Acid Catalysis in the Mutarotation of *N*-(*p*-Chlorophenyl)-β-D-glucopyranosylamine in Methanolic Medium

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The relationship has been studied between the rate of mutarotation of *N*-(*p*-chlorophenyl)-β-D-glucopyranosylamine and the concentration of a variety of substituted benzoic acids in methanol at 25 °C. Catalytic constants of these acids and of 2,6-dinitrophenol have been found to obey the Brønsted law of catalysis, the value of α being equal to 0.99. The mechanism of specific acid catalysis has been suggested for the anomerisation of *N*-(*p*-chlorophenyl)-β-D-glucopyranosylamine. It is concluded that in methanolic benzoate buffer solutions the reaction is of the general acid catalysis type.

While the mutarotation of sugars has been extensively studied over the past decades,[1,2] that of glycosylamines,[2,3] including nucleosides and other bioactive compounds containing the *N*-glycosidic linkage, has attracted less attention. One of the simpler and stable compounds of this type is *N*-(*p*-chloro)-phenyl-β-D-glucopyranosylamine which readily undergoes mutarotation in the presence of weak acids.[4]

The purpose of this study was to elucidate the mechanism of the acid-catalysed mutarotation of *N*-D-glucosides, which represents a complex reversible process.

Experimental

Reagents.—Methanol was dried with freshly calcined sodium sulphate, then refluxed over iodine-activated magnesium metal[5] and distilled. To remove basic impurities it was again distilled over tartaric acid (0.4 g of the acid per 1 dm^3 of methanol[6]). Finally the solvent was distilled over a Widmer column.

The catalysts were carefully purified by crystallization from water or ethanol–water mixtures.

N-(*p*-Chlorophenyl)-β-D-glucopyranosylamine was prepared by the so-called methanolic method,[7] whereby a mixture of α-D-glucose (10.8 g), methanol (70 cm^3), and previously steam-distilled *p*-chloroaniline (8.4 g) was refluxed for 5 h. After the mixture had been cooled, a precipitate fell out which was filtered off and crystallised twice from 96% ethanol. The m.p. of the product was 146 °C, initial specific rotation $[\alpha_0]^{25}_{546} = -137°$, equilibrium rotation $[\alpha_\infty]^{25}_{546} = -55°$ (*c* 0.579, methanol) (lit.,[8] m.p. 126 °C, $[\alpha]_D = -40°$; $[\alpha_\infty]_D$ −22.5°); m.p. 120–122 °C; $[\alpha]_D = -30°$ (lit.,[9] m.p. 146 °C; $[\alpha_0]^{25}_D$ −112° and $[\alpha_\infty]^{25}_D = -43°$ in methanol) (Found: C, 46.7; H, 5.9; N, 4.6. Calc. for $C_{12}H_{16}NO_5 \cdot H_2O$: C, 46.83; H, 5.91; N, 4.55%). The mass spectrum, taken by the FD technique on a MAT 711 spectrometer, gave *m/z* 289.4 ($M^{+\cdot}$).

In thin-layer chromatography, plates coated with silica gel G (Merck) were used. The R_F values in the system butan-1-ol–acetone (4:5) were 0.24, 0.65, 0.69, and 0.48 for α-D-glucose, *N*-(*p*-chlorophenyl)-α-D-glucopyranosylamine, *N*-(*p*-chlorophenyl)-β-D-glucopyranosylamine and α-methyl-D-glucopyranoside, respectively, whereas in the system butan-1-ol–acetone–water (4:5:1) the respective values were 0.40, 0.80, 0.80, and 0.60.

Measurements.—The rates of the reactions were measured polarimetrically on a Polamat A polarimeter (C. Zeiss, Jena) at 546 nm. The angle α_t was read to an accuracy of ±0.005°. Solutions were placed in 2 dm long water-jacketed tubes maintained at 25 ±0.1 °C. The concentration of the *N*-D-glucoside was 1.9×10^{-2} mol dm^{-3} throughout. After a weighed amount of the *N*-D-glucoside had been dissolved in methanol, a methanolic solution of the catalyst was added and the time of the reaction was recorded from the addition of the catalyst. Rate constants, *k*, were calculated by the least-squares method from the equation

$$\ln(\alpha_\infty - \alpha_t) = kt + \ln(\alpha_\infty - \alpha_0)$$

where *t* is time in minutes, α_0 is the calculated optical rotation of solution at $t = 0$, α_t is the angle of rotation of polarised light at time *t* read on the polarimeter, and α_∞ is the optical rotation at equilibrium. This was kept constant throughout and amounted to −0.60°. Each *k* value in Table 1 is an average of at least ten readings taken over the range $-1.20° < \alpha_t < -0.70°$. The accuracy of the determination of the rate constants was determined by the error (%) defined as $s\% = 100\ s/k$, where *s* is the mean standard error and *k* is the rate constant.

By potentiometric titration[10] based on the determination of $E_{\frac{1}{2}}$ of the indicator electrode at the moment of half-neutralisation of the base, the pK_a value (1.99) of *N*-(*p*-chlorophenyl)-D-glucopyranosylamine in methanol was determined. The measurements were run using a Mera–Elwro Model N 517 pH meter and a combined (glass–AgCl) electrode. Imidazole,[11] *p*-NO_2, *m*-NO_2, *p*-Cl, and *p*-CH_3 aniline derivatives[12] were used as standards. The base (2×10^{-4} mol) was dissolved in methanol (30 cm^3) and titrated with methanolic HCl solution (0.06 mol dm^{-3}). From the determined basicity constant of the *N*-D-glucoside, the equilibrium constant, *K*, was calculated for the reaction of this glucoside (S) and the catalysing acid (HA). Subsequently, the molar concentration of the protonated form of *N*-D-glucoside ($[SH^+]$) was calculated, along with the H^+ ion concentration in each solution (Table 2).

The *k* values measured in buffer solutions are shown in Table 3. Each of the constants was determined with an error of $s < 3\%$. The magnitudes of the errors are not included in Table 3 as most of the values are averages of several measurements. The buffer solutions prepared from benzoic acid ($K_a = 3.8 \times 10^{-10}$ in methanol[13]) and sodium benzoate contained (*a*) 0.1 mol dm^{-3} of the acid and 0.2 mol dm^{-3} of the salt; (*b*) 0.2 mol dm^{-3} of the acid and 0.2 mol dm^{-3} of the salt; (*c*) 0.2 mol dm^{-3} of the acid and 0.1 mol dm^{-3} of the salt.

In each of these solutions (10 cm^3), 0.05794 g of the *N*-D-glucoside was dissolved and variations in optical rotation were measured. Less concentrated solutions, (*a*) Nos. 1–5, (*b*) Nos. 7–11, and (*c*) Nos. 12–18 in Table 3, were prepared by appropriate dilution with methanol.

Table 1. Rate constants, k, of the mutarotation reaction of *N*-(*p*-chlorophenyl)-β-D-glucopyranosylamine in methanol *vs.* catalyst concentration.

Entry	Catalyst	$c/10^{-5}$ mol dm^{-3}	$k/10^{-3}$ min^{-1}	s(%)	$-\alpha_0^0$
1	*p*-Methoxybenzoic acid	0.048	1.80	1.2	1.51
		0.48	2.21	1.3	1.52
		0.95	3.03	0.6	1.52
		2.38	4.03	0.9	1.52
		4.76	5.82	0.9	1.50
		9.52	10.1	0.4	1.50
		47.6	42.8	0.6	1.51
		476	256	0.9	1.48
2	Benzoic acid	7.5	15.4	0.8	1.39
		13.9	34.7	0.6	1.35
		25.0	47.1	2.2	1.44
		40.0	61.9	0.9	1.50
		80.0	101	1.1	1.45
		80.0	128	1.1	1.42
		100	144	2.0	1.42
		100	119	1.2	1.44
		120	163	1.8	1.48
		120	186	1.3	1.42
		137	182	1.3	1.42
		160	212	1.4	1.44
		200	266	2.0	1.35
		200	273	0.9	1.42
		200	273	1.6	1.42
		330	430	1.5	1.48
		393	485	1.7	1.52
3	*m*-Chlorobenzoic acid	20.2	116	1.2	1.33
		20.2	101	1.0	1.34
		20.2	114	1.1	1.51
		20.2	99	1.8	1.50
4	*o*-Chlorobenzoic acid	0.91	24.3	0.6	1.51
		1.82	38.4	0.9	1.50
		3.65	72.8	1.1	1.48
		5.47	106	0.5	1.48
		8.21	161	0.6	1.48
		9.09	180	0.8	1.47
5	2,6-Dinitrophenol	20.2	1 180	2.4	1.46
		20.2	1 110	1.6	1.13
6	*o*-Nitrobenzoic acid	1.00	80.9	2.3	1.53
		2.00	171	0.6	1.40
		3.13	251	0.4	1.46
		4.30	340	0.8	1.43
7	3,5-Dinitrobenzoic acid	2.86	313	0.4	1.49
		3.33	372	0.7	1.57
		3.81	414	0.7	1.55
		4.76	547	0.6	1.46
8	Methanol		1.64	1.4	1.51
			1.49	1.9	1.52
			1.41	2.2	1.40
			1.72	1.3	1.50
			1.57	1.9	1.48

The pH measurements were run by using the above described pH meter calibrated against a methanolic solution of an oxalate buffer[14] (pH 5.79).

Results and Discussion

The acid-catalysed mutarotation of *N*-aryl-D-glucopyranosylamines in methanol[9] has been found to be controlled by reversible conversion of the more stable β anomer into the α one. The reversibility of this reaction is well documented by identical values of the mutarotation rate constants of both the β and α anomers of *N*-(*p*-methylphenyl)-D-glucopyranosylamine. The absence of other processes under these conditions was demonstrated by the fixed value of the optical rotation of solution at equilibrium. This finding was further confirmed by t.l.c. tests which failed to detect glucose and methyl glucoside in the solutions both after the addition of the catalyst and after completion of the reaction. These observations, together with the results of analyses shown in the Experimental section, lead to the conclusion that the substrate is a monohydrate of *N*-(*p*-chlorophenyl)-β-D-glucopyranosylamine (S_β) which undergoes $\beta \rightleftarrows \alpha$ interconversion under the influence of weak acids in methanol.

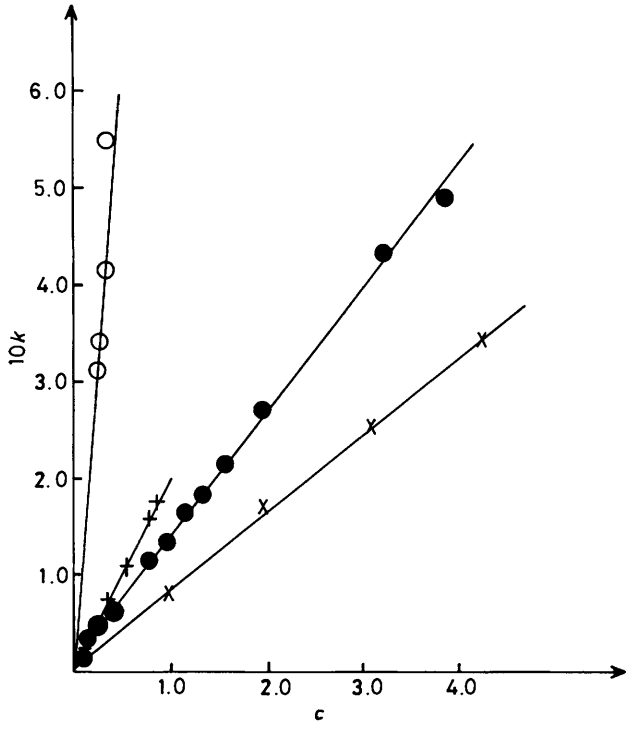


Figure 1. Rate constant k *vs.* concentration of: ●, benzoic acid (10^4 mol dm^{-3}); +, *o*-chlorobenzoic acid (10^6 mol dm^{-3}); ×, *o*-nitrobenzoic acid (10^5 mol dm^{-3}); and ○, 3,5-dinitrobenzoic acid (10^5 mol dm^{-3}).

The rate of anomerisation of *N*-(*p*-chlorophenyl)-β-D-glucopyranosylamine is linearly related to concentration of the acid catalyst (Figure 1) and can be described by equation (1)

$$k = k_c c + k_0 \quad (1)$$

where k is the measured reaction rate, k_c is a measure of catalytic efficiency of the acid, and k_0, which was determined precisely over a large concentration range, is 1.5×10^{-2} min^{-1} for the benzoic acid-catalysed reaction.

Catalytic coefficients for particular acids (Table 4) obey the Bronsted catalysis law as illustrated by Figure 2 and equation (2)

$$\log k_c = -\alpha p K_a + \log G \quad (2)$$

where $\alpha = 0.99$, $\log G = 11.4$ and regression coefficient $r = 0.999$. The catalysts obeying equation (2) have differences in the structure of their molecules. These are both *meta*- and *para*-substituted benzoic acids, benzoic acids carrying bulky *ortho*-substituents, and even 2,6-dinitrophenol. Consequently, the rate constant appears to be dependent only on the strength of the acid and not on the shape of its molecule. One may thus

Table 2. Rate constants, k, *vs.* proton concentration $[H^+]$ and *N*-D-glucoside cation $[SH^+]$.

Entry	Acid	$k/10^{-3}$ min^{-1}	$[H^+]/10^{-7}$ mol dm^{-3}	$[SH^+]/10^{-7}$ mol dm^{-3}	K
1	*p*-Methoxybenzoic acid	5.82	0.433	1.19	1.48×10^{-8}
		10.1	0.613	1.68	
		42.8	1.37	3.75	
		256	4.36	11.8	
2	Benzoic acid	15.4	0.837	2.38	3.80×10^{-8}
		34.7	1.19	3.25	
		47.1	1.59	4.36	
		61.9	2.02	5.51	
		115	2.85	7.79	
		132	3.19	8.71	
		163	3.49	9.55	
		182	3.73	10.2	
		212	4.04	11.0	
		271	4.52	12.3	
		430	5.80	15.8	
		485	6.32	17.3	
3	*m*-Chlorobenzoic acid	108	2.73	7.45	1.38×10^{-7}
4	*o*-Chlorobenzoic acid	24.3	1.05	2.87	4.68×10^{-7}
		38.4	1.49	4.08	
		72.8	2.12	5.80	
		106	2.60	7.11	
		161	3.19	8.72	
		180	3.36	9.18	
5	2,6-Dinitrophenol	1 145	9.72	26.6	1.78×10^{-6}
6	*o*-Nitrobenzoic acid	80.9	2.50	6.84	2.51×10^{-6}
		171	3.58	9.77	
		251	4.49	12.3	
		340	5.24	14.4	
7	3,5-Dinitrobenzoic	313	5.09	13.9	3.55×10^{-6}
		372	5.50	15.0	
		414	5.89	16.1	

Table 3. Catalysis of the mutarotation of *N*-(*p*-chlorophenyl)-β-D-glucopyranosylamine by benzoate buffers at 25 °C.

Entry	$[C_6H_5CO_2H]$/mol dm^{-3}	$[C_6H_5CO_2Na]$/mol dm^{-3}	$[CH_3OH_2^+]$/mol dm^{-3}	$k/10^{-3}$ min^{-1}
1	0.009	0.018	7.94×10^{-10}	2.40
2	0.0165	0.033	7.94×10^{-10}	3.87
3	0.033	0.067	7.94×10^{-10}	6.78
4	0.065	0.130	7.94×10^{-10}	13.1
5	0.075	0.150	7.94×10^{-10}	13.8
6	0.100	0.200	7.94×10^{-10}	18.8
7	0.018	0.018	1.66×10^{-9}	5.48
8	0.033	0.033	1.66×10^{-9}	8.84
9	0.067	0.067	1.66×10^{-9}	15.0
10	0.100	0.100	1.66×10^{-9}	21.9
11	0.130	0.130	1.66×10^{-9}	28.2
12	0.018	0.009	3.02×10^{-9}	7.25
13	0.033	0.0165	3.02×10^{-9}	9.85
14	0.067	0.033	3.02×10^{-9}	17.2
15	0.100	0.050	3.02×10^{-9}	25.2
16	0.130	0.065	3.02×10^{-9}	31.5
17	0.150	0.075	3.02×10^{-9}	34.4
18	0.180	0.090	3.02×10^{-9}	39.9
19	0.200	0.100	3.02×10^{-9}	44.7

speculate that the reaction is catalysed solely by the H^+ ions. The exclusive contribution of these ions is further supported by the Brønsted α value of 0.99. According to Brønsted,[18] reactions with coefficient α or β equal to 1 are specifically acid- or base-catalysed, respectively. On the other hand, Fife and co-workers[19] have reported reactions, in which the Brønsted coefficient $\beta = 1$, which were, however, general-base catalysed, because the rate-determining step was a proton transfer in a thermodynamically unfavourable direction. According to the commonly adopted view,[20] catalysis can be regarded as general

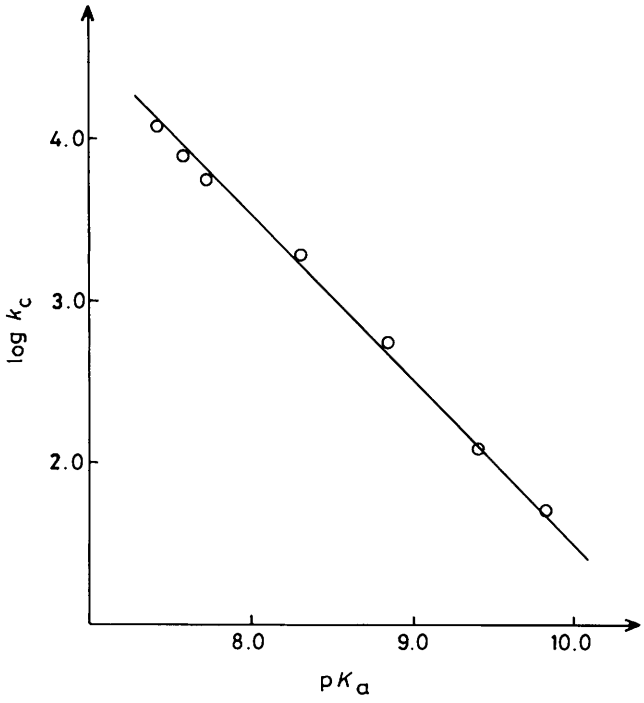


Figure 2. Bronsted plot for the mutarotation of *N*-(*p*-chlorophenyl)-β-D-glucopyranosylamine successively catalysed by 3,5-dinitrobenzoic acid, *o*-nitrobenzoic acid, 2,6-dinitrophenol, *o*-chlorobenzoic acid, benzoic acid, and *p*-methoxybenzoic acid.

Table 4. Numerical values of constants used for the calculation of coefficients in the Brønsted equation (2).

Entry	Acid	k_c/dm^3 mol^{-1} min^{-1}	log k_c	pK_a in methanol
1	*p*-Methoxybenzoic acid	53	1.72	9.83[15]
2	Benzoic acid	123	2.09	9.42[13]
3	*m*-Chlorobenzoic acid	535	2.73	8.86[13]
4	*o*-Chlorobenzoic acid	1 915	3.28	8.33[13]
5	2,6-Dinitrophenol	5 668	3.75	7.75[16]
6	*o*-Nitrobenzoic acid	7 760	3.89	7.6[12]
7	3,5-Dinitrobenzoic acid	12 198	4.09	7.45[17]

when the rate of the overall reaction is controlled by the proton-transfer step. Again, specific acid or base catalysis in multi-step reactions takes place when a step other than the proton transfer is rate limiting. Hence, to classify properly a reaction, the rate-determining step must be identified. To do this, the hydrogen-ion concentrations were measured in the solutions (Table 2). A logarithmic plot of the rate constant against the lyonium ion concentration/([$CH_3OH_2^+$]; further denoted as [H^+] for simplicity) is linear [equation (3)]:

$$\log k = -1.6\,\mathrm{pH} + 9.9 \qquad r = 0.999 \qquad (3)$$

Coefficients of this equation suggest the relationship given in equation (4). This correlation indicates that the rate of

$$k = 1.2\,[H^+]^2 + 1.6 \times 10^{-2} \qquad r = 0.999 \qquad (4)$$

anomerisation of *N*-(*p*-chlorophenyl)-β-D-glucopyranosylamine is controlled by the rate of proton transfer to a previously protonated form of the *N*-D-glucoside ($S_\beta H^+$). Consequently, the following three steps are suggested for conversion of the anomer β(S_β) into the anomer α(S_α). Reaction (6) undoubtedly

$$S_\beta + HA \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} S_\beta H^+ + A^- \qquad (5)$$

$$S_\beta H^+ + H^+ \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} S_\alpha H^+ + H^+ \qquad (6)$$

$$S_\alpha H^+ + A^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} S_\alpha + H^+ \qquad (7)$$

is the rate-limiting one. The rate of the overall process can thus be expressed as equation (8). As the *N*-D-glucoside is a weak

$$v = k_2[S_\beta H^+][H^+] \qquad (8)$$

base ($K_b = 2.0 \times 10^{-15}$), concentration [$S_\beta H^+$] is negligible and the principle of stationary states can be applied. If $k_{-1} \gg k_2$, $k_3 \gg k_{-2}$, and $[S_\alpha] = k_1k_2k_3/k_{-1}k_{-2}k_{-3}\,[S_\beta]$,[9] the rate constant can be described by equation (9) where k_0 is the rate

$$k = \frac{k_1k_2\,[H^+]}{k_{-1}\,[A^-]}[HA] + \frac{k_0k_2\,[H^+]}{k_{-1}\,[A^-]} \qquad (9)$$

of proton transfer from methanol to the substrate (S_β). Knowing that $[S_\alpha]/[S_\beta] = 0.22$,[9] one can demonstrate that k (Table 2) is equal to k_1/k_{-1}. Equation (9) can thus be rearranged as follows into equation (10).

$$k = k_2\frac{K_{HA}\,[H^+]}{K_{SH^+}\,[A^-]}[HA] + \frac{k_0k_2\,[H^+]}{k_{-1}\,[A^-]} \qquad (10)$$

Since

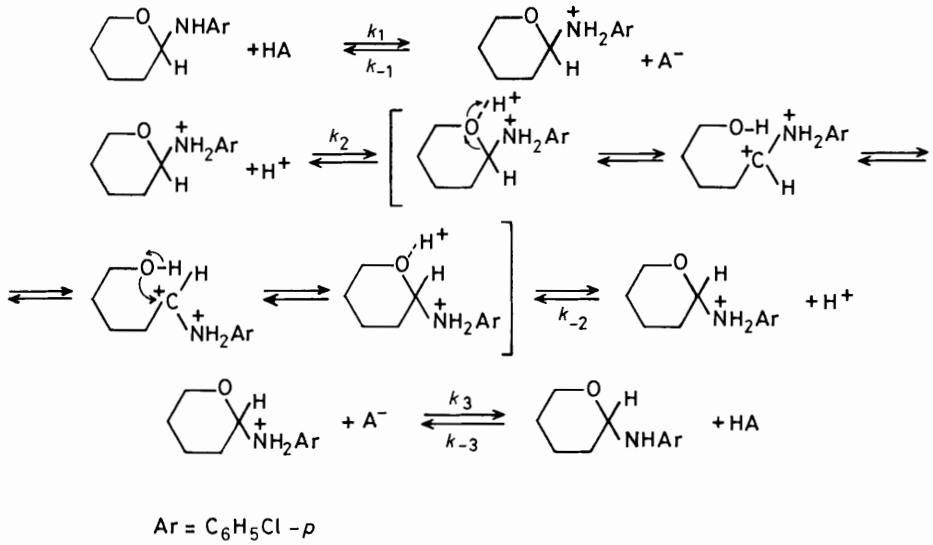
$$[A^-] = \frac{K_{HA}\,[HA]}{[H^+]}$$

we have

$$k = \frac{k_2}{K_{SH^+}}[H^+]^2 + \text{const.} \qquad (11)$$

Equation (11) is a generalisation of the experimental equation (4). The calculated k_2 value is 1.2×10^{10} min^{-1} (2.0×10^8 s^{-1}). The proton transfer occurs virtually during the slowest step, in spite of the fact that it was preceded by a preliminary rapid protonation of the substrate. Further, in accord with experiment, equation (11) shows that the rate of the reaction depends exclusively on the hydrogen-ion concentration and on the basicity of the *N*-D-glucoside. Accordingly, equation (11), along with $\alpha = 0.99$, provides satisfactory conditions for classifying the anomerisation of *N*-D-glucosides as specific-acid-catalysed.

Equation (9) and the data of Table 2 show that in all solutions the ratio [H^+]/[A^-] is 0.27, and constitute a basis for the linear dependence of k on the catalyst concentration [HA] [equation (1)]. On the other hand, equation (10) reveals, as has been found previously,[21] that the rate is linearly related to the acid strength of the catalyst and to the basicity of the *N*-D-glucoside. As the slowest step of reaction (6) is described by equation (8), it becomes clear as to why the addition of a neutral salt accelerates the mutarotation rate of *N*-(*p*-chlorophenyl)-β-D-glucopyranosylamine catalysed by benzoic acid.[22] This is caused by a preliminary salt effect.[18] Equations (9) and (10) also elucidate the retardation of the reaction after the addition of a salt with a common anion, [A^-].[23] To sum up, all the previous and the present experiments suggest the mechanism shown in the Scheme of the specific acid catalysis of anomerisation of *N*-(*p*-chlorophenyl)-β-D-glucopyranosylamine in methanol. Following a rapid and reversible protonation of the nitrogen atom in the molecule of substrate (S_β), another proton is slowly attached



Scheme. Mechanism of the anomerisation of *N*-aryl-D-glucopyranosylamines.

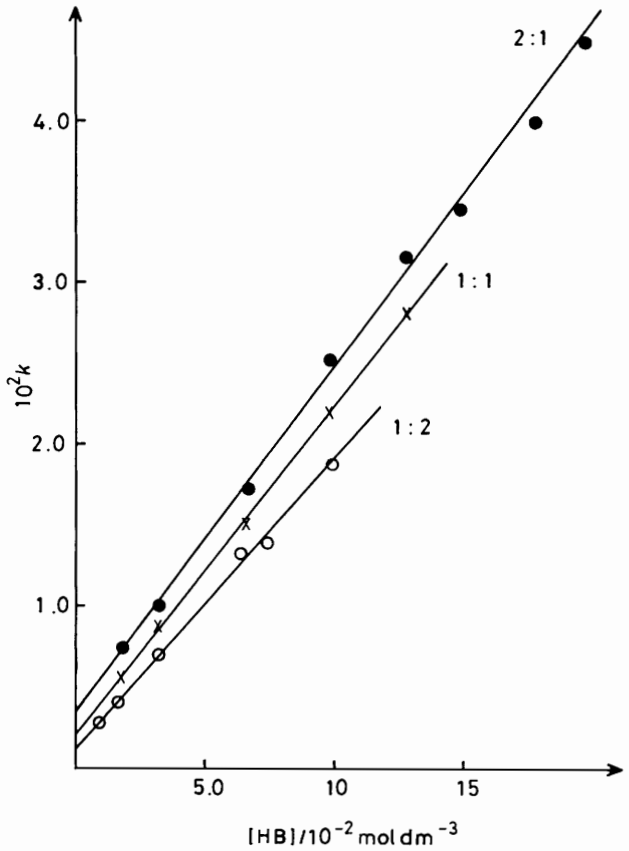


Figure 3. Rate constant *k vs.* buffer concentration. The acid/salt ratios are: ●, 2:1 (pH 8.52); ×, 1:1 (pH 8.78); and ○, 1:2 (pH 9.10).

to the ring oxygen in the $S_\beta H^+$ cation to give the pseudo-acyclic intermediate, SH_2^{2+}, in which the rotation about the C(1)–C(2) bond is possible as well as the change in the configuration of the anomeric carbon atom. Then, after the splitting off of one of the protons, the isomeric cationic species, $S_\alpha H^+$, is produced which reacts with the basic anion to afford the S_α anomer and to recover the catalyst, HA. This mechanism does not comply with those advanced so far[2,3] which are analogous to the mutarotation of glucose. This notwithstanding, elucidates all of the experimental findings.

Table 5. Parameters of the relation $k = k_{HB}[HB] + k_H[H^+]$ in buffer solutions.

$[C_6H_5CO_2H]/[C_6H_5CO_2Na]$	k_{HB}	$k_H[H^+]$	r
1:2	0.178	9.26×10^{-4}	0.999
1:1	0.201	1.90×10^{-3}	1.000
2:1	0.206	3.64×10^{-3}	0.999

The benzoic acid catalysed rate of mutarotation of *N*-(*p*-chlorophenyl)-β-D-glucopyranosylamine is markedly inhibited by sodium benzoate (Table 3). Appropriate measurements run in weakly basic buffer solutions show, however, that the acid catalysis is operative, because the rate increases upon lowering the pH of the solution at a fixed benzoic acid concentration [HB] (Figure 3).

However, when the formation of the high energy cationic intermediate is markedly impeded by a high $[A^-]$, the slowest step involves the attaching of any acid capable of appropriate polarisation of the substrate[20] required to effect the transformation. Under these conditions the reaction occurs in accordance with equation (12). By maintaining a fixed

$$k = k_{HB}[HB] + k_H[H^+] \quad (12)$$

hydrogen-ion concentration by dilution with appropriate buffer solutions, the catalytic coefficient of the molecules of benzoic acid, k_{HB}, could be determined (0.2 min^{-1}, Table 5). The free term in equation (12) is a linear function of $[H^+]$, and the calculated value of k_H is 1.2×10^6 min^{-1} ($r = 0.999$).

More detailed information on the mechanism of the general acid catalysis during the anomerisation of *N*-D-glucosides can be gained from additional studies, for instance in methanolic buffer solutions of different compositions.

Acknowledgements

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