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KINETICS OF THE LIQUID-PHASE HYDROBROMINATION OF ACETYLENE IN THE PRESENCE OF MERCURY SALTS

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A very limited number of works have been devoted to questions concerning the study of the liquid-phase catalytic interaction of acetylene with hydrogen halides in the presence of mercury salts (1,2). As a rule, these processes were studied under nonstationary conditions.

The hydrobromination of acetylene in the presence of mercury salts has been studied only in the vapor phase. There are indications that, in addition to vinyl bromide, various isomers of dibromoethane or their mixture are obtained (3), whereas for the reactions of hydrochlorination and hydroiodination under analogous conditions only asymmetric adducts were identified among the dihalo derivatives. In view of the possibility of obtaining both isomers of dibromoethane in the liquid-phase hydrobromination reaction, we considered a detailed study of this reaction to be of interest.

The investigations were carried out in an apparatus providing continuous feed of a mixture of precisely metered volumes of acetylene and hydrogen bromide, carefully purified of impurities, through a Schott filter into a reactor filled with contact solution. The latter was a solution of mercuric bromide in hydrobromic acid, the concentration of which corresponded to the saturation limit at the temperature of the experiment.*

From the vapor–gas mixture leaving the reactor, dibromoethane and vinyl bromide were condensed successively in a water condenser and in traps cooled with dry ice and acetone. Unreacted hydrogen bromide was absorbed by a known excess of titrated alkali; the return acetylene was collected in a special vacuum gasometer.

All experiments were carried out at a temperature of 100 ± 0.5° and a vacuum of 90–100 mm Hg, which ensured complete removal of the reaction products from the contact solution when conducting the process under stationary conditions. The volume of the contact solution in all experiments was 175 ml.

Distillation of the high-boiling condensates, washed with soda solution and water, from all cycles of acetylene hydrobromination experiments confirmed the

Fig. 1

Figure 1: Fig. 1

formation in the process indicated, in addition to vinyl bromide, of pure 1,1-dibromoethane (b.p. 107–108.5°, $n_D^{19} = 1.5126$).

A. Effect of the ratio of reagents on the degree of conversion of acetylene. In this series of experiments a contact solution with a concentration of $HgBr_2$ of 200 g/100 was used; the molar ratios $HBr : C_2H_2$ were varied within the limits $0.5 \div 4$ at a constant total volumetric rate of the reagents of 5.82 ± 0.18 l/hr, which corresponds to a contact time (τ) of 37.25 ± 1.1 sec.

It was found that both the overall degree of conversion of acetylene and the yield of vinyl bromide and ethylidene dibromide do not depend on the ratio of the reagents within the limits indicated above. The dependence obtained permits with complete obviously, to establish a zero kinetic order of the reaction with respect to hydrogen bromide.

B. Effect of contact time on the rate of hydro-bromination of acetylene. The experiments were carried out with a contact solution of the composition indicated above, at a constant ratio $\mathrm{HBr} : \mathrm{C_2H_2} \simeq 1 : 1$. The total volumetric flow rate of the reactants was varied within the range of 2–20 ml/hr, which corresponds to a contact time of 200–20 sec. The experimental results are presented in Fig. 1. Noteworthy is the relatively small change in the degree of conversion of acetylene (α_0) with τ (when the latter is increased 10-fold, the yield of reaction products increases only about threefold). This fact may be connected with considerable inhibition of the reaction by its products.

Fig. 1

Analysis of the experimental data shows that the ratio of the yields of the reaction products (vinyl bromide (α_1) and ethylidene dibromide (α_2)) does not depend on τ, fluctuating around the value

$$n = \frac{\alpha_1}{\alpha_2} = 2.61 \qquad (1)$$

within ±0.3, which can occur only in the presence of two independent parallel reactions obeying identical kinetic equations:

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* In view of a certain change in the concentration of HBr in the contact solution after dissolution of $HgBr_2$ upon heating to the temperature of the experiment, in the following presentation, for characterization of the composition of the contact solution, the number of grams of $HgBr_2$ per 100 g of H_2O (g/100) is used.

$$C_2H_2 + HBr \rightarrow CH_2{=}CHBr, \tag{a}$$

$$C_2H_2 + 2HBr \rightarrow CH_3{=}CHBr_2. \tag{b}$$

If this assumption is valid, the following equalities must hold:

$$K_0 = K_1 + K_2, \tag{2}$$

$$\frac{K_1}{K_2} = \frac{\alpha_1}{\alpha_2} = n = \text{const}, \tag{3}$$

where K_0, K_1, and K_2 are the rate constants of the overall conversion of acetylene, and of the formation of vinyl bromide and ethylidene dibromide, respectively.

The only kinetic equations satisfying the experimental data proved to be those derived by us from the assumption that both parallel reactions, each first order with respect to acetylene, are inhibited by both reaction products, with the degree of inhibition equal to unity. In general differential form these equations will have the form:

$$\frac{d\alpha_i}{d\tau} = K_i \frac{1-\alpha_0}{\alpha_0}. \tag{4}$$

From the relation $\alpha_0 = \alpha_1 + \alpha_2$ and equality (1) it follows that:

$$\alpha_0 = S\alpha_1 = (n+1)\alpha_2 \quad \text{and} \quad \alpha_1 = n\alpha_2, \tag{5}$$

where the operator S has the value

$$S = \frac{n+1}{n} = \text{const} = 1.382. \tag{6}$$

As a result of the corresponding substitutions and integration, the following expressions were obtained:

a) for the overall conversion of acetylene

$$K_0 = \frac{1}{\tau}\left(\ln\frac{1}{1-\alpha_0} - \alpha_0\right); \tag{71}$$

b) for the vinyl bromide formation reaction

$$K_1 = \frac{1}{\tau}\left(\frac{1}{S}\ln\frac{1}{1 - S\alpha_1} - \alpha_1\right); \tag{72}$$

c) for the ethylidene dibromide formation reaction:

$$K_2 = \frac{1}{\tau}\left(\frac{1}{n+1}\ln\frac{1}{1 - (n+1)\alpha_2} - \alpha_2\right). \tag{73}$$

The experimental values of α_i and the values of K_i calculated from equations (7) are summarized in Table 1.

Table 1

No.	τ, sec	α_0, %	α_1, %	α_2, %	n	$K_0 \cdot 10^4$	$K_1 \cdot 10^4$	$K_2 \cdot 10^4$
1	21.75	16.05	11.1	4.95	2.25	7.26	5.24	1.582
2	37.25	19.21	14.2	5.01	2.83	6.35	5.10	2.34
3	79.9	28.75	20.0	8.75	2.29	6.82	5.32	2.13
4	206.0	45.6	33.3	12.3	2.71	7.72	5.68	1.99
5	224.0	46.15	34.6	11.55	2.98	7.25	5.67	1.558
				Average . . .	2.61	7.08	5.42	1.92

The attainment of sufficiently good agreement among the K_i, whose mean values satisfy conditions (1) $\left(K_1 + K_2 = 7.34 \cdot 10^{-4},\ \frac{K_1}{K_2} = 2.82\right)$, confirms the assumptions stated above.

Thus, the kinetic measurements show the following: 1) the formation of 1,1-dibromoethane in the hydrobromination reaction of acetylene is the result of the direct simultaneous addition of two HBr molecules to C_2H_2, without the participation of vinyl bromide as an intermediate product, i.e., the reactions of vinyl bromide and ethylidene dibromide formation are two independent parallel reactions; 2) both parallel reactions are first order with respect to acetylene, with inhibition by both reaction products.

The parallel character of the reactions in the hydrobromination of acetylene is additionally confirmed by direct experimental evidence—the formation of another isomeric dibromoethane when vinyl bromide interacts with HBr. When vinyl bromide was hydrobrominated under analogous conditions, a reaction considerably slower than in the case of acetylene was observed (the degree of conversion of vinyl bromide was 8–10%, whereas the degree of conversion of acetylene was 30–35%), and the dibromo product proved to be almost pure 1,2-dibromoethane (b.p. 126.5–130°, $n_D^{23} = 1.5340$).

B. Effect of the concentration of mercuric bromide in the contact solution on the rate of hydrobromination of acetylene. This series of

Fig. 2

Figure 2: Fig. 2

experiments was carried out at a constant total volumetric flow rate of the reactants of 6.05 ± 0.42 nl/hr at the inlet to the reaction column, with a ratio $HBr : C_2H_2 \simeq 1 : 1$, on four samples of contact solutions containing $HgBr_2$ at 60, 150, 275, and 400 g/100. Measurements were made after 1.5–2 hours of operation, following a preliminary 15-minute purge with a mixture of nitrogen and HBr at the indicated rate, in order to attain the equilibrium concentration of HBr in the contact solution.

As is evident from Table 2, α_0 increases monotonically with increasing concentration of $HgBr_2$, α_1 passes through a maximum, and α_2 increases rather sharply.

Table 2

No.	C_{HgBr_2}	α_0, %	α_1, %	α_2, %	τ, sec	$K_0 \cdot 10^4$	$K_1 \cdot 10^4$	$K_2 \cdot 10^4$	lg$(K_0 \times 10^4)$	lg$(K_1 \times 10^4)$	lg$(K_2 \times 10^4)$	ε, V	$\frac{HBr}{HgBr_2}$
1	60	7.6	7.58	0	74.3	7.0	7	0	0.845	0.845	–	0.4935	10.80
2	150	27.7	25.4	2.3	83.5	43.8	40	3.8	1.641	1.602	0.580	0.5248	4.21
3	275	35.4	23.4	12.0	90.5	70.7	46.7	24.0	1.845	1.669	1.380	0.5414	2.25
4	400	41.8	20.7	21.0	97.1	134.0	66.2	67.8	2.127	1.821	1.831	0.5514	1.489

The indicated fact may be interpreted as an increase in the probability of a triple collision of an acetylene molecule with two catalyst molecules when the concentration of $HgBr_2$ is increased. It is known that in a solution of hydrobromic acid $HgBr_2$ forms stable complex anions: $HgBr_3'$ and $HgBr_4''$. The molar ratios $HBr : HgBr_2$ calculated by us (see Table 2) for the contact solutions tested convincingly show that practically all the mercury in the solution is present only in a complex-bound form and that, as the concentration of $HgBr_2$ in the contact solution increases, the concentration of the anion $HgBr_3'$ increases.

Fig. 2

There is every reason to believe that the reaction is catalyzed by the latter anion. The ion $HgBr_4''$, being coordinatively saturated, can hardly participate in the activation of acetylene. In addition, its concentration decreases with increasing concentration of $HgBr_2$ in the solution, which is due to an increase in the ratio $HgBr_2 : HBr$.

On the basis of the kinetic equations (7), for all four catalyst concentrations the rate constants of the reactions K_0, K_1, and K_2 were calculated; the values of each of these increase with increasing concentration of $HgBr_2$, with K_2 increasing faster than K_1 (see Table 2).

We suppose that activation of acetylene consists in the withdrawal by the catalyst of the π-electron doublet. If the rate-limiting stage of the acetylene hydrobromination process is activation of the latter, then there should be a correlation between the oxidizing potential of the contact solution, as a measure of its acceptor ability, and its catalytic activity. The oxidizing potentials of the contact solutions (ε) were measured at $t = 95 \pm 0.1^\circ$ according to a method previously described by one of the authors (4).

As is evident from Fig. 2, the linear dependence between $\lg K$ and ε is preserved for both hydrobromination reactions and for the overall conversion of acetylene; moreover, the only possible reason for the increase in the rate of the reactions with increasing ε is a decrease in the activation energy. The linearity of the function $\lg K = \varphi(\varepsilon)$ makes it possible to assert that the rate-limiting stage of the hydrobromination processes is activation of acetylene.

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CITED LITERATURE

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