

### Summary

Arsine reacts with sodium, potassium and potassium amide in liquid ammonia to form the corresponding alkali metal dihydrogen arsenide.

Arsine is regenerated from the dihydrogen arsenide salt by ammonium bromide in liquid ammonia.

Methyl chloride reacts with potassium di-

hydrogen arsenide in liquid ammonia to produce methylarsine. Some of the physical properties of methylarsine have been determined.

Potassium dihydrogen arsenide decomposes at temperatures in excess of 115° to produce hydrogen and a polyarsenide of potassium.

CHICAGO, ILLINOIS

RECEIVED AUGUST 11, 1937

---

## NOTES

---

### Oxidation-Reduction Potentials of Hydroxynaphthoquinones in Alkaline Solutions

BY ERIC G. BALL

Studies by Hill<sup>1</sup> on the oxidation-reduction potential of phthiocol (2-methyl-3-hydroxy-1,4-naphthoquinone) have shown that this compound gives titration curves in strongly alkaline solutions that indicate the formation of a semiquinone. In agreement with these findings I am able to report that phthiocol in 1.0 *M* sodium hydroxide gives a titration curve which is much steeper than that predictable on the basis of the two equivalent change reported previously at lower *pH* values.<sup>2</sup> Titrations performed by reduction with sodium hydrosulfite or by oxidation with potassium ferricyanide of phthiocol previously reduced with hydrogen and palladium black gave identical results. At *pH* 13.50 the mid-point potential ( $E'_0$ ) of the symmetrical titration curve is -0.555 volt. The slope of the curve may be defined by the usual equation if *n* is assigned the unorthodox value of 1.21. Procedures and standards employed were the same as described previously.<sup>2</sup> Modification of the Clark type shaking apparatus for *pH* determinations so as to exclude oxygen rigorously permitted consistent values to be obtained for 1 *M* sodium hydroxide solutions.

Lapachol was found to behave in a manner similar to phthiocol. At *pH* 13.50 the value of  $E'_0$  for this compound is -0.568 volt. The slope of the curve is, however, not as steep as that for phthiocol at this same *pH* value. In this connection it is of interest to note that the first and second dissociation constants of the reduc-

tant of phthiocol are larger than those for reduced lapachol.<sup>3</sup> Whether or not a relationship exists between these properties is not determinable without further data. An extension into more alkaline solutions of the studies previously reported<sup>3</sup> on similar hydroxynaphthoquinones might be enlightening since these compounds would probably behave in a manner similar to phthiocol and lapachol, and yet their reductants possess dissociation constants sufficiently different to test this hypothesis.

It was reported by Hill<sup>1</sup> that the change in slope of titration curves of phthiocol began at about *pH* 9.0. In view of this fact the data previously reported<sup>2</sup> for the titration of phthiocol at *pH* 10.50 and there interpreted as a two equivalence change have been reanalyzed carefully. When treated by the method of Reed and Berkson<sup>4</sup> the data fit the theoretical two equivalence curve within  $\pm 0.1$  mv. over the range 15-85% oxidation. It is true then, however, that the extremes of the curve deviate more than is normal in this unpoised region. If the end-point is chosen arbitrarily, a better fit can be obtained between the extremes of the curve and the theoretical, but then a deviation of  $\pm 1.0$  mv. is encountered over the range 15-85% oxidation. It is thus apparent that the interpretation of the data in this *pH* range is dependent upon slight variations in the investigator's choice of the end-point and the reliability of the potentials observed in the unpoised regions of the titration. In this connection it must be emphasized that unless the potentials recorded are corrected for those changes of *pH* which are caused by the

(3) Ball, *ibid.*, **114**, 649 (1936).

(4) Reed and Berkson, *J. Phys. Chem.*, **33**, 760 (1929); see also Clark and Perkins, *THIS JOURNAL*, **54**, 1228 (1932).

(1) Hill, *Proc. Soc. Exptl. Biol. Med.*, **35**, 363 (1936).

(2) Ball, *J. Biol. Chem.*, **106**, 515 (1934).

products formed in the oxidation-reduction process, and are also absolutely free from any drift throughout, such small deviations from the theoretical as encountered here cannot be accorded any significance. The latter requirement is especially important when dealing with compounds such as reduced phthiocol which is extremely susceptible to traces of oxygen at alkaline pH values. Since, however, the data here analyzed have met these requirements rigidly, I am inclined in agreement with Hill to consider the deviations from the theoretical encountered in the unpoised region of the curve as an indication that a change in slope of the curve has begun at least in the region of pH 10.5.

DEPARTMENT OF PHYSIOLOGICAL CHEMISTRY  
JOHNS HOPKINS UNIVERSITY SCHOOL OF MEDICINE  
BALTIMORE, MD. RECEIVED JULY 28, 1937

### The Action of Elementary Fluorine on Organic Compounds. IV. The Vapor Phase Fluorination of Ethane<sup>1</sup>

By JOHN D. CALFEE AND LUCIUS A. BIGELOW

In the third paper of this series<sup>2</sup> we have described the vapor phase fluorination of hexachloroethane over a copper gauze catalyst, with the production of *sym*-difluorotetrachloroethane. Since then this type of catalyst, originally suggested by Fredenhagen and Cadenbach,<sup>3</sup> has been

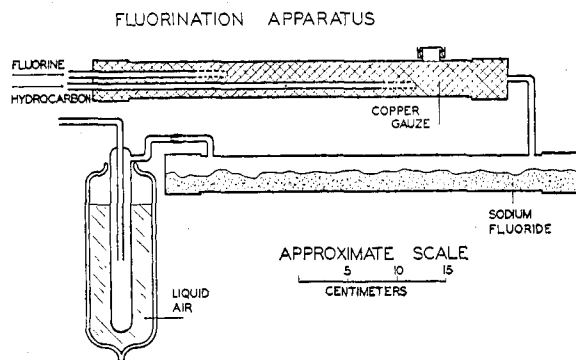


Fig. 1.—Apparatus for the vapor phase fluorination of ethane.

patented abroad;<sup>4</sup> but neither the above-mentioned writers nor the patent specifications have described the substitution of chlorine or hydrogen by fluorine with the formation of definite products

of known constitution. Also Ruff<sup>5</sup> has found that fluorine reacts vigorously with fluoroform, with the formation of carbon tetrafluoride and hexafluoroethane, and this observation has been confirmed in part, very recently, by Henne,<sup>6</sup> although details were not given in either case. In view of these considerations, it seemed a logical development to attempt the vapor phase fluorination of a simple saturated hydrocarbon, using a procedure similar to that which we had developed before.

Accordingly, we permitted ethane and fluorine to mingle within the meshes of a copper gauze coil, when a perfectly quiet, continuous reaction occurred. The gaseous products were freed from hydrogen fluoride, and condensed by means of liquid air. After preliminary purification, the material was distilled through a low temperature Podbielniak still at atmospheric pressure, making use of a simplified form of the excellent technique recently described by Booth and Bozarth.<sup>7</sup> At first there came over a considerable fore fraction (4–5 cc.) boiling at about  $-125^{\circ}$  and remaining liquid at  $-183^{\circ}$ , which was clearly carbon tetrafluoride (b. p.  $-128^{\circ}$ ). This was followed by two minor fractions, the first (1 cc.) at  $-88^{\circ}$  (ethane, b. p.  $-89^{\circ}$ ) and the second at  $-84^{\circ}$  (fluoroform, b. p.  $-84.4^{\circ}$ ,<sup>5</sup>  $-82.2^{\circ}$ ).<sup>6</sup> Then came the main product (5–6 cc.) boiling at  $-78^{\circ}$  and melting at  $-101^{\circ}$ , which constituted roughly a third of the material fractionated. This was unquestionably hexafluoroethane,  $C_2F_6$  (b. p.  $-78.3^{\circ}$ , m. p.  $-101^{\circ}$  according to Ruff).<sup>8</sup> Finally a small but definite fraction (1.0–1.5 cc.) was obtained at  $-48$  to  $-50^{\circ}$ , which we believe probably consisted of methylfluoroform,  $CH_3CF_3$  (b. p.  $-46.7^{\circ}$  according to Henne and Renoll),<sup>9</sup> although it could possibly have been methylene fluoride  $CH_2F_2$  (b. p.  $-51.6^{\circ}$  according to Henne).<sup>10</sup> Both are resistant to hydrolysis. A more complete discussion of these, and the other substances which were formed at the same time, will be reserved for later papers in this series.

From these results it appears to be established definitely that simple aliphatic hydrocarbons containing more than one carbon atom can be fluorinated directly in the vapor phase, with the formation of chemical individuals of known constitution, other than carbon tetrafluoride.

(1) Presented in part before the Organic Division at the Chapel Hill Meeting of the American Chemical Society on April 13, 1937.

(2) Miller, Calfee and Bigelow, *THIS JOURNAL*, **59**, 198 (1937).

(3) Fredenhagen and Cadenbach, *Ber.*, **67**, 928 (1934).

(4) British Patent 452,656; *C. A.*, **31**, 1042 (1937).

(5) Ruff, *Ber.*, **69**, 299 (1936).

(6) Henne, *THIS JOURNAL*, **59**, 1200 (1937).

(7) Booth and Bozarth, *Ind. Eng. Chem.*, **29**, 470 (1937).

(8) Ruff, *Z. angew. Chem.*, **46**, 739 (1933).

(9) Henne and Renoll, *THIS JOURNAL*, **58**, 889 (1936).

(10) Henne, *ibid.*, **59**, 1400 (1937).