Title	ISOTOPIC SEPARATION FACTOR OF SLOW DISCHARGE MECHANISM OF HYDROGEN ELECTRODE REACTION. II
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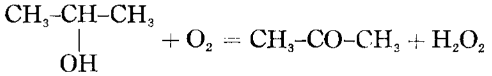
consumption of oxygen. On intercepting light, the consumption occurring steadily was found to cease apparently. Reillumination caused consumption of oxygen again to proceed, so that the photocatalytic oxidation of isopropylalcohol was almost reversible with respect to on or off of the light switch.

Now, in the case of oxidized zinc oxide, the photosensitized oxidation reaction took place quite similarly as the case on reduced zinc oxide while the reaction did not proceed without illumination beyond the period of 70 hours. However strikingly different behavior was that interception of light still permits the oxidation reaction to proceed with a speed almost equal to that of illumination. All the rate data for the oxidation of isopropylalcohol are shown in Fig. 1. Gas chromatographic and chemical analyses indicated that the product contains nothing other than acetone and hydrogen peroxide. The oxidation reaction may hence be expressed by



$$\underset{\displaystyle OH}{CH_3\text{-}\underset{|}{CH}\text{-}CH_3} + O_2 = CH_3\text{-}CO\text{-}CH_3 + H_2O_2$$

As shown previously,[1] adsorbed oxygen due to illumination was unable to desorb on intercepting light whereas photodesorption was fairly reversible. If it is accepted that the photoresponse of this kind should hold even during the progress of the oxidation reaction of isopropylalcohol, the different photocatalytic behavior shown above respectively on reduced and oxidized zinc oxide is not unexpected. Because the catalyzing surface of reduced zinc oxide varies, when oxygen is present, depending on whether the light is switched on or off whereas the surface of oxidized zinc oxide, once experienced illumination, may maintain its state even during the light is intercepted.

On the other hand, almost identical photocatalytic activity shown by the two zinc oxide samples during the initial stage, including the induction period and later, is unexpected and rather embarrassing. Further work is in progress.

ISOTOPIC SEPARATION FACTOR OF SLOW DISCHARGE MECHANISM OF HYDROGEN ELECTRODE REATION. II

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KEII and the present author[1] have theoretically calculated the electrolytic separation factor, S, of deuterium on the basis of the slow discharge mechanism

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with the result that $S=12\sim13$ irrespective of electrode materials. However, it was assumed in the above calculation that proton or deuteron to be discharged was that of hydroxonium ion which may be reasonable in the electrolysis of acidic solution.

The separation factor will be calculated in the present paper on the same basis but alternatively on the premise that proton or deuteron is discharged from water molecule as

$$H_2O + e \longrightarrow H(a) + OH^-$$

or

$$DHO + e \longrightarrow D(a) + OH^-$$

which is probable in alkaline solution, where $H(a)$ or $D(a)$ is adsorbed hydrogen or deuterium atom on the electrode metal. Only difference is that of the base H_2O or OH^- which holds proton or deuteron to be discharged, and hence S can readily be calculated according to the procedure described in the previous paper[1] by replacing the potential functions relevantly.

Dissociation energy, A_0, of the MORSE function of the proton or deuteron was estimated[2] at -379 Kcal/mol., in place of -263 Kcal/mol. in the former case, as the heat toning of the reaction

$$H_2O(l) = H^+(g) + OH^-(l, \infty),$$

where (l) or (g) signifies the liquid or the gaseous state and $OH^-(l, \infty)$ the hydroxyl ion in aqueous solution at infinite dilution. It was found by varying other parameters, i. e. a and r_e of the MORSE function and the distance y_L between the proton or deuteron and water molecule at the critical state along the normal to the electrode surface that S is considerably insensitive to their variation over a reasonable range.

The factor S was thus calculated at 12 (for Ni, Ag) and 13 (for Hg), changing A_0 only from -263 Kcal to -379 Kcal and reserving the previous values[1] of a, r_e and y_L. The former result $S=12\sim13$ for hydroxonium ion holds in the present case of water molecule quite unchanged. This confirms further the previous conclusion[1],[3] that the theoretical value of S depends practically only on the underlying mechanism.

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