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DEUTERATION OF ETHYLENE, PROPYLENE AND BUTENES ON Pt ELECTRODE IN DEUTERATED ACIDS – D_2O SOLUTIONS

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Deuteration of C_2, C_3 and C_4 olefins was conducted at a platinum electrode in 0.5M D_2SO_4 or 1M $DClO_4$-D_2O solutions. In each case studied, deuteroparaffins reveal a common feature of a two maxima distribution; one is at partially deuterated paraffins and the other at perdeuteroparaffin. Appearance of the two maxima distribution clearly indicates the presence of two reaction paths. Isomerization during the deuteration of butene isomers was found small, 10~30% of the total conversion.

Present authors have studied the reduction of ethylene on a platinum electrode in acid aqueous solution and confirmed the applicability of the associative mechanism proposed by Horiuti and Polanyi to the electrode system.[1-3] Deuteration of ethylene in $HClO_4$-H_2O gives deuteroethanes with a distribution where the fraction decreases in a successive manner with the increase in the number of D atoms. Such a distribution is taken as a substantial evidence for the rapid occurrence of the half hydrogenation step and its reverse in the Horiuti-Polanyi mechanism. The distribution was fairly approximated by the random distribution of D among the surface species at the atomic fraction of $f_D=0.15$.[3)]

The present work aims to test the random distribution by increasing f_D. A maximum in the distribution will be expected to shift to a deuteroethane containing more D atoms with the increase of f_D.

In experiment, the system of olefin + D_2 + D_2SO_4 (or $DClO_4$) + D_2O was used to enhance the deuterium atom % on the surface. The olefins used were C_2H_4, C_3H_6, 1-C_4H_8, cis-2-C_4H_8 and trans-2-C_4H_8 supplied from Takachiho Chemical Ind. Co., Japan. They were all purified by repeated distillation in vacuum. Deuterium gas was produced by decomposing D_2O (99.75%, Merck, Germany) over magnesium metal heated up to 500°C and purified by passing through molecular sieves 13X at -196°C. Electrolyte solutions were prepared from D_2O and D_2SO_4 (99.0%, CEA, France) or $DClO_4$ (Min 99%, Merck, Germany). Test electrode was a cylindrical smooth platinum net (apparent surface area, 42 or 81 cm^2) and anodically activated at 1.8V vs rhe for 2 min and then reduced at 0V for 1 min before use. Platinized platinum foils were used as the reference and counter electrodes, respectively. Immediately after the activation of the test electrode, the reaction was commenced at room temperature by circulating a reaction gas through the test electrode compartment of a three compartment type cell. The reaction gas was an atmospheric mixture of olefin, deuterium and helium. A helium gas was purified by a commercial purifier (Japan Pure Hydrogen Co. INC.) to 7N-purity. In the case of electroreduction, deuterium was not included in the reaction gas. Reaction products were analyzed by a gas chromatography with a column of silica gel (1.5m in length) for C_2 and C_3 paraffins and VZ7 (6m) for C_4 paraffin at 0°C, respectively. Each fraction was trapped out and subjected to a mass spectroscopic analysis.

Kinetic study shows that the initial rate of reduction, V_0, on a smooth Pt electrode on open circuit in 0.5M D_2SO_4 or 1M $DClO_4$-D_2O solution is expressed as

$$V_0 = k_D k_{C'} P_D P_{C'} / (k_D P_D + k_{C'} P_{C'})$$

where k_D and $k_{C'}$ are constant. P_D and $P_{C'}$ are the initial partial pressures of deuterium and olefin under investigation. The present experimental condition satisfies $P_D/P_{C'} < k_{C'}/k_D$ where the diffusion of deuterium is rate determining. Open circuit potential during the reaction stays at 80~120 mV, being far more positive than the reversible potential of the hydrogen electrode reaction. Such a deviation is one of the evidences for the above conclusion. Therefore, the diffusion of olefins is taken to be fast under the present conditions. However, olefins suffers D atom exchange only to a detectable extent during the reaction. This indicates an irreversible adsorption of olefins in agreement with a previous conclusion.[3)]

Figure 1, a~e, shows a distribution of deuteroparaffins formed by the

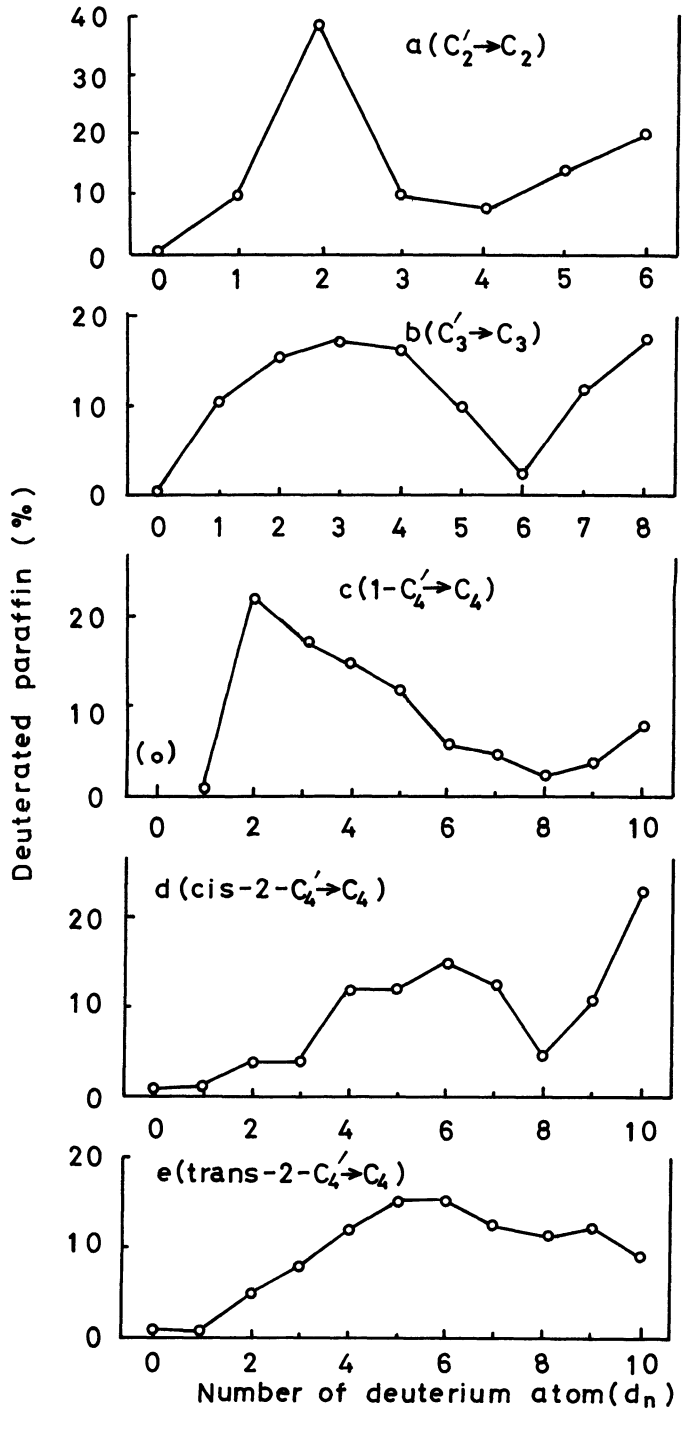

Fig. 1 Distribution of deuteroparaffins

Pressures of olefins and deuterium (mm Hg) conversion(%), and open circuit potential (mV vs rhe) are as follows. a (123,39,ca10, 175), b (62,124,ca10,112), c (30,48,9,99), d (30,20,6,102), e (30,29,3,78)

reduction of C_2H_4(Fig.1, a), C_3H_6(b), 1-C_4H_8(c), cis-2-C_4H_8(d) and trans-2-C_4H_8(e). These distributions were independent of the conversion within 10% and reproduced by electroreduction at the same potential as the open circuit potential. The coincidence of the results obtained by electroreduction suggests that the hydrogen atom takes part in the reaction via the same adsorption state, irrespective of being supplied from hydrogen molecule or from D^+ in solution and metal electron.

A clearly noticed common feature among a$\sim$e of Fig. 1 is the presence of two maxima against a single maximum expected from the random distribution. Perdeuterospecies are the most abundant isomer in one of the two segments in each distribution, though the case e is somewhat different. The other segment consisting of isomers with smaller number of D atoms, exhibits a maximum at d_2 for ethane and butane from 1-butene, d_3 for propane, and $d_5 \sim d_6$ for butane from 2-butenes, respectively. Such a distrubution of two maxima seems not to have been reported in gaseous heterogeneous hydrogenation catalysis. For example, Bond et al.4) examined the deuteration of $C_2 \sim C_4$ olefins on alumina-supported platinum (5 molar %)

in a temperature range of 0~150°C. Only one maximum at d_1, without the second maximum at perdeuterospecies, is reported. Their distribution is independent of the kind of olefins studied. It is, however, to be noted that alkanes of C_2 and C_3 subjected to the exchange, gives the U-shaped distributions where both mono- and per-deuterospecies are substantial.$^{5,6)}$

The result of Fig. 1e appears somewhat exceptional. It may be noticed that the fraction of perdeuterospecies is generally suppressed when the reaction undergoes at a less positive potential, i.e., at a condition that the ratio $P_D/P_{C'}$ approaches to $k_{C'}/k_D$. Effect of $P_D/P_{C'}$ is now under investigation in details.

In the case of C_4 olefins, hydrogenation of 2-butenes accompanies more enhanced isotopic exchange than that of 1-butene. A mean deuterium number in butane from 2-butenes is 5.9~6.5, whereas 4.1 in butane from 1-butene. Isomerization occurrs to an extent of 10 to 30%. Deuterium distribution in the isomerized butenes will be reported elsewhere.

The present two maxima distribution cannot be explained by the simple Horiuti-Polanyi mechanism. Two reaction paths must be assumed by taking into account, e.g., different adsorption states of olefin such as π and σ-type, two kinds of reaction sites with different activity for the half hydrogenation step of the Horiuti-Polanyi mechanism, dissociative adsorption of olefin, etc. The previous distribution obtained at low $f_D$$^{3)}$ was assumed as a first approximation to be the random one but considerable deviations were observed at d_0 and at the other end of the distribution, i.e., at d_3~d_5. Thus, it must be understood as a sum of the two distributions each corresponding to each reaction path. Reanalysis is now in progress.

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