V. A. KALYAVIN, T. A. SMOLINA, Corresponding Member of the Academy of Sciences of the USSR O. A. REUTOV

It is known that reactions of monoalkyl electrophilic substitution

1964

SovietRxiv

Abstract

Full Text

V. A. KALYAVIN, T. A. SMOLINA, Corresponding Member of the Academy of Sciences of the USSR O. A. REUTOV

ON BROMIDE-ANION CATALYSIS OF THE MONOMOLECULAR ISOTOPIC EXCHANGE OF BENZYLMERCURY HALIDES WITH MERCURIC HALIDE

It is known that reactions of monoalkyl electrophilic substitution

$$\mathrm{RHgX} + \mathrm{Hg}^{203}\mathrm{X}_2 \rightleftarrows \mathrm{RHg}^{203}\mathrm{X} + \mathrm{HgX}_2,$$

which proceed by a bimolecular mechanism, are catalytically accelerated by X^- anions capable of coordinating with mercury, in particular by bromide anion (^{1,2}). The action of the bromide anion is evidently associated with the following complex-formation reactions:

$$\mathrm{HgBr}_2 + \mathrm{Br}^- \rightleftarrows \mathrm{HgBr}_3^-, \tag{1}$$

$$\mathrm{RHgBr} + \mathrm{Br}^- \rightleftarrows \mathrm{RHgBr}_2^-. \tag{2}$$

In the present work we have studied the effect of additions of potassium bromide on the rate of the monomolecular reaction of isotopic exchange of *p*-nitrobenzylmercury bromide with radioactive mercuric bromide in dimethyl sulfoxide, where the stage controlling the rate of isotopic exchange, as we found earlier (^{3}), is the ionization of the organomercury compound.

The accelerating influence of bromide anion on the bimolecular substitution reaction is apparently determined by complex formation proceeding both according to equation (1) and according to equation (2). In the reaction of monomolecular substitution the accelerating influence of bromide anion should be determined by complex formation proceeding only according to equation (2).

$$O_2N{-}C_6H_4{-}CH_2{-}HgBr \underset{\text{fast}}{\overset{\text{slow}}{\rightleftharpoons}} O_2N{-}C_6H_4{-}CH_2^{(-)} + HgBr^{(+)}$$

$$Hg^{203}Br_2$$

$$\text{fast}$$

$$O_2N{-}C_6H_4{-}CH_2{-}Hg^{203}Br \underset{\text{fast}}{\overset{\text{slow}}{\rightleftharpoons}} O_2N{-}C_6H_4{-}CH_2^{(-)} + Hg^{203}Br^{(+)}$$

From the experimental results given in Table 1 it follows that the rate of monomolecular isotopic exchange changes substantially with variation in the concentration of potassium bromide; moreover, even at potassium bromide concentrations lower than the concentration of mercuric bromide, the exchange rate increases noticeably. Thus, at a potassium bromide concentration of 0.05 mol/l (mercuric bromide concentration 0.06 mol/l) the initial rate of exchange is 8 times higher than that in the absence of potassium bromide. This fact apparently indicates that even when there is a deficiency of potassium bromide in the system as compared with mercuric bromide, along with complex formation

Fig. 1. Dependence of the initial rate of the isotopic-exchange reaction of *p*-nitrobenzylmercury bromide with radioactive mercuric bromide in dimethyl sulfoxide on the concentration of potassium bromide. $[Hg^{203}Br_2] = 0.06$ mol/l; $[p\text{-}NO_2C_6H_4CH_2HgBr] = 0.03$ mol/l.

Table 1

Isotopic exchange of *p*-nitrobenzylmercury bromide with radioactive mercuric bromide in dimethyl sulfoxide in the presence of potassium bromide at 18° C*. $[Hg^{203}Br_2] = 0.06$ mol/l, $[NO_2C_6H_4CH_2HgBr] = 0.03$ mol/l; R and R_0 (mol/l · h) are the initial rates of exchange in the presence of KBr and without it, respectively; k_1 (h^{-1}) is the first-order rate constant of the exchange reaction

Exchange time	Degree of exchange, %	Exchange time	Degree of exchange, %
[KBr] = 0.00; $k_1 \cdot 10^4 =$ 14.7 h^{-1}; $R \cdot 10^4 =$ 0.442 mol/l · h; $R/R_0 =$ 1.0		[KBr] = 0.04 mol/l; $k_1 \cdot 10^4 = 70.6$ h^{-1}; $R \cdot 10^4 =$ 2.12 mol/l · h; $R/R_0 =$ 4.8	
20.5 h	7	20 h	20
43	11	40	36
71.5	17	70	50
138.5	26	100	67
211	38	150	78

Exchange time	Degree of exchange, %	Exchange time	Degree of exchange, %
306	49	[KBr] = 0.05 mol/l; $k_1 \cdot 10^4 = 121$ h^{-1};	
401.5	60	$R \cdot 10^4 =$ 3.6 mol/l · h; $R/R_0 =$ 8.0	
473	61	1 h	3
[KBr] = 0.01 mol/l; $k_1 \cdot 10^4 = 23.8$ h^{-1};		3	7
$R \cdot 10^4 =$ 0.714 mol/l · h; $R/R_0 =$ 1.6		6	12
5 h	3	22	36
26	7	46	57
94	25	69	67
142.5	41	93	81
213	54	141	95
261	60	190	99
310	70	262	97
[KBr] = 0.02 mol/l; $k_1 \cdot 10^4 = 33.0$ h^{-1};		309	97
$R \cdot 10^4 =$ 0.990 mol/l · h; $R/R_0 =$ 2.2		[KBr] = 0.06 mol/l; $k_1 \cdot 10^4 = 2560$ h^{-1};	
20 h	10	$R \cdot 10^4 =$ 77 mol/l · h; $R/R_0 =$ 174	
70	31	10 min	10
140	51	20	15
240	69	30	20
285	78	60	32
340	81	90	47
[KBr] = 0.03 mol/l; $k \cdot 10^4 = 46.8$ h^{-1};		120	55
$R \cdot 10^4 =$ 1.41 mol/l · h; $R/R_0 =$ 3.2		180	64
5 h	4	[KBr] = 0.07 mol/l; $k_1 \cdot 10^4 = 69000$ h^{-1};	

Exchange time	Degree of exchange, %	Exchange time	Degree of exchange, %
26	16	$R \cdot 10^4 =$ 2100** mol/l $\cdot$ h; $R/R_0 =$ 4700	
46	28	2 min	29
70	37	5	62
117	57	10	82
190	75	20	95
238	85	[KBr] = 0.09 mol/l; $k_1 \cdot 10^4 =$ 710000 h^{-1};	
286	87	$R \cdot 10^4 =$ 21000** mol/l $\cdot$ h; $R/R_0 =$ 47000	
		1 min	83
		2	96

* The method of kinetic measurements was described by us earlier (3).
** The constants have an approximate value, since the isotopic-exchange reaction proceeds very rapidly.

of mercuric bromide (equation (1)), complex formation of *p*-nitrobenzylmercury bromide takes place (equation (2)). It should be noted that, when potassium bromide is deficient, only a small part of it is bound into a complex with the organomercury compound, and only with an excess of potassium bromide does complex formation according to equation (2) begin to take place to a greater extent; as a result, the rate of isotopic exchange increases sharply. Thus, at a potassium bromide concentration of 0.09 mol/l (mercuric bromide concentration 0.06 mol/l), the initial rate of the isotopic-exchange reaction is 47,000 times higher than that in the absence of potassium bromide.

Figure 1 shows the dependence of the initial rates of the isotopic-exchange reaction of *p*-nitrobenzylmercury bromide with radioactive mercuric bromide on the concentration of potassium bromide. As can be seen, the curve for the dependence of the exchange rate on the potassium bromide concentration consists of three segments. In segment A* the rate increases by a factor of 8, in segment B by a factor of 21, and in segment C by a factor of 276; or, recalculated per 0.01 unit of concentration, the increase in rate in each of these segments is 1.6, 21, and 92, respectively.

It is of interest to compare the dependence obtained for the rate of monomolecular isotopic exchange on the amount of bromide anion with analogous dependences obtained by us for the S_E2 reaction of isotopic exchange of benzylmercury bromide with mercuric bromide (²) and by Ingold and co-workers for the S_E2

schematic chemical structures showing complex formation of
p-nitrobenzylmercury bromide, benzylmercury bromide, and methylmercury
bromide with bromide anion

Figure 1: schematic chemical structures showing complex formation of *p*-nitrobenzylmercury bromide, benzylmercury bromide, and methylmercury bromide with bromide anion

reaction of isotopic exchange of methylmercury bromide with mercuric bromide (^{1}). In the case of the exchange reaction of benzylmercury bromide, the curve for the dependence of the reaction rate on the concentration of bromide anion also consists of three segments, although there is no such abrupt jump on passing from segment A to segment B. Thus, in segment A the exchange rate increases by a factor of 2.7, and in segment B by a factor of 1.5; i.e., recalculated per 0.01 unit of potassium bromide concentration, in each of these segments the exchange rate increases by factors of 0.5 and 1.5, respectively. The curve for the dependence of the rate of isotopic exchange of methylmercury bromide with mercuric bromide, obtained by Ingold and co-workers, consisted of two segments with a point of inflection at a bromide-anion concentration equal to the concentration of mercuric bromide; i.e., there was no noticeable jump in rate on approaching a bromide-anion concentration equal to the concentration of mercuric bromide.

The presence of a jump in the rate of isotopic exchange, and its magnitude in the region of bromide-anion concentrations close to but lower than the concentration of mercuric bromide, can be explained by the different tendency toward complex formation with bromide anion of the organomercury compounds considered, among which *p*-nitrobenzylmercury bromide has the greatest tendency toward complex formation, and methylmercury bromide the least.

The different tendency toward complex formation of these compounds is especially noticeable in the region of bromide-anion concentrations exceeding the concentration of mercuric bromide. Thus, when the bromide-anion concentration is increased from a value equal to the concentration of mercuric bromide to a value equal to the sum of the concentrations of mercuric bromide and the organomercury compound, the rate of the isotopic-exchange reaction of *p*-nitrobenzylmercury bromide, benzylmercury bromide, and methylmercury bromide with mercuric bromide increases, respectively, by factors of 276, 10, and 2.3.

Moscow State University
named after M. V. Lomonosov

Institute of Organoelement Compounds
Academy of Sciences of the USSR

Received
20 IV 1964

CITED LITERATURE

1. H. B. Charman, E. D. Hughes, C. Ingold, *J. Chem. Soc.*, **1961**, 1142.

2. V. A. Kalyavin, T. A. Smolina, O. A. Reutov, DAN, **155**, No. 3, 596 (1964).

3. V. A. Kalyavin, T. A. Smolina, O. A. Reutov, DAN, **156**, No. 1, 95 (1964).

* The dependence of the exchange rate in segment A is in fact not strictly linear.

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.