Photo-acoustic Spectroscopic Evidence for Site–Site Interactions in a Bifunctional Surface-bonded Phase

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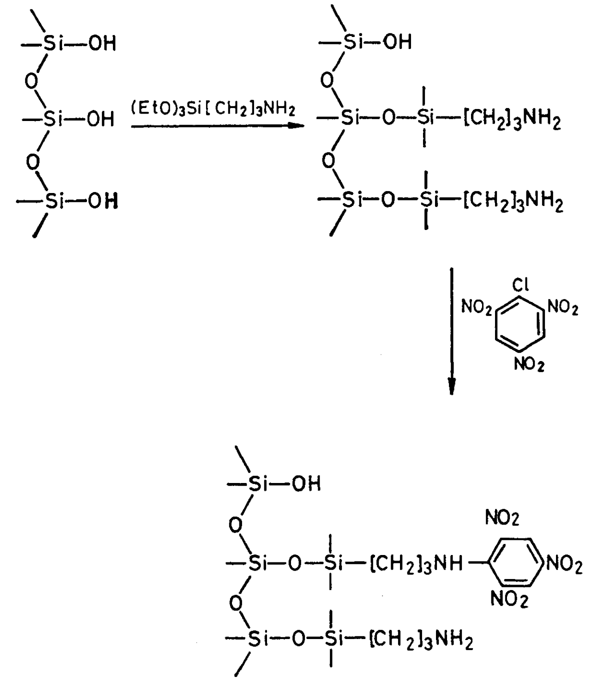
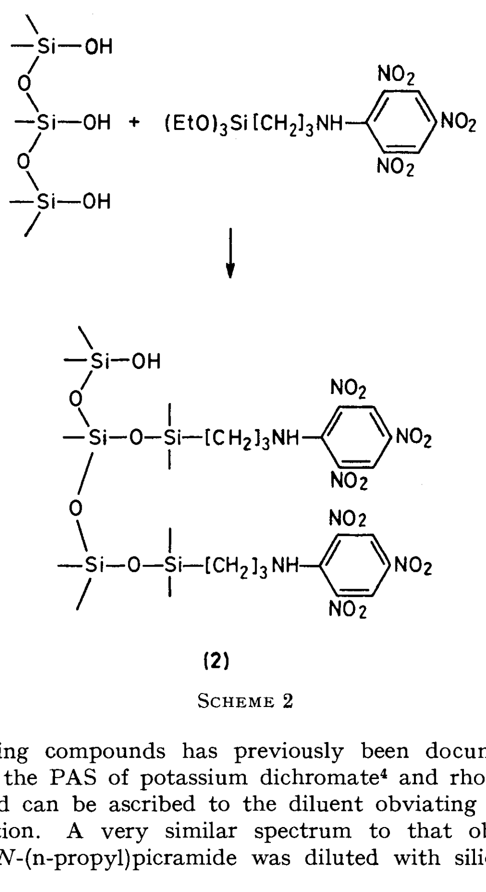
Summary The first direct, spectroscopic observation of interactions between surface-bonded organic molecules has been made.

We recently described the synthesis of two chemically bonded stationary phases for h.p.l.c., containing picramidopropyl groups linked to the surface of silica. The first phase (**1**) was prepared[1] by treatment of a preformed aminopropyl silica (1·4 amino-groups per nm^2) with picryl chloride (Scheme 1), leading to 22% derivatisation of the amino-groups in the phase (*i.e.* 0·31 picramidopropyl groups per nm^2). The second phase (**2**) was obtained[2] by synthesis of 3-picramidopropyltriethoxysilane and linkage of this to the surface of silica (Scheme 2) to give a bonded phase with 0·36 picramidopropyl groups per nm^2 and lacking in free amino groups. The h.p.l.c. elution behaviour of polycyclic aromatic hydrocarbons on both these bonded phases was consistent with the operation of a charge transfer retention mechanism.[1,2]



(**1**)

Scheme 1



(**2**)

Scheme 2

These phases have now been examined by photo-acoustic spectroscopy (PAS).[3] The spectrum of powdered *N*-(n-propyl)picramide showed an absorption band, the onset of which is around 540 nm; however, no clear maximum was observed. When the picramide was diluted with silica, maxima were observed (λ_{max} at *ca.* 410 and 320 nm). Increase in spectral resolution by diluting strongly light-absorbing compounds has previously been documented, *e.g.* in the PAS of potassium dichromate[4] and rhodamine B,[5] and can be ascribed to the diluent obviating optical saturation. A very similar spectrum to that obtained when *N*-(n-propyl)picramide was diluted with silica was

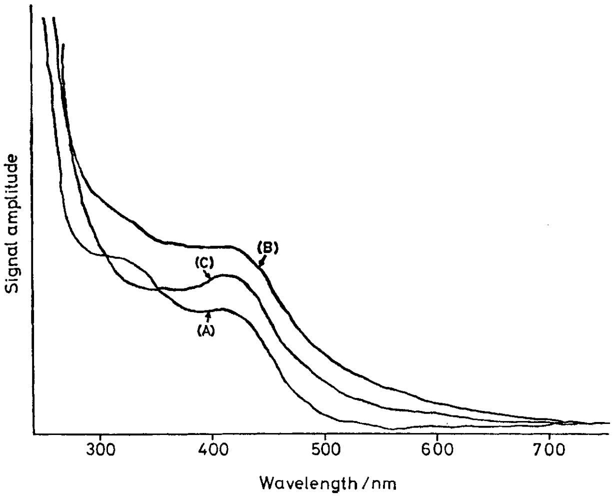


Figure. Photo-acoustic spectra obtained using EDT Research OAS 400. (A) Phase (**2**) + silica (1 : 1 w/w) (B) Phase (**1**) + silica (1 : 1 w/w) (C) Phase (**2**) + silica (1 : 1 w/w; 47 mg) doped with n-propylamine (71 mg) by evaporation of a mixture in CH_2Cl_2.

exhibited by phase (**2**). By contrast, phase (**1**) showed a totally different spectrum (Figure). It can be seen that this phase is absorbing light far to the red of 540 nm. We ascribe this as being due to a light-absorbing complex (σ- and/or π-complex) formed between some of the free amino-groups and picramide groups which are in close proximity. That such an absorption band can be produced by the interaction of bonded picramidopropyl groups with amino-functions was demonstrated by the observation that addition to phase (**2**) of n-propylamine gave a modified material exhibiting this new band (Figure).

PAS has been applied previously to the examination of only a few bonded phases.[6–8] Although one of these resembles our own phase (**1**), being prepared by reaction of aminopropyl silica with 2,4-dinitrofluorobenzene,[6] no unusual features for this phase were described. This is the first time that a direct, spectroscopic observation of complex formation between pairs of organic molecules bonded to a support has been made.

These results have implications not only for the chromatographic character of surface-bonded silica phases but also for the behaviour of surface-immobilised catalysts. The influence of site–site interactions in non-rigid polymer-immobilised catalysts has been recognised[9,10] but the possibility that such interactions may also be important in monolayer coatings bonded to rigid, inorganic supports has not been so clearly appreciated. PAS, whose range also extends into the near i.r. region of the spectrum where H-bonding interactions can be studied, is a powerful new tool for studying such effects.

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