On the Hydrolysis of Polysaccharides, I The Influence of Neutral Salts on the Acid Inversion of Sucrose

By

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In a course of the study of polysaccharides in our laboratory, the hydrolytic velocity of sucrose by the mineral acids was noticed to be modified to some extent by the presence of their salts, and the present communication deals with the experimental results.

In connection with the catalytic hydrolysis of sucrose in acid solution, especially in the presence of neutral salts, a large amount of research work has been done to confirm that the salts exert an influence on the reaction, and most of the investigators have attempted to explain this phenomenon in terms of the activity of the hydrogen ions in the reaction system[1].

According to H. Colin and A. Chandun the velocity of the hydrolysis of sucrose by HCl in the presence of neutral salts (KCl, KBr) depends not only upon the concentration of the salts but on that of the sucrose[2].

A solution of 20 gms. of purified sucrose was mixed with sulphuric acid and the salts, which diluted to 100 c.c. would give their desired concentration. The solution was transferred to the polarimeter tubes, and the readings taken at different time intervals, the temperature being maintained at 25°, 30° and 35°.

The reaction velocity constants were calculated according to the

1. Caldwell: Report Brit. Assoc. Adr. Sci., (1906) 267; W. C. Mc Lewis: Trans. Faraday Soc., **17**, 573 (1922); C. F. Kantz & A. L. Robinson: Jour. Am. Chem. Soc., **50**, 1023 (1928).

2. C. R., **192**, 1929 (1931).

formula: $K=\frac{2\,30}{t}\log\frac{\alpha_0-\alpha_\infty}{\alpha-\alpha_\infty}$,

t being the time in minutes, α_0 the initial rotation, α the rotation at a time t, α_∞ the final rotation.

20 % Sucrose, $\frac{N}{1}$ H_2SO_4, t=25°.

Time in minutes	α	K
0	6.68°	
81	5.33	0.00212
106	5.00	206
126	4.38	248
169	4.00	222
204	3.53	225
267	2.85	222
321	2.13	236
402	1.54	228
452	1.13	231
∞	1.87	

Mean 0.00226

$\frac{N}{1}$ H_2SO_4, t=30°.

Time in minutes	α	K
0	12.98°	—
48	9.38	0.00504
82	7.35	499
100	6.30	508
129	4.91	509
168	3.40	518
207	2.04	511
260	0.63	538
300	−0.22	517
379	−1.47	523
∞	−3.77	—

Mean 0.00514

$\frac{N}{1}$ H_2SO_4, t=35°.

Time in minutes	α	K
0	6.68°	
21	4.98	0.0104
41	3.78	099
59	2.53	110
75	2.20	098
103	1.43	090
143	0.43	089
183	−0.45	094
253	−0.99	085
∞	−2.00	

Mean 0.0096

$\frac{N}{1}H_2SO_4+\frac{N}{10}Fe_2(SO_4)_3$, t=25°.

Time in minutes	α	K′
	6.68°	
59	5.58	0.00233
86	5.23	216
118	4.48	252
145	4.21	235
185	3.78	224
235	3.20	222
305	2.10	251
385	1.36	253
435	1.08	244
∞	−1.87	

Mean 0.00237

20 % Sucrose, $\frac{N}{1}$ H_2SO_4 + $\frac{3N}{10}$ $FeSO_4$, t=25°.

Time in minutes	α	K′
0	12.78	
58	11.36	0.00153
123	9.53	146
156	8.83	174
243	6.88	179
306	6.01	170
363	4.83	178
453	4.38	154
573	1.91	183
∞	−3.92	

Mean 0.00167

$\frac{N}{1}H_2SO_4+\frac{N}{50}$ $FeSO_4$,

Time in minutes	α	K′
	6.78	
25	5.68	0.00544
51	4.96	467
83	3.88	491
114	3.03	516
152	1.71	580
203	1.36	485
240	0.76	496
∞	−1.87	

Mean 0.00511

$\frac{N}{1}H_2SO_4+\frac{N}{25}$ $FeSO_4$, t=30°.

Time in minutes	α	K′
	6.39	
22	5.63	0.00441
49	5.02	372
82	3.86	492
112	3.03	469
152	1.86	527
202	1.40	463
239	0.78	481
∞	−1.82	

Mean 0.00464

$\frac{N}{1}H_2SO_4+\frac{N}{2}FeSO_4$,

Time in minutes	α	K′
	7.18	
15	6.63	0.00406
46	5.75	363
71	4.88	400
89	4.63	360
132	3.75	348
173	2.76	372
271	1.26	373
331	0.42	392
388	0.13	365
∞	−2.12	

Mean 0.00375

$\frac{N}{1}H_2SO_4+\frac{N}{1}FeSO_4$, t=30°.

Time in minutes	α	K′
	6.96	
39	5.70	0.00394
70	4.88	383
89	4.40	384
126	3.78	354
173	2.88	350
223	1.88	384
276	1.38	363
332	1.03	335
388	0.88	300
∞	−0.187	

Mean 0.00361

$\frac{N}{1}H_2SO_4+\frac{N}{25}CuSO_4$, t=30°.

Time in minutes	α	K′
	6.73	
32	5.43	0.00515
45	4.98	508
80	3.93	495
101	3.18	531
185	1.58	497
245	0.62	511
287	0.02	535
358	−0.37	495
∞	−1.82	

Mean 0.00511

$\frac{N}{1}H_2SO_4+\frac{N}{50}Fe_2(SO_4)_3$, t=30°.

Time in minutes	α	K′
	13.13	
71	8.13	0.00500
111	5.63	536
164	3.40	532
215	1.85	523
269	0.32	541
329	−0.49	513
391	−1.49	532
∞	−3.57	

Mean 0.00525

$\frac{N}{1}H_2SO_4+\frac{N}{25}Fe_2(SO_4)_3$, t=30°.

Time in minutes	α	K′
	6.63	
37	5.13	0.00542
70	3.90	573
112	2.62	594
165	1.31	627
215	0.71	587
269	0.13	576
329	−0.37	573
∞	−1.62	

Mean 0.00582

$\frac{N}{1}H_2SO_4+\frac{N}{25}Fe_2(SO_4)_3$, t=30°.

Time in minutes	α	K′
	6.73	
33	5.28	0.00567
45	5.02	499
80	3.95	495
100	3.38	496
155	2.01	523
185	1.61	499
245	0.38	562
286	0.23	507
358	−0.23	478
∞	−1.76	

Mean 0.00514

$\frac{N}{1}H_2SO_4+\frac{N}{25}Al_2(SO_4)_3$, t=30°.

Time in minutes	α	K′
	6.76	
47	5.13	0.00451
81	4.18	444
100	3.56	470
128	2.78	490
168	2.18	458
206	1.51	442
258	0.88	453
298	0.15	500
381	−0.27	456
∞	−1.77	

Mean 0.00463

$\frac{N}{1}H_2SO_4+\frac{3N}{10}FeSO_4$, t=35°.

Time in minutes	α	K′
	6.68	
24	5.51	0.00613
48	4.40	646
68	3.48	689
109	2.13	696
150	1.61	599
218	0.13	666
277	−0.42	640
∞	−1.87	

Mean 0.00650

20 % Sucrose, $\frac{N}{1}H_2SO_4+\frac{N}{10}Fe_2(SO_4)_3$, t=35°.

Time in minutes	α	K′
	6.68	
14	5.53	0.0104
33	3.88	122
54	3.28	95
94	1.61	97
135	0.38	100
203	−0.79	105
264	1.78	
66		
		Mean 0.0104

In the following table, the first column gives the concentration of the salt, the second the velocity constant (K′) and the third the ratio $\left(\frac{K'}{K}\right)$ of the velocity constant to that (K) obtained in the absence of salt.

t=25°.

	K′	$\frac{K'}{K}$
$\frac{N}{10}Fe_2(SO_4)_3$	0.00237	1.049
$\frac{3N}{10}FeSO_4$	0.00167	0.739

t=30°.

$FeSO_4$	K′	$\frac{K'}{K}$
N/50	0.00511	0.994
N/25	0.00464	0.903
N/2	0.00375	0.730
N/1	0.00361	0.702
$Fe_2(SO_4)_3$		
N/50	0.00525	1.021
N/25	0.00582	1.132
N/25 K_2SO_4	0.00514	1.000
„ $Al_2(SO_4)_3$	0.00463	0.901
„ $CuSO_4$	0.00511	0.994

$t=35°$.

	K′	$\frac{K'}{K}$
$\frac{N}{10}Fe_2SO_{43}$	0.0104	1.083
$\frac{3N}{10}Fe(SO_4)$	0.0065	0.677

The temperature coefficient of the velocity constant $\frac{K_{35}}{K_{25}}$ was found by calculation to be 4.4, 3.9 and 4.2 in the sulphuric acid, $H_2SO_4+FeSO_4$, and $H_2SO_4+Fe_2(SO_4)_3$ solutions respectively.

The velocity of the reaction with sulphuric acid is accelarated by the presence of ferric sulphate within the experimental conditions, but the ferrous salt retards, and the presence of potassium and cupric salts has no effect on, the velocity constant. These facts can not be explained by attributing the phenomena to the change in the degree of ionization of the acid caused by the salts or by "monohydrol" (H_2O) occurring in the solvent.[1]

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1. L. E. Bowe: Jour Phy. Chem., **31**, 291 (1927).