of material by chromatographic adsorption on alumina.

Experimental[11]

Materials.—Pure isodurene was prepared according to Smith's method.[12] On careful fractionation of the product through a Fenske column, the middle fraction, b.p. 195.5–195.6°, $n^{20}{}_{\mathrm{D}}$ 1.5130, was collected and used for nitration.

The isodurene-rich isomeric mixture used as a convenient starting material for the preparation of large amounts of 4,6-dinitroisodurene was obtained by submitting the tetramethylbenzene filtrate, after separation of durene in the usual manner[13] to a number of further freezing processes each followed by centrifugation with an International Equipment Co. refrigerated centrifuge at successively lower equilibrium temperatures down to −23°. After each centrifugation, the equilibrium liquid was separated from the solid (durene) by filtration, except for the last two processes at −20 and −23°, respectively, in which the equilibrium liquid was decanted. The clear liquid thus obtained was directly used for nitration. From 130 g. of starting tetramethylbenzene filtrate, 95 g. of such a liquid was obtained.

Nitration Experiments.—These experiments were carried out in essential accordance with the procedure described in Part II,[1] with the exception of the mode of addition of the nitrating reagent. In the present work, better results were obtained when a solution of nitric acid in 98% sulfuric acid was prepared first and then added to the chloroform solution of the hydrocarbon.

(a) **Nitration of Isodurene.**—On dinitration of 1.005 g. of isodurene (0.0075 mole) with a stoichiometric amount of nitric acid, 1.31 g. of crude 4,6-dinitroisodurene was obtained. After two crystallizations from ethanol, the yield was 0.95 g. (57.5%) of white needles, m.p. 181.5–183.5°. After two further crystallizations, a constant melting point value of 182.5–183.5° was observed.

Unlike durene[1] and prehnitene,[14] isodurene shows no sharp color change at the end of the reaction with a stoichiometric amount of nitric acid.

(b) **Nitration of the Isodurene-rich Isomeric Mixture.**—A four-batch dinitration of 20.0 g. of the isodurene-rich isomeric mixture, obtained at −23° as described above, was carried out with a stoichiometric amount of nitric acid in a straight-wall beaker of 15-cm. height and 4-cm. width, to give a combined yield of 25.9 g. of crude product, m.p. 160–175°. After three crystallizations from ethanol, the yield of 4,6-dinitroisodurene was 14.4 g. (43%), m.p. 181.5–183.5°.

4-Nitro-6-aminoisodurene.—To a boiling solution of 14.4 g. of 4,6-dinitroisodurene (0.064 mole) in 400 ml. of ethanol, a solution of sodium disulfide (prepared from 50 g. of crystalline sodium sulfide and 6.5 g. of sulfur in 145 ml. of water) was gradually added. The mixture was refluxed for an over-all time of five hours; then most of the alcohol was removed by distillation and the residue was poured into ice water. After filtration, the collected product was dissolved in hot 10% hydrochloric acid and the resulting solution was filtered, if necessary. This solution was made alkaline by gradual addition of concd. ammonia, and the product which separated was collected by filtration and dried. A beautiful yellow powder, m.p. 139.5–140.5°, was obtained; the yield was 12.1 g. (97.5%).

Anal. Calcd. for $C_{10}H_{14}N_2O_2$: C, 61.84; H, 7.26; N, 14.42. Found: C, 61.51; H, 7.65; N, 14.49.

4-Nitroisodurene.—4-Nitro-6-aminoisodurene was diazotized and the resulting diazo-salt was treated with 50% hypophosphorous acid according to the procedure previously described for the corresponding durene compound.[3] The reaction mixture was kept in ice water for a fortnight and, after filtration, the collected product was thoroughly mixed with chloroform. The chloroform solution thus obtained was filtered from any inorganic material left behind and then worked up in the usual manner.[3] From 7.77 g. of nitroamino compound (0.040 mole), 5.37 g. of a crude, brown-yellow product was obtained. For decolorization and purification, the latter was dissolved in 90 ml. of dry petroleum ether (b.p. 40–60°), and the resulting solution was applied on a column of 90 g. of alumina for adsorption. Elution was continued with a 5% solution of absolute ethanol in dry petroleum ether until a brown-yellow band due to impurities reached the bottom of the column. On evaporation of the combined elution liquids, a very pale-colored crystalline residue of 5.18 g. (72.2%) of 4-nitroisodurene, m.p. *ca.* 40°, was obtained. On recrystallization from methanol, the melting point raised to 41–42°.

With only a small percentage decrease in the final yield, the reduction of the diazo-salt can be made faster by keeping the reaction mixture at room temperature for two days or so.

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[11] All melting points are uncorrected.

[12] L. I. Smith, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 360.

[13] Reference 12, p. 248.

[14] Unpublished studies.

Density and Refractive Index of Uranyl Fluoride Solutions[1]

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In the course of an ultracentrifugal investigation of uranyl fluoride solutions, their densities and refractive indices were measured as a function of concentration.

The measurements were carried out near 25 and 30° and if necessary extrapolated to 25.0 and 30.0° from the observed temperature coefficients. Most density data were obtained pycnometrically (25-cc. samples) and a few with gradient tubes.[2] The refractive index measurements were carried out with a Bausch and Lomb dipping refractometer (calibrated with "known" solutions) using sodium-D light (reproducibility ±0.00004).

The materials used and the analytical procedures were described earlier.[3] Although the accuracy of the density measurements was approximately one part in 10,000, the accuracy of the determinations at high UO_2F_2 concentration is considerably less, in view of the uncertainty in the uranium analyses (±0.2% in the uranium concentration).

1. **Density.**—The density data, which are listed in Table I, could be fitted to the quadratic equation

$$1/d = 1/d_0 + aF_2 + bF_2^2 \qquad (1)$$

where d is the density of the solution, d_0 the density of the pure solvent and F_2 the weight fraction of UO_2F_2. The empirical constants a and b were obtained from the intercept and slope of a plot of $(1/d - 1/d_0)/F_2$ *vs.* F_2, which is a straight line. At 25°, $a = -0.9120$ and $b = 0.0567$ and at 30°, $a = -0.9126$ and $b = 0.0569$ give satisfactory fit as shown in Table I. Dean[4] earlier measured densities of UO_2F_2 solutions in the range 13 to 66

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[1] This document is based on work performed for the Atomic Energy Commission at the Oak Ridge National Laboratory.

[2] (a) K. Linderstrom-Lang and H. Lanz, *Compt. rend. trav. lab. Carlsberg*, **21**, 315 (1938); (b) C. Anfinsen, "Preparation and Measurement of Isotopic Tracers," J. Edwards, Ann Arbor, Michigan, 1947, p. 61.

[3] J. S. Johnson and K. A. Kraus, THIS JOURNAL, **74**, 4436 (1952).

[4] G. R. Dean, Report CC 2092, September, 1944.

Table I

Density and Refractive Index of Uranyl Fluoride Solutions

	Density				Refractive index				Mole refraction
	25°		30°		25°		30°		
Wt. % UO_2F_2	d	$\Delta d^a \times 10^4$	d	$\Delta d^a \times 10^4$	n^{25}_D	$\Delta n^a \times 10^5$	n^{30}_D	$\Delta n^a \times 10^5$	(cc.) (25°)
1.002					1.33319	−1	1.33266	−4	17
2.495	1.0202[b]	0			1.33417	0	1.33366	−5	17.0
4.985	1.0443	0	1.0429	0	1.33586	0	1.33531	−2	17.0
5.025	1.0448	−1			1.33597	−8			17.1
7.481					1.33764	−2	1.33705	−2	17.1
9.607					1.33925	−10	1.33864	−7	17.2
10.20	1.0983	0	1.0967	0	1.33963	−5	1.33907	−7	17.1
15.01					1.34333	−6	1.34275	−7	17.04
20.09	1.2164	+2	1.2146	0	1.34756	−5	1.34692	−2	17.09
20.48	1.2219[b]	−2			1.34788	−2	1.34721	+3	17.01
24.89					1.35188	−1	1.35114	+9	17.06
30.10	1.3632	0			1.35705	0			17.09
30.18	1.3632	+13	1.3607	+15	1.35705	+6	1.35636	+11	17.21
33.39					1.36059	+1	1.35988	+5	17.09
40.30	1.5509	+4	1.5481	+6					
40.27					1.36888	−5	1.36825	−9	17.14
46.36					1.37726	−1	1.37647	+6	17.15
50.27	1.7893	+2	1.7859	+1	1.38316	+14	1.38239	+18	17.13
50.90					1.38439	−5	1.38370	−11	17.15
56.90					1.39503	+1	1.39418	+10	17.13
57.10					1.39542	0	1.39457	+9	17.13
61.12					1.40392	−26	1.40303	−15	17.14
61.63	2.1627	−1	2.1589	−15	1.40475	+2	1.40407	−9	17.11

[a] Δd and Δn are the differences: calculated values minus experimental values. [b] Measured by gradient tube method.

weight per cent. His densities agree with those calculated by equation 1 to *ca.* 0.1% except for the saturated solution, where his points scatter considerably more. Since his densities are reported to four significant figures, the agreement clearly is within his experimental error and indicates that there is no systematic error in the uranium analyses.

Assuming that the density of uranyl fluoride solutions follows equation 1, the apparent molal volume ϕ_v at 25° was computed by the equation

$$\phi_v = M_2(1/d_0 + a + bF_2) = 308.07(0.0909 + 0.0567F_2) = 28.0 + 17.5F_2 \quad (2)$$

where $M_2 = 308.07$ is the molecular weight of uranyl fluoride.

Since it had been shown earlier[3,5] that uranyl fluoride in the concentration range studied does not appreciably dissociate into ions (*i.e.*, essentially is a non-electrolyte under these conditions), the large variation of ϕ_v with concentration is surprising. For non-electrolytes ϕ_v would have been expected to change little with concentration.[6] It is of interest that extrapolation of ϕ_v to $F_2 = 1$ yields $\phi_v = 45.5$ cc. which may be compared with the molal volume $V = 48.3$ cc. of solid UO_2F_2 which was calculated from the crystallographic value of the density ($\rho = 6.38$).[7]

2. **Refractive Index.**—The results of the refractive index measurements are also listed in Table I. The refractive indices were fitted to the equation

$$n^t_D = n^{\circ t}_D + \alpha c + \beta c^{3/2} \quad (3)$$

where c is the concentration (molarity), α and β are constants, and where n^t_D and $n^{\circ t}_D$ are the measured refractive indices of the solutions and of water at temperature t, respectively. Satisfactory fit of the data to equation 3 was obtained at 25° using $\alpha = 0.02055$ and $\beta = -0.00185$ and at 30° using $\alpha = 0.02049$ and $\beta = -0.00183$. The deviations between experimental and calculated values are shown in Table I. It is believed that the scatter is due, to a large extent, to the inaccuracies in the analyses of the uranium solutions.

Values of the mole refraction (R) of UO_2F_2 were calculated according to the equation[8]

$$R = \frac{(n^2 - 1)}{(n^2 + 2)} \times \frac{1}{d}\left(\frac{1000}{m} + M_2\right) - \frac{(n^0)^2 - 1}{(n^0)^2 + 2} \times \frac{1}{d_0} \times \frac{1000}{m} \quad (4)$$

where m is the molality of the solution. The results of the calculations are also listed in Table I. Within the accuracy of the data, R appears to be constant ($R = 17.1 \pm 0.1$ cc.) and hence does not reflect the considerable change in the degree of dimerization of uranyl fluoride which occurs in this concentration range.

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(5) J. S. Johnson and K. A. Kraus, unpublished.

(6) See for example, H. S. Harned and B. B. Owen, "Electrolytic Solutions," Second Edition, Reinhold Publ. Corp., New York, N. Y., 1950, p. 260.

(7) W. H. Zachariasen, *Acta Cryst.*, **1**, 277 (1948).

(8) W. Geffcken, *Z. physik. Chem.*, **B5**, 81 (1929).

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Preparation of β-H-Perfluoro Alkanesulfonic Acids

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The synthesis of β-H-perfluoroethanesulfonic acid by the reaction of sodium bisulfite with tetrafluoro-