[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, BROOKHAVEN NATIONAL LABORATORY]

Quinone–Hydroquinone Exchange Reactions. II. Duroquinone and Durohydroquinone Exchange in Buffered Methanol Solution[1]

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A study has been made of the electron exchange reaction at 25° between duroquinone and durohydroquinone-α-^{14}C dissolved in methanol saturated with potassium biphthalate. The exchange reaction proceeds at a measurable rate with a half-life in the order of minutes. In the range of concentrations studied, the rate of reaction is approximately independent of the quinone concentration and first-order with respect to the hydroquinone.

Introduction

The previously reported[2] observation that an exchange reaction between duroquinone and durohydroquinone-α-^{14}C occurs in solution suggested that an investigation of the kinetics of quinone–hydroquinone exchange reactions should be undertaken. Such a study could conceivably lead to a better understanding of some of the factors governing the rates of electron-exchange reactions in general, since by a proper choice of substituents, the influence of such factors as steric hindrance, electrode potential and acidity of the hydroquinone could be separately evaluated.

As an example of a highly hindered quinone, duroquinone was selected for a first study. Since it has been observed that separations by means of liquid extractions rarely cause induced exchange, a solvent was sought from which one of the reactants could be selectively extracted. A practical solvent turned out to be methanol, from which duroquinone can be partially extracted by means of pentane, after the addition of a few drops of water to cause immiscibility. The methanol was saturated with potassium acid phthalate to act as a buffer.

Methanol solutions of durohydroquinone exposed to air quickly autoxidized with the production of duroquinone. In order to avoid this complicating reaction solutions were made up using vacuum line techniques with the rigid exclusion of air and mixed under pure nitrogen. Exposure to the air during extraction was only of a few seconds duration, during which no appreciable oxidation took place, as shown by runs in which duroquinone was initially absent.

The duroquinone samples were purified and analyzed for carbon and hydrogen percentage and for specific radioactivity. The method used consisted of a dry combustion, manometric determination of the water and carbon dioxide produced and counting of the carbon dioxide in a methane and carbon dioxide filled proportional counter tube. The procedure is described in detail elsewhere.[3]

Experimental

Preparation of Materials. Duroquinone.—Duroquinone was prepared by the method of Smith,[4] and recrystallized from methanol until it melted in the range 110–111°.[5]

Durohydroquinone-α-^{14}C.—1.00 g. of duroquinone-α-^{14}C prepared as previously described[2] and recrystallized from methanol until it melted at 110–111°, was dissolved in 10 ml. of methanol and added with stirring to a solution of 1 g. of sodium borohydride in 30 ml. of ethanol. The color was instantaneously discharged and a clear solution resulted. Forty ml. of distilled water and a drop of hydrochloric acid were added to the mixture which, on chilling, deposited a copious precipitate of white crystals. The crystals were filtered and dried, then heated to 170° under 0.05 mm. pressure in a sublimation tube. Pure white durohydroquinone, melting at 242–243°, sublimed in 93% yield. The specific activity of the product was 0.157 μc./mmole.

Methanol–Potassium Acid Phthalate.—Commercial absolute methanol was shaken for a week with excess primary standard potassium acid phthalate. Before using, the solution was checked with a Beckman *p*H meter using a standard glass electrode and invariably gave a reading within a few hundredths of a *p*H unit of *p*H 6.15.

Pentane.—Pure grade pentane obtained from the Phillips Petroleum Company was redistilled under nitrogen, b.p. 36°, and stored under nitrogen.

Typical Run.—A sketch of the apparatus is shown in Fig. 1. The methanol–potassium acid phthalate to be used in making up solutions was first degassed by placing about 150 ml. of it in the 200-ml. conical flask A. The flask was closed off by means of its stopcock, and the methanol was frozen by cautiously dipping the flask in liquid nitrogen. It was then attached to the line at B and the methanol was pumped on at $\sim 10^{-4}$ mm., while it thawed. One repetition of the freezing–thawing cycle gave essentially gas-free methanol. 420.0 mg. of duroquinone and 420.0 mg. of durohydroquinone-α-^{14}C were weighed out in 200-ml. stock solution storage bulbs such as C, and the bulbs were fitted with closures such as D. The flask containing the degassed methanol was then connected at F, the stock solution bulb containing duroquinone at E, and the system H, C, D evacuated. By proper manipulation of the stopcocks, the measuring pipet F was then filled, the overflow going into H. After a sufficient number of pipetfuls to make up the solution to 183.3 ml. were delivered into C, it was closed off, disconnected and shaken until solution was complete. The durohydroquinone was similarly made up. Properly made up solutions of durohydroquinone stayed colorless for months.

The stock solution bulbs were then connected to the exchange apparatus at I and J, and the apparatus chambers K, L and O were evacuated. Stopcocks M and N were closed and about 55 ml. of each of the stock solutions were metered into the 60-ml. calibrated storage burets K and L. Water at 25.0 ± 0.1° was circulated through the jacket S. The solutions were given a few hours to reach temperature equilibrium. Exactly 50 ml. of each solution was then drained into the reaction compartment O. Zero time was taken as that time at which half of the second component had been added. Mixing was accomplished by bleeding prepurified nitrogen gas through the nozzle T until a slight excess (about 1 cm. of mercury) pressure was present. Approximately 15-ml. aliquots were taken at 3-minute intervals by filling the sampler R until the siphon began to operate. The sample was drained into a 125-ml. separatory funnel containing 25 ml. of pentane and 0.7 ml. of water. The funnel was quickly stoppered and shaken, then the lower alcohol layer was drained into a waste bottle. With a little practice it was possible to perform the sampling and separation in a reproducible manner with a total time lapse of about 30 seconds.

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[1] Research carried out under the auspices of the Atomic Energy Commission.

[2] A. Bothner-By, THIS JOURNAL, **73**, 4228 (1951).

[3] R. C. Anderson, Y. Delabarre and A. Bothner-By, *Anal. Chem.*, **24**, 1298 (1952).

[4] L. I. Smith, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, New York, N. Y., 1943, p. 254.

[5] All melting points were taken on a Kofler hot stage micro melting point apparatus.

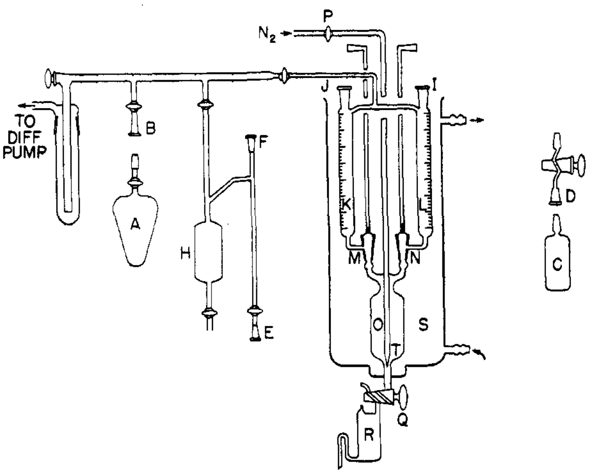


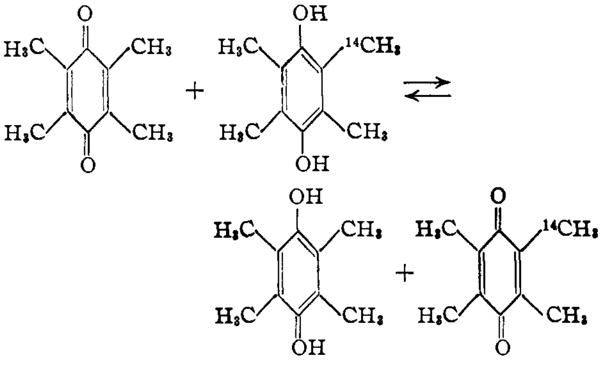
Fig. 1.—Apparatus for conducting exchange experiments *in vacuo.*

The samples were purified by sublimation under reduced pressure. For this purpose the pentane solution was poured into a 50-ml. centrifuge tube, protected from dust, and allowed to evaporate spontaneously to dryness. The residual quinone was taken up in 1 ml. of pentane and transferred to a sublimation tube. The pentane was evaporated by gentle warming. A water-cooling jacket was then slipped over the upper portion of the tube and the tube evacuated to a pressure of 15 mm. The lower end of the tube was immersed in a boiling water-bath. The quinone sublimed in a few minutes to a ring of yellow needles, m.p. 110–111°. The tube was removed and cut apart 2 cm. below the ring of needles. The sample was then ready for assay of its carbon-14 activity.

Radioassay.—The method of determination of specific carbon-14 activity has been described completely elsewhere.[3]

Results

The rate, R, of the exchange reaction



is given by the McKay law

$$R = \frac{ab}{a+b}\,\frac{\mathrm{d}\ln(1 - X_t/X_\infty)}{\mathrm{d}t} \tag{1}$$

where a is the gross macroscopic concentration of initially inactive duroquinone, b is the gross macroscopic concentration of initially active durohydroquinone, X_t is the specific activity of a duroquinone sample withdrawn at time t, and X_∞ is the theoretical specific activity of a duroquinone sample withdrawn when equilibrium has been reached. The points obtained by plotting $(1 - X_t/X_\infty)$ on semi-logarithmic coördinates against the contact time on the linear scale, should fall on a straight line the slope of which, m, may be related to equation (1) by the expression

$$m = \frac{\mathrm{d}\ln(1 - X_t/X_\infty)}{\mathrm{d}t} \tag{2}$$

A plot of the data from the run described in the Experimental section is shown in Fig. 2.

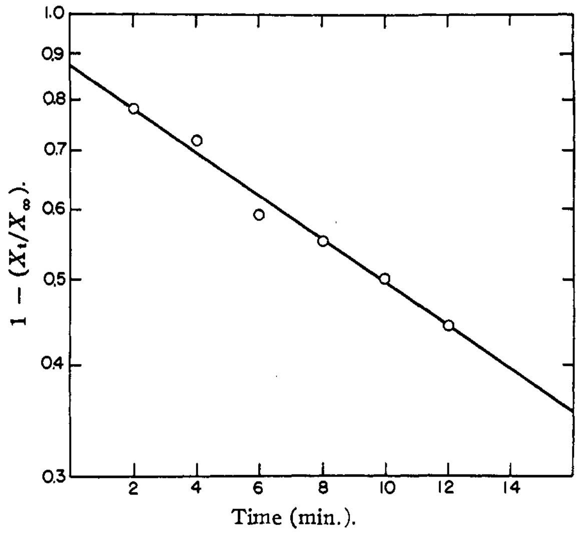


Fig. 2.—Rate of exchange in buffered methanol solution: (duroquinone) = 7.00×10^{-3} M; (durohydroquinone) = 6.91×10^{-3} M.

Using equations (1) and (2) it is possible to calculate the over-all rate of reaction R in one of these exchange reactions, given the concentrations of the reactants and the slope of the line in the McKay plot. Table I shows these rates calculated for five runs.

TABLE I

Run	Concentration × 10^3 M Duroquinone	Durohydroquinone	$R \times 10^5$, moles l.$^{-1}$ min.$^{-1}$
A	10.50	3.46	10.85
B	7.00	6.91	19.65
C	3.82	10.03	32.14
U	3.49	3.45	11.88
P	4.55	9.00	27.60

In order to solve the equation

$$R = ka^\alpha b^\beta$$

for k, α and β in terms of the parameters R, a and b three independent sets of data are needed. In this case we have five, and consequently an over-determined system. The principles of treating such systems by a least squares method have been described by DuMond and Cohen.[6] The equations derived from the data of runs A, B, C, U, P were weighted in the least squares answer proportionally to the number of individual observations in each run. The following values were obtained: $\alpha = -0.09 \pm 0.05$; $\beta = +0.91 \pm 0.05$; $k = (4.2 \pm 0.3) \times 10^{-5}$ min.$^{-1}$.

It is difficult to evaluate the reality of the deviations from integral order observed here. If real, such deviations may be caused by the presence of more than one reaction path leading to exchange, or may point to a free radical chain character for the mechanism.

On the other hand, a first-order rate dependent

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(6) J. W. M. DuMond and E. R. Cohen, *Am. Scientist*, **40**, 447 (1952).

on hydroquinone may be rationalized from the known facts. Michaelis and co-workers[7] have observed that strongly alkaline solutions of duroquinone and durohydroquinone exhibit paramagnetism consistent with the presence of a large proportion of the intermediate oxidation state, or semiquinone free radical. Formation of such free radicals may be expected to proceed rapidly from duroquinone and doubly charged durohydroquinone anions and is a logical path for the exchange reaction. In the relatively acid solutions employed in this study, the concentration of doubly-charged anion would be extremely low, and its rate of formation may be assumed to be rate-controlling. The reactions may be represented as

$$H_2Q^* \rightleftharpoons HQ^{*-} + H^+ \quad (3)$$

$$HQ^{*-} \rightleftharpoons Q^{*=} + H^+ \quad (4)$$

$$Q^{*=} + Q \rightleftharpoons Q^{*\cdot -} + Q^{\cdot -} \rightleftharpoons Q^* + Q^{=} \quad (5)$$

where H_2Q^* represents radioactive durohydroquinone, Q represents inactive duroquinone, $Q^{\cdot -}$ represents a semiquinone radical, etc.

This formulation implies that the rate of reaction (4) is slow. This seems rather unusual, but possible factors suppressing the rate are the low initial concentration of singly-charged hydroquinone anions in the solution, and the low second ionization constant for hydroquinones. A study of the effect of hydrogen-ion concentration on the rate of reaction is indicated.

Acknowledgments.—I wish to express my appreciation to Professor R. W. Dodson, to Dr. J. Silverman and to Dr. A. P. Wolf for helpful discussions, and to Miss Yvette Delabarre for the performance of a large number of analyses and isotopic assays.

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[7] L. Michaelis, M. P. Schubert, R. K. Reber, J. A. Kuck and S. Granick, THIS JOURNAL, **60**, 1678 (1938); L. Michaelis, *ibid.*, **63**, 2446 (1941).

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF HARVARD UNIVERSITY AND THE RICE INSTITUTE AND THE RESEARCH LABORATORY OF THE PAINT DIVISION OF THE PITTSBURGH PLATE GLASS COMPANY]

Pyrolysis of the Addition Product of Diphenyldiazomethane and 1,4-Naphthoquinone

BY ALFRED R. BADER AND MARTIN G. ETTLINGER

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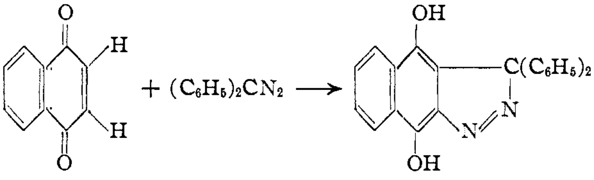
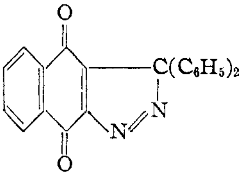
The pyrolysis product of 2,3-(3′,3′-diphenylisopyrazolo)-1,4-naphthohydroquinone previously formulated as a derivative of methylenecyclopropane consists of 4-hydroxy-1-phenyl-2,3-benzofluorenone, the major component, and 4-hydroxy-9-phenyl-2,3-benzo-1-isofluorenone.

During the study of the addition of diazo compounds to quinones, Fieser and Peters[1] pyrolyzed the azo compound I, the adduct of diphenyldiazomethane and 1,4-naphthoquinone, and isolated besides II and III a small portion of nitrogen-free fiery red needles, m.p. 274°. To the red substance, which dissolved in aqueous carbonate, formed a monoacetate, m.p. 245°, and was believed to be reducible to 2-benzhydryl-1,4-naphthohydroquinone, characterized as its diacetate and the quinone III, the unusual structure IV was tentatively assigned. The present investigation began with the idea that structure V, analogous to the known enols of 1,2-naphthoquinones,[2,3] might fit the properties of the red substance. The molecule V would form in base the resonant anion VI, which would be obtained also by removal of a proton from III. However, it was found that although both the red pyrolysis product and III formed purple solutions in hot alcoholic alkali, the pyrolysis product was recovered on acidification, whereas III furnished an unknown mixture. Furthermore, III did not yield well-defined products on treatment with sulfuric acid or with acetic anhydride and catalysts and thus gave no indication of the existence of a stable enol V.[2]

The red pyrolysate, m.p. 274°, was eventually found to be a mixture of two compounds which could not be separated by crystallization. The



I



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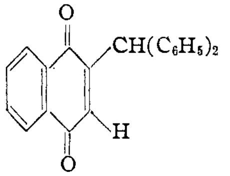
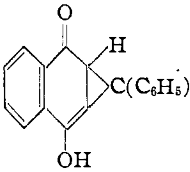
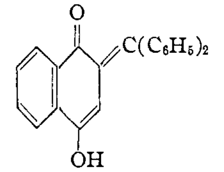


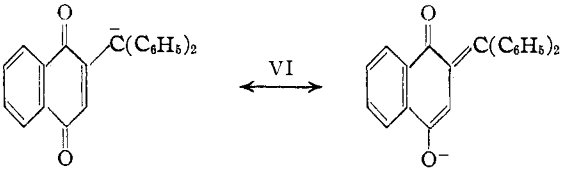
III



IV



V



VI

previously described acetate, m.p. 245°, was difficultly purifiable and furnished on hydrolysis an

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[1] L. F. Fieser and M. A. Peters, THIS JOURNAL, **53**, 4080 (1931).

[2] L. F. Fieser and J. L. Hartwell, *ibid.*, **57**, 1484 (1935).

[3] L. F. Fieser and M. Fieser, *ibid.*, **61**, 596 (1939); *cf.* F. Sachs and L. Oholm, *Ber.*, **47**, 955 (1914).