

# Technical

## A Study of Benzylphenols as Antioxidants

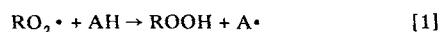
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### ABSTRACT

A series of benzylphenols has been evaluated as antioxidants for paraffin wax at 160 C. Introduction of the benzyl group to the *para*- and/or *ortho*-positions to the hydroxyl group on the benzene ring was shown to improve antioxidative activities of phenols. Excellent activities have been observed with benzylpyrocatechols and benzylresorcinol. Antioxidant activities of benzylphenol compounds increased with the decrease of  $^{13}\text{C}$  NMR chemical shifts ( $\delta$ ) of the ipso-carbon of the OH substituent.

### INTRODUCTION

In chemical industries, antioxidants have commonly been used to prevent deterioration due to the oxidation of organic materials — for example, petroleum hydrocarbons, lubricating oils, rubbers, polymers and foodstuffs. The oxidations on storage at room temperature or during various processings at high temperature have been well recognized as radical chain reactions. Such antioxidants as phenol and aromatic amine derivatives react as chain-breaking inhibitors of the peroxyradical:



The radical  $\text{A} \cdot$  from the antioxidant is less reactive and consequently it is difficult for a new chain reaction to become initiated, as was first reported by Bolland and ten Have (1).

During the course of our studies of phenol derivatives as antioxidants (2-6), the evaluations obtained by the oxidation test of paraffin wax at 160 C (2,3) were ascertained to

be applicable to the stabilization of a wide range of materials — for instance, lard (4), vitamin A (5), mineral oils (6) and grease (6). Furthermore, we have found that 1,3- or 1,4-*bis*(3,4-dihydroxybenzyl)benzene and 4-benzylpyrocatechol exhibit much higher antioxidative activity than nordihydroguaiuretic acid (3). Consequently, we conclude that compounds containing diaryl methylene with the phenolic hydroxyl group show high activity as an antioxidant.

In this paper, the antioxidative activities of benzylphenols on paraffin wax are determined by measuring peroxide values and are discussed in connection with their  $^{13}\text{C}$  NMR chemical shifts.

### EXPERIMENTAL PROCEDURE

#### Antioxidants

The 16 compounds studied in this experiment are listed in Table I. Benzylphenols were prepared by the reported method (7).

#### Measurement of $^{13}\text{C}$ NMR Spectra

The spectra of 1-15 were recorded on a JNM-PS-100/EC-100 FT spectrometer operating at 25.15 MHz with complete proton decoupling. Pulse width and repetition time were 10.2  $\mu\text{sec}$  for a 45° pulse and 6 sec, respectively. The spectra were observed as 2 mmol/mL solutions in  $(\text{CD}_3)_2\text{CO}$  with a spectral width of 6250 Hz. Chemical shifts were referred to internal standard TMS.

#### Determination of Antioxidative Activity

Antioxidative activities of 1-16 for paraffin wax (mp 52-

TABLE I

Activity of Antioxidant on Induction Period (hr) in the Oxidation of Paraffin Wax at 160 C, along with  $^{13}\text{C}$  Chemical Shift of the ipso-Carbon of the OH Substituent

Compound	Concentration (mol/kg of wax)					$\delta_c^a$ (ppm)
	$1 \times 10^{-3}$	$5 \times 10^{-3}$	$1 \times 10^{-2}$	$2 \times 10^{-2}$	$3 \times 10^{-2}$	
1. Phenol	1.7	1.5	1.5			157.9
2. Pyrocatechol	5.1	7.5	9.5			145.6
3. Resorcinol	1.8	2.9	4.0			159.0
4. Hydroquinone	3.5	3.9	5.0			150.8
5. Guaiacol	4.3	5.8	6.8			147.3
6. Hydroquinone monomethyl ether	3.5	4.0	4.8			151.8
7. 2-Benzylphenol	3.3	4.6	5.2	6.3	7.2	155.4
8. 4-Benzylphenol	2.7	4.1	4.4	5.7	6.4	156.1
9. 2,4-Dibenzylphenol	4.2	8.8	12.3	17.2	21.6	153.8
10. 3-Benzylpyrocatechol	22.0	37.0	49.0	63.5	80.0	145.0; 143.7
11. 4-Benzylpyrocatechol	24.0	42.0	54.0	84.0	110.5	143.7; 145.3
12. 4,5-Dibenzylpyrocatechol	22.5	41.0	64.0	90.5	117.0	143.5
13. 4-Benzylresorcinol	6.5	19.0	33.0	71.0	99.0	157.1; 156.2
14. 2-Benzylhydroquinone	5.8	15.0	23.0	36.0	50.0	148.3; 150.6
15. 2,5-Dibenzylhydroquinone	4.0	11.5	20.5	37.5	37.5	148.1
16. Diphenylmethane	1.3	1.3	1.5	1.6	1.8	
Control		(1.2)				

<sup>a</sup>The other shifts of these compounds have been reported in our previous paper (7).

54 C) were evaluated by measuring the time required to oxidize the wax to a given extent by dry air blowing (2 L/hr) at 160 C. The procedure was followed by Morawetz's method (8). To a melted 50 g of the wax, the antioxidant was added as an aliquot of an alcoholic solution. In order to remove the alcohol, the mixture was heated under reduced pressure, and then poured into a glass test tube (3.5 cm diameter). A constant-temperature oil bath was employed; it was equipped with an immersion heating element that afforded a temperature control of  $\pm 0.5$  C. The rate of the oxidation of the wax was followed by measuring the peroxide value (8). The induction period was defined as the time required to obtain a peroxide value of 50.

## RESULTS AND DISCUSSION

### Activity of Antioxidants

The data of antioxidative activities on compounds 1-16 which are denoted by induction period are listed in Table I. The results indicate that the introduction of a benzyl group on the *para*- and/or *ortho*-positions of the hydroxyl group on the benzene ring greatly increase their antioxidative activities. This may be illustrated by comparing the corresponding data of 1-4 and 7-15, respectively. Both pyrocatechol and resorcinol, 2 and 3, are poor antioxidants. However, their benzyl derivatives, 10-13, show excellent activities. Furthermore, 9 and 12, having dibenzyl groups, show much higher activities compared to those of 7 or 8 and of 10 or 11, having the monobenzyl group. On the contrary, the activity of 15, having dibenzyl groups, is inferior to that of 14, having the monobenzyl group, in various concentrations. The increased activities of the phenols by benzylation do not depend on the activity of a benzyl group since a benzyl group is known to be unaffected by an oxidizing agent and no activity could be detected in 16. Therefore, it can be considered that the high antioxidative activity of the benzylphenols is due to the effects of the phenolic hydroxyl group with the methylene group of the benzyl substituent. These benzylphenols, except for 15, increased their antioxidative activities as their concentrations were increased.

### Correlation between Antioxidative Activities and $^{13}\text{C}$ Chemical Shifts

In order to obtain the factors governing antioxidative activities of 1-15, an attempt was made to plot the ipso-carbon chemical shifts of the OH substituents against their induction periods in the case of the concentration of  $1 \times 10^{-2}$  mol/kg. Since these compounds, 10, 11, 13, and 14, exhibit two different shifts (see Table I), the shifts employed their average value. As can be seen in Figure 1, curve A denotes the relation in the benzylphenol system, and line B denotes that in the phenol system. Their induction periods in both systems, except for 3 and 13, increased with the decreasing of their chemical shifts. This fact indicates that the electron

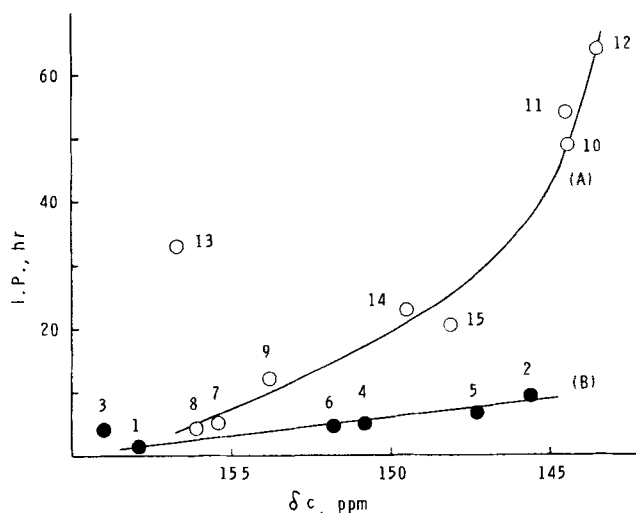


FIG. 1. Plot of the induction period (IP) vs the  $^{13}\text{C}$  chemical shift of the ipso-carbon of the OH substituent. Curve A: compounds 7-15. Line B: compounds 1-6.

density on the ipso-carbon of the OH substituent governs antioxidative activity. In our previous paper (9), it was proved that the transmission through the ipso-carbon to the oxygen atom depend mostly upon the resonance contribution. That is, the total  $\pi$ -electron density on the oxygen atom may be increased by increasing the electron density of the ipso-carbon. According to the proposal by Morokuma et al. (10), this will necessarily decrease the electronegativity of the oxygen atom and make the Coulomb integral of the  $\sigma$  orbital on the oxygen more positive. The reactivity of phenolic hydrogen for an electronegative radical (such as a peroxy radical in Eqn. 1) attack is greatly elevated by an increased  $\pi$ -electron density on the oxygen.

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