A Kinetic Study of the Reaction from Tetramethyl-p-benzoquinone to Tetramethylhydroquinone

By Chie MIYAKE, Takasuke MORI and Tadao SANO

(Received June 25, 1962)

The semiquinone free radical which appears during course of the oxidation-reduction reaction between quinone and hydroquine has been widely studied to ascertain the relation between the formation of the free radical and the condition of the reacting solution¹⁾, as well as its electronic structure. However, there is little conclusive information about the nature of these reactions because they are confused with fairly complicated side reactions.

The measurement of the magnetic susceptibility of the solution during the course of reaction was carried out with systems having duroquinone and various monosaccharides applied as reducing agents, considering that in these systems the side reactions need not be taken into account²⁾. The results have already been reported but are now dealt with from the view-point of chemical kinetics. The rates of the formation and decomposition of the tetramethyl-*p*-benzosemiquinone radical are empirically found to follow such simultaneous differential equations as:

$$dx/dt = -(k_1 + k_2 y)x$$
$$dy/dt = (k_1 + k_2 y)x - k_3 y$$
$$dz/dt = k_3 y$$

where x, y and z are the concentrations of tetramethyl-*p*-benzoquinone, tetramethyl-*p*-benzosemiquinone and tetramethyl-*p*-hydroquinone, respectively, after time t. k_1, k_2 and k_3 are rate constants. Figure 1 shows the relation between the experimental and calculated values using the equation as representative. The dependency of the rate constants k_1, k_2 and k_3 on the temperature at which the measurement was performed is represented in Fig. 2, which shows a good linearity. k_1 and k_3 are found to be proportional to the concentrations of such monosaccharide used as glucose, mannose or fructose, while k_2 is in parabolic proportion to those of every monosaccharide. The activation energy necessary for the formation of the free radical by the reaction of tetramethyl-*p*-benzoquinone with monosaccharide, that for the formation of the free radical by a reaction like the auto-reduction reaction between the

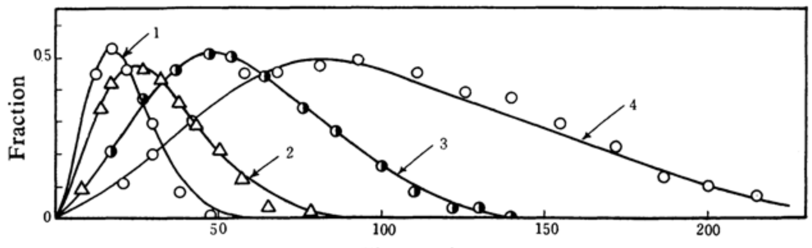

Fig. 1. Relation between experimental values and those calculated from equation.
—— calcd.; ○, ◑ and △ experimental
1 65 mg. of glucose, at 25.2°C 2 10 mg. of fructose, at 25.4°C
3 100 mg. of mannose, at 24.0°C 4 10 mg. of glucose, at 25.2°C

---

1) J. E. LuValle et al., "Technical Note on the Chemistry of Quinone", ASTIA Document Service Center, Arlington Hall Station, Arlington, Virginia, Report No. TOI 58-29 (1958).

2) H. Takaki, N. Kawai, C. Miyake and T. Morita, *J. Phys. Soc. Japan*, **13** 629 (1958).

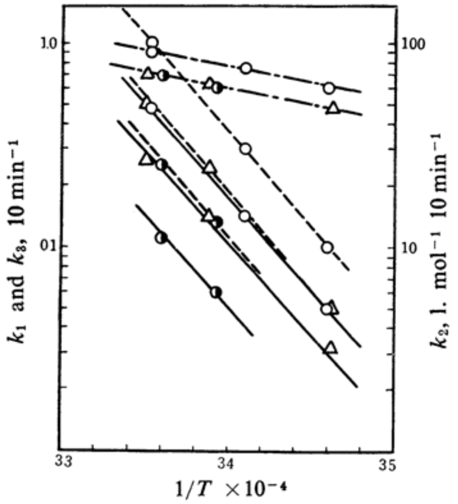

Fig. 2. Dependency of rate constants k_1, k_2 and k_3 upon temperature.
—— for k_1; —·— for k_2; ------ for k_3
○ 80 mg. of glucose
◑ 100 mg. of mannose
△ 10 mg. of fructose

free radical and tetramethyl-*p*-benzoquinone, and that for the decomposition of the free radical producing tetramethyl-*p*-benzohydroquinone are 40, 8 and 41 kcal./mol., respectively.

The details of this report will be published in the Technology Reports of Osaka University.

Department of Nuclear Engineering
Faculty of Engineering
Osaka University
Miyakojima-ku, Osaka