SHORT COMMUNICATIONS

Confirmation of the Catalytic Deuteration of Methyl Groups of p-Xylene by the Use of the Infrared and NMR Methods

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It has been considered generally that the catalytic isotopic exchange reaction of hydrogen atoms with deuterium oxide occurs much more difficultly at paraffinoid hydrocarbons than at benzenoid hydrocarbons. However, as reported already[1] the exchange reaction of *p*-xylene catalyzed by nickel powders occurs also at the hydrogen atoms of the methyl groups, judging from the mass-spectrometric and infrared data of the products. In order to confirm such an expected result, the same samples were analyzed by the NMR apparatus of high resolution type (Varian V-4300 B). The conclusion was the same as already obtained. However, it was found that the proton signal of the methyl groups splitted into three or five components. Such a splitting may be not only interesting as a sure evidence of the above conclusions, but also would be noteworthy as a rare case where spin-spin coupling between H and D nuclei attached to the same carbon atom was observed. Although the similar splitting phenomenon has been reported by some researchers[2], the NMR results also will be presented here preliminarily in connection with the essential point of the research.

Nickel powders were prepared by decomposing nickel formate, oxidizing with air at 300°C and reducing at 400°C with hydrogen for 8 hr. Exchange reaction was carried out in a sealed glass tube, which contained a known amount of pure *p*-xylene and deuterium oxide (99.7% D_2O) as well as nickel catalyst. During the reaction, the tube was kept in a thermostat without shaking. After the definite time the reaction was stopped, and the *p*-xylene was separated from both heavy water and catalyst.

As an example of the experiment the most deuterated run, (No. 5), in which the reactants *p*-xylene and D_2O, were 0.4792 g. and 0.4864 g., respectively, and which were carried out for 150 hr. at 100°C will be referred. The numbers of deuterium (d_i) atoms in *p*-xylene molecules, determined by the mass-spectrometer, were as follows (%):

$$d_0=0.2,\ d_1=2.0,\ d_2=9.0,\ d_3=23.5,\ d_4=32.6,$$
$$d_5=24.7,\ d_6=7.9,\ d_7=0.1,\ d_8=d_9=d_{10}=0.0.$$

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[1] Abstracts of the 12th Annual Meeting of the Chemical Society of Japan (1959), p. 85.

[2] (a) M. Karplus, D. H. Anderson, T. C. T. Farrer and H. S. Gutowsky, *J. Chem. Phys.*, **27**, 597 (1957); M. Karplus and D. H. Anderson, ibid., **30**, 6 (1957). (b) J. N. Schoolery, *Svensk, Kem. Tidskr.*, **69**, 185 (1957). (c) G. V. D. Tiers, *J. Chem. Phys.*, **29**, 963 (1958).

By the infrared method, three bands could be observed at the region of the C–D stretching bands, i. e. 2187, 2118 and 2047 cm^{-1} (broad). They can be ascribed to the bands of deuterated methyl groups, because in the case when the exchange reaction had been carried out by use of D_2SO_4 in order to deuterate the hydrogen atoms at the benzene ring[3], one C–D band appeared at 2254 cm^{-1}. This conclusion is not contradictory to the mass-spectrometric data, because *p*-xylene molecules highly deuterated more than six were negligibly small. Therefore it may be concluded that the exchange reaction proceeded practically at the six hydrogen atoms of the methyl groups (cf. Fig. 1).

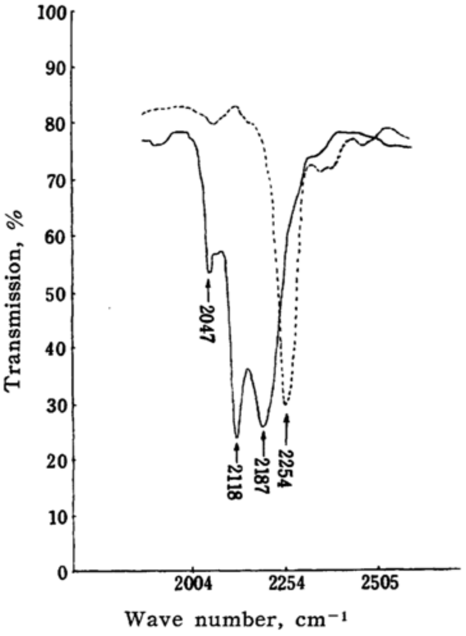

Fig. 1. Infrared absorption spectra of the deuterated samples.
——: Ni catalyst (deuterated degree= 39%)
------: H_2SO_4 catalyst (deuterated degree =23%)[3]

By the NMR measurements relative intensity ratio of the proton signals of the methyl and ring groups in the original *p*-xylene should be expected to be 3 : 2 in singlet. This ratio would be expected to change as the deuteration proceeded. Actually the sample in medium process changed it, and moreover the methyl group spectrum had a structure which could be considered as superposed singlet and triplet components. These structures may be assigned to spectra from protons in CH_3 groups and those in CH_2D groups, respectively. Though exact measurements were hard, the relative intensity ratio of the ring protons and the methyl ones (CH_3 and CH_2D) seemed to be almost the same. There was observed no appreciable change in the line shape of the ring protons. It may be difficult to decide whether the ring protons also were exchanged or not. However, the obtained results would suggest that the exchange reaction proceeded easily at the methyl groups. The other features of this spectrum was slight shift of the proton signals of CH_2D to higher field as reported by Tiers[2]. Unfortunately a strong signal from CH_3 groups prevented exact measurements of this kind, but the distorted line shape and the slight hump on the central strong component suggested this fact. This tendency was observed more clearly with the more deuterated sample (No. 5). The large sharp central line of the triplet disappeared, and a very weak quintet if compared with the singlet of the ring protons which remained still sharp and strong was observed on the methyl protons. This would suggest at least that the deuteration had proceeded more easily at the two methyl groups than at the ring groups. The observed quintet was very weak and distorted considerably. The observed J_{H-D} was about 2 c. p. s. The distortion might be caused by superimposed structures like singlet, triplet and quintet being slightly shifted each other. These features of NMR measurements confirmed clearly that the deuteration by this method would occur easily at the methyl groups and that the deuteration may take place step by step at the two methyl groups; i. e., roughly speaking, according to the scheme, $CH_3 \rightarrow CH_2D \rightarrow CHD_2 \rightarrow CD_3$.

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[3] T. Ueda, *Catalysts* (*Shokubai*), **1**, 1 (1959).