such an effect because they do not react sufficiently rapidly with anhydrous hydrogen bromide, because their halides catalyze the competing normal addition reaction, or because their halides inhibit the abnormal chain reaction.

3. Indices of refraction of 1,2- and 1,3-dibromopropanes have been redetermined.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT THE OHIO STATE UNIVERSITY]

Fluorinated Derivatives of Ethane and Ethylene. VI. Corrective Data

BY ALBERT L. HENNE AND EMIL G. WIEST

The determination of the fluorine position in some organic polyfluorides rests sometimes partly on reasons of analogy in physical properties. One of the lines of analogy most frequently used claims that when two polyfluorides are fully halogenated, they differ by only one or two degrees in boiling points, but by a substantially larger amount in freezing points. The asymmetrical compound boils lower and freezes higher than its symmetrical isomer. It proved therefore desirable to verify some of our very early data[1] which had been obtained on minute amounts, and did not seem as well in line as one might have wished, and also to clear up a marked discrepancy reported recently by Bigelow and co-workers.[2]

It is well established that $CClF=CClF$ boils about 21°.[1,3] Its isomer $CCl_2=CF_2$ was first reported to boil about 15°[1]; an unpublished repetition of the work[4] indicated 19°, which was regarded as well in line with expectations. However, the boiling point found by Bigelow is reported as 0°, a discrepancy which would very seriously undermine several phases of our previous work. The compound was, therefore, prepared once more, purified, measured and transformed into crystallizable derivatives. The experiments confirmed and slightly improved our preceding values. They also allowed an opportunity to correct a gross clerical error made on another compound.

1. $CCl_2=CF_2$.—The compound is obtained from well-crystallized CCl_3CClF_2 by reaction with zinc in alcohol. The reaction is swift, complete, and yields a single olefin, boiling at 18.9 to 19.0° (cor.). One half of the material was sent to Dr. Bigelow who rectified it, found a boiling point of 19–20°, a freezing point of -116 to $-115°$, and a molecular weight of 133 (theory 133).[5] These properties are (as would be expected) about two degrees lower than the boiling point of *cis*-$CClF=CClF$, and about 15° higher than its melting point.[1]

2. CCl_3CClF_2.—This compound was obtained by chlorination of the preceding one. The boiling point, 91.5°, and the melting point, 40.6°, confirmed our previously reported values.[1] The same operation, carried out by Dr. Bigelow, gave him a compound boiling close to 92°, and melting from 39 to 41°.

3. CCl_2BrCF_2Br.—This compound was obtained by bromination of $CCl_2=CF_2$. Its freezing point is 45.5° and its corrected boiling point 138.8–139.0°. This corrects the obviously wrong boiling point of 117.1° given in our first paper[1] and confirms the contention that symmetrical and asymmetrical fully halogenated compounds boil only one or two degrees apart (see following paragraph).

4. $CClFBrCClFBr$.—This compound was prepared as in our first paper, and the new experimental data are confirmations with only slight improvements. The freezing point is 32.9–32.6° and the corrected boiling point 139.8–140.0°. A comparison with the properties of the asymmetrical compound in the preceding paragraph shows the expected one degree difference in boiling point, and twelve degrees difference in freezing point.

5. CCl_3CF_3.—This derivative was obtained by chlorination of CH_3CF_3 in sunlight. According to our contentions, the melting point is the only physical property which should distinguish it markedly from its isomer, CCl_2FCClF_2. The corrected boiling point is 45.9° (nearly two degrees lower than that of CCl_2FCClF_2); freezing point 14.2°; d^{20}_4 1.5790 (improving the previously reported value); n^{20}_D 1.3610; the molecular refraction calculated from the new datac omes to 26.18, from which the refractive increment for fluorine is computed as 1.15. These values are

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(1) Locke, Brode and Henne, THIS JOURNAL, **56**, 1726 (1934).

(2) Bigelow, *et al.*, *ibid.*, **62**, 267 (1940).

(3) Booth, Burchfield, Bixby and McKelvey, *ibid.*, **55**, 2231 (1933).

(4) By Mary Renoll, in this Laboratory, in 1937.

(5) Private communication.

close to the corresponding values recorded for CCl_2FCClF_2 (extrapolated from 25 to 20°) of MR 26.12 and AR_F 1.13. The most important difference is, as expected, between the freezing points, *i. e.*, +14.2° for the asymmetrical CCl_3CF_3 and −36.4° for the symmetrical CCl_2FCClF_2.

Conclusion.—The experimental data confirm the contention that fully halogenated fluorides differ little in most of their physical properties, but markedly in their freezing points. The boiling point of an asymmetrical compound is very slightly lower, and its freezing point is markedly higher, than those of its symmetrical isomer.

Acknowledgment.—We wish to thank Dr. L. A. Bigelow for his very helpful spirit of collaboration in trying to clear the discrepancy between his data and ours.

Summary

Improved physical data are listed for $CCl_2{=}CF_2$, CCl_3CClF_2, CCl_2BrCF_2Br, $CClFBrCClFBr$ and CCl_3CF_3. The boiling point presented by Bigelow[2] for $CCl_2{=}CF_2$ was not duplicated. The method of predicting physical properties of fully halogenated fluorides by general analogy is sustained.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ROCHESTER]

Photochemical Studies. XXXI. A Systematic Study of the Near Ultraviolet Photochemical Decomposition of Acetone

BY DONALD S. HERR AND W. ALBERT NOYES, JR.

The photochemical decomposition of acetone vapor has been the subject of numerous investigations.[1] Much speculation concerning both primary and secondary processes has appeared in the chemical literature. It is quite evident, however, that a systematic study covering several variables, particularly intensity, pressure and temperature should be made as a prerequisite to further discussion concerning the mechanism of this reaction. This work has been performed with the hope of supplying some of the essential data.

An appreciable fraction of the photochemical decomposition of acetone proceeds by the over-all equation[2,3,4,5]

$$CH_3COCH_3 = C_2H_6 + CO \qquad (1)$$

Indeed, many quantum yields for this reaction have been based on analyses for carbon monoxide, the assumption being made that one molecule of acetone disappears for each molecule of carbon monoxide formed. However a second reaction takes place to a considerable extent at temperatures up to 60°.[6]

$$2CH_3COCH_3 = C_2H_6 + (CH_3CO)_2 \qquad (2)$$

Additional products not indicated by reactions (1) and (2) may be found at elevated temperatures, but these are to be ascribed to secondary reactions involving methyl radicals. Thus methane is found under such conditions,[7,8] but practically none is formed under conditions used in the present experiments.

A polymerization, supposedly aided by the presence of water, has been reported.[5] Evidence for this reaction is not satisfactory. Biacetyl, one of the products of reaction (2), is known to polymerize under some conditions.

The general conclusion may be drawn both from previous work and from the data herein presented that reactions (1) and (2) account within experimental error for all of the photochemical acetone decomposition at temperatures below 150° and in wave length regions which have hitherto been explored. In what follows this conclusion is accepted as a basis for discussion.

I. Experimental

The source of radiation was a high pressure mercury arc lamp. In order to obtain monochromatic 3130 Å. radiation, a thin silver film and a cobalt–nickel sulfate solution[9] 5 cm. in thickness were used. The spectrum transmitted by this combination was photographed and over 95%

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[1] For a recent summary see P. A. Leighton, *J. Phys. Chem.*, **42**, 749 (1938). The literature will not be cited in detail at this time, although reference to much of it will appear during the discussion.

[2] Berthelot and Gaudechon, *Compt. rend.*, **155**, 207 (1912).

[3] Bowen and Watts, *J. Chem. Soc.*, 1607 (1926).

[4] Kirkbride and Norrish, *Trans. Faraday Soc.*, **123**, 407 (1931).

[5] Damon and Daniels, THIS JOURNAL, **55**, 2363 (1933).

[6] Barak and Style, *Nature*, **135**, 307 (1935); Spence and Wild, *ibid.*, **138**, 206 (1936).

[7] Leermakers, THIS JOURNAL, **56**, 1897 (1934).

[8] Taylor and Rosenblum, *J. Chem. Phys.*, **6**, 119 (1938).

[9] Bäckström, *Naturwiss.*, **21**, 251 (1933).