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Abstract

Full Text

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On the Mobility of Hydrogen in the Methoxy Group of Aromatic Compounds as a Function of Other Substituents

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The isotopic method makes it possible not only to discover, but also to evaluate quantitatively, such effects of the mutual influence of atoms in molecules of organic substances that remained unknown as long as ordinary chemical methods of investigation were used. For example, by studying deuterium-exchange reactions catalyzed by a solution of potassium amide in liquid ammonia, it proved possible to detect (⁀1) the mobility of hydrogen atoms in a methoxy group bonded to an aromatic ring, and then to express it quantitatively (⁀2). The present work considers the question of how the mobility of hydrogen in a methoxy group is affected by the type of aromatic system, as well as by the nature and position of a second substituent in the benzene ring. Data are reported on the kinetics of deuterium exchange in the methoxy groups of anisole, isomeric methoxynaphthalenes, fluoroanisoles, dimethoxybenzene, and *p*-dimethylaminoanisole with a 0.06 *N* solution of potassium amide in liquid ammonia at $25° \pm 0.1°$. The following mean values of the first-order rate constants (sec^{-1}) were obtained:

Substance	$k \cdot 10^5$, sec^{-1}	lg *f*
I. Anisole	4.0 ± 0.3	–
II. 1-Methoxynaphthalene	7.7 ± 0.3	1
III. 2-Methoxynaphthalene	8.2 ± 0.3	0.7
IV. 2-Fluoroanisole	28 ± 3	6
V. 4-Fluoroanisole	9 ± 2	2
VI. 1,2-Dimethoxybenzene	8.3 ± 1.0	2.7
VII. 1,3-Dimethoxybenzene	3.6 ± 0.4	0
VIII. 1,4-Dimethoxybenzene	1.7 ± 0.4	−0.3
IX. 4-Dimethylaminoanisole	0.7 ± 0.1	−1.2

It had previously been suggested that the mobility of hydrogen atoms in a methoxy group bonded to an aromatic ring depends on the sum of the inductive effects of the oxygen atom and the aromatic ring. Webster (⁀3) considers the latter effect to be the main reason for the decrease in the basic strength of aromatic amines in comparison with aliphatic amines. The naphthalene ring is a better electron acceptor than the benzene ring. Therefore naphthylamines are weaker bases than aniline and, conversely, the dissociation constants of

Fig. 1

Figure 1: Fig. 1

naphthoic acids are greater than the dissociation constants of benzoic acid (ˆ4). Correspondingly, the rate constants of deuterium exchange in the OCD_3 groups of the isomeric methoxynaphthalenes are higher than in anisole.

If the mobility of the hydrogen atoms of the methoxy group is caused by displacement of the electrons of the CD bonds toward the oxygen atom and toward the benzene ring, then it must be assumed that, upon introduction of a second substituent into the latter, the rate of the exchange reaction in the methoxy group will depend on the change-

changes induced by a substituent in the electron density at the carbon atom to which the methoxy group is attached. An idea of what changes in the distribution of electron density at different carbon atoms of the benzene ring are caused by a given substituent under the conditions of the exchange reaction with base is given by the values of the partial rate factors (f) for deuterium exchange in the ortho-, meta-, and para-CD bonds of monodeutero derivatives with a solution of KNH_2 in NH_3 ([5]). In that case there should be a direct dependence between the values of f for the second substituent (in the position occupied by the methoxy group) and the rate constants of deuterium exchange of the methoxy group. Indeed, most of the experimental points obtained in this work lie close to the straight line of the graph plotted in the coordinates k–lg f (Fig. 1).

Anisole and the isomers of dimethoxybenzene containing deuterium in the methoxy groups were synthesized according to ([6]), the methylating reagent being $(CD_3)_2SO_4$ (see ([2])). Methoxynaphthalenes were obtained from naphthols ([7]), using CD_3OH as the methylating reagent (CD_3OD is not recommended, since deuterium may also enter the aromatic ring). 2- and 4-fluoroanisole with deuterium in the methoxy group were obtained by methylating the corresponding fluorophenols with $(CD_3)_2SO_4$ according to the procedure ([8]). A second preparation of 4-fluoroanisole was synthesized from 4-nitrophenol through the following stages: methylation with $(CD_3)_2SO_4$ analogously to ([9]), reduction of the nitro group (Sn + HCl), preparation of the diazonium borotrifluoride ([10]), followed by its thermal decomposition.

Fig. 1

The substances were carefully purified and diluted with preparations not containing deuterium. Usually the experiments were carried out with two independently synthesized or purified preparations of the substance. We give their constants (literature data are indicated in parentheses). I. n_D^{20} 1.5179 (1.5179); II. n_D^{14} 1.6260; n_D^{15} 1.6238 (n_D^{14} 1.6232); III. m.p. 72.0–73.0° (72.0°); IV. n_D^{24} 1.4940; b.p. 72° at 20 mm Hg (b.p. 193°); V. n_D^{20} 1.4880; 1.4880; VI. n_D^{21} 1.5320; 1.5335 (1.5341); VII $n_D^{22.5}$ 1.5233; 1.5255; VIII. m.p. 54.5–55.5°; 55.5–56.5°

(56°); IX. m.p. 46.5–47.5° (48°).

The experiments were carried out by the standard procedure adopted in the laboratory. The reaction was stopped by cooling the reaction mixture to −78° and adding NH_4Cl. For an experiment, 0.15 g of substance and 10 ml of a 0.06 N solution of KNH_2 in liquid NH_3 were taken. In each series an experiment was set up in which the volume of the solution was increased to 16–20 ml (marked with asterisks in Table 1). The constancy of the rate-constant values (sec^{-1}) indicated the absence of impurities neutralizing the amide.

In experiments with 2-fluoroanisole, the appearance of slight turbidity with time was noted, and the rate constants of the exchange reaction decreased when the duration of the experiments was increased. Therefore we give the results of the shortest experiments.

For isotopic analysis the substances were burned, the water was purified, and its density was determined by the drop method. Combustion of the fluoroanisoles was carried out by the method described in ([11]), and a check showed that it ensures the correctness of the isotopic analyses.

Table 1

Rate of deuterium-exchange reactions

	τ	C_v^0	C_v	$k \cdot 10^5$		τ	C_v^0	C_v	$k \cdot 10^5$
I. Anisole	0.5	3.73	3.44	4.5	VI. 1,2-Dimethoxybenzene	2	4.28	2.36	8.3
I. Anisole	4	3.73	2.21	3.7	VI. 1,2-Dimethoxybenzene	2*	4.28	2.28	8.8
I. Anisole	4	3.73	2.19	3.7	VI. 1,2-Dimethoxybenzene	3*	4.28	1.55	9.4
I. Anisole	4	3.73	2.14	3.9	VI. 1,2-Dimethoxybenzene	4	4.28	1.62	6.8
					VI. 1,2-Dimethoxybenzene	4*	4.28	1.37	7.9
II. 1-Methoxynaphthalene	2	4.29	2.54	7.3	VII. 1,3-Dimethoxybenzene	4	4.03	2.63	3.0
II. 1-Methoxynaphthalene	2	4.29	2.37	8.2	VII. 1,3-Dimethoxybenzene	4.3	4.08	2.26	3.8

	τ	C_v^0	C_v	$k \cdot 10^5$		τ	C_v^0	C_v	$k \cdot 10^5$
II. 1-Methoxynaphthalene	2*	4.29	2.44	7.8	VII. 1,3-Dimethoxybenzene	4.3*	4.08	2.13	4.2
II. 1-Methoxynaphthalene	4	4.23	1.37	7.8	VII. 1,3-Dimethoxybenzene	6	4.08	1.94	3.4
II. 1-Methoxynaphthalene	4	4.23	1.46	7.4					
III. 2-Methoxynaphthalene	2	4.26	2.38	8.1	VIII. 1,4-Dimethoxybenzene	4	4.26	3.34	1.7
III. 2-Methoxynaphthalene	2	4.26	2.41	8.0	VIII. 1,4-Dimethoxybenzene	5	4.37	2.93	2.2
III. 2-Methoxynaphthalene	4	3.91	1.29	7.8	VIII. 1,4-Dimethoxybenzene	5	4.37	3.03	2.1
III. 2-Methoxynaphthalene	4*	3.91	1.09	8.8	VIII. 1,4-Dimethoxybenzene	5*	4.37	3.44	1.3
					VIII. 1,4-Dimethoxybenzene	10	4.37	2.60	1.4
IV. 2-Fluoroanisole	0.5	4.30	2.27	31	IX. 4-Dimethylaminoanisole	4	4.40	4.06	0.6
IV. 2-Fluoroanisole	0.5	4.30	2.77	25	IX. 4-Dimethylaminoanisole	24	4.40	2.22	0.8
IV. 2-Fluoroanisole	0.5*	4.30	2.57	30	IX. 4-Dimethylaminoanisole	24*	4.40	2.20	0.8
V. 4-Fluoroanisole	3	2.01	0.76	9					
V. 4-Fluoroanisole	3*	2.01	0.61	11					
V. 4-Fluoroanisole	3	4.59	1.94	8					

	τ	C_v^0	C_v	$k \cdot 10^5$	τ	C_v^0	C_v	$k \cdot 10^5$
V. 4-Fluoroanisole	3*	4.59	1.71	9				
V. 4-Fluoroanisole	3.5*	2.01	0.86	7				

The results of the experiments on measuring the rate of deuterium exchange are given in Table 1, where C_v^0 and C_v are the concentration of D (at. %) in the water from combustion of the substance at the beginning of the experiment and after time τ (hours).

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Note: Figure translations are in progress. See original paper for figures.