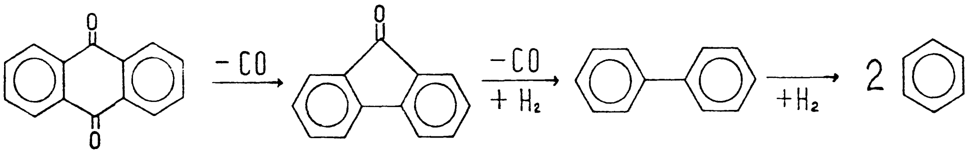
CHEMISTRY LETTERS, pp. 1103-1106, 1975. Published by the Chemical Society of Japan

THERMAL DECARBONYLATION OF QUINONES IN THE PRESENCE OF HYDROGEN

Tomoya SAKAI and Masayuki HATTORI
Department of Chemical Reaction Engineering, Faculty
of Pharmaceutical Sciences, Nagoya City University
3-1, Tanabedori, Mizuhoku, Nagoya 467

Non-catalytic thermal decarbonylation of quinone proceeded for 9,10-phenanthrenequinone, 1,4- and 1,2-naphthoquinones and p-benzoquinone as well as for 9,10-anthraquinone in the previous study.1) In the cases of 1,2-naphthoquinone and p-benzoquinone, however, the title reaction occurred only in 20 - 40% selectivity due to the consumption of feed quinones seemingly through simultaneous polymerization.

A novel reaction of anthraquinone (ANQ) was reported by the authors , which proceeded consecutively as shown below at ca. 600°C in the presence of hydrogen.

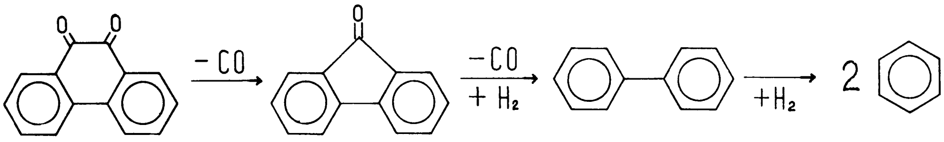


Occurrences of similar reactions were examined for 9,10-phenanthrenequinone (PHQ) 1,4- and 1,2-naphthoquinones (NPQ), and p-benzoquinone (BNQ), and their results combined with a short discussion were described in the present paper.

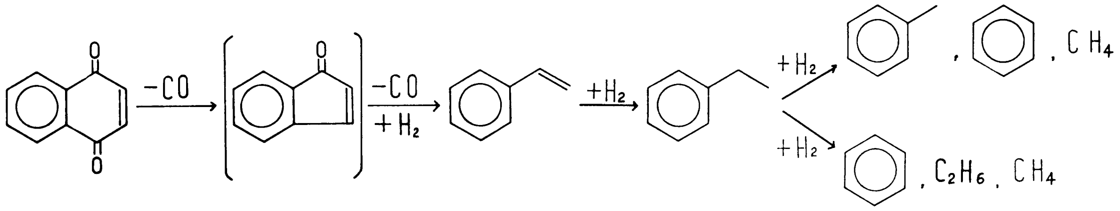
PHQ was synthesized according to the method of literature.2) Commercially available 1,4- and 1,2-NPQ and p-BNQ were used with or without purifications.3)4)5) The purities of feed materials were confirmed to be more than 99.9% by gas chromatographic analyses. Hydrogen was rectified through a heated copper gauze for removal of contaminated oxygen followed by a silica gel column for removal of water. Experiments were conducted by use of transparent quartz ampules of 20 mm i.d. and 130 mm length as reaction vessels. Quartz was used to attain an improved temperature profile throughout the reaction period by a sudden heating-up at the start and quenching at the end of the experiment. Detailed procedures and the methods of analyses were described in the previous paper.1)

Typical experimental results are summarized in Tables I - III. Conversion (%) was calculated based on the amount of unreacted quinones remained in a quenched ampule. Mass balance (%) was defined to be a ratio of the mass of total products measured from gas chromatographic peaks by use of three apparatus furnished with MS5A, silica gel, and silicone GE-SE30 to the mass of feed quinone. Accordingly, in the case where a polymerized compound of high molecular weight is formed, it results as the shortage in mass balance (%).

As listed in Table I, main products in the case of PHQ were CO, benzene, biphenyl and fluorenone, and minor ones were phenanthrene and fluorene. It is clear from the change of product distribution with time that a typical consecutive reaction scheme holds in this case similarly to that in the case of ANQ, although the reaction temperature was about 30 - 40°C lower for the reaction of PHQ than that in the case of ANQ to attain the corresponding conversions.



In the cases of 1,4- and 1,2-NPQ and p-BNQ, as listed in Table II and III, respectively, the shortages in mass balances were great and at the same time pretty large amount of CO_2 was formed. However, it can be said that the decarbonylation is still a main reaction course for the case of 1,4-NPQ. In this case, though indenone could not be detected as one of the products, the existences of styrene, ethylbenzene combined with CO at the initial stage of the reaction enabled us to propose the following reaction scheme.



Similar schemes can be assumed for the reaction of 1,2-NPQ and p-BNQ, although the shortages in mass balances were considerably large in both cases

Table I. Decarbonylation of PHQ

Temperature, °C	589	587	583	583	594	597	595	588
Reaction period, min.	2.5	5.0	7.5	10	15	30	60	120
H_2/PHQ molar ratio	10.1	10.7	11.1	10.9	10.7	10.8	10.6	11.4
Conversion, %	26.6	94.3	100.0	100.0	100.0	100.0	100.0	100.0
Moles of obtained compounds per 100 moles of feed								
CO	17.5	81.0	84.1	93.8	108.6	148.0	136.5	163.5
Benzene	0.0	0.0	0.0	0.4	1.4	13.6	32.0	65.9
Biphenyl	0.2	4.6	8.2	11.8	27.7	38.9	36.0	30.7
Fluorene	0.5	6.1	4.5	6.0	6.4	5.0	5.3	4.7
Fluorenone	16.7	54.3	78.5	55.2	30.4	5.6	0.9	0.0
Phenanthrene	0.0	0.0	0.0	0.0	0.2	0.9	1.9	2.3
PHQ	73.4	5.7	0.0	0.0	0.0	0.0	0.0	0.0
Total mole	108.3	151.7	175.3	167.2	174.7	212.0	212.6	267.1
Mass balance, %	90.8	71.9	88.9	74.1	67.2	63.4	63.7	75.2

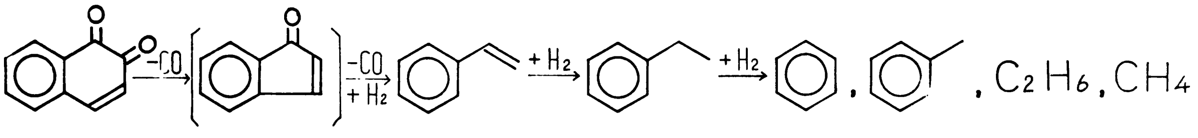
Table II. Decarbonylation of 1,4-NPQ and 1,2-NPQ

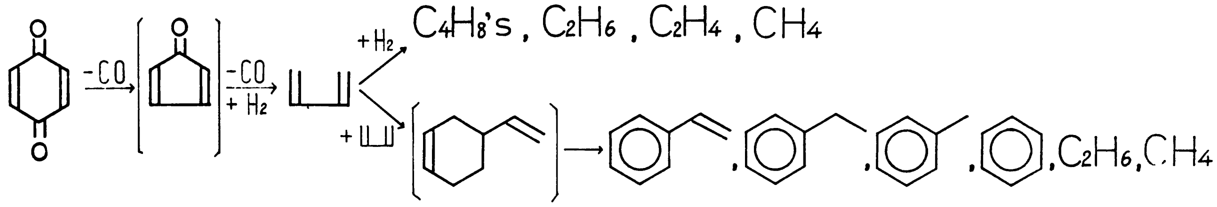
	1,4-NPQ						1,2-NPQ					
Temperature, °C	581	581	580	582	584	582	577	575	573	572	578	579**)
Reaction period, min.	5.0	7.5	10.0	15.0	20.0	30.0	5.0	7.5	10.0	15.0	30.0	15.0
H_2/NPQ, molar ratio	19.5	19.5	19.1	20.4	19.1	19.4	21.2	21.7	21.9	22.0	20.8	20.7
Conversion, %	51.3	88.7	97.4	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Mole of obtained compounds per 100 moles of feed												
CO	54.4	104.0	133.0	155.0	166.0	167.0	43.1	38.6	41.0	51.0	48.2	28.2
CO_2	2.7	10.6	5.0	7.2	5.1	5.1	16.8	16.8	16.4	16.4	17.4	18.9
Methane	t	3.6	6.6	16.1	21.8	36.3	0.9	1.0	1.3	2.6	5.2	2.0
Ethane	0.0	t	1.2	6.6	11.0	15.6	0.3	0.3	0.5	1.2	2.1	0.5
Benzene	0.7	3.1	5.2	11.7	17.3	24.9	0.7	0.9	1.3	3.0	4.2	2.0
Toluene	0.4	1.5	2.9	8.8	13.0	16.2	0.6	0.5	0.6	1.3	2.2	0.6
Ethylbenzene	1.1	7.3	13.6	18.8	14.6	7.1	2.3	2.7	3.8	5.3	2.7	1.4
Styrene	7.3	12.3	10.0	2.8	1.1	0.4	2.1	1.1	1.0	t	t	t
Indene	t	0.5	0.4	0.4	0.9	0.9	t	t	t	t	0.0	0.0
Peak 5*)	t	0.5	1.3	2.7	3.0	2.8	t	t	t	t	0.0	0.0
Naphthalene	0.4	0.5	0.7	1.4	2.3	3.6	t	t	t	0.9	2.0	t
1,4- or 1,2-NPQ	48.7	11.3	2.6	t	t	t	0.0	0.0	0.0	0.0	0.0	0.0
Total mole	115.7	155.2	182.5	231.5	256.1	279.9	66.8	61.9	65.9	81.7	82.0	53.6
Mass balance, %	65.1	49.6	50.2	61.0	66.5	70.1	16.1	15.0	16.2	20.6	21.1	12.9

*) Unidentified substance.

**) Sealed ampule was treated at 200°C for 10 min. before putting into the furnace maintained at 580°C.

caused probably by the polymerization of feed materials.





By use of high speed liquid chromatography, several higher molecular weight substances than feed quinones were detected in the products of these reactions. They have not been identified yet. Result of the experiment listed on the last column in Table II showed that polymerization of 1,2-NPQ proceeded even at 200°C and that the polymerization depressed the decarbonylation seriously. It is not clearly understood until present why the shortages in mass balance were large especially in the cases of 1,2-NPQ and p-BNQ. The reactive double bonds in the structures of these compounds may play some important role for the formation of high molecular weight substances.

Table III. Decarbonylation of p-BNQ

Temperature, °C	585	584	589	590	591
Reaction period, min.	2.5	5.0	7.5	10.0	30.0
H_2/BNQ molar ratio	9.9	9.7	9.6	10.0	10.0
Conversion, %	57.6	100.0	100.0	100.0	100.0
Mole of obtained compounds per 100 moles of feed					
CO	26.9	80.7	89.8	97.8	108.1
CO_2	2.6	7.5	7.4	7.3	7.5
Methane	t	1.0	2.7	5.4	17.0
Ethane	t	0.4	1.8	3.2	13.4
Ethylene	t	0.7	1.1	1.5	0.9
Acetylene	t	t	0.5	2.0	4.6
1-Butene	t	0.9	0.5	0.3	0.3
t-2-Butene	t	1.3	0.8	0.6	0.6
c-2-Butene	t	1.3	0.6	0.5	0.5
Butadiene	12.0	1.8	0.3	0.2	0.3
Benzene	0.5	2.1	3.0	3.5	5.8
Toluene	0.0	0.4	0.6	0.7	1.4
Ethylbenzene	t	0.4	0.8	0.9	0.2
Styrene	0.3	0.7	0.2	t	t
BNQ	42.4	0.0	0.0	0.0	0.0
Total mole	84.7	99.2	110.1	123.9	160.6
Mass balance, %	57.0	30.0	32.3	35.6	45.0

References

1) T. Sakai and M. Hattori, Chem. Lett., 617 (1974).
2) R. Wendland and J. Lalonde, Org. Syn., Coll. Vol. IV, 757 (1963).
3) E.A. Braude and J.S. Fawcett, ibid., Vol. IV, 698 (1963).
4) L.F. Fieser, ibid., Vol. II, 430 (1943).
5) H.W. Underwood and Jr., W.L. Walsh, ibid., Vol. II, 553 (1943).

(Received August 11, 1975)