KINETICS OF THE HYDROBROMINATION OF n-PROPYL ALCOHOL BY HYDROGEN BROMIDE IN AQUEOUS SOLUTIONS OF HBr AND HBr WITH H_2SO_4 CONTAINING HIGH CONCENTRATIONS OF ALCOHOL

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The kinetic laws for the formation of n-C_3H_7Br from n-C_3H_7OH and HBr in aqueous solutions with and without H_2SO_4 at 80-100°C have been described in [1]. In order to avoid a large change in the acidity of the medium during the course of the reaction, the experiments were carried out at relatively low initial concentrations of the reactants: 0.71-0.84 mole/liter n-C_3H_7OH in experiments with and without H_2SO_4 and 0.5 mole/liter HBr in the experiments with H_2SO_4. In the experiments in which no additions of H_2SO_4 were made, the HBr concentration was varied from 6.56 to 8.28 mole/liter. In this case, a decrease in the rate constant was recorded after high degrees of conversion had been achieved which may be attributable to a decrease in the acidity of the medium.

Both for theory and practice, the results of kinetic experiments on the formation of alkylbromides in aqueous solutions of strong acids with high concentrations of alcohol are of interest. It is important that two questions should be examined: 1) how to quantitatively take account of the change in the acidity of the medium during the course of a kinetic experiment when there is a decrease in the concentration of the strong acid; 2) how relatively high concentrations of the alcohol affect the true rate constant which characterizes the reactivity of the reagents.

The aim of the present work was to study these questions using the hydrobromination of n-C_3H_7OH by hydrogen bromide in aqueous solutions of HBr in the presence of H_2SO_4 as a catalyst and without H_2SO_4 as the example.

EXPERIMENTAL

The characteristics of the reagents, the technique used to carry out the kinetic experiments, and the method of calculating the changing concentrations of the alcohol, HBr, n-C_3H_7Br, the alkylsulfonic acid (n-$C_3H_7OSO_3H$), and H_2SO_4 have been described in [1].

All the experiments were carried out at 80°C and until the reaction had gone to completion. At certain concentrations of the reagents, an equilibrium is established between the alcohol and n-C_3H_7Br. The calculated concentration equilibrium constants K_p and the densities of the solutions at the moment of mixing the reagents and after the reaction had gone to completion, measured at 25°C, are shown in Table 1.

DISCUSSION OF RESULTS

The experiments in aqueous solutions without H_2SO_4 were carried out with concentrations of n-C_3H_7OH from 1.5 to 4.2 mole/liter and at HBr concentrations from 6.11 to 8.0 mole/liter. The acidity of the medium decreased sharply during these experiments due to the change in the concentration of HBr.

In the experiments on the hydrobromination in aqueous solutions of H_2SO_4, the initial concentration of the alcohol was varied from 1.45 to 4.23 mole/liter at relatively low concentrations of HBr (from 0.267 to 0.783 mole/liter). In this case, the change in the acidity of the medium during the course of an experiment was smaller than in the experiments with aqueous solutions of HBr. This is attributable not only to the use of low initial HBr concentrations but also to the formation of H_2SO_4 as a result of the hydrolysis of the propylsulfonic acid which is in equilibrium with the alcohol and H_2SO_4

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TABLE 1. Data on the Kinetics of the Formation of n-C_3H_7Br from HBr and n-C_3H_7OH at 80°C

C^0_{HBr}	$C^0_{C_3H_7OH}$	$C^0_{H_2SO_4}$	$C^0_{H_2O}$	ε	$-(H_0)_{in}$	$\beta = \frac{C_{C_3H_7OH}}{C_{C_3H_7OSO_3H}}$	$C^\infty_{C_3H_7Br}$	K_p	$(k_1')_0(h_0)_{in}$	$k_1(h_0)_{in}$	ρ_{in}	ρ_{final}
mole/liter									liter/mole· min		g/cm³	
0,991	0,74	8,46	32,3	0,605	3,93	*	0,698	$4{,}8\cdot10^{-4}$	$8{,}5\cdot10^{-3}$	$8{,}5\cdot10^{-3}$	1,5359	–
0,473	1,43	7,83	30,0	0,585	3,63	3,7	0,473	–	$3{,}4\cdot10^{-3}$	$4{,}3\cdot10^{-3}$	1,4416	1,4437
0,315	1,45	8,00	29,7	0,475	3,67	2,4	0,315	–	$3{,}2\cdot10^{-3}$	$4{,}5\cdot10^{-3}$	1,4433	1,4437
0,444	1,45	8,11	29,5	0,475	3,70	2,2	0,444	–	$3{,}6\cdot10^{-3}$	$5{,}2\cdot10^{-3}$	1,4464	1,4540
0,468	2,42	8,17	25,5	0,465	3,85	1,9	0,468	–	$5{,}8\cdot10^{-3}$	$8{,}8\cdot10^{-3}$	1,4436	1,4459
0,466	2,39	8,06	25,6	0,530	3,86	2,7	0,466	–	$5{,}8\cdot10^{-3}$	$7{,}9\cdot10^{-3}$	1,4333	1,4322
0,553	4,23	4,56	27,0	0,822	2,43	5,7	0,474	–	$2{,}6\cdot10^{-4}$	$3{,}1\cdot10^{-4}$	1,2344	1,2312
0,575	4.23	5,53	24,7	0,789	2,93	4,5	0,551	$2{,}3\cdot10^{-2}$	$8{,}5\cdot10^{-4}$	$1{,}0\cdot10^{-3}$	1,2874	1,2682
0,552	4,23	6,51	21,74	0,625	3,37	2,7	0,552	$1{,}7\cdot10^{-2}$	$2{,}3\cdot10^{-3}$	$3{,}1\cdot10^{-3}$	1,3284	1,3237
0,519	4,23	7,42	19,5	0,576	3,85	2,2	0,519	–	$5{,}9\cdot10^{-3}$	$8{,}5\cdot10^{-3}$	1,3762	1,3734
0,484	4,23	7,96	18,0	0,478	4,11	1,9	0,484	–	$1{,}1\cdot10^{-2}$	$1{,}7\cdot10^{-2}$	1,3982	1,3962
0,454	4,23	8,20	17,0	0,450	4,21	1,4	0,454	–	$1{,}2\cdot10^{-2}$	$2{,}1\cdot10^{-2}$	1,3981	1,4029
0,267	4,23	8,27	16,7	0,458	4,12	1,14	0,267	–	$8{,}3\cdot10^{-3}$	$1{,}6\cdot10^{-2}$	1,3885	1,3863
0,783	4,23	8,03	16,7	0,532	4,37	1,7	0,783	–	$1{,}5\cdot10^{-2}$	$2{,}4\cdot10^{-2}$	1,4150	–
6,11 †	4,20	–	30,0	0,914	2,85	–	3,31	$2{,}2\cdot10^{-2}$	$6{,}5\cdot10^{-4}$	$6{,}5\cdot10^{-4}$	1,287	–
7,23 ‡	2,48	–	34,6	0,758	3,05	–	2,48	–	$1{,}4\cdot10^{-3}$	$1{,}4\cdot10^{-3}$	1,3585	–
8,05	1,64	–	37,9	0,633	3,21	–	1,57	$7{,}2\cdot10^{-3}$	$2{,}4\cdot10^{-3}$	$2{,}4\cdot10^{-3}$	1,4333	–
8,28	0,73	–	41,0	0,599	3,07	–	0,73	–	$1{,}6\cdot10^{-3}$	$1{,}6\cdot10^{-3}$	1,4520	–

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* Only traces of the alkyl acid were found. ρ_{in} and ρ_{fin} are the densities at 25°C of the initial reaction mixture and the reaction mixture obtained at the end of the experiment.

† For the calculation of $(k_1')_0$, the segments of the kinetic curves up to x = 2.0 mole/liter were employed.

‡ For the calculation of $(k_1')_0$, the segments of the kinetic curves up to x = 1.89 mole/liter were employed.

$$n\text{-}C_3H_7OSO_2OH + H_2O \rightleftarrows n\text{-}C_3H_7OH + H_2SO_4$$

It follows that one should also allow for the change in the acidity of the medium during the course of the reaction in calculating the rate constants for hydrobromination in experiments with solutions of the reagents in H_2SO_4.

According to [1], the rate of formation of n-C_3H_7Br, when the acidity of the medium and the volume of the reaction mixture remain constant, is expressed by the equation

$$\frac{1}{V}\frac{dN_X}{dt} = k_1'\frac{N_{HBr}}{V}\frac{N_{ROH}}{V} - k_2'\frac{N_X}{V}\frac{N_{H_2O}}{V} \tag{1}$$

where N_X, N_{HBr}, N_{ROH}, and N_{H_2O} are the number of moles of the alkylbromide, HBr, the alcohol, and water in the reaction mixture respectively. k_1' and k_2' are the effective rate constants for the forward and reverse reactions, and V is the volume of the reaction mixture.

In Eq. (1), the total number of moles of the alchohol not bound up in the alkylsulfonic acid, and of the alkyl acid is denoted by N_{ROH}. As has been shown in [2], n-propylsulfonic acid is unreactive in the hydrobromination of alcohol with HBr and the concentration of the active species C_3H_7OH is reduced on account of its formation. Hence in analyzing the kinetic data from experiments using solutions of the reagents in H_2SO_4 in accordance with Eq. (1), account should be taken of the fact that the rate constant k_1' contains a factor which allows for the relative concentration of the reactive form of the alcohol. The n-C_3H_7Br which is formed is poorly soluble in the solution of the acid and is evolved into the gas phase where it partially condenses in the form of droplets which leads to a reduction in the volume of the reaction mixture. The densities ρ of the initial solution and the solution obtained after the reaction has gone to completion are practically identical. Hence, when x moles of n-propylbromide are formed in 1 liter of the initial solution and they are removed into the gas phase, the volume of the reaction mixture decreases by the amount

$$\lambda x = \frac{M_{C_3H_7Br}x}{1000\rho}$$

where $M_{C_3H_7Br}$ is the molecular weight of the alkylbromide. The initial volume of the reaction mixture is denoted by V_0 and the current volume of the reaction mixture $V = V_0(1 - \lambda x)$. When V is replaced by V_0 in Eq. (1) and we introduce the notation $N_X/V_0 = x$, and $N_{HBr}/V_0 = a$, $N_{ROH}/V_0 = b$, $N_{H_2O}/V_0 = C^0_{H_2O}$ for the initial solutions, then, for a constant acidity of the solution

$$\frac{dx}{dt} = \frac{k_1'(a-x)(b-x) - k_2'(C^0_{H_2O} + x)x}{1 - \lambda x} \tag{2}$$

In Eq. (2) and the subsequent equations, x has the meaning of the current concentration of the n-propylbromide if it had all remained in the solution. The rate constant k_1' changes in proportion to the acidity of the medium h_0 [1] and $k_1' = (k_1')_0 h_0$. The rate constant for the hydrolysis of n-propylbromide k_2' also includes a coefficient describing the solubility of n-C_3H_7Br in the reaction mixture. It follows from the data cited in [1] that k_2' only changes insignificantly when there is a change in the acidity of the medium. Under the conditions which were employed, the equilibrium of the hydrobromination reaction was strongly displaced in favor of n-C_3H_7Br, i.e., $k_2' \ll k_1'$. Hence, in order to simplify the calculations, we assume that k_2' also changes proportionally to h_0, i.e., $k_2' = (k_2)_0 h_0$. In calculating k_1', this assumption can only lead to significant errors when points on the kinetic curve close to equilibrium are employed. With the above assumption the rate of the reaction is described by the equation

$$\frac{dx}{dt} = \frac{[(k_1')_0(a-x)(b-x) - (k_2)_0(C^0_{H_2O} + x)x](h_0)_{cur}}{1 - \lambda x} \tag{3}$$

where $(h_0)_{cur}$ is the current acidity of the solution.

For integration, Eq. (3) is written as

$$\frac{dx}{dt} = \frac{(k_1')_0(m-x)(n-x)(h_0)_{cur}}{(1-K_e)(1-\lambda x)} \tag{4}$$

where

$$m + n = \frac{a + b + K_e C^0_{H_2O}}{1 - K_e};\quad n = C^{\infty}_{C_3H_7Br} = x^{\infty}\ (4)$$

K_e is the equilibrium constant for the hydrobromination expressed in concentration terms

$$K_e = \frac{(a - C^{\infty}_{C_3H_7Br})(b - C^{\infty}_{C_3H_7Br})}{(C^0_{H_2O} + C^{\infty}_{C_3H_7Br})\, C^{\infty}_{C_3H_7Br}}$$

$C^{\infty}_{C_3H_7Br}$ is the equilibrium concentration of n-propylbromide in the solution if it had not evaporated into the gas phase. By $C^{\infty}_{C_3H_7Br}$ we also denote the final concentration of n-propylbromide which would have been obtained in the solution during the complete conversion of the alcohol into n-C_3H_7Br subject to the condition that the latter completely remained in solution.

In order to integrate Eq. (3) it is necessary to express $(h_0)_{cur}$ in terms of the current concentrations of HBr, H_2SO_4, H_2O, and n-C_3H_7OH. It is impossible to measure the acidity functions of aqueous–propanol solutions of HBr and mixtures of HBr with H_2SO_4 at 80°C using the indicator method. The values of H_0 for the solutions under investigation at 80°C can be calculated on the basis of results presented in [2] where it was shown that at 25°C, the acidity functions of aqueous–alcoholic and aqueous solutions of a strong acid change by the same amount over the same range of γ (γ is the ratio of the sum of the concentrations of the strong acids to the sum of the concentrations of the bases). We assume that this law is also valid at higher temperatures. The acidity functions of aqueous solutions of strong acids can be measured by the indicator method. If these data are available, the acidity functions of aqueous–alcoholic solutions can also be calculated. In order to do this it is necessary to calculate the value of γ for the solutions under investigation and to find H_0 of an aqueous solution of the strong acid with the same value of γ from the tabulated data. The acidity functions of aqueous solutions of H_2SO_4 at temperatures above 25°C are known from [3]. These data have been used in [1] and in the present work to calculate H_0 for solutions of HBr and HBr with H_2SO_4 in aqueous–propanol mixtures.

It is known [4, 5] that, at 25°C and at concentrations of a strong acid in an aqueous solution of more than 4 moles per 1000 g water, there is a linear relationship between H_0 and the molality of the acid (the number of moles of the acid per 55.5 moles of water).

According to [2], the same relationship also holds at 25°C in the case of aqueous–alcoholic solutions of H_2SO_4 and a mixture of H_2SO_4 and HBr and is applicable to the mixtures investigated in this work. It can be expressed by the equation

$$-(H_0) = 55.5 \cdot \varepsilon' \gamma + d \tag{5}$$

The factor of 55.5 in this equation was introduced in order to refer the number of moles of the strong acid to 55.5 moles of the sum of the bases. It is expedient to refer to the number of moles of the acid per 55.5 moles of water and alcohol in the aqueous–alcoholic solution as the molality of the aqueous–alcoholic solution of the acid.

Water and alcohol molecules are the bases in aqueous–alcoholic solutions of H_2SO_4. Any alkyl acid present in the solution is not allowed for in the sum of the concentrations of the acids [2]. According to [2], a molecule of an alkyl acid binds a water molecule which is allowed for in the sum of the number of moles of the bases. In our case the acidity functions of the initial and current solutions can be expressed by the equations

$$\begin{aligned} -(H_0)_{cur} &= 55.5 \cdot \varepsilon' \frac{(y - z_{cur} - x)}{C^0_{H_2O} + C^0_{ROH}} + d \\ -(H_0)_{in} &= 55.5 \cdot \varepsilon' \frac{(y - z_0)}{C^0_{H_2O} + C^0_{ROH}} + d \end{aligned} \tag{6}$$

where y is the sum of the concentrations of H_2SO_4 and HBr in the initial solutions in mole/liter, z_0 is the concentration of the alkylsulfonic acid in the initial solution in mole/liter, z_{cur} is the concentration of the alkylsulfonic acid in the current solution subject to the condition that the volume remains constant during the course of the reaction, and ε' and d are constants which are temperature dependent but independent of the nature of the strong acid.

Since Eqs. (5) and (6) are empirical and have not been checked experimentally at temperatures exceeding 26°C, it is reasonable to assume that the constants ε' and d only retain their constancy over a narrow range of the acidity function at high temperatures. If these constants really remain constant even within the limits of a single H_0 unit, then this is acceptable for the description of the kinetic curves of experiments where the acidities of the initial and final solutions differ by an order of magnitude. In these experiments, the concentration of the strong acid decreases by almost 2-2.5 mole/liter. The coefficient τ is equal to the number of moles of the strong acid removed from the solution during the formation of 1 mole of n-alkylbromide.

Only the initial concentrations of water $C^0_{H_2O}$ and alcohol C^0_{ROH} are used in Eqs. (6) since the total number of moles of these components in the solution remains constant during the course of the reaction. From Eqs. (6) we obtain that

$$\frac{(h_0)_{\text{in}}}{(h_0)_{\text{cur}}} = 10^{\frac{\varepsilon' (x - z_0 + z_{\text{cur}}) 55.5}{C^0_{H_2O} + C^0_{ROH}}} = e^{\varepsilon x} \tag{7}$$

In experiments without additions of H_2SO_4, only 1 mole of the strong acid (HBr) is consumed in the formation of 1 mole of n-propylbromide. In the analysis of such experiments when there is no H_2SO_4 in the solution, the quantity $2.3 \cdot \varepsilon' \cdot 55.5/(C^0_{H_2O} + C^0_{ROH})$ is denoted by ε in Eq. (7).

It has already been mentioned above that, in experiments with H_2SO_4 solutions, the acidity also changes during the course of the experiment due to hydrolysis of the alkylsulfonic acid. The change in the concentration of the alkylsulfonic acid can be expressed in terms of x. It has been established by an experimental route that, during the course of the hydrobromination of n-C_3H_7OH, the ratio of the current concentrations of the alcohol and the alkylsulfonic acid is practically constant [1]. We shall denote this ratio by β.

$$\beta = \frac{C^0_{ROH} - x - z_{\text{cur}}}{z_{\text{cur}}} \quad \text{in the current solution}$$

$$\beta = \frac{C^0_{ROH} - z_0}{Z_0} \quad \text{in the initial solution}$$

Consequently

$$z_0 = \frac{C^0_{ROH}}{1+\beta}; \quad z_{\text{cur}} = \frac{C^0_{ROH} - x}{1+\beta}; \quad (x - z_0 + z_{\text{cur}}) = \frac{\beta x}{1+\beta}$$

Hence, in analyzing the experiments with solutions of the reagents in H_2SO_4, the quantity

$$\frac{2.3 \cdot \varepsilon' \cdot 55.5}{C^0_{H_2O} + C^0_{ROH}} \frac{\beta}{1+\beta}$$

is denoted by ε in Eq. (7). We shall represent the exponential function $e^{\varepsilon x}$ in the form of a series. In our experiments εx was not greater than 1.8. Hence, even at the maximum value of εx, only the first four terms in the series

$$e^{\varepsilon x} = 1 + \varepsilon x + \frac{(\varepsilon x)^2}{2} + \frac{(\varepsilon x)^3}{6}$$

are required to describe the change in h_0 and

$$(h_0)_{\text{cur}} = \frac{(h_0)_{\text{in}}}{1 + \varepsilon x + \frac{(\varepsilon x)^2}{2} + \frac{(\varepsilon x)^3}{6}} \tag{8}$$

When Eqs. (4) and (8) are solved simultaneously, we have

$$\frac{dx}{dt} = \frac{(k_1')_0 (m - x)(n - x)(h_0)_{\text{in}}}{(1 - K_e)\left(1 + \varepsilon x + \frac{(\varepsilon x)^2}{2} + \frac{(\varepsilon x)^3}{6}\right)(1 - \lambda x)} \tag{9}$$

As a result of the integration of Eq. (9), formula (10) is obtained for the calculation of the rate constant for the hydrobromination of n-C_3H_7OH by hydrogen bromide

$$\begin{aligned} &A \ln \frac{m - x}{n - x} + B \ln (m - x) + C \ln (n - x) + Dx + \\ &+ Mx^2 - Nx^3 = \frac{(k_1')_0 (h_0)_{\text{in}}}{1 - K_e} t + A \ln \frac{m}{n} + B \ln m + C \ln n \end{aligned} \tag{10}$$

When all four terms of the series are used, which is necessary in the experiments without H_2SO_4 where a lot of HBr is consumed, the coefficients in Eq. (10) are calculated using the formulas

$$A = \frac{(1 + \varepsilon n + \delta mn)(1 - \lambda n)}{m - n}; \quad \delta = \frac{\varepsilon^2}{2} + \frac{\varepsilon^3}{6}$$

$$B = (\varepsilon + \delta m)(1 - \lambda n) - (1 + \varepsilon m + \delta m^2)\lambda$$

$$C = n\left(\frac{\varepsilon^3}{6}n + \delta\right)(1 - \lambda n)$$

$$D = \left(\frac{\varepsilon^3}{6}n + \delta\right)(1 - \lambda n) - (\varepsilon + \delta m)\lambda$$

$$M = \frac{1}{2}\left[\frac{\varepsilon^3}{6}(1 - \lambda n) - \delta\lambda\right]; \quad N = \frac{\varepsilon^3}{18}\lambda$$

For the analysis of experiments where the change in εx is not greater than 0.5, it suffices to use just three terms in the series expansion of the exponential function $e^{\varepsilon x}$. In this case the coefficients appearing in Eq. (10) should be calculated using the formulas

$$A = \frac{\left(1 + \varepsilon n + \frac{1}{2}\varepsilon^2 mn\right)(1 - \lambda n)}{m - n}$$

$$B = \left(\varepsilon + \frac{\varepsilon^2}{2}m\right)(1 - \lambda n) - \left(1 + \varepsilon m + \frac{\varepsilon^2}{2}m^2\right)\lambda$$

$$C = \frac{\varepsilon^2}{2}n(1 - \lambda n); \quad D = \frac{\varepsilon^2}{2}(1 - \lambda n) - \left(\varepsilon + \frac{\varepsilon^2}{2}m\right)\lambda$$

$$M = -\frac{\varepsilon^2\lambda}{4}$$

In our calculations we took dilute solutions of a strong monobasic acid in a mixture of water and alcohol of fixed composition* as standard states of the values of H_0 for aqueous–propanol solutions. Hence the coefficient ε depends on the ratio of $C^0_{H_2O}$ to C^0_{ROH}. The coefficients ε' and ε were determined for each experiment in the following manner. The molalities of the initial $(55.5(y - z_0)/(C^0_{H_2O} + C^0_{ROH}))$ aqueous–alcoholic HBr and HBr/H_2SO_4 solutions and the aqueous–alcoholic HBr and HBr/H_2SO_4 solutions obtained at the end of the reaction $(55.5(y - z_T - x^\infty)/(C^0_{H_2O} + C^0_{ROH}))$ were calculated. Using the tabulated data, we found the values of H_0 for aqueous solutions of H_2SO_4 with the same molalities at the experimental temperature. The values of ε' were calculated by the simultaneous solution of the two equations (6). The values of ε were subsequently calculated using the known values of ε' and β. The values of H_0 for aqueous solutions at 80°C were determined using the linear relationship between H_0 and $1/T$ over a range from 25-90°C using the data cited in [3]. The points for 80°C did not lie on this line and they were not taken account of in constructing the graph. The kinetic curves for the hydrobromination of n-propyl alcohol are completely described by Eq. (10). Values of $(k_1')_0/(1 - K_p)$ were calculated from the tangent of the slope of the line plotted in the coordinates of Eq. (10). The values obtained for the constants $(k_1')_0$ are presented in Table 1. In the experiments without H_2SO_4, $(k_1')_0$ is the effective rate constant for hydrobromination in a solution with a constant acidity equal to $(h_0)_{in}$ subject to the condition that the volume of the solution does not vary during the course of the reaction.

In experiments with solutions of the reagents in H_2SO_4 $(k_1')_0$ is the ratio of the rate of reaction to the current total concentration of the alcohol (the totals of that not bound in the alkyl acid of the alcohol and of the alkyl acids) and HBr. Hence, $(k_1')_0$ includes the factor $(1 + \beta)/\beta$ which takes account of the fraction of the overall concentration of the alcohol which is in the reactive form. We denote the rate constant obtained after making allowance for the fraction of the reactive form of the alcohol by k_1 and according to [1]

$$k_1 = (k_1')_0 \frac{1 + \beta}{\beta}$$

As would be expected, k_1 varies linearly with the acidity $(h_0)_{in}$ · $\log k_1 + gH_0 = \text{const}$, $g = 0.99 \pm 0.01$, const = -5.92 ± 0.04.

It was found in [1], using an initial concentration of alcohol equal to ~ 0.75 mole/liter, that $g = 1.00 \pm 0.04$, const = -5.98 ± 0.13. The errors in these constants were calculated at a confidence level of 0.95 without taking account of the errors in the parameters h_0 and β. In [1], the errors in g and const were greater than in the present work which may be attributable to the failure to take account of the variation in h_0 during the course of the experiment. It should be noted that, when allowance is made for the variation in h_0, the main error in k_1 is introduced by the factor $(1 + \beta)/\beta$. This error lies within the bounds of 5-15% since β is calculated as the difference between two large quantities and the lower the concentration of the alcohol, the greater the error in β. Thus, the values of k_1/h_0, within the limits of the errors in the measurements, are the

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* As the result of the reaction taking place in the solution there is a small change in the ratio between the alcohol and water but we have neglected this in the calculations.

same in experiments with relatively low (~ 0.75 mole/liter) and high (up to 4.2 mole/liter) concentrations of alcohol in aqueous solutions of HBr, H_2SO_4, and H_2SO_4 with HBr.

As has already been mentioned above, its own standard state was chosen in calculating H_0 for each mixture of water and alcohol: a dilute solution of a strong monobasic acid in the mixture. If the values of h_0 of a dilute solution of the strong acid in water and in aqueous–propanol solutions containing up to 4.2 mole/liter C_3H_7OH are equal to the concentration of the acid then it may be asserted that, in these solutions, the true rate constant for the hydrobromination of alcohol is independent of the composition of the medium. If, however, at the same concentrations of the acid, the values of h_0 are different in the dilute aqueous and aqueous–alcoholic solutions of the strong acid then the result which is obtained is a consequence of a change in the acidity of the medium which has been referred to a single standard state and a change in the true rate constant.

CONCLUSIONS

1. The kinetic laws for the hydrobromination of n-C_3H_7OH by hydrogen bromide at 80°C in a solution with and without additions of H_2SO_4 have been investigated.

2. A method is proposed for taking account of the reduction in the acidity of the medium due to the consumption of HBr from the solution during the hydrobromination reaction. The kinetic curves are described by a second order equation for the reactions involving the formation of n-C_3H_7Br and its hydrolysis.

3. When the reagents are mixed, an equilibrium is rapidly achieved between n-C_3H_7OH, H_2SO_4, and n-$C_3H_7OSO_2OH$. The alkyl acid is unreactive in the hydrobromination of n-propyl alcohol.

4. The rate of reaction, referred to the current concentrations of HBr and the alcohol which is not bound up in the alkyl acid, varies proportionally to the acidity of the medium h_0. A dilute solution of the strong acid in the mixture was chosen as the standard state. At 80°C, this law is obeyed up to 4.2 mole/liter n-propanol in the solution.

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REACTION OF o-PHTHALONITRILE WITH ANILINE

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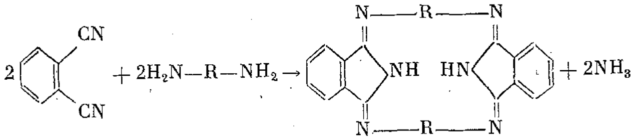
The work reported here is a continuation of our studies of the relationships and mechanism of formation of nitrogen-containing macroheterocycles, hexazocyclanes, which are obtained by the condensation of o-phthalonitrile with diamines in phenols



Since this reaction is complex and proceeds in many stages, it appeared desirable to investigate the reaction of phthalonitrile with a monoamine, aniline, as this reaction can be regarded as a model of the interaction of phthalonitrile with diamines.

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