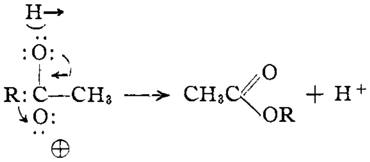

Kinetic work on this reaction is in progress.

Summary

It has been found that by the reaction of perbenzoic acid in chloroform with the cyclic ketones cyclopentanone, cyclohexanone and suberone, the lactones of the corresponding ω-hydroxy acids are formed in 70–97% yields.

The kinetics of the reaction have been briefly investigated. The reaction is clearly second order, and subject to acid catalysis.

A reaction mechanism has been proposed which involves an electron-deficient oxygen in an intermediate molecule, and a Whitmore-type shift of a group from carbon to this oxygen.

ROCHESTER 3, N. Y. RECEIVED FEBRUARY 14, 1949

[DEPARTMENT OF PHYSICS, DUKE UNIVERSITY]

Vapor Pressures of the Isomeric Trichlorobenzenes in the Low Pressure Region[1a]

BY G. W. SEARS[1b] AND E. R. HOPKE

The vapor pressures of the isomeric trichlorobenzenes have been reported in the region 1–760 mm.[1c] Since, in studies of the ultraviolet absorption spectra of these compounds in the vapor phase, which have been carried out in this Laboratory, vapor pressures are rather low, it was desirable to extend the known data into the region 0.01–1.0 mm. The measurements were made with a Rodebush manometer.

Compounds.—A purified sample of 1,2,3-trichlorobenzene was obtained through courtesy of Dow Chemical Co., Midland, Mich. The sample was further purified by recrystallization from ethyl alcohol. It was dried for two hours at 45°. The melting point range was from 52.55° to 52.70°. The 1,2,4-trichlorobenzene was Eastman Kodak Co. white label product. The material was vacuum distilled and only the center fraction was used in this investigation. The melting point range of the sample was from 17.05 to 17.40°. The 1,3,5-trichlorobenzene was Eastman Kodak Co. white label product. The material was purified by recrystallization from methyl alcohol. It was dried for two hours at 50°. The melting point range of the sample was from 63.45 to 63.50°.

Experimental.—The vapor pressure measurements were made with a Rodebush gage of the type used by Rodebush and Henry.[2] The calibration has been described previously by Sears and Hopke.[3,4] In this investigation only 1,2,4-trichlorobenzene was sufficiently volatile to have a vapor pressure in the gage range below room temperature. The remaining two isomers were heated above room temperature by placing part of the apparatus in an asbestos box whose temperature was maintained about 30° higher than the temperature of the condensed sample. This procedure has been previously described by the authors.[5]

Temperatures were measured with a calibrated 0–50° mercury-in-glass thermometer. The smallest scale division was 0.1°. Although the temperature was read to 0.02°, the accuracy of the vapor pressure measurements did not necessitate temperature readings to closer than 0.1°.

The samples were outgassed after inserting them into the apparatus by melting the compound, freezing it, and then pumping out the evolved gases. This process was repeated four or five times. It was found that the outgassing necessary to remove the last traces of a volatile impurity was slower for the 1,2,3-compound than for the other isomers.

Results.—The vapor pressure of 1,2,3-trichlorobenzene was measured over the range 16 to 30°. The vapor pressures of 1,2,4- and 1,3,5-isomers were measured over the temperature ranges 6 to 25° and 9 to 28°, respectively. Each set of data was treated by the method of least squares to fit an equation of the form

$$\log_{10} P = -(A/T) + B \qquad (1)$$

where P is the pressure in microns, T is the absolute temperature, and A and B are constants The ice-point was taken as 273.2° K. Since the temperature range of 1,2,4-trichlorobenzene includes the melting point, it was necessary to set up two equations to represent the vapor pressure curve of the solid as well as the vapor pressure curve of the liquid. Table I gives the constants of Equation (1) for the respective compounds.

TABLE I

	A	B
1,2,3-Trichlorobenzene (sol.)	3440.2	13.662
1,2,4-Trichlorobenzene (sol.)	3254.0	13.445
1,2,4-Trichlorobenzene (liq.)	2452.3	10.682
1,3,5-Trichlorobenzene (sol.)	2956.0	12.176

[1a] This investigation was assisted by the Office of Naval Research under Contract N6ori-107, Task Order I, with Duke University.

[1b] Present address: General Electric Co., Schenectady, N. Y.

[1c] Stull, *Ind. Eng. Chem.*, **39**, 517 (1947).

[2] Rodebush and Henry, THIS JOURNAL, **52**, 3159 (1930).

[3] Sears and Hopke, *J. Phys. Chem.*, **52**, 1137 (1948).

[4] Hopke and Sears, THIS JOURNAL, **70**, 3801 (1948).

[5] Sears and Hopke, *ibid.*, **71**, 1632 (1949).

Discussion.—The absolute error in these pressure measurements is estimated to be 4.8% (see ref. 3). This figure includes the error from temperature uncertainty. For each curve an average deviation has been calculated. This represents the self-consistency of the data in terms of closeness of fit to the least squares equation. The average deviations were 1.4 and 1.3% for 1,2,3-trichlorobenzene and 1,3,5-trichlorobenzene, respectively. The deviations were 1.8 and 0.7% for solid and liquid 1,2,4-trichlorobenzene, respectively.

The only available data on vapor pressures of the isomeric trichlorobenzenes are to be found in Stull's[1c] compilation and were taken from the Dow Chemical Co. files. Stull's data are for the high pressure region (*i.e.*, 1–760 mm.). For comparison, the present data were extrapolated to temperatures corresponding to Stull's values of one mm. in the case of the 1,2,3- and 1,2,4-isomers and of five mm. for the 1,3,5-isomer. The extrapolated pressures were approximately one half of those given in Stull's compilation. As is known equations of type (1) usually show deviations when extrapolated to different pressure ranges. Considering an extrapolation of Stull's values (obtained by plotting the original values on a Cox chart) downward to our values, a Cox chart was constructed for 1,2,4-trichlorobenzene and his values were graphically extrapolated to the melting point. This procedure gave a value of 0.235 mm. as compared to our measured value of 0.171 mm. In view of the uncertainties of extrapolations, the agreement was considered fair. A similar extrapolation could not be carried out for the other two isomers due to insufficient data in the solid phase.

The intersection of the vapor pressure curves of liquid and solid 1,2,4-trichlorobenzene was taken at 17.0°. The heat of vaporization of solid 1,2,4-trichlorobenzene calculated from Equation (1) and Table I is 14,900 cal./mole. The heat of fusion is then 3700 cal./mole and the entropy of fusion is 12.7 E.U.

Acknowledgment is made to the Dow Chemical Co., Midland, Mich., for giving us a purified sample of 1,2,3-trichlorobenzene.

Summary

The vapor pressures of the isomeric trichlorobenzenes have been measured with a Rodebush gage in the region 0.01–1.0 mm. Comparison of our values extrapolated to higher temperatures showed some disagreement with previously reported data. This result was briefly discussed.

RECEIVED MARCH 11, 1949

NOTES

Irradiated 7-Dehydrocholesteryl Halides

BY SEYMOUR BERNSTEIN, J. J. OLESON, HILDA B. RITTER AND KARL J. SAX

The preparation of 7-dehydrocholesteryl chloride and bromide has been reported recently by this Laboratory[1] and, independently, by Bide and co-workers.[2] We now wish to present the results of studies on the ultraviolet irradiation of these two provitamin D_3 derivatives.

The relationship between chemical structure and vitamin D activity is too well known to warrant discussion here. However, the biological effect of the replacement of the C-3 hydroxyl group of vitamin D_3 by halogen has hitherto been unknown.

7-Dehydrocholesteryl chloride and bromide in ether solution were irradiated with an ultraviolet lamp (Hanovia) in the usual manner. Samples of 7-dehydrocholesterol and ergosterol were similarly irradiated for control purposes. Two separate experiments were carried out under approximately the same conditions.

All samples were assayed by both the U. S. P. XII rat line test and the AOAC chick bone ash test. In the latter, the distal portion of the middle toe of one foot was used in place of the tibia for the ash determination according to Evans and St. John.[3]

The results indicated a conversion of approximately 25% of the ergosterol and 7-dehydrocholesterol to vitamins D_2 and D_3, respectively. On the basis of this conversion figure the irradiated halides were inactive for both species when tested at levels up to 10,000 units in the line test, and 50 units per 100 g. of diet in the chick test. U. S. P. reference cod liver oil was also used as a positive control, and gave the expected responses in each test.

We have assumed that irradiation of the halides gave, among other products, the desired vitamin D_3 chloride and bromide, and not, principally, tetraene hydrocarbons. This assumption may be supported by the following arguments: (1) spectrophotometric analyses of the irradiated solutions were approximately the same as the control solutions of ergosterol and 7-dehydro-

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[1] Bernstein, Sax and SubbaRow, *J. Org. Chem.*, **13**, 837 (1948).

[2] Bide, Henbest, Jones and Wilkinson, *J. Chem. Soc.*, 1788 (1948).

[3] Evans and St. John, *J. Assoc. Offic. Agr. Chem.*, **27**, 283 (1944).