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VARIABILITY OF SILICA SURFACES AS REACTION MEDIA

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Abstract: The properties of nine silica surfaces as reaction media are compared.

A number of unique products, unusual product ratios, unusually high rates, or features of mechanistic interest, have been noted when reactions are carried out on the surface of amorphous silica.[1] The silicas have usually been chromatographic, and often from unidentified commercial sources. Very few comparisons have been made of the properties of even two different silica surfaces as media for the same reaction.[1a,b] Such differences as have been found have usually been minor, except that a silica with more of the typical iron or titanium impurities will catalyze reactions that do not take place on a purer silica.[1a] This paper uses two medium effect parameters to evaluate the interchangability of nine silica samples.

One of the parameters is the rate of decomposition of anisoyl peroxide in slurries of the silica in CCl_4 at room temperature. This reaction, which will be described in detail in a future publication, is entirely or almost entirely polar, involving ion pairs formed on the surface of the silica. The rate serves as a measure of the extent to which the various surface environments favor this kind of ionic reaction. Although the rates varied from one sample to another, all were many orders of magnitude faster than the reaction in ordinary polar solvents at room temperature.

The other test is a measurement of the position of the absorption maximum in the reflectance spectrum of adsorbed p-nitroanisole, 1. The scaled frequency shift π^*_1 is one of the quantities averaged to establish the π^* solvatochromic scale of polarity and/or polarizability of liquid reaction media.[2] The property represented by π^* is an important component of what is loosely termed the 'polarity' of the medium. Whereas ordinary solvents have π^* values ranging from 0.00 for cyclohexane to 1.09 for water (one of the most polar), all of the silicas tested had π^*_1 values between 2.0 and 2.8. The polarity of the silicas is also very high by this measure.

Table I

Source	Rates[a] Dry[c]	Rc'd.	π^*_1[b]	Source	Rates[a] Dry[c]	Rc'd.	π^*_1[b]
Fisher S-157[d]	100	13	2.49	Will[e]	87	4	2.64
Fisher S-679, grade 923[f]	52	4	2.39	Sargent-Welch[g]	50	39	2.76
				Baker 40 μm[h]	22	13	2.12
Merck[i]	24	6	2.05	Will[j]	33	2	2.53
Baker 60-200[k]	14	5	2.25	Grace 923[l]	41		2.41

(a) Relative first-order rates at room temperature. 100 is approximately 10^{-2} sec^{-1}. (b) From reflectance spectra of 0.25 wt. % of p-nitroanisole on an oven-dried sample of the silica. (c) Dried for 3-4 hr at 140°, stored overnight in a vacuum desiccator over Drierite. (d) Fisher Chem. Co., 28-200M, S-157, grade 12, lot 753475, manufactured by Grace Davison. This is from the same lot number as the silica designated as P_0H_1 in ref. 1a. (e) Will Sci. Co., 28-200 mesh, no W85880, grade 12. (f) Fisher Chem. Co., 100-200 mesh, S-679, lot 710014, grade 923, ASTM D1319-61T, manufactured by Grace Davison. (g) Sargent-Welch, 28-200 mesh, SC14616, lot 4L 038. (h) J.T.Baker Chem. Co., silica gel for column, flash, or TLC plate chromatography, 40 μm av. diam., cat. no. 7024-1, lot 404355. (i) E. Merck, Silica Gel 60, 230-400 mesh, cat. no. 9385, lot 1128425. (j) Will Sci. Co., 100-200 mesh, WI 85893. (k) J.T. Baker Chem. Co., 60-200 mesh, for column chrom., 3405-5, lot 344338. (l) Grace Co., Davison Chem. Div., 100-200 mesh, grade 923, specifications MIL-D-3716 and/or Davison Commercial Grade H, Dav. code 923-08-08-226. This is the same grade and code number as the silica designated as P_1H_1 in ref. 1a.

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