[CONTRIBUTION FROM THE McGREGORY HALL OF CHEMISTRY, COLGATE UNIVERSITY]

Metalyl Compounds of Benzoylpyruvic Acid and its Esters[1]

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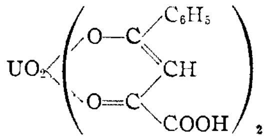
Methyl and ethyl esters of benzoylpyruvic acid react with the uranyl structure to form inner coördination complexes containing two moles of ester to one of metalyl. However, benzoylpyruvic acid formed a highly insoluble compound with uranyl ion, this product containing one mole of the acid to one of metalyl when preparations comprised the direct reaction between acid and uranyl, gentle hydrolysis of the ethyl ester complex, or acidification of sodium uranyl benzoylpyruvate. The ethyl ester forms an unstable complex with molybdyl ion, this compound containing two moles of ester for one of the metalyl.

As part of a program to measure polarizations of inner coördination complexes, this Laboratory has been concerned with the synthesis and characterization of compounds with the general formula MO_2 (β-diketone)$_2$, M being uranium, tungsten or molybdenum. Benzoylpyruvic acid was selected as a representative asymmetrical β-diketone whose carboxylic acid group might permit resolution of optical isomers. This specific use has been recorded for copper, zinc and beryllium complexes.[2]

It was believed that one uranyl structure would react with the β-diketone functions of two molecules of benzoylpyruvic acid to form



However, the product contained only one mole of benzoylpyruvic acid for one of uranyl structure.

Since this ratio of one mole of acid to one of uranyl structure indicated participation of the ionizable hydrogen of the carboxylic acid group, the methyl and ethyl esters of the acid were used. In both cases, the complexes contained two moles of β-diketone for one of uranyl structure.

Indirect synthesis of a compound containing two moles of acid was attempted by gentle hydrolysis of the ethyl ester complex, but the isolated products were benzoylpyruvic acid and an impure compound whose appearance, insolubility and analysis approached those of the monoacid compound. Thus elimination and rearrangement are indicated. A second attempted indirect synthesis comprised acidification of the reaction product of one mole of uranyl nitrate with two of disodium benzoylpyruvate. However, this yielded a solid resembling the monoacid compound in analysis and insolubility.

Attempts to synthesize corresponding molybdyl compounds succeeded only for bis-(ethyl benzoylpyruvato)-dioxomolybdenum, which was unstable on heating in solution or on standing in a sealed tube.

Attempts to synthesize the analogous tungstyl complexes failed although a yellow color appeared when the reactants were mixed.

Experimental

Benzoylpyruvic acid and an aqueous solution of its disodium salt were prepared by the condensation of acetophenone and ethyl oxalate in the presence of sodium ethoxide according to the method of Bromme and Claisen.[3] The methyl and ethyl esters were prepared by a modification of the Claisen condensation procedure reported by Maria Freri.[4] Commercial grades of acetophenone and ethyl oxalate were fractionated through a twelve-bulb, vacuum jacketed Snyder column. Acetophenone was collected at 199–200° (uncor.) and the ethyl oxalate at 183–184° (uncor.). Commercial absolute methyl and ethyl alcohol were dried by the method of Lund and Bjerrum.[5] Commercial sodium was cut under kerosene immediately before use. Molybdenum trioxide dihydrate was prepared by the method of Rosenheim.[6]

Loss of weight determinations were made under vacuum in a standard Abderhalden drying pistol containing phosphorus pentoxide.

A. Preparation of Bis-(methyl Benzoylpyruvato)-dioxouranium.—A warm methanol solution of 5.02 g. (0.01 mole) of uranyl nitrate hexahydrate was poured slowly with stirring into a warm methanol solution of 4.5 g. (0.023 mole) of methyl benzoylpyruvate. On cooling there precipitated 5.5 g. of orange solid which, on exposure to ambient air for several days, lost solvated methanol and became a yellow monohydrate. This changed to orange on drying at 70° in vacuum. The alcoholate and hydrate melted with effervescence at 155–156° (uncor.).

Anal. Calcd. for $C_{22}H_{18}O_{10}U \cdot 2CH_3OH$: C, 38.71; H, 3.52; U, 31.98; CH_3OH, 8.61. Found: C, 38.44; H, 3.54; U, 32.3; wt. loss on drying in vac. for 3 days at 65°, 8.4. Calcd. for $C_{22}H_{18}O_{10}U \cdot H_2O$: C, 37.83; H, 2.89; U, 34.09; H_2O, 2.58. Found: C, 37.56; H, 2.96; U, 34.20; wt. loss on drying in vac. for 3 days at 65°, 2.74.

B. Preparation of Bis-(ethyl Benzoylpyruvato)-dioxouranium.—Using 95% aqueous ethanol solutions of the reagents at 35°, 5.02 g. (0.01 mole) of uranyl nitrate hexahydrate was rapidly added to 5.5 g. (0.025 mole) of ethyl benzoylpyruvate. Fairly dense orange crystals, solvated with ethanol, separated after slow cooling. The melting point of these crystals rose from 97 to 139° on exposure to ambient air for 2 or 3 days, prolonged exposure resulting in partial decomposition. Vacuum drying (4 days at 45°) of the freshly precipitated crystals yielded the orange anhydrous compound which became a yellow dihydrate on exposure to ambient air.

Anal. Calcd. for $C_{24}H_{22}O_{10}U \cdot 2H_2O$: C, 38.71; H, 3.52; U, 31.98; H_2O, 4.84. Found: C, 38.38; H, 3.53; U, 32.04; wt. loss on drying in vac. for 4 days at 45°, 4.92.

C. Preparation of Sodium Uranyl Benzoylpyruvate.—Ten grams of the yellow primary product of the Claisen condensation of ethyl oxalate with acetophenone (before acidification) was dissolved in cold water, filtered and poured slowly into an aqueous solution of 5.02 g. (0.01 mole) of uranyl nitrate hexahydrate, forming a thick orange-yellow gel. After digestion on a steam-bath for 4 hours a finely divided yellow solid precipitated. This exhibited no melting point, darkening at about 325°.

Anal. Found: C, 23.10; H, 2.00; U, 45.50; ash, 59.1; wt. loss on drying in vac. 48 hours at 100°, 6.72.

Leaching with hot water and recrystallization from aqueous ethanol did not change the analysis significantly.

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[1] This work was supported by the Office of Naval Research and by a Frederick Gardner Cottrell Grant from the Research Corporation.

[2] W. H. Mills and R. A. Gotts, *J. Chem. Soc.*, 3121 (1926).

[3] E. Bromme and L. Claisen, *Ber.*, **21**, 1131 (1888).

[4] Maria Freri, *Gazz. chim. ital.*, **68**, 612 (1938); *C. A.*, **33**, 2488 (1939).

[5] H. Lund and J. Bjerrum, *Ber.*, **64**, 210 (1931).

[6] A. Rosenheim, *Z. anorg. Chem.*, **50**, 320 (1906).

D. Preparation of Uranyl Benzoylpyruvate. 1.—Using 95% aqueous ethanol solutions, 4.3 g. (0.0224 mole) of benzoylpyruvic acid was added slowly to 5.02 g. (0.01 mole) of uranyl nitrate hexahydrate. The finely divided yellow precipitate was digested for one hour on the steam-bath and filtered hot; yield 6.8 g. No solvent permitting recrystallization of this solid was found. The material darkened with apparent decomposition at 280°. The 48.7% U content of this solid showed that it had only one benzoylpyruvic acid per uranyl structure. Hence the preparation was repeated using half as much benzoylpyruvic acid: the product closely resembled the first in appearance and behavior.

Anal. Calcd. $C_{10}H_6O_6U$ anhyd.: C, 26.10; H, 1.31; U, 51.73. Found: C, 27.36; H, 1.29; U, 51.45, on correcting wet analysis for 2.98% wt. loss on drying.

2.—Acidification of an aqueous ethanol solution of the sodium uranyl benzoylpyruvate yielded a product having the same behavior and analysis as that of the direct preparation.

3.—The ethyl ester complex was boiled with water, the uranium content of the solid rising to 44.26% after 4 hours. At this time benzoylpyruvic acid was crystallized from the cooled filtrate; yield 20% predicated upon the elimination of one mole of acid from the ester complex.

E. Preparation of Bis-(ethyl Benzoylpyruvato)-dioxomolybdenum.—A mixture of 1.8 g. (0.01 mole) of molybdenum trioxide dihydrate and 7 g. (0.032 mole) of ethyl benzoylpyruvate was heated until solution of the oxide in the molten ester appeared complete (about 45 min.). A yellow solid crystallized from the hot benzene extract of the reaction mixture. This solid was unstable, changing to green on standing.

Anal. Calcd. $C_{24}H_{22}O_{10}Mo$: Mo, 16.94. Found: Mo, 16.7.

Discussion

The uranyl complexes of the methyl and ethyl esters of benzoylpyruvic acid have compositions consistent with the expectation of two β-diketone molecules per metalyl structure. The precise configuration of these compounds is, of course, not derivable from analytical evidence alone, several chelate ring formations being possible.

The uranyl compound of benzoylpyruvic acid appears to be a salt of the uranyl ion and the doubly ionized acid, this product being favored by its insolubility. The adequacy of the acid's double ionization was confirmed by conductometric titrations[7] in aqueous ethanol, of benzoylpyruvic acid and its ethyl ester with $Ba(OH)_2$, there clearly being two and one ionizable hydrogens in these materials, respectively. The analysis of the uranyl compound of sodium benzoylpyruvate definitely shows the presence of only one β-diketone per uranyl structure. Comparison of the U analysis for this preparation with the ash obtained upon its combustion appears to indicate a 1:1 atomic ratio of U and Na, but this evidence is not compelling.

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[7] We are indebted to W. L. Patchen for these measurements.

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A Molecular Orbital Theory of Organic Chemistry. I. General Principles

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By applying perturbation theory to the LCMO[12] modification of the usual semi-empirical molecular orbital treatment, a series of approximate expressions are obtained for the resonance energies bond orders and charge distributions in mesomeric systems which will later be shown to serve as a basis for a simple qualitative and semi-quantitative treatment of organic chemistry. This work is an extension of that of Coulson and Longuet-Higgins[8,9]; the extent to which it is novel is indicated.

The purpose of this series of papers is to present a general theory of organic chemistry which seems to offer important advantages over the current resonance theory.[2] The starting point for the present treatment is the familiar molecular orbital method in its original form,[3] without any of the subsequent refinements such as inclusion of non-orthogonality,[4] antisymmetrization,[5] or configurational interaction.[6] This simple version of the MO method is admittedly semi-empirical in that the basic parameters are determined from experiment rather than by *a priori* calculation, but it has proved remarkably successful in spite of its crudity. In any case the more refined treatments are far too complex for use in the present connection.

From approximate solutions of the MO equations, obtained by perturbation methods, it will prove possible on the one hand to derive qualitative relationships between molecular structure and physicochemical properties, and on the other to calculate in a very simple manner various molecular quantities (energies, charge distributions, etc.) of importance in chemistry. These calculations naturally share in the semi-empirical nature of the MO method in the form used here, but at least the results will all be obtained by rigorous reasoning within a framework of clearly stated approximations, and no appeal will be made to the kind of intuitive arguments on which the resonance theory[7] is based.

It should be emphasized at the outset that the general plan behind this treatment is not new, and

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[1] Reilly Lecturer, March-April, 1951. Present address: University of London, Queen Mary College, Mile End Road, London, E.1, England.

[2] *Cf.* G. W. Wheland, "The Theory of Resonance," John Wiley and Sons Inc., New York, N. Y., 1944.

[3] For a recent account of the method and references see A. Pullman and B. Pullman, "Les Theories Electroniques de la Chimie Organique," Masson, Paris, 1952.

[4] *Cf.* G. W. Wheland, THIS JOURNAL, **63**, 2025 (1941).

[5] M. Goeppert Mayer and A. L. Sklar, *J. Chem. Phys.*, **6**, 645 (1938).

[6] D. P. Craig, *Proc. Roy. Soc.* (*London*), **A200**, 474 (1950).

[7] This criticism applies to the resonance theory, not to the valence bond method which is a valuable and correct method of approximation. The connection between the two is by no means rigorous.