[CONTRIBUTION FROM THE ARGONNE NATIONAL LABORATORY]

Occurrence of the (4n + 1) Series in Nature

BY D. F. PEPPARD, G. W. MASON, P. R. GRAY AND J. F. MECH

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A small quantity of Np^{237}, the long-lived ancestor of the $4n + 1$ series, has been isolated from a natural source. The Th^{229} content of Th^{230} obtained from Belgian Congo pitchblende concentrate and of Th^{232} obtained from Brazilian monazite has been determined indirectly through isolation of the Ac^{225} daughter. The respective values for the mass ratio Th^{229} to Th^{232} in these sources is $(4.0 \pm 0.6) \times 10^{-11}$ and less than 3×10^{-14}. The mass ratio of U^{233} to U^{238} in the pitchblende concentrate and the monazite samples is set at $(1.3 \pm 0.2) \times 10^{-13}$ and less than $(4 \pm 2) \times 10^{-11}$, respectively. The maximum value for the mass ratio of Np^{237} to U^{238} in the Belgian Congo pitchblende concentrate is thus calculated to be $(1.8 \pm 0.4) \times 10^{-12}$, and the maximum value for the ratio of the respective neutron capture cross sections of U^{238} in the ore body for the $(n,2n)$ and (n,γ) reactions is set at $(1.3 \pm 0.6) \times 10^{-3}$. It is probable that the true values are much lower than these figures which are based on the assumption of zero contribution from the $Th^{232}(n,\gamma)$ reaction. The relative contributions of the $U^{238}(n,2n)$ and the $Th^{232}(n,\gamma)$ reactions cannot be calculated, but it seems likely that the latter reaction makes the larger contribution.

Introduction

The $4n$, the $4n + 2$ and the $4n + 3$ radioactive series, whose respective long-lived parent nuclides are Th^{232}, U^{238} and U^{235}, have long been known to exist in nature. The "missing" $4n + 1$ series, of which Np^{237} may be considered the long-lived genitor, was reported by Hagemann, *et al.*[1], and English, *et al.*[2], who prepared U^{233}, whose mass number conforms to the general formula $4n + 1$, by the $Th^{232}(n,\gamma)Th^{233} \xrightarrow{\beta} U^{233}$ reaction.

It has been pointed out by Seaborg[3] that uranium-bearing ores should contain trace quantities of Np^{237} formed by the $U^{238}\ (n,\ 2n)U^{237} \xrightarrow{\beta} Np^{237}$ reaction; and it has been suggested by Garner, Bonner and Seaborg[4] that uranium-bearing ores containing an appreciable relative quantity of thorium should contain some long-lived U^{233} formed as the result of the $Th^{232}(n,\ \gamma)Th^{233} \xrightarrow{\beta} U^{233}$ reaction. However, isolation of either Np^{237} or U^{233} from natural sources has not been reported, and except for the stable terminal member of the chain, Bi^{209}, the family of radioactive heavy nuclides corresponding to the formula $4n + 1$ has not been found in nature.[1]

In the work presently reported, Np^{237} was isolated from an aqueous waste resulting from the processing of Belgian Congo pitchblende concentrate.

The decay of Np^{237} leads to the formation of Th^{229} (α-active, 7.34×10^3 years),[1] and the decay of U^{238} leads to the formation of Th^{230} (α-active, 8.0×10^4 years).[5] Since the half-lives of these thorium isotopes are very long with respect to the time involved in processing an ore, but very short with respect to the age of the ore deposit, it follows that the ratio of Th^{229} to Th^{230}, by activity, should be identical to the ratio of Np^{337} to U^{238}, by activity, assuming that Th^{229} has been formed by no means other than Np^{237} decay. However, it is to be noted that Th^{229} will be formed if neutrons are captured by the Th^{232} present in small quantities.[1] This correction is of unknown magnitude and may approach 100%.

The ratio of Th^{229} to Th^{230} in a sample containing several grams of Th^{230} (ionium) which had been isolated, in this Laboratory, from an aqueous waste resulting from the processing of Belgian Congo pitchblende concentrate was measured by determining the content of Ac^{225}, a 10.0 day α-active daughter of Th^{229}.

The requirements of the technique are stringent, since a virtually weightless sample of Ac^{225} is required for determination of α-energies[6]; and actinium, a trivalent element, must be separated from divalent radium and lead, trivalent bismuth, and tetravalent thorium. In order to obviate the much more difficult problem of separating actinium from rare earths, the Th^{230} was exhaustively purified from rare earths (and Ac^{225}), and the Ac^{225} allowed to grow again.

Experimental

Isolation of Np^{237} from a Sample of Th^{230}.—In the isolation of approximately one microgram of naturally-occurring Pu^{239} from a uranium process waste,[7] the aqueous effluents from the first thenoyltrifluoroacetone extraction cycle were combined and set aside for further study. This composite aqueous phase was subsequently evaporated to dryness. The residue was dissolved in 0.5 M HNO_3, and the resulting solution made 0.1 M in $K_2Cr_2O_7$. After a heating period of several hours the solution was saturated with magnesium nitrate and contacted with eight equal-volume portions of diethyl ether (0.3 M in HNO_3) which were scrubbed successively with twelve half-volume portions of a solution 3.5 M in $Mg(NO_3)_2$ and 0.2 M in HNO_3. The combined ether extract was allowed to evaporate over water. This aqueous phase was evaporated to dryness.

The resulting residue was dissolved in 5 M HCl, and any plutonium present reduced to the trivalent state (leaving any neptunium present in the tetravalent state). The neptunium was then extracted into four successive portions of 0.4 M thenoyltrifluoroacetone in benzene from the diluted solution.[8] These organic phases were then scrubbed suc-

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(1) French Hagemann, L. I. Katzin, M. H. Studier, G. T. Seaborg and A. Ghiorso, *Phys. Rev.*, **79**, 435 (1950). The decay scheme of the $4n + 1$ series is given in this paper. The values for the half-lives, as well as the characteristic α-energies, of the members were also taken from this reference.

(2) A. C. English, T. E. Cranshaw, P. Demers, J. A. Harvey, E. P. Hincks, J. V. Jelley and A. N. May, *ibid.*, **72**, 253 (1947).

(3) G. T. Seaborg, *Chem. Eng. News*, **25**, 358 (1947).

(4) C. S. Garner, N. A. Bonner and G. T. Seaborg, THIS JOURNAL, **70**, 3453 (1948).

(5) The values for certain half-lives have been taken from the Table of Isotopes of G. T. Seaborg and I. Perlman, *Revs. Modern Phys.*, **20**, 585 (1948).

(6) The energies of the α-particles were determined by means of a multi-channel differential pulse analyzer: described by A. Ghiorso, A. H. Jaffey, H. P. Robinson and B. B. Weissbourd, Paper 16.8 in "The Transuranium Elements," National Nuclear Energy Series, Div. IV, Vol. 14B, McGraw-Hill Book Co., Inc., New York, N. Y., 1949.

(7) D. F. Peppard, M. H. Studier, M. V. Gergel, G. W. Mason, J. C. Sullivan and J. F. Mech, THIS JOURNAL, **73**, 2529 (1951).

(8) This procedure for separating neptunium from plutonium is reported by L. B. Magnusson, S. G. Thompson and G. T. Seaborg, *Phys. Rev.*, **78**, 363 (1950).

cessively with small portions of 1.0 *M* HCl, in order to decrease the content of Th^{230} and trivalent Pu^{239}, until the total α-activity of the composite organic phase (determined by measuring the α-disintegration rate of an aliquot evaporated on a 5-mil platinum disc) was reduced to 110 counts per minute.

In order to simplify the interpretation of later α-pulse data the absence of Th^{230} was proved. The proof was furnished by the removal of added Th^{234}.

Enough Th^{234} tracer was added to the organic phase to produce a total β-counting rate, under the counting conditions used, of 12,700 counts per minute. Following several hours of agitation to permit thorium isotope exchange, the organic phase was scrubbed successively with six small portions of 1.0 *M* HCl in order to strip the thorium from the organic phase. The entire organic phase was then evaporated on a 5-mil platinum disc. The total α-counting rate was 26 counts per minute, and the total β-counting rate was less than 50 counts per minute.

Alpha pulse analysis showed 7 α-counts per minute due to Np^{237}. Most of the remaining activity was due to Pu^{239}.

Isolation of Ac^{225} from a Sample of Th^{230}, No Tracer Added.—A sample of thorium as the nitrate, containing 8.77 ± 0.09 g. of Th^{230} (and 74 g. of Th^{232}), isolated from an aqueous waste resulting from the processing of Belgian Congo pitchblende concentrate for uranium, was extracted into approximately 10 liters of 0.6 *M* solution of thenoyltrifluoroacetone[9] in benzene at a *p*H of unity.[10] This solution was scrubbed with several small portions of 0.1 *M* $\mathrm{HNO_3}$ to remove traces of rare earths, yttrium and actinium. The solution was then allowed to age for 80 days to permit the growth of Ac^{225} from the Th^{229} present.

At the conclusion of the ageing period, the Ac^{225} was removed from the organic phase into a small volume of aqueous phase by scrubbing the organic phase with three successive 200-ml. portions of 0.1 *M* $\mathrm{HNO_3}$,[10] these aqueous phases being successively contacted with two 300-ml. portions of 0.6 *M* thenoyltrifluoroacetone in benzene followed by two 300-ml. portions of benzene. The benzene–thenoyltrifluoroacetone extracts containing the Th^{230} were combined, Ac^{227} tracer was added to a portion, and the extract allowed to age for the experiment described in the section, "Isolation of Ac^{225} from a Sample of Th^{230}, Tracer Added."

The composite aqueous phase, containing radium, bismuth and lead daughters of Th^{232}, of Th^{230} and of Th^{229} and relatively large quantities of Th^{230} and Th^{232} in addition to the desired Ac^{225}, was evaporated to dryness. The residue was dissolved in a small quantity of water, and the solution converted to 10 ml. of saturated ammonium nitrate, 0.3 *M* in $\mathrm{HNO_3}$.

This aqueous feed was then contacted successively with four 10-ml. portions of dibutoxytetraethyleneglycol[11] to extract thorium, followed by two 10-ml. portions of tributyl phosphate[12] to extract actinium, leaving radium in the aqueous phase. (Each of these organic phases had previously been pre-equilibrated with a large volume of saturated ammonium nitrate, 0.3 *M* in $\mathrm{HNO_3}$.) The aqueous feed was then followed, in the extraction cycle, by one 10-ml. portion of ammonium nitrate scrub (saturated ammonium nitrate, 0.3 *M* in $\mathrm{HNO_3}$).

The dibutoxytetraethyleneglycol phases were then discarded. The two tributyl phosphate phases, containing actinium and traces of radium, were contacted successively with two 5-ml. portions of ammonium nitrate scrub in order to reduce the radium content and then contacted successively with three 10-ml. portions of 4 *M* $\mathrm{HNO_3}$ in order to transfer the actinium to an aqueous phase. The aqueous reëxtract was scrubbed with carbon tetrachloride to remove traces of tributyl phosphate[13] and then evaporated to dryness with a heat lamp, taking care not to heat beyond dryness.

The residue was taken up in 2 ml. of saturated ammonium nitrate, and the above cycle of dibutoxytetraethyleneglyco and tributyl phosphate extractions repeated on a scale one-fifth of the foregoing. The final water reëxtract was evaporated to dryness, and the residue allowed to age for 24 hours to permit Ac^{228} and residual Pb and Bi isotopes, not of the Ac^{225} series, to die out to a low value.

Another extraction cycle on the same scale was then performed. The final aqueous reëxtract was then evaporated to dryness, and the container heated with 1 ml. of 0.02 *M* $\mathrm{HNO_3}$, which was then evaporated to about 0.2 ml. This solution was then saturated with ammonium nitrate and contacted successively in a single centrifuge cone with two 0.10-ml. portions of tributyl phosphate. The tributyl phosphate phases were combined, and an aliquot evaporated on a 5-mil platinum disc for α-counting[14] and for measurement of α-energies.[6] The data are listed in Table I. The α-pulse analysis curves are shown in Fig. 1. The two curves pertain to the identical aliquot counted at different bias settings and for different counting times.

Isolation of Ac^{225} from a Sample of Th^{230}, Tracer Added.—Using a shortened version of the preceding procedure, a sample of Ac^{227} was separated from its daughter activities. This isotope of actinium has two modes of decay, approximately 1.2% of the decaying atoms emitting α-particles, and the remainder emitting β-particles.[15] The energy of the β-particles is too low to permit the use of β-counting as an assay technique. However, standardization of an Ac^{227} solution by determination of the α-disintegration rate associated with a certain aliquot is easily accomplished if the α-particles emitted by the Ac^{227} may be distinguished from the α-particles emitted by the daughters of Ac^{227}. Consequently, a solution of this isotope was standardized immediately after purification by determining, through α-pulse analysis, the number of α-disintegrations per minute resulting from the α-branching of the Ac^{227} contained in an aliquot evaporated on a platinum disc. (The energy of the particles considered is sufficiently different from that of any of the Ac^{227} daughters that no difficulty is experienced if the sample is a freshly purified one.)

An aliquot of the standard Ac^{227} solution corresponding to 420 c./min. due solely to α-branching was added to a portion of the benzene–thenoyltrifluoroacetone extract, described in the preceding section, containing 5.31 ± 0.05 g. of Th^{230} (and 45 g. of Th^{232}). (This portion of the extract had been mixed with 300 ml. of 0.1 *M* $\mathrm{HNO_3}$ immediately following the isolation of an actinium fraction as described in the preceding section.) The mixture was agitated for approximately 30 min. each day to prevent the accumulation of Ac^{225}, as formed, on the walls of the container. The extract was allowed to age for 56 days.

An actinium fraction was then isolated by the method described in the preceding section. The final tributyl phosphate extract was evaporated, in approximately equal parts, on two 5-mil platinum discs. One of these samples was immediately subjected to α-pulse analysis (to determine that fraction of the total α-activity due to Ac^{227} and that due to Ac^{225} and its daughters), and the other was concurrently

TABLE I

ISOLATION OF Ac^{225} FROM Th^{230}

Expt.[a]	Th^{230}, g.	Ageing, days	Ac^{225} isolated, c./min.	Yield, %	Ac^{225} content, c./min.
1	8.77	80	227	..	..
2	5.31	56	153	44.5	344[b]

[a] Expt. 1 involved no Ac^{227} tracer. In Expt. 2, Ac^{227} tracer was added so that the chemical yield could be determined. [b] Since the feed solution of Th^{230} had aged 56 days and the period between isolation of the Ac^{225} sample from the Th^{230} and α-pulse analysis of the aliquot was 24 hr., the "Ac^{225} content" represents 76.4% of the maximum value.

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(9) Thenoyltrifluoroacetone was obtained from Dow Chemical Co.

(10) The extraction coefficients for actinium and thorium from an acidic aqueous phase into a benzene solution of thenoyltrifluoroacetone are given by French Hagemann, THIS JOURNAL, **72**, 768 (1950).

(11) Dibutoxytetraethyleneglycol was obtained from Carbide and Carbon Chemical Corporation.

(12) Tributyl phosphate, the *n*-butyl orthoester, was obtained from Commercial Solvents Corporation.

(13) This technique for removal of trace quantities of tributyl phosphate is recommended by J. C. Warf, THIS JOURNAL, **71**, 3257 (1949).

(14) Alpha counting was done with a methane proportional counter with an approximate 52% geometry factor. Beta counting was done on the first shelf of a Geiger-Müller counter filled with neon-amyl acetate gas, with a window thickness of approximately 2 mg./cm.^{2}, using appropriate aluminum absorbers to prevent counting of α-particles.

(15) M. Perey, *J. phys. radium*, **10**, 435 (1939); *J. chim. phys.*, **43**, 155 (1946). S. Peterson and A. Ghiorso, in "The Transuranium Elements," National Nuclear Energy Series, Div. IV, Vol. **14B**, Paper 19.10, McGraw-Hill Book Co., Inc., New York, N. Y., 1949.

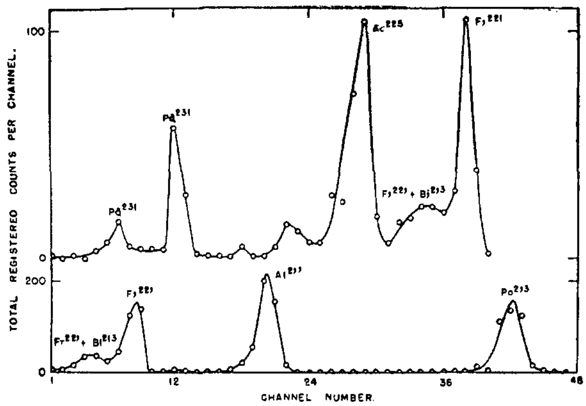

Fig. 1.—α-Spectrum of naturally occurring Ac^{225}.

subjected to α-counting in a counter calibrated at approximately 52% geometry.[14] The data are included in Table I. The α-pulse analysis curve is shown in Fig. 2. The bias setting and counting time differ from those used in obtaining the data of Fig. 1.

Isolation of an Actinium Fraction from a Th^{232} Sample, No Tracer Added.—A sample of thorium as the nitrate tetrahydrate,[16] containing approximately 1 kg. of Th^{232} was dissolved in approximately 14 liters of dibutoxytetraethyleneglycol by long stirring at room temperature. The clarified solution was scrubbed with six 500-ml. portions of 6 M ammonium nitrate. The extract, containing 985 ± 10 g. of Th^{232}, was then allowed to age for 56 days.

At the conclusion of the ageing period, the extract was contacted with four 250-ml. portions of ammonium nitrate scrub (saturated ammonium nitrate, 0.3 M in HNO_3) in order to strip the actinium, leaving the thorium in the organic phase. These aqueous phases were then separately and successively contacted with two 250-ml. portions of tributyl phosphate, in order to separate actinium from radium, etc.

The dibutoxytetraethyleneglycol phases were combined with the large dibutoxytetraethyleneglycol extract. Tracer Ac^{227} was added, and the extract allowed to age for the experiment described in the section, "Isolation of an Actinium Fraction from a Th^{232} Sample, Tracer Added."

The tributyl phosphate phases were then contacted successively with three 125-ml. portions of 4 M HNO_3. The combined aqueous re-extract, containing actinium and contaminants, was scrubbed with carbon tetrachloride to remove traces of tributyl phosphate and then evaporated to dryness with a heat lamp, taking care not to heat beyond dryness.

The residue was dissolved in a small quantity of water, and the solution converted to 10 ml. of saturated ammonium nitrate, 0.3 M in HNO_3. The technique used for the isolation of an actinium fraction from a Th^{230} sample was then used, beginning at the first dibutoxytetraethyleneglycol and tributyl phosphate cycle. The data are listed in Table II.

TABLE II

ISOLATION OF Ac^{225} FROM Th^{232}

Expt.[a]	Th^{232}, g.	Ageing, days	Ac^{225} isolated, c./min.	Yield, %	Ac^{225} content, c./min.
1	985	56	<5	..	..
2	962	73	<3	51.5	<6[b]

[a] Expt. 1 involved no Ac^{227} tracer. In Expt. 2, Ac^{227} tracer was added so that the chemical yield could be determined. [b] Since the feed solution had aged 73 days and the period between isolation of the Ac^{225} sample from the Th^{232} and α-pulse analysis of the aliquot was 24 hr., the "Ac^{225} content" represents 85.1% of the maximum value.

Isolation of an Actinium Fraction from a Th^{232} Sample, Tracer Added.—An aliquot of the standard Ac^{227} solution corresponding to 420 c./min. due solely to α-branching was added to the dibutoxytetraethylene glycol extract, containing 962 ± 10 g. of Th^{232}, described in the immediately preceding section. Following a 73-day ageing period, an actinium fraction was isolated according to the procedure of the preceding section, beginning with the saturated ammonium nitrate scrub. The data are included in Table II.

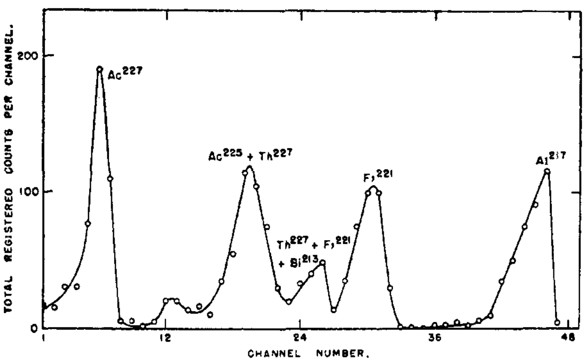

Fig. 2.—α-Spectrum of naturally occurring Ac^{225} with Ac^{227} tracer.

Results and Discussion

From the data of Table I, introducing limits of error, values for the following mass ratios, at secular equilibrium in the ore body, may be derived: Th^{229} to Th^{230}, $(3.4 \pm 0.3) \times 10^{-10}$; Th^{229} to Th^{232}, $(4.0 \pm 0.6) \times 10^{-11}$; and U^{233} to U^{238}, $(1.3 \pm 0.2) \times 10^{-13}$.

From the data of Table II, the mass ratio of Th^{229} to Th^{232}, at secular equilibrium in the ore body, is calculated to be less than 3×10^{-14}, corresponding to upper limits for the mass ratios U^{233} to Th^{232} and U^{233} to U^{238} of 7×10^{-13} and $(4 \pm 2) \times 10^{-11}$, respectively.

Assuming that all of the U^{233} present in the pitchblende concentrate was formed as the result of the $U^{238}(n, 2n)$ reaction, a maximum value of $(1.8 \pm 0.4) \times 10^{-12}$ may be set for the Np^{237} to U^{238} mass ratio in this deposit. The corresponding maximum value of $(1.3 \pm 0.6) \times 10^{-3}$ for the ratio of the respective neutron-capture cross-sections of U^{238} in the ore body for the $(n, 2n)$ and (n, γ) reactions may then be calculated, since the Pu^{239} to U^{238} mass ratio in the same deposit is $(1.5 \pm 0.2) \times 10^{-11}$.[7]

However, it appears likely that the $Th^{232}(n, \gamma)$ reaction is a considerably greater contributor to the U^{233} content than is the $U^{238}(n, 2n)$ reaction and that, therefore, the true values of the above ratios are much lower than the upper limits which have been determined.

The neutron flux is assumed to be contributed to by: the $M_1(\alpha, n)M_2$ reaction where M_1 is a light element such as Li, Si, Mg, etc.; spontaneous fission of U^{238}; induced fission of U^{235}; and cosmic rays. The importance of these various neutron sources in ore bodies has been discussed by Seaborg, *et al.*,[3,17] Levine, *et al.*,[18] Garner, *et al.*,[4] and Peppard, *et al.*[7]

Since the $M_1(\alpha, n)M_2$ reaction is almost certainly the major source of neutrons in monazite, it is logical to assume a much lower neutron flux in the monazite than in the pitchblende deposit, since the flux

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(16) The thorium nitrate, obtained from Lindsay Light and Chemical Co., had been isolated from a Brazilian monazite concentrate with approximate Th and U contents of 6 and 0.1%, respectively.

(17) G. T. Seaborg and M. L. Perlman, THIS JOURNAL, **70**, 1571 (1948).

(18) C. A. Levine and G. T. Seaborg, *ibid.*, **73**, 3278 (1951).

of α-particles sufficiently energetic to produce the (α, n) reaction is relatively very much lower in the monazite sample. The monazite also contains a much higher relative content of contaminants of high neutron-capture cross-sections than does pitchblende. Consequently, in a qualitative fashion, the fact that monazite has a much lower Th^{229} to Th^{232} ratio than does pitchblende is satisfactorily explained, even on the assumption that nearly all of the Th^{229} is present as the result of the $Th^{232}(n, \gamma)$ reaction.

CHICAGO 80, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE PURDUE RESEARCH FOUNDATION, PURDUE UNIVERSITY]

An Electron Diffraction Investigation of the Molecular Structures of Ketene, Carbonyl Fluoride and Tetrafluoroethylene[1]

BY T. TAYLOR BROUN AND R. L. LIVINGSTON

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The interatomic distances in ketene, carbonyl fluoride and tetrafluoroethylene have been determined by electron diffraction, using the visual correlation procedure. The following results were obtained: ketene, C=C = 1.30 ± 0.02 Å., C=O = 1.16 ± 0.02 Å. with ∠HCH and C–H assumed to be 117.5 ± 12.5° and 1.07 ± 0.02 Å., respectively; carbonyl fluoride, C–F = 1.32 ± 0.02 Å., C=O = 1.17 ± 0.02 Å. and ∠FCF = 112.5 ± 6°; tetrafluoroethylene, C–F = 1.30 ± 0.02 Å., C=C = 1.33 ± 0.06 Å. and ∠FCF = 114 ± 3°. The results for ketene are compared with an earlier electron diffraction investigation and with infrared and microwave results. The interatomic distances in C_2F_4 compare favorably with those obtained in a recent electron diffraction investigation in which the rotating sector was employed.

The interatomic distances in ketene have been determined both by electron diffraction and by spectroscopy. The electron diffraction results[2] gave C–C = 1.35 Å. and C–O = 1.17 Å. and were compatible with a linear arrangement of the carbon and oxygen atoms. A study of the infrared spectrum[3] of this compound did not yield sufficient data to fix all of the parameters, but a model with C–C = 1.300 Å. and C–O = 1.154 Å. was found to be in agreement with the infrared data. It was because of the disagreement between the electron diffraction and infrared results that the present reinvestigation of ketene was undertaken. It was felt possible to improve upon the early electron diffraction study since the results of that investigation were based upon measurements of only six features and gave an average deviation of 0.033 from the mean $s_{\text{calcd}}/s_{\text{obsd}}$ ratio. After the present investigation was started, the results of two microwave studies of ketene were published. The first of these[4] led to a preferred model with C–C = 1.333 Å. and C–O = 1.150 Å., while the second[5] gave the long C–O distance as 2.62 Å.; these results will be discussed later.

The interest in tetrafluoroethylene stems from the rather large differences which have been observed in the length of C–F bonds in various fluorine compounds. In methyl fluoride, this distance is 1.39 Å.[6]; in methylene fluoride, it is 1.36 Å.[7]; in fluoroform, it is still shorter.[8] It seemed interesting to be able to compare with the above distances the C–F distances in C_2F_4 and in F_2CO where the double bond on the same carbon atom might cause additional shortening. Such a shortening has been observed in the corresponding chlorine compounds.[9]

A comparison of the C–C bond distances in ketene and in ethylene with that in C_2F_4 should indicate whether or not the presence of the fluorine atoms has any effect on this bond length. Further, a comparison of the C–O distances in H_2CO and in F_2CO should permit one to determine if the fluorine atoms have any effect on this bond length.

Experimental

Ketene was prepared in this Laboratory by the thermal cracking of acetone.[10] After removal of acetone from the ketene by simple distillations, the product was subjected to rectification in a Podbielniak Hyd-Robot distillation column. The ketene distilled at a temperature of −73.8 ± 0.5° at 187 mm. and the sample used for the diffraction photographs was taken from the middle of this fraction. The sample was judged to be well above 99% in purity.

The carbonyl fluoride sample was provided by the Carbide and Carbon Chemicals Co. (Oak Ridge) operating under a contract with the U. S. Atomic Energy Commission. Infrared examination of the compound carried out at Oak Ridge indicated that the sample contained much less than 1% of impurities.

Two samples of tetrafluoroethylene were employed. One of these was obtained in this Laboratory by distillation of a commercial sample in the Podbielniak Hyd-Robot distillation column; a middle portion of the constant-boiling mixture was collected for photographing. The second was a specially purified sample supplied by Dr. C. F. Hammer of the Research Division, Polychemicals Department of the du Pont Company.

The electron diffraction photographs were prepared using an apparatus constructed by Professor H. J. Yearian of the Purdue Department of Physics. The wave lengths of the electrons were determined from transmission patterns of zinc oxide and were about 0.055 Å.; the camera distances were about 11 cm.

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(1) Contains material from the Ph.D. thesis of T. Taylor Broun, Purdue Research Foundation Fellow in Chemistry, 1949–1951.

(2) D. P. Stevenson and J. Y. Beach, *J. Chem. Phys.*, **6**, 75 (1938).

(3) G. Herzberg, Symposium on Molecular Structure and Spectra, The Ohio State University, June, 1947.

(4) B. Bak, S. Knudsen, E. Madsen and J. Rastrup-Andersen, *Phys. Rev.*, **79**, 190 (1950).

(5) H. R. Johnson, J. G. Ingersoll and M. W. Strandberg, *ibid.*, **82**, 327 (1951).

(6) V. Schomaker and D. P. Stevenson, THIS JOURNAL, **63**, 37 (1941).

(7) R. L. Livingston and C. R. Rice, to be published.

(8) See references 20–22.

(9) L. O. Brockway, *Rev. Modern Phys.*, **8**, 231 (1936).

(10) (a) Fieser and Fieser, "Organic Chemistry," D. C. Heath and Co., Boston, Mass., 1944; (b) R. O. Rice, J. Greenberg, C. E. Waters and R. E. Vollrath, THIS JOURNAL, **56**, 1760 (1934).