
**THE EVIDENCE AND APPLICATIONS OF EQUILIBRIA BETWEEN
HYDROXIDE AND ALKOXIDE IONS
IN AQUEOUS-ALCOHOLIC SYSTEMS**

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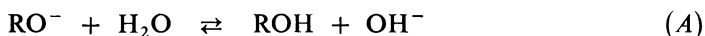
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The composition of solvolysis products of butyl bromide, acetanhydride, and benzoyl chloride has been followed in aqueous alcohol in alkaline and (except for butyl bromide) also in neutral regions. The results have been used as a piece of evidence of the existence of equilibrium between hydroxide and alkoxide ions and for evaluation of the possibility of calculation of the concentration ratio of hydroxide and alkoxide ions from the concentration ratios of the products as well as for evaluation of selectivities of the solvolytic reactions for mechanistic purposes.

The equilibrium (A) is established in alkaline mixtures of water and alcohol.



A real existence of equilibria between hydroxide and methoxide or ethoxide ions was confirmed within a wide range of concentrations of water and alcohol by means of relative proportions of the reaction products of the hydrolytic and alcoholic reactions of dinitrohalobenzenes¹⁻⁴, acetanhydride⁵, benzyl chloride⁶, phthalic anhydride⁶ and in reesterification reactions^{7,8}. There are not many reports showing the real existence of equilibrium (A). Therefore chemists often ignore this equilibrium. The aim of the present communication is to gather further evidence confirming the existence of equilibrium (A) and to show the consequences following therefrom. Another aim of this paper is to evaluate the possibility of calculation of the concentration ratio of alkoxide and hydroxide ions from that of the reaction products and to gather experimental material enabling utilization of selectivities of the solvolytic reaction for mechanistic purposes.

EXPERIMENTAL

Chemicals. Acetanhydride, benzoyl chloride, benzene, methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, methyl and ethyl benzoates, 1-propyl and 2-propyl acetates of p.a. purity grade (Lachema) were redistilled immediately before use. Sodium hydroxide, sodium perchlorate, and potassium iodide were also p.a. commercial products (Lachema). 1-Bromobutane⁹, methyl butyl ether¹⁰, and ethyl butyl ether¹⁰ were prepared according to known procedures.

Solvolyses. The solvolyses of butyl bromide were carried out in aqueous methanol ($c_{\text{BuBr}} = 0.805 \text{ mol dm}^{-3}$) and aqueous ethanol ($c_{\text{BuBr}} = 1.48 \text{ mol dm}^{-3}$) by action of sodium hydroxide of various concentrations. The reaction mixture was analyzed (after 24 h) by means of gas chromatography to estimate the content of butanol and methyl butyl ether and ethyl butyl ether, respectively. Dibutyl ether was not observed.

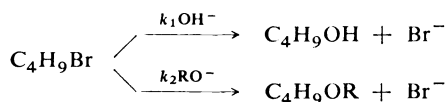
The initial concentrations of acetanhydride for the solvolyses in neutral mixtures water-1-propanol and water-2-propanol were 0.105 and 0.96 mol dm^{-3} , respectively. The reaction products were identified chromatographically after 24 h of reaction. The initial concentrations of acetanhydride for the solvolyses in alkaline mixtures of water and 1-propanol were 0.01 mol dm^{-3} . For solvolyses in alkaline mixtures of water and 2-propanol a small amount of solid sodium hydroxide was dissolved in the reaction mixture prior to addition of acetanhydride (whose resulting concentration was 0.96 mol dm^{-3}). The concentrations of the esters formed were estimated chromatographically after 5 min (water-1-propanol) or after 3 h (water-2-propanol).

For the solvolyses of benzoyl chloride, the solution of the substrate in benzene was added to aqueous methanol or ethanol (the resulting concentration of benzoyl chloride was $8.7 \cdot 10^{-3} \text{ mol dm}^{-3}$). For the solvolyses in alkaline region, small amounts of solid sodium hydroxide were dissolved in the reaction mixture prior to benzoyl chloride. The resulting solution was analyzed by means of gas chromatography (the content of the esters) either immediately (alkaline medium) or after 24 h (neutral medium). All the reactions were carried out at room temperature, since the selectivity of solvolytic reactions is known to change but little with temperature¹¹.

Analyses. All the analyses were carried out by means of a gas chromatograph Chrom 4 (Laborní přístroje, Prague) with a flame ionisation detector. The steel column (2.5 m, 3 mm) was packed with 15% Carbowax 20M on Chromaton NAW HMDS (0.16 to 0.20 mm). The analyses of the reaction mixtures of 1-bromobutane in aqueous methanol (ethanol) were carried out at the inlet temperature of 110°C , column temperature of 82°C (75°C), and detector temperature of 110°C . The flow rates: nitrogen 27, hydrogen 30, and air 500 ml min^{-1} . The analyses of the reaction mixtures of acetanhydride in aqueous 1-propanol (2-propanol) were carried out at the inlet temperature of 100°C , the column temperature of 69°C (61°C), and the detector temperature of 110°C . Flow rates: nitrogen 26, hydrogen 30, and air 500 ml min^{-1} . A glass column (1 m, 2 mm) packed with 3% FFAP on Inerton Super (0.16–0.20 mm) was used for the analyses of the reaction mixtures from benzoyl chloride and aqueous methanol or ethanol. The inlet temperature 120°C , the column temperature 100°C , the detector temperature 130°C . Flow rates: nitrogen 23, hydrogen 30, and air 500 ml min^{-1} . The reaction mixture to be analyzed was injected ($1 \mu\text{l}$) into the gas chromatograph by means of a Hamilton syringe (U.S.A.) of $10 \mu\text{l}$ capacity.

THEORETICAL

Scheme 1 describes the solvolyses of 1-bromobutane and other substrates investigated.



SCHEME 1

If both the reactions are first order in the nucleophile, OH^- or RO^- ions, which sometimes¹⁻⁴ but not always⁶ is the case, and first order in the substrate, then one can write Eq. (1) for the ratio of concentration increases of the reaction products. This equation can be integrated for zero initial concentration of the reaction products and for constant ratio $c(\text{OH}^-)/c(\text{RO}^-)$ throughout the reaction to obtain Eq. (2).

$$dc(\text{BuOH})/dc(\text{BuOR}) = k_1c(\text{OH}^-)/k_2c(\text{RO}^-) \quad (1)$$

$$k_1/k_2 = c(\text{BuOH}) \cdot c(\text{RO}^-)/c(\text{BuOR}) \cdot c(\text{OH}^-) \quad (2)$$

The logarithm of ratio of the rate constants is sometimes denoted as the reaction selectivity ($\log(k_1/k_2) = S$, see e.g. ref.¹²). Sometimes this function has been suggested as a mechanistic tool for differentiation between monomolecular and bimolecular reactions, since it is closely bound with the slowest reaction step¹³. If the slowest reaction step consists in a bond splitting followed by a faster reaction of the splitting products with nucleophiles, then the concentration ratio of the reaction products (unless sterical aspects are taken into account) is given by the concentration ratio of the nucleophiles, and the ratio of rate constants is close to one. With respect to the sterical aspects it turns out that for solvolytic reactions of the type investigated the water-methanol system is preferable.

If the slowest step consists in the addition of nucleophile to the substrate followed by a fast decomposition of the intermediate formed, then the additions of the two nucleophiles exhibit different velocities. In such case the concentration ratio of the reaction products does not correspond to the concentration ratio of nucleophiles, and the ratio of rate constants calculated from Eq. (2) is different from 1.

However, Eq. (2) has broader applications given by the fact that calculation of the equilibrium constant of Eq. (A) is connected with problems at present. The method by Rochester¹⁴ is connected with extrathermodynamic presumptions whose justification is not always clear. Therefore it is still useful to compare its results with those of the kinetic method¹⁻⁴ based on Eq. (2). It is based on the presumptions that if k_1 and k_2 are separately measurable and the rate constants are independent of or equally dependent on the medium, then it is possible to calculate the concentration ratio of alkoxide and hydroxide ions from the concentration ratio of the reaction products using Eq. (2). This method has already been critically evaluated⁶ but on a relatively narrow experimental basis. The present communication is designed to extend this experimental basis.

In the solvolysis of benzyl chloride a large dependence was found⁶ between the solvolytic reaction selectivity and the total concentration of base. Therefore we also investigated the solvolysis of butyl bromide at various overall concentrations of base. The results of these experiments should contribute to elucidation of the reaction formalism of the parallel reaction studied. If the solvolytic reaction is first

order in both $c(\text{RO}^-)$ and $c(\text{OH}^-)$, then a change in the overall concentration of base must not change the k_1/k_2 ratio obtained from Eq. (2). Hence the found concentration ratios of butanol and butyl alkyl ether were multiplied by the ratio of activities of alkoxide and hydroxide ions and introduced into Eq. (2). The equation (2) necessitates the multiplication by the concentration ratio of the corresponding ions which, however, has not been available. Therefore it was replaced by the ion activity ratio taken from refs^{6,14}.

RESULTS AND DISCUSSION

Tables I and II present the results of calculations of the k_1/k_2 ratios of solvolytic reaction of 1-bromobutane in the water-methanol and water-ethanol systems. From Table I it is obvious that the rate constant ratio k_1/k_2 found from Eq. (2) somewhat decreases with increasing concentrations of both methanol and base in the water-methanol system. In the water-ethanol system the respective changes are much less distinct. The changes in the ratio of rate constants with changes in concentrations of both base and alcohol, which are given in Table I, lead to the conclusion that the kinetic situation in the solvolytic reaction of 1-bromobutane probably is somewhat more complex than that following from Eq. (2). Hydrolyses and alcoholyses are not always of the same order with respect to hydroxide and alkoxide ions, respectively, however, the experiments described do not provide sufficient information for a discussion of kinetic formalism of the parallel reactions studied. They unambiguously indicate the real existence of equilibrium in the sense of Eq. (A) and the found change in the ratio of rate constants (calculated from Eq. (2)) connected with the change in the solvent composition (which is expressed in order of magnitude for the water-methanol system), they confirm the earlier opinion⁶ that the activity ratio of alkoxide and hydroxide ions cannot be calculated from the ratios of the rate constants and of the concentrations of reaction products experimentally found since the dependence of the rate constants on the solvent composition is not known and the kinetic formalism can also somewhat change with the solvent composition. In conclusion it can be stated that the rate constant ratio found in the water-methanol system considerably differs from 1. Hence it is in accordance with the $\text{S}_{\text{N}}2$ mechanism of the reaction studied¹⁵ and corresponds to the addition of hydroxide (alkoxide) ion to the substrate in the rate-limiting step. The results obtained in the water-ethanol system are less unequivocal. The activity ratios of alkoxide and hydroxide ions do not much differ in the water-methanol¹⁶ and water-ethanol⁶ systems. Hence the difference between the k_1/k_2 ratios in Tables I and II (which is expressed in order of magnitude) must be caused by lowered reactivity of ethoxide ions whose reasons are not quite clear. However, the selectivity cannot be used in this case for mechanistic discussions.

Due to the known difficulties connected with chromatographic determination

of acetic acid itself, we could only quantitatively estimate the acetate esters formed in the solvolyses of acetanhydride in the mixtures of water with 1-propanol or 2-propanol. Special attention was paid to the system water-1-propanol, since the existence of 1-propoxide ions has not yet been synthetically proved therein. Therefore we followed, at first, the proportion of the acetate ester formed during the solvolysis in 60% (by weight) 1-propanol in neutral and alkaline regions at various overall

TABLE I

The rate constant ratio k_1/k_2 obtained from measurements of alkaline hydrolysis of 1-bromobutane in aqueous methanol

wt. % MeOH	Total concentration of base, mol dm ⁻³			
	0.130	0.217	0.304	0.435
10	0.113	0.110	0.085	0.084
28.5	0.065	0.101	0.074	0.068
50	0.050	0.042	0.036	0.030
60	0.045	0.039	0.031	0.025
70	0.022	0.032	0.019	0.019
80	0.013	0.018	0.012	0.019
90	0.018	0.013	0.013	0.008

TABLE II

The rate constant ratio k_1/k_2 obtained from measurements of alkaline solvolysis of 1-bromobutane in aqueous ethanol

wt. % EtOH	Total concentration of base, mol dm ⁻³			
	0.12	0.20	0.28	0.40
10	7.31	5.14	5.15	5.33
20	6.88	7.46	7.87	7.93
30	7.93	8.87	9.70	13.82
40	3.81	3.22	2.81	2.76
50	2.78	2.39	2.45	3.95
60	1.96	2.16	2.33	2.41
70	2.23	2.56	1.58	1.58
80	3.50	4.35	3.74	3.91
90	2.56	2.20	2.40	2.15

concentrations of base. The below-given results thus obtained are not loaded with any presumptions ($c(\text{AA})$ means the initial concentration of acetanhydride).

Overall base concentration, mol dm ⁻³	0.00	0.02	0.03	0.04	0.05	0.06
$c(\text{ester})/c(\text{AA})$ in %	23.8	5.07	5.98	8.04	9.09	9.59

Obviously the fraction of the ester formed in alkaline region is lower in the order of magnitude for the most diluted concentrations of base as compared with the neutral region, but it increases with increasing base concentration. Therefrom it follows that the nucleophiles are different in the neutral and alkaline regions. As, however, acetic acid and 1-propyl acetate again are the reaction products, the existence of propoxide ions is thereby proved. From the increased proportion of the ester with increasing overall concentration of base it can be concluded that the hydrolytic and alcoholic reactions differ in their kinetic order with respect to the nucleophiles. The reaction is very fast and it has not yet been studied kinetically. Therefore, Eq. (1) was used for description of the reaction system, which means a certain simplification of the kinetic formalism. The fraction of acetanhydride which underwent hydrolysis was calculated from the difference between the known initial concentration of acetanhydride and the ester concentration determined after the reaction was finished. The ratio of rate constants of the hydrolysis and alcoholysis is expressed by Eq. (3),

$$k_1/k_2 = [c(\text{AA}) - c(\text{ester})] \cdot c(\text{RO}^-) / [c(\text{ester}) \cdot c(\text{OH}^-)] \quad (3)$$

where again $c(\text{AA})$ means the initial concentration of acetanhydride. In the calculation of the rate constant ratio according to Eq. (3) the concentration ratio of 1-propoxide and hydroxide ions again was replaced by the corresponding ratio of their activities taken from ref.¹⁷. The rate constant ratio thus calculated from Eq. (3) for the water-1-propanol system is given in Table III. From the table it can be seen that the share of alcoholysis in the overall hydrolysis is increased with increasing total base concentration. In order to find whether the increase in alcoholysis to the detriment of hydrolysis is due to neglecting of the difference between activities and concentrations, i.e. of the different dependence of the activity coefficients of 1-propoxide and hydroxide ions on ionic strength, we investigated the solvolysis of acetanhydride in 0.02 mol dm⁻³ NaOH ($I = 0.02$ mol dm⁻³) in 50% (by weight) 1-propanol. The ionic strength of solution was adjusted by addition of solid sodium perchlorate (up to $I = 0.08$ mol dm⁻³). The rate constant ratio found varied only within experimental error, hence the experimental results are not presented. This

finding allows the conclusion that the replacement of the concentration ratio by the activity ratio of alkoxide and hydroxide ions is correct and introduces no serious error, but the situation in the reacting system is somewhat more complex than that indicated by Eq. (3). However, our experimental material does not allow any increase in precision. Table III also gives the rate constant ratio of the neutral solvolysis of acetanhydride calculated from Eq. (4) which obviously is an analogue of Eq. (3).

$$k_1/k_2 = [c(\text{AA}) - c(\text{ester})] c(\text{ROH})/c(\text{ester}) c(\text{H}_2\text{O}) \quad (4)$$

From Table III it follows that the rate constant ratio of the neutral solvolysis changes with the solvent composition, which again prevents application of Eq. (2) to the calculation of the concentration ratio of 1-propoxide and hydroxide ions. From the table it is also obvious that the hydrolysis is far less preferred in neutral medium than in alkaline medium.

The results of investigation of the solvolytic reactions of acetanhydride in the water-2-propanol system are given in Table IV. Again the calculation of the rate constant ratio was simplified by adopting the ratio of activities of 2-propoxide and hydroxide ions taken from ref.⁶ and introducing it into Eq. (3). For calculation of the rate constant ratio in the neutral region we adopted Eq. (4). Comparison with Table III shows that the rate constant ratio of hydrolysis and alcoholysis of acetanhydride is ten times as large in the water-2-propanol system as in the water-1-propanol system due probably to the sterically less accessible oxygen atom in 2-propanol. In alkaline medium the reactivity differences are less distinct. In the case

TABLE III

The rate constant ratio k_1/k_2 obtained from measurements of neutral and alkaline solvolyses of acetanhydride in aqueous 1-propanol

wt. % 1-PrOH	Total concentration of base, mol dm ⁻³					
	0.00	0.02	0.03	0.04	0.05	0.06
10	0.43	12.8	10.5	8.1	7.6	6.9
20	0.65	37.7	29.7	27.9	19.9	18.2
30	0.84	36.7	31.9	31.1	29.8	25.7
40	1.16	44.0	38.4	38.0	33.7	30.4
50	1.32	40.6	31.4	29.3	23.4	22.9
60	1.44	66.8	56.1	40.8	35.7	33.6
70	1.63	102.0	59.9	49.1	27.0	26.3
80	1.76	116.8	75.8	45.2	36.4	31.4
90	2.24	70.5	53.5	26.0	18.6	17.8

of alkaline solvolysis of phenyl amidophosphates⁸ low (practically zero) reactivity of 2-propoxide ions was used to prove the reaction mechanism. Our results show that this procedure can only be used in the cases of sterically very much hindered

TABLE IV

The rate constant ratio k_1/k_2 obtained from measurements of solvolysis of acetanhydride in aqueous 2-propanol

wt. % 2-PrOH	Region	
	neutral	alkaline
10	4.65	47.7
20	5.00	43.3
30	5.56	63.1
40	6.22	72.5
50	6.28	74.3
60	7.31	75.0
70	9.51	79.4
80	9.53	17.9
90	13.26	2.2

TABLE V

The rate constant ratio k_1/k_2 obtained from measurements of solvolyses of benzoyl chloride in aqueous methanol and ethanol

wt. % ROH	Water-methanol		Water-ethanol	
	neutral	alkaline	neutral	alkaline
10	2.97	0.66	4.51	1.16
20	—	—	13.39	1.46
28.5	1.01	0.53	—	—
30	—	—	8.56	0.55
40	—	—	3.49	0.16
50	0.77	0.24	1.95	0.51
60	0.54	0.21	0.52	0.77
70	0.47	0.12	0.44	0.70
80	0.52	1.64	0.61	0.84
90	2.90	2.87	0.78	2.43

electrophiles, since the reactivity changes of acetanhydride in the systems water–ethanol⁵, water–1-propanol, and water–2-propanol are not very distinct. The results of Table IV agree qualitatively with those of solvolysis of phthalic anhydride⁶. With both the substrates a decrease in the rate constant ratio is observed in 80 and 90% (by weight) 2-propanol. The reasons of this phenomenon are not known yet.

Table V presents the experimental results of solvolyses of benzoyl chloride in the water–methanol and water–ethanol systems. In neutral region the k_1/k_2 ratio changes with the solvent composition in both the systems. This ratio is close to 1 in the former system, the solvolysis of benzoyl chloride proceeding by a spectrum of S_N1-S_N2 reactions with predominant share of the S_N2 mechanism¹⁸ or by an entirely associative mechanism¹⁹. However, the k_1/k_2 ratio is close to 1 within the whole concentration range of alcohol, which (together with refs^{18,19}) leads to the conclusion that the k_1/k_2 ratio differing from 1 by one or more orders of magnitude can serve as evidence in favour of a bimolecular process in the rate-limiting step. If the ratio is close to 1, then the rate constant ratio cannot provide reliable information about reaction molecularity. In alkaline region the solvolysis of benzoyl chloride is very fast, but the acid-base equilibrium (*A*) is probably established much faster. This explains different k_1/k_2 ratios in neutral and alkaline regions in both systems. In both the systems (water–methanol and water–ethanol) the k_1/k_2 ratio is close to 1 in alkaline region, which does not allow any conclusions to be made about the reaction molecularity.

In conclusion it can be stated that in the neutral solvolyses the k_1/k_2 ratios change with the solvent composition. The changes can be due to different dependences of the rate constants on the medium (as it was proved earlier⁶), but changes in kinetic formalism can contribute, too. These changes found in the neutral solvolyses (where the concentration of nucleophile is doubtless) prevent applications of Eq. (2) to calculations of the concentration ratio of alkoxide and hydroxide ions from kinetic data. The rate constant ratios k_1/k_2 in Tables I–IV have been calculated with the help of known activity ratios of alkoxide and hydroxide ions. If this ratio were considered constant for a given substrate in a binary solvent mixture within the whole range of concentrations of its components (as it is the case in the kinetic method), one would obtain different ratios of concentrations of alkoxide and hydroxide ions for a single mixed solvent depending on the substrate used. Hence the calculations of k_1/k_2 ratios provide information about applicability of kinetic methods to the calculations of concentration ratios of alkoxide and hydroxide ions. At present, the method by Rochester¹⁴ seems to be the only one suitable for the calculation of activity of alkoxide and hydroxide ions within a broader concentration range of alcohol. The estimation of molecularity of solvolytic reactions (if possible at all) by means of the selectivities is restricted to the water–methanol system, which follows from Tables I–III. Finally it can be stated (which was the main aim of the present work) that all the reactions studied – by their reaction products found in

alkaline medium – confirm the existence of the equilibrium between hydroxide and alkoxide ions in all the water–alcohol systems investigated.

REFERENCES

1. Tommila E., Murto J.: *Acta Chem. Scand.* **16**, 53 (1962).
2. Murto J., Tommila E.: *Acta Chem. Scand.* **16**, 63 (1962).
3. Murto J.: *Acta Chem. Scand.* **18**, 1029 (1964).
4. Murto J.: *Acta Chem. Scand.* **18**, 1043 (1964).
5. Mollin J., Nevěčná T., Čáp L., Schneiderová A.: *Chem. Papers* **41**, 745 (1987).
6. Mollin J., Pavelek Z., Kašpárek F.: *Collect. Czech. Chem. Commun.* **52**, 1115 (1987).
7. Sunderland B. B., Watts D. N.: *Int. J. Pharm.* **27**, 1 (1985).
8. Kašpárek F., Vavčiková K., Mollin J., Husek A.: *Collect. Czech. Chem. Commun.*, in press.
9. Marko M., Krasnec L.: *Základy preparativnej organickej chémie*, Vol. 1, p. 215. SNTL, Bratislava 1962.
10. Černý J. V., Černý M., Paleček M., Procházka M.: *Organická syntéza*, p. 211. Academia, Prague 1971.
11. Karton Y., Pross A.: *J. Chem. Soc., Perkin Trans. 2*, 1978, 595.
12. Bordwell F. G., Branca J. C., Cripe T. A.: *Isr. J. Chem.* **26**, 357 (1985).
13. Levine R. D.: *Isr. J. Chem.* **26**, 320 (1988).
14. Rochester C. H.: *J. Chem. Soc., Dalton Trans.* 1972, 5.
15. Ingold C. K.: *Structure and Mechanism in Organic Chemistry*, p. 306. Cornell University Press, London 1953.
16. Pavelek Z.: *Chem. Papers* **42**, 299 (1988).
17. Mollin J., Karásková E.: Unpublished results.
18. Bentley T. W., Harris H. C.: *J. Chem. Soc., Perkin Trans. 2*, 1986, 619.
19. Song B. D., Jencks W. P.: *J. Am. Chem. Soc.* **111**, 8470 (1989).

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