

Magnetic Studies on Reduction of Duroquinone by Monosaccharides

Hideo TAKAKI and Chie MIYAKE*

(Takaki Laboratory)

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In order to investigate magnetic change associated with reactions in which free radicals appear and disappear, a torsion pendulum magnetometer whose sensitivity is 1×10^{-10} c. g. s. e. m. u. per division was made with fused silica. By using this, processes of reduction of duroquinone with various monosaccharides, such as glucose, fructose and mannose can be traced from time to time during the reaction. The rate at which semiquinone radical appears and disappears was found to be proportional to the concentration of monosaccharide. From the relation between the initial rate of the reaction and the temperature at which it occurs, the apparent activation energy necessary for production of free radical was estimated to be about 24 kcal. per mol.

INTRODUCTION

In 1941 Michaelis proposed the existence of a free radical, durosemiquinone radical, in the solution in which the duroquinone is reduced to durohydroquinone¹². Very recently, many authors such as Venkataraman, Fraenkel, McConnell and Werts have adopted the straight forward method by means of electron spin resonance for the detection of the radical as well as for the determination of its electronic configurations¹³.

In order to review the above-mentioned authors' results, a sensitive pendulum magnetometer was designed and the reducing processes from duroquinone to durohydroquinone was magnetically observed especially in detail. In this paper are dealt with the results obtained with the solutions of duroquinone having the above-mentioned various monosaccharides and also with dependencies of the reaction upon temperature and concentration of the reducing agent. As a result, the apparent activation energy necessary for the formation of durosemiquinone radical was estimated.

APPARATUS

A sensitive torsion magnetometer was made with fused silica in the following way. As shown in Fig. 1, pendulum system of the magnetometer (C, M, B and B') is fixed to a tripod through a thin quartz fiber (A) in such a way that the center of gravity of the whole pendulum system may be placed in the position higher than that of the fulcrum. The solution to be measured is placed into a reaction vessel (B) and a suitable solution into a compensating vessel (B'). By placing the above-mentioned vessel symmetrically on either side of the truncated pole pieces of the

* 高木秀夫, 三宅千枝

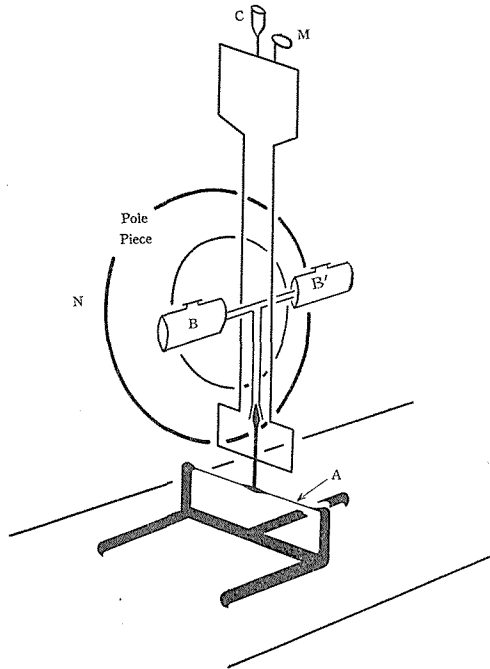


Fig. 1. Apparatus

electromagnet (N), diamagnetism of both the two kinds of solution can be offset and only the change of susceptibility related with the reaction can be taken out. The amount of the change can be measured directly from the deflection angle of the pendulum with the aid of a lamp-scale and a reflecting mirror (M). As has already been stated, the center of gravity (G) of the pendulum system is located at the height higher than that of the torsion wire. Hence, the restoring couple vector due to the torsion wire is much reduced by the couple vector of the gravity, which rotate the system in the opposite direction to that of the former. Thus, the sensitivity of the magnetometer is given by

$$\theta/f = r/(\tau - mgl)$$

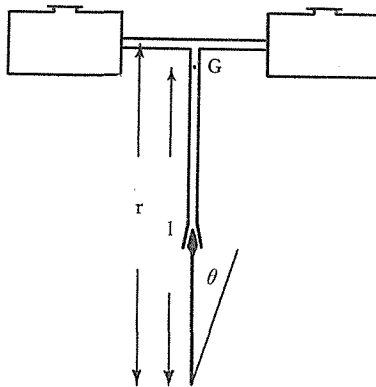


Fig. 2. Scheme of magnetometer.

where θ represents the deflection angle, f , horizontal component of paramagnetic attraction between the magnetic field and the solution, τ , torsion constant of the wire, l and r , the distance from the foot of pendulum to G and to the center of cylindrical vessel respectively; m , the total mass of the pendulum system, and g , the acceleration of gravity.

Sensitivity of our apparatus can be raised, when, by adding suitable mass to the top of the pendulum (C), we elevate its center of gravity, because $\tau - mgl$ becomes smaller. Hence a very high sensitivity is attainable, so far as $\tau - mgl$ is kept positive. The highest sensitivity ever reached by this adjustment was 1×10^{-10} c. g. s. e. m. u. volume susceptibility per division. It is one of the characteristic properties of our equipment that comparatively large sample solution can be measured with sufficient sensitivity.

The calibration of our magnetometer is carried out in the following way: first, a small counter weight, say, 1 mg. is mounted upon the dish attached to B. Next, the deflection due to this weight is determined, and then the scale constant per unit force (dyne/div.) is calculated. The paramagnetic attraction between the solution and the magnetic field is further expressed by

$$f = A\chi \int H \frac{\partial H}{\partial x} dx$$

where A is the cross sectional area of the vessel, and χ the paramagnetic volume susceptibility of the solution.

EXPERIMENTAL

Materials

Duroquinone. Duroquinone was manufactured, taking care not to include any ferromagnetic impurity.

Monosaccharides. The reducing agents used in this experiment were glucose, fructose and mannose of chemical grade reagent.

Pyridine. Analytical grade reagent was purified by redistillation.

Sodium hydroxide. Sample solution to be measured was prepared by the following procedures: About 10mg. of duroquinone was dissolved in 1ml. of pyridine, to which were added consecutively a given amount of monosaccharide solution and 1ml. of 1*N*-sodium hydroxide, and then diluted with water up to 5ml. The concentrations of duroquinone, pyridine and sodium hydroxide were kept constant throughout this experiment.

Measurements

By the use of the above newly designed apparatus, the change of the magnetic susceptibility of the solution was measured, which took place as the reaction proceeded with time. Fig. 3 shows the deflection of the pendulum magnetometer²³. The positive shift of the magnetometer in the figure corresponds to the accumulation of free radical.

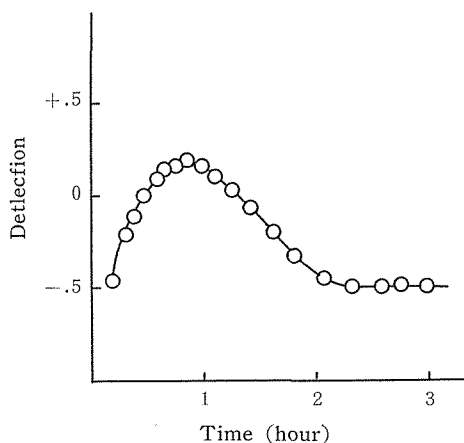
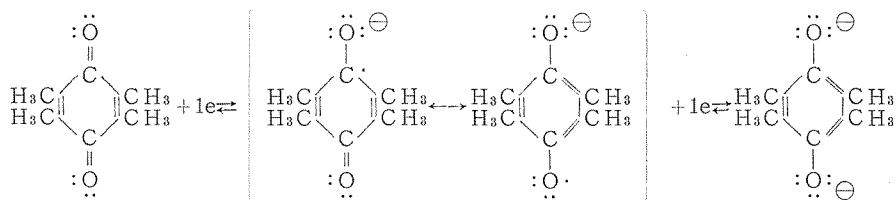


Fig. 3. Solution of 0.010 g. of duroquinone; 1 ml. of 1.0 *N* sodium hydroxide and 1 ml. of pyridine, mixed with water up to 5ml., and 20 mg. of glucose added.

RESULTS AND DISCUSSION

The reducing process of duroquinone, if its side reaction is neglected, can be simplified as follows⁴⁾.



In this equation semiquinone appears as the intermediate product. This product, however, is generally unstable due to the formation of compounds of diamagnetic dimer having quinhydrone type. Nevertheless, in the pH region of the present solutions, durosemiquinone can be considered to exist, because of its ionic nature allowing the resonance state between molecules or otherwise hyperconjugation in a molecule.

Thus, we can assume that the time-change of magnetic susceptibility during the reaction is only due to the paramagnetic increment arising from one unpaired electron contained in semiquinone. In general, the molar susceptibility of the substances having one unpaired electron is represented as follows⁵⁾.

$$\chi_{\text{mol}} = N g^2 J(J+1) \mu_B^2 / 3kT$$

where N is Avogadro's number; g , the spectroscopic splitting factor; J , the total angular momentum; μ_B , the Bohr magneton; k , the Boltzmann's constant; and T , the absolute temperature. At 25°C, volume susceptibility of 1 molar solution of the substance is 1.25×10^{-6} c. g. s. e. m. u. The concentration of duroquinone of the sample solution which we prepared is 0.012 molar. Therefore, if we assume that all of the solute molecules become semiquinone radical by the instantaneous reduction, then

we can expect the paramagnetic volume susceptibility to be 15×10^{-9} c. g. s. e. m. u. Therefore, by comparing the observed susceptibility of the solution with the value mentioned above, the concentration of semiquinone radical can easily be evaluated.

As can be seen in Fig.4, the rate with which the free radical appears and disappears is largest in the solution with fructose, smallest with mannose and intermediate with glucose.

In every monosaccharide, both the rate of production of free radicals and that of their decay are strictly in proportion to the concentration of monosaccharide (see Fig.5). The temperature dependency of the series of reactions is given in Fig.6. Assuming that all of the obtained magnetic susceptibilities have been caused only by the production of durosemiquinone, we can estimate the apparent activation energy necessary for the formation of free radical. From Figs.7 and 8 which show the initial rate of the progress of reaction in logarithmic scale plotted against the

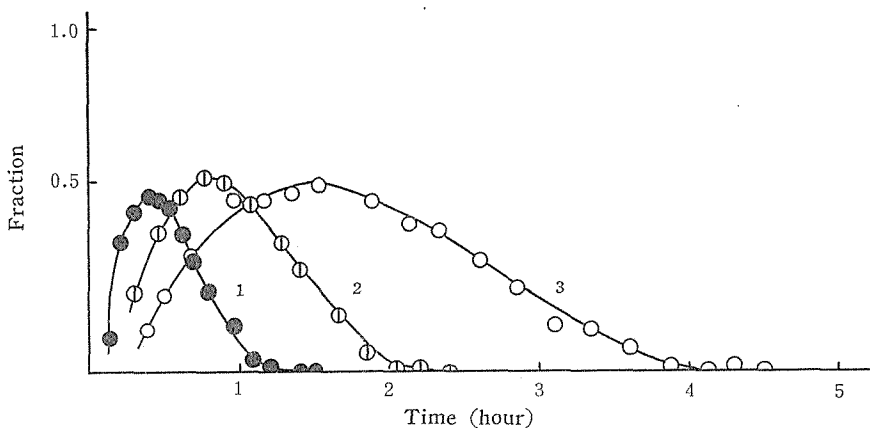


Fig. 4. Dependency of reaction upon kind of monosaccharide.

- 1: 10mg. of fructose,
- 2: 100mg. of mannose,
- 3: 10mg. of glucose.

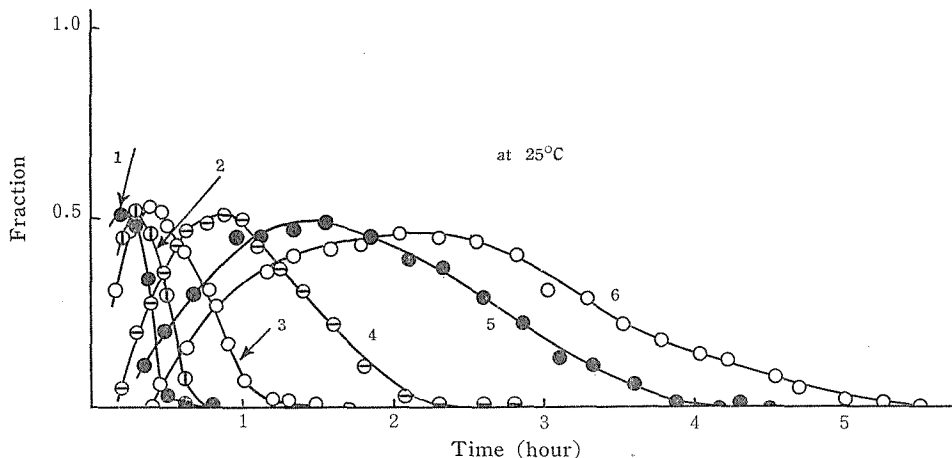


Fig. 5. Dependency of reaction upon concentration of monosaccharide (glucose).

- 1: 80mg., 2: 60mg., 3: 40mg., 4: 20mg., 5: 10mg., 6: 7.5mg.

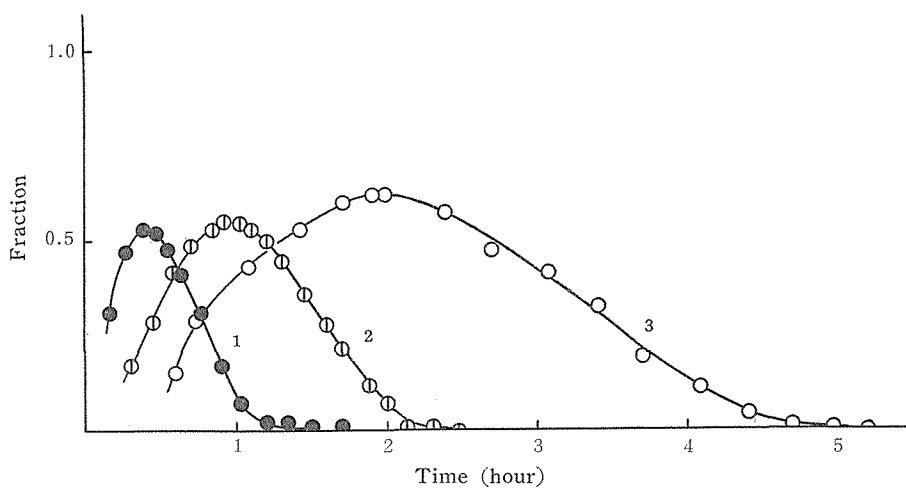


Fig. 6. Dependency of reaction upon temperature (40mg. of glucose solution).
1: at 25.2°C, 2: at 21.5°C, 3: at 16.8°C

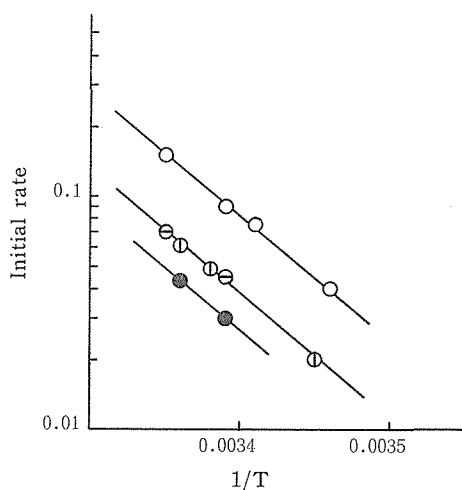


Fig. 7. Dependency of initial rate of reaction upon temperature.

- ⊖ : 40mg. of glucose,
- : 80mg. of glucose,
- : 100mg. of mannose,
- ⊕ : 150mg. of mannose

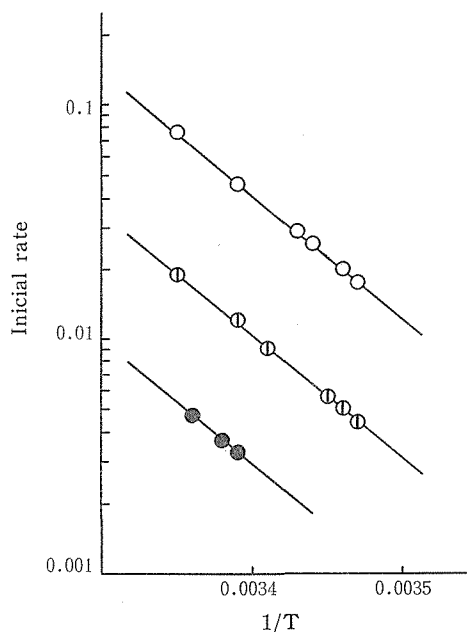


Fig. 8. Dependency of initial rate of reaction upon temperature.

- : fructose, ⊕ : glucose, ● : mannose

reciprocal of the absolute temperature, the apparent activation energy can be calculated. The value thus obtained is about 24 kcal. per mol.

SUMMARY

Descriptions are given in the following items.

- 1) Magnetometer with very high sensitivity (1×10^{-10} c. g. s. e. m. u. volume

susceptibility per division) by which the production of free radical in solutions can be detected.

2) Dependencies of the reducing reaction from duroquinone to durohydroquinone upon temperature and concentration of monosaccharide used as a reducing agent were examined.

3) The rate of reduction is greatest in solution with fructose, smallest with mannose and intermediate with glucose.

4) Tentative determination of the apparent activation energy required for the formation of semiquinone radical. The obtained value is about 24 Kcal per mol.

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