

The Effect of Mercuric Bromide on the Hydrolysis of Acetobromoglucose in Acetone

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In an earlier investigation ¹ it was found that the reaction between mercuric bromide, water and α -acetobromoglucose is of the second order, depending on the concentrations of mercuric bromide and acetobromoglucose and that β -2,3,4,6-tetraacetylglucose is the product of hydrolysis. Reactions between mercuric salts, water and R. Hal have earlier been studied by Nicolet and Stevens ², Roberts and Hammet ³, Read and Taylor ⁴, and Gand ⁵. Nicolet and Stevens find that the hydrolysis is catalysed by mercuric bromide, which seems to be deactivated by the reaction $\text{HgBr}_2 + 2\text{Br} \rightarrow \text{HgBr}_4^{2-}$.

Roberts and Hammet suppose that a carbenium ion is an intermediate in their reaction between benzylchloride, mercuric nitrate and water. The reaction is of the second order but is disturbed by the mercuric chloride formation and by a new substance $\text{C}_7\text{H}_7\text{OHgCl}$. Read and Taylor on the other side have found that the reaction $\text{RBr} + \text{H}_2\text{O} \rightarrow \text{ROH} + \text{HBr}$ [$\text{R} = -\text{CH}_3$, $-\text{O}_2\text{H}_5$, $-\text{CH}(\text{CH}_3)_2$ and $-\text{C}(\text{CH}_3)_3$.] is accelerated by mercuric bromide, but they did not get satisfactory rate constants unless they introduced an initial concentration of hydrogen bromide.

As the reaction α -acetobromoglucose + $\text{HgBr}_2 + \text{H}_2\text{O} \rightarrow \beta$ -2,3,4,6-tetraacetylglucose + HHgBr_3 differs from reactions of similar type it has been examined more closely. The reaction was followed in a polarimeter, so to interpret the data the mutarotation of β -2,3,4,6-tetraacetylglucose in acid medium had to be investigated (Table 1 and 2).

With Arrhenius equation one gets the activation energy 28700 cal. $k = 10^{19.6} \cdot e^{-28700/RT}$.

Table 2 gives the variation of k with the concentrations of water and hydrogen bromide.

Table 1. Mutarotation of β -2,3,4,6-tetraacetylglucose in acid solutions of various acidity and temperature.

1 mmole β -2,3,4,6-tetraacetylglucose, 1 mmole mercuric bromide, hydrogen bromide, acetone with 1% water ad 20 ml.

t° C	mmole HBr	10 ³ k min ⁻¹
15	1	5.5 ± 0.2
20	0.5	5.0 ± 0.2
20	1	12.6 ± 0.3
25	1	31.1 ± 0.3
30	1	67 ± 3

Table 2. Mutarotation of β -2,3,4,6-tetraacetylglucose in acid solutions of various water concentrations.

20.0° C · 0.5000g β -2,3,4,6-tetraacetylglucose, hydrogen bromide, water and acetone ad 20 ml.

mmole HBr	% H ₂ O	10 ³ k min ⁻¹
0.641	2	13.3 ± 0.1
1.30	1	122 ± 1
1.27	2	28.9 ± 0.5
1.28	4	7.98 ± 0.2
2.56	2	96.0 ± 1

The velocity increases with the hydrogen bromide concentration but the relation is not linear. Water is a negative catalyst as would be expected. As a base it neutralizes the acid that catalyses the reaction.

Table 3. Variation of the concentrations of acetobromoglucose and mercuric bromide.

20.0° C. Mercuric bromide, α -acetobromoglucose and acetone with 1% water ad 20 ml.

mmole HgBr ₂	mmole abg.	k liter · mole ⁻¹ · min ⁻¹
1.00	1.50	3.52 ± 0.05
1.00	1.00	3.44 ± 0.04
1.50	1.00	3.63 ± 0.05

Table 4. Effect of the temperature upon the second order reaction. 1 mmole mercuric bromide, 1 mmole α -acetobromoglucose, acetone with 1 % water ad 20 ml.

t° C	k liter · mole ⁻¹ · min ⁻¹
15	2.48 ± 0.02
20	3.44 ± 0.04
25	4.76 ± 0.04
30	6.70 ± 0.05

With Arrhenius equation one gets the activation energy 11600 cal · $k = 10^9$,²². $e^{-11000/RT}$.

From the results in Table 3 it is clear that the reaction is of the first order with regard to both acetobromoglucose and mercuric bromide. That the mercuric bromide that is consumed reacts to HHgBr₃ has already been proved¹ in two runs where the same amounts of acetobromoglucose reacted firstly with 0.567 mmole mercuric bromide, secondly with 1.013 mmole mercuric bromide + 0.451 mmole hydrogen bromide. The initial concentration of mercuric bromide, not bound as HHgBr₃, was the same in the two runs and the velocity of the reaction was also the same.

A few runs have been made at higher water concentrations (2 and 4 %). Here the mutarotation is slower and the corrections are smaller (Table 5).

Table 5. Effect of water concentration upon the second order reaction. 1 mmole acetobromoglucose, 1 mmole mercuric bromide, water and acetone ad 20 ml 20.0° C.

% H ₂ O	k liter · mole ⁻¹ · min ⁻¹
1	3.44 ± 0.04
2	4.19 ± 0.04
4	4.61 ± 0.04

The velocity increases slightly with the water concentration.

One acetolysis of α -acetobromoglucose has also been made in order to see if this reaction too proceeds with Walden's inversion. α -Acetobromoglucose was acetolysed in a mixture of acetic anhydride, acetic acid and sulfuric acid. This mixture is not stable, so an isomerisation of β -pentaacetylglucose to α/β -pentaacetylglucose had to be run at the same time with the same solution. A kinetic analysis proves that the α -acetobromoglucose first gives β -pentaace-

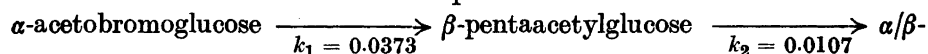
tylglucose, which then reacts to α/β -pentaacetylglucose. The experimental data and calculations based upon two theories (1 and 2 below) are given in Table 6.

Table 6. Acetolysis of acetobromoglucose.

(The table gives only a part of the observed values.) 0.500 g acetobromoglucose, 20 ml of a mixture of 50 ml acetic anhydride, 20 ml acetic acid and 3 ml sulfuric acid, 20.0° C.
 α -pentaacetylglucose \rightarrow α/β -pentaacetylglucose. $k = 0.0107 \text{ min}^{-1}$.

t min	α found	α calc.	
		1	2
0	9.21		
30	7.27	7.27	7.42
60	6.29	6.32	6.33
90	5.73	5.77	5.65
120	5.39	5.43	5.25
180	5.00	5.04	4.85
240	4.84	4.83	4.70
1200	4.62		

1. It is assumed that the reaction proceeds:



pentaacetylglucose.

2. It is assumed that the reaction proceeds: α -acetobromoglucose $\xrightarrow{k = 0.0165}$ α/β -pentaacetylglucose. (The best value.)

As the values calculated according to 1 show a maximum deviation of only 0.04, and those according to 2 deviate consistently over the entire range of values, it is clear that the acetolysis involves Walden's inversion.

The effect upon configuration by hydrolysis of compounds R · Hal, catalysed by mercuric salts, has not been observed earlier. The similar reaction, catalysed by silver salts, has however been studied in detail⁶. Here one generally finds inversion and a little racemisation.

The steric course of the reactions catalysed by silver salts is similar to that of the homogenous, unimolecular substitution (S_N1), so it is natural to suppose a similar mechanism. The rôle of the silver salts should be to facilitate the dissociation of the halogen ion. In the reaction studied here the rôle of the mercuric bromide is clear. A molecule HgBr_2 combines with a Br^- from the acetobromoglucose, and gives HgBr_3^- , which under the reaction conditions cannot react further. The resulting carbenium ion then reacts rapidly with water

and gives 2,3,4,6-tetraacetylglucose and H^+ . Unfortunately it is impossible to give a value for the optical purity of the 2,3,4,6-tetraacetylglucose formed, but from the data it is evident that it is rather pure, at least 90 % or higher.

The investigation of the effect of mercuric bromide on hydrolysis of R · Hal will be continued with β -*n*-octylbromide. The intention is to follow the hydrolysis with both polarimetrical and analytical methods.

EXPERIMENTAL

The acetobromoglucose was prepared by a method of Freudenberg ⁷ and recrystallized from ethyl ether.

The β -2,3,4,6-tetraacetylglucose was prepared by a method in Org. Syntheses ⁸.

The mercuric bromide was Merck's pro analysi. The acetone was dried over potassium carbonate and distilled. All reactions were made in polarimeter tubes with mantles, through which water from a thermostat circulated. The temperature of the thermostat fluctuated 0.1° C from the mean value, the fluctuations in the tube were smaller. In a typical run (Table 1). 1 mmole β -2,3,4,6-tetraacetylglucose was dissolved in 20 ml of a solution of 1 mmole mercuric bromide and 1 mmole hydrogen bromide in acetone with 1 % water. This solution was preheated in the thermostat to 25° C and as quickly as possible the solution was transferred to a polarimeter tube, 20 cm long. The rotation was determined at definite intervals.

t min	α	$10^2 \cdot \frac{1}{t} \log \frac{\alpha_\infty - \alpha_0}{\alpha_\infty - \alpha}$
0	0.20	
5	0.53	1.32
10	0.82	1.35
15	1.01	1.24
20	1.26	1.33
30	1.60	1.34
40	1.88	1.40
50	2.07	1.42
60	2.16	1.35
70	2.27	1.38
80	2.34	1.39
90	2.38	1.36
120	2.46	1.33
1200	2.52	

Mean value 1.35 ± 0.01

$K = (3.11 \pm 0.03) 10^{-2}$

In another typical run 1 mmole acetobromoglucose was dissolved in 10 ml acetone at 25° C and put in the thermostat. After 15 minutes 10 ml of a similar preheated solution

of 1 mmole mercuric bromide in acetone with 2 % water was added. As quickly as possible the solution was transferred to the polarimeter tube and the rotation determined at definite intervals.

(Only a part of the observed values is given here.)

t min	a	$a_0 - a$	$(a_0 - a)$ corr	x %	$\frac{1}{t} \cdot \frac{x}{a(a-x)}$
0	7.60	0			
2	5.29	2.31	2.32	31.9	4.69
4	3.98	3.62	3.67	48.9	4.79
6	3.31	4.29	4.39	58.6	4.72
8	2.86	4.74	4.90	65.4	4.73
10	2.53	5.07	5.31	70.8	4.85
12	2.40	5.20	5.52	73.6	4.65
14	2.24	5.36	5.76	76.8	4.73
16	2.14	5.46	5.95	79.4	4.82
18	2.07	5.53	6.10	81.3	4.83
20	2.02	5.58	6.24	83.2	4.95
25	1.93				
50	2.12				
1200	2.80				

Mean value 4.76 ± 0.04

The values were determined with 1 min intervals. In order to correct for the mutarotation of 2,3,4,6-tetraacetylglucose, as a first approximation the mutarotation was disregarded and the fraction β -2,3,4,6-tetraacetylglucose formed under each interval calculated.

From the velocity constant for the mutarotation it was calculated how much β -2,3,4,6-tetraacetylglucose had reacted to α -2,3,4,6-tetraacetylglucose and what this corresponded to in terms of optical rotation. In this calculation it was assumed that the velocity of the mutarotation varied in a linear way with respect to the concentration of HHgBr_3 , which is the same as the overall concentration of 2,3,4,6-tetraacetylglucose. Another assumption is that pure β -compound is formed by the hydrolysis. This assumption is justified by the consistency of the calculated reaction velocity constants. A repetition of this approximating calculation only led to corrections within the precision of the experiment.

SUMMARY

The rate of the reaction between mercuric bromide, α -acetobromoglucose and water has been determined in acetone at various relative concentrations and temperatures. The reaction was found to be of the first order with respect to both mercuric bromide and acetobromoglucose and was found to involve Walden's inversion. The concentration of water did not influence the velocity very much. The parameters of the Arrhenius' equation for the reaction were

determined. In order to interpret the data for this reaction, the mutarotation of 2,3,4,6-tetraacetylglucose in acid solutions of acetone-water has been studied. The acetolysis of acetobromoglucose with sulfuric acid has been shown to involve Walden's inversion.

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