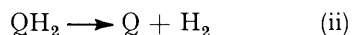
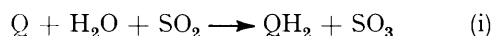


## Applications of High-potential Quinones. Part 12.<sup>1</sup> Studies on an Organic Reaction Cycle for the Production of Hydrogen from Water

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Quinones and sulphur dioxide are of potential use in an organic reaction cycle for water decomposition involving (i) reduction of the quinone with aqueous sulphur dioxide and (ii) dehydrogenation of the resulting hydroquinone by catalytic or other methods. Participation of water in stage (i) has been established by deuterium labelling in inert solvents. Procedures for partial transfer of hydrogen involving boron compounds in stage (ii) are discussed.

THE virtues of hydrogen as a non-polluting fuel are manifest,<sup>2</sup> and, if more economic processes can be developed for the breakdown of water into its elements, the hydrogen economy could become a reality. Inorganic reaction cycles for the decomposition of water into hydrogen and oxygen have been the subject of much recent study,<sup>3</sup> the main disadvantages being the high temperatures required for some of the individual stages, and the unfavourable equilibria involved in the endothermic reactions.<sup>4</sup> Organic 'energy cycles' have been relatively little investigated, and in this report we discuss a reaction cycle based upon the reduction of quinones with water and sulphur dioxide:



As well as forming hydrogen from water, this cycle has the advantage of converting sulphur dioxide into sulphuric acid, a process which could be of value in the removal of pollutant sulphur dioxide from the atmosphere.

*Stage (i): Reduction of the Quinone.*—Early work<sup>5</sup> on this type of system, using quinones of fairly low redox potential, revealed a variety of side reactions. (Addition of sulphite and related anions to unsubstituted quinones has long been of practical use in photography.<sup>6</sup>) With benzoquinone itself, and its simple derivatives, aqueous sulphur dioxide is oxidised to sulphuric acid, but addition of sulphite to the quinone nucleus also occurs, and the reaction can become quite complex.

High-potential quinones are particularly reactive towards aqueous sulphur dioxide (the reaction has been employed for some years in this laboratory to destroy excess of the quinone in procedures utilizing high-potential quinones for dehydrogenation), and the most useful of such quinones, chloranil and 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ), are fully substituted, thereby reducing the possibility of addition of sulphite to the benzoquinone nucleus.

No obvious reaction occurs when sulphur dioxide is bubbled through a solution of DDQ in benzene or dioxan—the solution remains clear orange. When water is added to the solution, dichlorodicyanohydroquinone

<sup>1</sup> Part 11, D. R. Brown and A. B. Turner, *J.C.S. Perkin II*, 1978, 165.

<sup>2</sup> C. Marchetti, *Chem. in Britain*, 1977, **13**, 219; C. A. McAuliffe, *ibid.*, 1973, **9**, 559.

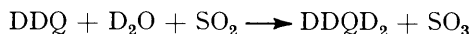
<sup>3</sup> T. H. Maugh, *Science*, 1972, **178**, 849.

<sup>4</sup> M. D. Archer, 'Phytochemistry,' *Chem. Soc. Specialist Periodical Reports*, 1975, vol 6, p. 739; 1976, vol. p. 561.

<sup>5</sup> J. W. Dodson, *J. Chem. Soc.*, 1914, 2435; 1930, 2498.

<sup>6</sup> K. T. Finley, 'Chemistry of the Quinonoid Compounds,' ed. S. Patai, Wiley, New York, 1974, pp. 936–939.

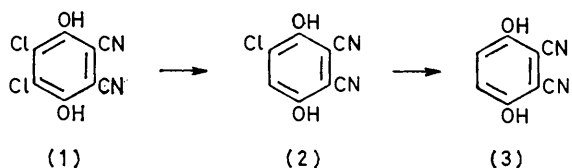
(DDQH<sub>2</sub>) is soon formed and the solution is rapidly decolourised. Precipitation of the hydroquinone is complete after a short time at room temperature. The participation of water in this reaction has been demonstrated by the use of deuterium oxide in place of water, when the isolated hydroquinone is found by mass spectral analysis to contain two deuterium atoms:



This confirms that water is split by the reagent system, with the hydrogen atoms of DDQH<sub>2</sub> arising by dehydrogenation of sulphurous acid. Similarly it has been shown by g.l.c. that 3,5-di-*t*-butyl-1,2-benzoquinone is reduced quantitatively by sulphur dioxide in the presence of water.

*Stage (ii): Dehydrogenation of the Hydroquinone.*—Nitric acid and other inorganic reagents such as lead and manganese dioxides can be conveniently deployed to reoxidise the hydroquinones,<sup>7</sup> albeit with re-formation of a molecule of water for each molecule of hydroquinone oxidised. Thus no systematic investigation of conditions under which the hydroquinone can be dehydrogenated, with recovery of the hydrogen as such, have been made. It is clear that quinones of high redox potential will yield hydroquinones which will be difficult to dehydrogenate, but our investigations have been mainly concerned with high-potential systems, since fully substituted quinones lacking alkyl substituents are less susceptible to side reactions.

Since solar energy would be the most convenient method of driving the hydrogen fuel cell, we first examined the photochemistry of DDQH<sub>2</sub>. This was found to undergo successive loss of the chlorine atoms when irradiated in aqueous methanol to give 2,3-dicyano-1,4-hydroquinone (3), and the ease of reaction



clearly indicated that DDQH<sub>2</sub> was unsuitable for use in a photochemical reaction cycle. The mono- and dechlorinated products were identified by g.l.c.–mass spectrometry of their trimethylsilyl ethers. Irradiation of the dicyanohydroquinone gave mainly very polar material, which appeared to be polymeric. Ferris and Antonucci<sup>8</sup> have recently obtained benzoxazole by photolysis of *o*-cyanophenol, and it is likely that the material of higher molecular weight contains polymerized oxazoles. G.l.c.–mass spectrometric analysis of the

<sup>7</sup> D. Walker and J. D. Hiebert, *Chem. Rev.*, 1967, **67**, 153.

<sup>8</sup> J. P. Ferris and F. R. Antonucci, *J. Amer. Chem. Soc.*, 1974, **96**, 2010, 2014.

<sup>9</sup> L. M. Jackman, *Adv. Org. Chem.*, 1960, **2**, 329.

<sup>10</sup> Ger. Offen., 2,263,942/1974 (*Chem. Abs.*, 1975, **82**, 61230q).

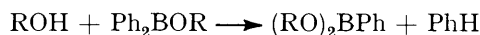
<sup>11</sup> Cf. C. Masters, A. A. Kiffen, and J. P. Visser, *J. Amer. Chem. Soc.*, 1976, **98**, 1357; H. Imai, T. Nishiguchi, and K. Fukuzumi, *J. Org. Chem.*, 1974, **39**, 1622.

traces of volatile products showed the major component to have a molecular weight of 193. It was tentatively identified as methyl 2-cyano-3,6-dihydroxybenzoate. No quinonoid products were detected.

*Catalytic Dehydrogenation.*—Catechols and hydroquinones are not noted for their ability to transfer hydrogen under mild conditions,<sup>9</sup> although it has been shown that catalytic dehydrogenation at high temperatures is a feasible approach for the recovery of hydrogen.<sup>10</sup> Our own attempts, using various systems both with and without hydrogen acceptor, to transfer hydrogen from these dihydric phenols to another molecule (or to produce molecular hydrogen) gave no indication that suitably mild conditions could be found. Results of experiments using the soluble catalyst trisphenylphosphinerhodium chloride, RhCl(PPh<sub>3</sub>)<sub>3</sub>, for the dehydrogenation of hydroquinone itself, in the presence of acetone as acceptor, under an inert atmosphere, were negative. Small amounts of benzoquinone were only obtained when we failed to exclude oxygen rigorously.

Attempts to transfer hydrogen from 3,5-di-*t*-butylcatechol (1) under both homogeneous<sup>11</sup> [RhCl(PPh<sub>3</sub>)<sub>3</sub> or RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> catalysts] and heterogeneous conditions (Pd–C catalyst) to a variety of acceptors failed.

*Boron Compounds.*—The use of hydrogen gas as a fuel for motor vehicles is subject to storage problems. Interstitial metal hydrides may provide a solution, but storage of the fuel in the form of the solid sodium borohydride or organoboranes for subsequent controlled regeneration is another possibility. Studies have therefore been undertaken on boron derivatives of the catechol (4) in the hope that hydrogen would be transferred as shown in the Scheme. However, formation of the dioxaborole (7) is the preferred route when the catechol (4) reacts with the ethanolamine complex of diphenylborinic acid (8). The borole (7) is readily prepared from the catechol (4) and phenylboronic anhydride by the method of Kuvila *et al.*<sup>12</sup> The adduct (5) could not be isolated, even when the reaction with the ethanolamine complex (8) was conducted at low temperature. The process (4) → (5) → (7) is analogous to the high-temperature dephenylation of borinic esters by monohydric alcohols:<sup>13</sup>



Whilst it does achieve partial transfer of hydrogen, it is difficult to see how the quinone (6) could be obtained readily from the borole (7), which is a particularly stable compound.

Anodic oxidation of DDQH<sub>2</sub> has recently been achieved with yields in the region of 75%.<sup>14</sup> To be of any use in an efficient cycle for water decomposition, the yield would have to be improved, and the process shown

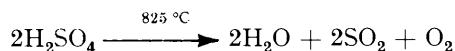
<sup>12</sup> H. G. Kuvila, A. H. Keough, and E. J. Soboczenski, *J. Org. Chem.*, 1954, **19**, 780.

<sup>13</sup> E. W. Abel, W. Gerrard, and M. F. Lappert, *J. Chem. Soc.*, 1958, 1451.

<sup>14</sup> U. H. Brinker, M. Tyner, and W. N. Jones, *Synthesis*, 1975, 671.

to be more economical than the direct electrolysis of water.

The sulphur dioxide used in the reduction of the quinone is itself oxidised to sulphuric acid, which can be recycled:<sup>2</sup>



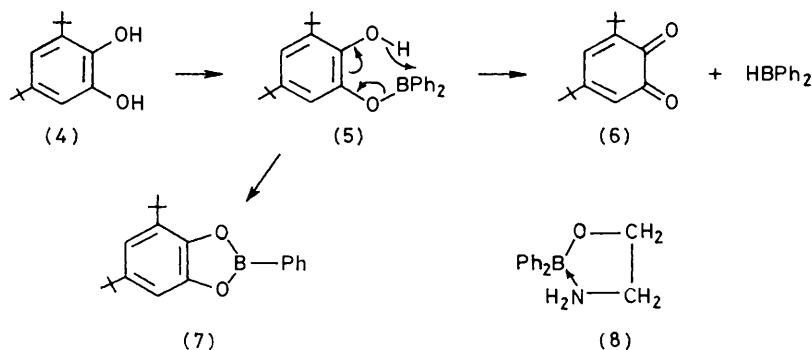
However, in an integrated chemical plant, this may not be necessary as the sulphuric acid could be an end-product.

Large-scale application of this type of cycle for hydrogen production will depend upon the discovery of

(500 mg; excess) was added, whereupon the yellow solution was slowly decolourised. G.l.c. showed quantitative conversion into 3,5-di-*t*-butylcatechol ( $t_R$  15.5 at 180 °C) after 3 h (the quinone had  $t_R$  13.5 at 180 °C).

*Attempted Transfer Hydrogenations.*—*General procedure.* A solution of 3,5-di-*t*-butylcatechol (100 mg) in the acceptor solvent (20 ml) was heated under reflux in the presence of a catalytic amount of transfer agent under nitrogen for 12 h. The resulting mixtures were examined by t.l.c. and g.l.c. No trace of quinone was detected when 5% Pd-C (for toluene, xylene, and acetone), or Rh(PPh<sub>3</sub>)<sub>3</sub>Cl (for acetone, butan-2-one, and cyclohexanone), or Ru(PPh<sub>3</sub>)<sub>3</sub>Cl<sub>2</sub> (for cyclohexanone, toluene, and cycloheptene) was used.

*2-Phenyl-4,6-di-*t*-butyl-1,3,2-benzodioxaborole.*—A solution



SCHEME 1

an efficient method for dehydrogenation of the hydroquinone or an efficient hydrogen transfer to boron. Material losses in the reduction stage of the cycle are small, but, so far, losses incurred in the dehydrogenation stage would make the process uneconomic.

#### EXPERIMENTAL

For general directions see Part 11.<sup>1</sup>

*Reduction of DDQ.*—(a) *With H<sub>2</sub>O-SO<sub>2</sub>.* Dry sulphur dioxide was bubbled through a solution of DDQ (258 mg, 1.1 mmol) in dioxan (10 ml) for 2 min, and the orange solution was left at room temperature for 30 min. No change was observed. Water (20 mg, 1.1 mmol) was added, and formation of a precipitate began after a few minutes. The solution was colourless after 4 h, when the precipitated hydroquinone (214 mg, 85%), m.p. >300°, was collected; *m/e* 230 (*M*<sup>+</sup>, 50%), 228 (*M*<sup>+</sup>, 100), 202 (16), and 200 (32). Its i.r. spectrum was identical to that of authentic DDQH<sub>2</sub>.

(b) *With D<sub>2</sub>O-SO<sub>2</sub>.* Sulphur dioxide was bubbled for 3 min through a solution of DDQ (646 mg, 2.8 mmol) in anhydrous benzene (20 ml). No change was observed. Deuterium oxide (280 mg, 14 mmol) was added to the orange solution, and a colourless precipitate was formed immediately. 5,6-Dichloro-2,3-dicyano-1,4-bisdeuterio-oxybenzene (507 mg, 79%), m.p. >300°, was collected (Found: *M*<sup>+</sup>, 229.9620. Calc. for C<sub>8</sub>D<sub>2</sub>Cl<sub>2</sub><sup>35</sup>N<sub>2</sub>O<sub>2</sub>: 229.9619); *m/e* 232 (*M*<sup>+</sup>, 50%), 231 (14), 230 (*M*<sup>+</sup>, 100), 229 (14), 204 (14), 202 (28), 111 (10), and 87 (18);  $\nu_{\text{max}}$ . 2 420, 2 260, 1 260, 1 080, 1 010, 945, and 895 cm<sup>-1</sup>).

*Reduction of 3,5-Di-*t*-butyl-1,2-benzoquinone.*—Sulphur dioxide was passed through a solution of the quinone (101 mg) in toluene (50 ml). No change was noted until water

of 3,5-di-*t*-butylcatechol (100 mg, 0.45 mmol;  $t_R$  7.5 min at 200 °C) and phenylboronic anhydride (47 mg, 0.45 mmol) in methanol (10 ml) was warmed to 50 °C. G.l.c. showed quantitative conversion into a new compound ( $t_R$  38 min at 200 °C) after a few minutes. (For comparison, under the same conditions catechol had  $t_R$  2.3 min and 2-phenyl-1,3,2-benzodioxaborole had  $t_R$  6.2 min.) After 30 min the solvent was removed *in vacuo* and the residual quinone was crystallised from methanol to give the dioxaborole as needles, m.p. 61–62° (99 mg, 71%) (Found: C, 77.7; H, 8.4%; *M*<sup>+</sup>, 307.9961. C<sub>20</sub>H<sub>25</sub>BO<sub>2</sub> requires C, 77.9; H, 8.1%; *M*<sup>+</sup>, 307.9964), *m/e* 308 (*M*<sup>+</sup>, 16%), 294 (13), 293 (100), and 292 (16);  $\delta[(\text{CD}_3)_2\text{CO}]$  1.35 (s, Bu<sup>t</sup>), 1.50 (s, Bu<sup>t</sup>), and 7.21, 7.50, and 8.08 (m, ArH),  $\nu_{\text{max}}$ . 1 600, 1 320, 1 260, 1 240, 1 130, 1 070, 1 020, 970, 850, 825, 755, 690, and 660 cm<sup>-1</sup>).

*Reaction of 3,5-Di-*t*-butylcatechol with Diphenylboronic Acid-Ethanolamine Complex.*—(i) Ethereal solutions (5 ml) of the catechol (100 mg, 0.45 mmol) and the borinate (100 mg, 0.45 mmol) were mixed at 20 °C. The solution became yellow after 3 h. Solvent was removed *in vacuo* at 20 °C, and the residual orange oil was washed with water (3 × 5 ml) to remove ethanolamine, redissolved in ether, and dried (MgSO<sub>4</sub>). Evaporation as before gave a gum which could not be crystallised; *m/e* 308 (16%), 294 (12), 293 (100), and 292 (15).

(ii) A solution of the catechol (100 mg) and the borinate (100 mg) in toluene (25 ml) was heated under reflux for 3 h, and evaporated to dryness *in vacuo*. The residual gum was crystallised from methanol to give the benzodioxaborole (90 mg, 65%), m.p. 60–62°, mixed m.p. 60–62° with material described above.

*Photolysis of DDHQ<sub>2</sub>.*—(a) *In aq.* MeOH. A solution of the hydroquinone (540 mg) in methanol (200 ml) and water (400 ml) was irradiated through Pyrex with a 500 W

medium-pressure Hanovia mercury arc for 7 h. After removal of the solvent *in vacuo*, p.l.c. of the residue on silica gel [developing with ethanol-toluene (1:3), and eluting the main mobile zone] gave material which, although it could not be purified further, appeared to be 2-chloro-5,6-dicyano-1,4-hydroquinone, *m/e* 196 ( $M^+$ , 16%), 194 ( $M^+$ , 100%), 166 (25), and 76 (13);  $\delta(\text{CD}_3\text{OD})$  7.2 (s);  $\nu_{\text{max}}$ . 3 600—3 300, 2 230, 1 245, 1 055, 980, and 855  $\text{cm}^{-1}$ .

G.l.c.-mass spectrometry on the crude photolysate after trimethylsilylation by the method of Klebe *et al.*<sup>15</sup> gave two main components: 1,4-bis(trimethylsilyloxy)-2,3-dicyanobenzene,  $t_R$  5.0 min at 190 °C; *m/e* 304 ( $M^+$ , 20%), 290 (22), 289 (100), and 73 (51); and 2-chloro-5,6-dicyano-1,4-bis(trimethylsilyloxy)benzene,  $t_R$  6.5 min at 190 °C; *m/e* 340 ( $M^+$ , 5%), 338 ( $M^+$ , 15%), 325 (33), 324 (15), 323 (100), and 73 (100). G.l.c.-mass spectrometry on the bistrimethyl-

silyl ether of DDQH<sub>2</sub>,  $t_R$  6.0 min at 220 °C, showed *m/e* 374 ( $M^+$ , 7%), 372 ( $M^+$ , 13%), 359 (50), 358 (12), 357 (85), and 73 (100).

(b) *In aq.* EtOH. A solution of the hydroquinone (120 mg) in ethanol (40 ml) and water (40 ml) was irradiated as above for 1 h. Work-up as before gave a brown gum which was subjected to p.l.c. on silica gel, developing with ethyl acetate-hexane (1:1). Elution of the zone  $R_F$  0.2 (blue fluorescence under u.v.) gave 2,3-dicyanohydroquinone (24 mg, 24%) as needles, m.p. 230° (decomp.) (from dioxan), identical (mixed m.p., i.r.) with an authentic sample.<sup>16</sup>

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<sup>15</sup> J. F. Klebe, H. Finkbeiner, and D. M. White, *J. Amer. Chem. Soc.*, 1966, **88**, 3390.

<sup>16</sup> K. Wallenfels, G. Buchmann, D. Hofmann, and R. Kern, *Tetrahedron*, 1965, **21**, 2239.