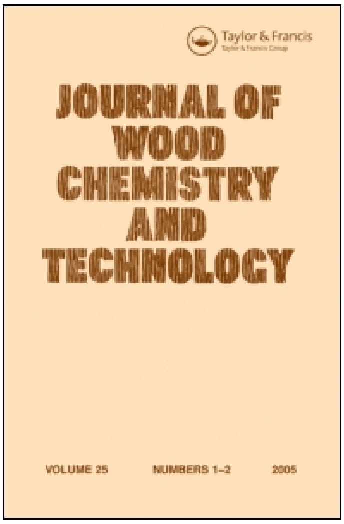

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GENERATION OF OXYGEN-CONTAINING RADICALS IN THE AQUEOUS MEDIA OF MECHANICAL PULPING*

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ABSTRACT

Mechanical treatments of veratrylglycerol-β-syringaldehyde ether (M) were conducted with a ceramic ball mill or a vibration ball mill in the presence of water and *n*-paraffin alcohols which were used as ·OH scavengers. Addition of 1% each of the alcohols to the milling process of Compound (M) greatly decreased the yields of the products, e.g. veratryl alcohol 2, vanillin 3, syringaldehyde 4, 3,5-dimethoxy-*p*-benzoquinone 5, 3,5-dimethoxy-*p*-hydroquinone 6 and others. Another addition of *n*-paraffin alcohols to aqueous media during the millings also significantly reduced the concentration of H_2O_2. When phthalic hydrazide (P) was treated in the mills in the aqueous media, triacetoxyphthalazine (1A), 3-acetoxyphthalic acid (2A) and other products were separated from the acetates of the reaction mixtures. Results mentioned above disclosed the generation of $\cdot O_2H$, ·OH, and ·H in the aqueous media during the mechanical treatments.

- This paper is Part XIII of the series: Mechanochemistry of Lignin.

INTRODUCTION

Generation of radical intermediates during the mechanical treatments of lignin and lignin model compounds has been reported previously.[1-7] Hon[1] observed the formation and decay behaviors of several kinds of mechanoradicals during millings of lignin by the method of ESR spectroscopy.Lee and Sumimoto[2] found that a number of mechanochemical conversions of *trans*-coniferyl alcohol methyl ether proceeded through the radical reaction mechanisms and were essentially similar to those of photochemical reactions. Lee et al[3] and Wu et al[4-5] compared the conversion products from β-O-4 and β-1 types of lignin model compounds treated by ball mills and concluded that the radicals were formed mainly *via* mechanically homolytic cleavages of Cα-Cβ, Cα-O or Cβ-O bonds in the model compounds.

In Part VII[5] of this series, however, it was mentioned that the mechanical treatments of veratrylglycerol-β-syringaldehyde ether (M) with a ceramic ball mill (CBM), a vibration ball mill (VBM) and a laboratory refiner in the aqueous media resulted in the formation of syringaldehyde ethyleneglycol ether 1, veratryl alcohol 2, vanillin 3, syringaldehyde 4, 3, 5-dimethoxy-*p*-benzoquinone 5, 3,5-dimethoxy-*p*-hydroquinone 6 and others as shown in Figure 1. Formation of these products from Compound (M) suggested that homolytic cleavage of the Cα-Cβ bond occurred first to give radicals (a) and (b). At the same time, three active species namely, $\cdot O_2H$, $\cdot OH$ and $\cdot H$ radicals were generated possibly by ultrasonic waves and reacted

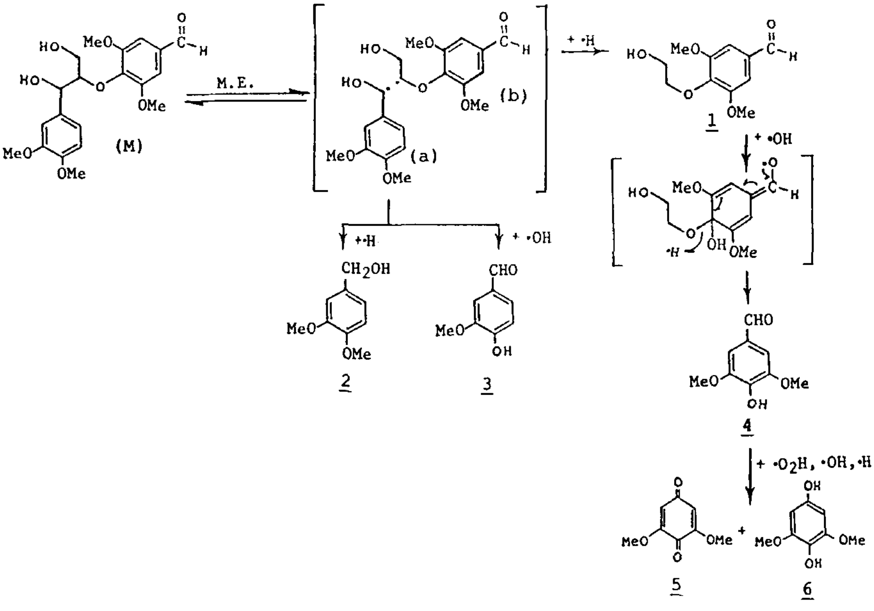

Figure 1. Major mechanochemical conversions of Compound (M) to form Compounds 1 to 6.

with radicals (a) and (b) in the aqueous media during the millings. The quinones and hydroquinones also were formed in the mechanical treatments of veratrylglycerol-β-(α'-methyl)syringyl alcohol ether[6] and a trimeric lignin model compound.[7]

Among the three radicals, $\cdot O_2H$ radical has been shown to be strongly related to oxygen in the mills by the following experiments. When Compound (M) was treated with the VBM in the aqueous media under nitrogen, the yields of 3,5-dimethoxy-*p*-benzoquinone 5 and 3,5-dimethoxy-*p*-hydroquinone 6 were reduced by about 90% as compared with those under air. The formation of Compounds 5 and 6 can be well explained by the mechanisms of Dakin-type radical oxidation of syringaldehyde 4 which requires $\cdot O_2H$, $\cdot OH$, and $\cdot H$ radicals.[5]

To prove the generation of the oxygen-containing radicals in the aqueous media during milling, various *n*-paraffin alcohols were added to the milling processes to evaluate the effect of radicals on the mechanochemical conversions of Compound (M). The paraffin alcohols are known to be effective scavengers for $\cdot OH$ radical.[8-10] On the other hand, phthalic hydrazide (P) can be used as the trapping agent for $\cdot OH$ radical.[11,12] After milling of Compound (P) with the CBM or the VBM in the aqueous media,the reaction mixtures were acetylated to give diacetoxyphthalazine (PA), triacetoxyphthalazine (1A), 3-acetoxyphthalic acid (2A), phthalic anhydride (3), and phthalic acid (4), respectively.

EXPERIMENTAL

^{1}H-NMR spectra were determined on a JNM-GX400 spectrometer (400 MHz) in $CDCl_3$ with TMS as an internal standard. Mass spectra (MS) were recorded on a Shimazu QP-1000 gas chromatography mass spectrometer (70 eV). High performance liquid chromatography (HPLC) was carried out on a JASCO TRIROTAR-Ⅱ with a column of DEVELOSIL-60-3(ϕ20 × 250 mm) using n-hexane /ethyl acetate / methanol as elution solvents.

Materials

Veratrylglycerol-β-syringaldehyde ether (M) was prepared as described in the previous paper.[5] Linter pulp was extracted with methanol before using. Paraffin alcohols and phthalic hydrazide (P) were purchased from Tokyo Kasei Chem. Co. and used without further purification.

Treatments of Compound (M) with a VBM

Each 50 mg of Compound (M) dissolved in 2 ml of dichloromethane was added to 500 mg of extracts-free linter pulp, and the solvent was removed *in vacuo* so that Compound (M) was dispersed homogeneously into the pulp. The resulting pulp was transfered to a VBM (SM-06, Yokohama Ind. Co.) and set in a dry box (Tokyo Air Engineering Co.) to exchange air with nitrogen. Then 5 ml of deionized water and 0.05 ml of glycerol or one of the paraffin alcohols in a syringe were added to the VBM. After being heated to about 100 °C in an autoclave, the VBM was vibrated for 15 min. The reaction mixture was extracted from the VBM successively with methanol, acetone and ethylacetate. The extracts were filtered, dried over Na_2SO_4 and evaporated *in vacuo* to give a residue which was acetylated with acetic anhydride and pyridine and separated by HPLC. Identification of the products was made by the comparison of their mps, MS- and ^{1}H-NMR spectra with those of authentic samples.

Measurement of Hydrogen Peroxide

Ten ml of deionized water and either 0.05 ml of glycerol or one of the paraffin alcohols was added to the VBM and treated at room temperature for 1 h. Then the reaction mixture was extracted from the VBM with 110 ml of deionized water. The aqueous solution was filtered and the concentration of H_2O_2 was determined by the method of iodometry.

Treatments of Phthalic Hydrazide with a VBM or a CBM

Each 100 mg of phthalic hydrazide (P) and 10 ml of water were added to either the VBM or the CBM (Nihon Kagaku Togyo Co.), and treated under the conditions shown in Table 2. The reaction mixture was extracted with methanol(700 ml x 3), and separated and purified as stated above.

Identification of the Reaction Products

Figure 1 shows the chemical structures of compounds isolated from the mechanochemical reaction mixtures of Compound (M). Identification of the compounds was described in details in the previous paper.[5]

When phthalic hydrazide (P) was treated with the mills in the aqueous media, the resulting reaction mixtures were acetylated and separated with HPLC. Phthalic anhydride (3) and phthalic acid (4) were determined by comparisons of mps, MS-spectra with those of the authentic samples. Compounds (1A) and (2A) were identified as follows:

Compound (1A): 1,3,8-triacetoxyphthalazine, mp. 176 °C, ^{1}H-NMR: 2.17-2.19 (9H, m, OAc x 3),7.51-7.82 (3H, aromatic protons). MS m/z (%): 305 (M^+ + 1, 7), 304 (M^+, 10), 264 (1), 263 (11), 262 (15), 221 (8), 220 (83), 179 (4), 178 (73), 120 (6), 92 (2), 63 (1) and 43 (100).

Compound (2A): 3-acetoxyphthalic acid, ^{1}H-NMR: 2.18 (3H, s, OAc),7.24-7.45 (3H, aromatic protons), 9.98 (1H, COOH), 10.05 (1H, COOH). MS(acetate) m/z(%): 224 (M^+, 5), 210 (10), 196 (4), 182 (7), 178 (15), 160 (14), 159 (54), 120 (10) and 43 (100).

RESULTS AND DISCUSSION

Effects of Paraffin Alcohols on Mechanochemical Conversions of Compound (M)

It is well known[8,9,10] that paraffin alcohols are effective scavengers for ·OH radical generated either chemically or physically in the aqueous media. According to Eriksson et al[10] all of ·OH radicals produced during the bleaching of chemical pulp with ozone can be removed by addition of methanol. Henglein and Korman[9] found that the ability of paraffin alcohols to scavenge ·OH radical increases with their increasing hydrophobicity. Therefore, it can be expected that if ·OH radicals are generated in the aqueous media of mechanical treatment and participate in mechanochemical conversions of Compound (M), the presence of paraffin alcohols will reduce the yields of reaction products due to scavenging of ·OH radicals.

The mechanical treatments of Compound (M) were conducted with a VBM at about 100 °C. Eight *n*-paraffin alcohols having carbon number of 1 to 10 were used. Each 0.05 ml of the paraffin alcohols was added to the VBM containing 50 mg of Compound (M) and 5 ml of water, and then treated for 15 min. Eight products and others were isolated from the reaction mixtures as shown in Figure 1 and Table 1. Veratrylalcohol 2 and syringaldehyde 4 were obtained in the largest yields, but *p*-benzoquinone 5 and *p*-hydroquinone 6 were low as compared with those in the absence of the alcohols.

As shown in Figure 2, the presence of the paraffin alcohols in the millings of Compound (M) greatly reduced the total yields of the products. Compared to 13.3% of the products in the absence of the alcohols, the amount of the products decreased to 9.6% in glycerol and to 3.6% in decanol. The alcohols with greater hydrophobicities seem to be more effective in decreasing the amounts of the products.

Figure 3 shows the changes of amounts of veratryl alcohol 2 and syringaldehyde 4 in the presence of the paraffin alcohols. The decrease trends of the two compounds are consistent to that of the total yields of the products, indicating that the paraffin alcohols mainly cause the decrease of degradation products. Based on the mechanisms proposed in Figure 1, the formation of veratrylalcohol 2 and syringaldehyde 4 is *via* addition of either ·H or ·OH radicals to the intermediate (a). When the paraffin alcohols were

Table 1 Effect of paraffin alcohols on yields of mechanochemical conversion products from Compound (M), (weight% on starting materials)

Additives	(M)	Conversion products 1	2	3	4	Others	Totals
----	64.5	1.6	4.2	0.2	6.9	0.3	13.2
Glycerol	72.1	1.2	2.9	0.5	4.4	0.6	9.6
Methanol	74.8	0.9	1.5	0.1	2.1	0.6	5.2
Ethanol	74.9	0.9	1.4	0.1	2.1	0.7	5.2
1-Propanol	80.5	0.7	1.2	0.1	1.7	0.8	4.5
1-Butanol	82.7	0.6	1.1	0.1	1.3	0.9	4.0
1-Hexanol	86.0	0.6	0.8	0.1	1.3	0.9	3.7
1-Octanol	87.4	0.5	0.9	0.1	1.2	0.8	3.5
1-Decanol	90.1	0.6	0.7	0.1	1.2	1.0	3.6

Note: (M). Veratrylglycerol-β-syringaldehyde ether; 1. syringaldehyde ethyleneglycol ether; 2. veratryl alcohol; 3 vanillin; 4. syringaldehyde; Others are the combined yields of p-benzoquinone 5, p-hydroquinone 6 and codensation products.

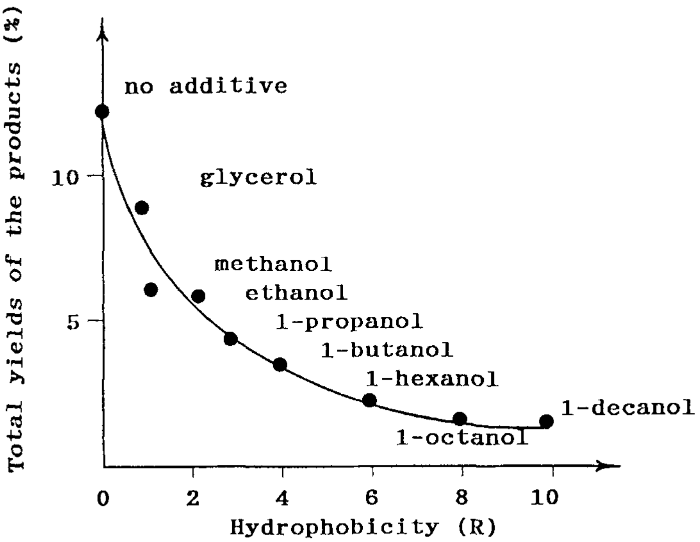

Figure 2. Effect of the paraffin alcohols on total yields of the mechanochemical conversion products from Compound (M).

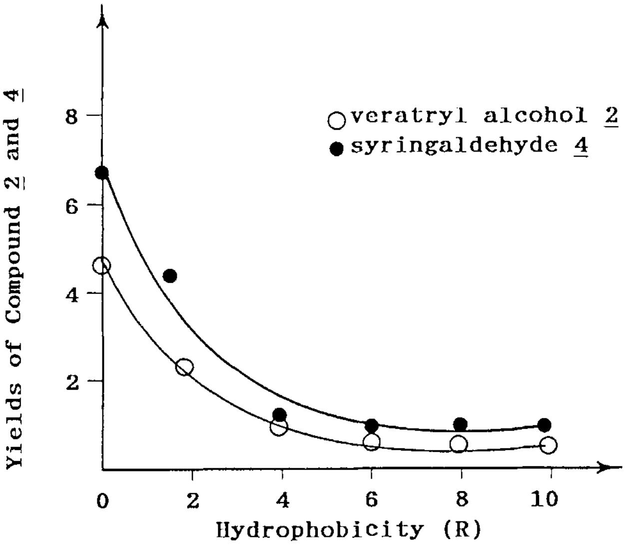

Figure 3. Effect of the paraffin alcohols on the yields of veratrylglycerol 2 and syringaldehyde 4.

present in the aqueous media, the generation of ·OH and ·H radicals may have been greatly inhibited so that the reactions to form veratrylalcohol 2 and syringaldehyde 4 were reduced dramatically.

On the other hand, based on the observation of Henglein and Korman,[9] concentrations of H_2O_2 coupled by two ·OH radicals in the aqueous media of sonication greatly decreased as the hydrophobicities of paraffin alcohols increased. A same decrement of concentration of H_2O_2 generated in the aqueous paraffin alcohols media during the millings with the VBM also was observed as shown in Figure 4. The decrease trend is consistent with those shown in Figures 2 and 3.

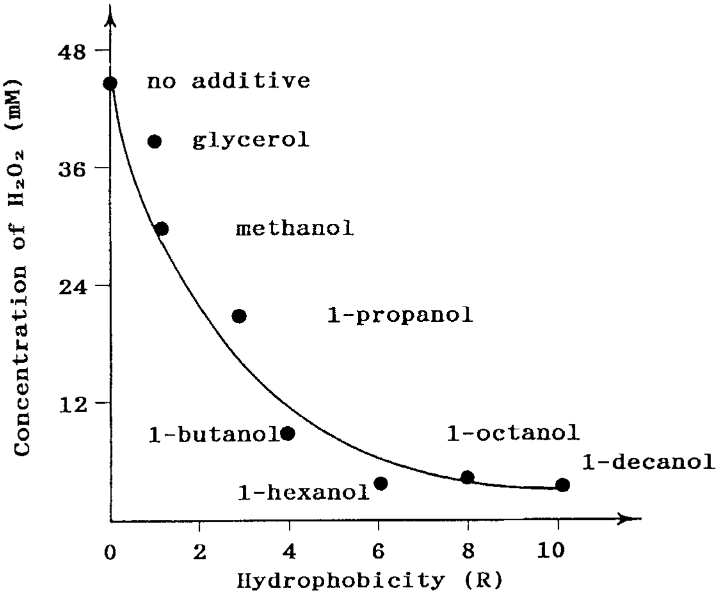

Figure 4. Effect of the paraffin alcohols on the concentration of H_2O_2 generated in the aqueous media of mechanical treatment.

Therefore, this confirms the ability of the paraffin alcohols to scavenge ·OH radicals in aqueous media of the mechanical treatments.

Confirmation of generation of OH radicals by using phthalic hydrazide (P)

Recently, Reitberger and Gierer[10] developed a new method to demonstrate the generation of ·OH radicals in both chemical and biochemical systems. The method is based on the special reaction of a phthalic hydrazide molecule (P) with a ·OH radical to give 3-hydroxyphthalic hydrazide (1). The latter can be oxidized by alkaline-H_2O_2 to give 3-hydroxyphthalic acid (2), which is combined with emission of strong chemiluminescence, to prove the presence of ·OH radicals.

To give a direct proof for the generation of ·OH radicals in the aqueous media of mechanical treatment with the ball mills, an attempt to isolate and identify 3-hydroxyphthalic hydrazide (1) was made. The mechanical treatments of phthalic hydrazide (P) were carried out in the aqueous media with either the VBM or the CBM. As a blank experiment, 100 mg of phthalic hydrazide (P) was added to the VBM, and treated for 1 h in the absence of water. In this case, almost no detectable reaction product was produced, indicating that no ·OH radicals were generated under the condition. When 100 mg of phthalic hydrazide (P) and 10 ml of deionized water were milled in the VBM for 1 h, several compounds were isolated from the acetates of the reaction mixture by the method of HPLC as shown in Figure 5. Based on their mps, MS-, and^{1}H-NMR spectra, the compounds were identified as diacetoxyphthalazine (PA), triacetoxyphthalazine (1A), 3-acetoxyphthalic acid (2A), phthalic anhydride (3) and phthalic acid (4), respectively.

Figure 6 shows the mechanisms for mechanochemical conversions of phthalic hydrazide (P) in the aqueous media to Compounds (1), (2), (3) and (4). The reaction mixtures including (P), (1), and (2) were acetylated to give Compounds (PA), (1A), and (2A). Since Compounds (1A) and (2A) have a 3-acetoxyl group, respectively, the formation of the Compounds in the millings of phthalic hydrazide (P) fully proves the gen-

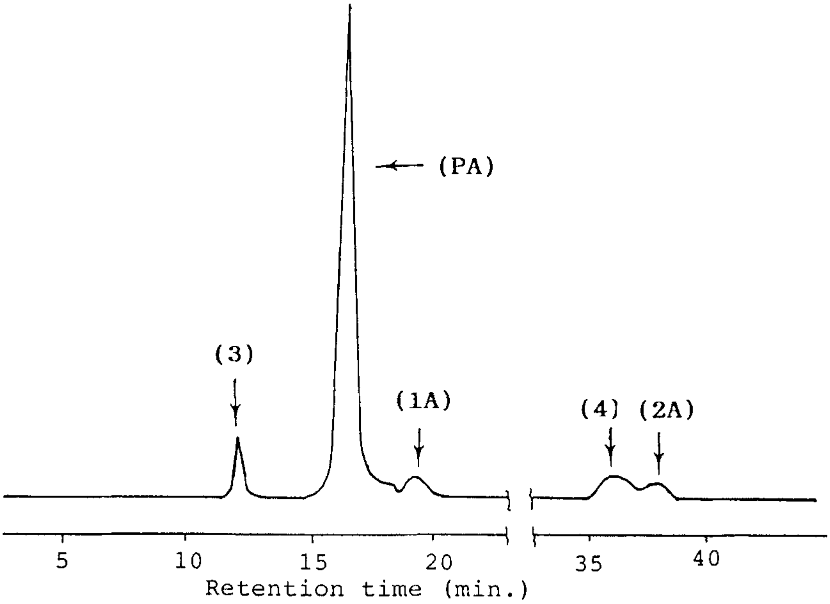

Figure 5. A HPLC chart of the acetates of mechanochemical reaction mixture of phthalic hydrazide (P) treated in a VBM.

eration of •OH radicals, which may be accompanied with $\cdot O_2H$ and •H radicals in the aqueous media of mechanical treatments based on the mechanochemical conversions of the lignin model compounds.[3-7]

The yields of the products from phthalic hydrazide (P) under various conditions were shown in Table 2. In the case of the CBM treatment, total yield of the products was only 1.8% compared to 10.3% in the VBM treatment. When the VBM treatment was carried out under N_2, the amount of Compound (2A) was reduced from 1.0% under air to only 0.2%. However, the yield of Compound (1A) increased from 2.3% to 3.6%. Decrease

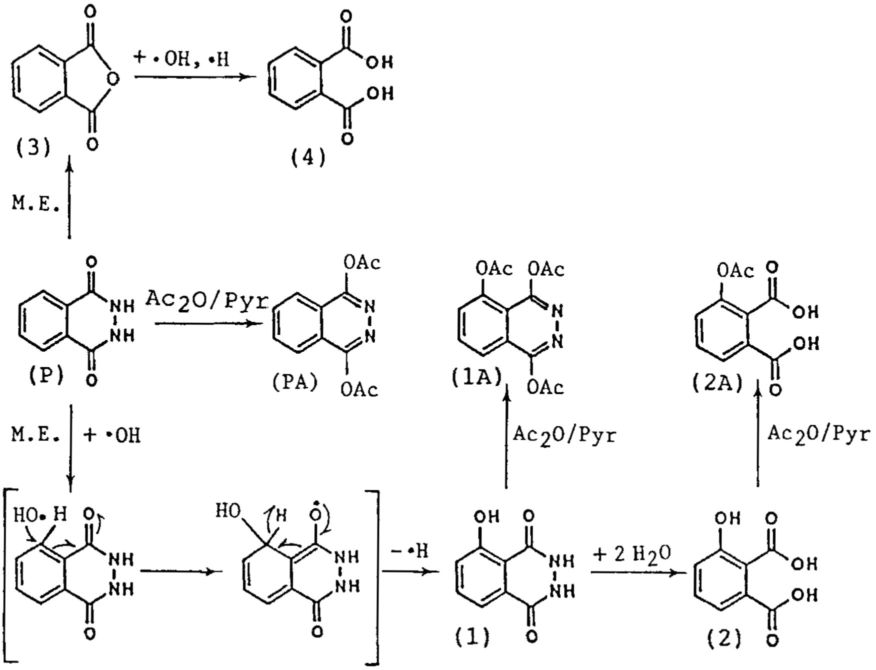

Figure 6. Mechanochemical conversions of phthalic hydrazide (P) to give Compounds (PA), (1A), (3), and (4).

Table 2 Yields of the mechanochemical conversion products of phthalic hydrazide (P) (weight% on starting material).

Reactors	Conditions		Conversion products				
		(PA)	(1A)	(2A)	(3)	(4)	Totals
CBM	Air, 1 h	94.3	0.3	0.1	0.2	1.2	1.8
VBM	Air, 1 h	88.9	2.3	1.0	2.8	4.2	10.3
VBM	Air, 2 h	86.4	1.4	3.1	3.2	6.4	14.3
VBM	N_2 , 1 h	92.1	3.6	0.2	1.4	3.8	9.3

Note: (PA) diacetoxyphthalazine; (1A) triacetoxyphthalazine;
(2A) 3-acetoxyphthalic acid; (3) phthalic anhydride;
(4) phthalic acid.

in the amounts of $\cdot O_2H$ radicals due to removal of O_2 in the VBM is apparently responsible for these changes. By extending treatment time of the VBM from 1 h to 2 h, the yield of Compound (1A) decreased from 2.3% to 1.4%,but the yield of Compound (2A) increased from 1.0 to 3.1%. This indicates that 3-hydroxyphthalic hydrazide (1) formed by phthalic hydrazide (P) and $\cdot OH$ radical may be further hydrated to 3-hydroxyphthalic acid (2).

CONCLUSION

Addition of the paraffin alcohols to the millings of veratrylglycerol-β-syringaldehyde ether (M) in the aqueous media greatly decreased yields of degradation products, e.g. veratryl alcohol 2, syringaldehyde 4, 3,5-dimethoxy-*p*-benzoquinone 5,3,5-dimethoxy-*p*-hydroquinone 6 and others. As shown in Figure 4, concentrations of H_2O_2 coupled by two $\cdot OH$ radicals in the millings also was reduced by the addition of the paraffin alcohols. These facts illustrate that $\cdot O_2H$, $\cdot OH$ and $\cdot H$ radicals were generated in the aqueous media during mechanical treatments and participated in the mechanochemical conversions of Compound (M).

Mechanical treatments of phthalic hydrazide (P) with the mills in the aqueous media furnished 3-hydroxyphthalic hydrazide (1), 3-hydroxyphthalic acid (2), phthalic anhydride (3), and phthalic acid (4). These facts proved the generation of $\cdot OH$ radicals in the aqueous media during mechanical treatments, which may be accompanied with the generation of $\cdot O_2H$ and $\cdot H$ radicals.

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