

OTS: 60-31,142

JPRS: 3375

10 June 1960

CONFIDENTIAL

HYDROGEN EXCHANGE OF PHENOL AND ITS ETHERS WITH SOLUTIONS
OF POTASSIUM AMIDE IN LIQUID DEUTEROAMMONIUM

- USSR -

by A. I. Shatenshteyn and A. V. Vedeneyev

DISTRIBUTION STATEMENT A
Approved for Public Release
Distribution Unlimited

19990528 092

Distributed by:

OFFICE OF TECHNICAL SERVICES
U. S. DEPARTMENT OF COMMERCE
WASHINGTON 25, D. C.
Price: \$0.50

U. S. JOINT PUBLICATIONS RESEARCH SERVICE
205 EAST 42nd STREET, SUITE 300
NEW YORK 17, N. Y.

FOREWORD

This publication was prepared under contract by the UNITED STATES JOINT PUBLICATIONS RESEARCH SERVICE, a federal government organization established to service the translation and research needs of the various government departments.

HYDROGEN EXCHANGE OF PHENOL AND ITS ETHERS WITH SOLUTIONS
OF POTASSIUM AMIDE IN LIQUID DEUTEROAMMONIUM

Following is a translation of an article by A. I. Shatenshteyn and A. V. Vedeneyev in *Zhurnal Obshchey Khimii* (Journal of General Chemistry), Vol. 28, No. 10, Moscow, October 1958, pages 2644-2652.

A previous report [1] showed that features of hydrogen exchange of phenol, its ethers, and aromatic amines with liquid DBr are determined by the effect of p, *π*-conjugation, while the different relationship to the proton and differences in coordinating capacity of oxygen and nitrogen atoms of the particular compounds are also important factors.

This article presents results obtained in the study of hydrogen exchange of phenol and its ethers with solutions of KND_2 in liquid ND_3 . They supplement our presentation of the interaction of atoms in the molecules of these substances and permit certain conclusions concerning the mechanism of hydrogen exchange. (These results were presented at a Meeting on the Use of Isotopes in April 1957. They were included in a dissertation by A. V. Vedeneyev, Physico-Chemical Institute imeni Karpov, 1955).

EXPERIMENTAL

The methods of operation were described earlier [2]. Particular attention was directed toward drying the equipment, starting substances, and solvent, since potassium amide reacts readily with moisture. The operations connected with taking a sample were performed either in a special "dry" room or in a stream of dry nitrogen. The samples of substances usually weighted 0.2-0.5 gram, and of solvent 3-5 grams. At temperatures up to 40° the experiments were performed in glass ampules, while at higher temperatures stainless-steel ampules were used. The preparations of phenol, anisole, and diphenyl ether were the same as used in the work with liquid DBr [1]. n is the number of hydrogen atoms exchanged for deuterium, calculated from the formula:

$$n = \frac{c_B \cdot N}{c_p \cdot \frac{c \cdot N_B \cdot N_O \cdot m_B}{N_p \cdot n_t \cdot m_p}}$$

where c_B and c_p^0 are the concentration of D in atom-% in water in which the substance was consumed and in solvent before the experiment; α is the coefficient of distribution of deuterium between the N-H and C-H bonds, equaling 0.92 [3]; N is the number of hydrogen atoms in the substance; N_0 is the number of exchangeable hydrogen atoms in the substance; N_p is the number of exchangeable hydrogen atoms in the solvent; n_t is the number of hydrogen atoms in the substance exchanged by a given time, calculated from the formula

$$n_t = \frac{c_B \cdot N}{\alpha c_p^0};$$

m_B is the number of moles of substance; and m_p the number of moles of solvent.

The rate constants of hydrogen exchange were calculated from a first-order equation.

Hydrogen exchange in phenol. Ignoring as a first approximation the ammonolysis of the potassium phenolate formed in the reaction with KND_2 , we assumed that an equivalent quantity of amide was consumed in dissolution of phenol. After the completion of the experiment on deuterium exchange the reaction mixture was poured into a dilute HCl solution. The phenol was extracted with ether, the ether solution dried over sintered Na_2SO_4 , and the phenol distilled twice in vacuo. After the experiments the phenol had a melting point of 40.5-41°. The results of the experiments are given in Table 1. The symbols in the tables are the same as those used in the previous report [1]: c_{KND_2} = concentration of potassium amide solution (n.), and c_B^1 = concentration of D in atom-% in water in which the tribromophenol was heated.

One is struck by the fact that hydrogen exchange in the phenolate ion is very slow. Exchange of all the hydrogen atoms would require heating for 200 hours at 120°. This is explained by the fact that the ring of the phenolate ion is negatively charged, and this makes it difficult for the ND_2^- ion to approach, which is a condition of exchange. If p, π -conjugation played an important role in exchange in the phenolate ion with solutions of KND_2 in ND_3 then the meta hydrogen atoms would be exchanged most of all, i.e., atoms at the points of minimum electron density. In order to check this assumption experiments 5, 6, and 8 (Table 1) were stopped when around one hydrogen atom had been exchanged as a statistical mean. The phenolate was transformed into phenol, and the latter into 2,4,6-tribromophenol. If exchange were concentrated on the meta hydrogen atoms, when the tribromophenol was heated the concentration (c_B^1) would be higher than when the phenol was heated (c_B). If the ortho and para hydrogen atoms were exchanged $c_B^1 = 0$.

As Table 1 shows (right-hand column), $c_B^1 < c_B$. This can be explained in that all hydrogen atoms in $C_6H_5O^-$ are exchanged with approximately equal probability. Apparently a strong base equalizes the differences in "acidity" of the hydrogen atoms on the aromatic ring in a manner similar to what usually happens with acids dissolved in protophilic solvents [4].

A comparison of the rate of exchange of the hydrogen atom in the phenolate ion and in benzene shows that when $c_{KND_2} = 0.4 n.$, then $k_{500} = 5 \cdot 10^{-6}$ and $8 \cdot 10^{-3}$ respectively (calculated on the basis of data in [5]), i.e., the phenolate ion reacts approximately 10^{-3} as fast.

Hydrogen exchange in anisole. A solution of anisole in ND_3 / KND_2 is light-green in color. The reaction mixture was cooled to -70° to stop the exchange. After the ammonia had been driven off at low temperature the anisole was distilled in vacuo over anhydrous copper sulfate, which collected the residual ammonia. In experiments lasting more than 24 hours, after the ammonia was removed a gelatinous mass remained from which anisole was extracted with absolute ether. The anisole constants remained unchanged after this treatment. The results obtained are given in Table 2. All the hydrogen atoms in the anisole were exchanged. Their great inequality can be seen from the kinetic curve (cf. Figure). In order to determine the sequence in which the hydrogen atoms were exchanged preparations were made tagged in various positions.

We then determined the number of D atoms remaining after treatment of these preparations with a solution of KNH_2 in NH_3 . The results are shown in Table 3.

A comparison of results shows that the ortho D atoms are exchanged very rapidly, followed by the meta atoms and, finally, by the hydrogen atoms in the para position. These data agree with the conclusions drawn by Roberts and collaborators [7]. Measuring the rate of exchange of D in isomers of monodeuteroanisole with a solution of KNH_2 in NH_3 at -33.5° they obtained the following values for the constants of the rate of exchange (sec^{-1}) for the ortho, meta, and para atoms: $9 \cdot 10^{-4}$, $1 \cdot 10^{-7}$, $1 \cdot 10^{-8}$. Deuterium exchange in monodeuterobenzene had a rate of $\sim 10^{-7} sec^{-1}$.

In order to compare the rate of exchange of hydrogen in the methoxy group with the slowest-exchanged H atom in the ring -- the para atom -- preparations of trideuteroanisole and 4-monodeuteroanisole were used.

Trideuteroanisole, $C_6H_5OCD_3$, was obtained by exhaustive exchange with a solution of KND_2 in ND_3 followed by treatment with HF. (Experiments, conducted with Ya. M. Varshavskiy and M. G. Lozhkina, showed that when liquid DF is used only the hydrogen atoms of the anisole ring are exchanged, while the methoxy group is not affected. These experiments will be described later.)

4-monodeuteroanisole, $C_6H_5DOCH_3$, was prepared from 2,4,6-trideuteroanisole by treating it twice (at room temperature for 10 minutes) with an 0.03-normal solution of KNH_2 . Under these conditions only the ortho hydrogen atoms are exchanged, and the para atom is practically untouched.

The rate of exchange of the para hydrogen atom in the ring was $3 \cdot 10^{-4} \text{ sec}^{-1}$, twice that of the methoxy group ($\sim 1.4 \cdot 10^{-4} \text{ sec}^{-1}$) (Table 4). Comparison of the rate of exchange of the para hydrogen atom in anisole with that of the hydrogen atoms in benzene shows that when $^{\text{c}}\text{KND}_2 = 0.27n$, $k_{250} = 3 \cdot 10^{-4}$ and $6 \cdot 10^{-4}$, respectively (data from [5] recalculated). Thus hydrogen exchange in benzene is approximately twice as rapid as that in the para position of anisole. The methoxy group is exchanged approximately 4 times more slowly than the hydrogen atoms in benzene.

If we assume that in hydrogen exchange in anisole with solutions of KND_2 in ND_3 the main role is played by the conjugation effect, then we should expect a completely different sequence of hydrogen exchange in the ring than that actually observed, specifically: meta > para > ortho. The actual diminution of the rate of hydrogen exchange in the anisole ring, which goes ortho > meta > para, causes us to suppose that the decisive factor in hydrogen exchange in anisole with solutions of KND_2 / ND_3 is the inductive effect of the oxygen atom.

In the work done in our laboratory we have frequently been struck by the profound analogy between deutron exchange with nucleophilic reagents and the reactions of metallation [8, 9]. But what is known concerning metallation of anisole?

Wittig and collaborators [10] have shown that when dimethyl anilin, anisole, and fluorobenzene are metallated with phenyl lithium only the ortho hydrogen atoms are exchanged, while the rate of metallation rises in a certain sequence. Wittig explained these results by saying that the electronegativity of the heteroatoms attached to oxygen (N, O, F) increases in the same sequence. Since the inductive effect attenuates rapidly along the carbon chain, the ortho hydrogen atoms will be protonized more easily than the other atoms. This is why the metal substitutes at the ortho atom and the rate of metallation decreases in this sequence. Roberts [7] showed that the law observed by Wittig is true also for the case of hydrogen exchange with solutions of potassium amide in liquid ammonia in isomers of monodeuterofluorobenzene and deuterioanisole. The rate constants for the reverse exchange of D in ortho, meta, and para monodeuterofluorobenzenes were, respectively: $4 \cdot 10^{-1}$, $4 \cdot 10^{-4}$, and $2 \cdot 10^{-5} \text{ sec}^{-1}$. Because of the great electronegativity of fluorine compared with oxygen the absolute value of the constant is higher for fluorobenzene than for anisole.

From the results which we have obtained it should be noted that all 8 hydrogen atoms could be exchanged in anisole, including those of the methoxy group. This fact was established as early as 1950 [11]. (It should be noted that in his article [7], Roberts not only fails to mention this fact, but also overlooks all the work done on hydrogen exchange in liquid ammonia in the laboratory of isotope reactions of the Institute imeni Karpov beginning in 1947. Roberts implies that the study of hydrogen exchange with solutions of potassium amide in liquid ammonia was begun in the USA in 1954.) Thus the aromatic ring affects the mobility of the hydrogen atoms in the C-H bonds which are not attached

to the oxygen atom. This is also confirmed by experiments with methoxy naphthalene [14]. This phenomenon is still more general: the effect of the aromatic ring on the aliphatic bond is transmitted even through the nitrogen atom. This follows from the complete exchange of hydrogen in dimethyl anilin and dimethyl naphthalene [11].

In connection with the foregoing it is interesting to compare hydrogen exchange in toluene and anisole with solutions of $\text{KND}_2 / \text{ND}_3$. In toluene [12], unlike anisole, the hydrogen atoms of the methyl group are exchanged much faster (250 times) than in the ring. The acidity of the hydrogen atoms of the toluene methyl group is so great that they are replaced in reaction with cesium [13].

What is the cause of hydrogen exchange in the OCH_3 group of anisole? On analogy with the effect of 6, π -conjugation (in toluene, for example), the effect of the ring on the mobility of the hydrogen atoms in the CH_3O group may be considered as the effect of π , p, 6-conjugation. This is indicated in Wiles' survey article [14]. He notes that when this type of conjugation exists the C-O bond in the anisole molecule should be shortened; this is confirmed by X-ray data. To be sure, caution should be observed in their interpretation, in the author's opinion.

It is quite possible that in this case a certain role is also played by an inductive shift of electrons toward the oxygen atom, causing protonization of the H atoms in the methoxy group. This assumption agrees with the results of experiments performed by Lauer and Day [15] on the exchange of deuterium which had been introduced chemically into phenyl-alkyl ethers in the position para to the alkoxy group. The solvent was glacial acetic acid, and H_2SO_4 the catalyst. It was found that the rate of electrophilic substitution of the para D atom in the aromatic ring increases in a sequence corresponding to the inductive effect of the alkyl group, specifically: $\text{CH}_3(3.0) < \text{C}_2\text{H}_5(4.0) = \text{C}_3\text{H}_7(4.0) < \text{iso-C}_3\text{H}_7(7.5)$. The figures in parentheses are rate constants ($\text{k} \cdot 10^4 \text{ sec}^{-1}$).

It should be noted, however, that the peculiarities of hydrogen exchange in anisole with solutions of potassium amide in liquid ammonia still cannot be explained only by the inductive effect of the oxygen atom in the methoxy group. For example, it is not known in such a case why the H atoms of the ring are exchanged more rapidly than the H atoms of the methoxy group. Since the inductive effect attenuates rapidly along the chain of carbon atoms, the H atoms in the methoxy group should have been exchanged more rapidly than the meta atoms, and particularly the para H atom. Obviously the mutual effects of atoms in the anisole molecule have peculiarities which require further study, and it is not yet possible to explain them from generally accepted points of view.

Hydrogen exchange in diphenyl ether. $(\text{C}_6\text{H}_5)_2\text{O}$ dissolves well in ND_3 . In the presence of KND_2 it gives yellow solutions. After the experiment the substance was isolated, like anisole, and distilled in vacuo over sodium. The constants remained unchanged after the experiment. The results of the exchange experiments can be seen in Table 5.

In only 15 minutes hydrogen exchange is almost completed. Under the same conditions less than one-third of the H atoms (1.8 out of 6) in benzene have been exchanged, in the anisole ring only the two most mobile ortho H atoms, and in diphenyl [12] around two H atoms. Consequently hydrogen exchange in diphenyl ether is considerably more rapid than in benzene, anisole, or diphenyl. If hydrogen exchange in $(C_6H_5)_2O$ with an ammonia base, like exchange with acid DBr [1], depended on p, π -conjugation, one should expect a slowing of hydrogen exchange in comparison to benzene. In fact, this exchange is faster, regardless of whether acid or base participates in the reaction.

Diphenyl ether differs from anisole in that the position of the methyl group, lacking π -electrons, is occupied by a phenyl group. The $(C_6H_5)_2O$ molecule is more highly polarizable ($20.8 \cdot 10^{-24} \text{ cm}^3$) than the anisole molecule ($13.1 \cdot 10^{-24} \text{ cm}^3$). Apparently in hydrogen exchange with a base this plays a certain role.

EVALUATION OF RESULTS

The data obtained in the study of hydrogen exchange in oxygen- and nitrogen-containing aromatic compounds with acid [1] and basic solvents permit drawing conclusions concerning the mechanism of hydrogen exchange. Ingold and collaborators [6], as early as 1934, showed that deuterium exchange in an acid medium is similar to electrophilic substitution. This position has been confirmed in numerous examples in our laboratory [8], particularly in the preceding article [1]. That article showed clearly that if saturation of the free electron pair of the nitrogen atom results in a drop in the level of electronegativity of the carbon atoms of the aromatic amine, and it therefore becomes more probable that acid deuterons will attach to them, then the exchange reaction is inhibited. This is convincing proof of the fact that a necessary condition for the exchange reaction with acid is attachment of D to the carbon atom of a C-H bond.

On the other hand for the exchange reaction to occur with the participation of base the hydrogen of the C-H bond must be protonized. At this point free carbene ions are formed (like the free carbonium ions in the reaction with acid). The fact that the substance is a proton donor in hydrogen exchange catalyzed by base is supported also by the profound analogy, frequently observed in our laboratory, between the metallation of aromatic substances with organoalkali compounds and hydrogen-exchange reactions in a basic medium [9]. A great deal of work now explains the mechanism of metallation with organoalkali compounds [16]. Bryce-Smith suggests that this mechanism be called "protophilic". The attack of the nucleophilic reagent is directed not to the carbon atom of the C-H bond (as occurs in nucleophilic substitution of hydrogen) but to the H atom. Only in the second stage does the metal cation attach to the negatively charged carbon atom. Hydrogen exchange catalyzed by the ND_2^- ion proceeds

in similar fashion. The ND_2^- ion attracts the hydrogen from the C-H bond in the form of a proton, and this permits the D from the ND_3 to attach to the carbon atom. This process must occur as a single act in an activated complex. This makes understandable the similarity between the laws of metallation of anisole and hydrogen exchange with an ammonia base. In Roberts' opinion [7] the primary attack of the ND_2^- ion does not involve the π -electron system of the ring, as happens in nucleophilic aromatic substitution.

Our views [9, 17] of the effect of the charge on the substance on the rate of hydrogen exchange, which have received supplementary confirmation in the present work, also agree with the above concept of the mechanism of exchange reactions.

We intend to supplement our investigations with data on hydrogen exchange in aromatic amines with solutions of potassium amide in liquid ammonia and on deuterium exchange with DF and DF / BF_3 in aromatic compounds with substituents containing oxygen and nitrogen. We also intend to measure the rate of deuterium exchange of unequal hydrogen atoms in diphenyl ether.

CONCLUSIONS

1. All the hydrogen atoms in the phenolate ion, diphenyl ether, and anisole are exchanged with a solution of KND_2 in liquid ND_3 . Since the amide ion is a very strong base, there is a sharp leveling of differences in acidity and reactivity in the exchange of unequal hydrogen atoms on the aromatic rings of the above substances.
2. In the phenolate ion hydrogen is exchanged at a rate 10^3 slower than in benzene. This is explained by the fact that the negative charge on the ND_2^- ion hinders its approach to the catalyst.
3. Hydrogen is exchanged considerably more rapidly in diphenyl ether than in benzene.
4. The rate of exchange of hydrogen in anisole falls in the sequence: ortho > meta > para > OCH_3 . This sequence shows that, unlike exchange with acid, an important role in hydrogen exchange in the ring with a base is played not by the effect of π, p -conjugation, but by the inductive effect of the oxygen in the methoxy group. The hydrogen in the latter is exchanged more slowly than the para atom of the anisole aromatic ring.
5. Various ideas concerning the mechanism of the hydrogen-exchange reaction with acids and bases have been expressed.
6. Methods have been given for preparing various anisoles: $\text{C}_6\text{D}_5\text{OCD}_3$, $\text{C}_6\text{H}_5\text{OCD}_3$, 2,4,6- $\text{C}_6\text{D}_3\text{H}_2\text{OCH}_3$, 3,5- $\text{C}_6\text{D}_2\text{H}_3\text{OCH}_3$ and n- $\text{C}_6\text{D}_4\text{OCH}_3$, using exchange reactions in various solvents.

BIBLIOGRAPHY

1. SHATENSHTEYN, A. I., VEDENEYEV, A. V., ALIKHANOV, P. P.: ZhOKh, 28, 2638 (1958).
2. SHATENSHTEYN, A. I., and IZRAILEVICH, Ye. A.: ZhFKh, 13, 1791 (1939); 26, 377 (1952).
3. SHATENSHTEYN, A. I., VASIL'YEVA, L. N., DYKHNO, N. M., and IZRAILEVICH, Ye. A.: DAN, SSSR, 85, 381 (1952).
4. SHATENSHTEYN, A. I.: Teorii kislot i osnovaniy [Theory of Acids and Bases], Moscow (1949).
5. SHATENSHTEYN, A. I. and IZRAILEVICH, Ye. A.: ZhFKh, 28, 3 (1954).
6. INGOLD, C. K., RAISIN, C. G., and WILSON, C. L.: Nature, 134, 731 (1934); J. Chem. Soc., 1936, 1635.
7. HALL, T. H., PICCOLINI, R., and ROBERTS, J. D.: J. Am. Chem. Soc., 77, 4540 (1955).
8. SHATENSHTEYN, A. I.: Usp. khim., 21, 914 (1952); in the symposium Voprosy kinetiki i t. d. [Problems of Kinetics, etc], published by the Acad Sci USSR, 649 (1954).
9. SHATENSHTEYN, A. I. and VYRSKIY, Yu. P.: DAN SSSR, 70, 1029 (1950); SHATENSHTEYN, A. I.: Usp. khim., 24, 377 (1955); Ukr. khim. zh., 22, 3 (1956).
10. WITTIG, G.: Angew. Chem., 66, 10 (1954).
11. SHATENSHTEYN, A. I., DYKHNO, N. M., IZRAILEVICH, Ye. A. VASIL'YEVA, L. N., and FAYVUSH, M.: DAN SSSR, 79, 479 (1951).
12. SHATENSHTEYN, A. I. and IZRAILEVICH, Ye. A.: DAN SSSR, 94, 923 (1954).
13. J. de POSTIS: C. r., 222, 398 (1946).
14. WILES, L. A.: Chem. Revs., 56, 329 (1956).
15. LAUER, W. M. and DAY, J. T.: J. Am. Chem. Soc., 77, 1904 (1955).

16. ROBERTS, J. D. and CURTIN, D. J.: J. Am. Chem. Soc., 68, 1658 (1946); BRYCE-SMITH, D.: J. Chem. Soc., 1954, 1079; BRYCE-SMITH, D., GOLD, V., and SACHELL, D. P. N.: J. Chem. Soc. 1954, 2743; GRONOWITZ, S. and HALVARSON: Ark. f. Ch., 8, 343 (1955).
17. SHATENSHTEYN, A. I. and YAKOVLEVA, Ye. A.: DAN SSSR, 105, 1024 (1955).

Received for publication
20 August 1957

Physicochemical Institute
imeni L. Ya. Karpov

Table 1

Hydrogen exchange in phenol

$c_{\text{KND}_2} = 1.19 \text{ n}$; $c_{\text{p}}^{\circ} = 9.10 \text{ atom-\%}$

Experi- ment Number	T (hours)	t°	* c_{KND_2}	$\frac{m_{\text{p}}}{m_{\text{B}}}$	$\frac{m_{\text{KND}_2}}{m_{\text{B}}}$	c_{B}	n	$\frac{1}{c_{\text{B}}}$
1	1	25	0.20	33	0.19	0.12	0.1	
2	12	25	0.46	49	0.64	0.21	0.2	
3	6	50	0.37	43	0.27	0.60	0.4	
	16	20						
4	8	50	0.20	44	0.24	0.90	0.6	
5	9	50	0.41	45	0.53	1.01	0.7	0.49
6	8	50	0.37	46	0.48	1.07	0.8	0.46
7	75	35	0.43	47	0.57	1.55	1.1	
8	19	50	0.40	45	0.51	2.04	1.5	1.03
	27	20						
9	221	100	0.53	54	0.42	5.90	4.3	
10	201	120	0.79	88	1.97	6.50	4.8	

* KND_2 concentration takes into account consumption to neutralize phenol.

Table 2

Hydrogen exchange in anisole ($c_{\text{KND}_2} = 0.028 \text{ n}$)

Experi- ment Number	T	t°	$\frac{m_p}{m_B}$	$\frac{m_{\text{KND}_2}}{m_B}$	c_p	c_B	n
1	15 min.	25	184	0.14	4.38	1.03	2.1
2	15 "	25	61	0.05	4.38	1.11	2.3
3	30 "	25	49	0.04	4.38	1.31	2.8
4	30 "	25	40	0.04	9.46	3.10	3.0
5	1 hour	25	40	0.03	4.38	1.48	3.2
6	1 "	25	47	0.04	4.38	1.53	3.2
7	2 "	25	48	0.04	4.38	1.77	3.8
8	3 "	25	41	0.03	4.38	1.87	4.1
9	3 "	25	43	0.03	4.38	1.95	4.1
10	6 "	25	44	0.03	4.38	2.33	4.9
11	6 "	25	85	0.06	4.38	2.42	5.0
12	22 "	20	41	0.03	4.38	2.75	5.9
13	89 "	20	40	0.03	9.46	6.55	7.0
14	144 "	20	47	0.01	9.46	7.66	7.6

2,4,6-trideuteroanisole was prepared by using dimethyl sulfate to methylate 2,4,6-trideuterophenol obtained by isotope exchange of hydrogen in phenol with a solution of alkali in D_2O [6].

Pendadeuteroanisole, $\text{C}_6\text{D}_5\text{OCH}_3$, was obtained by isotopic exchange with DF. The experiments on exchange with HF and DF were performed with Ya. M. Varshavskiy, to whom we extend our thanks.

Table 3

Experiments on reverse exchange with deuterized preparations of anisole,
at 25°

<u>Experi- ment Number</u>	<u>$\frac{^o}{c_p}$</u>	<u>Number of D Atoms</u>	<u>c_{KNH_2}</u>	<u>T</u>	<u>$\frac{m_p}{m_B}$</u>	<u>c_B</u>	<u>Remaining D Atoms</u>	<u>D Atoms Washed Out</u>
2,4,6-trideuteroanisole								
1	2.27	2.7	0.03	5 min.	60	0.87	1.0	1.7
2		3.0	0.10	5 "	51		1.0	2.0
3	2.27	2.7	0.04	30 "	66	0.77	1.0	1.7
4	2.27	2.7	0.04	30 "	50	0.77	1.0	1.7
5	2.27	2.7	0.03	30 "	63	0.74	1.0	1.7
6	2.27	2.7	0.04	1 hour	71	0.77	1.0	1.7
7	2.27	2.7	0.03	6 "	56	0.44	0.6	2.1
2,3,4,5,6-pentadeuteroanisole								
8	2.66	4.7	0.03	30 min.	52	1.29	2.5	2.2
9	2.66	4.7	0.03	6 hours	60	0.28	0.6	4.1
10	2.66	4.7	0.03	6 "	58	0.26	0.5	4.2

Table 4

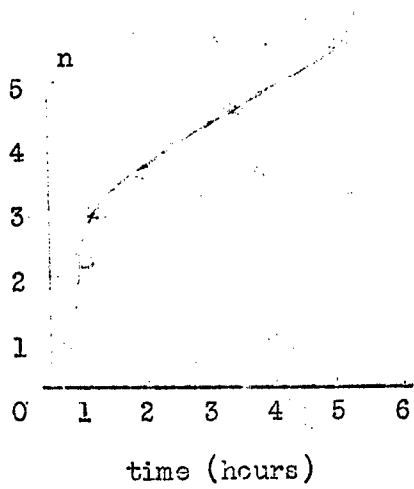
Kinetics of reverse exchange ($c_{\text{KNH}_2} = 0.27 \text{ n}$, 25°)

<u>Experi- ment Number</u>	<u>c_B^o</u>	<u>T (hours)</u>	<u>$\frac{m_p}{m_B}$</u>	<u>c_B</u>	<u>$k \cdot 10^{-4} \text{ sec}^{-1}$</u>
$\text{C}_6\text{H}_5\text{OCD}_3$					
1	3.27	1.0	105	2.08	1.3
2	3.27	1.5	127	1.58	1.3
3	3.27	1.5	160	1.53	1.4
4	3.27	2.0	168	1.11	1.5
4-monodeuteroanisole					
5	3.21	0.5	135	1.85	3.1
6	3.21	0.66	190	1.48	3.2
7	3.21	0.66	127	1.58	2.9
8	3.21	1.0	185	1.05	3.1
9	3.21	1.0	150	1.05	3.1
10	3.21	1.5	170	0.66	2.9

Table 5

Hydrogen exchange in diphenyl ether (25°)

<u>Experi- ment Number</u>	<u>T</u>	<u>c_{KND_2}</u>	<u>$\frac{m_p}{m_B}$</u>	<u>$\frac{m_{\text{KND}_2}}{m_B}$</u>	<u>c_p^o</u>	<u>c_B</u>	<u>n</u>
1	15 min.	0.028	62	0.05	4.38	3.07	8.1
2	15 "	0.046	190	0.25	5.34	4.42	9.1
3	20 "	0.049	63	0.09	5.36	4.03	8.7
4	1 hour	0.028	70	0.06	4.38	3.50	9.2
5	1 "	0.046	83	0.11	5.34	4.86	10.2



Kinetics of hydrogen exchange in anisole in an
0.03-normal solution of KND_2 in ND_3 at 25° .

5338

- END -