Host–Guest Complex Formation by a Solid–Solid Reaction

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Some host–guest complexes have been formed by mixing the components in the solid state, and complexation has been shown to proceed with some selectivity.

The formation of quinhydrone by a solid–solid reaction of quinone and hydroquinone has long been known.[1,2] Recently, Curtin and co-workers studied the mechanism of the solid–solid reaction and found that the quinone sublimes and its vapour attacks certain sides of the hydroquinone crystals preferentially.[3] We have now found that some hosts and guests form complexes with no charge-transfer interaction, like quinhydrone, by mixing these components in the solid state, and also that some selectivity including enantioselectivity, is apparent in the solid–solid reaction. One of the most interesting observations is the catalytic behaviour shown by the host compound in a photoreaction of the guest compound.

In a typical example, when a mixture of finely powdered 1,1,6,6-tetraphenylhexa-2,4-diyne-1,6-diol (**1**) and an equimolar amount of finely powdered benzophenone was agitated using a test-tube shaker (of the type specified in Table 1) for 0.2 h at room temp., a 1 : 1 complex involving these two compounds was formed. Using the same method, chalcone, pyridone, and *p*-dimethylaminobenzaldehyde formed 1 : 2 complexes with (**1**) (Table 1). Termination of the complex forming reaction was determined by m.p. measurements and by i.r. spectroscopy and the structure of the complex was identified by comparing its m.p. and i.r. spectrum with those of the complex prepared in solution.[4,5]

In the case of pyridone, which is present as a tautomeric mixture with 2-hydroxypyridine even in the solid state,[6] inclusion occurs only in the keto form. A similar result has been obtained from the complexation experiment in solution.[5]

9,10-Dihydroxy-9,10-diphenyl-9,10-dihydroanthracene (**2**) and 1,1-di(*o*-hydroxyphenyl)cyclohexane (**3**) also form complexes with some guest compounds by intimate mixing in the solid state (Table 1). However, some differences in complexation behaviour were observed between the solid state and solution experiments. In ethyl acetate, (**3**) formed a mixture of the 3 : 2 and 2 : 1 complexes, but only the 2 : 1 complex was formed in the solid state. Although no complexation of (**3**) and naphthoquinone occurs in any solvent, a 2 : 1 complex was obtained from the solid–solid reaction (Table 1).

Table 1. Host–guest complex formation by their solid–solid reaction.

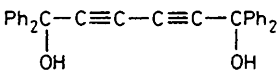
			Complex	
Host	Guest	Reaction time/h[a]	Host : guest	M.p./°C
(**1**)	Ph_2CO	0.2	1 : 1	96
(**1**)	Chalcone (**6**)	1.0	1 : 2	87—98
(**1**)	2-Pyridone	48	1 : 2	177—182
(**1**)	*p*-$Me_2NC_6H_4CHO$	24	1 : 2	148—149
(**2**)	Ph_2CO	24	1 : 1	127—130
(**3**)	*p*-Benzoquinone	24	2 : 1	Not clear
(**3**)	1,4-Naphthoquinone	48	2 : 1	96—104

[a] Agitated using a test-tube shaker of S-3 type from the Tokyo Rikakikai Co. Ltd.

By grinding *N,N,N′,N′*-tetraisopropyloxamide (**4**) and *p*-cresol by agate mortar and pestle, 1 : 2 and 1 : 1 complexes were formed depending on the amount of *p*-cresol used. In the case of a 1 : 2 ratio of (**4**) : *p*-cresol, the mixture turned to liquid on grinding and the 1 : 2 complex was formed quantitatively within one hour. In the case of a 1 : 1 ratio of reactants, the 1 : 1 complex was formed by grinding the mixture for 12 h to give a quantitative yield. The production of local high temperatures was not observed during the grinding; moreover these temperatures are not thought to cause the reaction since complexation proceeds even at about 0 °C.

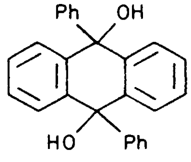
Enantioselective complexation of cyanohydrin with brucine in solution has been reported.[8] In this case, racemic cyanohydrin is completely converted into one enantiomer by complexation and racemisation through a brucine-catalysed equilibrium. Similar phenomena occurred in the solid state. When brucine and an equimolar amount of 1-cyano-2,2-dimethyl-1-phenylpropan-1-ol (**5**) was shaken for 24 h, a 1 : 1 complex was formed, which upon distillation gave optically active (**5**) {$[\alpha]_D$ +1.0°, 6.3% enantiomeric excess (e.e.)} in almost quantitative yield. However, optically active (**5**) was not obtained by distillation alone of (**5**) from a mixture with brucine. Therefore, the enantiomerisation and enantioselective complexation must occur in the solid state.

We also found that a combination of the solid phase complexation and irradiation is useful for a continuous

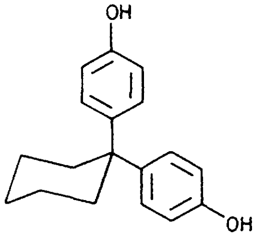


$Ph_2\underset{OH}{C}-C\equiv C-C\equiv C-\underset{OH}{C}Ph_2$

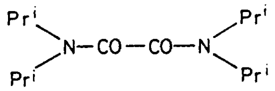
(**1**)



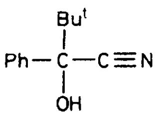
(**2**)



(**3**)

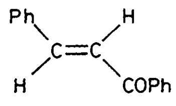


(**4**)

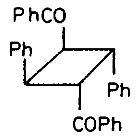


$Ph-\overset{Bu^t}{\underset{OH}{C}}-C\equiv N$

(**5**)



(**6**)



(**7**)

stereoselective photoreaction. For example, irradiation of a 1 : 1 mixture of (**1**) and chalcone (**6**) during shaking for 10 h gave the *syn*-head-to-tail dimer (**7**) in 80% yield.† Since the irradiation of (**6**) itself in a crystalline state gives a mixture of isomers of (**7**) in a poor yield,[9] and the irradiation of a 1 : 2 complex of (**1**) and (**6**) in the solid state for 6 h gives (**7**) in 90% yield,[4,5,10] the 1 : 2 complex is expected to be produced during the shaking. The irradiation is also effective for a 1 : 2 mixture of (**1**) and (**6**), since after 40 h of reaction under shaking conditions, (**7**) was obtained in 82% yield. Interestingly, this procedure is also effective for a 1 : 4 mixture of (**1**) and (**6**), since (**7**) was obtained in 87% yield after 72 h irradiation under the same conditions. This shows that (**1**) can be used repeatedly similar to a catalyst, *viz.* (**1**) which is released from the complexation with (**6**) by its photodimerisation goes on to form a complex with another molecule of (**6**).

In spite of the above, the mechanism of the complexation by the solid–solid reaction is not clear. The possibility of a solid–vapour reaction which has been postulated for the quinhydrone formation[3] seems not to be applicable to our reactions, except in the case of benzoquinone and naphthoquinone, because all the host and guest compounds used are not sublimable. Only the quinones are capable of being sublimed.

Received, 12th June 1986;‡ Com. 807

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† All irradiations were carried out using a high-pressure mercury lamp at room temperature.

‡ Received in revised form, 10th September 1986.