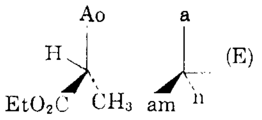
stereospecific hydrolysis.[3] In a variety of these substrates, of the asymmetric type Cabde and of the symmetric type Cabdd, the absolute steric sense of the hydrolysis, where determined, was[2] L. We are studying the effect of the alpha and beta acetoxyl substituent in place of the acetamido group in this reaction, and wish to report an inversion of antipodal reactivity in the hydrolysis of ethyl α-acetoxypropionate, $CH_3CH(OCOCH_3)$-$CO_2C_2H_5$.

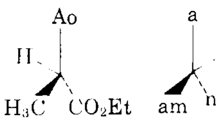
Ethyl *dl*-α-acetoxypropionate was subjected to the action of α-chymotrypsin, 12 mg./ml., at pH 7.8 in a pH-stat for 12 hours, hydrolysis stopping after about 50% reaction. Unhydrolyzed ester was recovered in 85% yield, α_{obsd} $-2.32°$, $[\alpha]^{22}D$ $-22°$, 5.3% in chloroform. Negative rotation also was observed in acetone, ethyl acetate and in ethyl *dl*-α-acetoxypropionate. Since the L-ester has negative rotation,[4] $[\alpha]^{22}D$ $-48°$, this indicates more rapid hydrolysis of the D-enantiomorph than the L from the racemate, and by a ratio of about 2.7 to 1. The product of hydrolysis, α-acetoxypropionic acid, was isolated from the hydrolysate in 85% yield α_{obsd} $+1.77°$, $[\alpha]^{22}D$ $+23.3°$, 3.8% in chloroform; it was characterized as the substituted ureide from 1,3-bis-(*p*-dimethylaminophenyl)-carbodiimide, m.p. 149–151°, $[\alpha]^{22}D$ $-17°$. *Anal.* Calcd. for $C_{22}H_{28}O_4N_4$: C, 64.06; H, 6.84; N, 13.58. Found: C, 63.94; H, 6.95; N, 13.62. D-α-Acetoxypropionic acid has positive rotation,[5] $[\alpha]^{22}D$ $+49°$, and this confirms the more rapid hydrolysis of the D-enantiomorph by a ratio of about 2.8 to 1.

Since such experiments with racemates may lead to results different from those found in study of the individual enantiomorphs[6a,b] the D(+) and L(−) ethyl α-acetoxypropionates were prepared and hydrolyzed separately by α-chymotrypsin, 5 mg./ml. at pH 7.2 in 0.1 N NaCl. The initial zero order rates of hydrolysis were determined at several concentrations, the first numbers in each set being the concentration, the second the rate: L: 2.84×10^{-3} M, 0.646×10^{-7} mole/l./sec.; 4.30, 0.800; 6.67, 0.969. D: 2.99×10^{-3} M, 1.08×10^{-7} mole/l./sec.; 5.26, 1.27; 6.19, 1.76; 7.34, 2.38. The separate enantiomorphs also lead to more rapid hydrolysis of the D compound, with the ratio in rates approaching a value in excess of 2 with increasing concentration of substrate, consistent with the results of the isolation experiments, which had been carried out on saturated solutions of the racemate. The data indicate that the L-enantiomorph has a more favorable K_m and a less favorable k_3; the absolute values of these kinetic parameters will require more extensive kinetic experiments. Enzymatic hydrolysis of the ethyl L-α-acetoxypropionate in a preparative experiment led to L-α-acetoxypropionic acid, characterized as its ureide derivative from 1,3-bis-(*p*-dimethylaminophenyl)-carbodiimide, m.p. and mixed m.p. with an authentic sample, 146–147°, $[\alpha]^{22}D$ $+48.6°$, 2.22% in chloroform.

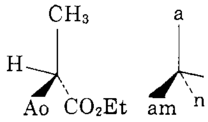
We suggest that ethyl α-acetoxypropionate may associate as an extended tetrahedron with α-chymotrypsin in two conformations. In both, the α-hydrogen assumes its normal orientation, presumably fitting into a restricted space, determining the sense of approach of the other three groups to the enzyme, E. In one conformation, which is preferred, I-L and I-D, the acetoxyl group (Ao), lacking the polar N–H of a typical acetamido substrate, associates with the non-polar site (a) of the enzyme at which the β-aryl groups of the natural substrates[7] normally associate. The L-enantiomorph does this more effectively than the D, but only with the D enantiomorph does this association place the ester group near the nucleophilic site (n) which leads to hydrolysis. In the second, somewhat less favored mode of association, II-L, the acetoxyl group associates with the acylamido site (am) and this leads to hydrolysis of the L enantiomorph, but not of the D. A similar analysis of the inversion of antipodal reactivity in the hydrolysis of 1-keto-3-carbomethoxytetrahydroisoquinoline,[8] indicates that the benzamido moiety in that substrate may be associating with α-chymotrypsin at the β-aryl site, the phenyl group being dominant in effecting association, leading to a rotation of 120° and a situation similar to that of I-D, as has been proposed by Hein and Niemann.[9]



I-L



I-D



II-L

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[3] S. G. Cohen, Y. Sprinzak and E. Khedouri, *J. Am. Chem. Soc.*, **83**, 4225 (1961).

[4] J. Kenyon, H. Phillips and H. G. Turley, *J. Chem. Soc.*, **127**, 399 1925).

[5] C. M. Bean, J. Kenyon and H. Phillips, *ibid.*, 303 (1936).

[6] (a) P. Rona and R. Ammon, *Biochem. Z.*, **181**, 49 (1927); (b) P. Rona and E. Chain, *ibid.*, **266**, 4806 (1933).

[7] H. Neurath and G. W. Schwert, *Chem. Rev.*, **46**, 69 (1950).

[8] G. E. Hein, R. B. McGriff and C. Niemann, *J. Am. Chem. Soc.*, **82**, 1830 (1960).

[9] G. E. Hein and C. Niemann, *Proc. Natl. Acad. Sci.*, **47**, 1341 (1961).

SAUL G. COHEN
JOHN CROSSLEY
EZRA KHEDOURI
ROBERT ZAND

DEPARTMENT OF CHEMISTRY
BRANDEIS UNIVERSITY
WALTHAM 54, MASSACHUSETTS

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RADON FLUORIDE[1]

Sir:

Shortly after Bartlett[2] reported the reaction of xenon with platinum hexafluoride, Claassen, Selig and Malm[3] prepared xenon tetrafluoride by direct combination of the elements. We have studied the reaction of trace amounts of radon with fluorine and found that radon forms a stable fluoride which is less volatile than XeF_4.

Gaseous radon (Rn^{222}), collected from an aqueous solution of radium chloride, was passed through

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[1] Based on work performed under the auspices of the U. S. Atomic Energy Commission.

[2] N. Bartlett, *Proc. Chem. Soc.*, 218 (1962).

[3] H. H. Claassen, H. Selig and J. G. Malm, *J. Am. Chem. Soc.*, **84**, 3593 (1962).

a drying tube filled with magnesium perchlorate, then into a prefluorinated metal vacuum line, and frozen into a cold trap at −195°. When the trap was warmed to −78°, it was demonstrated that the radon moved readily under vacuum into other parts of the line which were cooled to −195°. The position of the radon was determined by counting the 1.8 Mev. gamma activity of the daughter Bi^{214}. The Bi^{214} ($T_{1/2}$ = 19.7 min.), following Pb^{214} ($T_{1/2}$ = 26.8 min.), grew into equilibrium with the radon wherever it appeared and decayed where it disappeared, within several hours. The measurements were made with a 400-channel pulse height analyzer and two sodium iodide scintillation detectors, shielded by lead bricks.

In the first experiment in which the fluoride was prepared, a 5.1 microcurie amount of radon was condensed into a 5 cc. nickel reaction tube, fluorine was added to a pressure of 300 mm. and the mixture was heated to 400° for 30 minutes. The tube was cooled to −78°, and the excess fluorine was pumped off through a trap at −195°. It was found that a marked reduction in the volatility of the radon had occurred. The radon remained fixed in the tube, in a vacuum of 2×10^{-6} mm., when warmed in slow stages to 150°. At 230 to 250°, part of the radon moved out of the tube and condensed in the exit valve, which was at approximately 100°.

To ascertain whether the behavior of the trace radon was the same in the presence of macroscopic amounts of carrier, a mixture of xenon and radon next was fluorinated. A new 7-cc. nickel vessel, provided with a capillary inlet tube, was charged with 110 mm. partial pressure of xenon, 87 microcuries of radon, and 1200 mm. partial pressure of fluorine and heated to 400° for 25 minutes. The vessel was cooled to −78° while the excess fluorine was pumped off, then was warmed to 50° to allow the xenon fluoride formed to sublime under vacuum into a trap at −195°. The less volatile radon fluoride remained behind. When the vessel was heated gradually to 250°, the radon fluoride moved into the cooler section of capillary tubing.

We have found that radon alone, when heated to 400° in a nickel vessel, shows no evidence of reaction with the walls. When the vessel is cooled to room temperature or to −78°, the radon can be distilled as usual into a trap at −195°. In this respect our results are in agreement with the very early work of Rutherford and Soddy[4] and of Ramsay and Soddy,[5] who demonstrated that radon does not react with metals and a large number of other reagents.

The composition of the radon fluoride has not yet been determined. Attempts are being made to introduce samples of the fluoride into a time-of-flight mass spectrometer for stoichiometric analysis.

The fluoride can be reduced with hydrogen to quantitatively recover elemental radon. At 200° the compound appears to be stable in hydrogen, but at 500° and a hydrogen pressure of 800 mm. it is completely reduced within 15 minutes.

The tracer quantities of radon fluoride prepared thus far have shown no evidence of radiation decomposition from alpha particle emission. Samples have been stored for several days at room temperature without evolving any measurable amounts of elemental radon. The compound has been present in such dilute form on the inner surfaces of the container vessels that most of the energy of the alpha particles has been absorbed by the metal walls rather than by the compound. The radiation decomposition may be significant when larger amounts of the compound are prepared.

We wish to express our deep appreciation to Dr. W. M. Manning, Director of the Chemistry Division, for encouraging us to undertake this research and for his continued enthusiastic support. We also wish to thank Dr. J. E. Gindler for supplying the radium chloride solution.

CHEMISTRY DIVISION
ARGONNE NATIONAL LABORATORY
ARGONNE, ILLINOIS

PAUL R. FIELDS
LAWRENCE STEIN
MOSHE H. ZIRIN

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(4) E. Rutherford and F. Soddy, *Phil. Mag.*, [6] **4**, 580 (1902).

(5) W. Ramsay and F. Soddy, *Proc. Roy. Soc.* (London), **72**, 204 (1903).

TETRAPHENYLCYCLOBUTADIENE DERIVATIVES. V.[1] THE TETRAPHENYLCYCLOBUTENIUM DICATION

Sir:

The isolation of true carbonium-ion salts has been limited mainly to the monocations derived from polyarylmethanes and those singly charged species incorporated in "Hückel aromatic" systems. We wish now to report the first example of a stable, crystalline dicarbonium-ion salt, formally bearing adjacent positive charges, whose stability derives from an unusual combination of the above mentioned systems.

Bromination of tetraphenylcyclobutadiene-nickel bromide complex[2] with excess pyridinium hydrobromide perbromide yields (65%) 3,4-dibromotetraphenylcyclobutene[3] (II), (m.p. 173–174°; calcd. for $C_{28}H_{20}Br_2$: C, 65.1; H, 3.9; Br, 31.0; mol. wt., 517.2. Found. C, 64.9; H, 3.9; Br, 31.0; mol. wt. (osmometer) 540), whose structure is assigned on the basis of its spectral ($\nu_{\text{Raman}}^{\text{C=C}}$ 1627 cm.$^{-1}$(s), $\lambda_{\text{max}}^{\text{CH}_2\text{Cl}_2}$ 305 mμ (20,000)) and chemical properties.[4]

In contrast to the inert character of the vinylic bromine atoms of its valence isomer, *cis,cis*-1,4-dibromotetraphenylbutadiene,[2] the allylic bromines of II are extremely labile and give an instantaneous precipitate with alcoholic silver nitrate. In common with the trityl halides, II is un-ionized in solvents of moderate polarity,[5] but in liquid sulfur dioxide II dissolves sparingly to yield a red solution from which unchanged, colorless II is recovered on evaporation. Dissociation in anhydrous acids occurs readily, the strength of the acid determining whether one or both bromines undergo ionization. In hot glacial acetic or formic acid, solution occurs with evolution of one mole of hydrogen bromide,

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(1) Part IV, H. H. Freedman and D. R. Petersen, *J. Am. Chem. Soc.*, **84**, 2837 (1962).

(2) H. H. Freedman, *ibid.*, **83**, 2194 (1961).

(3) Abstracts, 141st National Meeting of the American Chemical Society, Washington, D. C., March, 1962, p. 26-O.

(4) II undergoes a number of remarkable chemical transformations some of which have been briefly summarized in the abstract cited in reference 3. Further details will be given in a forthcoming publication.

(5) This is indicated by the identity of the ultraviolet spectrum of II in tetrahydrofuran and in *n*-hexane.