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HYDROCRACKING OF 9,10-ANTHRAQUINONE

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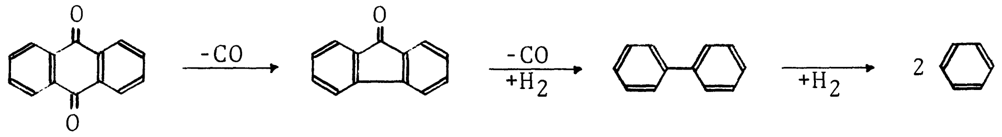
Non-catalytic hydrocracking of 9,10-anthraquinone at 600 - 900°C proceeded as a typical consecutive reaction yielding fluorenone plus CO in the first step, biphenyl plus CO and benzene in the succeeding steps. The found reaction which is expected to occur for general quinones has an important industrial meaning in the hydrocracking of petroleum heavy residues.

It was found that the non-catalytic hydrogenation of 9,10-anthraquinone (ANQ) yielded fluorenone, biphenyl, benzene and carbon monoxide (CO) at temperatures 600 - 900°C under atmospheric pressure. The reaction proceeded consecutively, yielding fluorenone plus CO in the first step, biphenyl plus CO and benzene in the succeeding steps.



(1)

The found reaction is expected to have an important industrial meaning in the hydrocracking of coal or petroleum heavy residues, in conjunction with the preliminary oxidation process of condensed aromatic rings.

A commercially available ANQ of 99.99% purity or more by gas chromatographic analysis was used without a further purification. Hydrogen from a cylinder was purified by a heated copper gauze for a small percentage of oxygen and was dried through a silica gel column.

The reaction vessel was a transparent quarz ampule of 20 mm i.d. and 130 mm long. Quarz was used to attain an improved temperature profile throughout the reaction period by a sudden heating-up and quenching. Amount of ANQ put in an ampule was ca. 15 mg (72 μ mol) and hydrogen pressure was around 400 mmHg. On the start of the reaction, six ampules were inserted in a stainless-steel block furnace, the temperature of which was maintained at ca. 600°C. After fixed reaction periods between 2.5 and 160 minutes, the ampules were taken out of the furnace one by one to quench immediately in a cooled water bath. The reaction products were gaseous and solid. Gaseous products were analyzed by gas chromatographs furnished with MS5A, carbowax and squalane columns. Solid products were dissolved in acetone in the absence of light and were analyzed by the silicone column gas chromatograph. Pyrene was added to the acetone solution as an standard substance.

Typical experimental results are summarized in Table I.

Table I. Decarbonylation of ANQ

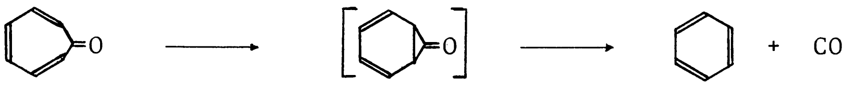
Temperature, °C	ca.600	ca.600	590	595	610	620	630
Reaction period, min	3.0	4.0	10.0	20.0	40.0	80.0	160.0
H_2/ANQ, molar ratio	9.5	10.0	10.5	11.3	11.7	12.4	12.2
Conversion, %	0.0	10.3	9.3	28.7	84.0	100.0	100.0
Mole of obtained compounds per 100 moles of feed							
CO	0.0	0.0	3.8	22.0	110.3	178.4	176.4
Benzene	0.0	0.0	0.0	t	8.1	84.8	133.6
Biphenyl	t	t	t	3.2	29.9	34.3	4.6
Fluorene	0.0	0.0	t	t	3.0	5.6	5.4
Fluorenone	0.6	1.8	4.1	14.9	21.4	t	t
Anthracene	t	t	t	t	0.9	1.8	1.6
ANQ	100.8	89.7	90.7	71.3	16.0	0.0	0.0
Unidentified polymer*	-	-	0.2	0.3	0.5	2.0	2.0
Total mole	101.4	91.5	98.8	111.7	190.1	306.9	323.6
Mass balance, %	101.4	91.3	95.2	90.3	78.9	91.3	86.9
$\frac{\text{CO obs.}}{\text{CO calc.}}$, %	-	-	92.7	103.3	119.5	112.2	119.0

* assumed to be ANQ dimer.

The temperature varied slowly along with the reaction period. The indicated temperature in Table I corresponds to that of the furnace at the withdrawal of each ampule from the furnace. Conversion was calculated based on the amount of ANQ remained in a quenched ampule. The main products were carbon monoxide, benzene, biphenyl and fluorenone. Very small amounts of methane, naphthalene, fluorene, anthracene, and unidentified high molecular weight compounds which were all together assumed to be ANQ dimer were detected by the glc analysis. Mass balance was calculated as the ratio of the mass of the compounds appeared in gas chromatogram to that of the feed ANQ. CO obs./CO calc. means the ratio of the amount of CO obtained to that of CO calculated from the stoichiometry of the reactions (1).

It is clear from Table I that a typical consecutive scheme holds in this reaction. An additional experiment conducted at ca. 800°C, residence time ca. 0.1 sec in a flow-type apparatus proceeded in the same scheme. By use of He instead of H_2 in the flow-type apparatus, fluorenone was a sole main product. No benzene nor biphenyl was formed.

Similar decarbonylation is reported to proceed thermally in the case of tropone and tropolone homologues.[1] In the case of tropone, it is proposed that the three membered ring compound is a possible intermediate of the decarbonylation reaction based on the orbital symmetry rule by Woodward and Hoffmann.[2]



(2)

Namely, the formation of such an intermediate is thermally allowed. As far as the orbital symmetry rule is concerned, since the same symmetrical situation is expected for ANQ,[3] the thermal decarbonylation of ANQ is not inconsistent with the Woodward - Hoffmann rule.

Another example is the thermal reaction of cathecol.[4] In this case butadiene and CO are produced. In the liquid phase, D. Hausigk[5] and D.G. Davies and P. Hodge [6] have recently succeeded in the cleavage of ANQ to yield benzoic acid and/or phthalic acid. No report has been found concerning the thermal decarbonylation of ANQ. The authors are now proceeding on the examination of the thermal decarbonylations of 9,10-phenanthrenequinone and 1,4-naphthoquinone in the presence of hydrogen.[7]

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