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The Reaction of Aliphatic Amines with *p*-Benzoquinone. The Effect of the Alkyl Group of Amines on the Reaction

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The most general reaction between quinones and amines has been established for both primary and secondary, aliphatic and aromatic.[1–5] *p*-Benzoquinone undergoes two nuclear substitutions, but single substitutions are frequently observed with secondary amines under selected conditions.

The ease with which an amine enters the quinone nucleus depends to a large extent on the nature of the amine.[6] Under the present conditions (see General Procedure), *p*-benzoquinone gave bis-(alkylamino)-*p*-benzoquinones with primary amines, but with secondary amines it gave monoamino derivatives only.

p-Benzoquinone forms substitution products with 1 or 2 mol of amine, accompanied by the reduction of 1 or 2 mol of the benzoquinone respectively. These substitution products undergo a reversible oxidation or reduction on the dropping-Hg electrode, like the system quinone-hydroquinone itself. To follow the chemical change, polarography has been used.

In the present work, the effects of the alkyl group of the amine on the pattern and the rate of the reaction of *p*-benzoquinone with amines were determined.

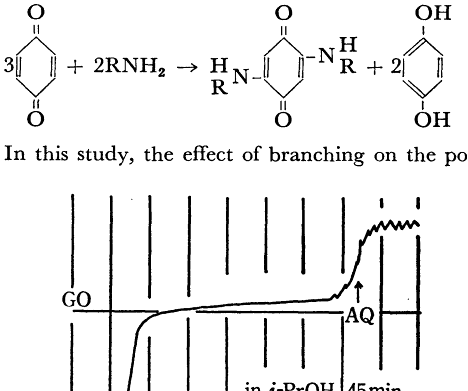
Experimental and Results

General Procedure of the Reaction of *p*-Benzoquinone with Amines. *p*-Benzoquinone (3×10^{-4} mol) was dissolved in 10 m*l* of isopropanol or ethanol, and into the resulting solution we added amine (2×10^{-4} mol) with constant stirring at 25°C. At regular time intervals, 0.1 m*l* aliquots of the reaction mixture were taken out and diluted to 10 m*l* with a polarographic base solution (isopropanol: phosphate buffer = 1 : 1). This dilution practically quenched the reaction. Any oxygen was removed from the solution by bubbling it with nitrogen, and the oxygen-free solution was subsequently polarographed by an ordinary method.

Materials and Apparatus. *p*-Benzoquinone (mp 116°C) was purified by the sublimation of commercially available chemicals. The amines used were commercially available and were identified by means of gas chromatography. The buffers used were prepared by the method of Sörensen in our laboratory.

The gas-chromatographic determinations were made with a Yanagimoto Gas Chromatograph, GCG-5DH, while the polarographic determinations were made with a Yanagimoto Pen Recording Polarograph, PA-102.

The Reaction of Primary Amines with *p*-Benzoquinone. In the reaction of *p*-benzoquinone with alkylamines in alcohols at ordinary temperatures, *p*-benzoquinone undergoes two nuclear substitutions, as is shown in Eq. (1).



(1)

In this study, the effect of branching on the position

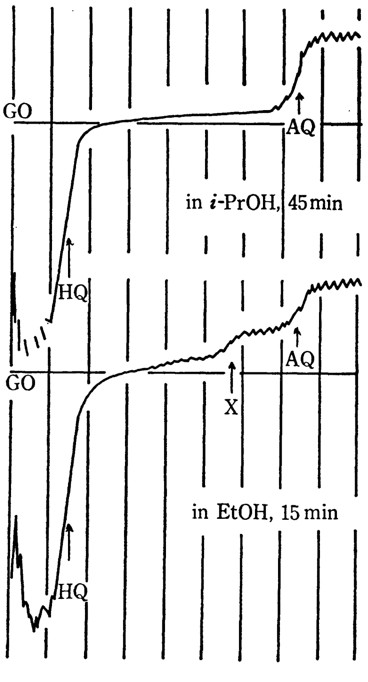


Fig. 1. Polarograms for the reaction of *p*-benzoquinone with *s*-butylamine. (1) in isopropanol after 45 min; (2) in ethanol after 15 min.
HQ; Hydroquinone
X; Unknown product
GO; Galvano. Zero Line

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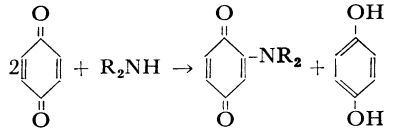
1) R. N. Harger, *J. Amer. Chem. Soc.*, **46**, 2540 (1946).
2) F. Mylius, *Ber.*, **18**, 468 (1885).
3) A. W. Hofman, *Proc. Roy. Soc.*, **13**, 4 (1863).
4) M. Martynoff and G. Tsatsas, *Bull. soc. chim.*, **14**, 52 (1947).
5) O. Suchanek, *J. prakt. Chem.*, **90**, 467 (1914).
6) H. Suida and W. Suida, *Ann.*, **426**, 116 (1918).

of the carbon atom adjacent to the nitrogen atom of the amine upon the rate of the reaction between alkylamine and *p*-benzoquinone was determined. Furthermore, the effect of the solvents, ethanol and isopropanol, upon the reaction was studied.

According to the procedure described above, methylamine, ethylamine, *n*-propylamine, and *n*-butylamine reacted with *p*-benzoquinone to form 2,5-bis(alkylamino)-*p*-benzoquinone in isopropanol or ethanol at 25°C within 5 min. In the case of isopropylamine and *s*-butylamine, the completion of the reaction in isopropanol required 45 min, the reaction in ethanol required only 15 min, but this was produced an unknown by-product which showed a cathodic wave (see Fig. 1). In the case of the *t*-butylamine-*p*-benzoquinone reaction in isopropanol, the rate of the reaction was still slower; even after 120 min the reaction had not been completed and a part of the quinone remained. In ethanol, *t*-butylamine did not give 2,5-bis(*t*-butylamino)-*p*-benzoquinone under the present conditions, though the quinone used decreased and hydroquinone was produced.

The Reaction of Secondary Amines with *p*-Benzoquinone. With alkylamines, *p*-benzoquinone gives bis(alkylamino)-*p*-benzoquinones; with dialkylamines, *p*-benzoquinone gives monoamino derivatives only.



(2)

In the present work, a study of the condensations of *p*-benzoquinone with dialkylamines was made; the experimental conditions were the same as in the general procedure except for the use of isopropanol only as a solvent.

In these reactions, their rates depended upon the kind of alkyl group in the amine used. In this report, dimethylamine, diethylamine, di-*n*-propylamine, and di-*n*-butylamine were used.

The quinone used disappeared within one minute in the case of dimethylamine, within 90 min in the case of diethylamine, and within 180 min in the cases of di-*n*-propylamine and di-*n*-butylamine. The rate of the reaction of *p*-benzoquinone with dialkylamines depends to a large extent on the size of the alkyl group of the amine in the case of the lower dialkylamine members.