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49. Mamoru Kamiya, Tatsunori Hamaoka, and Takao Kwan : Relative Rates of Photo-excited Quinones for the Reaction with Isopropyl Alcohol.*1

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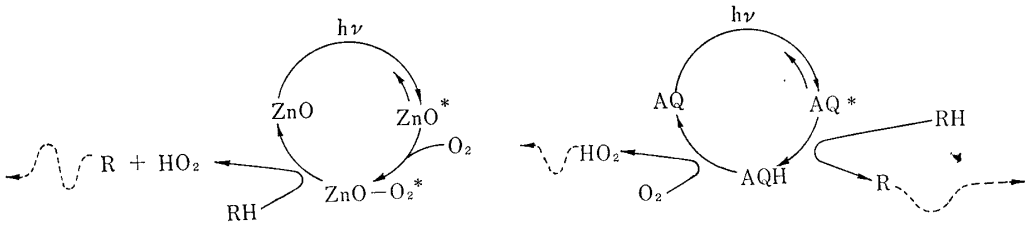
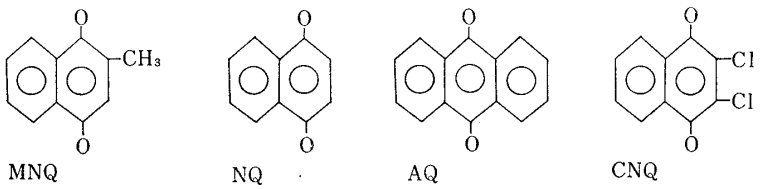
Photosensitizers are often regarded as catalysts; they accelerate the rate of a chemical reaction under illumination and participate repeatedly in the reaction. It has been shown in this laboratory that zinc oxide[1,2] and anthraquinone[3] act as photocatalysts for the oxidation of isopropyl alcohol; the two catalysts appeared to give acetone and hydrogen peroxide as the products. It was considered, however, that zinc oxide, absorbing lights, activates molecular oxygen whereas anthraquinone activates alcohol. The photoprimary processes are schematically shown as below.



Here, RH denotes isopropyl alcohol, AQ anthraquinone and AQH semiquinone radical.

It is known that photo-excited quinones abstract hydrogen atom from α-carbon of alcohol molecule.[4] Little information is available, however, concerning the relative rates of photo-excited quinones for such act, although the photocatalytic activity of anthraquinone sulfonate for the oxidation of various alcohols has been worked out by Wells.[5]

In the present paper we shall show a comparative study on the reactivities of various photo-excited quinones for the oxidation of isopropyl alcohol. Special interest will be laid on the relative importance of the photo-excited quinones, denoted as M*, to abstract hydrogen atom from alcohol as compared with their deactivation processes. The quinones studied here along with the purpose are :



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1) I. Komuro, Y. Fujita, T. Kwan : Bull. Chem. Soc. Japan, **32**, 884 (1959).
2) A. Ikekawa, M. Kamiya, Y. Fujita, T. Kwan : *Ibid.*, **38**, 32 (1965).
3) M. Kamiya, Y. Fujita, T. Kwan : Shokubai (Catalyst), **6**, 15 (1964).
4) J. L. Bolland, H. R. Cooper : Nature, **172**, 413 (1953); Proc. Roy. Soc., A225, 405 (1954).
5) C. F. Wells : Trans. Faraday Soc., **57**, 1703, 1719 (1961).

Experimental

A given amount of each quinone, purified by recrystallizations in ethyl alcohol, was dissolved in 50 ml. pure isopropyl alcohol. The solution was put in a cylindrical reaction vessel made of Pyrex and having a flat bottom, and was stirred magnetically under a constant oxygen pressure.

The volume of oxygen, consumed upon illumination, was determined by a burette kept in a thermostat. The whole apparatus used is shown in Fig. 1.

The light source was a 100W high pressure mercury lamp supplied by Ushio Kogyo Co. Lights were filtered by a Mazuda glass filter UV D2 so that lights of 3000~4000 Å wave lengths could pass through. The light intensity was varied by inserting blackened copper nets between the reaction vessel and the light source. The amount of hydrogen peroxide was determined by iodometry and acetone by colorimetry after the reaction with 2,4-dinitrophenylhydrazine in an alkaline medium.

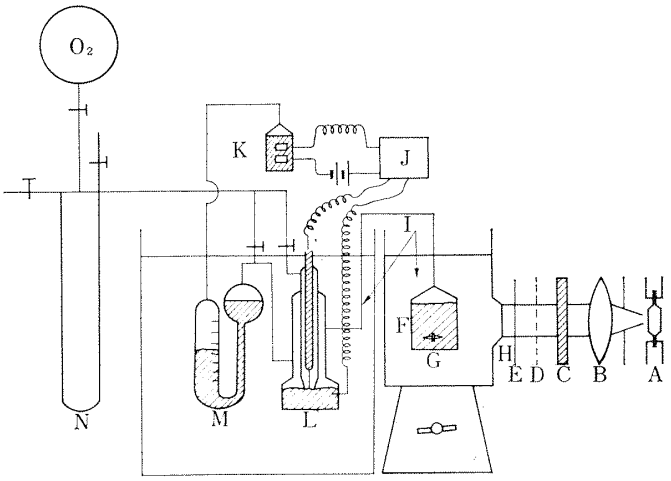

Fig. 1. Apparatus for the Measurement of Photo-oxidation of Alcohol

A: High pressure mercury lamp B: Quartz lens C: Glass filter D: Blackened copper net E: Shutter F: Reaction vessel G: Stirrer H: Quartz window I: Thermostat J: Relay K: Electrolytic cell L: Manostat M: Gas burette N: Mercury manometer

Results and Discussion

Preliminary studies have shown that the absorption of oxygen takes place at room temperature only when lights were illuminated and that the stoichiometry of the reaction occurred was: $(CH_3)_2CHOH+O_2 \rightarrow (CH_3)_2CO+H_2O_2$. The rate of oxygen uptake was then investigated against oxygen pressures, temperatures, quinone concentrations and light intensities. The experimental circumstance was so chosen that the rate was independent of oxygen pressures as well as of quinone concentrations. The dependence of the alcohol concentration on the rate was also investigated, when necessary, using benzene as the solvent.

Inspection of quantum yields for the oxygen consumption at various temperatures and also of the temperature dependence of the reaction rate over a wide range of temperature has led to a view that the photo-oxidation of isopropyl alcohol by quinones is characterized by a non-chain mechanism at ordinary temperature and that chains propagate gradually with increasing temperature. In accordance with these kinetic trends and also with spectroscopic and ESR studies on the nature of semiquinone intermediates,[3] the following mechanism was proposed as the main pathways.

$$M \xrightarrow{I_a} M^*$$

$$M^* \xrightarrow{k_0} M$$

$$M^* + RH \xrightarrow{k_1} MH + R$$

$$MH + O_2 \xrightarrow{k_2} M + HO_2$$

$$R + O_2 \xrightarrow{k_3} RO_2$$

$$RO_2 \xrightarrow{k_4} (CH_3)_2CO + HO_2$$

$$HO_2 + RH \xrightarrow{k_5} R + H_2O_2$$

$$2HO_2 \xrightarrow{k_6} H_2O_2 + O_2$$

where I_a stands for the rate of photo-excitation of quinones present and k_0, k_1,……are the rate constants of the respective steps.

The steady state treatment relevant to the above mechanism yields Eq. (1).

$$-\frac{d[O_2]}{dt} = \frac{I_a k_1[RH]}{k_0 + k_1[RH]} + \frac{k_5}{\sqrt{k_6}} \sqrt{\frac{I_a k_1[RH]}{k_0 + k_1[RH]}}\,[RH] \qquad (1)$$

Dividing both sides of Eq. (1) by I_a, we obtain an expression for the overall quantum yields Φ.

$$\Phi = \Phi_0 + \frac{k_5}{\sqrt{k_6}} \sqrt{\Phi_0}\,[RH] \frac{1}{\sqrt{I_a}} \qquad (2)$$

where

$$\Phi_0 = \frac{k_1[RH]}{k_0 + k_1[RH]} \qquad (3)$$

Eq. (2) assumes that a plot of Φ against $1/\sqrt{I_a}$ may yield a straight line with an intercept Φ_0. I_a can be determined either by a chemical actinometry or by a kinetic method. Uranyl oxalate actinometry gave 1.14×10^{-7} mole/L. sec. for I_a. On the other hand we have determined I_a kinetically after Wells[5] as follows.

It is noted at least with AQ and MNQ that the overall photo-oxidation process does not involve chains around room temperature. This means that the second term of the right of Eq. (1) is negligible as compared with the first term below room temperature. Thus, the following relation should be valid.

$$\frac{1}{-|d[O_2]/dt|} = \frac{1}{I_a} + \frac{k_0}{k_1} \frac{1}{I_a[RH]} \qquad (4)$$

In fact, a linear relationship was found to hold between $1/-d[O_2]/dt$ and $1/[RH]$ with AQ and MNQ respectively, as shown in Fig. 2 for MNQ, when the concentration of alcohol was low enough, although it appeared to deviate at high concentrations. Probably the deactivation constant k_0 would not remain constant over a wide range of concentrations. From the intercept of the straight line of Fig. 2, I_a was found to be 1.89×10^{-7} mole/L. sec. This extrapolated value, I_a, will only be approximate. However, it may serve as a guide for the relative photocatalytic activity of the quinones under investigations.

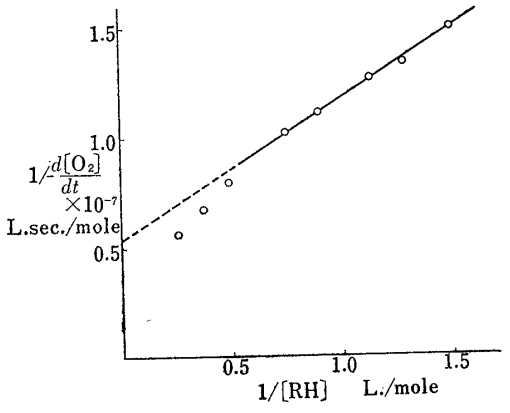

Fig. 2. Reciprocal Relation between the Rate of Oxygen Uptake and the Concentration of Isopropyl Alcohol

M: MNQ T: 25°

Substitution of the I_a-value kinetically determined for Eq. (2) yielded a linear relation for Φ against $1/\sqrt{I_a}$. The plot of this kind obtained with MNQ is shown in Fig. 3. It is noted that three straight lines at temperatures 20, 40, and 60° respectively have a common intercept at $\Phi_0 = 0.96$.

Such was the case also with NQ, AQ, and CNQ. In Fig. 4 are shown the plots obtained at the temperature 40° with respect to all the quinones investigated.

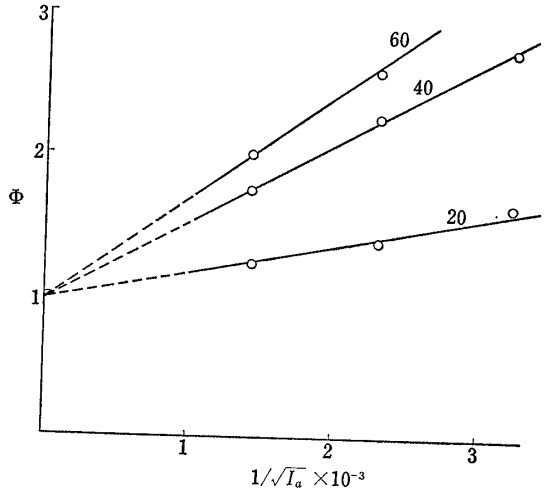

Fig. 3. The Relationship between Φ and $1/\sqrt{I_a}$ at 40°
M: MNQ, NQ, AQ, and CNQ.

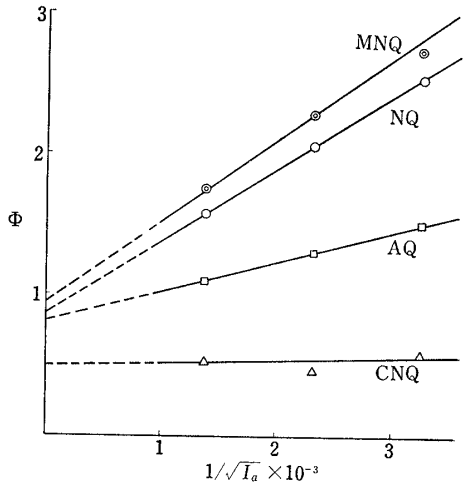

Fig. 4. The Relationship between Φ and $1/\sqrt{I_a}$ at 20, 40, and 60°
M: MNQ

Since Φ_0 is readily derived from the intercept of Fig. 4 with respect to each of the quinones, k_1/k_0 can be evaluated from Eq. (3) keeping in mind that [RH]=13.3 mole/L. The k_1/k_0 values evaluated in this way are listed in Table I.

Table I. Kinetic Data for the Photo-oxidation of Isopropyl Alcohol by Quinones

	MNQ	NQ	AQ	CNQ
$-d[O_2]/dt$ mole/L. sec. $\times 10^7$ 40°	4.36	3.98	2.51	0.91
k_1/k_0	1.78	1.09	0.72	0.09

The ratio k_1/k_0 is obviously a measure of the relative importance of the photo-excited quinone M* to abstract hydrogen atom from alcohol as compared with its deactivation. Thus, the data of Table I may indicate that either k_1 is of the sequence: MNQ>NQ>AQ>CNQ or k_0 is reversal. It is quite possible that both effects counteract each other.

Now, quite apart from k_0, it would be of some value to discuss the relative rates of the photo-excited quinones for the step with regard to the energy of reaction. The

$$M^*+RH \xrightarrow{k_1} MH+R$$

energy of reaction, q, may be expressed by

$$q=\{E(M^*)+E(RH)\}-\{E(MH)+E(R)\}$$
$$=\{E(M^*)-E(MH)\}+\{E(RH)-E(R)\}$$

where E(M*), E(RH) etc. are the total electronic energies of M*, RH etc. Since E(RH) −E(R) is invariable, the only variable should be E(M*)−E(MH). Let us assume $\pi\rightarrow\pi$ transition for M→M*. The $n\rightarrow\pi$ transition, as proposed by Bridge and Porter[6] for quinone sensitizations, was not taken into consideration because it was considered to be so weak as compared with $\pi\rightarrow\pi$. The change in q may now be given by

$$\Delta q=\Delta\{E^{\pi}(M^*)-E^{\pi}(MH)\}$$

6) N. K. Bridge, G. Porter: Proc. Roy. Soc., A224, 259, 276 (1952).

To see the relative magnitude of q with the four quinones, the total electronic energies were calculated according to the Hückel MO method.[7] The OH group of semiquinone radical was assumed not to join the resonance of π-electrons. The calculated energies are shown in Table II with parameters*[3] chosen in the calculations.

Table II. Difference in the Total π-Electron Energies between M* and MH

	MNQ	NQ	AQ	CNQ
$E^{\pi}(M^*)-E^{\pi}(MH)$	$\alpha+2.67\beta$	$\alpha+2.58\beta$	$\alpha+2.60\beta$	$\alpha+2.97\beta$

α: Coulomb integral β: Exchange integral

$\alpha_O=\alpha_C+1.2\beta_{C-C}$ $\alpha_{Cl}=\alpha_C+2.0\beta_{C-C}$ $\beta_{C-O}=1.56\beta_{C-C}$ $\beta_{C-Cl}=0.4\beta_{C-C}$ $\alpha_{H_3}=\alpha_C-0.5\beta_{C-C}$

$\alpha_{C_2}=\alpha_C-0.1\beta_{C-C}$ $\alpha_{C_1}=\alpha_C$ $\beta_{C_2-H_3}=2.5\beta_{C-C}$ $\beta_{C_1-C_2}=0.7\beta_{C-C}$

From the data of Table II, q may be considered to decrease in the order : NQ> AQ>MNQ>CNQ. This order coincides with the observed one except MNQ provided that k_1 parallels with q. As mentioned already, the role of k_0 in the observed sequence must also be taken into consideration. Unfortunately the machanism of the deactivation process is largely unknown. According to Kuboyama,[8] however, who very recently observed the phosphorescence spectra with MNQ and NQ, the life-time of the photo-excited MNQ is long as compared with NQ. It is apparent that the long life-time of MNQ* is in accordance with the highest photocatalytic activity of MNQ. In contrast, literatures[9] show that the phosphorescence life-time for photo-excited Cl-naphthalene is much shorter than that for naphthalene. The poor photocatalytic activity revealed in CNQ might partly be due to the short life-time for CNQ*. Further works are required for detailed discussions of the sequence.

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Summary

The ratio of the reaction rates of the photo-excited quinones with isopropyl alcohol as compared with their deactivation has been determined using methylnaphthoquinone, naphthoquinone, anthraquinone and dichloronaphthoquinone as photocatalysts. The sequence of the ratios was found to be methylnaphthoquinone>naphthoquinone>anthraquinone>dichloronaphthoquinone. Attempts were made to correlate this sequence with the electronic energies of the photo-excited state of the respective quinone as well as of the corresponding semiquinone radical. The importance of the life-time of the photo-excited methylnaphthoquinone was pointed out in connection with its highest photocatalytic activity.

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*[3] Parameters adopted for the calculations were taken from A. Streitwieser, Molecular Orbital Theory for Organic Chemists, John Wiley and Sons, Inc., New York, 1961.

7) See for instance R. Daudel, R. Lefebvre, C. Moser : "Quantum Chemistry," Methods and Applications, Interscience Publishers, Inc., New York, 1959.
8) A. Kuboyama : International Conference on Photochemistry, Tokyo, 1965.
9) See for instance M. Koizumi : Photochemistry, p. 303, Asakura, 1963.