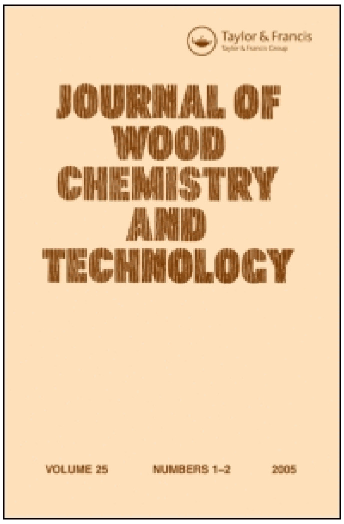

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DEGRADATION OF LIGNIN WITH OZONE
-Reactivity of Lignin Model Compounds Toward Ozone-

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ABSTRACT

In order to elucidate the reactivities of different types of lignin-structural units toward ozone, various lignin model compounds were ozonized. The results obtained are summarized as follows:

1) An α-carbonyl type structure is much more stable against ozone than a benzyl alcohol type structure.

2) A guaiacyl nucleus reacts faster with ozone than a veratryl one.

3) Biphenyl and phenylcoumaran structures react readily with ozone. However, a biphenyl structure of veratryl nuclei is very stable against ozone.

4) From the results of molecular orbital calculations, Pz orbitals (LUMO) of ozone form bonding orbitals to those (HOMO) of lignin aromatic nucleus at C_3 and C_4 positions. Furthermore, the squares of LCAO coefficients of C_3 and C_4 positions are greater than those of other positions in Pz orbital (HOMO) of lignin aromatic nucleus. This suggests that ozone reacts selectively with the lignin aromatic nucleus at C_3-C_4 position.

0277-3813/83/0304-0399$3.50/0

1. INTRODUCTION

It is well known that ozone attacks lignin aromatic nuclei selectively and brings about ring opening[1-6]. Accordingly, ozone is expected to be a promising bleaching agent in pulp and paper industries.

In previous papers[4,5], it was reported that several lignin model compounds such as β-aryl ether type compounds with a benzyl alcoholic group or an α-carbonyl group and bi-phenyl type compounds were ozonized and the reaction products were isolated and identified.

In the case of benzyl alcohol type compounds, the main course of the reaction was reported to be the oxidative cleavage of aromatic rings at the C_3-C_4 position to form muconic acid derivatives. In the case of α-carbonyl type compounds, the aromatic rings were rather stable and the product with a hydroxy group on the β-carbon which was formed through the cleavage of β-ether linkages, was isolated.

With respect to the reactivity of lignin toward ozone, the effects of functional groups of lignin structural-units on the reactivity is not yet fully clarified.

Kojima et al.[3] reported that ring opening proceeded faster at the ring which had more substituents, and that the reactivities of dimeric lignin model compounds were in the following order; biphenyl> phenylcoumaran> aryl ether. Since ozone is an electrophilic reagent, it is important to consider the effect of electron density of the lignin aromatic nucleus on the reactivity toward ozone.

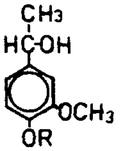
In this paper, the effects of ring substituents and inter-unit linkages of lignin on the reactivity toward ozone were investigated. The effect of electron density of the lignin aromatic nucleus on the reactivity was also discussed.

2.EXPERIMENTAL

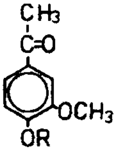
2.1 Model compounds

Lignin model compounds used are shown in Fig. 1. In order to investigate the reactivities of a guaiacyl and a veratryl nucleus with a benzyl alcohol or an α-carbonyl group, monomeric model compounds [1] - [4] were used. Dimeric model compounds [5] - [13] were used for the evaluation of the effects of inter-unit linkages in lignin structures.

Among the compounds [5] - [8] which have β-aryl ether structures, the compounds [5] and [6] and the compounds [7] and [8] have benzyl alcohol and α-carbonyl groups, respectively. Although compounds [9]



[1] R = H
[2] R = CH_3



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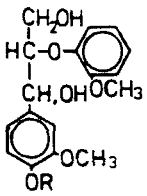

[5] R = H
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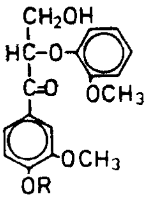

[7] R = H
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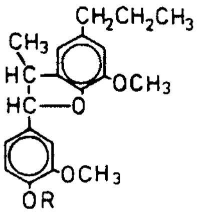

[9] R = H
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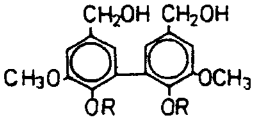
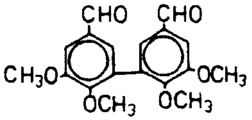


[11] R = H
[12] R = CH_3



[13]

Figure 1 Lignin model compounds.

and [10] are phenylcoumaran structures, it is difficult to compare directly the reactivities of these compounds with those of the other compounds, because the side chains of these compounds have alkyl substituents.

2.2 Synthesis of model compounds

Compounds [1] and [2] were prepared by the reduction of compounds [3] and [4] with $NaBH_4$, respectively. Compound [3] was obtained commercially. Compound [4] was obtained by the methylation of compound [3] with diazomethane. Compounds [5] and [7] were synthesized by Hosoya's method[7]. Compounds [6] and [8] were prepared by Adler's[8] and Pearl's[9] methods, respectively. Compound [9] was obtained according to the report of Leopold[10] and compound [10] was prepared by the methylation of [9]. Compounds [11] - [13] were synthesized by the method of Pew[11].

2.3 Ozonization of model compounds

Model compounds of 0.25 mmol were dissolved in 30 ml of methanol. The concentration of ozone in O_2 flow was kept at 3 % and the flow rate of O_2 was 0.5 l/min.. The reaction temperature was 6-7°C. Ozonization of compounds [2] and [4] were followed by GLC to determine the residual amount of the starting substances. In the case of the other compounds, high pressure liquid chromatography (HPLC) was used. The GLC and HPLC conditions were as follows:

GLC: Instrument; Yanagimoto G-80, Detector; FID, Column; QF-1, Carrier gas; He (flow rate; 15 ml/min.), Column temp.; 180 °C

HPLC: Instrument; Waters ALC/GPC-244, Detector; UV (254 nm), Column; μ-Bondapak C_{18}, Solvent; H_2O/MeOH (compd. [9] and [10]; 3/7, compd. [11]; 7/4, compd. [13]; 2/3, the others; 1/1)

2.4 Calculations of molecular orbitals of lignin model compounds

The calculations of molecular orbitals were carried out to investigate the reaction sites of lignin aromatic nuclei and the reactivities of lignin model compounds toward ozone. Molecular orbitals of unsaturated compounds were calculated by HMO (Huckel molecular orbital) method. Program of HMO calculation and parameters of substituents were referred to Kikuchi's program[12] and Yonezawa's table[13], respectively. Model compounds containing saturated side chains such as vanillyl alcohol were calculated by CNDO/2 method using Q.C.P.E program[14]. The calculations were carried out on a HITAC 8700/8800 computer at The Computer Center of The University of Tokyo.

Although co-ordinates of molecular structures are necessary for CNDO/2 calculations, crystal structural data of lignin model compounds have not yet been obtained, so that co-ordinates were calculated using interatomic distances of analogous compounds[15].

The structure of a model compound used for CNDO/2 calculation is shown in Fig. 2. It was assumed that C_8, C_{10}, O_7, O_9, O_{11}, H_{12}, H_{13}, H_{14} and aromatic ring lie on the same plane.

Although total energy depends on configurations, the sign of coefficient of molecular orbital cannot be inverted.

3. RESULTS AND DISCUSSION

3.1 Reactivities of model compounds

Reactivities of model compounds [1] - [4] are shown in Fig.3. Benzyl alcohol type structures [1] and [2] showed great reactivities. Especially, apocynol [1], having phenolic OH, was very reactive and was not detectable after 20 min. of ozonization. α-Carbonyl type structures [3] and [4] were much more stable against ozone and the starting substances were still detectable even after 60 min. of ozonization. Acetoguaiacone [3], having a phenolic OH, was a little more reactive with ozone than acetoveratrone [4].

Reactivities of β-aryl ether [5] - [8] and phenylcoumaran [9] and [10] structures are shown in Fig.4. In our earlier paper, it was reported that the aromatic rings of β-aryl ether structures [5] and [6], were cleaved at the C_3-C_4 position of A ring (Fig.5)$^{4)}$. B ring was more stable against ozone than A ring. Accordingly, the reactivities of these two compounds were similar to those of apocynol [1] and its methyl ether [2]. In the case of the reaction of β-aryl ether structures which have α-carbonyl groups (compounds [7] and [8]), the cleavage of B ring preceeds that of A ring, because the α-carbonyl group stabilizes the A ring against ozone$^{5)}$. Therefore, these two compounds [7] and [8] showed the same reactivity. As phenylcoumaran structures [9] and [10] have alkyl side chains, the reactivities of these compounds cannot be directly compared with those of other compounds. However, these two compounds reacted very fast with ozone.

Although it was reported that B ring of phenylcoumaran structure [9] and [10] was attacked by ozone faster than A ring$^{3,16)}$, there is still a possibility that A ring is attacked because the reactivities of these two compounds were a little different from each other. The reactivities of biphenyl structures [11] -[13] are shown in Fig.6. Dehydrodivanillyl alcohol [11] and dehydrodiveratryl aldehyde [13] were more reactive with ozone than other benzyl alcohol type and α-carbonyl type structures, respectively.

Even though it has a benzyl alcoholic OH, dehydrodiveratryl alcohol [12] was very stable against ozone. It is considered that the difference

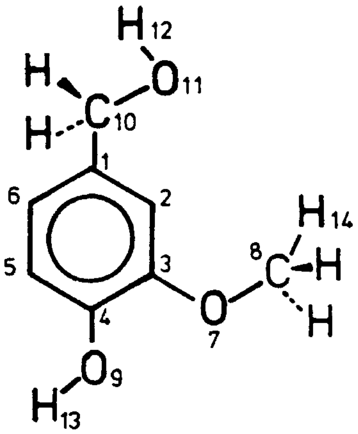


Figure 2 Structure of a lignin model compound used for CNDO/2 calculation.

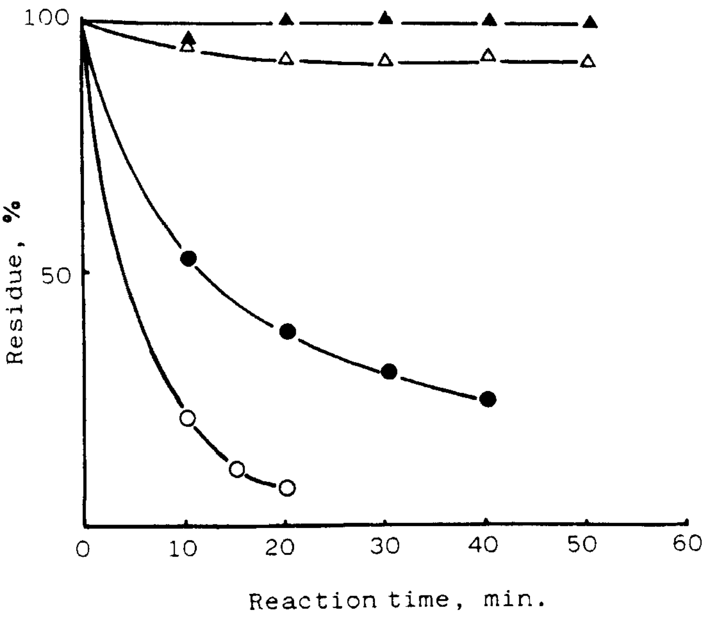


Figure 3 Reactivities of lignin model compounds-[I].

○ --- compd.[1], ● --- compd.[2]
△ --- compd.[3], ▲ --- compd.[4]

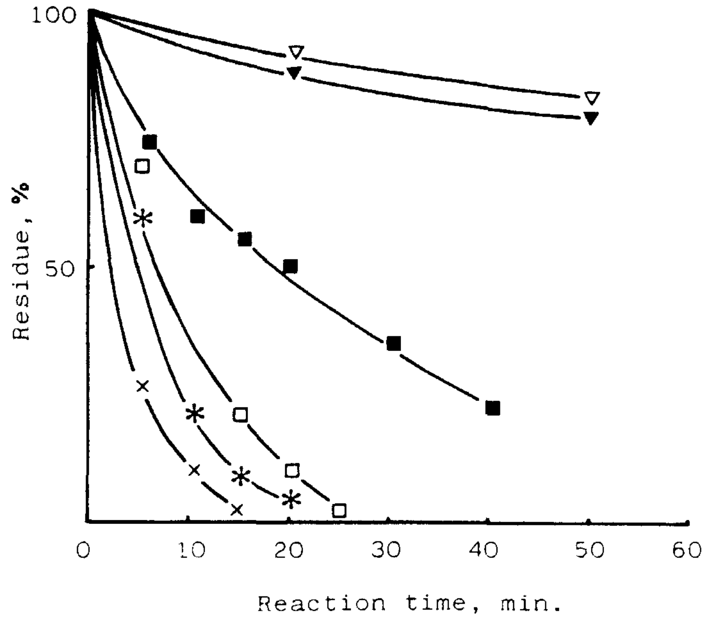


Figure 4 Reactivities of lignin model compounds-[II].

□ --- compd.[5], ■ --- compd.[6], ▽--- compd.[7]
▼--- compd.[8], ✱--- compd.[9], ×--- compd.[10]

in reactivity between compounds [11] and [12] is due to the steric effect of the methoxyl group at C_4 of aromatic nucleus. The effects of substituent groups of lignin model compounds on the reactivity toward ozone were summarized in Fig.7. Benzyl alcohol type compounds are more reactive with ozone than α-carbonyl type compounds, and the guaiacyl nucleus is attacked by ozone faster than the veratryl one.

Although the effects of inter-unit linkages of lignin structural units on the reactivity toward ozone are complex, the reactivity of a β-aryl ether structure is affected by substituent groups on an α-carbon of a side chain, as is similar to that of monomeric model compounds. Phenylcoumaran structures are very reactive with ozone. The reactivities of biphenyl structures are remarkably different depending on whether it contains a guaiacyl or veratryl nucleus.

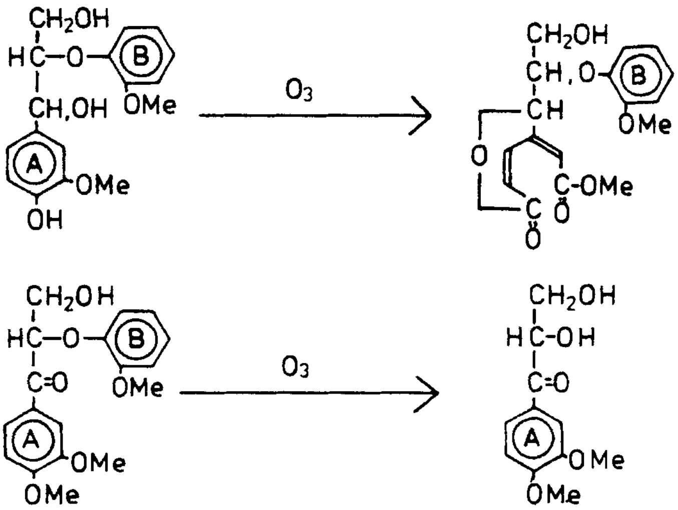


Figure 5 Ozonolysis of lignin model compounds[4,5].

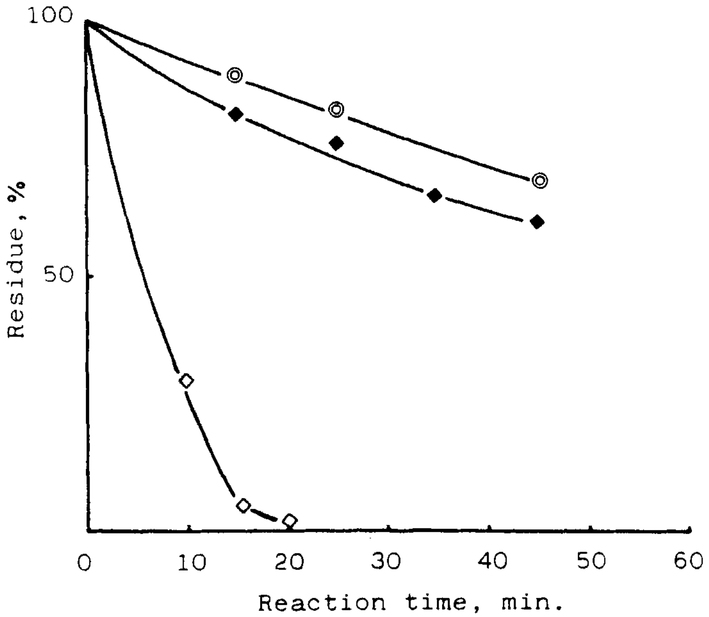


Figure 6 Reactivities of lignin model compounds-[III].

◇ --- compd.[11], ◆--- compd.[12]
◎ --- compd.[13]

3.2 Evaluation of molecular orbital calculation

Electron densities of lignin model compounds calculated by the HMO method are listed in Table 1. Ozone, being a electrophilic reagent, is considered to attack a center of high electron density.

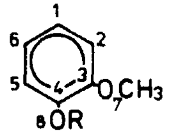
However, in consequence of molecular orbital calculations of guaiacol [14] and veratrol [15], the C_3 and C_4 positions of an aromatic ring, which are most reactive with ozone, have the lowest electron densities. Total bond orders of compound [14] and [15] are also shown in Fig.8. Again, the C_3-C_4 position of these compounds have lowest bond orders. From the results of reactivities of model compounds toward ozone, a guaiacyl nucleus was more reactive than a veratryl nucleus. However, the electron density at the C_4 position of guaiacol [14] is lower than that of veratrol [15]. Furthermore, the total bond order of guaiacol at the C_3-C_4 position is less than that of veratrol, as opposed to the results of ozonization experiments. Accordingly, the reactivities of lignin model compounds toward ozone cannot be explained on the basis of electron density or double bond character.

With respect to the attack of ozone at C_3-C_4 position of lignin aromatic nucleus, it was postulated, to explain the experimental results, that HOMO (Highest occupied molecular orbital) of lignin aromatic nucleus overlaps with LUMO (Lowest unoccupied molecular orbital) of ozone in Pz orbital. This assumption was referred to as HOMO-LUMO interaction in Diels-Alder reactions17,18). As molecular orbital calculation of HMO method is not quantitative and molecular orbital of saturated compounds cannot be calculated by HMO method, CNDO/2 method was used with regard to this evaluation. LCAO (linear combination of aromatic orbital) coefficients of vanillyl alcohol [17] are listed in Table 2.

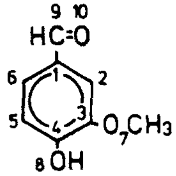
The square of LCAO coefficient shows the probability of the presence of an electron. In the case of vanillyl alcohol, absolute values of LCAO coefficients of C_3-C_4 positions are comparatively great and the carbon with an OH group as a substituent has a greater absolute value of LCAO coefficient than that with an OMe group. Moreover, HOMO of the C_3-C_4 position in the lignin aromatic nucleus and LUMO of 1 and 3 positions of ozone form bonding orbitals with each other. Namely, as is shown in Fig.9, LCAO coefficients of HOMO (C_3 and C_4 positions) of lignin aromatic nucleus and LUMO (1 and 3 positions) of ozone have the same sign. Furthermore, as the sign of the LCAO coefficient (2 positions) of ozone coincides with that of oxygen atoms in methoxyl and phenolic OH groups, repulsion will not take

Table 1 Electron densities of lignin model compounds by HMO method.

Position	Compounds		
	[14]	[15]	[16]
1	1.038	1.039	1.067
2	1.064	1.052	0.9568
3	1.027	1.017	1.022
4	1.007	1.017	0.9357
5	1.047	1.052	1.057
6	1.052	1.039	0.9560
7	1.894	1.893	1.895
8	1.872	1.893	1.800
9	-	-	0.6341
10	-	-	1.636



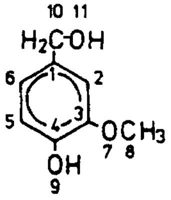
[14] R=H
[15] R=CH_3



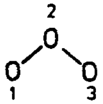
[16]

Table 2 LCAO coefficients of lignin model compounds and ozone (calculated by CNDO/2)

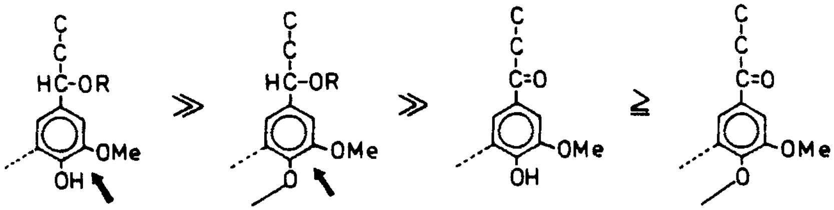
Position	HOMO of Compd. [17]	Position	LUMO of Ozone [18]
1	0.3971	1	0.5237
2	0.0828	2	-0.6719
3	-0.3291	3	0.5237
4	-0.4260		
5	-0.1931		
6	0.3294		
7	0.2908		
8	-0.0401		
9	0.3620		
10	-0.1729		
11	0.1922		



[17]



[18]



R = H, Alkyl, Aryl

Figure 7 Reactivities of various types of lignin structures toward ozone.

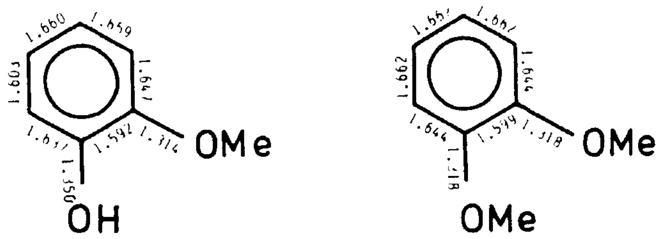


Figure 8 Total bond order of lignin model compounds calculated by HMO method.

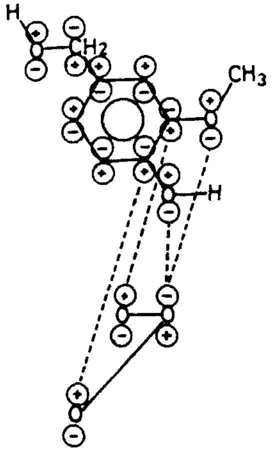


Figure 9 Signs of LCAO coefficients (HMO of lignin aromatic nucleus and LUMO of ozone).

place in the reaction of ozone with the lignin aromatic nucleus at the C_3-C_4 position.

From the viewpoint of HOMO-LUMO interaction, it can be elucidated that ozone attacks selectively the C_3-C_4 position of lignin aromatic nucleus and that a guaiacyl nucleus is more reactive with ozone than a veratryl one.

4. CONCLUSION

In order to clarify the behavior of lignin during ozonization, the reactivities of lignin model compounds toward ozone were investigated. Among the monomeric model compounds, α-carbonyl type structures are more stable against ozone than benzyl alcohol type ones. A guaiacyl nucleus is more reactive with ozone than a veratryl one.

With respect to the effect of inter-unit linkages on the reactivity of lignin model compounds toward ozone, the reactivity of a β-aryl ether structure is similar to that of corresponding monomeric model compounds. Phenylcoumaran structures are easily attacked by ozone. A biphenyl structure with veratryl nuclei is very stable against ozone even if it is a benzyl alcohol type compound, probably because of steric hindrance.

In consequence of the calculation of HMO method, the electron density of lignin aromatic nucleus at C_3-C_4 position, which is easily attacked by ozone, is lower than the other positions. Especially, the carbon with phenolic OH group on it has the lowest electron density. Accordingly, the reactions of lignin model compounds with ozone cannot be elucidated on the basis of electron density and double bond character. With regard to this point, HOMO-LUMO interaction was considered to explain the reaction of lignin with ozone. Namely, LCAO coefficients (HOMO) of lignin aromatic nucleus at the C_3 and C_4 positions have comparatively large values. Moreover, the C_3 and C_4 positions of lignin aromatic nucleus (HOMO) and the 1,3 position of ozone (LUMO) form bonding orbitals. LCAO coefficient squared (Pz orbital) of the carbon with a phenolic OH group is greater than that with a methoxyl group which indicates that a guaiacyl nucleus should be more reactive with ozone than a veratryl one.

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