Tetrahedron Letters Vol. 21, pp 2581 - 2584
0040-4039/80/0622-2581$02.00/0

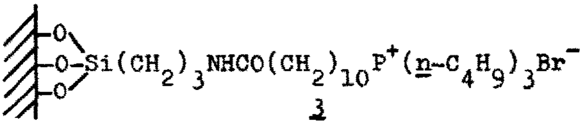
SILICA GEL SUPPORTED PHOSPHONIUM SALTS AS MICELLAR AND PHASE TRANSFER CATALYSTS

Pietro Tundo* and Paolo Venturello
Istituto di Chimica Organica dell'Università, I-10125 Torino, Italy.

Summary: Phosphonium salts immobilized on silica gel have been found to be both micellar and phase-transfer catalysts.They are able to exchange their parent anions with the anions present in an aqueous solution and promote, in catalytic amounts, the decarboxylation of 6-nitrobenzisoxazole-3-carboxylate to give 2-cyano-5-nitrophenolate, a test for micellar catalysis.

Micellar catalysis is due to substrate binding and to a change in its environment.[1]

$\underline{n}$-$C_{16}H_{33}N^+(CH_3)_3Br^-$ 1 $(\underline{n}$-$C_4H_9)_4P^+Br^-$ 2



$\equiv$O$_3$Si$(CH_2)_3NHCO(CH_2)_{10}P^+(\underline{n}$-$C_4H_9)_3Br^-$

3

Onium salts of long hydrocarbon chain having a hydrophylic head, such as 1, are typical micelle forming surfactants, and have been supported on cross-linked polystyrene.[2] Conversely 2, equally soluble in water, cannot form micelles, but is very active as a phase-transfer catalyst.[3] Although 1 and 2 have similar functions, each one can efficientily work according to only one of the above mentioned mechanisms.

Depending on the way in wich the reaction is carried out, phosphonium salts supported on silica gel,[4] such as 3, can act either as phase-transfer or micellar catalysts.

In the presence of an organic phase under phase-transfer conditions the activity of 3 strongly depends on the adsorption of the organic substrate and its mechanism is exactly like the mechanism of soluble catalysts.[5]

We report here the high activity of phosphonium salts supported on silica gel as insoluble catalysts to mimic functions of micelles. In water 3 works via adsorption, rapidly exchanges its anions with the aqueous solution, and provides a hydrophobic environment. In fact 3 (1.3 mequiv $[PR_4]^+$ /g, 100-140 mesh) decolorizes the 1.0×10^{-4} M aqueous solutions of several dyes such as cresol red, methyl red, toryn, bromcresol green and potassium picrate, by exchanging its bromine with the corresponding dyes anions.

Linear relationships between the decreases of the u.v. absorbances of these solutions and the grams of functionalized silica added are followed.

Addition of salts can affect the adsorption on 3 of an unbuffered $1.0x10^{-4}$ M aqueous solution of potassium picrate. The observed trend (figure) does not resemble the classical exchange of anions in the phase-transfer catalysis, but rather parallels the known effects of such salts on the micellar catalyzed reactions.[6,7]

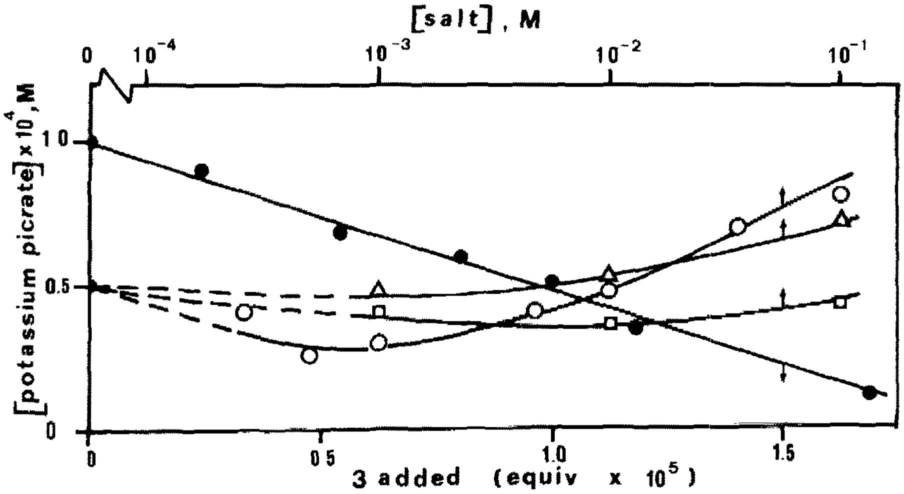
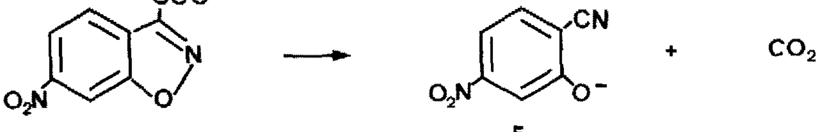


figure - Potassium picrate adsorption on 3 (100 mL of an unbuffered aqueous solution, $1.0x10^{-4}$ M) (-●-). Effect on the adsorption of salts added to a 100 mL $1.0x10^{-4}$ M unbuffered aqueous solution of potassium picrate containing $1.0x10^{-5}$ equiv of 3 (-□- KCl, -○- KI, -△- NaOTs).

Rate constants for decarboxylation of 6-nitrobenzisoxazole-3-carboxylate 4 depends highly on the nature of the environment.



4

5

This decarboxylation is, as compared with water (k_d= $0.06x10^{-4}$ s^{-1}, T=30°C)[7], 95 times faster in micellar 1 (molar ratio 1/4=195, T=25°C)[6]; 1300 times faster in cationic polysoaps: partially laurylated poly(4-vinylpyridine) and poly(2-ethyl-1-vinylimidazoate, as catalysts (molar ratio polysoap/4=50, T=30°C)[7]; 1300 times faster with quaternized polyethylenimines (molar ratio polyethylenimine/4=2, T=25°C; the molecular weight of polyethylenimine was 24 000)[8]; 14 000 times faster with polycrown ethers (molar ratio polycrown/4=50, CsCl 0.02 M, T=25°C).[9]

Sheer suspensions of unfunctionalized silica gel in 2.0×10^{2} M aqueous solutions of cetyltrimethylammonium (and phosphonium) bromide and N-cetylpyridinium bromide do not enhance, or rather slightly inhibit the decarboxylation of 4, compared with the rate of such micellar catalysts alone.

Table - Effect of the addition of 3, salts, phase-transfer catalyst and unfunctionalized silica gel on the aqueous decarboxylation of 4[a].

	ratio of		
Catalyst	catalyst	salt	$k_d\times10^{4}$ s^{-1}
	to carboxylate		
3	0.05	-	1.1
3 + KCl	0.05	10	1.2
3 + KI	0.05	10	0.5
3 + NaOTs	0.05	10	0.7
2	1.0	-	0.07
silica gel[b]	-	-	0.08
2 + silica gel[b]	1.0	-	0.09

[a] 5.0 mL of a solution 2.7×10^{-2} M in water buffered with borate (pH=9) at 30°C.

[b] Unfunctionalized silica gel, 100 mg.

0.05 molar equivalents of 3 (5.2 mg, 6.7×10^{-3} mmol) in 5.0 mL of a solution 2.7×10^{-2} M of 4 (borate buffer, pH=9) at 30°C catalyze the decarboxylation to give 2-cyano-5-nitrophenolate 5, stirring very slowly, simply to avoid concentration gradients in the water solution; the observed pseudo-first-order rate constants (k_d)[10] was $k_d=1.1\times10^{-4}$ s^{-1}. During the reaction the catalyst is red, showing the effect of the less polar milieu on which 5 is adsorbed (compared with water, λ_{max}=400 nm).

The phase-transfer catalyst 2 and the unfunctionalized silica gel pratically do not affect the rate of decarboxylation; this can be changed however by addition of salts (Table).

On the contrary of 1, the micellar microenvironment of 3 of course is not dependent on the concentration of surfactants since it represents another insoluble phase and thus the k_d are linearly dependent on the catalytic amount of 3, with a slope of 0.20 (r=0.997; k_dx10^{4} s^{-1} vs. mol equiv.x10^{2} of 3).

Experiments carried out with an excess of 3 25 times higher than the carboxylate (2.7x10^{2} M) showed that both 4 and 5 are entirely adsorbed by the catalyst; the variation of the colour from yellow to orange-red is very rapid: visual observations estimated $t_{1/2} \leqslant 20$ s, corresponding to $k_d \geqslant 350\text{x}10^{4}$ s^{-1}; this value is very near to one obtained by Smid[9] with polycrown ethers.

The rate acceleration is derived from formation of hydrophobic ion pairs between carboxylate anion and supported onium salt. Moreover the catalytic centers are compelled together, in a given environment because are immobilized on a solid matrix. The silica skeleton, which is also fully permeable toward the water solutions, recalls the function of the tertiary structure in the catalytic pattern of the enzymes.

The high catalytic activity of 3 should be important, because on such insoluble systems it is possible to optimize the factors controlling the catalysis, by changing the nature and the lipophilicity of the system and the hardness of the supported onium salt.

References and Notes

1) a)J.H. Fendler, E.J. Fendler "Catalysis in Micellar and Macromolecular Systems", Academic Press: New York,1975 and Adv.Phys.Org.Chem. 1970, 8,271;
   b)K.L. Mittal "Solution Chemistry of Surfactants", Plenum: New York, 1979.
2) J.M. Brown, J.A. Jenkins, J.Chem.Soc.,Chem.Commun., 1976, 458.
3) a)W.P. Weber, G.W. Gokel "Phase-Transfer Catalysis in Organic Synthesis", Springer-Verlag: Berlin, 1977.
   b)C.M. Starks, C. Liotta "Phase-Transfer Catalysis", Academic Press: New York, 1978.
4) P. Tundo, J.Chem.Soc.,Chem.Commun., 1977, 641 and P. Tundo, P. Venturello, J.Am.Chem.Soc.. 1979, 101, 6606.
5) P. Tundo, P. Venturello, unpublished results.
6) C.A. Bunton, M.J. Minch, J. Hidalgo, L. Sepulveda, J.Am.Chem.Soc., 1973, 95, 3262.
7) T. Kunitake, S. Shinkai, S. Hirotsu, J.Org.Chem., 1977, 42, 306.
8) M.F. Dampier, C-W. Chen, H.W. Whitlock Jr., J.Am.Chem.Soc., 1976, 98, 7064.
9) S.C. Shah, J. Smid, J.Am.Chem.Soc., 1978, 100, 1426.
10) The kinetics were measured by taking 50 µL samples from the reaction mixture and, after suitable diluition, were monitored by u.v. at 400 nm in water. The increases of the band of 2-cyano-5-nitrophenolate followed correct pseudo-first-order relationships: $k_d = (1/t)\ln a_\infty/(a_\infty - a_t)$, correlation coefficients being better than 0.998.

(Received in UK 16 April 1980)