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Reaction Intermediates in the Hydrogen Exchange of Propene on Cation-Exchanged Resin Studied by Microwave Spectroscopy

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Reaction intermediates in the hydrogen-exchange reaction of propene over deuterated cation-form sulfonic resin were studied by means of microwave spectroscopy. In the cases of Fe-form and Ni-form sulfonic resin, the results were explained by the process via the 2-propyl-type intermediate, while the reaction intermediate for Hg-form resin was demonstrated as an allyl-type complex.

INTRODUCTION

Catalytic behavior of a cation-exchanged ion exchanger provides important information about the catalytic role of the heterogenized cation on polymer surfaces. Catalytic properties of cation-exchanged inorganic ion exchangers, such as zeolites (*1*) and silica–alumina (*2*) have been investigated in detail in various reactions. However, there has been little investigation concerned with the application of cation-form ion-exchange resins and metal complexes bound on ion-exchange resins to heterogeneous catalysis.

We have reported on the heterogeneous catalyses in the isomerization of butenes (*3*) and the hydrolysis of esters (*4*) over various cation-exchanged sulfonic resins and clarified the properties of their active sites by the adsorption of basic gases (*5*). In the course of these studies, it was found that the catalytic activities and selectivities in the isomerization of butene can be interpreted in terms of the acidic nature of the metal cation on the resin (*3*) and that the adsorbed water, ammonia, and olefins are stabilized by the effect of the crystal field on the metal cations (*5*). Furthermore, the catalytic activities of H-form and Hg-form resins were much higher than those expected from their electronegativities (*3*). These facts suggest that the reaction mechanisms or the intermediates for these two cations are different from those of the others.

In order to determine a reaction intermediate, microwave spectroscopy has been successfully applied to the isomerization of butenes and the hydrogen exchange of propene over various catalytic systems (*6*). For example, using this technique, the four d_1-geometrical isomers and the seven d_2-isomers of propene can be identified with high resolution and high sensitivity.

Kondo *et al.* (*6a*) have proposed a new method to determine the reaction intermediates for the hydrogen-exchange reaction of propene by following the change in the distributions of the d_1- and d_2-isomers during the reaction. According to this method, one can distinguish seven typical distribution patterns, each of which depends on different reaction intermediates, assuming that no multiple-exchange process is present but that only one successive process plays the main role in the reaction, i.e., (1) 1-propyl, (2) 2-propyl, (3) 1-propenyl, (4) 2-propenyl, (5) σ-allyl, (6) π-allyl, and (7) concerted mechanism.

In the present paper, the reaction inter-

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mediates for the hydrogen–deuterium exchange reaction of propene were studied on the deuterated Fe-form, Ni-form, and Hg-form sulfonic resins by means of the microwave technique in an attempt to elucidate the catalytic properties of these types of catalysts.

EXPERIMENTAL

A crosslinked sulfonate polystyrene of macroreticular structure, Amberlyst-15, obtained from Organo Company Ltd., was treated with a 2 *N* NaOH solution so that the active protons on the resin were completely substituted for sodium ions. The Na-form resin (ion exchange capacity 3.77 meq/g Na-form resin), thus prepared, was impregnated with a 0.1 *N* solution containing the desired transition-metal nitrate, $Fe(NO_3)_3$, $Ni(NO_3)_2$, or $Hg(NO_3)_2$, for over 1 week, in a manner similar to that previously described (*3*). The resultant cation-form resins were filtered, dried *in vacuo,* and then heated at 80°C for 1 week to remove the residual water in the small pores of the resin. The transition-metal-form resins are written as AMNaFe, AMNaNi, and AMNaHg, respectively. The amounts of the transition metal on the resin, determined by the EDTA method, were 0.97 mmol Fe^{3+}/g AMNaFe dry, 1.15 mmol Ni^{2+}/g AMNaNi dry, and 1.45 mmol Hg/g AMNaHg dry.

The hydrogen–deuterium exchange reaction between the deuterated cation-form resin and propene was carried out in a conventional closed circulation system (340 ml). The catalyst sample (ca. 1.30 g) was evacuated at 120°C for 3 hr and then treated overnight with 6 ml of D_2O (>99.5% purity; Wako Chemicals Co., Ltd.). It was heated up to 60°C to promote the exchange of deuterium for hydrogen on the resin. After the deuteration process was repeated three times, the resin catalyst was finally evacuated at 100 or 150°C, prior to use for the reaction. The initial pressure of propene was about 300 Torr. The reaction was followed by analyzing the deuterium content in propene with a mass spectrometer, and the distributions of the d_1- and d_2-isomers were determined by means of microwave spectroscopy. The detailed procedures of the analysis are described elsewhere (*6a*).

RESULTS AND DISCUSSION

The change in the deuterium distribution in propene-d_1, C_3H_5D, during the hydrogen–deuterium exchange reaction on AMNaFe is shown in Fig. 1. Since no propene-2-d_1 was detected throughout the reaction, 1-propyl, $\underset{*}{\mathrm{C}}\mathrm{H_2CHDCH_3}$, 2-propenyl, $\mathrm{CH_2{=}}\underset{*}{\mathrm{C}}\mathrm{{-}CH_3}$, and protonated cyclopropane should not be intermediates of this reaction (*6a*). The composition of d_1-propene isomers was found to be nearly 40% propene-1-d_1 and 60% propene-3-d_1 from the initial stage of the reaction, and furthermore, the ratio between the two isomers of 4 : 6, which is equal to the equilibrium ratio, was maintained during the reaction. Consequently, the concerted mechanism and the π-allyl mechanism are excluded since their composition will start at 0% of propene-1-d_1 and 100% of propene-3-d_1 (see Fig. 5).

It is known that in the case of the exchange reaction via the 2-propyl intermediate, only two isomers should be produced, as shown in Eq. (1) (*6a*).

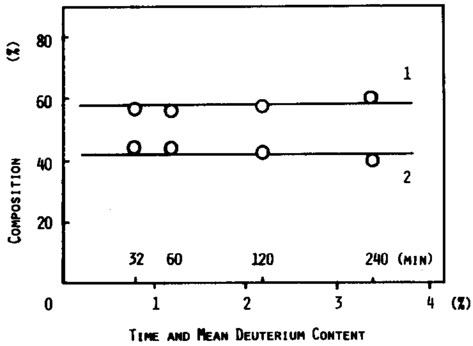

FIG. 1. Distribution of propene-d_1 isomers during the hydrogen-exchange reaction between propene and deuterium over AMNaFe evacuated at 100°C. Mean deuterium content (%) is represented by $\phi_D = 100\left(\sum_{1}^{6} id_i \Big/ 6\sum_{0}^{6} d_i\right)$. (1) $CH_2{=}CH{-}CH_2D$, (2) $CHD{=}CH{-}CH_3$.

$$CH_2{=}C_HCH_3 \underset{-D}{\overset{+D}{\rightleftharpoons}} CH_2D\underset{*}{C}HCH_3 \xrightarrow{-H} \begin{cases} CHD{=}CHCH_3 & 40\% \\ CH_2DCH{=}CH_2 & 60\% \end{cases} \qquad (1)$$

The 2-propyl intermediate, $CH_2D\underset{*}{C}HCH_3$, will be formed by addition of a deuterium from the catalyst to propene, and the exchange will proceed by dissociating one of the five hydrogens on the two methyl groups. If it is assumed that the secondary kinetic isotope effect can be neglected, the probabilities of the dissociation of hydrogen from CH_2D and CH_3 are equal. Therefore from the initial stage of the reaction the ratio of the two isomers is expected to be equal to that of the equilibrium.

The distribution pattern shown in Fig. 1 is in good agreement with this expected behavior, and it is concluded that the reaction on AMNaFe evacuated at 100°C proceeds through the formation of the 2-propyl intermediate.

This indicates that some hydrogen source is still present on the Fe-form resin, which is able to play a role in the catalysis. This hydrogen can be considered to be acidic in nature, as evidenced by adsorption of ammonia (*5*), catalytic activity for the polymerization of propene (*7*), and the isomerization of *n*-butenes (*3*). Therefore the 2-propyl intermediate above can be considered as 2-propylcarbonium ion. This observation is consistent with the fact that 2-propylcarbonium ion is also confirmed on several protonic-type solid acids, i.e., D_3PO_4 (*6a*, *8*), D_2SO_4 (*6a*), and deuterated *p*-toluenesulfonic acid (*9*).

In order to study the effect of the preevacuation temperature, the deuterated AMNaFe was evacuated at 150°C for 2 hr and subjected to the reaction. Figure 2 shows no significant difference in the deuterium distribution from that of AMNaFe evacuated at 100°C in Fig. 1, except that the rate of the exchange of deuterium decreased slightly. This indicates that the mechanism via 2-propyl intermediate is also valid for AMNaFe evacuated at 150°C.

It should be noted that when AMNaFe was preevacuated above 100°C for 2 hr, the rate for the polymerization of propene decreased as the temperature increased, reaching 0 at 180°C, whereas the isomerization of *n*-butenes increased with temperature up to 160°C (*7*). Since the propenyl-type intermediates were not demonstrated on AMNaFe evacuated at 150°C, the Lewis-type acid site due to Fe^{3+}, if formed by removing some of the hydroxyl groups on it by preevacuation, would not act as the

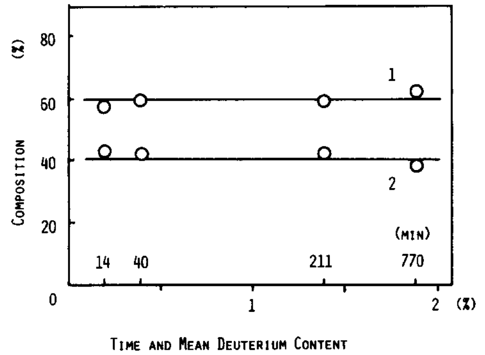

FIG. 2. Distribution of propene-d_1 isomers during the hydrogen-exchange reaction between propene and deuterium over AMNaFe evacuated at 150°C. (1) $CH_2{=}CH{-}CH_2D$, (2) $CHD{=}CH{-}CH_3$.

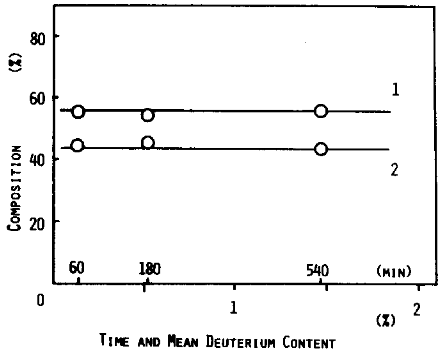

FIG. 3. Distribution of propene-d_1 isomers during the hydrogen-exchange reaction over AMNaNi evacuated at 100°C. (1) $CH_2{=}CH{-}CH_2D$, (2) $CHD{=}CH{-}CH_3$.

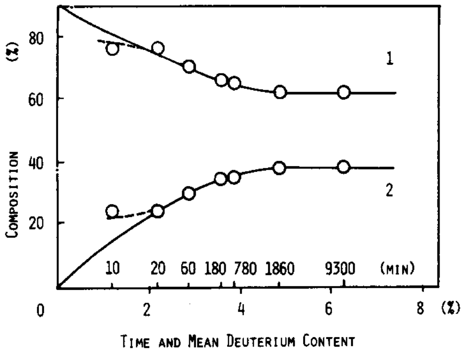

FIG. 4. Distribution of propene-d_1 isomers during the hydrogen-exchange reaction over AMNaHg evacuated at 100°C. (1) $CH_2{=}CH{-}CH_2D$, (2) $CHD{=}CH{-}CH_3$.

active site which facilitates the formation of an alkenyl-type intermediate.

The result for AMNaNi evacuated at 100°C is given in Fig. 3. The general features of the deuterium distribution during the reaction are quite similar to those for AMNaFe in Figs. 1 and 2. No propene-2-d_1 was detected. These facts demonstrate that in the case of Ni-form sulfonic resin, the main process of the exchange reaction is through the 2-propylcarbonium ion.[2]

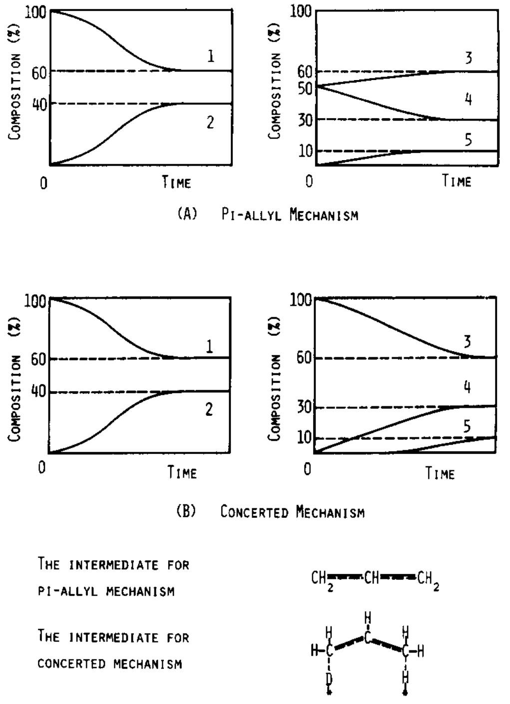

FIG. 5. Change in the deuterium distribution of propene-d_1 and propene-d_2 during the hydrogen-exchange reaction. (A) π-Allyl mechanism, (B) concerted mechanism. (1) $CH_2{=}CH{-}CH_2D$; (2) $CHD{=}CH{-}CH_3$; (3) $CHD{=}CH{-}CH_2D$; (4) $CH_2{=}CH{-}CHD_2$; (5) $CD_2{=}CH{-}CH_3$.

The deuterium distribution pattern for AMNaHg shown in Fig. 4 is quite different from the others. But similar to the cases of AMNaFe and AMNaNi, propene-2-d_1 was not detected. However, the initial compositions of propene-3-d_1 and propene-1-d_1 were above 80 and below 20%, respectively, and the former decreased and the latter increased as the reaction proceeded until they attained the equilibrium values of 60 and 40%, respectively. This pattern is consistent with those for the π-allyl, the concerted mechanism, and the dynamic σ-allyl,[3] as shown in Fig. 5. The change in the distribution of d_2-propene was not obtained because of the low concentrations detected. However, the relative ratio propene-1,3-d_2/propene-3,3-d_2 was about 1/2 at 31 hr (ϕ_D = 4.9%) and 1/1.5 at 165 hr (ϕ_D = 6.2%). The concerted mechanism is therefore excluded, since with it the ratio is expected to be 100/0 initially and at the final stage of the reaction, 60/30. Furthermore, the above ratios are close to that for the π-allyl intermediate (and the dynamic σ-allyl intermediate at higher tempera-

[2] A small deviation of the deuterium distribution in Fig. 3 from the ideal pattern for the 2-propyl mechanism may be accounted for by two factors: (1) The low S/N ratio in the low-content region of these deuterated species. Similar tendencies were also observed for the initial stages in Figs. 1 and 2. (2) Copresence of another minor process which might effect an increase in the formation of propene-1-d_1 and thus a decrease in that of propene-3-d_1. However, it is very difficult to determine the contribution of this minor process using only this method.

[3] In the case of the dynamic σ-allyl intermediate, the pattern alters from that for the σ-allyl at low temperatures to that for the π-allyl at higher temperatures (*6a*). Thus, the possibility of the mechanism through the dynamic σ-allyl cannot be completely excluded from the present data.

tures),[3] where it is expected to be 50/50 at the start and 60/30 at equilibrium. Thus, the hydrogen-exchange reaction on Hg-form resin proceeds through the π-allyl intermediate (or the dynamic σ-allyl under the higher-double-bond shift).

The small discrepancy of the first plot in Fig. 4 from the ideal pattern for the π-allyl process might stem from inaccuracies due to low concentrations, or from the copresence of another process; e.g., the 2-propyl intermediate, which would contribute to decrease propene-3-d_1 and thus increase propene-1-d_2.

These conclusions for the three different cation-form sulfonic resins seem to be reasonable since the soft acidic metal cations of Hg^{2+} have greater affinity to form a more stable π-complex with olefins than the hard-acid-type cations, Fe^{3+}, Ni^{2+}, and H^+, where the secondary carbonium ion is more stabilized.

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