Solid-state solvolysis induced *via* charge-transfer complexation by solid-phase grinding followed by contact with solvent vapor

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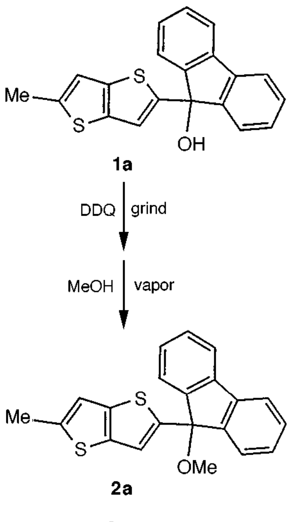
When 9-thienothienylfluoren-9-ol derivatives were ground together with DDQ then exposed to methanol vapor, solvolysis occurred to yield 9-methoxyfluorenes *via* the generation of a radical cation by solid-state single-electron transfer.

While organic reactions are usually carried out in solvents, solid-state reactions have also been extensively investigated.[1] The solid-state reactions between two different compounds have been realized by grinding a mixture of powdered reactant and reagent[2] or by using co-crystals in which two reactant molecules are preorganized in reactive positions.[3] Both of these methodologies, however, cannot be applied to solvolysis, for which dissolution of substrates in solvents is inevitable. We have recently achieved solid-state photosolvolysis[4] in the crystalline host–guest inclusion complexes with EtOH as a guest component.[5] We now report here on novel solid-state solvolysis by solvent vapor induced by solid–solid contact followed by gas–solid contact, from which a new consequence of solid-state grinding can be deduced.

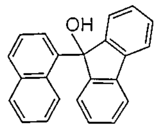
In a typical run, an equimolar mixture of 9-thienothienylfluoren-9-ol **1a** and dichlorodicyanoquinone (DDQ) was ground in a mortal and pestle and the resulting dark green solids were exposed to MeOH vapor below 5 °C for 6 h (Scheme 1). The resulting solids were shown to include a methoxy-substituted product **2a** in 42% yield. DDQ was recovered quantitatively. When substrate **1a** was ground alone and then exposed to MeOH vapor, the reaction did not occur at all, indicating that DDQ acts as a catalyst.[6]

Similarly, ethanolysis and propanolysis were accomplished for **1a** as well as for naphthyl-substituted **1b** and diols **1c** and **1d** to give the corresponding alkoxy derivatives in 5–32% yields. For **1a** and **1d**, tetracyanoethylene (TCNE) also promoted the solvolysis to give the methyl ethers in 70 and 51% yields, respectively, along with 16% of the dimethyl ether in the latter.

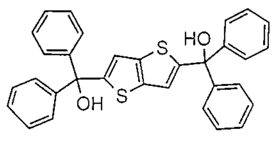


Scheme 1

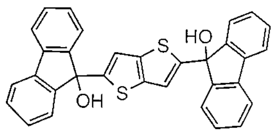
On the other hand, tetracyanoquinodimethane (TCNQ) and *p*-chloranil caused no solvolysis. In all cases, the solid states were retained throughout the procedure of grinding and exposure.



1b



1c

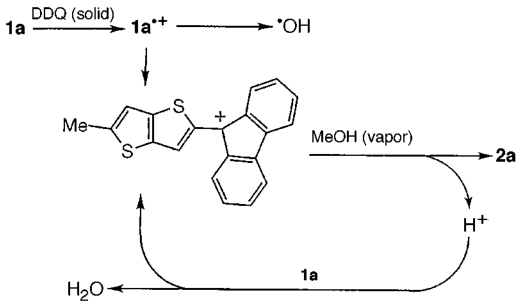


1d

The colored solids obtained by solid-state grinding of **1a** with DDQ exhibited an absorption maximum at 650 nm ascribed to a CT band, as measured by solid-state reflectance spectroscopy. EPR signals were observed for these solid samples.‡ Crystalline charge-transfer complexes were not obtained *via* recrystallization of **1a** and DDQ from MeCN solution. This was also the case for **1b** and **1c**; the charge-transfer complexation was realized only by grinding these compounds with the electron acceptor in the solid-state. The resulting solids exhibited EPR signals and solvolysis occurred upon solid–vapor contact.

For **1d**, a crystalline 1:1 charge-transfer complex was obtained from a highly concentrated colored solution of **1d** and DDQ in MeCN. In sharp contrast to the solids obtained by solid-state grinding, those obtained by recrystallization exhibited no EPR signals and did not undergo solvolysis upon exposure to solvent vapor. Furthermore, the ground mixture of **1d** and DDQ exhibited a charge-transfer band maximum (653 nm) at longer wavelength than the complex obtained by recrystallization (629 nm). All the above observations indicate that the solid-state grinding generates radical ions and that these species are essential to promote the solvolysis by vapor.

Catalytic effects of π-donors in the acetolysis of 2,4,7-trinitro-9-fluorenyl *p*-toluenesulfonate has been reported,[7] in which the π-donors are assumed to polarize the C-O bond leading to easy heterolytic bond cleavage. The present results appear to be different from such type of catalytic solvolysis in a solution. It has been quite often observed that radical cations generated *via* single-electron transfer undergo the cleavage of a σ-bond.[8] In order to see if such reaction occurs in the radical cation of **1a**, we have carried out the electrochemical oxidation of **1a** in MeOH and ascertained the formation of **2a**. This finding, however, does not settle the mechanism, because the precursor species to **2a** are only slightly generated in the ground solids; the spin concentration of the ground solids is estimated to be only 2% at most from the EPR signal intensity and furthermore **2a** is formed in mear trace amounts when the ground mixture is dissolved in MeOH. Thus the carbocation



Scheme 2

species should be propagated in the solid phase upon gas-solid contact.

As a most plausible mechanism at this stage, we assume that the methoxy substitution occurs in a catalytic chain process initiated by a small amount of the cation generated from the radical cation of **1a**, as depicted in Scheme 2.§ The acid-catalysed ether formation in the solid state was supported by the occurrence of the ethoxy substitution in a crystalline inclusion complex[9] **1d**·(EtOH)$_2$ upon grinding with toluene-*p*-sulfonic acid without solvent.

The reasons why only the ground mixtures of the substrates and acceptors show EPR signals and hence undergo the solvolysis by vapor should be discussed. The substrates used in this work are not planar molecules, and have irregular shape and conformational freedom. For such molecules, close packing in a periodic donor–acceptor arrangement is not easily attained upon recrystallization,¶ as noted already. On the other hand, solid-state grinding would force some of the molecules closer together while still being free from lattice control, and hence permit much stronger charge-transfer interactions than those in crystalline charge-transfer complexes derived from a solution.

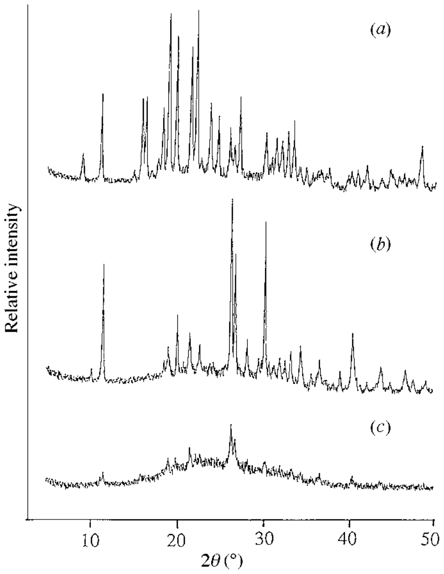


Fig. 1 Powder X-ray diffraction patterns of (*a*) **1a**, (*b*) DDQ and (*c*) a ground mixture of **1a** and DDQ

The above explanation is in line with the results of a powder X-ray diffraction study. The diffraction intensities of the ground solids of **1a** with DDQ decrease significantly as compared with those of each component (Fig. 1), indicating the collapse of the crystalline phase without reorganization into a new charge-transfer crystal phase. Despite the inability of the mixtures to give co-crystal packing, the charge-transfer contacts are strong enough to induce single-electron transfer, which could be partially due to the use of the planar moieties on **1a**. It has been reported that crystalline charge-transfer complexes can be formed by grinding together solid donor and acceptor components.[10] Such behavior has also been encountered for planar donor and acceptor molecules that can also co-crystallize from solution. Thus, it seems reasonable that the reactivity of the present solvolysis system using solvent vapor depends not only on the electron accepting and donating abilities, but also on the molecular shape, of the substrates and electron acceptors.

Notes and References

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‡ For the ground solids of **1a** and DDQ, an EPR signal occurs at $g = 2.0043$ with a simple profile of a type usually observed for monoradical species.

§ Alternatively the collapse of the radical cation to form H$^+$ and an alkoxy radical would be possible. In this case also H$^+$ would give the cation which enters into the chain process.

¶ Most of the substrates in this work act as host species for clathrate crystals, indicating that it is difficult for these compounds to crystallized without incorporation of other guest molecules. See also ref. 9.

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