Kinetic Studies on the Reactivity of Triphenylmethyl Cations Adsorbed on Silica, Alumina, and Aluminosilicate

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The apparent rate constants k' of different surface-mediated reactions of three nucleophiles 1,4-cyclohexadiene, triethylsilane, and isobutylvinyl ether with triphenylmethylium ions have been determined for three different solid acid catalysts and various triphenylmethylium precursors ($R^1R^2R^3C{-}X$, X = SCN, OH, Cl, or Br). Generation of triphenylmethylium ions [$R^1R^2R^3C^+$] was used for kinetic measurements when $R^1R^2R^3C{-}X$ derivates are chemisorbed to the solid acid catalysts. The catalysis of those surface-mediated reactions by a silica, an alumina, and an aluminosilicate has been studied in a slurry of dichloromethane at ambient temperature. The value of k' increases in the order $OH^- < SCN^- < Cl^- < Br^-$ and silica < alumina < aluminosilicate. The log k' can be correlated with the pK_s of the corresponding HX from $R^1R^2R^3C{-}X$ or the acidity of the solid acid (Adolph, S.; Spange, S.; Zimmermann, Y. *J. Phys. Chem. B* **2000**, *104*, 6429−6438) indicating the importance of the effective surface concentration of [$R^1R^2R^3C^+$] on the apparent rate constant. It is also shown that the specific rate constant of the surface-mediated reaction can be interpreted in terms of Mayr's nucleophilicity parameters of the π-nucleophile (N) and the pK_{R^+} values of the carbenium ion derived from polar reactions in homogeneous solution.

Introduction

The quantification of the catalytic activity of solid acid catalysts and heterogeneously induced organic reactions is an important field of materials research and catalysis.[1−15] This area of research has been stimulated by the application of improved adsorption-calorimetric and solid-state NMR spectroscopic methods and techniques to well-established solid catalyst materials in examining their surface properties.[4−10] Related to this topic, the mechanism of heterolytic dissociation of arylmethyl compounds for producing carbenium ions on solid acids was studied by several authors during the last 3 decades.[16−23] In 1939, Weitz first reported that chlorotriphenylmethane becomes yellow-colored when adsorbed on silica from a benzene solution.[16] Leftin studied the chemisorption of various triphenylmethane derivatives on aluminosilicates.[17] Other authors studied the infrared, UV/vis, and ^{1}H MAS NMR spectra of these adsorbates.[18−23] Recently, "ship in the bottle" synthesis of substituted triarylmethylium ions in HY-zeolites were reported by several authors.[24−28] Also, photochemically generated carbocations in zeolites have been used for studying their reactivity with various nucleophiles.[28,29]

However, the absolute reactivity of a carbenium intermediate generated on the surface of a catalyst is difficult to determine because the rate of the reaction (RG) observed depends on three independent parameters: the second-order rate constant (k_2), the concentration of the carbenium intermediate [R^+], and the concentration of the nucleophilic educt [N] for the reaction under study (eq 1).[30,31] Despite the well-documented chemisorption

$$-d[R^+]/dt = -d[N]/dt = RG = -k_2[R^+][N] \qquad (1)$$

process of halogeno arylmethanes to silica,[16,20−22,32] some questions remain whether a halide−carbenium ion pair adsorbed on silanol or a silanolate−carbenium ion pair is present. $(C_6H_5)_3$-CCl chemisorbed on solid acids is likely present in an equilibrium state similar to its heterolytic dissociation, which is caused by weak Lewis acids ($ZnCl_2$, $SbCl_3$) or acceptor solvents.[31,33,34] (Chart 1). Because the heterolytic dissociation of the carbenium precursor R−X is incomplete (eq 2), even in

$$R{-}X \overset{K}{\rightleftharpoons} [R^+] + X^- \qquad (2)$$

homogeneous solution often observed, then only the relative reactivity, an apparent rate constant k_{app}, of the reaction can be determined.[30] The value of k_{app} includes the product of k_2K (K from eq 2). If the equilibrium constant K of eq 2 is known, then k_2 can be calculated.

In the previous paper, we studied the kinetics of the surface-mediated hydride transfer reaction of 1,4-cyclohexadiene (CHD) with triphenylmethylium to be catalyzed by 30 different solid acid catalysts.[23] We showed that the relative rate constant ($k' = k_{app}$), the product of $k_2K = k_2f[R^+]$, depends significantly on the acidity of the solid acid catalyst. The parameter f is a theoretical correction factor for transforming the volume concentration (mol L^{-1}) into the surface concentration (mol m^{-2}). As acidity parameters for the solid acids, we did make use of Kamlet−Taft's α and Gutmann's acceptor number, AN.[35] We suggested that the acidity of the solid acids is preferably responsible for generating an effective concentration of [R^+].

Extensive and detailed kinetic studies by Mayr and others showed that the rate constant of a polar reaction of an electrophile (carbocation) (S_N1-type) with several structurally different nucleophiles can be described by linear free energy (LFE) relationships.[31,36−41] On the basis of many kinetic results

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CHART 1: Altenative Chemisorption Mechanisms of Chlorotriphenylmethane on Silica Or Alumina Surface Sites

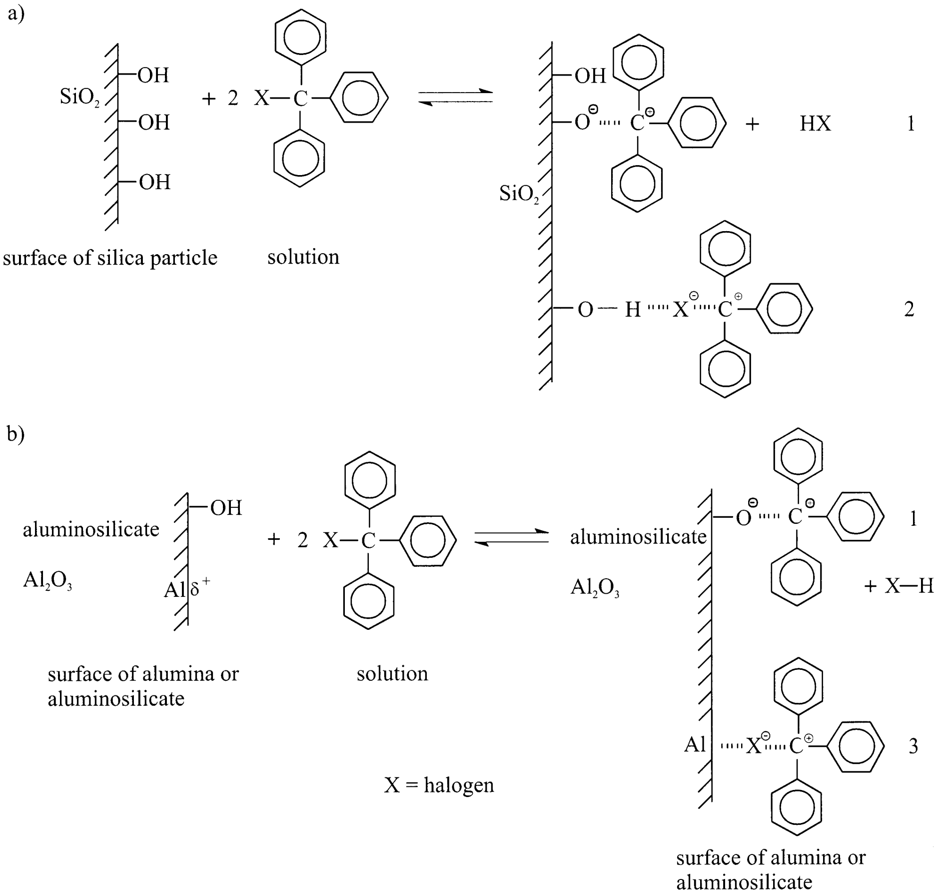
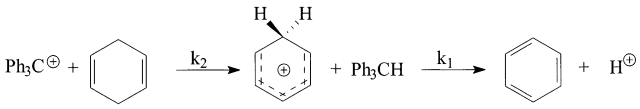


CHART 2: Hydride Transfer Reaction of 1,4-Cyclohexadiene with Surface-Coordinated Triphenylmethylium



and studies, the following LFE relationship for k_2 (from eq 1) has been established:

$$\ln k_2 = s(E + N) \tag{3}$$

where E is the electrophilicity parameter of an electrophile and N is the nucleophilicity parameter of a nucleophile;[31,36] s is a coefficient that approaches 1. The E parameters have been reported for several compounds and intermediates, carbocations, diazonium ions, aldehyde−Lewis acid adducts and others.[31,36] The N parameters are known for olefins, aromatics, amines, silanes, and silyl enol ethers.[30,31,36−38,40,41] In this work, we will investigate the influence of the counterion X of the triphenylmethylium precursor [$(C_6H_5)_3C-X$; X = Cl, OH, Br, NCS] and of substituents of the triphenylmethylium [$(4\text{-}RC_6H_4)_3C^+$, R = −OCH_3, −Cl, −CH_3] on the apparent rate constant of the model reaction.

The surface-mediated hydride transfer reaction of 1,4-cyclohexadiene (CHD), as the reagent, with $(C_6H_5)_3C^+$ has been used as model reaction. The hydride transfer reaction of CHD with $(C_6H_5)_3C^+$ BF_4^- in dichloromethane solution, as well as that of CHD with chemisorbed $(C_6H_5)_3C^+$ on solid acids yield quantitatively $(C_6H_5)_3CH$ and benzene (Chart 2).[21, 37, 42]

The benzenonium intermediate has a strong BrØnsted acidity ($pK_{RH^+} = -24$).[43] Therefore, the proton-transfer reaction occurs faster than the first step, the hydride ion transfer reaction.

In ref 22, we have reported that chlorodiarylmethanes react with CHD on silica yielding diarylmethane and benzene. The HCl formed does not significantly accelerate the reaction rate. In preliminary studies,[22] we used diphenylcarbenium ions, which undergo various reactions with olefins on silica. Unfortunately, competing reactions disturb clean kinetic investigations. Therefore, triphenylmethyl cations have been chosen for a deeper kinetic study. In the discussion part, we will also make use of four kinetic values taken from our previous paper.

We expect to answer the following question: Is it possible to find a reasonable correlation between kinetic data of Mayr from LFE relationships in solution[31,36] and kinetic data (k_{app}) from a polar model reaction on the solid acid catalysts? For these studies, the suitability of other π-nucleophiles for surface-mediated polar reactions with carbenium ions will be investigated from the kinetic point of view. The compounds chosen for these checks are shown in Chart 3.

For this work, we used those solid acid samples as investigated in the previous paper.[23] The acidity of the solids ranges in terms of the Hammett acidity scale between $H_o = 4.4$ (Aerosil 300®) and $H_o = -9.3$ and -10.5 (aluminosilicates) and of the Kamlet−Taft HBD scale between $\alpha = 1.06-1.08$ (silicas) and $\alpha = 1.7$ (aluminosilicate).[35]

Experimental Section

Materials. The chemical composition and physical properties of the solid acid catalysts used are summarized in Table 1. They were commercially available products.

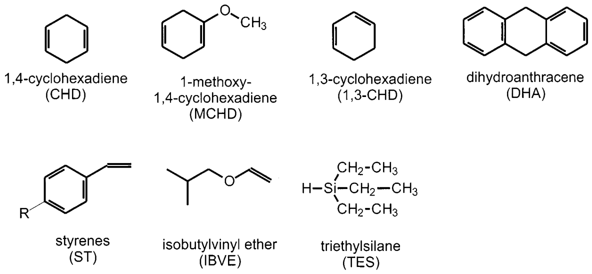
Triphenylmethanol (Merck) was recrystallized from benzene before use.

TABLE 1: Solid Acids Used in This Paper, Their Chemical Compositions, Physical Properties, Surface Polarity Parameters, and Source

solid acid sample	BET surface area [$m^2\ g^{-1}$]	specific pore vol [$cm^3\ g^{-1}$]	avg pore diam [nm]	α	π	source
SiO_2, Aerosil 300	240			1.14	1.05	Degussa
SiO_2 KG SG 432	315	1.42	nd	1.14	0.98	Grace
Al_2O_3, SP 18-8510	131	0.72		1.53	0.33	Grace
aluminosilicate, Siral 5	296	0.46	3.1	1.69	0.36	Condea

[a] nd = not determined.

CHART 3: Nucleophiles That Are Checked for Kinetic Studies with Carbenium Ions Adsorbed on Solid Acid Catalysts



Chlorotriphenylmethane and bromotriphenylmethane (Merck) were recrystallized from a benzene/hexane (20/80) mixture that contains 2% acetyl chloride and bromide, respectively.

Triphenylmethylisothiocyanate was synthezised from chlorotriphenylmethane and sodium rhodanide in acetone as solvent.[44]

The halogenodiphenylmethane derivatives were synthesized from the corresponding carbinols and dry HCl gas in the presence of anhydrous $CaCl_2$ in benzene according to ref 45. Their purity was checked by ^1H NMR spectroscopy. The diphenylcarbinols were commercially available products (Lancaster, Aldrich, Merck). They were recrystallized before use.

1,4-Cyclohexadiene (CHD) was purchased from Merck, dried over CaH_2, and purity-checked by GC (gas chromatography) before use. Triethylsilane (Merck), dihydroanthracene (Merck), and 1-methoxy-1,4-cyclohexadiene were used as received. Styrene, *p*-methoxystyrene, 1,3-cyclohexadiene, and isobutylvinyl ether were distilled under reduced pressure in the presence of CaH_2 before use.

Dichloromethane (Merck, analytical grade) was freshly distilled over CaH_2 and stored under dried argon.

Synthetic Procedures. *Soluble Fraction.* Into a 25 mL Schlenk-bottomed flask, 1 g of the solid acid catalyst (Aerosil 300) was weighed, which had been equilibrated with the atmosphere at 400 °C for at least 24 h. The flask was stoppered and allowed to cool under dry argon atmosphere. Then, a solution containing 15 mmol of the substrate (halogenoarylmethyl component) in 20 mL of dichloromethane was added. The resulting suspension was stirred, and a 15 mmol amount of the nucleophile was added.

After continued shaking for the indicated amount of time, the suspension was filtered, and the filtrate was washed with three 15 mL portions of dichloromethane. The silica cook was separately investigated (see below). The combined organic fractions were washed with aqueous $NaHCO_3$ and water. Then, the combined organic fraction was dried with anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residual organic oil was directly used for the ^1H NMR analyses.

Functionalized Adsorbent (Solid Acid). The silica cook obtained after filtration and washing was carefully dried in a vacuum. Then the carbon content was determined by quantitative elemental analyses. To remove the organic fraction, the silica cook was treated with aqueous NaOH and stirred for 12 h. After neutralization with aqueous HCl, the organic fractions were extracted with three portions of 10 mL of dichloromethane, dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The residual organic oil or solid was directly used for the ^1H NMR or HPLC analyses.

Identification of the Compounds. All compounds, [1:1] adducts, their elimination products and indane derivatives, and their spectral data are known from the literature.[34a,b,50,52]

Kinetic Measurements. The procedures for kinetic measurements have been reported in detail in ref 23.

UV/vis Spectroscopic Measurements. The UV/vis absorption maxima of the triphenylmethyl compounds adsorbed on the solid acid catalyst were recorded using a diode array UV/vis spectrometer (MCS 4 Carl Zeiss) with glass fiber optics. The concentration of the triphenylmethyl compound was about 1−10 mg per gram of catalyst. The transparent silica/1,2-dichloroethane suspensions were measured as previously reported.[23]

Brunauer−Emmett−Teller (BET) Measurements. The BET surface area was measured with nitrogen at 77 K using a Sorptomatik 1900 (Fisons).

Correlation Analyses. The correlation analyses were done with the statistics program Microcal Origin, version 5.0, SR2 from Microcal Software.

Results

UV/vis Spectroscopy. According to the question whether a chemical reaction or a reversible chemisorption takes place, we have investigated the influence of temperature on the triphenylmethyl ion concentration on the surface. For the experiments, we have chosen dichloromethane as solvent. The intensity of the corresponding carbenium UV/vis absorption on silica Aerosil 300 has been shown for $(C_6H_5)_3CCl$ and $(4\text{-}CH_3OC_6H_4)_2CHCl$(AnAnCHCl) adsorption in Figure 1.

The degree of heterolytic dissociation of chlorotriphenylmethane on silica in a dichloromethane slurry is strongly temperature-dependent and reversible: with decreasing temperature, the intensity of the visible triphenylmethylium absorption increases three times from 20 to −75 °C. The same result is found for the adsorption of $(4\text{-}CH_3OC_6H_4)_2CHCl$ on Aerosil 300. Therefore, the heterolytic dissociation process of the central carbon−halide bond of $(C_6H_5)_3CCl$ and $(4\text{-}CH_3OC_6H_4)_2CHCl$ on silica occurs similarly for both compounds. Accordingly, the behavior of R−X on solid acids is related to the heterolytic dissociation process of R−X caused by Lewis acids in solution.[33,46,47]

Studies on the Reaction of $R^1R^2R^3CCl$ on Silica with π-Nucleophiles. As possible nucleophilics for kinetic measurements, we have tested aromatics, olefins, triethylsilane, and hydride ion donating π-electron systems, because n-donors such as amines can also evidently interact with the solid acid, which leads to a partial deactivation of the catalyst.[48] Also, surface-

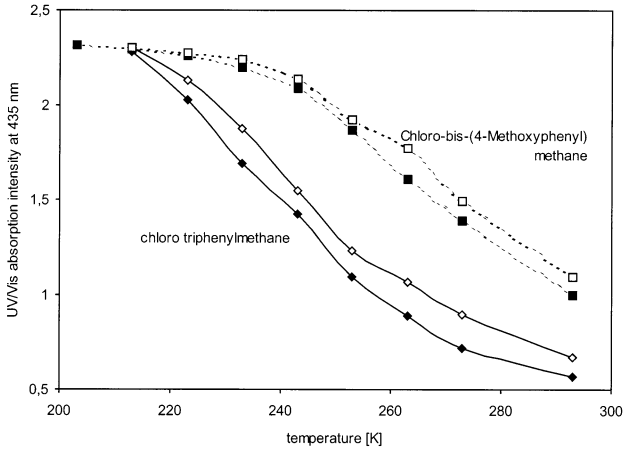


Figure 1. Intensity of the triphenylmethylium and bis(4-methoxyphenyl)methylium carbenium UV/vis absorption on Aerosil 300 as function of the temperature in a dichloromethane suspension: (filled points) while cooling; (unfilled points) while warming up (1, 0.2683 g Aerosil 300, 0.14 g chlorotriphenylmethane, 15 mL dichloromethane; 2, 0.2785 g Aerosil 300, 0.066 g chlorobis(4-methoxyphenyl)methane, 15 mL dichloromethane). The lines are a guide for the eye of the reader.

mediated reactions of electrophiles are suppressed completely in moderate HBA (hydrogen bond accepting) solvents such as THF.[49]

Aromatic compounds do not well react with diarylmethylium ions on silica. Only the highly reactive aromatic compounds 1,3-dimethoxybenzene and 1,3,5-trimethoxybenzene give the Friedel−Crafts product in good yield.[50] However, they do the same reaction when the corresponding carbinols (R^1R^2CHOH) are used in acetic acid as solvent because only a very low concentration of the carbocation is required for such reactions.[51] Thus, for highly reactive aromatics, the heterogeneous catalyst affords no progress. However, it should be mentioned at this point that in some cases an unprecedented electron donor−acceptor (EDA) complex formation between the carbenium ion on silica and the arene component takes place.[50] Those EDA complex formations on silica suppress the Friedel−Crafts-product formation and are associated with a strong color formation of the silica particle slurry.[50] Therefore, aromatic compounds have not been used for the kinetic measurements.

Para-substituted styrenes [$R^3C_6H_4CH{=}CH_2$] ($R^3 = H, -CH_3$) react with chlorodiarylmethanes (R^1R^2HCCl) to the covalent [1:1]-product [$R^1R^2CH-CH_2-CHCl-C_6H_4R^3$] on silica. Despite the good yield (85−90%) and high purity of the [1:1] product isolated from the surrounding solution phase, about 10−15% of byproducts remain strongly fixed on the silica particles after the heterogeneously induced reaction.[26,25,32] Indane derivates and allylium ions remain strongly fixed on the solid acid catalyst, as also reported by Garcia and Corma.[26] Because of these competition reactions,[52] a clean kinetic study is not really possible.

1,3-Dienes such as isoprene give the [1:1] product with AnAnCHCl on silica in low yield, but cyclohexa-1,3-diene (1,3-CHD) gives two products: the [1:1] adduct (20%) and $AnAnCH_2$ (50%) and benzene.[52a] This result is in contrast to its reaction in solution in which only the [1:1] adduct formation occurs.[31a] Therefore, 1,3-CHD should be considered as a hydride donor rather than as a 1,3-diene when used in surface-mediated reactions with carbenium ions (see below).

Chlorotriphenylmethane [$(C_6H_5)_3CCl$] on silica does not react with 1-octene ($N = -2.03$). With styrene ($N = 0.78$) on silica, only a slow reaction has been observed within a reaction time of 24 h at room temperature in dichloromethane as solvent. The rate for producing the [1:1] adduct of olefins with $R^1R^2R^3CCl$ on silica is quite low because of the three sterically hindered aryl groups.[53] It seems that the disturbing steric influence of the third aryl group on the addition reaction with a 1-olefin is even enhanced for triphenylmethylium when adsorbed on a surface. Therefore, only the addition reaction of triphenylmethylium with the fairly strong nucleophile isobutylvinyl ether has been considered for the kinetic studies. $(C_6H_5)_3CCl$ reacts quantitatively with vinyl ethers to the [1:1] addition product when a large excess of $(C_6H_5)_3CCl$ is used (see kinetic procedure). The apparent rate constant determined for the reaction of $(C_6H_5)_3C^+$ with isobutylvinyl ether ($N = 4$) on silica is $k' = (1.77 \pm 0.1) \times 10^{-5}\ s^{-1}\ m^{-2}$ ($\log k' = -4.75$).

TABLE 2: Measured log k' Values for the Model Reaction of Several Nucleophiles with $(C_6H_5)_3CX$ on Three Different Solid Acid Catalysts[a]

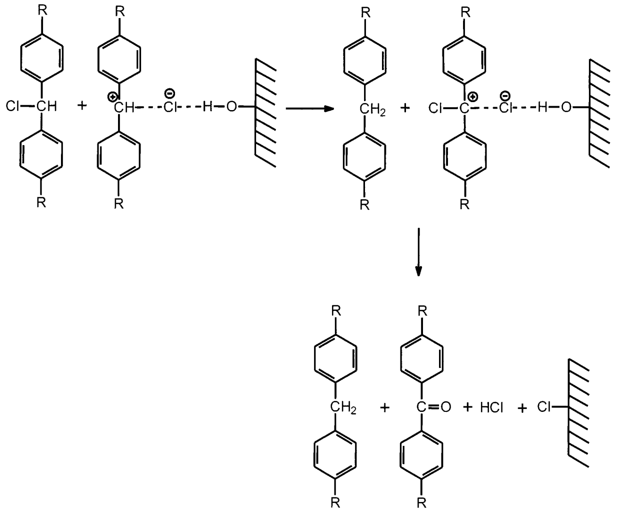
reaction	solid acid	log k'	pK_s (of HX)[b]	N[c]
$(C_6H_5)_3CCl$ + CHD	silica	−6.475	−7	0.09
$(C_6H_5)_3CCl$ + TES	silica	−5.16	−7	3.02
$(C_6H_5)_3CCl$ + IBVE	silica	−4.75	−7	4.00
$(C_6H_5)_3CCl$ + CHD	alumina	−5.79	−7	0.09
$(C_6H_5)_3CCl$ + TES	alumina	−4.69	−7	3.02
$(C_6H_5)_3CCl$ + IBVE	alumina	−4.09	−7	4.00
$(C_6H_5)_3CBr$ + CHD	silica	−6.31	−9	0.09
$(C_6H_5)_3CNCS$ + CHD	silica	−7.87	1.9	0.09
$(C_6H_5)_3COH$ + CHD	silica	−8.072	15.74	0.09
$(C_6H_5)_3CCl$ + CHD	aluminosilicate	−5.701	−7	0.09
$(C_6H_5)_3CBr$ + CHD	aluminosilicate	−5.456	−9	0.09
$(C_6H_5)_3CNCS$ + CHD	aluminosilicate	−6.376	1.9	0.09
$(C_6H_5)_3COH$ + CHD	aluminosilicate	−7.32	15.74	0.09

[a] [$(C_6H_5)_3CCl$] = 0.5 g; [CH_2Cl_2] = 25 mL; T = 295 K. [b] pK_s values for HX were taken from ref 56. [c] Nucleophilicity parameters for 1,4-cyclohexadiene, triethylsilane, and isobutylvinyl ether were taken from refs 36−38.

Reaction of Hydride Donors with Carbenium Ions on Solid Acids. In extension to our further studies, we have also investigated the reaction of other dienes such as 1-methoxy-1,4-cyclohexadiene (MCHD), dihydroanthracene (DHA), and 1,3-CHD (see the previous section) with several $R^1R^2R^3CX$ compounds on silica. Also, triethylsilane has been used for comparison.

Usually, MCHD or 1,3-CHD reacts with carbocations under formation of the [1:1] addition product according to ref 31. We have found that the silica surface-mediated reaction of the $AnAnCH^+$ with either MCHD or 1,3-CHD gave a mixture of several products. However, the reaction responsible for the fraction of the main product is the hydride transfer reaction from either MCHD or 1,3-CHD to $AnAnCH^+$. With MCHD about 80% $AnAnCH_2$ and benzene are observed beside oligomers and the [1:1] product. For the reaction of 1,3-CHD with $AnAnCH^+$ on Aerosil 300, a share of 50% hydride transfer products ($AnAnCH_2$ and benzene) is observed by the ^1H NMR analyses of the product mixture. The reaction of $AnAnCH^+$ with dihydroanthracene (DHA) proceeds smoothly to $AnAnCH_2$ and anthracene. No side products are detectable in the mixture. Unfortunately, the reaction of $(C_6H_5)_3C^+$, $AnAnCH^+$, $AnPhCH^+$, and $TolTolCH^+$ (Tol = 4-$CH_3C_6H_4$−) on silica with DHA does not go to completion. The reaction comes to a dead stop at about 50−60% conversion, and an equilibrium state between the products and educts is observed. Therefore, the reaction of $R^1R^2R^3CCl$ or R^1R^2CHCl with DHA on silica was not suitable for clean kinetic studies. Triethylsilane reacts quantitatively with $R^1R^2R^3CCl$ on silica and alumina to $R^1R^2R^3CH$ (Table 2). The apparent rate constants determined for the reactions of CHD and triethylsilane with $R^1R^2R^3CCl$ on silica and aluminosilicate, respectively, are compiled in Table 2.

CHART 4: Disproportionation Reaction of Chlorobis(4-methoxyphenyl)methane with Bis(4-methoxyphenyl)-methylium on a Silica Surface to Bis(4-methoxyphenyl)-ketone and Bis(4-methoxyphenyl)methane



Rate and yield of $R^1R^2R^3CH$ formed decrease with decreasing the nucleophilicity parameter of the hydride donor used as follows: triethylsilane > CHD > DHA.[37] For each triphenylmethyl ion used with CHD, a complete conversion to $R^1R^2R^3CH$ and benzene has been established. Therefore, we have used the hydride transfer reaction of CHD with surface-mediated carbocations as reference reaction to determine the reactivity of the carbenium.

However, there exists another problem for halogenodiarylmethanes on silica, because AnAnCHCl itself can react as a hydride donor with $AnAnCH^+$ (see Chart 4). This type of reaction is a disproportionation yielding finally AnAnCO and $AnAnCH_2$.

AnAnCO is formed by the reaction of $AnAnCCl^+$ with silanol groups. It could be independently shown that the dichloride of AnAnCO, AnAnCClCl, reacts spontaneously with silica forming first $AnAnCCl^+$ ($\lambda = 530$ nm)[54] and HCl. Then $AnAnCCl^+$ reacts with silanol groups, and a chlorinated silica surface and AnAnCO are formed after 15 min.[22] A similar disproportionation reaction of AnAnCHOH to $AnAnCH_2$ and AnAnCO occurs when AnAnCHOH has been treated with hexamethyldisilazane and trifluoromethane sulfonic acid.[55] The disturbing reaction (Chart 4) becomes of importance when such nucleophiles are used that are weaker nucleophiles than the precursor halogeno component, R^1R^2CHCl. Within 12 h reaction time, AnAnCHCl undergoes no conversion to $AnAnCH_2$.

Influence of the Leaving Group X. The rate constant of the reaction of $(C_6H_5)_3CX$ with CHD to be catalyzed by silica and aluminosilicate, respectively, is strongly affected by the nature of X^- as shown in Table 2. On increase of the basicity of X^- ($OH^- > SCN^- > Cl^- > Br^-$) ($pK_s$ values for the corresponding acid HX of the anions are also given in Table 2),[56] k' decreases significantly. This result has been found independently of the nature of the solid acids, which differ significantly in their surface acidity.

Influence of the Structure of the Carbocation. As mentioned, CHD reacts very well with $R^1R^2R^3C^+$ carbenium ions on silica. The specific rate constants for the reaction of several $R^1R^2R^3C^+$ cations with CHD to be catalyzed with silica are compiled in Table 3.

TABLE 3: Apparent Rate Constants (log *k*′) for the Silica-Catalyzed Hydride Transfer Reaction of 1,4-Cyclohexadiene with Various Chlorodi- and Chlorotriarylmethane Derivates ($R^1R^2R^3C-Cl$) in Dichloromethane at 295 K

R_1	R_2	R_3	log k'	pK_{R^+}[a]
C_6H_5	C_6H_5	H	-7.37[b]	-13.17
$4\text{-}CH_3C_6H_4$	$4\text{-}CH_3C_6H_4$	H	-7.34[b]	-9.92
$4\text{-}CH_3OC_6H_4$	C_6H_5	H	-7.23[b]	-8.16
$4\text{-}CH_3OC_6H_4$	$4\text{-}CH_3OC_6H_4$	H	-6.44[b]	-5.57
C_6H_5	C_6H_5	C_6H_5	-6.47	-6.63
$4\text{-}CH_3C_6H_4$	C_6H_5	C_6H_5	-6.78	-6.02
$4\text{-}CH_3OC_6H_4$	$4\text{-}ClC_6H_4$	C_6H_5	-7.76	-4.54
$4\text{-}CH_3OC_6H_4$	C_6H_5	C_6H_5	-7.88	-3.40

[a] The pK_{R^+} values for the corresponding di- and triarylmethylium ions were taken from refs 57 and 58. [b] Values were taken from ref 22.

For triphenylmethylium ions, on increase of the stability of $R^1R^2R^3C^+$ as expressed by their pK_{R^+} values,[57] the rate of the reaction with CHD decreases. This is a clear indication that the rate of the reaction in this section of carbenium reactivity is controlled by the electrophilicity of the carbenium (k_2) and not by the concentration of $[R^1R^2R^3C^+]$. That means that the amount of k_2 contributes stronger to k' than $[R^+]$.

In a previous paper, we have studied the reaction of R^1R^2CHCl with CHD and determined the relative reactivity for this reaction.[22] There is a distinct difference in the kinetic plot of the hydride transfer reaction of CHD with carbenium ions whether $R^1R^2R^3C^+$ or $R^1R^2CH^+$ is investigated. The kinetic plot for $R^1R^2R^3C^+$ gives a straight line up to 90% conversion.[23] $R^1R^2CH^+$ carbenium ions also react fairly well with CHD, but the kinetic plot approaches a straight line only in the first stage of the reaction up to 30% conversion of CHD. Therefore, we have only utilized this part of the curve in determining the apparent rate constant. The apparent rate constant for the reaction of $AnAnCH^+$ (with AnAnCHCl as the precursor) on silica with CHD amounts to $k' = 3.65 \times 10^{-7}\ s^{-1}\ m^{-2}$ (log $k' = -6.43$). This rate constant is slightly larger than that for the reaction of $(C_6H_5)_3C^+$ with CHD, $k' = 3.35 \times 10^{-7}\ s^{-1}\ m^{-2}$ (log $k' = -6.47$) determined under the same experimental conditions. We think that the sterical influence of the phenyl rings upon the rate of the hydride transfer reaction is not so dramatic when the reaction occurs on solid surfaces as observed for the olefin addition with di- and triarylmethyl carbenium ions, which have similar electrophilicity. The reason for this result is likely that the mobility and accessibility of the carbenium is retarded as a whole, which averages the steric influences. Therefore, we have used the results from triphenylmethylium as the reference system despite Mayr's argument that electrophilicity parameters for triarylmethylium ions cannot be determined.[37]

Discussion

According to the theory of the kinetic approach from eq 3, the logarithm of the rate constants are used for linear correlation analyses between the *E* and *N* parameters and the kinetic parameter k'.[31]

An important question remained from our previous paper: Is it justifiable to separate the influence of the part of the k_2 term and the $[R^+]$ term from the k' value for a surface-mediated reaction?[23] Because of the multiple adsorption mechanism of $(C_6H_5)_3CX$ on surfaces of solid acids containing both Lewis and BrØnsted acid sites, it is still not clear whether the two terms k_2 and $[R^+]$ adequately reflect their influence upon an individual k' for a distinct surface site.

Feigel and Kessler investigated the influence of the nature of X^- on the heterolytic dissociation of several triphenylmethyl

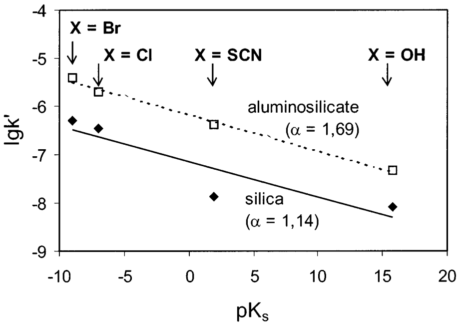


Figure 2. Relationships between the relative rate constant (log k') for the reaction of 1,4-cyclohexadiene with $(C_6H_5)_3CX$ as function of the basicity of the leaving anionic group X^- (expressed by their corresponding pK_s values) for two solid acid catalysts, a silica (SG 432) with $\alpha = 1.14$ and an aluminosilicate (Siral 5) with $\alpha = 1.69$.

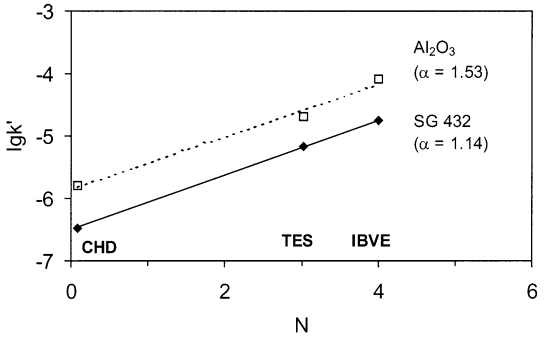


Figure 3. Relationships between the relative rate constant (log k') for the reaction of 1,4-cyclohexadiene, triethylsilane, or isobutylvinyl ether with $(C_6H_5)_3CCl$ as function of the nucleophilicity parameter E of the nucleophile for two solid acid catalysts, a silica (KG SG 432) with $\alpha = 1.14$ and an alumina (Al_2O_3 SP 18−8510) with $\alpha = 1.53$.

and tropylium ions in solution.[46] They showed that the equilibrium constant from eq 2 significantly increases for R−X in decreasing the pK_s of the corresponding acid HX. The correlation of log k' with pK_s of X^{-56} for the reaction of CHD with $(C_6H_5)_3CX$ is shown in Figure 2 for silica and aluminosilicate.

It is clearly seen that for each solid acid used a separate curve is obtained. Both plots occur parallel to each other. Assuming that k_2 is independent of the solid acid used, then the differences in the catalytic activity are only caused by the $[R^+]$ term. This presumption seems justified because the dipolarity/polarizability term (π^* parameter), which should affect k_2,[23] for the two solid acids is quite similar.[35] Consequently, the decrease of k' in increasing the basicity of X^- is evidently a concentration effect. The stronger the acidity of the solid acid is and the lower the bonding energy of the C−X bond is, the faster occurs the reaction of the carbenium with an external nucleophile. This is also an indication that the nucleophile does not influence the heterolytic dissociation process of R−X. Figure 3 shows the plots of the log k' values for three different reactions as function of the nucleophilicity parameter N value for two different solid acid catalysts. The influence of the nucleophilicity of the nucleophilic component on the apparent rate constant appears almost identical for different solid acids. This shows that the constant selectivity principle is also valid for heterogeneously induced polar reactions.

As mentioned, the k' value involves both the rate constant k_2 of the elementary step and the concentration of immediately generated triphenylmethylium per square meter solid acid catalyst. Therefore, not only these options, the variation of either the elementary step or the concentration of $R^1R^2R^3C^+$, depending on the nature of the solid acid catalyst, but also the nature of $R^1R^2R^3C^+$ must be considered in interpretation of the results.

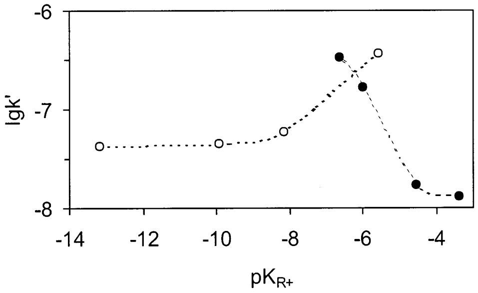


Figure 4. Relationships between the apparent rate constant of the model reaction (log k') of 1,4-cyclohexadiene with chlorodiarylmethanes (○) on silica (Aerosil 300) (from ref 22) and chlorotriphenylmethanes (●) on silica (Grace) and the pK_{R^+} of the corresponding carbenium.

For the model reaction in dichloromethane, the rate constant (log k') of the reaction of CHD with $R^1R^2R^3C^+$ (X = Cl) and $R^1R^2CH^+$ (X = Cl), respectively, have been determined for silica as solid acids. Figure 4 shows the log k' values determined as function of the electrophilicity (pK_{R^+}) of the carbenium generated, because Mayr's E parameters for triphenylmethylium ions are still not available.[37] The log k' values for the reaction of CHD with $R^1R^2CH^+$ (X = Cl) have been taken from our previous paper.[22]

The largest apparent rate constant for the hydride transfer reaction of CHD with carbenium ions on silica has been found for $AnAnCH^+$ (X = Cl). For the initiation of the cationic surface polymerization of isobutylvinyl ether on silica, the same result has been found.[20b] $AnAnCH^+$ is also the most effective initiator on MCM-41 for initiating the cationic host−guest polymerization of cyclohexyl vinyl ether.[45]

According to Mayr, Gorath, and Lang,[37] it is expected that k_2 should steadily increase from $(4\text{-}CH_3OC_6H_4)(C_6H_5)_2CCl$ (p$K_{R^+} = -3.4$) to $(C_6H_5)_2CHCl$ (p$K_{R^+} = -13.17$) from the right to the left. They used BCl_3 as catalyst, which is evidently a much stronger Lewis acid than silica or alumina. Therefore, the chlorodiarylmethanes are almost completely ionized with BCl_3. The value of K from eq 3 decreases in the same order for silica and BCl_3. For $(C_6H_5)_2CHCl$ and chlorobis(4-methylphenyl)methane (TolTolCHCl), the characteristic UV/vis absorptions of the corresponding carbenium ions are expected at $\lambda = 435$ nm and $\lambda = 462$ nm, respectively.[59] They cannot be observed on silica. This is an indication that the surface concentration of $(C_6H_5)_2CH^+$ or $TolTolCH^+$ on silica is below 10^{-7} g mol^{-1}. As one is moving further left in Figure 4 (p$K_{R^+} < -7$), one will be dealing with predominantly covalent material. Now, the apparent rate constant will decrease with increasing Lewis acidity of the cations because structural variation affects the equilibrium constant to a greater degree than the rate constants.[60] Consequently, for carbocations with high reactivity, the surface-mediated hydride transfer reaction is controlled by the concentration of the carbenium intermediate. For carbocations with low reactivity (p$K_{R^+} > -6$), the reaction is controlled by the intrinsic reactivity of the carbenium itself.

Therefore, calculations of multiple linear correlations between log k' and N, pK_s, and the surface acidity α are only reasonable for an individual carbocation. The result of the multiple least-squares analysis for log k' versus the α, pK_s, and N parameters for the reaction of $(C_6H_5)_3CX$ with nucleophiles catalyzed by solid acids (SA) is shown in Figure 5 and eq 4 (r = correlation

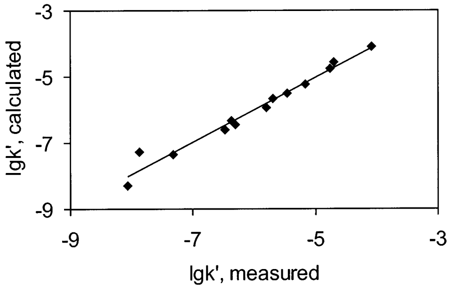


Figure 5. Calculated versus measured log k' values according to eq 4 for the influence of three independent parameters (pK_s of HX, the Kamlet−Taft acidity α of the solid acid catalyst, and the nucleophilicity parameter N of the educt [N]) on the reaction of $(C_6H_5)_3CX$ with N catalyzed by a solid acid.

coefficient; sd = standard deviation; F = significance).

$$\log k'[(C_6H_5)_3CX/SA + N] = -8.785 + 1.499\alpha \text{ (of SA)} - 0.075\mathrm{p}K_s \text{ (of X}^-) + 0.466N \quad (4)$$

$$n = 13; \quad r = 0.986; \quad \mathrm{sd} = 0.236; \quad F < 0.0001$$

Despite the restricted data set of $n = 13$, the excellent quality and significance of the correlation eq 4 is a promising result, which shows that LFE relationships are a suitable tool for quantification of surface-mediated polar organic reactions. Equation 4 also demonstrates the importance of the acid−base interaction of the solid acid catalyst with the substrate for generating the carbenium intermediate. Therefore, for a fixed carbenium precursor, the choice of the solid acid catalyst is of great importance. It seems that for a given pair of reactants for which E and N are known from model investigations from solution, the rate of the heterogeneously catalyzed reaction is solely dependent on both the basicity of the precursor and the acidity of the solid acid catalyst, which are important for the effective surface concentration of R^+. That would mean that the rate constant of the elementary step k_2 is hardly affected by the nature of the solid acid catalyst. However, this presumption seems only valid for heterogeneous catalysts in which the active sites are easily accessible or are located on the external surface of the solid acid. This problem will be studied by our group in future.

Conclusion

The apparent rate constant of a polar reaction catalyzed by a moderately strong solid acid is strongly dependent on the nature of the carbenium (R^+) precursor R−X, the acid strength of the solid, and the nucleophilicity of the olefinic educt. The solid acid can be similarly treated like a Lewis acid, which has been used as catalyst for polar reactions in solution. The apparent rate constant of a polar reaction is also significantly dependent on the basicity of the leaving anionic group X^-. Thus, for each precursor R−X dependent on both the nature of R^+ and the solid acid catalyst, the maximum rate constant as function of X^- can be changed.

The nucleophilicity of the educts determine the rate of the reaction with constant selectivity independent of the solid acid strength or basicity of the leaving anionic group X^-. Therefore, the results in this paper demonstrate that Mayr's E parameters derived from solution may also be suitable to describe relative reactivity of polar electrophilic reactions catalyzed by various moderately strong solid acid catalysts. These parameters can in turn be used to evaluate the catalytic activity of a special catalysts for a specific polar reaction of interest.

The main problem arisis from the choice of suitable nucleophiles to study kinetics of heterogeneous reactions, because seldom a clean kinetic plot is observed because interfering reactions occur.

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