Thermal Decarbonylation of Quinones and Related Compounds in the Presence of Hydrogen (Part 2) Hydroquinones and Related Compounds

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Decarbonylation was the main process in the thermal reactions of 9,10-phenanthrenediol, 1,4-naphthalenediol, catechol, hydroquinone and resorcinol in the presence of hydrogen at 500—600°C. A parallel minor reaction was dehydration. The rates of decarbonylation for the above compounds, excluding resorcinol, were smaller than those for the corresponding quinones. The phenol-type or phenoxyl-type structure would not be the key structure for a reaction intermediate in decarbonylation, but would be an intermediate structure in dehydration of the quinones.

1. Introduction

Few studies have been reported on the thermal decarbonylation of hydroquinones and their related compounds, however, a report on thermal reaction of catechol (CTC) appeared in 1931¹⁾. The main products of the thermal reaction of CTC were CO and butadiene similar to that of the present study. However, no kinetic performance of the reaction was revealed there. The study on thermal reaction of phenol (PHN) in the presence of H₂ to form benzene by dehydration was extensively made but no such study was made on the accompanying minor decarbonylation reaction.

Analogous to the thermal reaction of several quinones which was reported in the preceding paper²⁾, decarbonylation was the main process in the thermal reactions of 9,10-phenanthrenediol (PHDO), 1,4-naphthalenediol (NPDO), CTC, hydroquinone (HYQ) and resorcinol (RSC) at 500—600°C. Even 1-naphthol (NPTO) and PHN were partially decarbonylated. Decarbonylation of PHDO and NPDO took place after the dehydrogenation of these compounds to form the corresponding quinones, phenanthrenequinone (PHQ) and naphthoquinone (NPQ), respectively. Dehydration, a side reaction to form phenanthrene (PHT) and naphthalene, proceeded but slightly. In the cases of CTC, HYQ and RSC, both decarbonylation to form unsaturated hydrocarbons, mainly butadiene, and dehydration to form PHN took place simultaneously. In the case of NPTO and

PHN the rate of decarbonylation was very slow and dehydration predominated.

2. Experimental

PHDO was synthesized according to the method found in literature³⁾. Other reagents were commercially available and used with or without purification. Purities of all reagents were confirmed by glc analysis to be better than 99.9%. The contaminated oxygen in the diluent gas, H₂ or He, was removed with a heated copper gauze and the water formed was removed by a silica gel column. The molar ratio of diluent gas to feed stock or substrate was about 10. Experimental apparatus, procedures and methods for product analysis were similar to those reported earlier²⁾. Conversion (%) of the substrate was calculated from the amount of unreacted substrate that remained in the quenched ampule. Mass balance (%) was defined as the ratio of the mass of total compounds recovered to that of feed substrate.

3. Results and Discussion

Typical experimental results of the thermal reaction of PHDO are listed in **Table 1** along with those of PHQ conducted under the corresponding reaction conditions. PHDO was analyzed as PHQ in the present study because dehydrogenation of PHDO to PHQ can be realized quantitatively in the glc column at 200°C. The time course of product formation at 600°C is illustrated in **Fig. 1**.

From **Table 1** and **Fig. 1**, it is clear that decarbonylation proceeds by producing CO, fluorenone (FLR), biphenyl (BPH) and benzene. How-

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Table 2 Decarbonylation of NPDO

	NPDO						NPQ			
Temperature (°C)	546	551	550	602	603	602	550	552	580	582
Reaction Period (min)	5.0	20.0	80.0	8.0	15.0	40.0	15.0	30.0	10.0	40.0
H ₂ to Substrate Molar Ratio	9.7	10.5	10.6	10.9	10.9	11.3	48.3	48.5	19.1	20.0
Conversion (%)	67.1	93.9	100.0	100.0	100.0	100.0	64.7	95.0	97.4	100.0
Mole of Compounds Obtained per 100 Moles of Feed										
CO	13.4	54.0	80.4	81.5	98.9	118.2	43.1	101.2	133.0	183.0
CH ₄	0.0	0.0	0.0	0.0	0.0	0.0	2.7	11.9	6.6	42.2
C ₂ H ₆	0.0	2.3	7.1	3.1	9.3	15.2	0.0	1.3	1.2	17.4
C ₃ H ₈	1.2	5.6	0.0	2.4	1.5	0.0	} 1.2	} 2.7	} 5.8	} 5.9
CO ₂	1.1	3.4	5.4	2.9	3.5	4.4				
Benzene	1.0	12.3	15.2	2.9	7.6	15.8	0.8	3.5	5.2	31.0
Toluene	0.0	1.8	5.1	1.7	5.0	7.8	tr	0.9	2.9	16.6
Ethylbenzene	0.5	6.0	10.2	6.0	8.4	1.0	1.4	11.7	13.6	3.6
Styrene	1.3	3.3	0.8	4.2	1.9	tr	3.6	4.6	10.0	tr
Indene	tr	0.6	0.9	1.7	2.5	0.7	tr	0.4	0.4	1.4
Peak No. 5, 6*)	—	—	—	—	—	—	0.6	2.8	1.3	2.1
Naphthalene	0.1	0.7	2.1	1.4	2.4	4.6	0.3	0.6	0.7	4.2
Peak No. 8, 9*)	—	—	—	—	—	—	2.5	4.3	—	—
NPQ	32.9	6.1	tr	0.0	0.0	0.0	35.3	5.0	2.6	tr
Mass Balance (%)	38.7	31.9	37.7	27.5	37.4	41.8	50.0	62.4	50.4	75.0

*) Unidentified substance

Table 3 Pyrolysis of NPTO or PHN

	NPTO		PHN	
Temperature (°C)	602	602	598	600
Reaction Period (min)	25.0	60.0	15.0	60.0
H ₂ to NPTO or PHN Molar Ratio	11.1	10.8	10.2	10.1
Conversion (%)	66.5	97.1	7.7	40.6
Mole of Compounds Obtained per 100 Moles of Feed				
CO	7.0	14.5	tr	1.6
CH ₄	0.0	0.0	0.0	2.0
C ₂ H ₆	tr	1.7	0.0	3.0
Benzene	0.0	0.0	5.9	33.9
Toluene	tr	1.5	—	—
Styrene	0.0	tr	—	—
Indene	2.7	5.1	—	—
Naphthalene	30.4	50.8	—	—
NPTO or PHN	33.5	2.9	92.3	59.4
Total Mole	73.6	76.5	—	—
Mass Balance (%)	64.1	56.3	97.9	88.7

strate or with NPQ to form high molecular weight substances, causing a substantial deficiency in the mass balance. In the pyrolysis of NPTO listed in **Table 3**, the rate of consumption of NPTO was smaller than that of NPDO in **Table 2**. Dehydration predominated over decarbonylation in case of the monohydroxy compound. At the same time, the mass balance in the NPTO experiment was better than that in the NPDO pyrolysis. These facts suggest that the serious deficiency in mass balance for NPDO pyrolysis is caused by both phenoxyl-type radical and its acceptor or the olefinic double bond. When decarbonylation of NPDO proceeds *via* the NPQ type structure, the reactive double bond at the 2,3-position would function

Fig. 3 Time Course of Reaction of CTC at 600°C (H₂)

as a chain growth unit, thus giving larger amounts of high molecular weight substances. All these facts and discussions are analogous to those of PHDO pyrolysis described above.

Typical experimental results for the thermal reaction of CTC are summarized in **Table 4**, and those for thermal reactions of HYQ, RSC and *p*-benzoquinone (*p*-BNQ) in **Table 5**. Data for *p*-BNQ reaction carried out under H₂ dilution are given for understanding the reaction of HYQ better. Both H₂ and He were used as diluents in these reactions. However, for CTC, HYQ and RSC, no appreciable difference was observed in the initial rates of each substrate consumption

Table 4 Decarbonylation of CTC

Diluent	H ₂			He		
Temperature (°C)	600	600	600	595	598	600
Reaction Period (min)	2.5	5.0	10.0	2.5	5.0	10.0
Diluent to Substrate Molar Ratio	10.3	10.5	10.3	10.3	10.0	10.2
Conversion (%)	58.0	85.3	100.0	41.2	100.0	100.0
Mole of Compounds Obtained per 100 Moles of Feed						
CO	86.3	159.4	179.8	41.5	171.0	180.2
CH ₄	0.7	9.6	37.8	tr	14.0	28.5
C ₂ H ₆	tr	2.4	10.5	tr	1.7	3.1
C ₂ H ₄		3.6	8.0	tr	4.9	6.2
CO ₂	0.3	0.8	0.9	tr	0.5	0.5
C ₂ H ₂	0.1	0.7	12.6	0.1	0.3	0.6
C ₃ H ₆	0.3	3.3	8.3	0.7	3.9	6.3
C ₄ H ₈	3.4	8.0	4.8	5.4	7.7	2.8
C ₄ H ₆	6.2	3.3	0.6	10.4	5.3	1.3
Benzene	3.7	3.2	5.0	1.2	6.7	9.1
Toluene	0.2	0.7	1.6	0.4	2.9	4.3
Styrene + Ethylbenzene	0.1	0.6	1.0	—	—	—
PHN	3.8	5.0	4.3	1.4	3.8	3.6
CTC	42.0	14.7	0.0	58.8	0.0	0.0
Mass Balance (%)	75.2	73.4	75.0	79.8	66.6	71.7

Fig. 4 Time Course of Reaction of CTC at 600°C (He)

Fig. 5 Time Course of Reaction of HYQ at 600°C

and of CO formation between the two diluents, H₂ and He, as shown in **Figs. 3** and **4** for the cases of CTC. **Figs. 5** and **6** illustrate, therefore, the time courses of the molar amounts of reactants and products of the HYQ and RSC reactions under He dilution, respectively.

It is clear from **Table 4** and **Figs. 3** and **4** that primary products in the thermal reaction of CTC are CO, hydrocarbons, consisting mostly of butadiene, and PHN under H₂ dilution, while PHN shifts from a primary reaction product to a successive reaction product under He dilution. Benzene was a typical successive reaction product and its yield did not decrease with reaction period under the present reaction conditions. It might

be formed not only through dehydration of PHN but also through Diels-Alder reaction between butadiene and olefins followed by dehydrogenation^{4),5)}. This is supported by the following two observations that PHN was dehydrated very slowly at 600°C and under H₂ dilution as listed in **Table 3** and that the yield of benzene was higher for He dilution than for H₂ dilution owing presumably to the higher concentrations of butadiene and olefins at the initial stages of the reaction. It is a reasonable result that, under He dilution, the yield of PHN and, at the same time, the rate of hydrocracking of butadiene and olefins are smaller than those under H₂ dilution.

Similar reaction courses can be postulated for

Table 5 Decarbonylation of HYQ and RSC

Substrate	HYQ				RSC				<i>p</i> -BNQ		
Diluent	H ₂		He		H ₂		He		H ₂		
Temperature (°C)	598	601	596	600	600	599	600	602	589	590	590
Reaction Period (min)	5.0	15.0	5.0	15.0	10.0	40.0	10.0	40.0	5.0	10.0	20.0
Diluent to Substrate Molar Ratio	10.3	10.0	10.0	10.0	10.5	9.8	9.8	9.8	10.3	10.3	10.5
Conversion (%)	17.8	58.1	11.5	64.8	18.6	83.3	28.7	83.1	100.0	100.0	100.0
Mole of Compounds Obtained per 100 Moles of Feed											
CO	16.5	69.0	21.4	98.2	14.0	65.5	16.5	69.1	94.2	103.4	107.4
CH ₄	0.9	18.2	0.8	13.2	9.5	67.8	3.6	31.8	3.7	10.4	18.3
C ₂ H ₆	0.8	8.8	tr	1.8	1.7	26.7	0.0	2.5	1.1	3.3	8.2
C ₂ H ₄	tr	3.2	tr	3.2	tr	1.0	0.0	2.3	2.5	3.2	3.4
CO ₂	3.7	0.5	tr	0.9	4.0	12.4	5.6	24.3	9.7	8.5	8.2
C ₂ H ₂	0.1	3.6	0.1	0.6	0.8	6.8	0.0	tr	0.6	2.5	5.1
C ₃ H ₈	0.3	3.6	0.4	3.5	2.2	0.3	0.7	1.7	1.5	2.4	1.6
C ₄ H ₁₀ 's	0.6	2.0	1.6	2.3	0.6	tr	0.3	0.1	2.6	1.5	0.5
C ₄ H ₆	0.3	0.5	2.9	1.7	0.2	tr	0.2	0.1	0.9	0.2	0.1
Benzene	0.4	1.5	0.4	4.1	0.9	6.0	0.4	2.9	4.5	4.3	5.4
Toluene	0.2	0.7	tr	1.7	0.2	0.7	0.2	1.8	0.6	0.8	1.3
Styrene + Ethylbenzene	0.0	tr	—	—	tr	0.0	—	—	1.2	1.3	1.0
PHN	3.2	15.6	2.1	7.9	11.1	21.9	3.0	5.7	2.1	6.7	10.5
HYQ	82.2	41.9	82.5	35.2	—	—	—	—	37.2	31.9	26.2
RSC	—	—	—	—	81.4	16.7	71.3	16.9	0.7	0.9	1.0
<i>p</i> -BNQ	—	—	—	—	—	—	—	—	(Naphtha- lene) tr	(Naphtha- lene) 0.0	(Naphtha- lene) 0.0
Mass Balance (%)	92.0	84.1	92.5	78.7	100.2	81.0	82.2	61.2	77.9	80.4	82.2

Fig. 6 Time Course of Reaction of RSC at 600°C

the reactions of HYQ and RSC based on the results shown in **Table 5** and **Figs. 5** and **6**. Decarbonylation was the main and primary process for all cases. The ratio of rates of decarbonylation was about 15:2:1 for CTC:HYQ:RSC. As already mentioned, the absolute rate as well as the above ratio was maintained nearly constant in both reactions under H₂ and under He dilution. The ratio of dehydration rate, *i.e.*, the formation of PHN, was about 4:2:1 for CTC:HYQ:RSC under H₂ dilution, and under He dilution, the absolute rate

of dehydration was naturally much less. The difference in the rates of decarbonylation and dehydration for these reactants is interesting in that it is related to the structures of the reactants and the mechanisms of decarbonylation and dehydration. The reactants, CTC and HYQ, which can be converted to the quinone structure, are decarbonylated more readily than RSC. However, CTC is more rapidly decarbonylated than HYQ because CTC is converted to *o*-quinone while HYQ is converted to *p*-quinone. It is known that *o*-quinones are decarbonylated more readily than *p*-quinones²⁾.

Decarbonylation of *p*-BNQ in the presence of H₂ proceeded more than 3 times as fast as that of HYQ. No *p*-BNQ was found in the products of HYQ pyrolysis, but instead, HYQ and PHN were found in the products of *p*-BNQ hydrocracking. Thus, HYQ should not be considered as an intermediate compound of *p*-BNQ decarbonylation, but instead, *p*-BNQ should be considered as an intermediate compound of HYQ decarbonylation. Another difference between the reaction of *p*-BNQ and that of HYQ was the substantial amount of CO₂ formation in the former case.

This CO₂ formation is a characteristic feature of RSC pyrolysis. However, the mechanism of CO₂ formation is still not clearly understood, but it can be said that CO₂ is formed *via* intramolecular

mechanism. The reasons are that, first, CO_2 was never detected in the products of NPTO, PHN or FLR pyrolysis⁶⁾, *i.e.*, a molecule having only one oxygen atom in its structure never produces CO_2 on pyrolysis, and, second, in the case of 1,4-naphthoquinone pyrolysis⁷⁾, the rate of CO_2 formation remained almost unchanged with varying H_2 dilution ratio.

Although analysis of unidentified high molecular weight substances has not been performed in these experiments and although discussion on the mechanism of product formation may not be sufficient, certain conclusions could be drawn as follows. Aromatic dihydroxy compounds undergo decarbonylation as the corresponding quinones in the presence of H_2 . The hydroxy compound formed may

not be an intermediate compound of quinone decarbonylation but may be an intermediate compound of dehydration which is a minor reaction of quinone hydrocracking.

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要 旨

水素存在下におけるキノンおよび関連物質の熱的脱カルボニル (第2報)

ハイドロキノンおよびその関連物質

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9,10-フェナントレンジオール (PHDO), 1,4-ナフトレンジオール (NPDO), カテコール¹⁾ (CTC), ハイドロキノン (HYQ) およびレゾルシノール (RSC) の各物質もキノン類と同様に水素存在下 500~600°C で脱カルボニルする。副反応として脱水も一部進行する。1-ナフトール (NPTO) やフェノール (PHN) も極く一部脱カルボニルするけれども、この場合は脱水が主反応である。

実験装置や方法は既報の通りである²⁾。PHDO は文献の方法³⁾ で合成し、精製した。

PHDO の実験条件と結果を比較のためフェナントレンキノン (PHQ) の結果と合わせて Table 1 に掲げた。Table 1 と Fig. 1 に示したように PHDO も PHQ と同様に CO, フルオレノン (FLR), ビフェニル (BPH) およびベンゼンを生成した。しかし、PHDO の場合は PHQ より原料消耗速度は大きいにもかかわらず、CO 生成速度は小さく、glc で検出できる全生成物の収率が悪かった。脱水によるフェナントレン (PHT), フルオレノンの量も多かった。実験の物質収支が悪い訳は Eq. 1 で生成するフェノキシル型ラジカルによるものと考えられる。

NPDO の実験結果を 1,4-ナフトキノン (NPQ) のそれと合わせて Table 2 と Fig. 2 に示した。NPDO, NPQ とともに脱カルボニルが進行して CO, C₂H₄, スチレンを、また脱水によりナフトレンを生成した。NPDO では脱水が顕著で、また物質収支も悪かった。これはフェノキシル型ラジカルの生成

に起因するものと考えている。ナフトール (NPTO) では脱水が主として進行する事実 (Table 3) がそれを支持している。

Table 4 に CTC の, Table 5 に HYQ, RSC および *p*-ベンゾキノン (*p*-BNQ) の実験結果を示した。CTC, HYQ, RSC については H₂ 希釈と He 希釈で CO 生成速度に差はなかった。CTC について両希釈ガスの実験結果を Figs. 3 と 4 に示した。Figs. 5 と 6 には He 希釈下での HYQ と RSC の実験結果を示した。CTC の熱反応での主生成物は CO とブタジエンを主とする炭化水素および PHN であった。反応後期にベンゼンが生成するのは PHN の脱水とブタジエンとオレフィンの環化的付加、脱水素によるものと考えられる^{4),5)}。

HYQ や RSC でも同様に脱カルボニルと脱水による PHN の生成がみられた。脱カルボニルの速度比は CTC:HYQ:RSC についておよそ 15:2:1 であり、脱水の速度比は 4:2:1 であった。CTC と HYQ は脱水素してキノン構造をとりうるので脱カルボニル速度が大きいと考えられる²⁾。*p*-BNQ の脱カルボニル速度は HYQ のそれより3倍大きく、また *p*-BNQ の反応生成物中に HYQ が存在するのに対して HYQ の脱カルボニル反応の生成物中に *p*-BNQ が存在しない事実も認めている。反応生成物中に存在する CO₂ については、その生成機構が明らかではない^{6),7)}。最も顕著に CO₂ を生成する RSC についてその生成機構を考えてみることは興味深い。

本研究の重要な結論はキノン類の脱カルボニル反応はヒドロキシル構造を通過して進むのではないこと、ヒドロキシル構造は副反応である脱水反応の中間体であろうということである。

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Keywords

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