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.

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-

(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).

cholesterol; and (2) in view of the relative stability[1] of the starting materials, it was reasonable to assume that vitamin D_3 chloride and bromide would be stable (but to a lesser extent) under the conditions of the experiments. In connection with the latter argument it should be pointed out that 7-dehydrocholesteryl bromide was recovered in 77% yield when refluxed for five hours in xylene with aniline. No attempt was made to isolate the irradiated products in a pure state.

In summary, it may be stated that replacement of the hydroxyl group in vitamin D_3 by chlorine or bromine gave products devoid of vitamin activity.

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Halide Catalysis in the Reaction of Cerium(IV) with Arsenic(III)

BY ROBBIN C. ANDERSON, JAMES A. LASATER AND DAVID LIPPMANN

Lang[1] observed that halides were effective catalysts for the oxidation of arsenite with permanganate. Willard and Young and others[2] have noted similar effects on the oxidation of arsenite by ceric salts.

In these earlier experiments emphasis was usually placed on analytical uses. The concentrations of halide used were large (0.02–2 M) and most experiments were carried out in presence of hydrochloric acid. The experiments reported in the present paper were undertaken to obtain quantitative data on the rate effects of small concentrations of added salts and thus to obtain evidence on the mechanism of the catalytic action.

Experimental.—The apparatus and procedures were essentially those of Moore and Anderson.[2] Reactions were carried out in an all-glass system under nitrogen. Equivalent quantities of cerium (IV) sulfate and sodium arsenite were used and changes in concentration determined by titrating samples of the reaction mixture at various time intervals with iron(II) ammonium sulfate, using orthophenanthroline indicator.

For the present series of experiments, all reagent mixtures contained 0.02 mole/l. of cerium (IV) sulfate, 0.01 mole/l. of sodium arsenite and 0.355 mole/l. of sulfuric acid. Sufficient halide was added to the arsenite solution before mixing to provide the desired final concentration of catalyst.

Results.—The chloride, bromide and iodide had a definite catalytic effect even at very low concentrations. Colors of the free halogens could be detected in the experiments in which the largest concentrations of halide were present, and in some cases the characteristic odor was also detectable.

(1) Lang, Z. anorg. Chem., **152**, 197 (1926).

(2) H. H. Willard and Philena Young, THIS JOURNAL, **50**, 1376 (1928); E. H. Swift and C. H. Gregory, ibid., **52**, 901 (1930); J. W. Moore and R. C. Anderson, ibid., **66**, 1476 (1944).

In contrast to the cerium(IV)–arsenic(III) reaction itself, which shows a complex, third-order type dependence on concentration,[2] the halide-catalyzed reactions were pseudo first-order reactions. For a given catalyst concentration, straight lines were obtained when log c (where c is one-half the concentration of oxidant at time t) is plotted against the time t. Typical results for a run using 0.01 M sodium bromide as catalyst are shown in Fig. 1. (c is expressed in g.-ions/l.) The simple titration method used in these preliminary tests would not distinguish between the cerium(IV) present and some other oxidizing agent which might be formed by reaction of cerium(IV) with the halide, but the close correlation with first-order type dependence on concentration indicates these systems react differently from the cerium(IV) and arsenic(III) solutions.
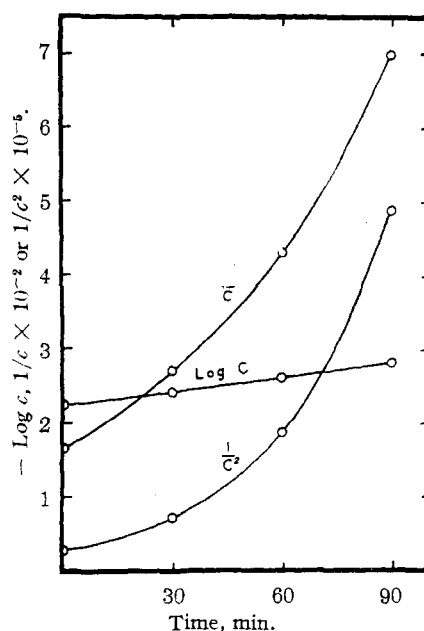

Fig. 1.—Order of reaction.

In general, the order of effectiveness as catalysts is $I^- > Br^- > Cl^-$. Reaction in the presence of iodide was too fast to be measured by the titration method. Comparison of the effects of chloride and bromide is shown in Table I. k is the pseudo first-order constant determined

TABLE I

Catalyst	Concn. of catalyst (g.-ions/l.)	k(min. $^{-1}$) (psuedo first-order constant)
Cl$^-$	0.02	0.016
	.01	.011
	.005	.024
	.001	.006
Br$^-$	.02	.018
	.01	.014
	.005	.011
	.001	.050