isotropic phase of *t*-butyl chloride and *t*-butyl bromide were grown from the liquids in the capillaries. Oscillation diagrams were obtained at −45 ± 3° and −35 ± 3°, respectively. The reflections for both crystals could be indexed on the basis of face-centered cubic unit cells with a_0 = 8.40 ± 0.05 Å. for the chloride and 8.78 ± 0.05 Å. for the bromide. Extrapolations from the known densities of the liquids indicate that there are in each case four molecules per unit cell. The computed density of *t*-butyl chloride is 1.04 at −45° and that of *t*-butyl bromide is 1.34 at −35°.

Discussion

A stationary molecule of low symmetry cannot of itself form the pattern unit of a lattice of high symmetry. In such cases some form of disorder, rotational or orientational, must be present. In both *t*-butyl chloride and *t*-butyl bromide there is only one molecule per lattice point. Molecules of both compounds possess axes of threefold symmetry but do not possess the two-fold symmetry axes needed if the molecules are to be stationary in the cubic unit cells found.

Values of F_{hkl}, based on several postulated types of disorder, were computed for comparison with values of $F_{observed}$. In the case of both compounds, intensities calculated on the basis of molecules rotating freely (or randomly oriented about one mean position)[5] showed variation of calculated *F*'s approximately in accord with those observed.

To improve the agreement between $F_{observed}$ and $F_{calculated}$ calculations were made by assuming rotation or orientational disorder about several positions along the carbon–halogen axis between the central carbon and the center of mass. In the case of the chloride the best fit to the observed data is at a point 0.46 Å. from the central carbon. The center of mass is 0.49 Å. from the central carbon. The best fit for the bromide was 0.41 Å. from the central carbon. The center of mass is 0.87 Å. away from the central carbon. Table I shows a comparison of computed and observed data.

TABLE I

COMPARISON OF CALCULATED AND OBSERVED STRUCTURE FACTORS

	t-Butyl chloride		*t*-Butyl bromide	
hkl	$F_{calcd.}$	$F_{obsd.}$	$F_{calcd.}$	$F_{obsd.}$
111	10.0	10.0	10.0	10.0
200	7.3	7.0	7.4	7.5
220	−0.1	..	1.1	1.4
311	0.0	..	−1.0	0.8
222	−0.5	2.9	−1.3	2.8

The distance between the molecular centers is 5.94 Å. in the case of the chloride, and 6.20 Å. for the bromide. By use of Pauling's value for the van der Waals radius for a methyl group,[6] it is found that the spherical volumes swept out by molecules rotating or randomly oriented about the centers determined above have diameters of 7.5 Å. for both cases. It is evident that rotation of the molecules is subject to steric restriction. The available X-ray data indicate that the restriction is not great enough to preclude reasonably good agreement between observed intensities and intensities calculated on the assumption of molecules with spherical symmetry on the average.

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(5) W. H. Zachariasen, "Theory of X-Ray Diffraction in Crystals," John Wiley and Sons, Inc., New York, N. Y., 1945, p. 213.

(6) L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1949, p. 189.

The Reaction between Calcium Hydroxide and Uranyl Nitrate Solutions[1]

BY CHARLES TANFORD,[2] ROBERT L. TICHENOR[3] AND H. A. YOUNG[4]

Tridot[5] has shown recently that the precipitates obtained from uranyl salt solutions by the addition of ammonia, sodium hydroxide or potassium hydroxide solutions have many points in common including the following: (1) the hydroxide is precipitated only after addition of 1.5 to 1.6 moles of base per mole of uranium; (2) the initial precipitate is $UO_3 \cdot xH_2O$; (3) this precipitate reacts with additional base to form a di-uranate such as $2UO_3 \cdot K_2O$; (4) in an excess of base, the mono-uranate, $UO_3 \cdot Na_2O$, can be prepared, but on washing with water this loses alkali until it reaches the composition of the di-uranate.

These results of Tridot are consistent with observations we made in 1945 while investigating the reaction between calcium hydroxide and uranyl salt solutions. As shown in Table I, considerably more than one equivalent of hydroxyl ion per mole of uranium must be added to stoichiometric uranyl nitrate solutions before a precipitate is obtained. In agreement with Tridot, we found the color of a solution of uranyl salt to deepen as the base is added even though no precipitate has appeared. Thus, between *p*H 4.1 and 5.5 the optical density at 4300 Å. of a 0.00685 *M* uranyl nitrate solution to which dilute $Ca(OH)_2$ solution was being added increased about 2.5-fold.

TABLE I

FORMATION OF INITIAL PRECIPITATE BY ADDITION OF 0.02 *M* $Ca(OH)_2$ TO URANYL NITRATE SOLUTIONS

U concn. at turbidity point	Equiv. OH^-/mole U at turbidity point
0.00187	1.92
.00442	1.64
.00716	1.68
.0173	1.60

Also, the initial precipitates contained very little calcium; the atomic ratio U/Ca was found to lie between 36 and 64.

Table II summarizes experiments on the dependence of the *p*H of precipitation on the uranium concentration; the *p*H decreases as the uranium concentration increases. The table also indicates that equilibrium in the precipitation is attained slowly, for after the initial precipitate is observed, the *p*H decreases in 24 hours by 0.8 to 1.1 *p*H units.

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(1) Done under contract W-7401-eng-23 for the Manhattan Project by Tennessee-Eastman Corporation at Oak Ridge, Tennessee in 1945.

(2) Department of Chemistry, State University of Iowa, Iowa City, Iowa.

(3) Thomas A. Edison, Inc., West Orange, New Jersey.

(4) Division of Chemistry, University of California, Davis, California.

(5) G. Tridot, *Ann. Chem.*, [12] **5**, 358 (1950).

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	$(U)(OH^-) \times 10^{11}$	$(U)(OH^-)^2 \times 10^{19}$	Final pH^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.

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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) $J1_1$ 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).