NOTES

The Epimerization of Glucose-1-C^{14} [1]

By Aksel A. Bothner-By and Martin Gibbs

The mechanism (or mechanisms) by which the epimerization of glucose proceeds in alkaline solution is not clearly established, the commonly accepted intermediate formation of an enediol being inconsistent with the results of the investigations of Fredenhagen and Bonhoeffer[2] concerning the conversion of glucose to fructose in heavy water. A rearrangement of the carbon chain of glucose during the course of the reaction has not been excluded by any earlier work and could conceivably occur. Such a rearrangement would be detectable using glucose-1-C^{14} which has recently become available.[3] We have performed this experiment and our results indicate that no rearrangement takes place.

Experimental

1.3 mg. of glucose-1-C^{14} having a specific activity of 120 mμc/mg.[4] was diluted with 30 mg. of inactive glucose and dissolved in 0.2 ml. of saturated calcium hydroxide solution. The solution was kept at 70° for 2 hours,[5] then chilled and passed over 1 g. each of Amberlite IR-100-H and IRA-400 ion exchange resins. The volume with washings was 6 ml. The mixed sugars were diluted with 25 mg. of cold glucose and were degraded by the method of Wood, Lifson and Lorber.[6] The specific activities obtained were: for the glucose carbon atoms 1 and 6, 4.4 mμc/mg. of carbon; carbon atoms 2 and 5, 0.1 mμc/mg.; carbon atoms 3 and 4, 0.09 mμc/mg. A similar distribution of label in the lactic acid was obtained by degrading glucose-1-C^{14} which had not been epimerized.[7]

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[1] Research carried out at Brookhaven National Laboratory under the auspices of the U. S. Atomic Energy Commission.

[2] Fredenhagen and Bonhoeffer, *Z. physik. Chem.*, **A181**, 392 (1938).

[3] Sowden, *Science*, **109**, 229 (1949).

[4] The glucose-1-C^{14} was most generously furnished us by Prof. J. C. Sowden.

[5] Lobry deBruyn and Van Ekenstein, *Rec. trav. chim.*, **14**, 203 (1895).

[6] Wood, Lifson and Lorber, *J. Biol. Chem.*, **159**, 475 (1945).

[7] Gibbs, Dumrose, Bennett and Bubeck, *ibid.*, **184**, 545 (1950).

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Separation of Seventh Group Anions by Ion-Exchange Chromatography

By R. W. Atteberry and G. E. Boyd

An extension of the techniques of ion-exchange chromatography to the separation and concentration of anionic species has been made possible by virtue of the recent commercial availability of several stable mono-functional strong base anion exchange polymers.[1,2] The principles governing anion fractionation are the same as those previously applied in the separation of the rare earths.[3,4] This communication reports the efficient separation of the halide anions and of pertechnetate from perrhenate ion. The separation of Cb(V) and Ta(V), and Zr(IV) and Hf(IV) through the formation of their complex halide anions has been described in a recent publication from this Laboratory.[5]

Halide Separations.—The fractionation was conducted by placing approximately 0.7 m. e. quantities of ammonium bifluoride, chloride, bromide and iodide on the topmost portion of a 0.72 sq. cm. × 91.5 cm. cylindrical bed of 100/120 mesh Dowex-2 initially in the nitrate form, and then eluting the mixture at a flow rate of 1.3 ml./min. at room temperature with a 1 *M* $NaNO_3$ solution adjusted to a *p*H of 10.4 with NaOH. The course of the separation was followed by continuously monitoring the radioactivity in the effluent from the bed. The 37 m. Cl^{38}, 34 h. Br^{82} and 8.0 d. I^{131} were used as indicators. Fluoride was determined chemically. Figure 1a shows the results taken from a typical experiment. The identities of the various activity peaks were established by measurements of decay and radiation characteristics on aliquots taken from the effluent. Interestingly, the first peak contained over 90% of the starting fluoride together with a

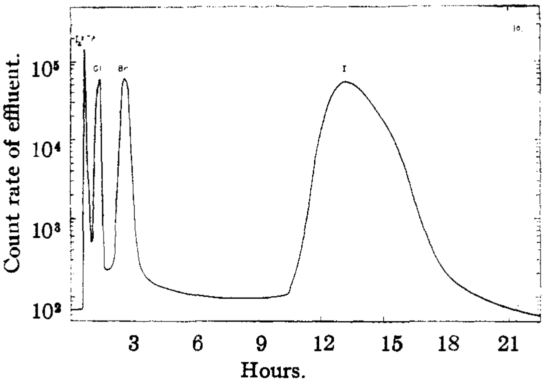

Fig. 1.—(a) Halide separation.

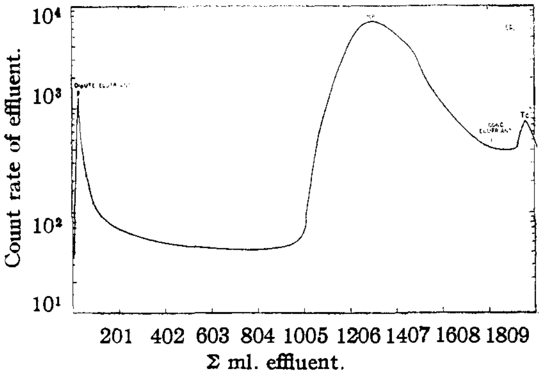

Fig. 1.—(b) Rhenium–technetium separation.

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[1] Dow Chemical Company, Midland, Michigan.

[2] Resinous Products Division, Rohm and Haas Co., Philadelphia, Pa.

[3] B. H. Ketelle and G. E. Boyd, This Journal, **69**, 2800 (1947).

[4] S. W. Mayer and E. R. Tompkins, *ibid.*, **69**, 2866 (1947).

[5] K. A. Kraus and G. E. Moore, *ibid.*, **71**, 3855 (1949).

small amount of the 8.0 d. iodine activity, suggesting possibly the occurrence of an interhalide complex anion. The completeness of the separations is indicated by peak to trough ratios ranging from 100 to 600.

Group VIIB Separations.—The three transition elements Mn, Tc and Re are known to form oxygenated anions of the type XO_4^- when present in their respective heptavalent oxidation states. The separation of these anions by use of an ion-exchange column should be possible, therefore, provided they are stable in the systems employed. Such proved not to be the case with permanganate which was found to react with the exchanger. Pertechnetate, although unstable in acid solution, is stable in alkaline solutions, and, if a strong base exchanger is used, it can be separated from perrhenate ion. The fractionation of trace amounts of technetium from microgram amounts of rhenium was conducted using a 0.72 sq. cm. × 51 cm. cylindrical bed of 100/120 mesh Dowex-2 initially in the sulfate form. The mixture of 90 h. Re^{186} and 6.0 h. Tc^{99m}, placed at the top of the bed as NH_4ReO_4 and NH_4TcO_4 in solution, was prepared by dissolving slow neutron irradiated molybdenum metal known to contain 2–3 p. p. m. rhenium impurity in concentrated sulfuric acid and distilling. The distillate containing the Tc and Re (and perhaps other volatile activities from impurities) was diluted, the mixed rhenium and technetium sulfides precipitated and then dissolved in ammoniacal hydrogen peroxide to give perrhenate and pertechnetate, respectively. The separation by elution was conducted at a flow rate of 1.7 ml./min. at room temperature with a solution 0.1 *M* in $(NH_4)_2SO_4$ and NH_4SCN adjusted to a *p*H of 8.3–8.5 with NaOH. The identity of the activity in the first peak (Fig. 1b) which appeared immediately as would be expected with cations was not established. When the second activity peak (identified as rhenium) had dropped by a factor of *ca.* 20 the concentration of eluant was increased to 1.0 *M*, maintaining the *p*H constant, in order to bring out the technetium which was shown to be well over 99% pure by its decay with a 6.0 h. period over ten half-lives. The reversal of the order of elution of Re and Tc with regard to atomic weight may be of interest.

Finally, it may be remarked that anion exchange columns filled with the new strong-base exchangers have been found to be somewhat less efficient than the nuclear sulfonic acid type cation exchangers, all other variables such as particle size, flow rate, temperature, etc., being the same. In the foregoing halide separations approximately 200–250 theoretical plates were shown, whereas with cations roughly twice as many stages are usually found with beds of the same depth. This difference may result in part, if not entirely, from the approximately twofold lower exchange capacity of the anion exchangers.

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Kinetic Analysis of Consecutive Irreversible Second Order Reactions[1]

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The kinetic analysis of consecutive reactions[2] of the type $A + B \rightarrow C;\ C + B \rightarrow D$ has not been generally feasible because of the difficulty of devising analytical expressions for the concentrations of *A*, *B*, etc., as functions of *t*. In practice this difficulty has usually been circumvented by adjustment of the reaction conditions so that the reaction is kinetically first order, for example by use of a large excess of the reactant *B*. However, in those cases in which the progress of the reaction is followed by measuring the concentration of *B* it is clearly undesirable to drown out its kinetic order by the use of a large excess.

A practical method for the determination of the kinetic constants for consecutive second order reactions has occurred to us, and while the principle is extremely simple it does not seem to have been used before. Let *a*, *b* and *c* represent the concentrations of *A*, *B* and *C*, respectively. If one sets up the differential rate equations

$$\mathrm{d}a/\mathrm{d}t = -k_1ab \qquad (1)$$

$$\mathrm{d}b/\mathrm{d}t = -k_1ab - k_2cb \qquad (2)$$

$$\mathrm{d}c/\mathrm{d}t = k_1ab - k_2cb \qquad (3)$$

it is apparent that these may be readily converted to equations of first order type by introduction of the parameter $\theta = \int_0^t b\mathrm{d}t$. Since $\mathrm{d}\theta = b\mathrm{d}t$

$$\mathrm{d}a/\mathrm{d}\theta = -k_1a \qquad (4)$$

$$\mathrm{d}b/\mathrm{d}\theta = -k_1a - k_2c \qquad (5)$$

$$\mathrm{d}c/\mathrm{d}\theta = k_1a - k_2c \qquad (6)$$

Equations 4 through 6 constitute a readily integrable set with the solutions

$$a = a_0e^{-k_1\theta} \qquad (7)$$

and, assuming $c_0 = 0$

$$b = b_0 - a_0\,[2 - 2e^{-k_1\theta} - k_1(e^{-k_2\theta} - e^{-k_1\theta})/(k_1 - k_2)] \qquad (8)$$

$$c = k_1a_0(e^{-k_1\theta} - e^{-k_2\theta})/(k_2 - k_1) \qquad (9)$$

The relationship between θ and *t* is readily established by plotting *b* against *t* and integrating graphically. The data giving *b* as a function of *t* are then converted to the θ basis and subsequently handled as a first order process.

Swain[3] has given a method of treatment for consecutive first order reactions which involves matching experimental points at selected stages of the reaction (15, 35 and 70% of completion) against standard curves calculated for various ratios of k_2/k_1 at these stages. We have found it more convenient to determine the values of k_1 and k_2 by a curve matching technique as follows: introduce the new variables $x = k_1\theta$ and $y = k_2/k_1$. Equation 8 now becomes

$$b = b_0 - a_0[2 - 2e^{-x} - (e^{-x} - e^{-xy})/(y - 1)] \qquad (10)$$

By plotting $(b_0 - b)/a_0$ against log *x* for various values of *y*, one obtains a family of S-shaped curves. The experimental curve relating $(b_0 - b)/a_0$ to log θ is then compared with the calculated *y*-family and an approximate value for *y* may be estimated. It is then possible to construct new curves for values of *y* in this neighborhood and thereby fit the experimental curve as closely as the data allow. The value of k_1 may be deduced from the lateral displacement of log θ against the log *x* scale which gives the best fit

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[1] Journal Paper No. J-1779 of the Iowa Agricultural Experiment Station, Ames, Iowa; Proj. 1116.

[2] Chien, THIS JOURNAL, 70, 2256 (1948).

[3] Swain, *ibid.*, 66, 1696 (1944).