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Abstract

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MIGRATION OF THE METHYL GROUP IN THE TOLUENE MOLECULE UNDER THE INFLUENCE OF ALUMINUM BROMIDE AND HYDROGEN BROMIDE

In a number of previous works ([1–3]) we have shown that the use, in studying the processes of isomerization of compounds labeled at a definite position of the aromatic nucleus with radioactive carbon, makes it possible to establish the paths of migration of the migrating substituent relative to its initial position in the molecule. By this method it was shown, in particular, that the conversion of α-methylnaphthalene and α-chloronaphthalene into the β-isomers over an aluminosilicate catalyst proceeds by an intramolecular shift of the substituent from the α- to the adjacent β-position.

Of great interest is the question of the mechanism of migration of substituents in benzene derivatives, which differ from compounds of the naphthalene series by a considerably greater equalization of the aromatic C–C bonds. Taking this equalization into account, Dewar allowed the possibility of free migration of the migrating group along the π-electron contour of the benzene nucleus ([4]). As applied to migration of the methyl group, Dewar' s hypothesis met with objections. In the opinion of a number of investigators ([5–7]), the isomeric transformations of xylenes under the influence of such catalytic systems as $Al_2Cl_6 + HCl$, $Al_2Br_6 + HBr$, and $BF_3 + HF$ proceed as a result of an intramolecular stepwise shift of the methyl group.

As we noted earlier ([8]), the mechanism of migration of substituents in the benzene nucleus is expediently studied using monosubstituted benzenes labeled in the nucleus with radioactive carbon as an example. The present work reports results obtained in the isomerization of toluene-1-C^{14} under the influence of aluminum bromide and hydrogen bromide.

Toluene dissolves aluminum bromide in the presence of hydrogen bromide with the formation of an orange-red layer of approximate composition $6C_6H_5CH_3 + Al_2Br_6 + HBr$. It is believed ([9]) that in this process a proton adds to the toluene molecule with formation of an ionized σ-complex solvated by several (on average five) molecules of toluene. On decomposition of such a complex, kept for 8 days at 0°, with water, "unchanged" toluene is isolated ([10]). The formation of products of intermolecular redistribution of methyl groups (benzene, xylenes, etc.) was not observed in this case.

At the same time, xylenes under the action of aluminum bromide and hydrogen bromide at 0—25° isomerize as a result of migration of the methyl group in the nucleus ([6]). It could therefore be expected that, in the case of toluene as well, under similar conditions a change in the position of the methyl group in the molecule takes place. The experiment, as shown below, confirmed this supposition.

The complex prepared by the interaction of toluene-1-C^{14} with aluminum bromide and hydrogen bromide was kept for 6 hr at 20°. The toluene-x-C^{14}, isolated by decomposition of the complex with water, was subjected to cleavage according to a scheme developed by us earlier ([8]), which makes it possible to determine the dis-

determination of radioactivity in the benzene ring:

$$\text{toluene} \xrightarrow{\mathrm{Ca(NH_3)_6}} \cdots \longrightarrow \mathrm{CH_3CO(CH_2)_4COOH} \longrightarrow \mathrm{CH_3CH_2CH_2CH_2CH_2CH_2COOH}$$

$$\longrightarrow \mathrm{CH_3(CH_2)_3CH_2COC_6H_5} \longrightarrow \mathrm{CH_3(CH_2)_4C(=NOH)COC_6H_5} \xrightarrow{-\mathrm{C_6H_5COOH}\ (I)} \mathrm{CH_3(CH_2)_4CONH_2}\ (II)$$

$$\longrightarrow \mathrm{CH_3(CH_2)_4COOH} \longrightarrow \mathrm{CH_3(CH_2)_3CH_2COC_6H_5} \longrightarrow \mathrm{CH_3(CH_2)_3C(=NOH)COC_6H_5}\ (III) \xrightarrow{-\mathrm{C_6H_5COOH}\ (IV}$$

$$\longrightarrow \mathrm{CH_3(CH_2)_3CONH_2}\ (V) \longrightarrow \mathrm{CH_3(CH_2)_3NH_2} + \mathrm{CO_2}\ (VI)$$

The relative molar radioactivities found for compounds I—VI were used to calculate the distribution of radioactivity in the ring of toluene-x-C^{14}, obtained upon decomposition of the complex (see Table 1). These data make it possible to decide the question of the mechanism of migration of the methyl group during the isomerization of toluene-1-C^{14}.

In the case of intramolecular stepwise displacement of the methyl group, the isomerization of toluene-1-C^{14} may be represented by the following scheme:

$$\text{toluene-1-}C^{14} \rightleftarrows (VII) \rightleftarrows (VIII) \rightleftarrows (IX) \rightleftarrows (X) \rightleftarrows \text{toluene-4-}C^{14},$$

with interconversions of the σ-complexes (VII)—(XII) proceeding with rate constants k,

and with formation of toluene-2-C^{14} and toluene-3-C^{14}.

Assuming that the rate constants of interconversion of the σ-complexes VII—XII are identical, the change in the concentrations of toluenes labeled in positions 1, 2, 3, and 4 (respectively T_1, T_2, T_3, and T_4) as a function of time can be expressed by the system of differential equations:

$$\frac{dT_1}{d\tau} = ka\,(T_2 - 2T_1);$$

$$\frac{dT_2}{d\tau} = ka\,(2T_1 + T_3 - 2T_2);$$

$$\frac{dT_3}{d\tau} = ka\,(T_2 + 2T_4 - 2T_3);$$

$$\frac{dT_4}{d\tau} = ka\,(T_3 - 2T_4),$$

where a is the degree of protonation of toluene under the experimental conditions, equal to the ratio of the concentration of the σ-complex to the concentration of toluene.

Table 1

Ratio between the isotopic isomers of toluene-C^{14} during the isomerization of toluene-1-C^{14}

Fractions of isotopic isomers	Found experimentally	Calculated from the value T_1/T: by equations (1–4)	Calculated from the value T_1/T: by equations (5)
T_1/T	0,759	–	–
T_2/T	0,221	0,223	0,096
T_3/T	0,019	0,017	0,096
T_4/T	0,0007	0,0006	0,048

Solving these equations, we obtain:

$$T_1/T = \frac{1}{6}\left(1 + 2e^{-ka\tau} + 2e^{-3ka\tau} + e^{-4ka\tau}\right), \tag{1}$$

$$T_2/T = \frac{1}{3}\left(1 + e^{-ka\tau} - e^{-3ka\tau} - e^{-4ka\tau}\right), \tag{2}$$

$$T_3/T = \frac{1}{3}\left(1 - e^{-ka\tau} - e^{-3ka\tau} + e^{-4ka\tau}\right), \tag{3}$$

$$T_4/T = \frac{1}{6}\left(1 - 2e^{-ka\tau} + 2e^{-3ka\tau} - e^{-4ka\tau}\right), \tag{4}$$

where $T = \Sigma T_i$.

Thus, knowing for some instant of time the fraction of unisomerized toluene-1-C^{14} (T_1/T), one can calculate from equation (1) the value of $e^{-ka\tau}$ and then, using equations (2)–(4), calculate the relative amounts of toluenes-2-C^{14}, -3-C^{14}, and -4-C^{14} in which these isotopic isomers should have been formed in the case of a stepwise migration of the methyl group.

If, however, the isomerization of toluene-1-C^{14} occurs in such a way that the methyl group, having detached from the C_1 atom, then bonds with equal probability to any of the six carbon atoms of the benzene ring, the ratio between the toluenes-2-C^{14}, -3-C^{14}, and -4-C^{14} formed, as can readily be shown, must satisfy the following condition:

$$\frac{T_2}{T} = \frac{T_3}{T} = 2\frac{T_4}{T} = \frac{2}{5}\left(1 - \frac{T_1}{T}\right). \tag{5}$$

Such a mechanism for migration of the methyl group could, for example, occur if the isomerization proceeded through the stage of formation of a "delocalized π-complex" ([6]) or a "parachute-type complex" (cf. ([11])).

Table 1 gives the experimentally found ratio between the isotopic isomers of toluene-C^{14} and the ratios calculated for the two isomerization mechanisms considered. Comparison of these data leaves no doubt that the migration of the methyl group during the isomerization of toluene-1-C^{14} proceeds by an intramolecular stepwise shift.

We also intended to carry out the isomerization of toluene-1-C^{14} at other temperatures and to determine the activation energy of this process. However, when the part of the investigation described above had been completed, we became aware of a communication by Dutch chemists ([12]), who, using an entirely different method for the cleavage of toluene, performed similar work and found that the activation energy of the reaction under consideration is $ $22 kcal/mole. Our data on the mechanism of migration of the methyl group and the results of the Dutch investigators are in complete agreement.

Experimental Part

Isomerization of toluene-1-C^{14}. Into a suspension of anhydrous aluminum bromide (35 mmole, calculated as $AlBr_3$) in 106 mmole of commercial toluene-1-C^{14} (specific activity 0.216 mCu/mmole), dry hydrogen bromide was passed for 25 min at 20°. The resulting clear orange-red solution was kept for 6 h at 20°, and then the complex was decomposed by adding ice. The separated toluene was washed with a solution of soda and with water and dried over anhydrous sodium sulfate, and then over metallic sodium. The IR spectrum of an analogous sample of toluene obtained in a model experiment did not differ from the spectrum of pure toluene.

Cleavage of toluene-1-C^{14}. The toluene isolated from the complex was converted by the previously described procedure ([8]) into enanthic acid. By reaction of the acid chloride of the latter with benzene in the presence of aluminum chloride ([13]), enanthophenone was prepared; yield 64%, b.p. 129–131°

(6 mm). Nitration of enanthophenone and isolation of the α-nitroso derivative (yield 33%, m.p. 34.0–35.5°) were carried out by the procedure ([14]). α-Isonitrosoenanthophenone was cleaved by the action of concentrated sulfuric acid (see ([15])) into benzoic acid (yield 90%, m.p. 121.8–122.5°) and caproic acid amide (yield 64%, m.p. 100–101°). The amide was hydrolyzed by boiling with a 20% solution of caustic potash for 5 h to caproic acid, and the latter was converted, analogously to that described above, into caprophenone, yield 73%, b.p. 140–141° (16 mm),

and then into α-isonitrosocaprophenone, yield 63%, mp 52-53° (from petroleum ether). On treatment of α-isonitrosocaprophenone with concentrated sulfuric acid, benzoic acid was obtained, yield 88%, mp 121.5-122.0°, and valeric acid amide, yield 36%, mp 95-97°. The carbon dioxide obtained in the cleavage of valeric acid amide by the Hofmann reaction (cf. (1)) was trapped with barium hydroxide. Yield of barium carbonate 93%.

Table 2

Results of radioactivity measurements

Compound	Mp after recrystallization, °C	Calculated, C, %	Found* C, %	Activity of $BaCO_3$ sample "of infinite thickness," imp/min	Relative molar radioactivity, imp/min
C_6H_5COOH (I)	122.0–122.5	68.2	68.5, 68.0	1 965	13 755
$CH_3(CH_2)_4CONH_2$ (II)	100.5–101.5	62.7	62.3, 62.2	18 460	110 760
$CH_3(CH_2)_3C(=NOH)COC_6H_5$ (III)	52.0–53.0	70.2	70.2, 70.1	9 225	110 700
C_6H_5COOH (IV)	122.2–122.7	68.2	68.9, 68.0	173	1 210
$CH_3(CH_2)_3CONH_2$ (V)	102.5–103.4	59.2	59.4, 59.0	21 700	108 500
CO_2 (VI)	–	–	–	188	188

* Control of completeness of combustion by the Van Slyke method (cf. (1)).

Table 2 gives the results of radioactivity measurements of compounds I–VI. The radioactivity of the samples before and after recrystallization remained constant within the accuracy of the measurements ($\pm$2%).

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REFERENCES

1. N. N. Vorozhtsov Jr., V. A. Koptyug, ZhOKh, **28**, 372 (1958).
2. N. N. Vorozhtsov Jr., V. A. Koptyug, ZhOKh, **30**, 999 (1960).
3. N. N. Vorozhtsov Jr., V. A. Koptyug, A. M. Komagorov, ZhOKh, **31**, 3330 (1961).
4. M. J. S. Dewar, *Bull. Soc. Chim. France*, 1951, 71; *Theoretical Organic Chemistry*, London, 1959, p. 179.
5. D. A. McCaulay, A. P. Lien, *J. Am. Chem. Soc.*, **74**, 6246 (1952).
6. H. C. Brown, H. Jungk, *J. Am. Chem. Soc.*, **77**, 5579 (1955).
7. R. H. Allen, L. D. Lats, *J. Am. Chem. Soc.*, **81**, 5289 (1959).
8. V. A. Koptyug, I. S. Isaev, N. N. Vorozhtsov Jr., DAN, **137**, 866 (1961).
9. H. C. Brown, W. J. Wallace, *J. Am. Chem. Soc.*, **75**, 6268 (1953).
10. H. C. Brown, C. R. Smoot, *J. Am. Chem. Soc.*, **78**, 2176 (1956).
11. Ya. K. Syrkin, V. I. Yakersen, S. E. Shnol, ZhOKh, **29**, 187 (1959).
12. H. Steinberg, F. L. J. Sixma, *Rec. Trav. Chim. Pays-Bas*, **81**, 185 (1962).
13. L. N. Nikolenko, K. K. Babievskii, ZhOKh, **25**, 2231 (1955).
14. I. F. Mikhailova, L. N. Nikolenko, *Izv. SO AN SSSR*, no. 4, 128 (1962).
15. L. N. Nikolenko, I. F. Mikhailova, A. V. Chistyakova, *Izv. SO AN SSSR*, no. 7, 73 (1960).

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