BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 2695—2697 (1969)

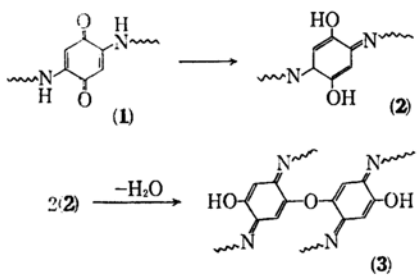
Amino-quinoid Polymeric System. The Thermal Reaction of 2,5-Bis(*n*-butylamino)-*p*-benzoquinone

Kazuyuki SUGITA*1 and Ju KUMANOTANI

The Engineering Research Institute, Faculty of Engineering, The University of Tokyo, Yayoi, Bunkyo-ku, Tokyo

(Received January 9, 1969)

Previously we have demonstrated that the 2,5-bis(aliphatic-amino)-*p*-benzoquinone nucleus (**1**), incorporated in the polymer chain, is quite sensitive to heat and can react to give (**2**) and (**3**), through isomerization and subsequent intermolecular condensation respectively, as follows:[1]



In order to elucidate the thermal reaction of (**1**) in detail, a model pyrolysis of 2,5-bis(*n*-butylamino)-*p*-benzoquinone was investigated at 195°C by means of IR spectroscopy, GLC, TLC, and pyrolytic gas chromatography. As the pyrolysis products, water, ammonia, *n*-butane and propane, 2-*n*-butylamino-*p*-benzoquinone, 2-amino-5-*n*-butylamino-*p*-benzoquinone, and 3-*n*-butylamino-7-hydroxy-9-*n*-butyl-carbazolquinone (1,4) were identified; unknown butylated butylamino-benzoquinoid and oligo-quinoid compounds were also separated.

On the basis of these results, the following reactions can be proposed for the pyrolysis reaction of 2,5-bis(*n*-butylamino)-*p*-benzoquinone: (a) the above reactions, isomerization and condensation, (b) the fission of the carbon and nitrogen bond in the alkylamino group and, (c) the migration reaction of the *n*-butylamino group. Furthermore, the distribution of the pyrolysis products and the change in the composition of the gaseous products as a function of time (see Fig. 1) show that the reactions (a) and (b) make a more significant contribution to the pyrolysis than (c), and that the reaction (a) precedes the reaction (b). This conclusion agrees well with those previously obtained for the amino-quinoid polyester system.[1]

Experimental

Materials. 2,5-Bis(*n*-butylamino)-*p*-benzoquinone (designated as Q-BuA), mp 163.5—164.5°C, was prepared by the known method[2] (Found: N, 11.19%, Calcd for $C_{14}H_{22}O_2N_2$: N, 11.16%).

Instrumental Analyses. The polarographic potential and the spectroscopic data were measured in the manner which has been described before.[3]

Pyrolysis of Q-BuA. The pyrolysis condition was established beforehand to give a major amount of the products in the minor components. Q-BuA (100 mg) in an evacuated ampoule (dia., 22 mm; length, 150 mm) fitted with a stop cock was pyrolyzed at 195°C for 3 hr in an oil bath and then cooled to room temperature.

Identification of Products. *Gaseous Products.* For IR spectroscopy the gaseous products generated in the ampoule were transferred through the cock to a cell which had previously been evacuated at 1 mmHg. The spectrum exhibits bands at 800—1200 cm^{-1} and 2880 and 2970 cm^{-1} that are characteristic of ammonia and alkanes respectively. The hydrocarbon was certified to be a mixture of *n*-butane and propane (4 : 1 in molar ratio) by the use of an Ohkura Chromatograph MS-1100 equipped with a Yanagimoto Active Alumina Column containing a tailing reducer (column temperature, 83°C; split temperature, 60°C; filament current, 120 mA; sensitivity, 1 mV; carrier gas, helium of 1.2 kg/cm^2).

Liquid Products. The liquid product that condensed on the inside wall of the ampoule was dissolved in dried methanol and submitted to GLC under conditions to be described later. The liquid product was thus revealed to be identical with water.

Solid Products. A solution of the solid products obtained from 5.00 g of Q-BuA in 200 m*l* of hot methanol was cooled to room temperature, refrigerated overnight, and filtered to give reddish crystals (4.28 g) and a mother liquor. The latter solution was concentrated to 50 m*l* at room temperature under the reduced pressure of an aspirator, refrigerated overnight, and filtered to give reddish crystals (0.40 g) and a methanol solution. The reddish crystals (4.68 g) were confirmed to be identical with Q-BuA by TLC using the same procedure

*1 Present address: Department of Graphic Engineering, Faculty of Engineering, Chiba University, Yayoi-cho, Chiba City.

1) J. Kumanotani, K. Sugita, S. Kazama and T. Yoshikawa, This Bulletin, **42**, 1130 (1969).

2) C. M. Martini and F. C. Nachod, *J. Am. Chem. Soc.*, **73**, 2953 (1951).

3) J. Kumanotani, F. Kagawa, A. Hikosaka and K. Sugita, This Bulletin, **41**, 2118 (1968).

as that described for the separation of butylamino-toluquinones.[3] The methanol solution was applied in lines on 30 plates of the silica-gel layer (1.0mm thick). The separated zones on the gel layer were scraped off and extracted with 100 m*l* of chloroform and then with 100 m*l* of methanol. The extract was evaporated to dryness at room temperature *in vacuo*. The operation by TLC was repeated three or five times in order to obtain sufficiently-isolated zones. Finally *ca.* 50 mg of each product was obtained.

Upon the identification of the mono- and di-amino-quinoid compounds, the following data were applied:[3] for monoamino-quinoid derivatives, $\nu_{max}^{CHCl_3}$ 3350 cm^{-1} (m. ν_{N-H}), 1620—1640 and 1570—1600 cm^{-1} (s. $\nu_{C=O}$); $\lambda_{max}^{CHCl_3}$ (π–π^*), 270—300 mμ; $E(1/2)$ (*vs.* SCE), −0.3—−0.35 V; for diamino-quinoid derivatives, $\nu_{max}^{CHCl_3}$ 3350 (m. ν_{N-H}), 1640 (m. $\nu_{C=C}$), 1580 (s. $\nu_{C=O}$), 1505 (s. amido II-type band) and 1460 cm^{-1} (m. δ_{C-H} in plane); $\lambda_{max}^{CHCl_3}$ (π–π^*), 330—350 mμ; $E(1/2)$ (*vs.* SCE), −0.45—−0.6 V.

The compounds identified, together with the unknown compounds, are presented below, along with their physico-chemical constants and characteristic spectral data.

2,5-Bis(*n*-butylamino)-*p*-benzoquinone: R_f, 0.20; recrystallized from chloroform as reddish crystals, mp 163.0—164.5°C (Found: N, 11.20%). This compound was found to be identical with Q-BuA by the mixed-melting-point method.

2-*n*-Butylamino-*p*-benzoquinone: R_f, 0.26; recrystallized from chloroform as reddish crystals; $E(1/2)$, −0.33 V (*vs.* SCE). IR in a KBr disk: 3350 (s. ν_{N-H}), 1665 (m. $\nu_{C=C}$), 1630 and 1590 (s. $\nu_{C=O}$), and 1505 cm^{-1} (s. amido II-type band). UV: $\lambda_{max}^{CHCl_3}$ 282 and 488 mμ.

2-Amino-5-*n*-butylamino-*p*-benzoquinone: R_f, 0.03; recrystallized from a mixed solvent of pyridine-chloroform (1 : 9 by volume) as purple-brown scales, mp 225°C (decomp.); $E(1/2)$, −0.46 V (*vs.* SCE).

Found: C, 61.68; H, 7.26; N, 14.36%: mol wt (VPO), 207. Calcd for $C_{10}H_{14}O_2N_2$: C, 61.84; H, 7.27; N, 14.42%; mol wt, 194.

IR in $CHCl_3$: 3520 and 3390 (m. ν_{N-H}), 1655 (m. $\nu_{C=C}$), 1585 and 1550 (s. $\nu_{C=O}$), and 1515 cm^{-1} (s. amido II-type band).

UV: $\lambda_{max}^{CHCl_3}$ 337 (ε 30000), 500 mμ (ε 450).

NMR in dimethyl sulfoxide: 2.3—2.9 (2H, 2(N–H), broadened), 2.8—3.2 (1H, N–H, broadened), 4.68 (1H on the quinoid ring) and 4.86τ (1H on the quinoid ring); in pyridine: 6.8—7.1 (2H, –NH–C$\underline{H}_2$–CH_2–, quartet coupled with N–H and –C$\underline{H}_2$–), 8.3—9.0 (4H, two methylene groups) and 8.8—9.3 τ (3H, one methyl group).

3-*n*-Butylamino-7-hydroxy-9-*n*-butyl-carbazolquinone (1,4): R_f, 0.04; recrystallized from chloroform, yellowish-brown powder, mp 180.7—181.5°C; $E(1/2)$, −0.48 V (*vs.* SCE) (Found: N, 8.01%). This compound was identified because it showed no drop in melting point when mixed with the authentic sample that had been previously prepared by the present authors.[4]

Butylated butylamino-benzoquinoid compound: R_f, 0.08; recrystallized from chloroform as reddish-purple plates, mp 81—84°C; $E(1/2)$, −0.14 V (*vs.* SCE).

Found: C, 66.54; H, 9.02; N, 8.64%; mol wt (VPO), 311. Calcd for $C_{18}H_{30}O_3N_2$: C, 67.05; H, 9.38; N, 8.69%; mol wt, 322.

IR in $CHCl_3$: 3385 (m. ν_{N-H}), 1660 (m. $\nu_{C=C}$), 1590 (s. $\nu_{C=O}$), 1515 cm^{-1} (s. amido II-type band).

UV: $\lambda_{max}^{CHCl_3}$ 346 (ε 9400), 495 mμ (ε 1700).

NMR in $CDCl_3$: 3.57 (1H on the quinoid ring), 4.49 (1H on the quinoid ring), 6.2—6.6 (2H, >N–C$\underline{H}_2$–CH_2–, triplet coupled with –C$\underline{H}_2$–), 6.6—7.1 (2H, –NH–C$\underline{H}_2$–CH_2–, quartet coupled with N–H and –C$\underline{H}_2$–), 7.7—8.1 (2H, –C$\underline{H}_2$– adjacent to the N, O, or quinoid ring, quartet coupled with –C$\underline{H}_2$– and another proton), 8.1—8.9 (12H, six methylene groups) and 8.8—9.3 τ (9H, three methyl groups).

From the above data, it became evident that this compound has such groups as *n*-C_4H_9–, *n*-C_4H_9–N<, and *n*-C_4H_9–NH– and a *p*-benzoquinone nucleus.

Oligo-quinoid compound: obtained from the zone of the starting line; recrystallized from chloroform as a dark brown substance, mp 120—140°C; $E(1/2)$, −0.55V (*vs.* SCE).

Found: C, 63.83; H, 7.61; N, 9.01%; mol wt (VPO), 342.

IR in $CHCl_3$: 3200—3500 (broadened, ν_{O-H}), 2850—3050 (m. ν_{C-H}), 1580 (s. $\nu_{C=O}$), 1515 (m. $\nu_{C=N}$), 1460 (m. δ_{C-H} in plane) and 1220 cm^{-1} (m. ν_{C-O-C}).

UV: $\lambda_{max}^{CHCl_3}$ 260 (ε 13000), 330 (ε 11700), 465 (ε 2220), 495 (ε 2050) and 550 mμ (ε 1230).

The above results show that the compound has the following groups: OH, –O–, >C=NH, and >C=N–C_4H_9, and the *p*-benzoquinone nucleus (cf. (3)).

Distribution of Pyrolysis Products of Q-BuA. The distribution of the products obtained from 10.0 mg of Q-BuA was examined by the extraction of the zones developed on a thin-layer chromatogram: 8.9 mg (85 mol% for the starting material) of Q-BuA, 0.6 mg (4.4 mol%) of the oligo-quinoid compound, 0.2 mg (2.5 mol%) of 2-amino-5-*n*-butylamino-*p*-benzoquinone, 0.1 mg (0.7 mol%) of the carbazolquinone, and traces of 2-*n*-butylamino-*p*-benzoquinone and the butylated butylamino-benzoquinoid compound.

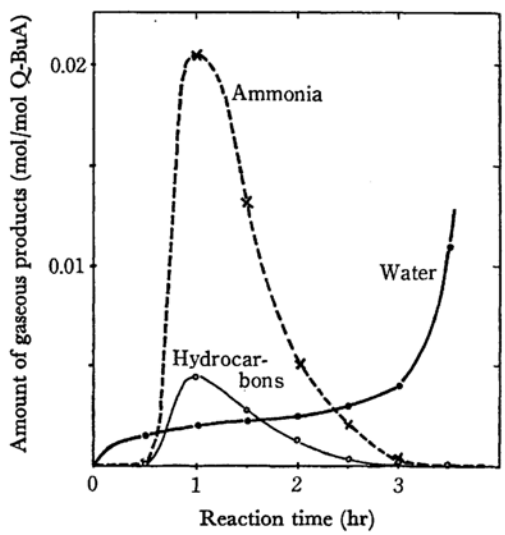


Fig. 1. The variation of the amount of gaseous products generated in the pyrolysis of Q-BuA at 195°C.

4) K. Sugita and J. Kumanotani, This Bulletin, **42**, 2043 (1969).

Pyrolytic Gas Chromatography. Its system was similar to that described by Yoshimi *et al*:[5] the pyrolytic cell was equipped with a Kotaki Super Fractioner GU-21. The column was prepared and the GLC operated in the manner reported by Amemiya.[6] Upon the pyrolytic gas chromatographic analysis, the peaks in a gas chromatogram of the products were assigned to *n*-butane, ammonia, and water. Q-BuA (100 mg) in a cell into which a stream of helium was introduced was heated in an oil bath kept at 110°C until no gas chromatographic peak of water could be detected. Then the cock was turned to close the sample cell and the cell was heated in an electric furnace kept at 195(±2)°C. The gaseous products which formed and accumulated in the cell over a 30-min period were run into the gas chromatograph with a stream of helium for a 10-sec interval by turning the cock, and then the cock was reversed in order to close the cell. The procedures of 30-min-pyrolysis and 10-sec-running of the gaseous products were repeated alternately for 3.5 hr. Thus, Fig. 1 was derived from the gas chromatograms where a normalization method was applied within a relative error of ±5%. Among the pyrolysis products, ammonia would be formed by the hydrolysis of the imino groups in the oligo-quinoid compound.

The authors wish to thank Mr. Masayoshi Yamao for his favor to provide the glass apparatus for the pyrolytic GLC. Thanks are also due to Associate Professor, Hiroo Tominaga of This University for the GLC measurements on the hydrocarbons.

5) N. Yoshimi, T. Yamauchi, M. Yamao and N. Tanaka, *Kogyo Kagaku Zasshi* (*J. Chem. Soc. Japan, Ind. Chem. Sect.*), **65**, 1131 (1962).

6) R. Amemiya, "Gaschromatography," Kyoritsu-shuppan, Tokyo (1957), p. 76.