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SURFACE VS. BULK REACTIVITY IN A SOLID-STATE METHYL TRANSFER

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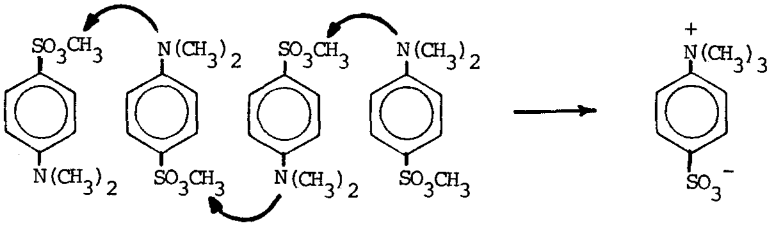
Summary. A methyl transfer in the crystalline state proceeds more slowly at the surface (as monitored by diffuse reflectance IR) than within the bulk solid (as monitored by NMR). Moreover, reaction intermediates accumulate only at the surface. These results are explained in terms of structural differences between the external and internal regions.

Methyl p-(dimethylamino)benzenesulfonate (A) rearranges to p-(trimethylammonium)benzenesulfonate zwitterion (B) about 25 times faster[1] as a solid at 81° than as a melt at 95°. Although solutions of A at 25° are stable indefinitely, reaction in the solid at 25° is half-over in 7 days. Isotope scrambling studies indicate that the fast solid-state methyl transfer takes place intermolecularly rather than intramolecularly.[1] X-ray data[1] reveal that the molecules of crystalline A are oriented such that the nitrogens are almost perfectly aligned with respect to an adjacent methyl group:



A B

Presumably, the reaction occurs by a chain mechanism during which the $N\cdots CH_3$ distance of 3.54 Å diminishes to the N/C bond length. This methyl transfer, considered a classic example of an orientation-related acceleration, has been subjected to more recent investigations including a Raman phonon spectroscopy study[2] and an extended Hückel calculation[3]. Our past experience with reactions at crystal surfaces[4,5] led us to wonder about the details of the reaction and, in particular, how the chemistry at the crystal surface compares with that inside the bulk crystal. We find, as described below, that the two regions behave quite differently.

Crystalline A, sieved to a 297-420 μ particle size, was placed in a test tube and thermostated at 50 ± 0.5°. Samples were removed periodically, mixed with 3:1 D_2O/CD_3OD (a solvent in which both A and B dissolve), and subjected to NMR analysis. A "% yield vs. time plot", obtained from the disappearance of an A peak at 3.1 ppm and from a corresponding formation of a B peak at 3.7 ppm, showed that the reaction reaches >98% at 24 ± 0.5 hours. When the experiment was repeated with A that had been powdered to a particle size less than 210 μ, the reaction time was distinctly longer: 48 ± 0.5 hours. This dependence of rate on particle size, not previously reported in the literature, was our first indication that surface phenomena may be playing a role in the reaction. As a consequence, we examined the reaction by diffuse reflectance infrared spectroscopy, a method which monitors only the outer regions of the solid.

Reaction samples (297-420 μ) at 50° were periodically cooled, mixed with a 100-fold excess of KBr, and placed in the sample holder of a Perkin-Elmer 983 IR spectrophotometer equipped with a data station and a Harrick diffuse reflectance attachment. Each mixture was scanned 10 times, averaged, plotted in a Kubelka-Munk format, flattened, and smoothed. The amount of product as a function of time was determined from the intensities of several peaks (*e.g.* 1452, 1350, and 1160 cm^{-1}) relative to an unchanging baseline point (4000 or 1720 cm^{-1}). Two conclusions are evident from the IR data: (a) The surface reaction is decidedly slower than the bulk reaction: 71 hours were required for the IR spectra to attain constancy. (b) The surface reaction is more complex than the bulk counterpart as indicated by a 2-fold rate discrepancy depending on which particular IR peak was scrutinized. This fact, plus the appearance of IR peaks belonging neither to A nor B, indicates the presence of intermediates. Although we were unable to characterize the intermediates, very likely they are ion-pairs of methyl *p*-(trimethylammonium)benzenesulfonate and *p*-dimethylaminobenzenesulfonate anion mentioned by Gavezzotti and Simonetta[3]. Our "whole crystal" NMR analyses were unable to detect these intermediates which, apparently, accumulate only at the crystal surface in low concentrations.

Molecular mobility and disorder, known to exist at solid surfaces[6,7], can explain the observed disparity between the NMR and IR-based rates. Since the molecules are more poorly aligned at the surface, methyl transfer rates in this region are reduced (as with the melts mentioned in the first paragraph). Disorder at the surface likewise impedes Bergman's chain mechanism[1], leading to a stepwise reaction and formation of intermediates. To our knowledge this represents the first example of discrete surface and bulk processes detected in a solid-state organic reaction.

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