at 47-50° after crystallization from benzene-petroleum ether mixture.

A separation of this mixture of isomers was effected by adsorption of the material (2.0 g.) on alumina from its benzene solution. The benzene eluates of the "flowing chromatogram" (0.55 g.) melted at 146-147° after crystallization from the same solvent. When mixed with the "*trans*"-isomer of Ludutsky[4,9] (m. p. 147-148°) the compound melted at 145.7-146.7°. The subsequent ether eluate (0.81 g.) from the same chromatogram could be crystallized from benzene-petroleum ether mixture and melted at 47-50°.[14] Vacuum sublimation of this material gave a crystalline sublimate, m. p. 43-46°. The residue melted at 58-61°.

The product obtained from the aqueous alkali (1.50 g.) was crystallized from Skellysolve B. The first crop of crystals, m. p. 110-120°, weighed 150 mg. Three crystallizations from benzene-ligroin raised the melting point to 141-142°. The mixture with the octahydro compound of Hoehn[5] (m. p. 144-145°) melted at 141-142°.

Ultraviolet Absorption Spectra.—The ultraviolet absorption spectra of the compounds were determined in 95% alcohol in approximately 0.0002 molar solution with a Beckman spectrophotometer.[15] The results are given in Table I.

TABLE I

ULTRAVIOLET ABSORPTION SPECTRA OF THE RACEMIC COMPOUNDS

Compound	$\epsilon\lambda$max. 225 mμ	$\epsilon\lambda$max. 280 mμ	$\epsilon\lambda$min. 250 mμ
I	3.803	3.205	2.023
II	3.868	3.232	2.281
III	...[a]	3.274	2.286
V[b]	4.119	3.477	2.441

[a] Not determined. [b] Racemic hexestrol.

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(14) The unusual behavior on adsorption is perhaps explained by the formation of a complex compound between the isomers. This would also explain the reported difficulties in separation.[4]

(15) Absorption spectra by Dr. E. E. Pickett, University of Missouri.

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The Half-Life of Protactinium (Pa^{231})

BY Q. VAN WINKLE,[1a] R. G. LARSON[1b] AND LEONARD I. KATZIN

The half-life of protactinium (Pa^{231}), the parent of actinium in the actino-uranium decay series, has been determined by a number of investigators. Values have been reported which range from 12,500 years to 32,000 years.[2,3,4] In view of the indirect methods used in the determinations, and their wide scatter, a redetermination of the protactinium half-life value has been made through direct determination of the specific activity with the aid of modern methods for counting alpha particles. A value of 34,300 ± 300 years has been found using the formula Pa_2O_5 for the ignited oxide of protactinium.

Experimental

Two samples of protactinium oxide were used in the half-life determinations. One was taken from material which had been isolated and purified by Larson, Katzin and Hausman,[5] and the second was taken from a preparation which had been isolated and purified by Thompson, Van Winkle and Malm.[6] These samples were given an additional purification by precipitating protactinium as the hydrated oxide from 0.5-1.0 *N* nitric acid either by heating on a boiling water-bath for five minutes (sample 1), or through precipitation with hydrogen peroxide added to 3% concentration (sample 2).

Samples of hydrated oxide were slurried into platinum crucibles using 1 *N* nitric acid, then dried and ignited to constant weight in a muffle furnace at 700-800°. Weighings were made on a semimicro balance with a sensitivity of 0.15 scale divisions per 10 micrograms. After ignition to constant weight, the oxide was made soluble by adding concentrated hydrofluoric acid and evaporating to dryness. The dried material was dissolved in 6 *N* hydrochloric acid solution (sample 1) or 1 *N* nitric acid (sample 2) and made up to volume. Aliquots of these two solutions were evaporated on platinum counting discs for determination of the alpha emission rate. Results are based on four aliquots of sample 1 and six aliquots of sample 2.

Aliquots from both sample solutions were analyzed spectrographically for impurities in the protactinium. We wish to thank Dr. Frank Tomkins for performing these analyses.

Determination of alpha particle emission rate was made with a counter having a mixture of argon and carbon dioxide at atmospheric pressure flowing through the chamber. The counter has been described by Jaffey.[7] Its effective counting yield is 51.7% and its coincidence loss has been estimated as 1.26% per 100,000 counts per minute.

Results

The data obtained have been summarized in Table I. The values appearing in line 3 for the weight of oxide were obtained by correcting the weight in line 2 for the impurities revealed by the spectrographic analysis. The corrections were made on the basis of the corresponding oxides. Sample 1 contained 1.5% iron, 0.15% calcium and 0.035% magnesium by weight. Impurities in sample 2 were less than the minimum detectable

TABLE I

Sample	1	2
Atm. ignited oxide, mg.	0.72	2.86
Cor. wt. oxide, mg.	0.705	2.86
Solution volume, ml.	5.00	49.63
Aliquot, μl.	25.0	50.35
Av. counting rate (cor.) of aliquot (51.7% counting yield)	153,500	128,100
Specific activity (counts/min./g. Pa)	5.11×10^{10}	5.18×10^{10}
Half-life, years	34,700	34,300

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(2) O. Hahn, *et al.*, *Ber. Berlin. Akad.*, 278 (1927); *Naturwiss.*, **16**, 454 (1928); *Z. angew. Chem.*, **42**, 926 (1929); *Naturwiss.*, **20**, 505 (1932); **15**, 803 (1927).

(3) J. H. Mennie, *Phil. Mag.*, [6] **46**, 684 (1923).

(4) A. von Grosse, *Ber.*, **61**, 243 (1928); *Naturwiss.*, **20**, 505 (1932).

(5) R. Larson, L. I. Katzin and E. Hausman, Plutonium Project Record, Vol. 17B, no. 6.3.

(6) R. C. Thompson, Q. Van Winkle and J. G. Malm, Plutonium Project Record, Vol. 17B, no. 6.4.

(7) A. H. Jaffey, Plutonium Project Record, Vol. 14A, Chapter 17.

a formula for the oxide of Pa_2O_5, the half-life of the protactinium is calculated, using the relation $\lambda T = \log_{e}2$, where λ is the disintegration constant and T is the half-life. Since the two samples give the same half-life value within experimental error, the rather more precise value of sample 2 is taken, namely, 34,300 ± 300 years.

The largest uncertainty in the measurements may actually be the structure of the ignited protactinium oxide. We are indebted to Professor W. H. Zachariasen for a study of the X-ray structure of the powder. Although the patterns obtained are complex, there seems to be evidence for a possible PaO_2 structure. If the composition of the ignited material is actually the dioxide composition, the half-life value given would be low by approximately 3%.

Discussion

The presently reported value of the Pa^{231} half-life, 34,300 years, is higher than any appearing in the literature. The closest correspondence is found with the 1932 value of von Grosse, namely, 32,000 years.[4] This value was obtained from presumedly pure macro amounts of the isotope; the values given in the earlier literature are based on growth into purified uranium of the protactinium. These early determinations depend on measuring current intensities in an alpha electroscope, knowing the number of ion pairs produced for both protactinium alphas and U^{238} alphas, and knowing precisely the ratio of activity of U^{235} and U^{238} in natural uranium. The method is beset with corrections and imperfectly known constants, and is inherently inaccurate. Correction of the original data with present values of the constants involved fails to raise the values to the level reported here, although a certain amount of consistency between different determinations by similar techniques can be found. The determination of von Grosse with macro amounts of the isotope eliminated some sources of error, but the determination again was dependent upon knowledge of the number of ion pairs produced per alpha particle, and comparison with alpha emission of uranium as measured in an electroscope. A source of error unknown to von Grosse is the fact that one-eighth the alpha particles emitted by protactinium differ in energy from the rest by some 300 kev.[8] The determination by direct counting of alpha particles, as carried out in our experiments, is therefore the least questionable of the procedures used. The uncertainty of the experimental value is probably well below 1%. A revision of approximately 3% must be made in the value if it is shown that the protactinium oxide obtained under our experimental amounts, so no correction was made. Assuming conditions is PaO_2 rather than the expected Pa_2O_5.

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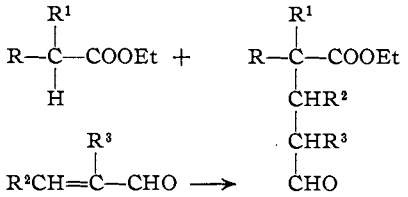
1,4-Addition Reactions. IV. Addition of Malonate Systems to Alkyl Substituted Acroleins[1]

BY DONALD T. WARNER AND OWEN A. MOE

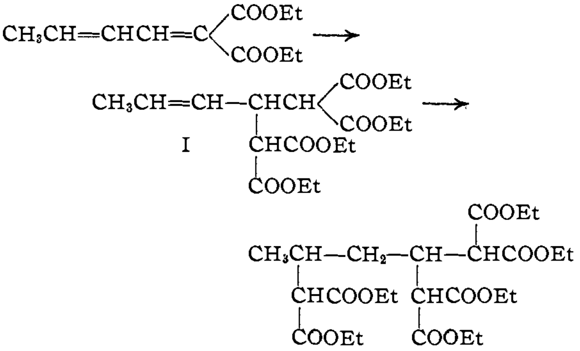
In previous publications[2,3] the 1,4-addition of malonate systems to acrolein has been disclosed. The present report concerns the 1,4-addition of malonate systems to alkyl substituted acroleins such as crotonaldehyde and methacrolein (α-methylacrolein).

The addition of ethyl malonate, ethyl ethylmalonate, ethyl acetamidomalonate and ethyl acetamidocyanoacetate to methacrolein and crotonaldehyde proceeded to yield the corresponding aldehydo compounds. The aldehydo compounds were characterized either as the phenylhydrazones or as the 2,4-dinitrophenylhydrazones.



The catalytic reduction of γ-acetamido-γ,γ-dicarbethoxy-α-methylbutyraldehyde yielded the corresponding carbinol (4-acetamido-4,4-dicarbethoxy-2-methyl-1-butanol) which may prove to be of interest in the synthesis of δ-hydroxyleucine.[4]

Farmer and Mehta[5] reported the reaction between ethyl malonate and crotonaldehyde in the presence of a "fractional molecular proportion" of sodium ethoxide at 0°. By this means, these investigators attempted to show that the formation of the double addition product II from cro-



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