TABLE II

VARIATION OF PPTN. *p*H WITH TOTAL U CONCN. AT CONSTANT CALCIUM ION CONCN.

Molar concns. (Ca^{++})[a]	Molar concns. (U)	Pptn. *p*H	(U)(OH$^-$) × 10^{11}	(U)(OH$^-$)^2 × 10^{19}	Final *p*H[b]
0.00438	0.000510	6.19	0.79	1.23	..
.00438	.000510	6.20	.81	1.29	5.40
.00442	.000837	6.04	.91	1.00	4.89
.00438	.000839	5.99	.81	0.79	4.98
.00442	.00142	5.87	1.05	.78	4.80
.00342	.00352	5.50	1.11	.35	4.45
.00451	.00353	5.55	1.26	.45	4.48
.0159	.000502	6.12	0.66	.87	..
.0159	.000502	6.09	.62	.76	..
.0152	.000825	5.895	.65	.51	..
.0161	.00141	5.695	.70	.35	4.80
.0161	.00141	5.80	.89	.44	4.88
.0158	.00348	5.49	1.07	.33	4.51
.0167	.00560	5.47	1.66	.49	4.43
.0146	.00675	5.35	1.5	.34	4.48
.0161	.0175	5.06	2.0	.23	4.23

[a] Calcium nitrate added initially to bring the Ca^{++} concentration to the indicated values at the moment of precipitation. [b] After 24 hours standing.

Equation 1-3 represent a possible formulation of the reaction which leads to the initial precipitate. Here 1.5 moles of hydroxyl ion per mole of uranium

$$UO_2^{++} + H_2O \longrightarrow UO_2OH^+ + H^+ \quad (1)$$

$$2UO_2OH^+ \longrightarrow UO_3UO_2OH^+ + H^+ \quad (2)$$

$$UO_3UO_2OH^+ + H_2O \longrightarrow UO_3UO_2(OH)_2 + H^+ \quad (3)$$

are required to form $UO_3UO_2OH^+$, and precipitation should begin when that number is exceeded in accord with the data of Table I. These equations are similar to the suggestion of Best, Taub and Longsworth[6] that polymeric $(UO_3)_xUO_2^{++}$ ions are formed as uranyl salt solutions are made alkaline.

Table III shows the ratio Ca/U found in the precipitates prepared by the addition of 0.02 *M* $Ca(OH)_2$ to 0.0014 *M* $UO_2(NO_3)_2$ until the indicated *p*H values are reached. When the precipitates were allowed to stand in contact with the supernatant liquid, the *p*H fell to final values about 1.0 unit below those reached initially. The calcium content of the precipitate increased both with the time of standing and with the *p*H of precipitation. We conclude that the composition of the precipitate is approaching $CaUO_4$.

TABLE III

ANALYSIS OF PRECIPITATES

Pptn. *p*H	Remarks	Atomic ratio Ca/U in ppt.
5.50	Shaken 6 days, final *p*H 4.59	0.016
4.93	Allowed to stand several hours	.024
4.91	Allowed to stand several hours	.028
7.50	Freshly pptd. substance	.089
7.50	Shaken 5 days, final *p*H 6.20	.132
8.75	Freshly pptd. substance	.190
8.75	Shaken 5 days, final *p*H 7.30	.209
10.00	Allowed to stand 5 minutes	.312
10.00	Allowed to stand 45 minutes	.349
10.00	Allowed to stand 1 hour	.455
10.83	Shaken 5 days, final *p*H 10.49	.625
11.00	Allowed to stand 2 hours	.695
11.00	Allowed to stand 1 hour	.800

The precipitate appeared either flocculent or granular, and on long standing the flocculent form changed into the granular material. Excess lime promoted the formation of the granular precipitate.

Table IV gives the amount of uranium found in solutions prepared at various *p*H values. The concentration decreases with increasing *p*H and with the time of standing.

TABLE IV

CONCENTRATION OF URANYL ION IN SOLUTIONS OF VARYING *p*H PREPARED BY ADDITION OF CALCIUM HYDROXIDE TO URANYL NITRATE SOLUTIONS

Pptn. *p*H	Time maintained at that *p*H	Concn. of U, mg./l.[a]
4.50	Several days	48.0
7.00	10 minutes	5.2
7.50	10 minutes	1.25
7.50	10 minutes	1.05
8.00	10 minutes	0.71
8.50	10 minutes	.43
8.75	10 minutes	1.43
8.85	10 minutes	.52
9.00	10 minutes	.67
9.50	10 minutes	.62
10.00	10 minutes	.60
10.00	10 minutes	.52
10.00	1 hour	.48
11.00	10 minutes	.45
11.00	1 hour	.29

[a] Measured by means of the polarographic technique of Tichenor, Crompton and Young, to be published.

Experimental

Calcium hydroxide solutions were prepared by dissolving freshly prepared calcium oxide in water and filtering off any precipitated calcium carbonate. Stock solutions of uranyl nitrate were prepared by dissolving U_3O_8 in concentrated nitric acid. *p*H measurements indicated these solutions to be nearly stoichiometric[6]. Reactions were carried out in a nitrogen atmosphere to avoid introduction of carbon dioxide. A Beckman Model G *p*H meter was used with a potassium chloride–agar bridge between the calomel electrode and the reaction mixture.

WEST ORANGE, NEW JERSEY RECEIVED MARCH 28, 1951

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[6] R. J. Best, D. Taub and L. G. Longsworth, Report A-380, November 24, 1942.

The Crystal Structure of Potassium Bromorhenate(IV)[1]

BY D. H. TEMPLETON AND CAROL H. DAUBEN

The compound K_2ReBr_6 seems to have been first prepared by Krauss and Steinfeld[2] who reported no structure determination. We have shown by X-ray diffraction that its structure is the K_2PtCl_6 type,[3] as are those of K_2ReCl_6[4] and K_2ReF_6.[5]

Dr. Z. Zimmerman Hugus of this Laboratory prepared single crystals of potassium bromorhenate by dissolving ReO_2 in hydrobromic acid and

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[1] For a table of observed and calculated *F* values, and a copy of a photographic Fourier section, order document 3246 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting $1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $1.05 for photocopies (6 × 8 inches) readable without optical aid.

[2] F. Krauss and H. Steinfeld, *Ber.*, **64**, 2552 (1931).

[3] J 1₁ type, *Strukturbericht*, **1**, 429 (1937), **3**, 121 (1937).

[4] B. Aminoff, *Z. Kristallographie*, **94**, 246 (1936).

[5] O. Ruff and W. Kwasnik, *Z. anorg. Chem.*, **219**, 78 (1934).

crystallizing the potassium salt. These crystals were well formed cubes, very dark red in color.

The powder diffraction pattern, taken with copper Kα X-rays ($\lambda = 1.5418$ Å.) corresponds to a face-centered cubic lattice with $a = 10.445 \pm 0.005$ Å. With four molecules to the unit cell, the density is calculated to be 4.34 g./cm.$^{-3}$. The intensities of most of the reflections were estimated visually from a rotation photograph taken about the (100) axis. Weissenberg photographs were used to obtain several reflections absent or not resolved in the rotation pattern. The magnitudes of 95 independent structure factors (all that are permitted by the space group up to $(\sin \theta)/\lambda = 0.64$) were calculated from these data after correction for Lorenz, polarization, and velocity factors. No correction was made for absorption other than to average the results for equivalent reflections. The crystal was a cube with edges about 0.1 mm. long.

Preliminary calculations showed these data to be consistent with the structure

Space group O_h^5—Fm3m; $Z = 4$
4 Re in 4(a): (000) + F.C.
8 K in 8(c): $\pm$ ($^1/_4$ $^1/_4$ $^1/_4$) + F.C.
24 Br in 24(e): $\pm$ (x00; 0x0; 00x) + F.C.

with the parameter x approximately 0.25. Signs of the structure factors were calculated on this basis; only seven were negative. An optical Fourier summation of the electron density made according to Huggins[6] for a section through a rhenium atom and four bromine atoms showed the series to be sufficiently convergent to give well-resolved peaks for the atoms. A numerical summation of the same series along the edge of the unit cell (Fig. 1) showed the bromine maximum at $x = 0.2410$. A series containing the same terms but using coefficients calculated for $x = 0.242$ gave a maximum at 0.2436. If a "back-shift" correction of -0.002 is applied, the experimental result is 0.239 ± 0.004.[7] The probable error was estimated from the rate of change of a few structure factors of large indices with change in x.

The calculated values of F are based on atomic form factors from the "Internationale Tabellen."[8] No temperature correction was made. It is possible that the absorption error in part compensates the temperature effect, allowing reasonably good agreement throughout the range of diffraction angles. The percentage discrepancy, $100\,(\Sigma\,||F_{\text{obsd.}}| - |F_{\text{calcd.}}||)/\Sigma\,|F_{\text{obsd.}}|$, is 25% for $x = 0.242$, which is as good as was expected because of the crude visual estimates and the neglect of absorption and temperature corrections. In view of the simplicity of the structure, further refinement of the observations was not deemed necessary.

The bromine–rhenium distance in the bromorhenate ion is 2.50 ± 0.04 Å. If the covalent radius of bromine is taken[9] as 1.14 Å., the octahedral radius of rhenium is 1.36 Å., in good agreement with the value 1.38 Å. calculated in the same way from K_2ReCl_6.

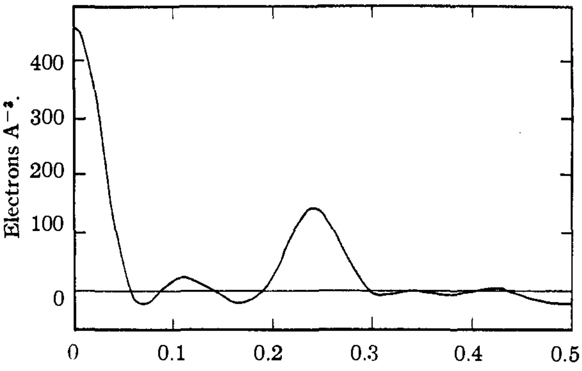

Fig. 1.—Electron density at (x00) in K_2ReBr_6. F_{000} is included in the calculation.

We wish to thank Dr. Hugus for making available the crystals. This research was supported by the U. S. Atomic Energy Commission.

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(6) M. L. Huggins, THIS JOURNAL, **63**, 66 (1941).

(7) We are indebted to Dr. V. Schomaker who independently derived the coefficients C_h from our tabulated values of F_{hkl}, and who computed the two series by a punched-card method. We checked his maxima by computing $d/dx\ \rho(x00) = -2\pi\Sigma hC_h \sin 2\pi hx$ for a few values of x near 0.24 for each series.

(8) "Internationale Tabellen zur Bestimmung von Kristallstrukturen," Edwards Brothers, Ann Arbor, Michigan, 1944, II, pp. 572–573.

(9) L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, New York, 1942, p. 165.

DEPARTMENT OF CHEMISTRY AND RADIATION LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA
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4-Carboxyazelaic Acid

BY JOHN F. TINKER

The sodio derivative of 2-carbethoxycyclopentanone reacts with esters[1] of 4-bromobutyric acid in alcohol solution to yield esters of 4-carboxyazelaic acid.

4-Carboxyazelaic Acid (1,4,7-Tricarboxyheptane).—In a 500-cc. 3-necked flask, equipped with a Hershberg stirrer with a rubber seal, a reflux condenser with a drying tube, and a dropping funnel, was placed 8.0 g. (0.33 gram-atom) of metallic sodium; 80 cc. of anhydrous methanol was added dropwise, and the mixture stirred until the sodium had dissolved. Methyl 2-ketocyclopentanecarboxylate[2] (47.5 g. 0.33 mole) was added rapidly, the mixture stirred for a few minutes, and 60.5 g. (0.33 mole) of methyl 4-bromobutyrate[1] was added. The mixture was refluxed for 3 hours, and allowed to stand overnight. The mixture was poured onto 100 g. of ice in a 500-cc. separatory funnel, made basic with a little dilute alkali, and separated. The aqueous phase was extracted with three 100-cc. portions of chloroform, and the combined organic layers carefully fractionated. Nineteen grams of methyl adipate was obtained (b.p. 70–75° at 3 mm., refractive index 1.4277 at 24° sodium D line), and 56 g. (70% of theoretical) of trimethyl 4-carboxyazelate (b.p. 135–137° at 3 mm., n_D 1.4464 at 24°; d^{24}_4 1.088; molar refractivity calcd. 65.1, found 67.3). The triester has a single, sharp adsorption band in the carbonyl region of the infrared at 5.70 mμ, in dilute carbon tetrachloride solution. A sample redistilled for analysis through a short helix-packed column boiled at 121–123° (uncor.) at 0.3 mm. (bath temperature 170–175°).

Anal. Calcd. for $C_{13}H_{22}O_6$ (274.3): C, 56.92; H, 8.08. Found: C, 56.55; H, 7.69.

One gram of the triester was refluxed with 25 cc. of 2% hydrochloric acid until it had dissolved, the solution evap-

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(1) For the preparation of these esters see J. Tinker, *J. Org. Chem.*, in press.

(2) G. Komppa and A. Talvitie, *Ann. Acad. Sci. Finnicae*, Ser. A **57**, No. 15, 3 (1941); *C. A.*, **38**, 5496^8 (1944).