TABLE I

SOLUBILITY PRODUCT CONSTANTS OF 16 METALLIC SULFIDES AT 25° AND THE DATA[a] USED IN THEIR CALCULATIONS

Compound	$\Delta F_f°$, kcal. Metallic sulfide	$\Delta F_f°$, kcal. Metallic ion	K_{sp}
PbS	−22.15	− 5.81	8×10^{-28}
Tl_2S	−21.0[b]	− 7.755	7×10^{-20}
ZnS	−47.4	−35.184	8×10^{-25}
CdS	−33.6	−18.58	7×10^{-27}
HgS	−10.22[c]	39.38	3×10^{-52}
Cu_2S	−20.6	12.0	1×10^{-48}
CuS	−11.7	15.53	8×10^{-36}
Ag_2S	− 9.56[d]	18.430	7×10^{-50}
NiS	−18.8[b]	−11.1	2×10^{-21}
CoS	−21.8[b]	−12.3	8×10^{-23}
Co_2S_3	−47.6[b]	29.6	10^{-124}
FeS	−23.32	−20.30	5×10^{-18}
MnS	−47.6[b]	−53.4	1×10^{-11}
Ce_2S_3	−293.0[b]	−170.5	6×10^{-11}
La_2S_3	−301.2[b]	−172.9	2×10^{-13}
Bi_2S_3	−39.4	15	10^{-96}

[a] Except where otherwise noted the free energy data are from F. D. Rossini, *et al.*, *Natl. Bur. Stds. Circ.*, 500 (1950). [b] Calculated from heat content data taken from reference "a" and estimates of entropy made by the method recently proposed by W. M. Latimer, THIS JOURNAL, **73**, 1480 (1951). [c] J. R. Goates, A. G. Cole and E. L. Gray, *ibid.*, **73**, 3596 (1951). [d] J. R. Goates, A. G. Cole , E. L. Gray and Neal D. Faux, *ibid.*, **73**, 707 (1951).

the values of 1×10^{-91} and 1.6×10^{-72}(?) should certainly be discarded.

The value of 7.1×10^{-61} was reported by A. F. Kapustinsky and I. A. Makolkin[8] and was supposed to have been calculated from the $\Delta F_f°_{Bi_2S_3}$ given by Kelley (−39.14 kcal.).[9] It appears, however, that an error was made in these calculations, for the $\Delta F_f°_{Bi^{+++}}$ which corresponds to Kapustinsky and Makolkin's solubility product constant value is the unreasonable value of −9.5 kcal.

The value given in the table was calculated from the $\Delta F_f°_{Bi_2S_3}$ given by the Bureau of Standards[3] and a value for the $\Delta F_f°_{Bi^{+++}}$ that was calculated from data reported by Feitknecht.[10] There is some question as to the accuracy of this last value, but it appears reasonable, and since its effect on the solubility product constant is much less than that of the sulfide ion, the value of the solubility product constant given seems to be a reasonable approximation.

---

(8) A. F. Kapustinsky and I. A. Makolkin, *Acta Physiochim., U. R. S. S.*, **10**, 259 (1939).

(9) K. K. Kelley, *U. S. Bur. of Mines, Bul.* 406, 63 (1937).

(10) W. Feitknecht, *Helv. Chim. Acta*, **16**, 1307 (1933).

DEPARTMENT OF CHEMISTRY
BRIGHAM YOUNG UNIVERSITY
PROVO, UTAH

RECEIVED OCTOBER 22, 1951

The Chlorination of Diisopropyl Ether at Low Temperatures[1,2]

BY GEORGE E. HALL AND ICLÂL SIREL

The chlorination of diethyl ether at −20° or lower yields α,α'-dichlorodiethyl ether rather than the α,β-dichlorodiethyl ether obtained at higher temperatures.[3] The present investigation was made to determine whether this low temperature orientation to the α-position is also found with diisopropyl ether. Chlorination of diisopropyl ether under the conditions used with diethyl ether gave no more than traces of α-chlorinated ethers, as determined by hydrolysis of the products and Volhard chloride determinations. The chlorination mixture distilled over a wide range and fractional distillation, both at atmospheric and reduced pressures, failed to give sharp fractions. 1,3-Dichloropropanone was the only substance isolated. This product indicates a cleavage during chlorination not found with diethyl ether.

Henry's method,[4] using isopropyl alcohol and acetone, failed to give α-chlorodiisopropyl ether, desired for comparison with the chlorination products.

Experimental

Chlorination of Diisopropyl Ether.—Seventy-two grams (0.710 mole) of purified[5] anhydrous diisopropyl ether were placed in a Pyrex flask fitted with a thermometer, mechanical stirrer and gas inlet tube and protected from moisture. The flask was immersed in a Dry Ice–acetone-bath and irradiated with a 275-watt reflector sun lamp at a distance of 30 cm. Dry chlorine was slowly passed into the ether at −20 to −25° until 53.0 g. (0.746 mole) had been absorbed, requiring 8.5 hours. Gases escaped as the reaction mixture warmed to room temperature, leaving a net gain of 30.8 g. Distillation and redistillation under reduced pressure gave 12.0 g. of material boiling at 83–88° (33 mm.) which solidified in the ice-box. Repeated crystallization from chloroform gave colorless needles with the following properties: m.p. 42.0–43.0° (cor.); b.p. 172–172.5°; n^{25}_{D} 1.4773; volatile at room temperature; lachrymatory; soluble water, alcohol, ether; reduces Fehling solution. These properties are in agreement with those reported for 1,3-dichloropropanone.[6]

Anal. Calcd. for $C_3H_4Cl_2O$: C, 28.35; H, 3.18; Cl, 55.91; mol. wt., 127.0. Found: C, 28.56; H, 3.18; Cl, 55.40; mol. wt.,[7] 128.4.

---

(1) From the Master's thesis of Iclâl Sirel.

(2) This work was carried out under contract with the Office of Naval Research.

(3) G. E. Hall and F. M. Ubertini, *J. Org. Chem.*, **15**, 715 (1950).

(4) L. Henry, *Bull. acad. roy. Belg.*, [3] **25**, 439 (1893); *Ber.*, **26**, Referate, 933 (1893).

(5) A. I. Vogel, *J. Chem. Soc.*, 618 (1948).

(6) E. H. Huntress, "Organic Chlorine Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 91.

(7) Cryoscopic method, *dl*-camphor solvent.

MOUNT HOLYOKE COLLEGE
SOUTH HADLEY, MASS.

RECEIVED SEPTEMBER 19, 1951

The Preparation and Spectrophotometric Estimation of 2-Amino-7-hydroxyfluorene[1]

BY HELMUT R. GUTMANN

The preparation and properties of 2-amino-7-hydroxyfluorene are of considerable interest since this phenolamine is a likely intermediate in the metabolism of the carcinogen 2-aminofluorene.

The synthesis of this compound from 2-amino-7-nitrofluorene was first reported by Bielschowsky.[2] 2-Amino-7-hydroxyfluorene melting at 271° was obtained in unrecorded yield. Goulden and Kon[3] prepared 2-amino-7-hydroxyfluorene starting with 2-aminofluorenone.

---

(1) This investigation was supported by Research Grant C-1066 from the National Cancer Institute of National Institutes of Health, Public Health Service.

(2) F. Bielschowsky, *Biochem. J.*, **39**, 287 (1945).

(3) F. Goulden and G. Kon, *J. Chem. Soc.*, 930 (1945).