I III VI

(IV) and 1,6-dihydroxycyclodecane (V). Table I contains the analytical data.

TABLE I

OXYGEN-18 ANALYTICAL DATA[a]

	Atom % excess oxygen-18			
	Starting compounds	Methanol run	Acetic acid run	
Benzoic acid (II)	1.35 1.38			
Perbenzoate (I)	1.37 1.37			
Benzoate (III)		1.29 1.30[b]	1.23[b]	
Benzyl alcohol (IV)		1.16 1.17	1.19 1.20	
1,6 - Dihydroxycyclodecane (V)		0.024 0.026[c]	0.012 0.014[c]	

[a] Analyzed by the method of W. E. Doering and E. Dorfman, THIS JOURNAL, 75, 5595 (1953). Normal isotopic abundance was taken as 0.204 atom % oxygen-18. [b] The diminution in oxygen-18 content in these samples probably occurred in their purification by crystallization from methanol–water, see M. Bender, ibid., 73, 1626 (1951). [c] A sample of inactive diol showed 0.204% oxygen-18.

Inspection of the data shows that no more than 2% of the excess oxygen-18 is found in the diol and the rest remains as carbonyl oxygen during the rearrangement. These results are inconsistent with the formation of an ion pair in which O^β and O^γ become equivalent,[5] and also rule out a quasi-ring transition state in which O^γ of I would become O^β of III. A very attractive explanation of these results involves a concerted shift of the benzoate group, with retention of its structural integrity in all respects, at the same time that carbon is migrating to oxygen. Such a process can be represented in terms of VI, which can be either a transition state or very short lived intermediate. A structure of the general type exemplified by VI can also be used to describe the details of other internal ion pair rearrangements.[1]

Acknowledgment.—The author wishes to thank Dr. J. E. H. Hancock for his help and advice in carrying out the oxygen-18 analyses.

DEPARTMENT OF CHEMISTRY
YALE UNIVERSITY   DONALD B. DENNEY
NEW HAVEN, CONNECTICUT

EVIDENCE FOR QUADRIVALENT CURIUM: X-RAY DATA ON CURIUM OXIDES[1]

Sir:

The preparation of several curium oxides has been carried out and their X-ray lattice constants measured. These unequivocally show the existence of an oxide with a O/Cm ratio more nearly 2/1 than 1.5/1 on the basis of lattice constants.

Cm^{244}, an alpha emitter of ~19.2 years[2] half-life,

(1) This work was sponsored by the U. S. Atomic Energy Commission.

(2) C. M. Stevens, M. H. Studier, P. R. Fields, J. F. Meek, P. A. Sellers, A. M. Friedman, H. Diamond and J. R. Huizenga, Phys. Rev. 94, 974 (1954).

obtained from pile irradiation of Pu^{239} by the reactions $Pu^{239} \xrightarrow{n} Pu^{240} \xrightarrow{n} Pu^{241} \xrightarrow{n} Pu^{242} \xrightarrow{n}$ $Pu^{243} \xrightarrow{\beta^-} Am^{243} \xrightarrow{n} Am^{244} \xrightarrow{\beta^-} Cm^{244}$, was used for most of the work although Cm^{242}, a 162-day emitter,[3] was used initially. The Cm^{244} was purified at Argonne National Laboratory, with 3% Ca as the only impurity present to more than 0.5% except for Am which was present in the amount of 0.8% at the time of analysis. A subsequent oxidation to Am(VI) with precipitation of the curium as curium trifluoride should have reduced the amount of Am by a factor of from 2 to 10.

In all cases, the initial preparation of the sample consisted of precipitation of curium(III) oxalate in the capillary and ignition of this compound *in situ* in an atmosphere of oxygen at ~400°. Such oxides were black in color.

With Cm^{244}, 10 micrograms of material with X-ray exposures of 20 hours were found satisfactory. With the shorter-lived Cm^{242}, it was found necessary to use $\leqslant 1/2$ microgram and exposures of <1 hour. The longer exposures were made in a 114.6 mm. diameter camera with Eastman Type A film using filtered copper radiation; the shorter exposures in a 60-mm. diameter camera with no-screen film using unfiltered copper radiation.

Curium sesquioxide was prepared by the thermal decomposition of the black oxide at 600° at 10^{-4} mm. pressure; the product was white or faint tan in color. X-Ray analysis showed it to be cubic in structure with $a_0 = 5.50 \pm 0.01$ Å. for the pseudo cube. As can be seen in Table I, this is reasonable for the compound Cm_2O_3.

TABLE I

CUBIC OXIDE XO_2, X_2O_3 COMPOUNDS

X	Lattice constants X_2O_3 (Å.), $a_0/2$	Source	Lattice constants XO_2 (Å.)	Source
U	....		5.4700 ± 0.0001 at 25°C.	F. H. E.[4]
Np			5.4341 ± 0.0002	Present work
Pu	5.52 ± 0.01	F. H. E.[4]	5.3960 ± .0003	work
Am	5.515 ± .005	D. H. T.[5]	5.376 ± .001	Present
Cm	5.50 ± .01	Present work	5.372 ± .003	work

Curium oxide, black, obtained from air ignition gave $a_0 = 5.43$ Å. One oxide was prepared by treatment with an ozone–oxygen stream at 650° followed by slow cooling to 300° in the gas stream. Another oxide sample was made by heating Cm_2O_3 in 1 atm. of oxygen to 650° with slow cooling in the gas. The lattice constant obtained from these two differently treated samples was 5.372 ± 0.003 Å.

In Figure 1 the best values of the dioxides obtainable are plotted against atomic number. Redeterminations were made of NpO_2 (prepared in 1 atm. hydrogen at 1000°), PuO_2 (prepared in 1 atm. oxygen at 600° with slow cooling), and AmO_2 (prepared in a stream of ozone at 600° with slow cooling), in order to obtain accurate values of the

(3) G. C. Hanna, B. G. Harvey and N. Moss, Phys. Rev., 78, 617 (1950).

(4) F. H. Ellinger, unpublished data.

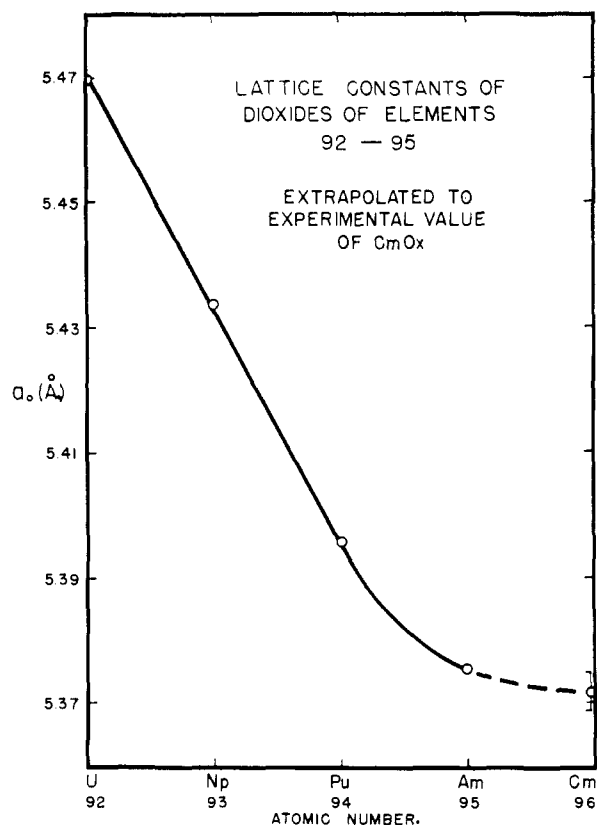(5) D. H. Templeton and Carol H. Dauben. THIS JOURNAL, 75, 4560 (1953).

LATTICE CONSTANTS OF
DIOXIDES OF ELEMENTS
92 — 95

EXTRAPOLATED TO
EXPERIMENTAL VALUE
OF CmOx

Fig. 1.

lattice constants. A reasonable extrapolation of the smooth curve would give ~5.37 for the expected value of CmO_2. Our value of 5.372 would indicate that the ratio of O/Cm must be close to 2, showing the existence of an "average valence" of Cm approaching 4.

UNIVERSITY OF CALIFORNIA   L. B. ASPREY
LOS ALAMOS SCIENTIFIC LAB.   F. H. ELLINGER
P. O. Box 1663   S. FRIED[6]
LOS ALAMOS, NEW MEXICO   W. H. ZACHARIASEN[7]
          RECEIVED JANUARY 31, 1955

(6) Argonne National Laboratory, Lemont, Illinois.

(7) Consultant to Los Alamos Scientific Laboratory; present address: University of Chicago, Chicago, Illinois.

CRYSTALLINE HIGH POLYMERS OF α-OLEFINS

Sir:

No crystalline polymers of olefinic hydrocarbons containing asymmetric carbon atoms in the principal chain of the macromolecules have been reported. Such a lack of crystallinity has been explained[1] by considering such polymers as copolymers of two types of random distributed monomeric units, differing only in the configuration of their dissymmetric group.

Using various heterogeneous solid catalysts which will be described elsewhere,[2] we have synthesized linear crystalline polymers of α-olefins and we are now reporting some properties of

(1) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, New York, 1953, p. 56.

(2) Details on the polymerization processes will be published in the Journal of Polymer Science and Atti dell'Accademia Nazionale dei Lincei.

crystalline polypropylene, poly-α-butylene, and polystyrene. Depending on the structure of the catalyst, different amounts (ranging from 0 to 100%) of the polymerization products are crystallizable and can be separated easily from the much more soluble non-crystalline polymers by solvent extraction. In the case of polypropylene and polystyrene the X-ray diagrams of drawn fibers show reflections from about fifty different planes. Both equatorial and higher order X-ray reflections of polystyrene may be indexed on the basis of a hexagonal cell with $a = 21.9$ Å., and $c = 6.65$ Å. (space-group R 3c or R $\bar{3}$c). One of the two different crystal forms we observed for the poly-α-butylene seems to have a similar cell with $a = 17.3$ Å. and $c = 6.7$ Å. We have not yet collected sufficient data to establish the correct unit cell of polypropylene: the identity period along the fiber axis c is, in this case, 6.50 Å.; the equatorial X-ray reflections may be indexed on the basis of an oblique cell with $a = 6.56$ Å., $b = 5.46$ Å. and $\gamma = 106°$ 30'.

In Table I the physical properties of the crystalline polypropylene and poly-α-butylene have been compared with those of the corresponding solid non-crystallizable substantially linear polymers obtained as by-products by the same polymerization processes.

The new crystalline polyhydrocarbons show higher melting point, higher density and lower solubility in organic solvents, than the corresponding "amorphous" polyhydrocarbons having intrinsic viscosity of the same order of magnitude.

The infrared spectra[3] of crystalline polypropylene, of melted samples of the same polymer and of the "amorphous" polypropylene show between 2 and 7.5 μ the high adsorption regions characteristic of hydrocarbons. The wave lengths of the absorption bands between 7.5 and 15 μ in normal and polarized light have been reported in the Table II. Most of the differences between the infrared spectrum of the crystalline and of the non-crystalline polypropylene[4] disappear on melting the crystalline product and reappear after cooling the melted sample.

The large number and the cleanness of the X-ray reflections obtained from drawn fibers of the new polyhydrocarbons demonstrate the unusual regularity of their chain structure. By comparing X-ray and density data are seen that each stretch of principal chain, included in the elementary cell, corresponds to three monomeric units (-CH₂-CHR- and therefore contains an odd number of asymmetric carbon atoms.

For these reasons we have excluded the presence of sequences of asymmetric carbon atoms having alternatively d and l configuration in the principal chain of the polymer, as was proposed for the crystalline poly-alkylvinyl ethers.[5]

(3) A Beckmann IR 2, a Perkin–Elmer model 112, and a Perkin–Elmer model 21 spectrometer with NaCl prisms have been used.

(4) The infrared spectra of the crystalline and of the linear not crystallizable polypropylene are very different from infrared spectra of branched polypropylene produced using AlBr₃ as catalyst.

(5) C. E. Schildknecht, et al., Ind. Eng. Chem., 40, 2104 (1948); C. E. Schildknecht, S. T. Gross and A. O. Zoss, ibid., 41, 1998 (1949); C. E. Schildknecht, A. O. Zoss and F. Grosser, ibid., 41, 2391 (1949).