Characterization Data for Chloroacetone, 1,1-Dichloroacetone, and 1,3-Dichloroacetone

EDGAR D. SMITH and WILLIS L. THORNSBERRY
Department of Chemistry, Graduate Institute of Technology, University of Arkansas, Little Rock, Ark. 72203

Purified samples of chloroacetone and the two isomeric dichloroacetones have been characterized by means of infrared and ultraviolet spectroscopy, polarography, and gas chromatography. Vapor pressure–temperature data are also presented for these compounds, showing that 1,1-dichloroacetone boils significantly lower than chloroacetone at reduced pressures, whereas their boiling points are practically identical at atmospheric pressures.

IT IS well known that chloroacetone and 1,1-dichloroacetone have the same boiling point at atmospheric pressure (*2*). However, it has not been generally recognized that 1,1-dichloroacetone boils significantly lower than chloroacetone at reduced pressures. Table I summarizes the smoothed data obtained from a Cox Chart plot (*4*) of the vapor pressure–temperature data obtained from various literature sources and from the present work. These data are in good agreement with the literature references for chloroacetone and for 1,1-dichloroacetone. For 1,3-dichloroacetone, three out of the four reduced-pressure boiling points cited in the literature fit the Cox Chart plot, while the fourth (87° C./12 mm.) falls badly off this linear plot.

Gas Chromatographic Data. The chlorinated acetone samples were well separated on a 1-meter × ¼-inch aluminum column packed with acid-washed Porapak Q (*3*). This column was operated at 210° C. with a helium flow rate of 70 ml. per minute. The samples were injected on-column with an injector temperature of 230° C. and a detector temperature of 250° C. Under these conditions, the retention times were 4.2, 7.2, and 14.2 minutes for chloroacetone, 1,1-dichloroacetone, and 1,3-dichloroacetone, respectively. The relative peak sharpness (Q) values (*8*) were approximately 6.0, with symmetrical peaks for chloroacetone and 1,1-dichloroacetone, and only slight tailing observed for the 1,3-dichloroacetone.

Spectrophotometric Data. The infrared and ultraviolet absorption spectra of the pure chloroacetone samples are shown in Figures 1 and 2, respectively. The infrared spectra were recorded as capillary films between salt plates and the ultraviolet spectra taken in 95% alcohol solvent. All of these data seem consistent with the structure of these compounds, with the exception of the ultraviolet absorption peak for chloroacetone at 237 $m\mu$. This absorption is believed to be caused by mesityl oxide, a ketone that is reported to be a by-product of the chlorination of acetone (*1*). The wavelength of absorption corresponds exactly to that reported for mesityl oxide, and the molar absorbance indicates that about 0.25% mesityl oxide was present in the chloroacetone sample (*6*).

Table I. Smoothed Vapor Pressure–Temperature Data for Chloroacetone and the Isomeric Dichloroacetones

	Boiling Point, ° C.		
Pressure, Mm. Hg	Chloro-acetone	1,1-Dichloro-acetone	1,3-Dichloro-acetone
20	30.0	19.0	75.0
40	43.0	33.5	90.0
80	58.0	49.0	106.0
160	75.0	68.0	124.0
320	93.0	88.0	143.0
760	118.5	118.5	172.0

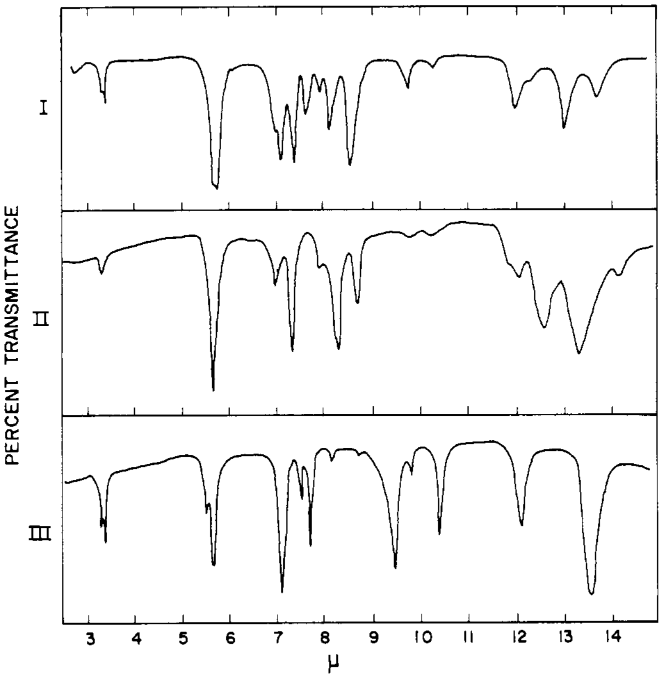

Figure 1. Infrared spectra of chloroacetone (I), 1,1-dichloroacetone (II), and 1,3-dichloroacetone (III); liquid films

Polarographic Data. The polarographic data obtained for the chloroacetone samples have been summarized and discussed by Hall and Harris in a recent publication from these laboratories (*7*). An appreciably higher diffusion current constant was obtained for chloroacetone than that reported by Elving and Van Atta (*5*). Presumably, this attests to the high purity of the samples used in the present study, although the increase seems too large (48%) to be due to this factor alone.

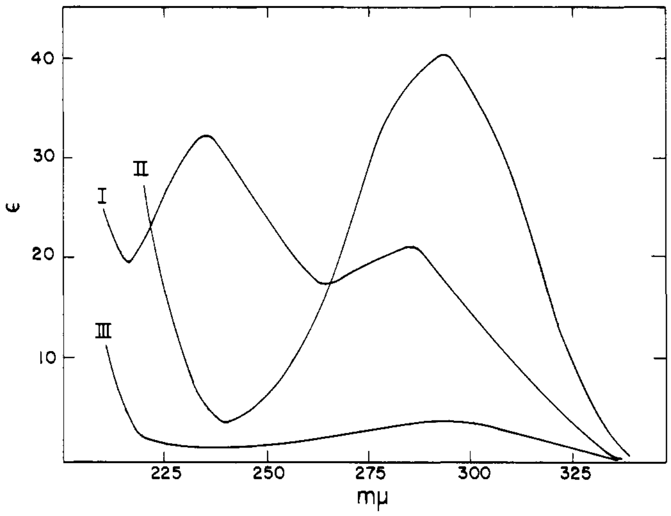

Figure 2. Ultraviolet spectra of chloroacetone (I), 1,1-dichloroacetone (II), and 1,3-dichloroacetone (III); 95% alcohol solvent

EXPERIMENTAL

Materials. Chloroacetone obtained from Eastman Organic Chemicals Department was analyzed by gas chromatography and ultraviolet spectrophotometry. As received, it contained about 2% water, 2% 1,1-dichloroacetone, and 1% of an impurity tentatively identified as mesityl oxide. Distillation of this material was carried out at 110 mm. of Hg pressure. After removal of the water and 1,1-dichloroacetone, a distillation cut boiling at 67° C. was obtained which was assayed at 99.5% purity based on chromatographic tests and chlorine analyses.

1,1-Dichloroacetone was obtained by distillation of a crude sample obtained by overchlorination of the commercial chloroacetone sample above. After a 40% molar excess of chlorine had been passed through the chloroacetone sample maintained at 25–30° C., the resulting crude dichloroacetone contained approximately 6% chloroacetone, 68% 1,1-dichloroacetone, 18% 1,3-dichloroacetone, 6% higher chlorinated acetones, and 2% water. After removal of the water, a fraction boiling at 59° C. at 110 mm. of Hg was obtained with a purity estimated at 99.2%.

1,3-Dichloroacetone was used as received from Eastman Organic Chemicals Department. It was a white crystalline material melting at 41–43° C. and was assayed at 99.5% purity.

Apparatus. The distillation column used was a Nester-Faust annular Teflon spinning band type. Tests with a *n*-heptane–methylcyclohexane mixture showed it to contain about 40 theoretical plates at total reflux. All characterization data were obtained with standard commercial instrumentation as follows: Matronics Model 500 gas chromatograph, Perkin-Elmer Model 21 infrared spectrophotometer, Bausch and Lomb Spectronic 600 ultraviolet and visible spectrophotometer, Sargent Model XXI polarograph.

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Solubility Isotherms for Calcium Fluoride in Nitric Acid Solution

MALCOLM W. WILDING and DONALD W. RHODES
Idaho Nuclear Corp., Idaho Falls, Idaho 83401

Solubility isotherms at 24°, 35°, 50°, and 70° C. were determined in the system CaF_2–HNO_3 in the range 0.1 to 10M HNO_3.

CALCIUM fluoride is one of several solid compounds produced during the calcination of fluoride containing highly radioactive wastes in the Waste Calcining Facility at the Idaho Chemical Processing Plant (*1*). This solid eventually must be dissolved in decontaminating solutions containing nitric acid during clean-up of the scrubbing system. Inasmuch as solubility values for calcium fluoride in nitric acid at various temperatures did not appear to be available in the literature, solubility values were obtained experimentally at four different temperatures and various concentrations of nitric acid.

EXPERIMENTAL

Reagent-grade anhydrous calcium fluoride (CaF_2), J. T. Baker analyzed reagent containing 0.025% SO_4, 0.01% Cl, 0.002% Fe, and 0.003% heavy metals as the main impurities, was used after heating 48 hours at 105° C. to obtain constant weight. Weighed samples (1 gram) of the dried CaF_2 were then contacted with 50 ml. of nitric acid in the range 0.1 to 10*M* HNO_3 and heated for 170 hours at 24°, 35°, 50°, and 70° C. The test samples, which were contained in polyethylene bottles, were agitated periodically. All samples were filtered through 0.45-micron-diameter pores before