The carbonate fractions are seen to contain on the order of 0.3–0.35 part per million of protactinium, which is mainly bound with the acid-insoluble silicious portion of this fraction. The ionium, present to some 15–20 parts per million, is found in the readily soluble portion of the fraction. Information furnished about the carbonate fraction is that it is 215 parts by weight for 580 parts by weight of the crude ore—*i. e.*, 37%. For pitchblende which is 65% by weight U_3O_8, this indicates that on the order of two-thirds the original protactinium content of the ore was dissolved in the sulfuric-nitric acid treatment, and precipitated by the carbonate treatment, with more than three-fourths of the ionium content following the same path. The apparent high level of ionium in the sulfate residues is in part at least a reflection of the fact that much of the soluble portion of the ore has been removed, giving a bulk concentration. For example, removal of the uranium alone gives a concentration of about three-fold. It is interesting to note that the radioactivity surviving to the ether residues is practically entirely ionium (together with a certain amount of uranium). It is difficult to assign a concentration factor for this material, but it must be rather large due to the previous treatments.

On the basis of the results obtained, a number of milligrams of protactinium and approximately one-half gram of ionium (with three times as much Th^{232}) have been obtained in pure state, from a carbonate fraction.[9,10,11] The yields obtained for the protactinium correspond to 50–60% of the material indicated by preliminary analysis. No attempt was made to obtain complete recovery of ionium.

(9) K. Kraus and Q. Van Winkle, "PPR," Vol. 17B, No. 6.2.

(10) R. Larson, L. I. Katzin and E. Hausman, *ibid.*, Vol. 17B, No. 6.3.

(11) R. C. Thompson, Q. Van Winkle and J. G. Malm, *ibid.*, Vol. 17B, No. 6.4.

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The Melting Point of Lead Bromide

BY L. M. KNOWLES

The literature references to lead bromide may be divided into two general groups which report the melting point at approximately 370°[1] and 495°,[2] respectively. Recent investigations in this Laboratory, which are summarized below, reveal that the cause of this discrepancy was the failure of many investigators to procure pure lead bromide. We have determined the melting point of lead bromide to be 370.0 ± 0.2° for various rates of heating and cooling; in contact with platinum, quartz, Vycor, Pyrex and magnesium oxide crucibles; and under atmospheres of air and nitrogen, and *in vacuo*. Each sample, tested chemically and spectroscopically both

(1) Ramsay and Eumorfopoulos, *Phil. Mag.*, **41**, 360 (1896); Herrmann, *Z. anorg. allgem. Chem.*, **71**, 287 (1911); C. Sandonnini, *Gass. chim. ital.*, **41**, II, 145 (1911); Lorenz and Fox, *Z. physik. Chem.*, **63**, 109 (1908); Tubandt and Eggert, *Z. anorg. Chem.*, **110**, 219 (1920); Mönkemeyer, *Neues Jahrb. Mineral. Geol.*, **22**, (B. B.) 1 (1906); Calingaert, Lamb and Meyer, THIS JOURNAL, **71**, 3709 (1949).

(2) Czepinski, *Z. anorg. allgem. Chem.*, **19**, 208 (1899); Goodwin and Kalmus, *Phys. Rev.*, **28**, 1 (1909); Helfstein, *Z. anorg. Chem.*, **23**, 255 (1900); Weber, *ibid.*, **21**, 305 (1899); Ehrhardt, *Ann. Physik*, **24**, 215 (1885); Camelley, *J. Chem. Soc.*, **33**, 278 (1878).

before and after each thermal run, contained at least 99.7% lead bromide. Temperature measurements with iron-constantan and platinum-platinum 10% rhodium thermocouples, gave a consistent melting point of 370.0 ± 0.2°. In no case was a value near 495° obtained.

The literature references to lead bromide are wholly inadequate in reporting methods of preparation or analyses. Consequently, it is impossible to determine the true composition of the material reported to melt near 495°. However, recent unpublished data from our laboratory on the lead bromide–lead oxide system show a persistent transformation temperature at 497° for compositions of 35–55 mole % lead oxide. It is this oxybromide transition temperature which the authors reporting the higher value probably measured.

The accepted correlation of the heat capacities and heat of fusion of lead bromide is the work of Kelley.[3] Unfortunately Kelley's calculations are based on the physical properties of a lead bromide sample reported to melt at 488°. Consequently, the accepted specific heat equations and other thermodynamic data apply to the basic salt rather than to pure lead bromide.

(3) Kelley, *U. S. Bureau of Mines Bull.*, **371**, 31 (1934); **383**, 61 (1935); **476**, 95 (1949); Quill, "The Chemistry and Metallurgy of Miscellaneous Materials, Thermodynamics," McGraw-Hill Book Co., Inc., New York, N. Y., 1950; Natl. Bur. Standards, Selected Values of Chemical Thermodynamic Properties, Table I: 27–8, Sept. 30, 1948; Table II: 27–2, Sept. 30, 1948.

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The Interaction of Diacyl Peroxides with Diazomethane

BY JOHN E. LEFFLER[1]

Diacyl peroxides might be expected to react with diazomethane either by analogy with acid anhydrides[2] or by analogy with sources of free radicals like hexaphenylethane.[3] However, no reaction was found between benzoyl peroxide and diazomethane in ether solution, the peroxide being recovered unchanged. This result may be due to a lesser degree of positive charge on the carbonyl group of the peroxide. The resonance form shown below would be of lower energy in the peroxide than in the acid anhydride, since in the anhydride the positive charge would be adjacent to the positive end of a carbonyl group.
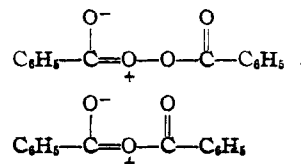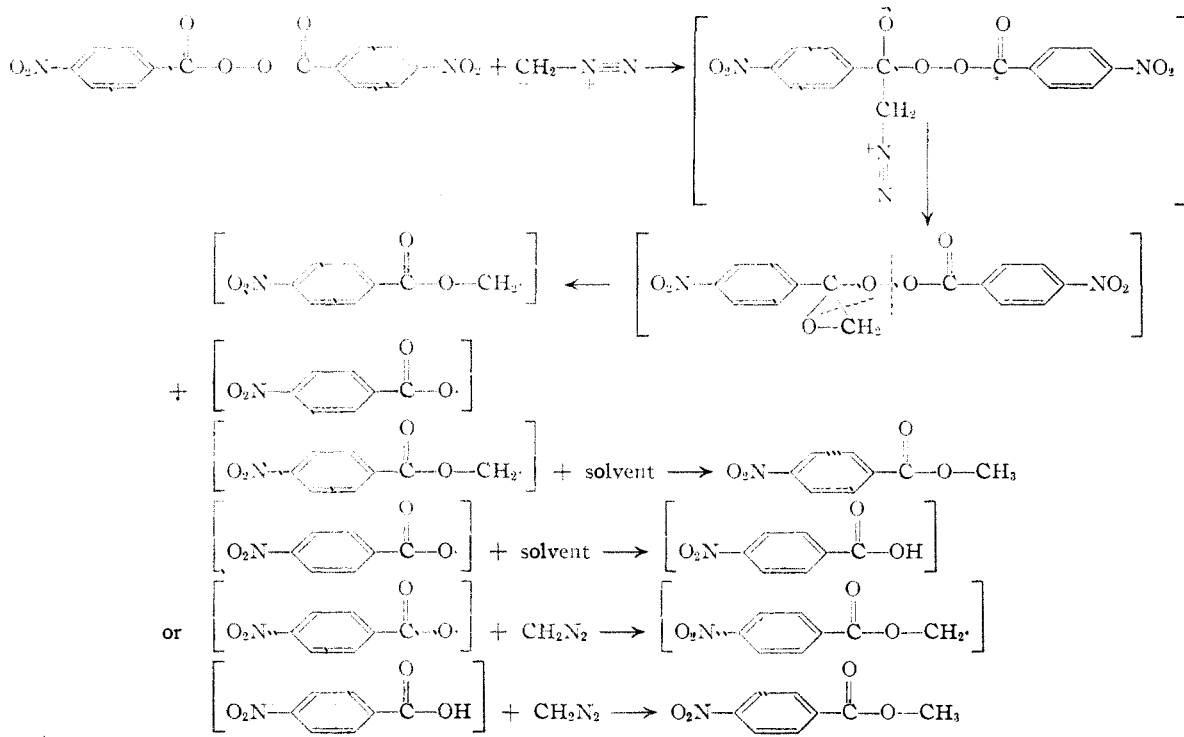
(1) Department of Chemistry, Florida State University, Tallahassee, Florida.

(2) Bradley and Robinson, THIS JOURNAL, **52**, 1558 (1930).

(3) Schlenk, *Ann.*, **394**, 183 (1912).

In order to counteract this effect, the reaction was tried with bis-(p-nitrobenzoyl) peroxide. The p-nitro group favors the reaction by withdrawing electrons and increasing the positive charge on the carbon atom of the carbonyl group. The reaction between bis-(p-nitrobenzoyl) peroxide and diazomethane in ether gave methyl p-nitrobenzoate. A control experiment showed that the peroxide alone is unchanged under the same conditions, hence the methyl p-nitrobenzoate is not the result of methylation of p-nitrobenzoic acid formed by independent decomposition of the peroxide. The influence of nitro groups on the reaction makes it seem likely that the first step is an ionic one, as in the scheme[?]

of the latter from cold ether gave 1.5 g., m. p. 90–92.5°, identified as methyl p-nitrobenzoate by a mixed melting point. Similar experiments with benzoyl peroxide and a large excess of diazomethane gave the peroxide back unchanged; heating or addition of methanol caused faster loss of the diazomethane, but still did not induce any reaction with the benzoyl peroxide.

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Di-2-picolylmethane

BY NELSON J. LEONARD AND JOSEPH H. BOYER

Ladenburg[1] in 1888 reported the synthesis of a compound, bis-(1-methyl-2-pipecolyl)-methane

Since the methyl p-nitrobenzoate recovered corresponds to only about one half of the peroxide consumed, it is possible that some radical induced decomposition of the peroxide or wastage of radicals from the peroxide by combination with radicals from the solvent may occur.

Experimental

To a solution of 6.6 g. (0.02 mole) of bis-(p-nitrobenzoyl peroxide) in 5 l. of ether was added a solution of diazomethane[5] made by adding 6.8 g. (0.05 mole) of nitrosomethylurea to a cold, stirred mixture of ether and concd. potassium hydroxide solution and drying the ether layer over solid potassium hydroxide.

The reaction mixture was allowed to stand overnight at room temperature and then allowed to evaporate to dryness. The residue, crystallized from chloroform–methanol gave 2.2 g. of unreacted peroxide and 2.0 g. of crude methyl p-nitrobenzoate, m. p. 84–90°. Repeated crystallization

(4) Leffler, Chem. Rev., **45**, 385 (1949).

(5) Eistert, "Neuere Methoden der präparativen organischen Chemie," Vol. I, Edwards Bros., Ann Arbor, 1947, p. 397.

(I), which he regarded as analogous to the Lupin alkaloid sparteine.[2] Even the best guide at that time as to the structure of the alkaloid was an incorrect postulate of Ahrens[3]; moreover, the correct structure (II) of sparteine was not established conclusively until 1936.[4] It is somewhat surprising, therefore, to compare I with II and to perceive in what measure Ladenburg actually
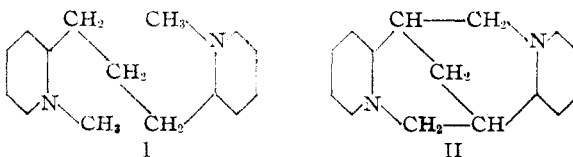
(1) Ladenburg, Ber., **21**, 3100 (1888).

(2) For leading reference, see Leonard and Beyler, THIS JOURNAL, **72**, 1316 (1950).

(3) Ahrens, Ber., **21**, 825 (1888).

(4) Clemo, Morgan and Raper, J. Chem. Soc., 1025 (1936).