with 0.25 ml. of 0.01 *M* sodium metaperiodate and 0.10 ml. 10 *N* H_2SO_4 for 20 minutes at 40°. Then 0.20 ml. of 0.10 *M* sodium arsenite was added and allowed to stand for 10 minutes at room temperature. The formaldehyde liberated was determined by the method of MacFadyen.[6] The compound yielded 1.81 moles of HCHO per mole of reducing sugar. When the unknown was reduced with KBH_4 before oxidation with HIO_4, the amount of HCHO liberated remained unchanged. A 3-ketopentose alone among the five carbon sugars possesses two terminal α-glycol groups and forms 2 moles of HCHO upon periodate oxidation. Prior reduction to the pentitol has no effect upon this ratio. This evidence must be regarded as presumptive rather than definitive since some 2-ketoses have been reported to form more than one mole of HCHO, although, according to Jackson,[7] the reaction producing 1 mole of HCHO predominates.

On reduction with borohydride, ribitol and xylitol were formed, as indicated by paper chromatography. To 1.5 μmoles of the unknown in 0.6 ml. of water, 0.20 ml. of a 0.01 *M* solution of KBH_4 was added and the mixture allowed to stand at room temperature for 20 minutes before adding 0.10 ml. of 2 *N* HCl to stop the reaction. The solution was de-ionized, lyophilized and taken up in 0.10 ml. of water. Upon paper electrophoresis in borate buffer, the unknown yielded three spots. As can be seen in Table I, a small amount of the unreduced compound remained at the end of the reaction while two new spots, corresponding to ribitol and xylitol, appeared. This result is unique for the 3-ketopentose with the *erythro* configuration since a *threo* 3-ketopentose would yield only one alcohol, arabitol.

TABLE I

The paper electrophoresis was performed at room temperature over a three-hour period. The potential remained constant at 500 volts while the amperage increased slightly from 10–12 ma. during the run. The solvent was 0.05 *M* borate buffer adjusted to *p*H 10. The spots were developed with the periodate spray of Metzenberg and Mitchell.[8]

Compound	Distance migrated from origin in cm.
Arabitol[a]	6.6
Ribitol[a]	7.4
Xylitol[a]	5.8
Unknown	9.1
Unknown after reduction	9.2, 7.4, 5.7

[a] The pure pentitols were generously provided by Dr. H. G. Fletcher of this Institute.

The second peak observed in the original fractionation procedure also produced a maximum at 600 mμ in the cysteine–carbazole reaction and appeared closely related to but not identical with the 3-ketopentose. As isolated from the column the solution had a faint blue color and contained copper in the ratio of 1 mole of copper to 2 moles of reducing sugar. The significance of this fraction is being further investigated.

Transketolase apparently plays no role in the conversion of ribulose phosphate to xylulose phosphate by spleen extracts,[1] as is also the case in certain bacterial preparations.[9] Therefore, we should like to suggest that the evidence presented above is consistent with the concept that the reaction proceeds through an ene-diol intermediate involving carbons 2 and 3 of ribulose. A tentative series of reactions may then be written which provides a mechanism for the formation of D-xylulose from D-ribulose and which also postulates the formation of 3-ketopentose. This formulation supports the view of Dische and Shigeura who proposed, on the basis of preliminary evidence, that the isomerization of ribose 5-phosphate leads to the formation of more than one carbonyl five carbon compound.[10] It should be further noted that a possible mechanism is hereby provided for the formation of L-xylulose from D-ribulose although, at the moment, experimental evidence for this is non-existent.

(6) D. A. MacFadyen, *J. Biol. Chem.*, **158**, 107 (1945).

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(8) R. L. Metzenberg and H. K. Mitchell, THIS JOURNAL, **76**, 4187 (1954).

(9) P. K. Stumpf, unpublished data.

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RECEIVED DECEMBER 22, 1954

RADIATION-INDUCED Ce(III)-Ce(IV) EXCHANGE IN AQUEOUS NITRIC AND SULFURIC ACIDS[1]

Sir:

The mechanism postulated by Allen[2] for the reduction of Ce(IV) in 0.4 *N* H_2SO_4 by radiation assumes a reaction of the form

$$Ce(III) + OH \longrightarrow Ce(IV) + OH^- \qquad (1)$$

as a vital step in the mechanism. Heretofore there has been no unequivocal experimental demonstration that any reaction involving the oxidation of Ce(III) actually does take place in irradiated cerium systems.

At the suggestion of Prof. Henry Taube[3] of the University of Chicago we have investigated the radiation-induced Ce(III)–Ce(IV) exchange in nitric and in sulfuric acid media.

Solutions containing unlabeled Ce(IV) and labeled Ce(III) were irradiated with unfiltered 50 kvp. X-rays from a tungsten target. After irradiation, the Ce(IV) was extracted with butyl phosphate[4] and the specific activity of this fraction determined. The radiation-induced exchange was calculated from this observed exchange rate by subtracting the spontaneous (thermal) exchange rate, which was determined by independent measurements.

The results are presented in Fig. 1 and Table I. We believe the exchange yields to be reliable to within 5–10% and the dosimetry yields to within 2%.

(1) This work was done under the auspices of the Atomic Energy Commission.

(2) A. O. Allen, *Radiation Research*, **1**, 85 (1954); Brookhaven National Laboratory Report BNL-1498.

(3) Consultant, Los Alamos Scientific Laboratory.

(4) J. C. Warf, THIS JOURNAL, **71**, 3257 (1949).

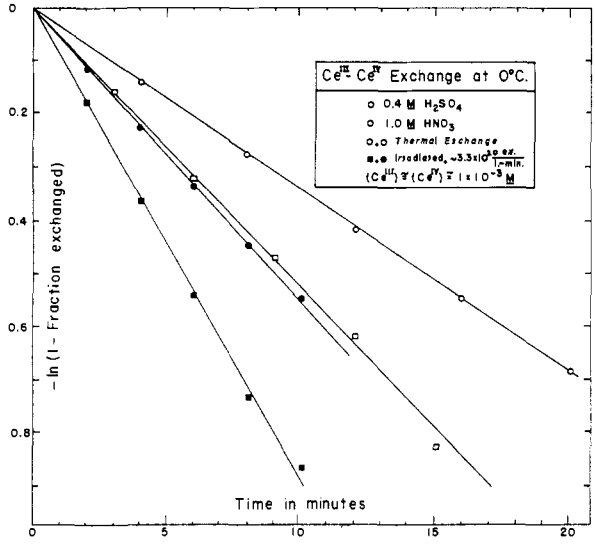

Fig. 1.

TABLE I

DOSIMETRY AND EXCHANGE DATA AT 0°

Observed rate of ferrous oxidation in 0.4 M H_2SO_4: 77.7 μmole/liter-minute $G_{Fe(III)}$ = 14 ions/100 ev. (assumed for low energy X-rays)

Medium	Rate Ce(IV) reduction (μmoles/l.-min.)	Radiation-induced exchange rate (μmols/l.-min.)	$G_{Ce(III)}$ (ions/100 ev.)	$G_{exchange}$ (ions/100 ev.)
0.8 N H_2SO_4	18.2	17.8	3.28	3.2
1.0 N HNO_3	46.1	9.6	8.32	1.7

All experiments were performed at 0° in order to minimize the contribution from the spontaneous thermal exchange process. G_{OH} values of 2.23–2.58 have been reported in the literature[5] for similar irradiation conditions at room temperature. This is certainly in the same range as our $G_{exchange}$ value found in H_2SO_4 and is highly suggestive that the inclusion of equation (1) in the ceric sulfate reduction mechanism is indeed valid.

In the HNO_3 system, the high $G_{Ce(III)}$ and low $G_{exchange}$ values are consistent with the above interpretation if it may be assumed that G_{OH} = 3.2, equal to the observed $G_{exchange}$ in the H_2SO_4 system. Since $G_{exchange}$ in HNO_3 is only 1.7, there remain about 1.5 OH radicals per 100 ev. which are free to react with the system in some other manner. If any of the following reactions occur, all of which are energetically possible under the experimental conditions employed, the additional reducing power of the solution would be sufficient to account for the large value of $G_{Ce(III)}$ in nitric acid.

$$OH + NO_3^- + H^+ = HO_2 + HNO_2 \qquad E^\circ = -0.16^6$$

$$2OH + NO_3^- + H_2O + H^+ = 2H_2O_2 + HNO_2 \qquad E^\circ = +0.22$$

$$3OH + NO_3^- + H_2O + H^+ = 3H_2O_2 + NO \qquad E^\circ = +0.24$$

We are currently engaged in extensive studies of the radiation-induced exchange in both the Ce(III)–Ce(IV) and Tl(III)–Tl(I) systems. Although Ce(III) and Ce(IV) possess opposite ionic charges in H_2SO_4 solutions,[7] the observed spontaneous exchange rate does not seem to differ greatly from that found for the nitric acid system,[8] in which both exist as cations. For this reason, a kinetic investigation of the spontaneous cerium exchange in H_2SO_4 is also planned.

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RECEIVED JANUARY 13, 1955

STEROIDS AND RELATED PRODUCTS. II.[1] THE SYNTHESIS OF 11-DEHYDRO-17α-METHYLCORTICOSTERONE ACETATE

Sir:

The important biological properties of 17-methylated estradiol,[2] testosterone[3a,b,c] and other androgens, such as Δ^5-3β,17β-dihydroxy-17α-methylandrostene[3a,4] and the recently described 17aα-methyl-D-homotestosterone[5] and 17α-methyl-19-nortestosterone,[6] of progesterone[7a,b,c] and desoxycorticosterone[1,8a,b] made the synthesis of 17-methyl adducts of 11-oxygenated adrenal cortical hormones desirable. I now wish to record the synthesis of 11-dehydro-17α-methylcorticosterone acetate (IV), a biologically active homolog of 11-dehydrocorticosterone acetate and analog of cortisone acetate.

Reaction of 3α-acetoxy-11,20-diketopregnane (I) with one mole of bromine gave a product from which the 17-monobromo derivative Ia[9] [m.p. 168–170°, $[\alpha]^{25}D$ 0.8° (c 0.864, $CHCl_3$); calcd. for $C_{23}H_{33}O_4Br$: C, 60.92; H, 7.34; Br, 17.63. Found: C, 60.86, 61.14; H, 7.47, 7.43; Br, 17.51, 17.45], a dibromide to which, according to present evidence, structure Ib should be assigned [m.p. 177°, $[\alpha]^{24}D$ 22.3° (c 1.121, $CHCl_3$); calcd. for $C_{23}H_{32}O_4Br_2$: C, 51.89; H, 6.06; Br, 30.03. Found:

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