Subsequent to contact ion pair formation, the solvent-separated ion pair is formed. For ethanol/acetonitrile mixtures ([EtOH] < 10 M), the electron transfer results in the formation of the solvent-separated ion pair. We observe contact ion-pair formation prior to hydrogen bonding in these systems. The formation of the solvent-separated ion pair from the contact ion pair is found to be controlled by an entropy of activation. Furthermore, the kinetics are found to be termolecular, second order in ethanol monomer concentration.

Acknowledgment. This work is supported by a grant from the National Science Foundation, CHE-8117519.

Registry No. Ph_2CO, 119-61-9; $PhNEt_2$, 91-66-7; Dabco, 280-57-9; Ph_2Co radical anion, 16592-08-8; Dabco radical cation, 54159-20-5; $PhNEt_2$ radical cation, 63224-14-6.

Anion-Exchange Properties of Ammonium Salts Immobilized on Silica Gel

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Received March 26, 1982

Abstract: The synthesis and aqueous anion-exchange properties are reported for ammonium salts immobilized on silica gel by alkyl chains of various lengths. Since the exchange properties of these systems are strongly affected by the polar inorganic matrix and its hydrophobic covering, these new anion-exchange supports have properties that are quite different from those of known polystyrene resins.

Benzyltrimethylammonium salts immobilized on insoluble polystyrene-type matrices are widely used as ion-exchange resins,[1] chromatographic supports,[2] and insoluble solid reagents.[3] When the methyl groups bound to the positive heteroatom are replaced with bulkier, lipophilic *n*-butyl groups, these systems can act as phase-transfer catalysts and activate the reagent anion in the organic phase, although they remain insoluble.[4] Tri-*n*-butyl onium salts have also been anchored to silica gel[5,6] and alumina[6] through alkyl chains, which on the one hand make the support more lipophilic, and on the other, when used as phase-transfer catalysts, facilitate anion exchange between the immiscible organic and aqueous phases. Silica gels with hydrophobic covering have been known for some time, and their application in the areas of chromatography and HPLC has been developed.[7] Lately, silica matrices supporting unspecified ammonium salts (presumably alkyltrimethyl) have become commercially available and their use is recommended in anion exchange, nucleotides, and enzyme chromatography.[8]

We report here the synthesis and anion-exchange properties of four new systems in which ammonium salts of different lipophilicities are anchored to silica gel via alkyl spacer chains of various lengths. These new systems have exchange, regeneration, and adsorption properties quite different from those of known polystyrene anion-exchange resins.

Table I. Regeneration and Anions Exchange on 4(Br⁻) via Aqueous $NaHCO_3$[a]

$$\underset{(0.16)}{4(\mathrm{Br}^-)} \xrightarrow{\mathrm{NaHCO_3}\ 5\%} \underset{(<1 \times 10^{-3})}{4(\mathrm{HCO_3}^-)} \xrightarrow{\mathrm{HCl}\ 0\ 2\ \mathrm{N}} \underset{(0.17)}{4(\mathrm{Cl}^-)} \xrightarrow{\mathrm{NaHCO_3}\ 5\%}$$

$$\underset{(<1 \times 10^{-3})}{4(\mathrm{HCO_3})} \xrightarrow{\mathrm{TsOH}^b\ 0.2\ \mathrm{N}} 4(\mathrm{TsO}^-) \xrightarrow{\mathrm{NaHCO_3}\ 5\%} \underset{(<1 \times 10^{-3})}{4(\mathrm{HCO_3}^-)}$$

$$\xrightarrow{\mathrm{HBr}\ 0.2\ \mathrm{N}} \underset{(0.16)}{4(\mathrm{Br}^-)}$$

[a] These consecutive exchanges were carried out successively treating 6.0 g of 4(Br⁻) with 50.0 mL of the reported aqueous solutions, slowly stirring for 5 min with $NaHCO_3$ 5% by weight and 2 min with acid solutions, at room temperature. In parentheses are the titers (Cl⁻ and Br⁻) as mequiv of X⁻/g. [b] *p*-Toluensulfonic acid.

Table II. Ammonium Chloride Functionalized Silica Gels Starting from the Corresponding Ammonium Bromide[a]

starting ammonium bromide (titer)	outcoming ammonium chloride (titer)
4(Br⁻) (0.16)	4(Cl⁻) (0.17)
6(Br⁻) (0.23)	6(Cl⁻) (0.24)
7(Br⁻) (0.43)	7(Cl⁻) (0.43)
8(Br⁻) (0.79)	8(Cl⁻) (0.79)

[a] The exchanges were carried out successively treating ammonium bromide functionalized silica gels (6.0 g) with $NaHCO_3$ 5% by weight (50.0 mL) and HCl 0.2 N (50.0 mL) according to eq 1. The number in parentheses are the titers as mequiv of X⁻/g.

Results

All systems were prepared from nonfunctionalized silica gel (Merck No. 7734, pore diameter 60 Å, specific surface area 500 m^2/g) sieved to a 212–106 μm particle size (70–130 mesh).

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(2) (a) Heftmann, E. "Cromatography"; Reinhold: New York, 1961; Chapters 11, 12; (b) Lederer, E.; Lederer, M. "Chromatography", 2nd ed.; Elsevier: Amsterdam, 1957; Division II; (c) "CRC Handbook Series in Chromatography"; CRC Press, Inc.: Palm Beach, FL, 1972.

(3) (a) Sherrington, D. C. In "Polymer-Supported Reactions in Organic Synthesis"; Hodge, P.; Sherrington, D. C. Ed.; Wiley: New York, 1980. (b) Cainelli, G.; Contento, M.; Manescalchi, F.; Mussatto, M. C. *Synthesis* **1981**, 302–303, and references therein.

(4) (a) Regen, S. L. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 421–429. (b) Molinari, H.; Montanari, F.; Quici, S.; Tundo, P. *J. Am. Chem. Soc.* **1979**, *101*, 3920–3927. (c) Regen, S. L.; Besse, J. J. *Ibid.* **1979**, *101*, 4059–4063. (d) Tomoi, M.; Ford, W. T. *Ibid.* **1981**, *103*, 3821–3828, 3828–3832.

(5) (a) Tundo, P. *J. Chem. Soc., Chem. Commun.* **1977**, 641–643. (b) Tundo, P.; Venturello, P. *J. Am. Chem. Soc.* **1979**, *101*, 6606–6613. (c) Tundo, P.; Venturello, P. *Ibid.* **1981**, *103*, 856–861.

(6) Tundo, P.; Venturello, P.; Angeletti, E. *J. Am. Chem. Soc.*, following paper in this issue.

(7) Iler, R. K. "The Chemistry of Silica"; Wiley: New York, 1979.

(8) Majors, R. E. *J. Chromatog. Sci.* **1977**, *15*, 334–351; **1980**, *18*, 488–511.

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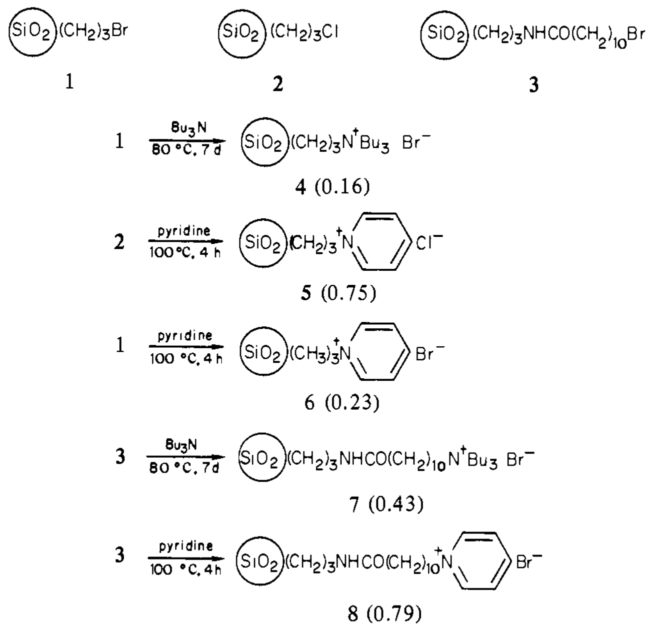
Scheme I



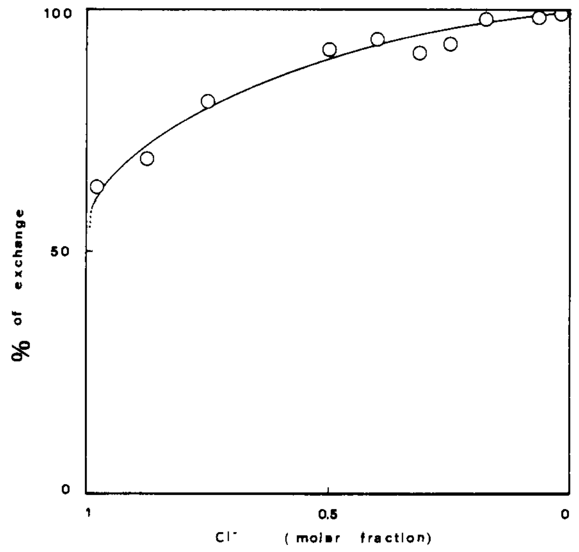


Figure 1. Competitive Cl^--HCO_3^- exchange in **5**(Cl^-).

The synthesis of **1** and **3** was reported previously.[6] **2** was prepared following the procedure for **1** by reaction of silica gel with 3-chloropropyltrimethoxysilane in refluxing toluene.

Reaction of these systems with the suitable tertiary amine gave immobilized ammonium salts **4**–**8**. The ammonium salt concentration is reported in parentheses as mequiv of Q^+/g in Scheme I where the circles indicate the inorganic matrix, and the siloxane functions binding the alkyl chains are omitted.

Systems **4**–**8** were found to be stable in 5% aqueous $NaHCO_3$ (by weight). No changes in the exchange properties of **4** were noted after six weeks. In this solution, the original anion is exchanged with HCO_3^- (see Discussion). The stability of the linkage between the silica and the organic functions in acidic media was tested for **7**; after 15 h at room temperature in $HClO_4$ (0.1 N) and treatment with $NaHCO_3$ and HBr according to Table I this system kept its original titer in Br^- ions.

Figure 1 shows the percent loss in Cl^- load for system **5**(Cl^-) as a function of the Cl^- molar fraction in the aqueous solution. The functionalized support's greater affinity for HCO_3^- than for Cl^- is clearly seen. Because of this peculiarity, these functionalized silica gels can be regenerated. The anions quantitatively exchanged simply by treatment with the acid of the anion to be introduced, as shown in Table I. By this procedure, the Br^- anions of **4**, **6**, **7**, and **8** were exchanged with Cl^- anions (Table II) in two steps performed by slowly stirring the resin in the corresponding aqueous solution (eq 1). In order to measure the exchange properties of

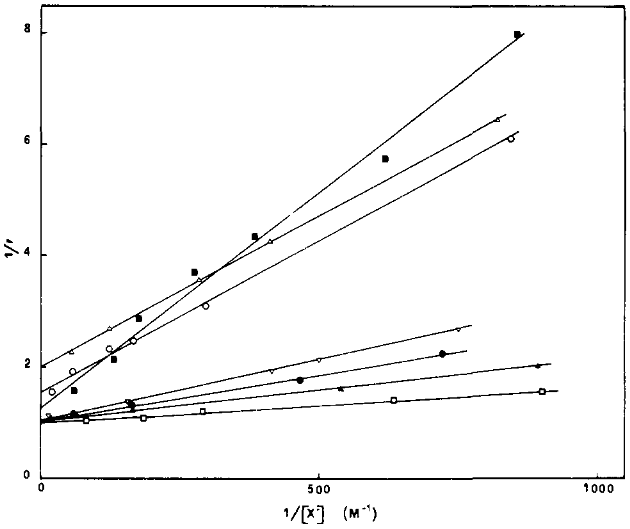
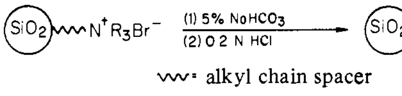


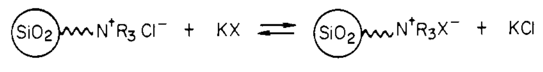
Figure 2. Exchange isotherms for some anions on **7** (Br^-): (□) KI; (▲) $KClO_4$; (●) $HClO_4$; (▽) C_6H_5COONa; (○) $CH_3(CH_2)_2COONa$; (△) CH_3COONa; (■) KCl. Data plotted according to eq 4.



$$\text{SiO}_2\text{∿∿}N^+R_3Br^- \xrightarrow[(2)\ 0.2\ N\ HCl]{(1)\ 5\%\ NaHCO_3} \text{SiO}_2\text{∿∿}N^+R_3Cl^- \quad (1)$$

∿∿ = alkyl chain spacer

4(Cl^-)–**8**(Cl^-) with anions in aqueous solution, according to eq 2, these supports were brought to equilibrium in an aqueous solution containing equal molar ratios of KCl and KX, with Cl^- concentrations 40 times higher than in the resin.



$$\text{SiO}_2\text{∿∿}N^+R_3Cl^- + KX \rightleftharpoons \text{SiO}_2\text{∿∿}N^+R_3X^- + KCl \quad (2)$$

Table III reports these results as well as those for Spherosil QMA[9] and the literature data for the Dowex 1 resin. Differences between silica and polystyrene supports, particularly with regard to very hydrophilic anions (F^-, HCO_3^-, and HSO_4^- are seen (Table III). Moreover, the behavior of these systems in the anion-exchange process is clearly influenced both by the type and the quantity of the hydrophobic covering.

Greater details on the exchange processes and the ionic bond to the solid support were obtained by studying the anionic exchange between **7** (Br^-) and some acids and their alkaline salts.

$$7(Br^-) + MX \overset{K}{\rightleftharpoons} 7(X^-) + MBr \quad (M = H, Na) \quad (3)$$

A given quantity of **7**(Br^-) was placed in solution containing various concentrations of the anion in question, until equilibrium was reached. Residual bromide anion on the functionalized silica was then measured potentiometrically and the resulting data were analyzed according to the treatment of Klotz[10]

$$1/r = 1/n + 1/nK[X^-] \quad (4)$$

where $1/r$ is the moles of immobilized onium salt/mol of exchanged anion, n is the molar fraction of exchanged anion (Br^- in this case) to the infinite concentration of the competing anion in aqueous solution, K is the equilibrium constant of eq 3, and $[X^-]$ is the residual concentration of the competing anion in water after the exchange. This treatment not only allows the above constants to be determined but also shows whether the exchange affects the structure of the support.[11] If it does, there is no linear

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[9] Sperosil QMA was a generous gift of Rhône-Poulenc Ind., France. It is silica gel (particle size 100–200 μm, pore diameter 1250 Å, specific surface area 25 m^2/g) functionalized with $-(CH_2)_{6-7}N^+(CH_3)_3$, having a Cl^- content of 0.29 mequiv/g.

[10] Klotz, I. M.; Walker, F. M.; Pivan, R. B. *J. Am. Chem. Soc.* **1946**, *68*, 1486–1490.

Table III. Competitive Cl^-–X^- Anion Exchange in Aqueous Solutions on Onium Salt Functionalized Silica Gels and Polystyrene Resin[a]

supports	anion source													
	KF	KCl	KBr	KI	$KHCO_3$	NaN_3	KNO_3	$KHSO_4$	HCOONa	CH_3COONa	C_6H_5·COONa	$C_{10}H_7$·COONa[b]	$CH_3C_6H_4$·SO_3Na[c]	C_6H_5ONa
4 (Cl^-)	7.0	1.0	1.3	1.7	>30	4.6	2.0	>30	2.0	2.3	5.9	>30	4.1	>30
5 (Cl^-)	2.7	1.0	1.9	3.5	4.7	4.2	3.5	9.9	1.7	1.8	3.5	>30	4.9	>30
6 (Cl^-)	3.0	1.0	1.1	1.3	>30	2.3	1.5	>30	2.8	2.8	4.5	5.5	4.8	>30
7 (Cl^-)	1.1	1.0	2.2	5.8	2.7	4.3	4.0	3.0	0.9	0.9	9.6	>30	7.6	>30
8 (Cl^-)	0.9	1.0	2.1	4.1	2.1	3.2	1.3	14	1.0	0.9	6.4	7.1	9.8	>30
Spherosil QMA[d]	0.3	1.0	2.3	4.2	0.7	1.8	2.1	9.3	0.6	0.5	2.8	3.2	12	5.4
Dowex 1[e]	0.09	1.0	2.8	8.7	0.5	–	3.0	4.1	0.22	0.17	–	—	–	5.2

[a] KCl; 20 mmol; MX, 20 mmol; immobilized onium salt, 0.1 mequiv; H_2O, 10.0 mL, slowly stirred for 15 h at room temperature. The reported values represent the selectivity toward Cl^- and are calculated in accordance with the formula given in the Experimental Section. [b] Sodium 1-naphtate. [c] Sodium *p*-toluenesulfonate. [d] See ref 9. [e] Data from ref 13.

Table IV. *K* and *n* Values for Some Anions, Determined for **7**(Br^-) According to Eq 4[a]

salt or acid	$K \times 10^{-2}$, M^{-1}	*n*
$HClO_4$	6.50	0.95
$KClO_4$	10.30	0.94
HI	23.10	0.97
KI	31.40	0.88
HCl	3.50	0.74
KCl	11.00	0.57
CH_3COOH	0.30	0.17
CH_3COONa	3.75	0.50
$CH_3(CH_2)_2COONa$	3.10	0.62
C_6H_5OH	0.00	0.00
C_6H_5ONa	11.90	1.00
C_6H_5COONa	3.10	0.62
$CH_3C_6H_4SO_3H$	5.80	0.95
$CH_3C_6H_4SO_3Na$	6.50	0.93

[a] See Experimental Section for procedures.

correlation between $1/r$ and $1/[X^-]$. Figure 2 shows the course of the exchange according to eq 4 of **7**(Br^-) with KI, $KClO_4$, $HClO_4$, C_6H_5COONa, $CH_3(CH_2)_2COONa$, CH_3COONa, and KCl, and Table IV reports the *n* and *K* values for some acids and their salts. While strong acids exchange more than their salts, the latter form stronger bonds. The mole fraction of anion exchanged decreases with the strength of the acid. As the anion becomes more lipophilic, the mole fraction exchanged and the binding constant increase. The case of phenol is interesting in this respect: although it is absorbed by the lipophilic covering (see below), it does not release Br^- ions in aqueous solution. These results were confirmed for **4**(Br^-) and **7**(Br^-) under different conditions (see Experimental Section) in Br^-–X^- competitive exchange reactions. Subsequent to reaching equilibrium, the residual X^- aqueous concentration (UV analysis) and the Br^- content of the solid support were measured. This experiment was also designed to establish whether the lipophilic covering (greater in **7** than in **4**) participates in the adsorption of the acid and its corresponding salt and/or in facilitating exchange with the bromide counterion of the onium salt.

Results in Table V show that nonfunctionalized silica gel in water adsorbs neither the anions nor their conjugate acids, while the presence of a hydrophobic covering in **3** promotes striking adsorption of both (in the order acids > salt). These data show that the silica skeleton in **4** and **7** does not affect adsorption, although it plays a decisive role in conferring good water wettability on the entire system.

Discussion

Anion Affinity of Onium-Functionalized Silica Gel. The importance of the silica support in the anion exchange processes is clearly evident from data in Table III. In systems **4–8**, inorganic anion selectivity is lower than that in the corresponding polystyrene resins. In systems with less covering (**4** and **6**), greater affinity for hydrophilic anions is observed (Table III). F^- ion becomes competitive with I^-, and both HSO_4^- and HCO_3^- are retained more readily than I^-, N_3^-, and NO_3^-. This inversion may be attributed to the properties of silica gel. As it competes with the water in solvating the anions, a microenvironment may be created in which the free energy of the system is lowered (especially for highly hydrophilic anions). However, as compared with the polystyrene resins, the selectivity toward less hydrophilic anions ($C_6H_5COO^-$, $C_{10}H_7COO^-$, $CH_3C_6H_4SO_3^-$, and $C_6H_5O^-$) does not vary greatly. In this case, the properties of the hydrophobic covering become important.

The effect of greater or lesser hydrophilicity of the positive head on the exchange properties of the systems is not easily explained. On the one hand, **6** has greater affinity than **4** for some very hydrophilic anions, while on the other the behavior of **8** and **7** is the reverse.

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(11) Smid, J.; Shah, S. C.; Sinta, R.; Varma, A. J.; Wong, L. *Pure Appl. Chem.* **1979**, *51*, 111–122.

Table V. Exchange and Adsorption of Phenols, Sulfonic Acids, and Their Salts on Functionalized Silica Gel[a]

compound	support					
	4(Br^-)		7(Br^-)		3	unfunctd silica gel,
	% Br^-_{exch}[b]	% $comp_{ads}$[c]	% Br^-_{exch}[b]	% $comp_{ads}$[c]	% $comp_{ads}$[d]	% $comp_{ads}$[d]
phenol	49	25	0	77	65	–
sodium phenoxide	100	0	91	38	59	–
picric acid	92	29	90	39	96	0
sodium picrate	86	0	99	20	90	0
p-toluenesulfonic acid	69	20	63	36	82	0
sodium *p*-toluenesulfonate	81	0	70	22	80	0
1-naphthalenesulfonic acid	92	13	92	29	90	0
sodium 1-naphthalenesulfonate	91	3	94	22	85	0
sodium 9-anthracenesulfonate	100	5	98	46	100	0
1 pyrenesulfonic acid	97	79	90	91	–	0
sodium 1-pyrenesulfonate	100	3	100	53	–	0

[a] KBr, 0.10 mequiv, acid, 0.20 mequiv (neutralized with 0.20 mequiv of NaOH in the case of the sodium salt); 4 or 7, 0.10 mequiv; (1.0 g of support in the case of 3 and unfunctionalized silica); H_2O, 10.0 mL, slowly stirred for 15 h at room temperature. [b] The exchanged Br^- was argentometrically determined on the recovered 4 and 7 and referred to the initial Br^- content. [c] The % compound adsorbed was determined as the difference between $(A_0 - A)/A_0 \times 2 \times 100$ (A_0 and A are the UV adsorption of the title compounds at their λ_{max}, before and after the exchange) and the observed % Br^- exchanged. In this way exchange and adsorption are comparable: for example, phenol on 4 (original titer 0.16 mequiv of Br^-/g) is present in 0.08 mequiv/g as exchanged and 0.04 mequiv/g as adsorbed (0.49 × 0.16 and 0.25 × 0.16, respectively). [d] Determined as $(A_0 - A)/A_0 \times 100$.

Under phase-transfer catalysis or extractive alkylation conditions, the onium salt selectivity for various anions is a determining factor for the reaction to proceed and is enhanced by the organic solvent. For example, Starks has reported selectivity ratios in toluene–water for various anions and onium salts:[12] for $(C_{18}H_{21})_3N^+CH_3$, $Cl^-:Br^-:I^-$ = 1.00:16.5:5000; for $(C_{10}H_{21})_3N^+CH_3$, $Cl^-:F^-$ = 1.00:0.02; for $(C_{18}H_{33})_2N^+(CH_3)_2$, $Cl^-:HSO_4^-:HCO_3^-$ = 1.00:0.02:0.05. The observed order is inversely proportional to anion hydrophilicity. For functionalized benzyltrimethylammonium polystyrene resins (Dowex 1, Ⓟ-$C_6H_4CH_2N^+(CH_3)_3$ Cl^-), this affinity remains essentially unchanged although the differences are somewhat smaller.[13] The ion-exchange resin, which acts as the organic phase in this case, is highly impregnated with water molecules with great affinity for the polar onium salts (for example, benzyltrimethylammonium chloride is very soluble in water and Dowex resin is swollen with water). Strong anion solvation diminishes selectivity and increases affinity for the highly hydrophilic anions. Silica gel-functionalized onium salts behave in this manner. The situation for onium salts bound to silica gel **4–8** is indeed more complex than for Dowex 1 resin since a completely water-wettable polar matrix is surrounded by a multilayer lipophilic covering. This covering consists of 3 or 15 atom linear alkyl chains with either a very hydrophilic onium salt (pyridinium salt) or a typical phase-transfer catalyst (tributylammonium salt) at the end. Systems **4–8** also vary in the amount of covering. Although they share the same functionalizing system, **5** and **6** differ in the number of surface siloxanic groups bonded to the covering (greater in **5** than in **6**).

Affinity for very hydrophilic anions is an important factor in the regeneration of systems **4–8** after their use in chromatography, phase transfer catalysis, and reactions as supported solid reagents. In particular, because of their great affinity for HCO_3^-, they may be converted into the desired form by treatment with HCO_3^- followed by the acid of the anion. Anion exchange is simple and rapid, requiring only a few minutes; conversely, for functionalized benzyltrimethylammonium resins, this process was usually carried out in a chromatographic column with 1 N NaOH as eluent.

Amount of Exchange and Binding Constant. The binding constant (K) and the amount of exchange (n) for several anions in aqueous solution with the long chain immobilized ammonium salt on silica (eq 3) have been calculated according to eq 4.

For monovalent anions, some of which are shown in Figure 2, the good linear correlation between $1/r$ and $1/[X^-]$ implies that ion exchange leads to no modification in the three-dimensional structure of the support. Organic anions such as $C_6H_5O^-$, $C_6H_5COO^-$, and $CH_3C_6H_4SO_3^-$ also show good linearity, although some of the organic compound is adsorbed on the lipophilic covering of the support. The resulting spatial alteration of the alkyl chains of **7** is relatively small since it does not affect the statistical anion-exchange process.

The lack of linearity between $1/r$ and $1/[X^-]$ for $KHSO_4$, K_2SO_4, H_2SO_4, and K_2CO_3 (not shown) may be due to the fact that these anions are present in their mono- or divalent forms. Unlike proteins,[10] soluble polymers,[11] and liposomes,[14] silica gels remain unaffected by the addition of salts or organic compounds.

It is of interest to note that strong acid can remove Br^- from the support more completely (larger n value) even if they form a weaker bond (smaller K value) than the corresponding conjugate bases. As the dissociation of the acid decreases, this effect diminishes drastically (consider $HClO_4$, $K = 6.50 \times 10^2$, $n = 0.95$, in comparison with CH_3COOH, $K = 0.30 \times 10^2$, $n = 0.17$) until it disappears (C_6H_5OH) completely. The phenomenon may be understood by considering that the salts are less readily adsorbed by the support than the corresponding acids since the greater charge separation requires more polar interaction than the support can provide. This in turn leads to a greater concentration of acid than salt on the inorganic silica skeleton, thus shifting the equilibrium. On the other hand, the exchange of anions coming from salts leads to a sharp charge separations. The salt is adsorbed little or not at all by the lipophilic covering, and the Br^- anions exchanged are present only in the aqueous solution.

Deducing the different behavior of the acids from their salts in exchange processes difined by eq 3 is difficult. However, the higher K values observed for the salts in comparison with those of their acids (Table IV) indicate stronger interactions between the onium salt and its counterion in neutral than in acidic media.

Adsorption and Exchange. Data in Table V show that the adsorption processes occur together with anion exchange, and that the adsorption correlated with the lipophilicity of the covering (greater in **7** than in **4**) and of the adsorbed compound (greater for pyrenesulfonic acid and pyrenesulfonate than for toluenesulfonic acid and toluenesulfonate).

The greater polarity of the salts causes them to be poorly adsorbed on **4** and **7**, and conversely, the anions of the salts exchange well. On the other hand, the corresponding acids are

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[12] Starks, C. M.; Liotta, C. "Phase Transfer Catalysis"; Academic Press: New York, 1978; p 24.

[13] Wheaton, R. M.; Bauman, W. C. *Ind. Eng. Chem.* **1951**, *43*, 1088–1093. These authors report for Dowex 2 resin, Ⓟ $C_6H_4CH_2N^+(CH_3)_2CH_2CH_2OH$ Cl^- (a more hydrophilic support) an enhanced affinity for hydrophilic anions (OH^-, HCO_3^-, etc.) and a lowered selectivity with respect to Dowex 1 resin.

[14] (a) Fendler, J. H.; Fendler, E. J. "Catalysis in Micellar and Macromolecular Systems"; Academic Press: New York, 1975. (b) Gross, L.; Ringsdorf, H.; Schupp, H. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 305–325.

more readily adsorbed by the covering, but they exchange less completely. These results are also in accord with the data reported in Table IV and in Figure 2.

Conclusion

Onium salts immobilized on silica gel present a quite different situation from any previously known exchange resin. Importantly, structures can be varied relatively easily which result in markedly altered exchange properties. Conversely, in cross-linked polystyrene resins, the selectivity properties may be partially altered only if the onium salt functionalization is varied. Combined with facility for regeneration, these factors make the use of silica gel supports valuable in anion exchange and ionic and liquid chromatography as well as in phase-transfer catalysis.

Experimental Section

General Methods. Argentometric titrations were performed with a Metrohm-Erisau Multi-Dosimat E 415 with a combined silver electrode in the presence of nitric acid. The hal^- titers were not corrected for the weight change of the supports due to the anion exchange and/or adsorption. Ultraviolet measurements were obtained with a Beckman UV-DGB spectrophotometer. All organic and inorganic reagents were ACS grade or have been previously described. **1** and **3** contained 0.40 and 0.69 mequiv of Br^-/g, respectively.

3-Chloropropyl-Functionalized Silica Gel 2. The procedure previously described for **1**[5] was followed: 40.0 g of activted silica gel and 12.0 g of 3-chloropropyltrimethoxysilane in 200 mL of anhydrous toluene yielded 48.5 g of functionalized silica gel. Determination of organic chlorine yielded 1.0 mequiv Cl^-/g.

Syntheses of 4–8. The precursor halogen-functionalized silica gels (10.0 g) were degassed under vacuum in tributylamine or pyridine and were then heated to 80 °C for 7 days or to 100 °C for 4 days, respectively. After cooling, the immobilized onium salts were filtered and washed several times with diethyl ether, methanol, and diethyl ether to yield 10.25, 10.75, 10.23, 10.32, and 10.25 g of **4**, **5**, **6**, **7**, and **8**, respectively. Titration of ionic halide yielded for **4**, 0.16; **5**, 0.75; **6**, 0.23; **7**, 0.34; **8**, 0.60 mequiv of Q^+/g.

The lower onium salt content found in the case of tributylammonium-functionalized silica gels, in comparison with the analogous pyridinium and tributylphosphonium ones, is attributable to the lower nucleophilic reactivity of tributylamine: no attempt was made to improve the functionalization.

Competitive Cl^-–X^- Exchange. A mixture containing 2.5 mL of 0.8 M KCl aqueous solution (20 mmol), 2.5 mL of 0.8 M KX or NaX aqueous solution, 5.0 mL of deionized H_2O (no change was observed using bidistilled and nitrogen-deaerated water), and 0.1 mequiv of **4–8** corresponding to 0.59, 0.13, 0.41, 0.23, and 0.13 g respectively, was slowly stirred for 15 h at room temperature; 0.34 g of Spherosil QMA (0.29 mequiv of Q^+/g) was also used. The solution was then filtered and washed repeatedly with water until anions had completely disappeared from the mother liquor and then with methanol and diethyl ether. After air evaporation of the solvent, the Cl^- present on the supports was measured argentometrically (0.01 N $AgNO_3$). The affinity of the systems for the various anions as compared to Cl^- (Table III) was calculated with the followng formula

$$(\text{mL Ag}^+_{\text{theor}} - \text{mL Ag}^+_{\text{used}})/\text{mL Ag}^+_{\text{used}}$$

where mL Ag^+_{theor} is the number of milliliters of 0.01 N $AgNO_3$ required to titrate an equal quantity of support before the exchange.

Competitive Cl^-–HCO_3^- in 5(Cl^-). Various amounts of 1.0 N NaCl aqueous solution and 1.0 N $NaHCO_3$ aqueous solution (7.8 mL in total, corresponding to 8.0 mequiv of (Cl^- + HCO_3^-), 2.2 mL of H_2O, and 0.20 mequiv of **5**(Cl^-) (0.27 g) were slowly stirred for 15 h at room temperature. The support was then filtered and washed with water until the Cl^- had disappeared; this was followed by washing with methanol and diethyl ether. After solvent evaporation, the Cl^- content was determined argentometrically with 0.01 N $AgNO_3$.

***n* and *K* Determination.** A 0.25-g sample of **7**(Br^-) (0.58 g) was placed in 50 mL of aqueous solution containing various quantities of salt or conjugate acid (ranging from 0.10 to 5.0 mmol). The suspensions were then slowly stirred for 15 h at room temperature; 10.0-mL aliquots of each solution were then taken and potentiometrically titrated with 0.01 N $AgNO_3$ to determine the Cl^- in aqueous solution. The quantity of Cl^- on the support and the residual X^- in solution were calculated by difference. The plots of $1/r$ vs. $1/[X^-]$ had correlation coefficients between 0.989 and 0.999.

Adsorption and Anion Exchange on 4(Br^-) and 7(Br^-). A 0.10-mequiv sample of KBr, 0.10 mequiv of **4** and **7** (0.625 and 0.290 g, respectively), and 0.20 mequiv of the acid in question (0.20 mequiv of NaOH was added in the case of the sodium salt) in 10.0 mL of H_2O, was degassed and slowly stirred for 15 h at room temperature. After suitable dilution, aliquots of the aqueous solution were analyzed by UV spectroscopy and compared with standard solutions of the compounds in question. Systems **4** and **7** were then filtered and washed thoroughly with water, methanol, and diethyl ether before air-drying. Nonexchanged bromide was titrated potentiometrically (0.01 N $AgNO_3$), and the percentage of exchanged bromine on the support was calculated. The percentage of compound present on the support was calculated from UV data. The difference between the two measurements is reported as the adsorbed percentage and is arbitrarily referred to the quantity of immobilized onium salt.

Acknowledgment. This research was supported by the Consiglio Nazionale delle Ricerche (Progetto Finalizzato 'Chimica Fine e Secondaria', Contract No. 80 02173 95).

Phase-Transfer Catalysts Immobilized and Adsorbed on Alumina and Silica Gel

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Abstract: Onium salts immobilized on alumina have been shown to be effective phase-transfer catalysts in comparison to analogous soluble catalysts adsorbed on silica or alumina. Appreciable selectivity has been observed in the nucleophilic substitution reaction with aqueous potassium iodide toward halide of different sizes (1-bromobutane, 1-bromooctane, and 1-bromohexadecane). Alumina and silica gel immobilized onium salts can also act very effectively as reagents when used in stoichiometric quantities.

Three methodologies have been developed in phase-transfer catalysis. In liquid–liquid phase-transfer catalysis (LL-PTC)[1] the reaction is run in a two-phase system: the reactant is in the organic phase while the nucleophile is located in the aqueous phase. In solid–liquid phase-transfer catalysis (SL-PTC)[2] the reaction is run in a heterogeneous solid–solvent system: a solid salt is used as the source of the reactive anion while the reagent is dissolved in the solvent. In the third and most recent method, gas–liquid phase-transfer catalysis (GL-PTC),[3] the reaction is run without solvent and the organic reagent is located in the gas phase. In

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