Structural studies of solid and solution phase reaction products between 
*p*-benzoquinone and 2-aminobenzoic acid

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Solid and solution phase reaction products between 
*p*-benzoquinone and 2-aminobenzoic acids have been 
characterized using XRD, EPR, NMR and electronic 
spectra. The solid state reaction product is assigned as 1:1 
addition complex while the solution phase reaction 
product is 1:2 oxidative addition product of 
*p*-benzoquinone with aminobenzoic acid; both are charge 
transfer complexes.

The preparation of charge transfer complexes from 
solid-solid reactions is of current interest1–5. Some 
of the merits of solid state reactions have been listed 
recently6. The use of solvents and its effects can be 
avoided if a reaction goes to completion in the solid phase.

Curtin et al1–3 have prepared a number of 
crystalline complexes between polymethylated quinones and hydroquinones as stable crystalline solids both in solution and solid phase reactions. Recently, we have also prepared charge transfer complexes between *p*-benzoquinone and *o*-, *m*-, and 
*p*-aminobenzoic acids and have reported that these 
are loose Mulliken CT complexes which lose colour 
due to sublimation of *p*-benzoquinone on keeping in air. Now, we have found that these complexes are quite unstable in solution phase and that their solution in acetonitrile transforms to give addition products.

The present note reports the structures of solid and 
solution phase reaction products in the reaction of 
*p*-benzoquinone and 2-aminobenzoic acid as obtained from XRD, NMR, EPR, mass and UV-vis 
spectral studies. This is the first study of such compounds in which the two products differ in the nature of interaction and in stoichiometry.

**Experimental**

Benzoquinone was repeatedly crystallized from 
AR benzene (m.pt. 113°C). All other reagents were 
from Koch-Light. The coloured complexes were 

obtained from solid state reactions by grinding the 
solid reactants in pestle and mortar for 20 min. The 
solution phase reaction product was obtained by 
mixing the reactants in acetonitrile. This mixture was 
refluxed for 6 h and the precipitates recrystallized 
from acetonitrile. Separation of the various products 
was carried out by column chromatography using 
silica gel (BDH) as adsorbent, benzene and benzene + methanol were used as eluants. All the fractions 
collected from column chromatography were 
compared with chromatograms of reaction mixture 
for checking their identity. The EPR spectra was 
recorded on spectrophotometer type JES-FE 3XG. 
The PMR spectra of solid and solution phase reaction 
products and of pure components were recorded in 
DMSO and D$_2$O + DMSO mixture to check the 
exchangeable signals on a JEOL-PMX60 spectrometer. The UV/VIS spectra were recorded in 
methanol on spectrophotometer Shimadzu 240. 
X-ray powder pattern of the two reaction products 
and of pure components were recorded on PW 1820 
diffractometer using Cu K$_\alpha$ radiation.

**Results and discussion**

Figure 1 shows XRD data of the reactants and 
products obtained from solid and solution phase 
reactions in case of *p*-benzoquinone and 
2-aminobenzoic acid. Table 1 further shows that the 
d-values with corresponding intensities for the two 
products do not match at all. The results thus show 
that the products are crystalline and that the solid and 
solution phase reaction products are different.

The solution of solid-solid adduct of *p*-benzo-
quione and 2-aminobenzoic acid on refluxing in 
acetonitrile gave dark brown precipitates. These were 
purified by recrystallization from acetonitrile to get 
dark red crystals, m.p. 327°C, M$^+$ m/e 378. Its $^1$H NMR 
showed a 2H singlet at 66.5 (benzoquinone), 8H 
multiplet at 67.0-8.3 (anthranilic acid) along with two 
exchangeable 2H singals at 610.8 and 615.7 due to 
-NH and -COOH protons. Its IR spectrum 
showed the absence of NH$_2$ group. From these 
spectral data, this product could be assigned as 1:2 
obxidative addition product of *p*-benzoquinone with 
2-aminobenzoic acid. This product could also be 
obtained by refluxing the solution of *p*-benzoquinone 
and 2-aminobenzoic acid in acetonitrile for 6h. The 
filtrate on column chromatography gave reduced 
form of *p*-benzoquinone and 2-aminobenzoic acid. 
Therefore *p*-benzoquinone with 1 equivalent of
aminobenzoic acid gives 1:2 adduct and hydroquinone along with unreacted 2-aminobenzoic acid. Thus on refluxing the solution of p-benzoquinone and 2-aminobenzoic acid (1:1) in acetonitrile for 6h TLC showed three spots due to (i) hydroquinone (ii) a product and (iii) unreacted acid. From these results we envisaged that 2-aminobenzoic acid initially adds on benzoquinone-then another benzoquinone molecule oxidizes this adduct and gets itself reduced which further undergoes addition of 2-aminobenzoic acid and oxidation to get the final product. So stoichiometrically, 3-equivalents of p-benzoquinone should be sufficient to react with 2 moles of 2-aminobenzoic acid as,

So on refluxing 3 equivalents of quinone with 2 equivalents of 2-aminobenzoic acid, 2 equivalents of hydroquinone could be isolated. These observations further support that p-benzoquinone sometimes participate in oxidation of intermediate adduct.

Similarly p-benzoquinone with 3-aminobenzoic acid and 4-aminobenzoic acid in the solution phase gives oxidative addition products. The formation of these products would be discussed in a subsequent paper in the near future.

Solid-solid reaction product however cannot be analyzed by column chromatography because mixing with the solvent may cause further reaction and give a product as obtained in solution phase reaction. The H NMR of solid phase reaction product of p-benzoquinone + 2-aminobenzoic acid shows 4H singlet due to p-benzoquinone at 6.58 and 4H multiplet due to 2-aminobenzoic acid at 7.0 to 7.88. In addition, it shows 2H exchangeable signals at 8.18 due to NH2 and 1H exchangeable signal at 6.98 due to -OH. From the spectral data, the compound is assigned as 1:1 CT complex of p-benzoquinone with 2-aminobenzoic acid.

The EPR spectral data for reactants and products showed that both the solid phase and solution phase reaction products gave EPR signals with g value 2.01 and 2.03 respectively although the reactants gave no signal.

<table>
<thead>
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<th>Table 1—X-ray diffraction data for reactants and products</th>
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<td>p-Benzoquinone</td>
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The UV-VIS spectra of solid phase reaction product shows λ_max at 225, 280 and 410 nm, whereas solution phase product gives λ_max at 245, 285, 335, 390 nm max reactants- p-benzoquinone (λ_max: 270, 435 nm) and 2-aminobenzoic acid (λ_max: 245, 335). On the basis of these studies, the solution phase reaction product and solid phase reaction product have been assigned the structures I and II.

In I and II, electron transfer occurs from aminobenzoic acid to benzoquinone as shown by arrows.

References