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CATALYTIC ISOTOPIC "ISOMERIZATION" OF DEUTERATED TOLUENE-d_1 ON PLATINUM BLACK

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It was reported(1) that toluene-d_1 deuterated at a ring hydrogen changed apparently into its isotopically isomeric species, if platinum or nickel was used as the catalyst. Since such "isomerization" (I) is very interesting in itself as a kind of self-exchange reactions, not only a part of the result on platinum will be reported preliminarily, but also the result on the exchange reaction (II) of toluene-d_1 with H_2O will be compared with that of the reaction (I):

$$C_7H_7D + XH_2O \longrightarrow C_7H_8 + XHDO \qquad \text{(II)}$$

Experimental apparatus and procedure were quite similar to those used in the study of exchange reaction (III):

$$C_8H_{10} + XD_2O \longrightarrow C_8H_{10-x}D_x + XHDO \qquad \text{(III)}$$

where C_8H_{10} denotes paraxylene(2)

Ortho- and meta-deuterated toluenes were prepared respectively from corresponding tolylmagnesium bromide by the reaction with deuterium oxide.

Experimental conditions as well as mean d_1 % ($\bar{d}_1 = \sum_i i d_i$) of both reactions and products are shown in Table 1, where Mn or On denotes the Run n with respect to meta- or ortho-deuterated toluene-d_1, respectively. Distribution of d_i, determined by the mass spectrometric method, and percentage of the substituted position are shown in Table 2, where MS denotes the standard run of the meta-substituted sample etc. Substituted positions were determined semi-quantitatively by the infrared absorption spectrum.

Judging from analysis on the product in the reaction (II), it was found that (i) deuterium atoms were transfered from the meta-position to the other ring positions and also to the methyl position (Fig. 1), and (ii) that concentration of d_1 decreased markedly as to be expected by the dilution effect of water. Nevertheless, in spite of the decrease of mean deuterium content, concentration of d_2- and d_3- species increased, though slightly, in the products (compare M3 and M4 with MS in Table 1 and 2).

Table 2 and Figures indicate, however, that the result of the reaction (I) includes several important differences from that of the reaction (II); (i) total deuterium content did not change practically, even though d_0- and d_2-species were produced markedly, and also d_3-species to some extent (Table 2); (ii) all the runs teach us that reactivity of hydrogen at the methyl and ortho-position was negligibly

Table 1. Exchange and Isomerization of Toluene-d_1

Amount of Pt black = 0.50 g

Reaction		Reactant			Reaction		Product
		Toluene g	$\bar{d}_1$ %	H_2O g	Temp. °C	Time hr.	Toluene $\bar{d}_1$ %
II	M3	0.499	90	0.500	100	110	37
	M4	0.505	90	0.501	80	150	41
I	M7	0.499	93	none	60	30	92
	M10	0.505	93	none	100	100	ca. 93*
	02	0.500	89	none	100	10	88

N.B. Number with * were estimated by the absorption of IR spectra.

Table 2. Mass Spectrometric and Infrared Results of the Products

	d_1-Distribution % of toluene-d					Substituted Position (%)			
Run	d_0	d_1	d_2	d_3	$\bar{d}_1$	CH_3	ortho	meta	para
MS	$10._6$	$88._8$	$0._4$	$0._2$	90	0	0	89	1
M3	$68._5$	$26._3$	$4._7$	$0._5$	37	16	8	7	6
M4	$66._4$	$27._0$	$5._6$	$1._0$	41	16	12	7	6
MS	$7._8$	$91._7$	$0._6$	$0._0$	93	0	0	92	1
M7	$22._6$	$64._1$	$12._3$	$1._0$	92	0	0	83	9
M10	--- unmeasured ---				ca. 93	0	2	48	43
OS	$12._6$	$86._6$	$0._8$	$0._0$	89	2	86	0	1
02	$27._8$	$57._2$	$13._3$	$1._7$	88	2	75	5	6

CH out-of-plane deformation

775 cm^{-1}	toluene-o-d
797 cm^{-1}	toluene-m-d
837 cm^{-1}	toluene-p-d

CD streching vibration

2165 cm^{-1}	methyl group
2185 cm^{-1}	
2265 cm^{-1}	benzene ring

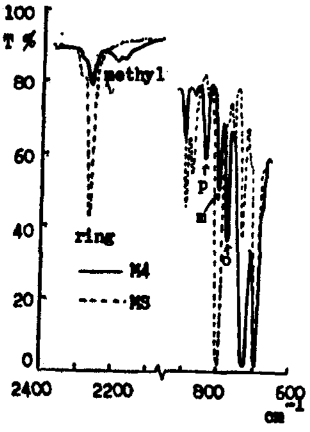


Fig. 1 IR spectra of the deuterated toluene (Reaction II).

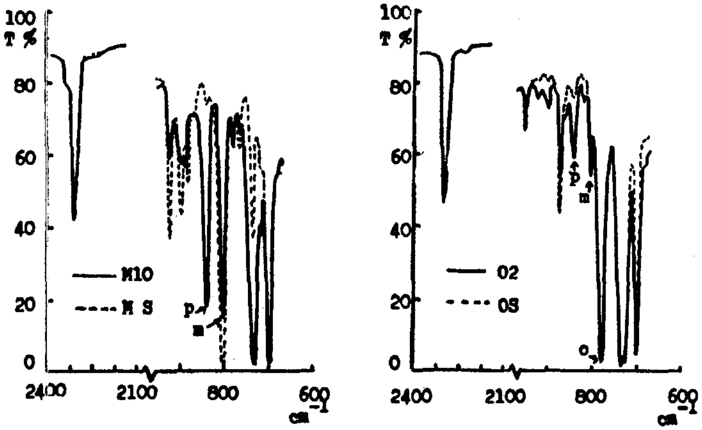
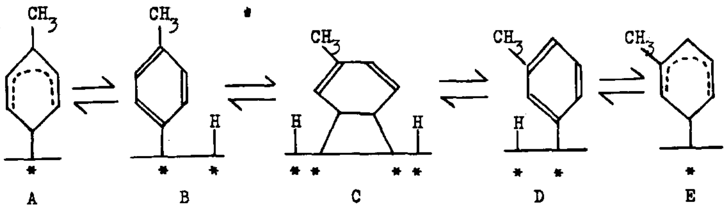


Fig. 2 IR spectra of the deuterated toluene (Reaction I).

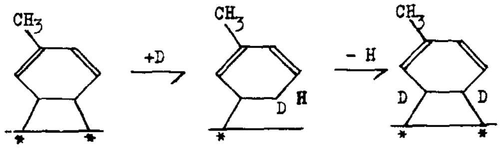
small if compared to that of the other positions.

From the three findings obtained above, the reaction (I) seems to be a kind of isotopic isomerization superposed by self-exchange reaction. However, spreading of d_1-distribution can be explained of the reaction (I) proceeded not intramolecularly but by the reaction between different toluene-d_1 molecules, and comparing the concentration of d_2 and d_3 species with that of substituted position, this reaction might be classified to a self-exchange one rather than to an isomerization.

The peculiar activity of ortho-position may suggest that scission of C-H (or C-D) bond at this position is more difficult than at the other positions, considering that this tendency could not be observed in the reaction (II). It is not probable, therefore, that toluene molecule is adsorbed, keeping its benzen ring parallel to the platinum surface. Due to steric hindrance of the methyl group, adsorption will not occur at the ortho-position to the surface, and the dissociative state of adsorption may realize as shown by A and E, and the reaction may proceed by reverse reactions $B \rightleftharpoons C \rightleftharpoons D$ in the following scheme:



By combining the above processes, formation of d_0, d_2 and d_3 species from d_1 species can be explained easily. Besides, a part of the products may be obtained by another mechanism via cyclo-hexadienyl intermediates; e.g., in case of formation of d_2 from d_1,



C F G

The second mechanism, which was already applied in the exchange reaction (III)$^{(2)}$, is to be applied to the reaction (II), but the D and H atoms in the above scheme must be supplied from and received by water molecule instead of toluene molecule, because it is possible that bond-scission of ring hydrogen does not occur in reaction (II) due to the poisoning effect of water. However, exchange of methyl hydrogen is to be explained by its scission of C-H bond, followed by indirect addition of deuterium via water, due to energetic reason.$^{(2b)}$

Reference

1. T. Ueda and K. Hirota, Presented at the 18th Annual Meeting of Chem. Soc. of Japan, April 3, 1965.
2. K. Hirota and T. Ueda, (a) Bull. Chem. Soc. Japan **35**, 228 (1962); (b) "Proc. of the Third Intern. Symp. on Catalysis," P. 1238, Amsterdam (1965).