special reflectance technique. A quartz plate is used as the bottom of the closed cell containing the solid sample in the liquid. The sensor head for measuring the reflectance spectra is located at this quartz plate. The UV/vis spectrum of the adsorbed dye can be monitored after particles sedimentation.

Details of the dye-loaded solid acid preparation for the UV/vis measurements in the various solvents are given in the Results.

Determination of the Polarity Parameters. The following dual correlations have been used to calculate the Kamlet–Taft parameters of the solid acid/solvent interface^{26,27} (r is the correlation coefficient, sd is the standard deviation, n is the number of solvents, and F is the significance)

$$\alpha = -7.900 + 0.453\nu_{\max}(\mathbf{1}) \times 10^{-3} + 0.021\nu_{\max}(\mathbf{2}) \times 10^{-3} \quad (4)$$

$$r = 0.95; sd = 0.17; n = 34; F = 0.000$$

$$\pi^* = 13.889 - 0.251\nu_{\max}(\mathbf{1}) \times 10^{-3} - 0.320\nu_{\max}(\mathbf{2}) \times 10^{-3} \quad (5)$$

$$r = 0.57; sd = 0.15; n = 36; F = 0.000$$

The two equations have been calculated using $\nu_{\max}(\mathbf{1})$ and $\nu_{\max}(\mathbf{2})$ measured in 36 solvents and the Kamlet–Taft solvent parameters as the reference system. The procedure has been outlined in ref 30.

Correlation Analyses. The correlation analyses were done with the MS Office program EXCEL 2000.

Results and Discussion

The influence of the solvent on catalytic activity and surface polarity of inorganic solid acids has been studied currently using two silicas, an alumina, and an aluminosilicate batch (for physical properties see Table 1).

Catalytic Activity as a Function of the Solvent Polarity. The surface-mediated hydride-transfer reaction of 1,4-cyclohexadiene (CHD) with $(\text{C}_6\text{H}_5)_3\text{C}^+$ generated by chemisorption of chlorotriphenylmethane (see Chart 1) was carried out to determine the catalytic activity of the solid acids. $(\text{C}_6\text{H}_5)_3\text{CCl}$ was used as the triphenylmethyl cation precursor because it can be easily activated on each solid acid catalyst used. This molecule and the solvatochromic probe dyes **1** and **2** are similar in size.^{16a} Thus, catalytic active surface sites that are observed by the two different types of compounds, either solvatochromic probes or $(\text{C}_6\text{H}_5)_3\text{CCl}$, are expected to be of similar shape and size.

TABLE 3: Rate Constants $\log k'$ for the Hydride-Transfer Reaction of 1,4-Cyclohexadiene with Triphenylmethyl Cation Catalyzed by Various Solid Acids Measured in Ten Solvents

no.	solvent	KG 60	SG 432	Al ₂ O ₃	Siral 40 S 713
1	<i>n</i> -hexane	−6.35	−6.18	−5.65	−5.43
2	cyclohexane	−6.34	−6.56	−5.93	−5.49
3	CCl ₄	−6.68	−6.69	−5.94	−5.46
5	toluene	−7.27	−6.70	−5.83	−5.81
7	chloroform	−7.05	−7.14	−6.38	−5.87
8	anisole	−7.80	not measured	−6.74	−6.25
9	DCM	−6.74	−6.33	−5.65	−5.50
11	DCE	−6.63	−6.28	−5.93	−5.61
15	nitromethane	−6.96	−6.17	−6.46	−6.41
17	acetonitrile	−8.00	−7.71	−7.44	−6.75

TABLE 4: Results of Correlation Analyses of the Rate Constant $\log k'$ for the Solid Acids Used between Each Other for the Hydride-Transfer Reaction from CHD to Surface-Generated Triphenylmethyl Cation

	SG 432		Al ₂ O ₃		Siral 40 S 713	
KG 60	$r = 0.80$	$F = 0.01$	$r = 0.82$	$F = 0.004$	$r = 0.85$	$F = 0.002$
SG 432			$r = 0.77$	$F = 0.01$	$r = 0.55$	$F = 0.12$
Al ₂ O ₃					$r = 0.86$	$F = 0.001$

The concentration of the triphenylmethyl cation generated on the surface is strongly dependent on the nature of the solvent. Using acetonitrile or nitromethane, only a weak yellow color attributing to the $(\text{C}_6\text{H}_5)_3\text{C}^+$ ion ($\lambda_{\max} = 412/432$ nm) on the catalysts surface is observed. In contrast, the surface becomes intense yellow in dichloromethane or cyclohexane owing to the chemisorption of $(\text{C}_6\text{H}_5)_3\text{CCl}$.

Solvents with $\beta > 0.4$ are excluded from the kinetic studies, because the triphenylmethyl cation reacts with such solvents (ester, ketones) or forms inactive adducts (dimethylformamide, dimethyl sulfoxide).^{34,35}

The rate constants ($\log k'$) determined for the model reaction catalyzed by the solid acids in the different solvents are summarized in Table 3. The error bar is negligible for $\log k'(\pm 0.02)$.

In all solvents (excluding nitromethane), the catalytic activity of the inorganic solid acids expressed by $\log k'$ increases in the order silica < alumina < aluminosilicate. In nitromethane, these differences of the rate constants between silica and aluminosilicate are averaged. The difference of $\log k'$ for any catalyst in the various solvents is smallest for silica KG 60 [$\Delta(\log k') = 1.32$ from, *n*-hexane to acetonitrile] and largest for alumina [$\Delta(\log k') = 1.79$, from *n*-hexane to acetonitrile].

The catalytic activity of each of the three solid acids is differently influenced by a solvent, because linear correlations of the rate constants $\log k'$ as a function of solvent between the four catalysts are not obtained. Of course, the mediocre correlation coefficients from Table 4 show a trend.

One result is very clear: the rate of the hydride-transfer reaction decreases with increasing HBA ability of the solvent. This is demonstrated by the correlation of $\log k'$ as a function of β of solvent for instance (see Figure 1). Results of correlation analyses are compiled in Table 5.

The results represented in Figure 1 and Table 5 are obvious, because acid–base interactions between acidic surface sites and solvents decrease the HBD acidity of the catalysts.

As mentioned in the Introduction, the catalytic activity of a solid acid in the hydride-transfer reaction of CHD with surface-generated triphenylmethyl cation is a function of the surface acidity in CH_2Cl_2 .²⁵

k' apparently decreases with increasing π^* of the solvent (see Figure 2). This can be explained by either $[\text{R}^+]$ or k_2 decreasing (eq 1). Mayr has shown that a slight increase of k_2 takes place

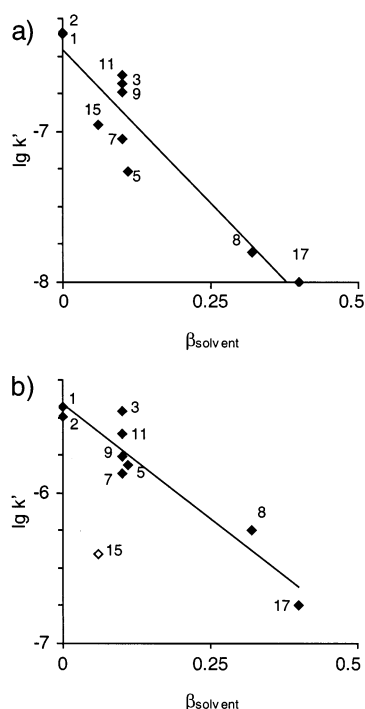


Figure 1. Rate constant $\log k'$ of the hydride-transfer reaction from CHD to triphenylmethylum on silica KG 60 (a) and aluminosilicate Siral 40 S 713 (b) as a function of the basicity of the solvent β_{solvent} .

TABLE 5: Results of Correlation Analyses of the Catalytic Activity of Solid Acids in the Hydride-Transfer Reaction of CHD to Triphenylmethylum as a Function the Solvents Basicity (β Value) ($\log k' = X + b\beta$)

solid acid	X	b	r	sd	n	F
KG 60	-6.46	-4.07	0.93	0.21	10	<0.0001
SG 432	-6.25	-3.50	0.81	0.32	9	0.009
Al_2O_3	-5.72	-3.69	0.84	0.32	10	0.002
Siral 40 S 713 ^a	-5.39	-3.08	0.93	0.18	9	0.0003

^a Value of nitromethane is not included.

with increasing solvent polarity for those reactions.²¹ Thus, the result in Figure 2 is likely attributed to a concentration effect that can be interpreted similarly to the influence of the β term, because a high π^* term of solvents corresponds to polar groups having acidic and basic sites.^{21,35}

The hydride-transfer reaction runs comparatively faster in CH_2Cl_2 , DCE, and nitromethane, which have π^* values larger than 0.8. Perhaps that rate increase is caused by the dipolarity of the solvent, because triphenylmethylum ions can desorb in the solvent phase. It is known that a hydride-transfer reaction occurs also in the surrounding solution phase when solid sedimentation takes place for specific silica batches. Silica particles react with an excess of chlorotriphenylmethane, yielding $(\text{C}_6\text{H}_5)_3\text{C}^+\text{HCl}_2^-$, which is soluble in CH_2Cl_2 .¹⁶ Because a simultaneous reaction in the surrounding solvent occurs, one cannot exclude that an influence on the overall rate constant takes place. For CH_2Cl_2 , the effect on k' is of minor importance.¹⁶

The rate constant of the model reaction shows no dependence on π^* of the solvent using alumina or aluminosilicate as the catalyst's.

However, multiple correlation analyses unambiguously indicate the significant influence of the solvents basicity β on $\log k'$ and show clearly that the rate constant of the surface-mediated hydride-transfer reaction of CHD with triphenylmethylum is not significantly dependent on the dipolarity/

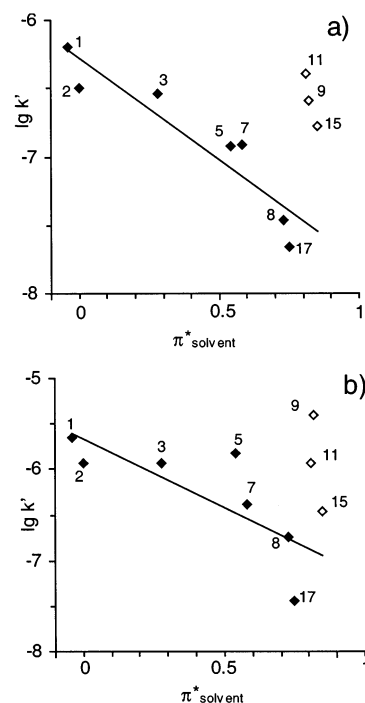


Figure 2. Rate constant $\log k'$ of the hydride-transfer reaction from CHD to triphenylmethylum on KG 60 (a) and alumina (b) as a function of the dipolarity/polarizability of the solvent π^*_{solvent} .

polarizability of the solvent. This result implies that k_2 of eq 1 is hardly influenced by the solvent.

Surface Polarity as a Function of the Solvent Polarity. Surface polarity as a function of solvent has been investigated to understand the influence of a solvent on the polarity of the inorganic solid acid/solvent interface.

The indicator dye **1** is insoluble in weakly polar solvents such as *n*-hexane, cyclohexane, toluene, CCl_4 , or THF (nos. 1–6, 8, and 10 in Table 2).^{30a} For the systems in these media **1** was adsorbed on solid acid from dichloromethane solution, and then filtered, washed, and dried. **1**-loaded solid acid sample was suspended subsequently in the corresponding solvents.²⁶

From moderately or strongly polar solvents (nos. 6, 10, 12–14, 16, and 17 in Table 2), Michler's ketone, **2**, adsorbs only weakly on solid acids. Thus, in the resulting UV/vis spectrum of dye measured in the slurry, interference from both the adsorbed and dissolved fractions occurs. Separate spectra of the two fractions were obtained by measuring the UV/vis spectra of the slurry and the supernatant solution after the particles sedimentation.

The main UV/vis absorption band at about $\lambda_{\text{max}}(\mathbf{2}) = 395 \pm 4$ nm is only observed for the silica.²⁶ UV/vis spectra with a second or third UV/vis absorption maximum of Michler's ketone are observed when it is adsorbed on alumina or aluminosilicate.¹⁷ The UV/vis absorption band of **2** at about $\lambda_{\text{max}}(\mathbf{2}) \approx 370$ –400 nm indicates weakly acidic Brønsted sites, i.e., a silanol-like environment. The other one at about $\lambda_{\text{max}}(\mathbf{2}) \approx 500$ nm is attributed to an oxycarbenium ion of **2**, which is produced by selectively complexing the carbonyl oxygen of **2** either by a proton or Lewis acid.^{36,37} In previous papers,^{17,36a} we have shown that one can distinguish between these two options by surface titration of adsorbed **2** with pyridine and 2,6-di-*tert*-butylpyridine, respectively, as competing bases. In principle, two values of the α and π^* parameters of alumina and aluminosilicate can be determined using the two different $\lambda_{\text{max}}(\mathbf{2})$ values of adsorbed **2** in eqs 4 and 5.¹⁷

TABLE 6: UV/Vis Absorption Maxima of Fe(phen)₂(CN)₂ (1) and Michler's Ketone (2) When Adsorbed on Silica Alumina and Aluminosilicate, Respectively, in Solvents at $T = 293$ K as Well as Polarity Parameters α and π^* of the Resulting Solid/Solvent Interface Calculated from Eqs 4 and 5 (Numbers of Solvents According to Table 2)

solvent no.	alumina						aluminosilicate							
	$10^3\nu_{\max}(1)$ (cm ⁻¹)	$10^{-3}\nu_{\max}(2)$ (cm ⁻¹)	α		π^*		$10^{-3}\nu_{\max}(1)$ (cm ⁻¹)	$10^{-3}\nu_{\max}(2)$ (cm ⁻¹)	α	π^*	α_1	α_2	$\pi^*_{\pi_1}$	$\pi^*_{\pi_2}$
			α_1	α_2	$\pi^*_{\pi_1}$	$\pi^*_{\pi_2}$								
1	19.5 ^a	26.8	21.5	1.49	1.38	0.42	2.13	19.9 ^a	26.5	21.1	1.66	1.55	0.43	2.13
2	19.1 ^a	26.7	21.1	1.32	1.20	0.56	2.35	19.9 ^a	26.5	21.3	1.68	1.57	0.40	2.08
3	18.9 ^a	26.6	21.1	1.22	1.11	0.63	2.41	19.8 ^a	26.5	21.1	1.68	1.50	0.40	2.18
4	19.0 ^a	28.1		1.32		0.12		19.6 ^a	27.2	20.5	1.55	1.41	0.25	2.40
5	19.4 ^a	26.3	21.3	1.43	1.33	0.60	2.20	19.6 ^a	26.2	20.7	1.53	1.42	0.59	2.33
6	18.9 ^a	28.8		1.25		-0.07		19.6 ^a	28.0	20.4	1.59	1.43	-0.01	2.44
7	18.9	26.7	21.9	1.22	1.12	0.59	2.13	19.5	26.4	20.7	1.48	1.37	0.55	2.37
8	19.5 ^a	26.6	20.6	1.51	1.38	0.48	2.39	20.0 ^a	26.0	20.4	1.73	1.61	0.53	2.31
9	19.2	27.0	22.1	1.36	1.26	0.45	1.99	19.5	26.2	20.5	1.48	1.36	0.60	2.44
10	19.3 ^a	26.5	20.9	1.38	1.27	0.59	2.37	19.8 ^a	28.2	20.7	1.68	1.52	-0.11	2.30
11	19.0	27.0	22.0	1.26	1.16	0.50	2.09	19.4	26.2	20.5	1.45	1.33	0.64	2.44
12	18.5	<i>b</i>												
13	18.7	<i>b</i>												
15	19.4	27.7		1.39		1.30		19.9	26.5	20.5	1.68	1.56	0.40	2.32
17	19.5	24.2	22.6	1.53	1.42	0.12	1.75	20.7	25.7	20.7	2.02	1.91	0.47	2.08

^a Preadsorption of Fe(phen)₂(CN)₂ from dichloromethane. ^b No adsorption from this solvent, a separation of ν_{\max} of adsorbed dye from that of the overall dye fraction is not possible.

TABLE 7: Results of the Multiple Correlation Analyses of $\nu_{\max}(\text{indicator})$ When Adsorbed on Various Solid Acids as a Function of Solvent Polarity Parameters α , β , and π^* [$10^3\nu_{\max}(\text{indicator})_{\text{solid acid}}(\text{cm}^{-1}) = X + a\alpha + b\beta + s\pi^*$]

solid acid	indicator	X	a	b	s	r	sd	n	F	remark
KG 60 ^a	1	18.88		-2.43		0.95	0.16	13	< 0.0001	
	2	26.43			-1.37	0.91	0.22	9	0.0006	
SG 432 ^a	1	18.39		-1.11		0.65	0.27	11	0.03	
	2	18.07	+1.44	-1.12	+0.53	0.96	0.10	12	< 0.0001	
alumina	1	26.77			-1.44	0.72	0.48	10	0.02	
	2, $\nu_{\max}(2)_1$	20.41		-2.66		0.97	0.11	7	0.0003	$\beta > 0.3$
Siral 40	1	23.56		+9.22		0.94	0.61	6	0.005	$\beta > 0.3$
	2, $\nu_{\max}(2)_1$	20.82		-2.32		0.98	0.08	6	0.0004	$\beta > 0.3$
	2, $\nu_{\max}(2)_2$	26.01		+2.87		0.74	0.55	12	0.006	
	2, $\nu_{\max}(2)_2$	21.21			-0.84	0.95	0.10	11	< 0.0001	Figure 5

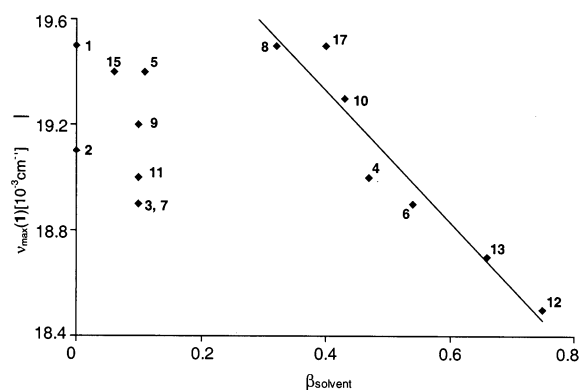
^a Results are taken from ref 27b.

The results of UV/vis spectroscopic measurements of indicators 1 and 2, respectively, when adsorbed on alumina and aluminosilicate as well as calculated α and π^* parameters of the solid acid/solvent interfaces are summarized in Table 6.

α and π^* of alumina and aluminosilicate determined in polar solvents such as acetonitrile, nitromethane, or acetone show unprecedented large α values, because manifold interactions do occur. Therefore, α and π^* data calculated for those solvent/solid acid interfaces represented in Table 6 are apparent values that reflect cooperative effects. Solvent/probe, probe/solid acid/solvent, and chemisorbed solvent/solid acid/probe interactions contribute to the UV/vis shift of the adsorbed probe. For that reason, a detailed discussion of the specific data in Table 6 seems too speculative in light of solely solvatochromic results. However, the large α values of aluminosilicate in CH₃CN and CH₃NO₂ are striking. According to ref 9b, solvent-assisted proton transfer to the probes likely occurs in these solvents, resulting in large α_1 and moderate $\pi^*_{\pi_1}$ values. Thus, large α values are not absolutely consistent with high catalytic activity. Similar results have been found for H₃PW as a solid acid catalyst.³⁸ Because a small fraction of mobile protons interact with 1, then a too large α results. In this case it does not correspond to concentration of active surface sites, which are actually responsible for the rate of the polar reaction.

Multiple LSE correlation analyses of $\nu_{\max}(\text{probe})$ adsorbed on solid acid catalysts with the Kamlet-Taft solvent parameters give reasonable results (Table 7).

HBA properties of a solvent decrease α of the acidic groups on the surface of Al₂O₃. Solvents possessing $\beta > 0.3$ cause a

**Figure 3.** UV/vis absorption maxima of Fe(phen)₂(CN)₂ 1 when adsorbed on alumina as a function of the β value of the solvent used at $T = 293$ K (number of the solvents is according to Table 2).

significant bathochromic shift of $\nu_{\max}(1)_{\text{alumina}}$ with increasing solvent basicity (Figure 3).

As already mentioned, two separate UV/vis absorption bands of 2 appear when adsorbed on alumina. The UV/vis absorption band at a shorter wavelength ($\lambda \approx 380$ nm) shifts hypsochromically with increasing β value ($\beta > 0.3$) of the solvent. Thus, the UV/vis absorption maximum of 2 adsorbed on alumina appearing in the section between $\lambda = 360$ –380 nm of the UV/vis spectrum is preferentially attributed to acid–base interactions.

The different positions of the second UV/vis absorption band of 2 at $\lambda \approx 500$ nm on alumina cannot be quantified by means

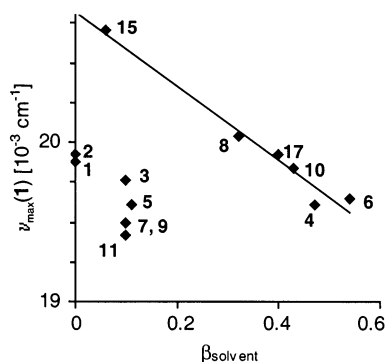


Figure 4. UV/vis absorption maxima of $\text{Fe}(\text{phen})_2(\text{CN})_2$ when adsorbed on aluminosilicate Siral 40 S 713 as a function of the β value of the solvent used $T = 293 \text{ K}$ (numbers of the solvents according to Table 2).

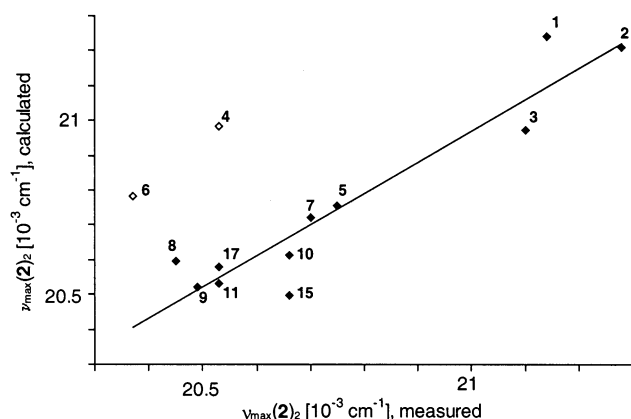


Figure 5. Calculated versus measured values of UV/vis absorption maximum $\nu_{\max}(2)_2$ of Michler's ketone adsorbed on Siral 40 S 713 as a function of π^* of the solvent used at $T = 293 \text{ K}$ (for numbers of the solvents, see Table 2; calculation according to correlation analysis in Table 7).

of correlation analyses using β and π^* of the solvents. Probably, structurally different species of **2** when adsorbed on alumina as a function of solvent are present.¹⁷ This result is in contrast to that when **2** is adsorbed within MCM-41 channels from different solvents. In this case a correlation between $\nu_{\max}(2)$ and π^* of the solvent is observed.^{26b}

Acid–base interactions between surface sites of the aluminosilicate/solvent interface and adsorbed **1** predominate, as seen by the bathochromic shift of **1** with increasing β of the solvent (Figure 4).

The oxycarbenium UV/vis absorption maximum derived from **2** [$\nu_{\max}(2)_{2,\text{aluminosilicate}}$], which is observed when **2** is adsorbed on aluminosilicate, is significantly dependent on the dipolarity/polarizability of the solvent (Figure 5). This result agrees completely with that observed for the adsorption of Michler's ketone on MCM-41^{26b} but disagrees with that when **2** is adsorbed on alumina.

Because the position of the second UV/vis absorption band of **2** on the surface of alumina is hardly influenced by the dipolarity/polarizability of the solvent, a different adsorption mechanism of **2**, compared to silicas and aluminosilicates, is indicated. Probably, **2** is adsorbed on Lewis-acid sites of alumina that are not strongly affected by external solvents.

Catalytic Activity as a Function of the Surface Polarity.

To show whether the influence of solvent changes both surface acidity and catalytic activity, we have correlated $\log k'$ with the α values (α_1 of alumina and aluminosilicate) determined from Table 6. α and π^* of the two silicas as a function of solvent are taken from our recent paper, too.^{26b} Considering all data, no reasonable multiple correlation results.

However, the specific rate constant $\log k'$ increases linearly for each specific solvent with increasing surface acidity of the inorganic solid acid/solvent interface. This is shown in Figure 6a–f. The strength of catalytic activity silica < alumina < aluminosilicate seems to be valid independent of the respective solvent used, as indicated by independent functions $\log k' = f(\alpha)$ obtained for each solvent.

The results in Figure 6 show that catalytic activity of the solid acid catalyst and interfacial polarity of the solid acid/solvent interface seem to be associated properties. Therefore, the polarity parameters of the solid acid/solvent interface that has been built up seem of importance rather than the rigid parameters of the pure components (solid acid or solvent) because a specific solvent is considered. That means the solvent must be considered in a complex sense, as both a solute and dielectric media as a function of its nature. The best fit $\log k' = f(\alpha)$ has been obtained for cyclohexane as solvent. Therefore,

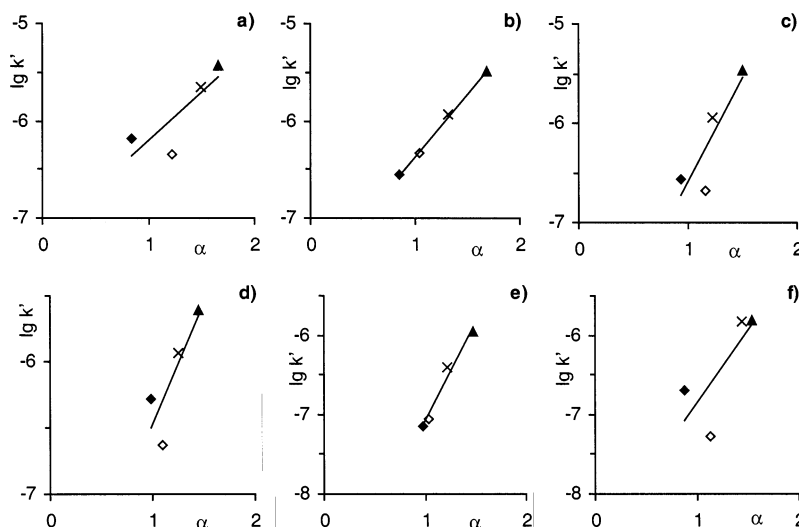


Figure 6. Rate constant $\log k'$ of the hydride-transfer reaction from CHD to triphenylmethylium on different catalysts in *n*-hexane (a), cyclohexane (b), CCl_4 (c), DCE (d), chloroform (e), and toluene (f) at $T = 293 \text{ K}$ as a function of the surface polarity α in the current solvent (KG 60 (\diamond), SG 432 (\blacklozenge), alumina (\times), aluminosilicate (\blacktriangle)).

for kinetic studies on solid acid/liquid interfaces, this solvent is recommended.

Some solvents such as nitromethane or halogenoalkanes show anomalies in the LSE relationship. The reason for this result is likely the uncertain β value for those solvents, because it is difficult to differentiate gradually β in the range between 0 and 0.3.³⁹

After finishing this study, a promising paper by Abraham et al.⁴⁰ appears, reporting on a deeper study on the basicity of chloro substituents of solvents and related compounds. These β values are of interest as solute properties to use in correlation analysis to further studies in this field.

Conclusion

The rate of the hydride-transfer reaction of 1,4-cyclohexadiene with surface-generated triphenylmethyl cation is strongly influenced by the surrounding solvent. The acidity of the solid catalysts surface decreases with increasing solvents basicity, because a decrease of the catalytic activity takes place.

The interaction of a solvatochromic probe with a surface environment in various solvent/solid acid slurries can be investigated by measuring the UV/vis absorption band of the probe when adsorbed on solid acids in slurries. Acid–base interactions dominate between the probe and the solid acid surface, as shown by correlation analyses of $\nu_{\text{max}}(\text{probe})$ with the Kamlet–Taft polarity parameters of the solvent. α and π^* of solid acid/solvent interfaces of alumina and aluminosilicate have been determined by LSE relationships from volume concepts.

For each solvent, the catalytic activity of the inorganic acid increases as follows: silica < alumina < aluminosilicate. Linear correlations of α (solid acid/solvent interface) with $\log k'$ are obtained for each individual solvent.

The results have also shown that solvent influence on catalytic activity and interfacial polarity can be treated with empirical concepts derived from LSE relationships. In accordance to previous papers,¹⁶ the results support that the reactivity of $(\text{C}_6\text{H}_5)_3\text{C}^+$ on a solid acid catalyst is preferentially determined by its concentration and not by affecting the second-order rate constant according to eq 1.

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