on the curves, particularly at the low θ values. The numerical value of k_2 is then simply k_1y.

The principles of this method of kinetic treatment may be readily extended and applied to more complex systems; an example of such an extension is the approximate analysis of the periodate oxidation of the Schardinger dextrins which will be reported in another paper.[4]

[4] French and McIntire, THIS JOURNAL, 72, in press (1950).

CHEMISTRY SECTION
IOWA AGRICULTURAL EXPERIMENT STATION
AMES, IOWA
RECEIVED APRIL 24, 1950

Ion Charge and Exchange Rates with Ion-exchange Polymers

BY G. E. BOYD, A. W. ADAMSON AND L. S. MYERS, JR.

At this time it is possible to report certain early observations on the influence of cationic charge on exchange rates with a synthetic ion-exchange polymer.[1] The uptake of ions bearing one, two and three charges, respectively, from dilute hydrochloric acid solutions was measured as a function of time using a flow technique[2] and radioactive isotopes as tracers: 14.8 h. Na^{24}, 1.62×10^5 y. U^{233} and 275 d. Ce^{144}. Since the exchanger had been equilibrated with a solution of the same macro-composition as that which subsequently contained radio-tracer, negligible changes took place in the composition of the exchanger and in the ionic strength of the external solution. Accordingly, the rate process observed was that which occurs at equilibrium. The exchange velocity diminished rapidly as the ionic charge increased (Fig. 1). As a consequence of the existence of several kinetic mechanisms, considerable overlap was found. As previously,[2] three rate processes could be distinguished: (a) a first order film diffusion process (F) for systems in which the exchanging ion showed a large equilibrium distribution coefficient, K_d, in favor of the exchanger; (b) a particle diffusion mechanism (P); and (c) an "intermediate" rate process (I) which resulted from the coupling of F and P. The rate constants for the systems of Fig. 1 are summarized in Table I.

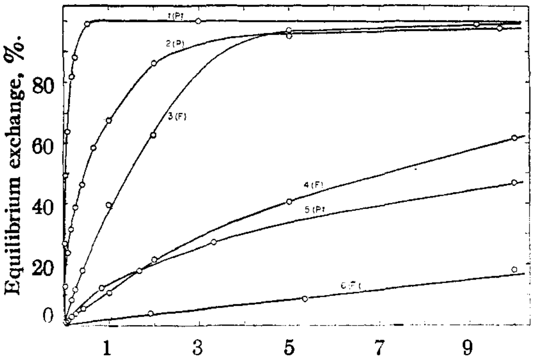

Fig. 1.—Effect of ion charge on cation exchange rates: (P) particle diffusion and (F) film diffusion mechanism: curve 1, Na^+ from 0.1 N HCl; curve 2, UO_2^{++} from 0.3 N HCl; curve 3, Na^+ from 0.001 N HCl; curve 4, UO_2^{++} from 0.033 N HCl; curve 5, Ce^{+++} from 0.5 N HCl; curve 6, Ce^{+++} from 0.1 N HCl.

TABLE I

RATE CONSTANTS FOR THE EXCHANGE OF VARIOUS IONS IN DILUTE HYDROCHLORIC ACID SOLUTIONS AT 25° (AVERAGE PARTICLE RADIUS = 0.0178 CM.)

System	Equilibrium distribution coefficient, K_d	Rate constant Observed	Rate constant Adjusted to $K_d = 10^4$	Mechanism
Na^+ from 0.001 N HCl	1810	9.3×10^{-3} sec.$^{-1}$	16.8×10^{-4}	Film diffusion[a]
UO_2^{++} from 0.003 N HCl	4660	2.0×10^{-3}	9.3×10^{-4}	Film diffusion[a]
Ce^{+++} from 0.1 N HCl	52,500	1.4×10^{-4}	7.1×10^{-4}	Film diffusion[a]
Na^+ from 0.1 N HCl	25	3.7×10^{-6} cm.^{2} sec.$^{-1}$		Particle diffusion
UO_2^{++} from 0.3 N HCl	55	3.6×10^{-7}		Particle diffusion
Ce^{+++} from 0.5 N HCl	3890	9.4×10^{-9}		Particle diffusion

[a] Film diffusion data corrected to a constant flow rate of 10 ml./cm.^{2}/sec.

The differences in the film diffusion rate constants depend in part on K_d according to the equation[2]: $k(\text{sec.}^{-1}) = 3D^1/rK_d\delta$ where r is the particle radius, and δ the "film thickness." The variation which persists after correcting to a common K_d (see column 4, Table I) results from the differing coefficients, D^1, for the ions in the film.

Diffusion through the cation exchange polymer must be governed by other factors. Not only do the ions move more slowly than in aqueous solutions, but there is also a much more pronounced dependence on charge. The internal diffusion coefficients,[2] D^i, appear to be independent of K_d and external flow rate, and to depend only on the nature and composition of the exchanger, on the temperature and perhaps on the ionic strength of the external solution. Independently of the nature of the polymer or of the character

---

[1] Amberlite IR-1, Rohm and Haas Company, Philadelphia, Pa. This material is presumed to have been a cross-linked phenol–formaldehyde polymer containing structurally bound methylene sulfonic acid groups solely responsible for the exchange capacity at low pH values.

[2] G. E. Boyd, A. W. Adamson and L. S. Myers, Jr., THIS JOURNAL, 69, 2836 (1947).

of the velocity controlling step, the higher the ion charge the slower the exchange.[3]

(3) This document is based on work performed for the Atomic Energy Project at Oak Ridge National Laboratory.

CHEMISTRY DIVISION
OAK RIDGE NATIONAL LABORATORY
P. O. BOX P
OAK RIDGE, TENNESSEE

RECEIVED MAY 25, 1950

The Nitration and Bromination of Tetraacetyl-β-D-glucopyranosylbenzene

BY JAMES M. CRAIG AND WILLIAM A. BONNER

While tetraacetyl-β-D-glucopyranosylbenzene (I) and related compounds have been known for several years[1] and the α-anomer of I has been discovered recently,[2] the chemical reactions of these compounds have been limited so far to those characteristic of the glycosyl side chain. The potentially more significant reactions of the aromatic nucleus, which might lead to series of aromatic derivatives possessing stable, water-soluble side chains of high molecular weight, have not yet been explored. In this note we wish to report the application of two typical aromatic-type reactions, nitration and bromination, to the benzene nucleus of I.

When I, dissolved in a mixture of acetic acid and acetic anhydride, was warmed with cupric nitrate, nitric oxide was evolved and the nitration mixture yielded a yellow sirup from which *p*-(tetraacetyl-β-D-glucopyranosyl)-nitrobenzene(II) m. p. 165–165.5°, $[\alpha]^{28}\mathrm{D}$ $-40.3°$, could be isolated in 22% yield. The structure of II was established by oxidation to *p*-nitrobenzoic acid. II could be deacetylated readily to *p*-(β-D-glucopyranosyl)-nitrobenzene, m. p. 181.5–182.5°, $[\alpha]^{25}\mathrm{D}$ 22.6°. The mother liquors from which II was obtained yielded a yellow glass, $[\alpha]^{28}\mathrm{D}$ 60.5°, on evaporation. This produced only a trace of *p*-nitrobenzoic acid on oxidation, and no other isolable product. The high positive rotation of this glass and the failure to isolate an aromatic acid on its oxidation, suggest that the nitration was accompanied by considerable degradation, since pure I was the starting material. When the usual mixture of nitric and sulfuric acids was employed in the nitration of I a glass, $[\alpha]^{27}\mathrm{D}$ 45.4°, was obtained, but this yielded only traces of a high melting solid product, and its oxidation similarly yielded only minute amounts of substances which appeared to be *o*- and *p*-nitrobenzoic acids.

Attempts to brominate I in acetic acid or chloroform, either at room or reflux temperatures, were unsuccessful. When I was dissolved in bromine containing fused ferric chloride and allowed to stand seven hours, the product was a yellow glass. By reacetylation and crystallization from 2-propanol 1-(tetraacetyl-β-D-glucopyranosyl)-3,4-dibromobenzene (III), m. p. 164.5–165°, $[\alpha]^{30}\mathrm{D}$ $-29.0°$, could be obtained. Its structure was substantiated by oxidation to 3,4-dibromobenzoic acid. The mother liquors producing III yielded a second crop of crystalline material, m. p. 105–108°, $[\alpha]^{24}\mathrm{D}$ $-28.8°$, on concentration. This material appeared to be a mixture of III and *p*-(tetraacetyl-β-D-glucopyranosyl)-bromobenzene (IV). When the above bromination was conducted for about three hours instead of seven, the product was approximately the same mixture of III and IV. It was not possible to separate this mixture into its components by recrystallization from 2-propanol, but its composition was supported by analysis and oxidation to *p*-bromo- and 3,4-dibromobenzoic acids.

Experimental Part

***p*-(Tetraacetyl-β-D-glucopyranosyl)-nitrobenzene (II).**—The nitrating reagent was prepared by adding cupric nitrate trihydrate (40 g., 0.165 mole) to a mixture of acetic anhydride (56 ml.) and acetic acid (24 ml.). To this reagent was slowly added tetraacetyl-β-D-glucopyranosylbenzene (8.0 g., 0.0196 mole) dissolved in a mixture of acetic anhydride (48 ml.) and acetic acid (32 ml.). The temperature of the reaction mixture was raised from an initial 40 to 50° on the water-bath, causing a gentle evolution of nitric oxide. After twenty minutes the reaction was cooled and poured into one liter of ice-water, and the aqueous solution allowed to stand for four hours. The viscous, dark amber gum which precipitated was dissolved in ether (50 ml.) and the aqueous solution extracted five times with 50-ml. portions of ether. The combined ether solutions were washed with small portions of cold water, cold, saturated sodium bicarbonate solution, and finally with cold water. The clear ether solution, dried over anhydrous sodium sulfate, was evaporated to give 9.1 g. of a yellow, semi-crystalline glass. This was crystallized from 2-propanol to yield two crops of yellow solid: 0.34 g., m. p. 151–156°, and 1.95 g., m. p. 155–161°. These were combined and recrystallized twice to yield 1.94 g. (21.9%) of pure *p*-(tetraacetyl-β-D-glucopyranosyl)-nitrobenzene, m. p. 165–165.5°, $[\alpha]^{28}\mathrm{D}$ $-40.3°$ (*c*, 2.284, chloroform).

Anal. Calcd. for $C_{20}H_{23}O_{11}N$: C, 52.98; H, 5.11; N, 3.09. Found: C, 53.31; H, 5.15; N, 3.26, 3.23.

A 78-mg. sample of the pure material was oxidized with alkaline potassium permanganate to produce *p*-nitrobenzoic acid, m. p. 237–239°, mixed m. p. with an authentic sample 236–237°.

The original 2-propanol mother liquors were concentrated to dryness leaving a yellow glass, $[\alpha]^{28}\mathrm{D}$ 60.5° (chloroform), from which further crystalline material could not be isolated. An alkaline permanganate oxidation of 1.0 g. of this glass produced only a trace of *p*-nitrobenzoic acid, and no other solid product was recovered.

***p*-(β-D-Glucopyranosyl)-nitrobenzene.**—*p*-(Tetraacetyl-β-D-glucopyranosyl)-nitrobenzene (0.50 g.) was dissolved in methanol (25 ml.) saturated with ammonia (14.6 g. of NH_3 in 100 ml.). The solution stood for twenty-four hours, then was evaporated to dryness. The yellow crystalline residue was extracted several times with warm absolute ether to remove acetamide. The remaining crystalline residue (0.34 g.) was recrystallized from ethyl acetate to give pure *p*-(β-D-glucopyranosyl)-nitrobenzene in the form of light yellow platelets, m. p. 181.5–182.5°, $[\alpha]^{25}\mathrm{D}$ 22.6° (*c*, 1.24, methanol).

Anal. Calcd. for $C_{12}H_{15}O_7N$: C, 50.52; H, 5.30; N, 4.91. Found: C, 50.42, 50.65; H, 5.47, 5.56; N, 4.95, 5.05.

Acetylation of 64 mg. of the pure material with acetic

---

(1) Hurd and Bonner, THIS JOURNAL, 67, 1664, 1759, 1972, 1977 (1945).

(2) Bonner and Craig, *ibid.*, 72, 3480 (1950).