Kinetic Studies on Dehydrogenation Reaction of 5,6-Dihydro-2,4(1*H*,3*H*)-pyrimidinediones in Aqueous Solution Induced by Argon Arc Plasma or Hydrogen–Oxygen Flame

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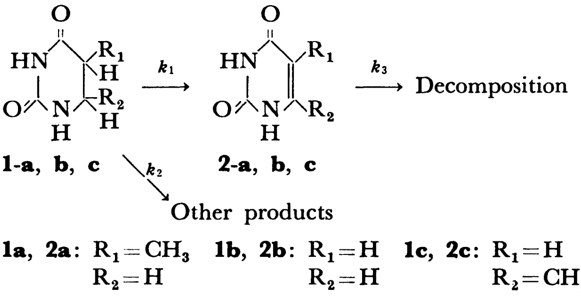
Synopsis. 5,6-Dihydro-2,4(1*H*,3*H*)-pyrimidinediones underwent dehydrogenation at the 5- and 6-position producing 2,4(1*H*,3*H*)-pyrimidinediones in aqueous solution induced by argon arc plasma or flames. From consideration based on the kinetic study of this reaction, it was found that abstraction of a hydrogen atom took place preferentially at the 6-position of the dihydropyrimidinediones.

Although various types of plasma chemistry have been reported,[1] most of these are chemical reactions in the gaseous phase or onto the solid phase. Few organic reactions in aqueous solution using plasma have been performed except for contact glow discharge electrolysis.[2] We recently reported a few aqueous-phase reactions induced by argon arc plasma or flames.[3–5] When argon arc plasma or flames of various gases mixed with oxygen were kept in contact with aqueous solution containing organic compounds, a very powerful and clean oxidation reaction took place without adding any oxidizing agent. For example, aliphatic amines were oxidized to amino acids,[3] and direct hydroxylation of aromatic rings proceeded in aqueous solution of phenyl-containing amino acids.[4] The active oxidizing species could be hydroxyl radicals which exist in flames, or which are produced by dissociation of water by high energy argon arc plasma.

In the present study, it was found that 5,6-dihydro-2,4(1*H*,3*H*)-pyrimidinediones underwent dehydrogenation at the 5- and 6-position producing 2,4(1*H*,3*H*)-pyrimidinediones in aqueous solution induced by argon arc plasma or flames. This paper reports the kinetics of the dehydrogenation and the reaction mechanism.

Results and Discussion

The substrates used here were 5,6-dihydro-5-methyl-2,4(1*H*,3*H*)-pyrimidinedione (**1a**), 5.6-dihydro-2,4(1*H*,3*H*)-pyrimidinedione (**1b**) and 5,6-dihydro-6-methyl-2,4(1*H*,3*H*)-pyrimidinedione (**1c**) (Scheme 1). The time courses of the yield of product (**2c**) and the decay curves of the substrate (**1c**) are shown in Figs. 1 and 2, which were obtained by using argon arc plasma and hydrogen–oxygen flame, respectively. The yields of pyrimidinediones increased with the reaction time and then decreased because of the decomposition of the products. Table 1 shows the maximum yield and its reaction time for each substrate. The order of the maximum yields of the products are as follows: **2c**>**2b**>**2a**, in both energy sources.



1a, 2a: $R_1=CH_3$ $R_2=H$ **1b, 2b**: $R_1=H$ $R_2=H$ **1c, 2c**: $R_1=H$ $R_2=CH_3$

Scheme 1.

Table 1. Maximum Yields and Thier Reaction Times for Each Substrate and the Energy Source

	1a-2a	**1b-2b**	**1c-2c**
Ar arc plasma	1.0% (40 min)	2.3% (60 min)	6.8% (40 min)
H_2-O_2 flame	2.4% (60 min)	4.0% (100 min)	6.4% (60 min)

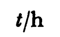


Fig. 1. The time course of the yield of **2c** through dehydrogenation reaction of **1c** by argon arc plasma; (○—○) **1c**, (●—●) **2c**.

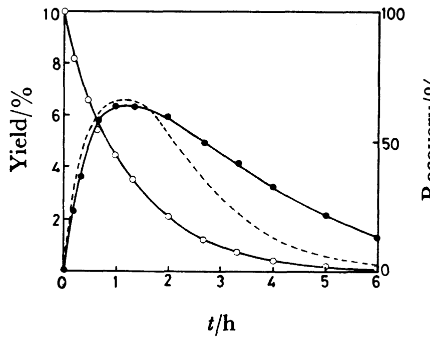


Fig. 2. The time course of the yield of **2c** through dehydrogenation reaction of **1c** by hydrogen–oxygen flame; (○—○) **1c**, (●—●) **2c**.

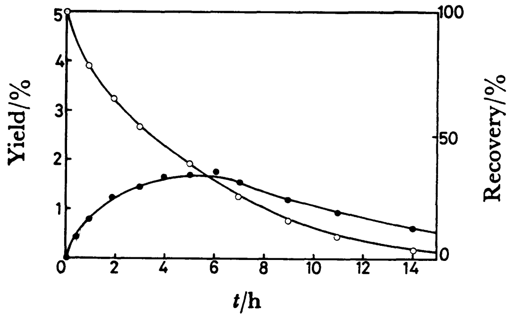


Fig. 3. The time course of the yield of **2b** through dehydrogenation reaction of **1b** by acetylene–oxygen flame; (○—○) **1b**, (●—●) **2b**.

This dehydrogenation reaction could proceed by the action of hydroxyl radicals, which were produced through dissociation of water molecule by high energy argon arc plasma, or transferred into the aqueous reaction mixture from the flames.[3–5] The dehydrogenation reaction was also effected by an acetylene(C_2H_2)–oxygen flame instead of a hydrogen–oxygen flame (Fig. 3). The rate of the dehydrogenation reaction with this flame was lower than that with a hydrogen–oxygen flame. This could be due to the lower hydroxyl radical abundunce in the acetylene–oxygen flame.

This reaction proceeded as a first-order reaction with respect to the decay of the substrate. This result was attributed to the large number of active species provided. Accordingly, it was also confirmed that the decay of the product proceeded as a first-order reaction from individual experiments. The reaction pathway could be explained as shown in Scheme 1, where k_1+k_2 and k_3 are the rate constants for the decay of the substrate and the product, respectively. The rate expression for the reaction is given by

$$\frac{d[P]}{dt} = k_1[DHP_0]e^{-(k_1+k_2)t} - k_3[P], \tag{1}$$

where [P] represents the concentration of the product, and [DHP_0] stands for the concentration of the substrate at t=0. Eq. 1 gives

$$[P] = -\frac{k_1}{k_1+k_2}[DHP_0](e^{-(k_1+k_2)t}-1) - k_3\int_0^t [P]dt. \tag{2}$$

The value of k_1+k_2, k_3, and k_1 are shown in Table 2. The theoretical curves are represented in Fig. 1 and Fig. 2 by dotted line, using Eq. 3 which is obtained from Eq. 1.

$$[P] = \frac{k_1}{k_3-k_1-k_2}[DHP_0](e^{-(k_1+k_2)t}-e^{-k_3t}). \tag{3}$$

The value of $k_1/(k_1+k_2)$, which represents the ratio of the dehydrogenation reaction, are shown in Table 2. It is apparent that the ratio of $k_1/(k_1+k_2)$ on **1c** was higher than that of others. These results show that the dehydrogenation reaction of **1c** took place easier than the others.

It has been known that the radical abstraction of a hydrogen atom is observed at the site with higher electron density.[6] For the substrates used, the electron density is lower at the 5-position than at the 6-position owing to the electron-withdrawing effect of a carbonyl group at the 4-position. In addition, in the case of **1c**, the electron density at the 6-position should be highest owing to the inductive effect of the methyl group.

Table 2. Rate Constants of Dehydrogenation Reaction for Each Substrate and Energy Source

Substrates	Rate constants (min^{-1})			$k_1/(k_1+k_2)$
	k_1+k_2[a]	k_3[b]	k_1[c]	
1a–2a*	2.02×10^{-2}	2.14×10^{-2}	6.38×10^{-4}	0.032
1b–2b*	2.11×10^{-2}	2.04×10^{-2}	1.07×10^{-3}	0.028
1c–2c*	1.97×10^{-2}	2.06×10^{-2}	3.73×10^{-3}	0.19
1a–2a**	1.33×10^{-2}	3.03×10^{-2}	1.21×10^{-3}	0.096
1b–2b**	1.25×10^{-2}	2.94×10^{-2}	1.63×10^{-3}	0.16
1c–2c**	1.27×10^{-2}	2.76×10^{-2}	3.59×10^{-3}	0.28

* Ar arc plasma. ** H_2–O_2 flame.

a) The values k_1+k_2 were obtained from the data up to 80 min after the begining of the reaction for both argon arc plasma and hydrogen-oxygen flame. b) The values k_3 were obtained from the data up to 80 min or 40 min after the begining of the reaction for argon arc plasma or hydrogen-oxygen flame, respectively. c) Using Eq. 2, the values of k_1 were estimated by averaging the values of each 20 min after 20 min up to 80 min or 180 min of the reaction, carried out by argon arc plasma or hydrogen-oxygen flame, respectively. The term $\int_0^t [P]dt$ was estimated by the area of the figure in comparison with that of a standard.

Based on the considerations mentioned above, the experimental results suggest that the preferential redical abstraction took place at the 6-position. Therefore, **1c** had the highest value of $k_1/(k_1+k_2)$.

The chemical reactions in aqueous solution induced by flames or argon arc plasma are a new type of chemistry. The reaction is also interesting from the chemical evolutionary point of view. The reaction could be regarded as a model for the solar plasma-induced reaction in the primitive hydrosphere, when the primitive Earth had no magnetic field and low atmospheric pressure.

Experimental

Materials. Compound **1b** was prepared by the method of Dakin.[7] Other substrates were commercial products. Their purities were checked by high performance liquid chromatography (HPLC).

Apparatus and Procedures. The apparatus used is shown in Fig. 4. The plasma torch used for the plasma induced reaction was a non-transferred type plasma torch (Nippon Welling Co., Wellpen NP-7). The conditions to produce plasma jet were: argon, 1.5 $dm^3\,min^{-1}$; electric current, 40 A; electric voltage, 15 V. The plasma torch was immersed into the solution of the substrate 1 cm below the surface and the plasma jet was directly applied into the solution. The flame used in the dehydrogenation reaction was a hydrogen–oxygen flame, and the flow rates of gas

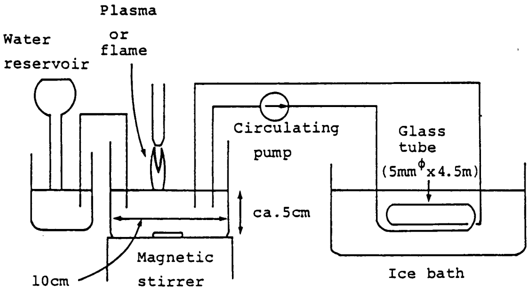


Fig. 4. Apparatus for the plasma- or flame-induced reaction.

($dm^3\ min^{-1}$) were 1.5 (hydrogen) and 0.8 (oxygen). A flame from a burner nozzle was blown onto the solution 3 cm above the surface. The temperature of the solution was kept at 40—50 °C throughout the reaction by circulating the solution through a glass tube immersed in an ice bath. The concentration of the substrates were 2.5×10^{-2} mol dm^{-3} and the volumes of the reaction mixture were 0.3 and 0.5 dm^3 for the flame and plasma, respectively. At appropriate time intervals, 0.5 ml aliquots of the solution were withdrawn and analyzed with HPLC. The column used for HPLC was Finepak C_{18} (JASCO 4.6 mm i.d.×25 cm; eluent: H_2O–CH_3OH) and UV detector (230 nm) was used. Quantitative analyses were carried out by comparison with authentic samples.

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