Tetrahedron Vol. 49, No 1, pp. 105-112, 1993
Printed in Great Britain

0040-4020/93 $5.00+.00

SOLID STATE REDOX CHEMISTRY OF HYDROQUINONES AND QUINONES

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(*Received in UK* 1 *October* 1992)

***Abstract** : Solid state ceric ammonium nitrate (CAN) oxidation of hydroquinones to the corresponding quinones, gives best results when operating with ultrasonic irradiation. Nitrogen dioxide plays a key role in these "solid-solid" oxidations. The oxidation of hydroquinones to quinones can also be achieved in a unique "solid-solid-solid" reaction, i.e., by using a limited amount of CAN in the presence of a full equivalent of a solid cooxidant such as* $KBrO_3$. *Reduction of quinones with sodium dithionite in the solid state gives rise to the corresponding highly colored quinhydrones and, eventually, to hydroquinones.*

Solid state organic chemistry has attracted considerable interest in recent years.[1] Remarkable regio and steroselectivity has been found in several solid state reactions such as phenol coupling,[2] ketone reduction,[3] inclusion phenomena,[4] photochemistry,[5] and some others.[6]

Herein we describe solid state redox chemistry of quinones[7a] and hydroquinones.[7b] To outline, we report that ceric ammonium nitrate (CAN)[8] oxidizes hydroquinones to the corresponding quinones and, more interestingly, that this oxidation can be carried out with only a limited amount of oxidant provided that a full equivalent of a third solid component such as potassium bromate is also present![9] Conversely, quinones can be reduced to the corresponding quinhydrones in the solid state by the action of sodium dithionite.

The oxidation of hydroquinones by CAN[10] was carried out by grinding together with a pestle and mortar both the hydroquinone substrate (HYQ) and reactant (CAN) for a few minutes (5-10) and keeping the solid mixture in a closed vial for several days, with occasional shaking (Method A). Table 1 (Entries 1-6) illustrates the results obtained with the hydroquinones shown in Fig 1. Color changes were noticed immediately after grinding (from gray to yellow or yellow-orange) as well as the formation of red-brown vapours of nitrogen dioxide ($NO_2^{\bullet}$).[11] In accordance with the view that this gaseous oxidant takes part in the oxidation, best results are observed when the solid mixture was kept in a closed vessel (entries 1-6, Table 1).[12]

As illustrated in Table 1 (entries 1-6), (almost) quantitative yields of quinones were achieved when a 1:1 (CAN : HYQ) stoichiometry was used. Lower CAN ratios gave lower conversions and yields, and higher ratios

(2:1 or 3:1) induced progressive browning, only substantially reduced yields (or none) of quinones being obtained by extraction with ether.

Table 1

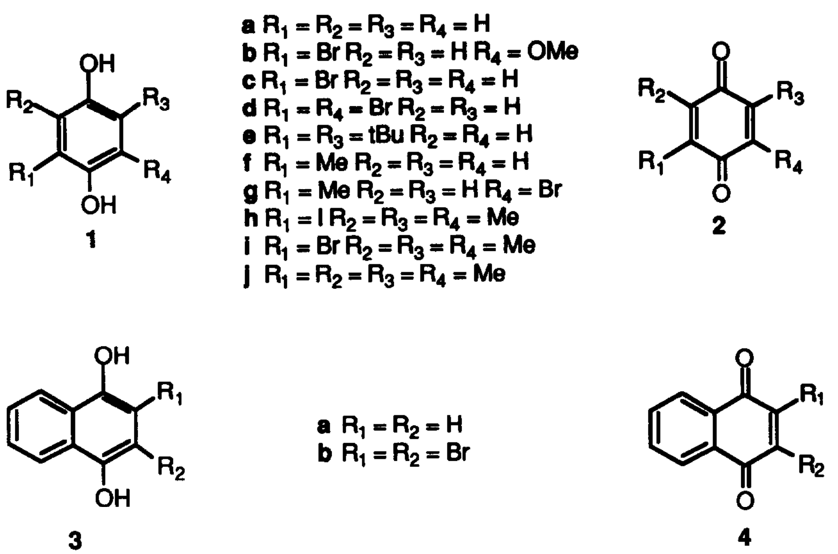
Solid State CAN and CAN/$KBrO_3$ Oxidation of Hydroquinones (HYQ)

Entry	Substrate (HYQ)	CAN:$KBrO_3$:HYQ molar ratio	Oxidation Method	Time (days)	Conversion (%)	Yield of Quinones **2** or **4** (%)
1	**1a**	1 : 0 : 1[c]	A	2	100	**2a** (84)[e]
2	**1b**	1 : 0 : 1[c]	A	2	100	**2b** (87)[e]
3	**1c**	1 : 0 : 1[c]	A	2	100	**2c** (85)[e]
4	**1d**	1 : 0 : 1[c]	A	2	100	**2d** (88)[e]
5	**1e**	1 : 0 : 1[c]	A	2	100	**2e** (98)[e]
6	**3a**	1 : 0 : 1[c]	A	2	100	**4a** (93)[e]
7	**1e**	0.04 : 1 : 1[c]	B	12	100	**2e** (80)[e]
8	**1d**	0.04 : 1 : 1[c]	B	12	100	**2d** (72)[e]
9	**1e**	0.04 : 1 : 1[b]		12	55	**2e** (55)[d]
10	**1e**	1 : 1 : 1[a,c,f]		13	27	**2e** (27)[d]
11	**1d**	0.04 : 1 : 1[b]		12	53	**2d** (53)[d]
12	**1d**	0: 1 : 1[b]		12	0	**2d** (0)[d]

a.-Separately grounded and mixed together. b.-Open vessel. c.-Closed vessel (septum). d.-Determined by GC. e.-Isolated. f.-A gentle stream of argon was passed occasionally through the mixture.

Interestingly, conversion of the hydroquinone into the corresponding quinone was observed (entries 7-12,Table 1) when a limited amount of CAN was used together with a second solid oxidant such as $KBrO_3$ (Method B).[13] Best results of this unique "solid-solid-solid" reaction were found when using a 0.04: 1: 1 molar ratio of CAN: $KBrO_3$: HYQ (entries 7,8, Table 1), respectively. It is worth noting that: (1) neither potassium chlorate nor potassium iodate, under otherwise identical conditions, served for the same purpose; (2) in the absence of $KBrO_3$ only partial (8.5-10%) conversion could be achieved and (3) $KBrO_3$ alone (1 equiv.) was found to be inert (entry 12, Table 1) towards hydroquinones.[13]

Once again, optimum yields were obtained by working in a closed vessel (entries 7, 8, Table 1) rather than on an open one (entries 9 and 11 Table 1). Curiously enough, when the three solid mixture was (occasionally) flushed out with a gentle stream of argon (to remove gases) only a very low yield of quinone (27%) was observed even when a full molar equivalent of CAN was employed (Table 1, entry 10).



1

a $R_1 = R_2 = R_3 = R_4 = H$
b $R_1 = Br\ R_2 = R_3 = H\ R_4 = OMe$
c $R_1 = Br\ R_2 = R_3 = R_4 = H$
d $R_1 = R_4 = Br\ R_2 = R_3 = H$
e $R_1 = R_3 = tBu\ R_2 = R_4 = H$
f $R_1 = Me\ R_2 = R_3 = R_4 = H$
g $R_1 = Me\ R_2 = R_3 = H\ R_4 = Br$
h $R_1 = I\ R_2 = R_3 = R_4 = Me$
i $R_1 = Br\ R_2 = R_3 = R_4 = Me$
j $R_1 = R_2 = R_3 = R_4 = Me$

2

3

a $R_1 = R_2 = H$
b $R_1 = R_2 = Br$

4

Fig 1

The oxidation rate, which is not significantly affected by temperature is, however, appreciably accelerated (25 to 50 times faster) by ultrasonic irradiation in a commercial ultrasonic cleaning bath (Method C), or even manual shaking. Actually, efficient oxidation of a variety of hydroquinones was achieved when using the optimized conditions (closed vessel, ultrasonic irradiation) of Method C (Table 2).

Table 2

Solid State CAN Oxidation of Hydroquinones (HYQ) with Ultrasonic Irradiation (Method C)

Entry	Substrate (HYQ)	CAN : HYQ Molar Ratio	Time (hours)	Conversion (%)	Isolated Yield of Quinones **2**, **4** (%)
1	**1b**	$1:1^c$	2	100	**2b** (98)
2	**1f**	$1:1^c$	2	100	**2f** (95)
3	**1g**	$1:1^c$	2	100	**2g** (96)
4	**1h**	$1:1^c$	2	100	**2h** (95)
5	**1i**	$1:1^c$	2	100	**2i** (98)
6	**1e**	$1:1^c$	2	100	**2e** (98)
7	**3a**	$1:1^c$	2	100	**4a** (95)
8	**3b**	$1:1^c$	2	100	**4b** (96)

c.- Closed vessel (septum).

As a test for selectivity, oxidation (Method C) of hydroquinone **1e** was carried out in the presence of 1,4-dimethoxybenzene for a short period of time. The fact that only quinone **2e** was obtained from the crude reaction mixture is in agreement with the inertness of 1,4-dimethoxybenzene towards oxidation by CAN in the solid state.[14]

From a mechanistic viewpoint it can be assesed that dinitrogen tetraoxide[15] or, rather, nitric acid-dinitrogen tetraoxide mixtures[11] plays a key role in the oxidation of hydroquinones to quinones. Whereas this is likely to be undisputed[11,16] it could be argued that, at least in part, a solid-solid reaction is also taking place. Actually we found that hydroquinones are oxidized, at room temperature, by either CeO_2[17] (obtained by thermal decomposition of CAN at 500 °C for 5 h) or commercial $Ce(SO_4)_2.4H_2O$. Under either one of these conditions, however, oxidation occurs only to a partial extent (35%, GLC determined) even when excess Ce (IV) reagent was used (52-62%, GLC determined).

The reverse operation, i.e. reduction[19] of quinones to the quinhydrone[20] or hydroquinone stage can also be carried out (at least in part) in the solid state by using solid sodium dithionite as the reducing agent.[21] The reaction is best achieved by grinding together both substrate and reactant (large excess) with a pestle and mortar. The reaction rate is significantly slower when substrate and reactant were independently grounded and then mixed (and shaked) together. A strong violet color (or otherwise; see Table 3) develops during the grinding process in a number of cases. For some others only a faint blue color is seen whereas no color change is observed for other examples even after a prolonged period of time. Color vanishes somewhat slowly (5h for benzoquinone; 24 h for naphthoquinone) when the solid mixture is left in an open flask for longer periods of time. The resulting solid material (almost white) contains mostly hydroquinone (extracted from the solid with the aid of ether). If, instead, the solid mixture is left in a closed vessel, the reduction rate is considerably reduced (after 4 days the violet color still remains) therefore suggesting that surrounding gaseous water is key for the reaction to take place till the hydroquinone stage. Ultrasonic irradiation brought no significant modification to the observed rate of reduction. An increase in temperature (50 °C) leads to an slight increase in the overall rate of reduction.

Table 3

Solid State Sodium Dithionite Reduction of Quinones

Entry	Quinone	Color observed	Entry	Quinone	Color observed
1	**2a**	Deep violet	5	**4a**	Blue-grey
2	**2i**	Red-violet	6	**4b**	No color change
3	**2e**	No color change	7	**2b**	No color change
4	**2h**	Deep brown	8	**2j**	Faint violet

All attempts at detecting the intermediate stages of the reduction by spectroscopic means were somewhat frustrating. On the one hand, e.s.r spectroscopy of the blue-violet solid mixtures was inconclusive due to the strong signal of the $SO_2^{\bullet}$ radical. On the other hand, ^{13}C CPMAS spectroscopy of the freshly prepared, deep blue solid obtained by grinding together benzoquinone and dithionite (1:20 ratio) showed only the presence of quinone (189.8, 137.7 ppm) contaminated with a small amount of quinhydrone (186.6, 149.9, 134.3, 118.5 ppm), by comparison with the reported spectra.[22] The spectrum of the same sample, taken after 30 days (color had almost vanished), showed signals corresponding to hydroquinone. Unfortunately, though, the expected primary product of reduction, i.e. the disodium salt of quinhydrone could not be detected thus suggesting that surrounding water acts as the proton source.

Reaction changes were also followed by IR spectroscopy as reported by Curtin and Paul[23] for the solid state formation of quinhydrones. A series of spectra were obtained on a 3 days period. Additional dithionite was added every day and the mixture grounded again. The spectra showed the slow disappearence of the carbonyl absortion at 1655 cm^{-1} and the simultaneous appearence of a signal at 1630 cm^{-1} assigned to the carbonyl absorption of the corresponding quinhydrone. Therefore, we conclude that color changes that are visible since the beguining of the reaction (grinding) are in fact due to the formation of superficial quinhydrones.[24] Reduction of the inner quinone molecules might be the result of proton-electron transfer phenomena[25] which is accelerated by pressure and temperature.

According to the above reasoning, sodium dithionite solid state reduction of quinones should be highly dependent on the donor and acceptor properties of hydroquinones and quinones as well as on steric hindrance, as reported by Curtin and Paul[26]. As shown in Table 3, this is in agreement with our observations since either the presence of very large substituents or halogen atoms provoke a significant decrease in reaction rate (entries 3, 6, 7 Table 3).

In summary, the solid state oxidation of hydroquinone can be achieved with a number of Ce (IV) reagents, the most efficient being cerium ammoniun nitrate (CAN). Ultrasonic irradiation strongly accelerates the oxidation process. Apparently this "solid-solid" reaction involves the action of a gaseous one electron oxidant ($NO_2^{\bullet}$). Remarkably, the oxidation of hydroquinones can even be carried out efficiently by means of a three solid ("solid-solid-solid") reaction i.e., by using a limited amount of CAN in the presence of a full equivalent of a third solid component ($KBrO_3$). Conversely, reduction of quinones to the hydroquinone stage can be carried out in the solid state using solid sodium dithionite as reducing agent. The reduction involves the formation of intermediate quinhydrones, surrounding gaseous water being the proton source required for these processes.

Acknowledgements. We gratefully acknowledge financial support by the DGICYT (Project MAT 91-0032). Thanks are due Dr. O. Arjona (U. Complutense. Madrid) for obtaining CPMAS spectra

EXPERIMENTAL PART

General -All melting points are uncorrected and were taken on a capillary melting point apparatus. Proton NMR spectra were obtained on Varian FT-80A, or Bruker AMX 300 instruments, in $CDCl_3$, using Me_4Si as internal standard, unless otherwise noted. Electron impact mass spectra were recorded on a Hewlett-Packard 5988A GC/MS spectrometer, operating at 70 ev ionizing energy. Infrared spectra were recorded on a Hitachi 260-10 infrared spectrophotometer.

The standard workup procedure employed throughout involved extraction of the solid mixture with ether, followed by drying the organic extracts over anhydrous sodium sulphate and evaporation in vacuo. The residue was analyzed by GC/MS and crystallized.

All hydroquinones and quinones employed were either commercially available or prepared according to the reported procedure.

Solid State Oxidation of Hydroquinones 1. General Procedures.

Method A: By Ceric Ammonium Nitrate (CAN) The hydroquinone **1** (1 mmol) and CAN(1 mmol) were grounded together with the aid of a pestle and mortar. The free flowing powder was introduced in a test tube (or vial) and capped with a rubber septum. On shaking, a red-brown gas appeared on the upper part of the tube. The color of the solid mixture smoothly changed from grey to yellow or yellow-orange. The vial was kept aside for the time indicated and shaken occasionally. The standard workup yielded crude quinones which were analyzed by GC/MS for conversion and crystallized from the appropriate solvent (entries 1-6, Table 1).

Method B: By Ceric Ammonium Nitrate (CAN)/Potassium Bromate. The hydroquinone **1** (1 mmol), CAN(0.04 mmol) and potassium bromate (1 mmol) were grounded together with the aid of a pestle and mortar, and the mixture set aside in a capped vial for the time shown. The standard workup yielded quinones **2d** and **2e** in good isolated yield (entries 7 and 8, Table 1).

Method C: By Ceric Ammonium Nitrate (CAN) under Ultrasonic Irradiation. The same procedure as Method A above except that the mixture, in a capped vial, was irradiated with a commercial ultrasonic bath for 2 hours. The standard workup yielded quinones **2** in good isolated yields (Table 2).

The following compounds were found to be identical to commercial samples: **1,4-Benzoquinone 2a**, mp 112-114°C; **2-Methyl-1,4-benzoquinone 2f**, mp 68-9 °C; **1,4-Naphthoquinone 4a**, mp 120-1 °C.

6-Bromo-2-methoxy-1,4-benzoquinone 2b. Yellow needles (87 % yield), mp 162-3 °C (lit[27] mp 161-2 °C). ^{1}H NMR: 3.85 (s, 3H), 5.95 (d, 1H, J= 2 Hz), 7.19 (d, 1H, J= 2 Hz) ppm.

2-Bromo-1,4-benzoquinone 2c. Orange needles (85 % yield), mp 54-5 °C (lit[28] mp 56.5 °C). ^{1}H NMR: 6.88 (m, 2H), 7.25 (d, 1H, J= 2 Hz) ppm.

2,6-Dibromo-1,4-benzoquinone 2d. Yellow plates (87 % yield), mp 128-130 °C (lit[29] mp 131-2 °C). ^{1}H NMR: 7.32 (s) ppm.

2,5-Ditertbutil-1,4-benzoquinone 2e. Yellow needles (98 % yield), mp 149-150 °C (lit[30] mp 150-2 °C). ^{1}H NMR: 1.26 (s, 18H), 6.48 (s, 2H) ppm.

2-Bromo-6-methyl-1,4-benzoquinone 2g. Solid (96 % yield), mp 93-4 °C (lit[31] mp 94-5 °C). ^{1}H NMR: 2.14 (d, 3H), 6.65 (m, 1H), 7.24 (d, 1H) ppm.

2-Iodo-3,5,6-trimethyl-1,4-benzoquinone 2h. Orange plates (95 % yield), mp 72 °C (lit[32] mp 71-73 °C) ^{1}H NMR: 2.09 (s,3H), 2.04 (s,3H), 2.30 (s, 3H) ppm.

2-Bromo-3,5,6-trimethyl-1,4-benzoquinone 2i. Solid (98 % yield), mp 78-80 °C (lit[33] mp 78-80 °C). ^{1}H NMR: 2.00 (s, 3H), 2.03 (s, 3H), 2.10 (s, 3H) ppm.

2,3-Dibromo-1,4-Naphthoquinone 4b. Solid (96 % yield), mp 216-8 °C (lit[34] mp 218 °C). ^{1}H NMR: 7.79 (m, 2H), 8.18 (m, 2H) ppm.

Solid State Sodium Dithionite Reduction of Quinones. General Procedure

Quinone (1 mmol) and sodium dithionite (20 mmol) were grounded together with the aid of a pestle and mortar. Intense color changes were immediately observed (Table 3) in most cases. After several hours in an open vessel, the color completely vanished. The standard workup yielded hydroquinones **1**. Since commercial ether contains up to 8% water, some reduction might have occurred during extraction. Acccordingly, yields given below refer to overall observed yields.

The following compounds were found to be identical to commercial samples: **Hydroquinone 1a** (74 % yield), mp 172-5 °C;.**1,4-Dihydroxynaphthalene 3a** (78% yield), mp 205-7 °C

2,5-Ditert-butyl-hydroquinone 1e. Obtained in 85 % yield, mp 210-1°C (lit[35] mp 213-4°C). ^{1}H NMR: 1.36 (s, 18H), 6.56 (s, 2H) ppm.

2-Iodo-3,5,6-trimethyl-hydroquinone 1h. Obtained in 81 % yield, mp 132-5 °C (lit[32] mp 135-6°C). ^{1}H NMR: 2.16 (s, 3H), 2.25 (s, 3H), 2.39 (s, 3H) ppm.

2-Bromo-3,5,6-trimethyl-hydroquinone 1i. Obtained in 79 % yield, mp 180-2 °C (lit[36] mp 185 °C). ^{1}H NMR: 2.11 (s, 3H), 2.18 (s, 3H), 2.29 (s, 3H) ppm.

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