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THERMAL DECARBONYLATION OF CATECHOL, HYDROQUINONE AND RESOLSINOL

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Decarbonylation proceeded as the main primary process in thermal reactions of catechol, hydroquinone, and resorcinol at 500 - 600°C under H_2 or He dilution. An accompanying minor process was dehydration to form phenol. The rate of decarbonylation of hydroquinone pyrolysis was smaller than that of p-benzoquinone pyrolysis under H_2 dilution.

Analogous to the thermal reaction of several quinones which was reported previously,[1,2] decarbonylation was the main primary process in the thermal reaction of catechol (CTC), hydroquinone (HYQ) and resorcinol (RSC) at 500 - 600°C. Features of the present reactions, however, differed from those of quinones in the following points. First, the effect of H_2 dilution which was observed in the decarbonylation of anthraquinone, fluorenone or 1,4-naphthoquinone[3] was not found in the present case, i.e., the rate of decarbonylation remained unchanged either by H_2 or by He dilution. Second, decarbonylation in the present case under H_2 dilution was accompanied by simultaneous dehydration which gave phenol (PHN) as one of the main primary products of the reaction.

Purities of reactants, CTC, HYQ, RSC and PHN, were confirmed to be more than 99.9% by gas chromatographic analysis. Deoxygenated and dried H_2 or He was employed as a diluent gas to the reactant. Molar amount of a diluent gas was around 10 times as much as that of the reactant. Reaction vessel was a transparent quartz ampule of 20 mm i.d. and 130 mm length. Six sealed ampules were subjected to the reaction at one time by inserting them into a six-holed SUS 27 block furnace maintained at 500 - 600°C. After fixed reaction periods, t = 2.5-60 min., each ampule was taken out of the furnace one by one to be quenched immediately in a water bath. Amounts of products and remaining reactant were determined by three sets of gas chromatographs.[1]

Typical experimental results are summarized in Table I. Other than the results for the reactions of CTC, HYQ and RSC, those for p-benzoquinone (p-BNQ) and PHN were listed in the table to get a better understanding for the feature of successive processes in the reaction. Conversion x (%) was calculated based on

Table I. Decarbonylation of Catechol, Hydroquinone, Resorcinol, p-Benzoquinone and Phenol

	C T C			H Y Q		R S C		p-BNQ	P H N
Diluent	H_2		He	H_2	He	H_2	He	H_2	H_2
Temperature, °C	600	500	600	600	600	600	600	590	600
t, min	2.5	20.0	2.5	15.0	15.0	20.0	20.0	2.5	60.0
x, %	33.3	34.4	41.2	65.5	64.8	49.0	51.4	29.7	40.6
	Mole of obtained compounds per 100 moles of feed								
CO	39.9	40.0	41.5	49.8	98.2	35.1	34.7	34.1	1.6
Methane	0.7	0.4	t	18.2	13.2	31.1	14.1	t	2.0
Ethane	t	0.0	t	8.8	1.8	9.1	0.6	t	3.0
CO_2	0.3	0.0	t	0.5	0.9	12.0	13.9	5.0	0.0
Ethylene	t	0.0	t	3.2	3.2	1.6	0.5	t	—
Acetylene	0.1	t	0.1	3.6	0.6	5.9	t	t	—
Propylene	0.3	0.2	0.7	3.6	3.5	2.4	1.6	t	—
Butenes	3.4	3.6	5.4	2.0	2.3	0.5	0.3	t	—
Butadiene	6.2	2.5	10.4	0.5	1.7	0.1	0.2	0.9	—
Benzene	3.7	0.5	1.2	1.5	4.1	2.0	1.1	2.6	33.9
Toluene	0.2	t	0.4	0.7	1.7	0.5	0.8	t	—
Styrene	0.1	t		t		t		0.4	—
Phenol	8.1	1.7	1.4	15.0	7.9	17.0	4.6	t	—
Hydroquinone	—	—	—	—	—	—	—	9.8	—
Unreacted feed	66.7	65.6	58.8	34.5	35.2	51.0	48.6	70.3	59.4
Mass balance, %	91.8	80.8	90.4	71.3	78.7	91.1	72.8	94.3	88.7

the amount of reactant remained in a quenched ampule. Mass balance (%) was defined to be a ratio of the mass of total compounds recovered which were measured from gas chromatographic peaks to the mass of feed reactant. Accordingly, whenever any compounds of high molecular weight were formed, there was a shortage in mass balance (%).

Overall course of the reaction is illustrated as amount of product vs. reaction period curves in Figure 1 for the case of CTC under H_2 dilution, or under He dilution, at around 600°C. There is an apparent induction period for both cases. The batch system apparatus employed in these experiments was responsible for this induction period. From a blank test of temperature measurement at the beginning of the reaction, it was concluded that no real induction period existed in these reactions.

It is clear from Figure 1 that primary products in the thermal reaction of CTC are CO, hydrocarbons mostly butadiene, and PHN in the case of H_2 dilution, while PHN shifts to a secondary product in the case of He dilution. Benzene was a typical secondary product and never decreased in its yield 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 facts that PHN dehydrated very slowly under these reaction conditions (Table I) and that the yield of benzene was higher in the case of He dilution than that of H_2 dilution caused by higher concentrations of butadiene and olefins at the initial stage of the reaction. It is reasonable in the case of He dilution that the yield of PHN

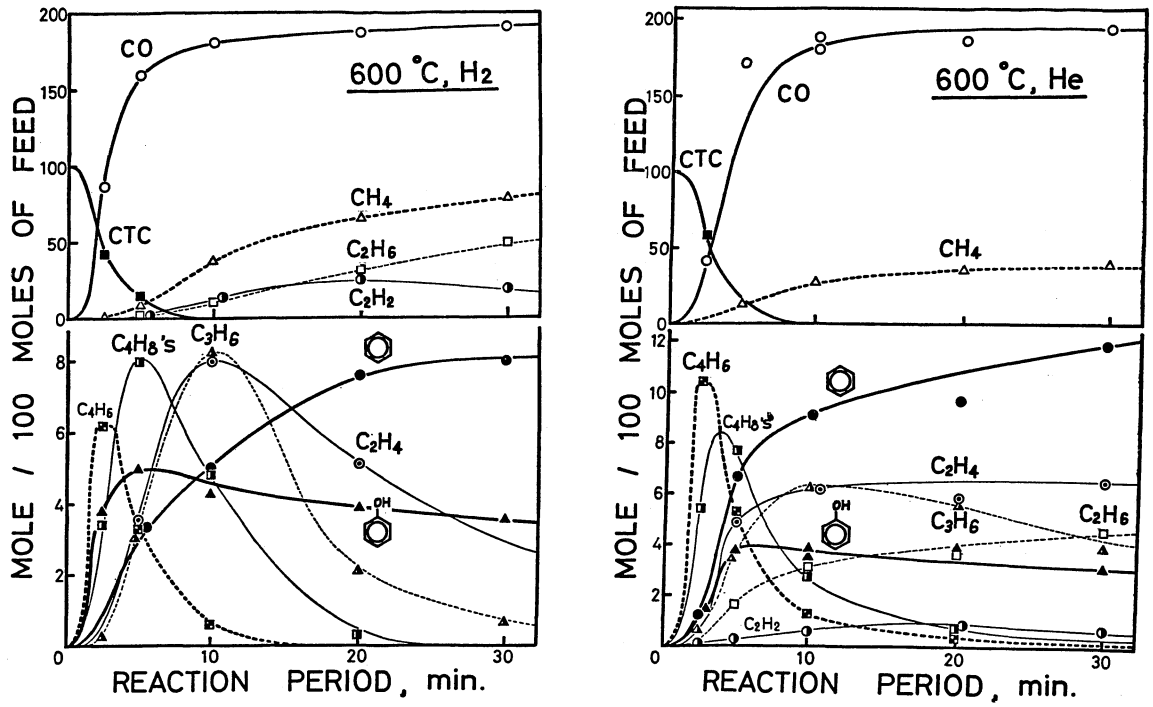

Figure 1. Decarbonylation of CTC under H_2 or He dilution.

and at the same time the rate of hydrocracking of butadiene and olefins are smaller than those in the case of H_2 dilution.

Similar reaction course can be postulated for the reactions of HYQ and RSC. Decarbonylation was a main and a primary process for all cases. The ratio of rates of decarbonylation was around 15 : 2 : 1 for CTC : HYQ : RSC. The absolute rate as well as the above ratio were maintained nearly constant in both reactions under H_2 and He dilution. On the contrary, the ratio of rates of dehydration, i.e., formation of PHN, was around 4 : 2 : 1 for CTC : HYQ : RSC in the case of H_2 dilution. The absolute rate of dehydration was naturally much decreased in the case of He dilution. Differences in the rates of decarbonylation and those of dehydration among these reactants are interesting facts in relation to the structure of reactants and the mechanisms of both decarbonylation and dehydration which are expected to be clarified in the future. Decarbonylation of p-BNQ in the presence of H_2 proceeded more than 3 times faster than that of HYQ. No p-BNQ was found in the products of HYQ pyrolysis, while HYQ and PHN were obtained in the products of p-BNQ hydrocracking. Another difference between the reaction of p-BNQ and that of HYQ was a pretty large amount of CO_2 formation in the former case.

Concerned with the CO_2 formation, it was also a characteristic feature of RSC pyrolysis. By now, the mechanism of CO_2 formation is not clearly understood. However, it can be said that CO_2 is formed via an intramolecular mechanism. Reasons are that CO_2 was never detected in the products of PHN or fluorenone pyrolysis, i.e., the reactant molecule which has only one oxygen atom in its structure never produced CO_2 on pyrolysis, and that, in the case of 1,4-naphthoquinone pyrolysis,[6] the rate of CO_2 formation remained almost unchanged by varying H_2 dilution ratio.

Although the results are not yet conclusive, the facts obtained in the present work are expected to be a valuable information to the elucidation of the mechanism of hydrodecarbonylation of quinones. Extensive studies are under way on the pyrolysis of 1,4-cyclohexanedione or other ketones.

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