
REACTIONS OF AROMATIC RADICAL-ANIONS AND ETHYLLITHIUM WITH SILICA GEL AND BRÖNSTED ACIDS

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Electric conductivities of radical-anions prepared from several aromatic compounds (biphenyl, naphthalene, benzophenone, anthracene, phenanthrene) and sodium in tetrahydrofuran have been measured and a suitability of radical-anions for titration of silica gel and acid impurities in liquid media have been investigated. The reactivity of the radical-anions and ethyllithium with acidic hydrogen of silica gel hydroxy groups is approximately equal in spite of substantial differences in structure and bonding character of the above compounds. Highest amounts of radical-anions and ethyllithium are decomposed by thermally non-activated silica gel (1.7 to 1.8 mmol g⁻¹ for Davison, grade 952). With the increasing temperature of dehydration of silica gel (200–900°C), the amount of decomposed organometallic compounds decreases approximately linearly.

Aromatic radical-anions and ethyllithium are organic compounds of alkali metals^{1,2}. They react readily with H₂O and substances containing acidic hydrogen. Ethyllithium evolves ethane in reaction with H₂O and substances containing acidic hydrogen³. The reaction of radical-anions with H₂O can be visualized² as a precipitative acid-base reaction (Ar = arene):



Radicals ArH[•] may combine or react with other radical-anions², which results in the consumption of one molecule of radical-anion per molecule of water. NaOH formed is virtually insoluble in THF medium. It allows the determination of radical-anion concentration by acidimetric titration.

Silica gel is porous, fine-grained SiO₂ with high internal surface area. The surface is formed by siloxane bonds, free and hydrogen-bonded OH groups and adsorbed H₂O. A number of papers^{3–14} have been devoted to the structure and reactivity of silica gel. Surface of silica gel contains both Brönsted and Lewis acidic centra, the distribution of their acidity being extraordinarily wide^{3,4}. Alkalimetric titrations^{3,4}, adsorptions from gaseous and liquid phases^{3,4}, reactions with various reagents,

such as organometallics^{3-6,9}, halides and halogen derivatives^{3-6,c,14} have been reported, frequently with spectral data (IR, NMR, EPR).

The structure and reactivity of silica gel is dependent on the procedure of its preparation and further processing. Thermal dehydration of silica gel consists of a large number of elementary physical and chemical processes taking place in pores, some of them being reversible. Condensed and physically adsorbed H₂O is removed at low temperatures. Last traces of H₂O are efficiently removed^{3,15,16} at 100–200°C. A further increase of temperature brings about dehydration of pairs of vicinal silanol groups, forming siloxane groupings Si–O–Si. At high temperatures, OH groups migrate on the silica gel surface and originally distant groups get in contact and dehydrate¹⁵. Some siloxane groupings exhibit a changed bond angle, thus being energy-rich. Their reactions, e.g. with Me₃Al, Me₃SiCl, CCl₄, NH₃, and TiCl₄, usually at higher temperatures have been described^{5,6,8,15}. Reaction of silica gel with above listed compounds is usually slow owing to a large pore volume and narrow pores of silica gel^{3,6,8} and to a low reactivity of some compounds. Certain reactions may not be quantitative and an equilibrium is established^{3,4,6}. Different methods yield non-consistent values of OH group concentration on silica gel surface. Therefore, we tried to find compounds reacting quantitatively with silica gel OH groups. Reaction of silica gel with aromatic radical-anions has not been reported. The present paper deals with an interaction of silica gel with aromatic radical-anions in THF and with ethyllithium in heptane. It also describes measurements of some properties of solutions of the organometallics and discusses their usage in laboratory praxis to titrate Brönsted acids.

EXPERIMENTAL

Materials

Silica gel (Davison Chemical Co., U.S.A., grade 952), was dehydrated in a quartz vessel in purified nitrogen stream at 200–900°C for 6 hours; the vessel was then evacuated until it cooled down (c. 30 min). Thermally untreated samples of silica gel were prepared by 100 h evacuation in a glass vessel at 20°C and $1 \cdot 10^{-2}$ Pa. In both cases a layer of silica gel was stirred mechanically or pneumatically so that the evolved water was effectively removed. Specific surface area was measured using the BET method and the following values were obtained for various temperatures of heat treatment: 285 m² g⁻¹ (20–600°C), 278 m² g⁻¹ (800°C), and 218 m² g⁻¹ (900°C). Pore volume values calculated using nitrogen desorption isotherm were 1.8, 1.7, and 0.85 cm³ . g⁻¹, respectively, and the maximum of pore size distribution was at 20 nm. Dehydrated silica gel was stored in sealed glass ampoules which were subsequently opened in inert atmosphere.

Aromatics — naphthalene, anthracene, phenanthrene, biphenyl, and benzophenone (all pure, product of Lachema, Czechoslovakia) — were recrystallized and before use volatiles were removed ($1 \cdot 10^{-2}$ Pa, 2 h). Sodium and lithium (both Lachema, Czechoslovakia) were freed from impurities by a mechanical removal of the surface layer in an inert atmosphere. Before use, alkali metals were cut to small pieces (c. 10 mg). For the preparations of low concentrations of radical-anions sodium was distilled in vacuo.

Heptane, p.a. (Loba Feinchemie, Austria), was tested for the absence of aromatics and then distilled; it was freed from water and oxygen by distilling-off at least 15% of its volume in highly pure nitrogen at elevated temperature. Tetrahydrofuran (THF), p.a. (Loba Feinchemie, Austria), 2,5,8-trioxanonane (diglyme), p.a., and 2,5,8-pentaoxatetradecane (tetraglyme), p.a., (both Merck-Schuchard, W. Germany), were predried by a prolonged stirring with metallic sodium and then vacuum-distilled into storage ampoules containing fresh sodium and benzophenone. Before each procedure fresh THF or glyme was distilled from the storage solution of radical-anions into an evacuated vessel. Ethyl chloride, pure (VCHZ Kolín, Czechoslovakia). Ethanol, chemical grade, and 1-octanol, chemical grade (both Lachema, Czechoslovakia), were twice distilled and stored under nitrogen atmosphere.

Nitrogen, high purity grade (Technoplyn, Czechoslovakia), was purified in columns containing Cu-catalyst (BASF, W. Germany) and molecular sieves A3; the sum of water and oxygen contents was under 1 ppm.

Instruments

Operations were carried out in a high-vacuum line with pure nitrogen supply at a pressure lower than $1 \cdot 10^{-2}$ Pa.

Infrared spectra of silica gel in the range $4\ 000-8\ 000\text{ cm}^{-1}$ were measured using a Perkin-Elmer 330 instrument. Silica gel was placed into an quartz 1 cm cell and dry CCl_4 was poured in to obtain the slurry concentration of 16–17 wt. %. Bands at $5\ 235\text{ cm}^{-1}$ (H_2O) and $4\ 425$, $4\ 505$, and $7\ 140\text{ cm}^{-1}$ (OH groups) were evaluated.

Electric conductivity of solutions was measured using a Radiometer Copenhagen CDM 2c instrument with a standard Pt electrode (two parallel Pt plates of 50 mm^2 each area placed at 5 mm distance, back sides sealed in glass).

Preparation of Aromatic Radical-Anion Solutions and their Reactions with Brönsted Acids

A SIMAX glass apparatus (Fig. 1) containing a reaction vessel with a volume calibration was connected to a high-vacuum line ($<1 \cdot 10^{-2}$ Pa) via a ground joint which enables a turning of the whole apparatus. Vacuum drying of the vessels lasting at least 3 h was several times interrupted by a highly pure nitrogen flushing. THF was vacuum-distilled from a storage vessel containing a blue solution of benzophenone sodium into the cooled mixture of an aromatic and sodium in a reaction vessel with magnetic stirring bar. After heating to room temperature, stirring was commenced and the formation of radical-anions was monitored through electric conductivity measurement by means of sealed-in Pt electrode. A maximum concentration was reached within 2–3 h. Higher concentrations of radical-anions (above $10^{-2}-10^{-1}\text{ mol l}^{-1}$) were prepared in common vacuum glass lines fitted with ground joints. Very low concentrations of radical-anions were prepared in all-glass sealed vacuum lines employing seal-off and break-seal techniques^{1,17}; reaction vessels were evacuated at elevated temperature to remove surface-bonded water. Samples of radical-anion solutions were taken out against nitrogen stream and dosed employing polyethylene syringes with polyethylene tubings flushed thoroughly with purified nitrogen. Concentration of radical-anion solutions was determined via acidimetric titration: 0.5–1.0 ml of THF solution of radical-anions was added to 20 ml of stirred ethanol–water mixture (1 : 1 by weight) containing two drops of Bromocresol Green and the NaOH solution formed was titrated with 0.01 or 0.1M-HCl, the colour change in the equivalent point being from blue to yellow.

Reactions of radical-anions with H_2O , ethanol or 1-octanol were examined in apparatus depicted in Fig. 1. Water, ethanol, and 1-octanol solutions in dry THF, diglyme, and tetraglyme (concentration range $0.001\text{--}0.3\text{ mol l}^{-1}$) were prepared under nitrogen atmosphere and aliquots consecutively syringed into the reaction vessel containing radical-anion solution. Concentration drop of the latter solution was measured from a conductivity drop or by acidimetric titration of aliquot sample after NaOH sedimentation.

Reaction of Radical-Anions with Silica gel

Titration of silica gel was performed in apparatus depicted in Fig. 2. To a slurry of dry silica gel in pure THF at 25°C , a solution of aromatic radical-anion in THF ($c. 0.1\text{ mol l}^{-1}$) was added slowly under magnetic stirring from a side storage bulb. At the beginning of titration, the solution discoloured fast; then the colour was disappearing slowly and silica gel gradually began to gain colour; at a certain point of titration, a weak colouration of solution was permanent while silica gel was coloured rather intensively. The colour of silica gel corresponded to that of radical-anion and it could be removed immediately by adding Brönsted acids (e.g. water or alcohol); thus an adsorption of radical-anions on silica gel can be visually checked. The adsorption may be chemical due to a non-zero amount adsorbed at zero concentration in solution. Further addition of radical-anion solution to the silica gel slurry was bringing about a colour deepening in both solution and silical gel. Titration of silica gel to the equivalent point, i.e. to the appearance of a permanent weak colour of solution fixed the total amount of radical-anions reacting with OH groups (and possibly with siloxane bonds) as well as that chemically adsorbed on silica gel at virtually zero concentration of radical-anions in solution. The last amount was determined by back-titration of the silica gel slurry with a water solution in THF (0.1 mol l^{-1}) up to discolouration of silica gel.

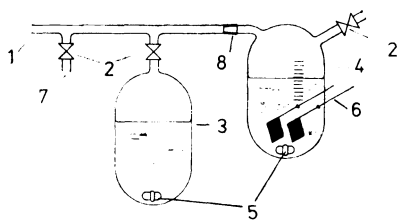


FIG. 1

Apparatus for preparation of radical-anion solutions and their reaction with Brönsted acids: 1 high-vacuum line attachment, 2 two-way stopcock, 3 storage bulb for THF or glyme, 4 reaction vessel, 5 stirring bar, 6 standard Pt electrode, 7 nitrogen supply, 8 ground joint

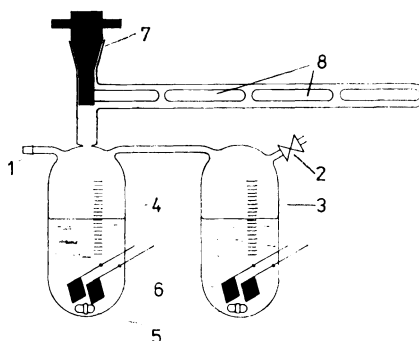


FIG. 2

Apparatus for reaction of silica gel with radical-anions: 1 high-vacuum line attachment, 2 two-way stopcock, 3 storage bulb for radical-anion solution, 4 reaction vessel, 5 stirring bar, 6 standard Pt electrode, 7 stainless steel breaker, 8 silica gel vials

A reverse titration was also carried out. A known amount of silica gel (0.5–2.0 g) was added to 20–50 ml of radical-anion solution of a known concentration (max. 0.05 mol l^{-1}) in THF. The slurry was stirred vigorously and the conductivity drop was measured. After reaching the equilibrium (30–60 min) the concentration of radical-anions was redetermined through the acidimetric titration: the slurry was titrated slowly with the solution of H_2O in THF (0.1 mol l^{-1}), first to discoloration of the solution (with simultaneous drop of conductivity) and then to discoloration of the intensively coloured silica gel. The weights and concentrations were chosen so as to decrease the radical-anion concentration after reaction with silica gel under 0.01 mol l^{-1} ; thus the titration was run at a level corresponding to virtually zero concentration in solution. From the difference between the total amount of radical-anions consumed by silica gel and the amount adsorbed on silica gel (reacting with H_2O), the amount of radical-anions that reacted with OH and siloxane groups of silica gel was determined.

Ethyllithium Preparation and its Reaction with Silica Gel

Ethyllithium was prepared from ethyl chloride and metallic lithium in heptane according to Applequist and O'Brien¹⁸. Its concentration determined by acidimetric titration¹⁸ was 0.050 mol l^{-1} .

Air-thermostated SIMAX glass apparatus depicted in Fig. 3 was employed for measurement of ethane evolution in reaction of ethyllithium with silica gel. The weighed glass vials containing 0.3–0.5 g of silica gel were consecutively broken into magnetically stirred heptane solution (15 ml) of ethyllithium (0.05 mol l^{-1}) which was contained in a glass reaction vessel of pre-determined volume. The amount of ethane liberated was measured manometrically. Time de-

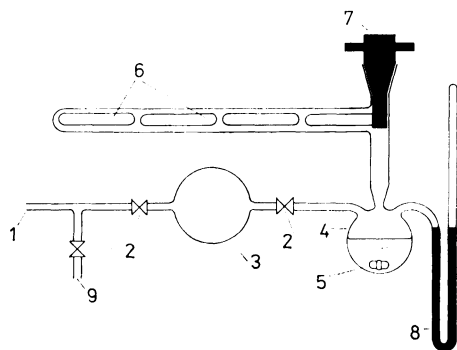


FIG. 3

Apparatus for measurement of ethane evolved: 1 high-vacuum line attachment, 2 two-way stopcock, 3 bulb of constant volume, 4 reaction vessel, 5 stirring bar, 6 silica gel vials, 7 stainless steel breaker, 8 mercury manometer with nonius, 9 nitrogen supply

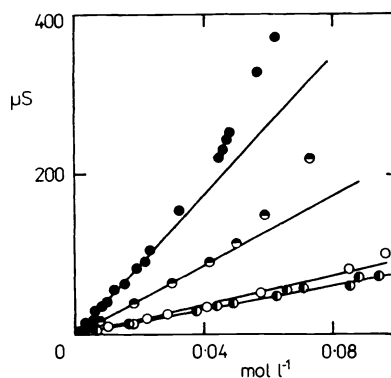


FIG. 4

Electric conductivity (in μS) of radical-anion solutions (Na^+ArH^-) in THF as a function of their molar concentration (20°C): ● benzophenone, ○ naphthalene, ● biphenyl, ● phenanthrene

pendence of pressure increase was recorded and the amount of ethane after reaching equilibrium (1–3 h) was determined. The solubility of ethane in heptane (determined using the same apparatus but with weighed amounts of 1-octanol instead of silica gel) is 0.221 mol l^{-1} at 25°C and partial pressure of 101.3 kPa . Corrections on volume changes and on nitrogen content in vials were made on basis of a blank experiment. The measurement of ethane amount evolved were reproducible within 2–3%.

RESULTS AND DISCUSSION

Electric Conductivity of Radical-Anion Solutions

Conductivities found for the radical-anion solutions in THF at 20°C are presented in Fig. 4. The conductivity is proportional to the concentration at low concentrations while a steeper increase has been observed at higher concentrations due to the ion aggregation¹. The best fit equation for the conductivity of $\text{Na}^+(\text{phenanthrene})^-$ solution in the $0.001\text{--}0.3 \text{ mol l}^{-1}$ range is

$$\kappa = 1.2 \cdot 10^4 \cdot c^{1.18},$$

where κ is conductivity in μS and c is concentration in mol l^{-1} .

Reaction of Aromatic Radical-Anions with Brønsted Acids

Stoichiometry of the reaction of radical-anions in THF (concentration range 0.001 to 0.3 mol l^{-1}) with H_2O solution in THF (concentrations 0.006 and 0.13 mol l^{-1}) has been studied. The drop of radical-anion concentration was measured conductometrically and checked by the acidimetric titration. The reactions proceeded very fast and the amount of radical-anion consumed was equal to the amount of H_2O added under all conditions investigated, thus confirming the published mechanism². The equivalent behaviour was found for reactions of radical-anion solutions in diglyme (concentration range $0.001\text{--}0.3 \text{ mol l}^{-1}$) with H_2O solution in THF, diglyme, or tetraglyme, and for reactions of radical-anions in THF or diglyme (concentration range $0.001\text{--}0.2 \text{ mol l}^{-1}$) with ethanol or 1-octanol solutions in THF or diglyme (concentration range $0.001\text{--}0.2 \text{ mol l}^{-1}$).

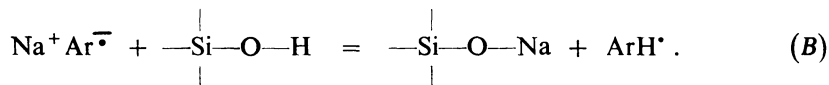
Solutions of radical-anions were used to remove traces of impurities from gases which do not react with radical-anions (nitrogen, rare gases, paraffins, olefins). If an effective gas-liquid mass exchange is assured and radical-anion solution components of low volatility are selected (such as phenanthrene, tetraglyme), concentrations of the impurities which react with radical-anions can be lowered to an immeasurable level.

Radical-anion solutions were employed to determine (quite often quantitatively) the content of Brønsted acids in various liquid and gaseous media. The quantitative

determination requires a consideration of volume and solvation ability changes resulting from the change of the solution composition.

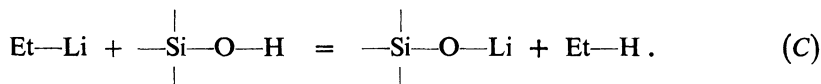
Reaction of Radical-Anions and Ethyllithium with Silica Gel

The reaction of radical-anions with OH groups of silica gel can be described as follows (Ar = arene):



The amount of radical-anions consumed by silica gel (including the chemically adsorbed amount) as determined by the standard titration procedure was the same as that found in the reverse titration. Benzophenone, phenanthrene, and naphthalene were used as the aromatic components of radical-anions; the results obtained were independent of the type of aromatic used.

Reaction of ethyllithium with silica gel in heptane can be described as



The amount of ethane formed corresponds to the quantity of acidic hydrogen.

The amounts of $\text{Na}^+(\text{phenanthrene})^{\cdot-}$ and Et—Li reacted with silica gel activated at 20–900°C are shown in Fig. 5. These two quantities do not differ from each other within experimental error (5–10%). Both reagents differ substantially in their molecule sizes and in the polarity of carbon–metal bonds. Considering an extremely high reactivity of these substances and a proportional drop of the OH group signal

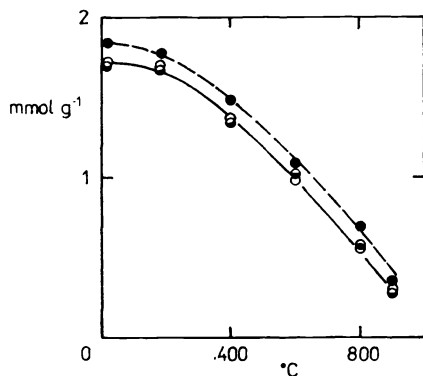


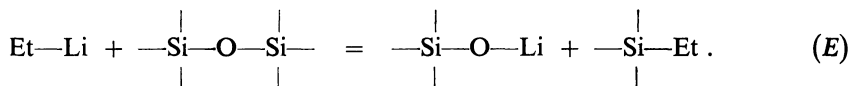
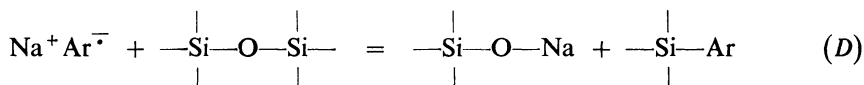
FIG. 5
Influence of dehydration temperature of silica gel on reaction of silica gel with $\text{Na}^+(\text{phenanthrene})^{\cdot-}$ in THF and with ethyllithium in heptane (20°C): ○ consumed amount of $\text{Na}^+(\text{phenanthrene})^{\cdot-}$, ● sum of consumed and adsorbed amount of $\text{Na}^+(\text{phenanthrene})^{\cdot-}$, ● evolved amount of ethane

in infrared spectra of silica gel (4 425, 4 505, and 7 140 cm^{-1}) after the reaction with radical-anions and ethyllithium, it can be concluded that both substances react quantitatively and stoichiometrically with OH groups on silica gel surface. According to infrared spectra a certain part of OH groups (2–5%) is left intact in reactions with both reagents. These may be inaccessible OH groups the presence of which was demonstrated in pressed discs of silica gel⁵ or OH groups in micropores¹⁵.

The thermally untreated silica gel exhibit the maximum possible value of 3.6–3.8 OH groups per nm^2 (calculated from Fig. 5) which decreases only slightly with increasing activation temperature up to 200°C. By refluxing silica gel in H_2O for 8 h and evacuating at 20°C for 100 h it contained again 3.6–3.8 OH groups per nm^2 . The amount of physically bonded H_2O under these conditions is negligible as can be seen from absence of 5 235 cm^{-1} signal in infrared spectra. The published values of maximum amounts of the surface OH groups of silica gel are 2.9–5.5 OH per nm^2 (refs^{3,5-10,13}), rarely higher^{12,13,19}. These values however were found by extrapolating experimental data after activating silica gel at least at 100°C. The contents of free H_2O have not been reported which may lead to an overestimation of the OH group content at low temperatures of activation (see e.g. the dependence on the activation time⁸).

The found amounts of reacted radical-anions and ethyllithium per square unit of silica gel surface decrease linearly with the increasing temperature of activation of silica gel in the range of 200–900°C. A steeper decrease with the increasing temperature is usually reported^{6-8,10,14} though also a linear dependence has been found^{14,19,20}. The scatter of published values of OH groups content is rather high which may be caused by unequal experimental procedures (reaction times, reaction effectiveness, corrections accepted) and by differences in silica gel samples (method of preparation, thermal history, free water content, surface area, pore size distribution, etc.). The agreement of our data with the published results strongly suggests suitability of the titration methods for the characterization of surface composition of silica gel.

Radical-anions and ethyllithium as strong nucleophiles may react with strained Si–O–Si bonds:



These reactions may be responsible for a certain difference between the amounts of radical-anions consumed and ethane from ethyllithium formed. The difference is

negligible in the present study, therefore it can be concluded that his reaction does not take place to a great extent.

The amount of radical-anions chemisorbed on silica gel Davison, grade 952, is 0.2–0.3 molecule per nm² and it is apparently independent of the activation temperature (Fig. 5). A certain dependence on the activation temperature, however, cannot be excluded due to a high experimental error involved ($\pm 50\%$).

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