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REPORT [redacted] 50X1-HUM

CD NO.

UNCLASSIFIED
JUL 29 1954
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COUNTRY	USSR	DATE OF INFORMATION	1950
SUBJECT	Scientific - Chemistry, deuterium		
HOW PUBLISHED	Thrice-monthly periodical	DATE DIST.	1 May 1950
WHERE PUBLISHED	Moscow/Leningrad	NO. OF PAGES	4
DATE PUBLISHED	21 Feb 1950	SUPPLEMENT TO REPORT NO.	
LANGUAGE	Russian		

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SOURCE Doklady Akademii Nauk SSSR, New Series, Vol LXX, No 6, 1950.

COMPARISON OF THE ACIDITY OF VERY WEAK ACIDS

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Submitted 24 October 1949
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/A Digest.7

Using the protophilic properties of liquid ammonia, the acidity of weak acids like acetamide and urea could be determined by the author(1). The underlying principle can also be used to determine hydrogen mobility in hydrocarbons and other substances which, from the chemical point of view, function as acids in organometallic compounds(2). Using deuteroammonia as a solvent, the proton of the solute can be considerably loosened, and exchange of the proton for a deuteron effected. C-H groups which do not readily enter into an exchange reaction with heavy water or deuteroalcohol, even in the presence of alkali (4,6), can be easily brought into reaction with deuteroammonia, particularly in the presence of potassium amide ($\sim$ 0.25N). Then the differences in exchange reaction rates are especially pronounced, so that a quantitative comparison of the mobility of hydrogen and its capacity for ionization in compounds where the hydrogen does not have much mobility becomes possible(5).

The two appended tables show results obtained by the author for a number of compounds. In Table 1, α is the coefficient of the distribution of deuterium between the organic substance and the solvent and n the number of atoms of hydrogen exchanged for deuterium. The results in Table 2 were calculated according to the formula $\alpha n = N\frac{c}{c_0}$, where N is the total number of hydrogen atoms in the organic compound, c the concentration of deuterium in the water resulting from the combustion of the compound after exchange, and c_0 the concentration of deuterium in deuteroammonia. The rate constant was calculated according to the equation for a monomolecular reaction. The values of αn were determined experimentally in the cases of indene and acetophenone ($\alpha n = 2.4$), and also for fluorene ($\alpha n = 1.7$). For all other substances it was arbitrarily assumed that $(\alpha n)_{\infty} = 1$. Shown in parentheses are values of the rate constant which have been calculated for the purpose of orientation on the basis of a proximate value

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for the energy of activation. Along with the rate constants for the reaction of isotope exchange, Table 2 lists conventional constants of ionization (pK = -lgK).

It is known that hydrogen bound to oxygen or nitrogen enters into an exchange reaction instantaneously even in heavy water. Consequently, the method of isotope exchange cannot contribute anything of value as far as the comparison of hydrogen mobilities in compounds of this type is concerned. According to A. I. Brodskiy (5), this is due to the presence of a free pair of electrons in nitrogen or oxygen. Deuterium combines with the electron pair and a proton is simultaneously split off. On the other hand, a deuteron can combine with a carbon atom only after the hydrogen bound to the latter has been ionized. This is a process which requires an expenditure of activation energy. The reaction rate will be higher when the hydrogen passes into the ionic state more easily. In other words, there is a parallelism between the reaction rate constants and the ionization constants.

Using liquid ammonia in which potassium amide had been dissolved, all hydrogen atoms of naphthalene could be replaced with deuterium. Similarly, hydrogen atoms of the methyl group of toluene could be replaced and exchange reactions with other compounds having a low mobility of hydrogen carried out.

BIBLIOGRAPHY

1. A. I. Shatenshteyn, Theory of Acids and Bases, 1949
2. K. A. Kocheshkov and T. V. Talalayeva, Synthetic Methods in the Field of Organometallic Compounds, issue No 1, 1949
3. J. B. Conant and G. W. Wheland, J. Am. Chem. S., Vol LIV, p 1212, 1932; W. K. McEwen, ibid, Vol LVIII, p 1124, 1936
4. G. P. Miklukhin, Uspekhi Khimii (Progress of Chemistry), Vol XVII, p 663, 1948 [redacted] 50X1-HUM
5. A. I. Brodskiy, Izv AN SSSR (News of the Academy of Sciences USSR), Chemical Series, No 1, 1949 [redacted] 50X1-HUM
6. M. Kharash, W. Brown, and J. McNab, J. Org. Chem., Vol II, p 36, 1937

[Tables follow]

Table 1. Comparison of Isotope Exchange Reaction Rates in Deuteroalcohol (or heavy water) and Deuteroammonia

Substance	Deuteroalcohol or Heavy Water			Deuteroammonia			~0.25 N Potassium Amide Solution in Deuteroammonia		
	^{o}C	Time of Interaction (hr)	α n	^{o}C	Time of Interaction (hr)	α n	^{o}C	Time of Interaction (hr)	α n
Indene	100	5	0.01	0	3	1.16	20	5 min.	1.9
Acetophenone	110	97	0.14	0	3	0.21	20	5 "	2.4
Fluorene	25	3300	0	25	1	0.12	20	5 "	0.18
Fluorene	110	670	0	120	10 min	1.6	-	-	-
p-Nitrotoluene	110	48	0	120	48	1.8	-	-	-
Triphenylmethane	100	3600	0*	120	72	0.08	50	24	0.7**
Naphthalene	-	-	-	120	96	0.03	25	9	7.1**
Diphenylmethane	25	3500	0	120	96	0.02	50	120	2.6**
Toluene	150	50	0*	-	-	-	120	144	2.2

* In the presence of alkali

** Determination made by N. M. Dykhno

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Table 2. Constants of Isotope Exchange Reaction Rates in Deuteroammonia* and Conventional Ionization Constants of Weak Acids

Substance	Rate Constant (min $^{-1}$)			Ionization Constant pK = -lgK	
	k_{25°	k_{50°	k_{120°	Data from Conant and Wheland (3)	Data from McEwen (3)
Methyl alcohol	Instantaneous	-	-	-	16
Diphenylamine	"	-	-	-	23
p-Toluidine	"	-	-	-	27
Indene	1×10^{-3}	-	(6×10^{-1})	22	21
Acetophenone	3×10^{-4}	-	-	20	19
Fluorene	4×10^{-5}	2×10^{-4}	(1×10^{-2})	24	25
m-Dinitrobenzene	-	2×10^{-5}	-	-	-
p-Nitrotoluene	1×10^{-6}	4×10^{-6}	6×10^{-4}	-	-
α - Picoline	-	-	2×10^{-5}	-	-
Quinaldine	-	-	1×10^{-5}	-	-
Triphenylmethane	-	-	2×10^{-6}	28.5	33
Acenaphthene	-	-	2×10^{-6}	-	-
Naphthelene	-	-	6×10^{-6}	-	-
Sodium formiate	-	-	6×10^{-7}	-	-
Sodium acetate	-	-	4×10^{-7}	-	-
Diphenylmethane	-	-	3×10^{-7}	29.5	35

*The values of rate constants determined in the present investigation and listed here are purely for the purpose of comparison and orientation.

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