[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, UNIVERSITY OF CHICAGO, CHICAGO, ILLINOIS]

The Oxidation of Captive *p*-Aldehydobenzoate

BY R. T. M. FRASER AND HENRY TAUBE

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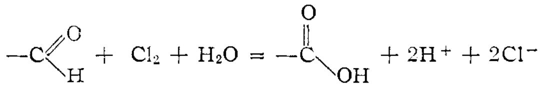
When the *p*-aldehydobenzoatopentammine cobalt(III) ion is oxidized by Cl_2 or by H_2O_2 (catalyzed by Mo(VI)), the corresponding terephthalato complex is formed as product, but when Co^{+++} aq, $S_2O_8^=$ (catalyzed by Ag^+) or alkaline permanganate is used, the oxidation of the ligand leads to reduction of Co(III). The feature which determines the course of the reaction is apparently this: a $2e^-$ oxidizing agent does not involve the Co(III) center, but a $1e^-$ oxidizing agent does.

A simple method for preparing many complexes of the series $(NH_3)_5Co(III)$–L (where L is a ligand attached to Co(III) by a carboxylate group) is to heat a mixture containing the ligand distributed between the acid and salt form with the ion $(NH_3)_5CoOH_2^{+++}$. However, when this procedure is applied in an attempt to prepare the acid terephthalato complex, the product is largely the binuclear rather than the mononuclear complex.[1] The acid terephthalato complex is of special interest in connection with studies on electron transfer through bridging groups, and an effort was therefore made to prepare it by another route. The method which proved successful was first to prepare the *p*-aldehydobenzoato complex, which was then oxidized by suitable reagents. The results obtained in the oxidation studies themselves proved to be so interesting, related as they are to earlier experiments on the oxidation of oxalate attached to Co(III)[2] and to the issue of electron transfer through conjugated systems, that we are making a separate report dealing with them.

Methods and Results

Preparation of the *p*-Aldehydobenzoatopentamminecobalt(III) Complex.—A solution containing $(NH_3)_5CoH_2O(ClO_4)_3$ and an equimolar mixture of *p*-carboxybenzaldehyde and its sodium salt was warmed at 80° for 2 hr. The solution was cooled, made strongly acid with $HClO_4$ and filtered. The precipitate was washed with hot water, the filtrate was allowed to cool, and the precipitate which formed was filtered off, washed with alcohol and then with ether and dried. The purity of the preparation was checked by making an analysis for ClO_4^- (% Cl: calcd., 13.89; found, 13.8).

Cl_2 as Oxidizing Agent.—A solution 0.05 *M* in the Co(III) complex was cooled in an ice-bath and Cl_2 was passed through it for 40 min. The reaction mixture was placed in a vacuum desiccator and Cl_2 was removed by evacuation. A test on the product solution failed to show Co^{++}, but titration with alkali showed that acid had developed in the solution equivalent to the conversion of 91% of the aldehyde complex to the terephthalato.



$$-\mathrm{C}\begin{smallmatrix}\nearrow\mathrm{O}\\ \searrow\mathrm{H}\end{smallmatrix} + Cl_2 + H_2O = -\overset{\overset{\displaystyle O}{\|}}{C}\searrow_{OH} + 2H^+ + 2Cl^-$$

Chlorine was the oxidizing agent used in the preparation of the terephthalatopentammine-cobalt(III) complex. The perchlorate salt precipitates in almost pure form when the product solution is acidified with perchloric acid.

Reaction with H_2O_2 Catalyzed by Mo(VI).—The reaction mixture was made up 0.01 *M* in the Co(III) complex, 5 *M* in H_2O_2 and 5×10^{-4} in $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$. Aliquots were withdrawn after 10, 60 and 120 min. and titrated with standard alkali. The increase in acidity in the 10–60 min. interval corresponded to oxidation to the terephthalato complex of 58% of the aldehyde and in the 60–120 min. interval to 23% additional. No cobaltous ion was detected in the final solution. The results show that the oxidation of the aldehyde is substantially complete in 120 minutes and that the terephthalato complex is the principal reaction product. If $(NH_3)_5CoOH_2^{+++}$ were formed, its presence would be revealed in the titration with alkali; any terephthalic acid set free would form a precipitate.

MnO_4^- as Oxidizing Agent.—In acid solution MnO_4^- reacts only slowly with the aldehydo complex and the system was not investigated thoroughly under these conditions. But in 0.5 *M* NaOH reaction takes place rapidly, the color of the solution changing from red to green. The product solution was acidified with HCl, whereupon a white precipitate formed, and the solution became almost colorless. The solution was centrifuged, and the precipitate was washed with dilute HCl, centrifuged and dried. Titration with alkali showed that 86% of the theoretical yield of terephthalic acid was obtained. It should be mentioned that the terephthalato complex resists the treatment with alkaline permanganate. From the observation that the solution after acidifying becomes virtually colorless, we can conclude that Co(III) has been reduced in the reaction of the complex with MnO_4^- and set free as Co^{++}.

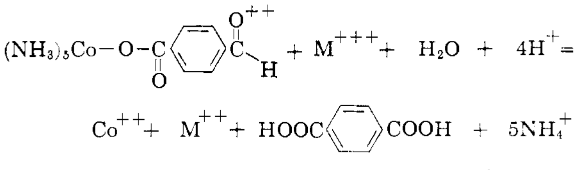
Reaction with $S_2O_8^=$, Catalyzed by Ag^+.—A solution 0.03 *M* in complex, 0.3 *M* in $K_2S_2O_8$ and 0.05 *M* in Ag^+ was prepared. The red color of the original solution gradually faded until the solution was essentially colorless. A white precipitate formed which on being collected was shown by infrared analysis to be largely silver terephthalate. The solution at the end of the experiment contained Co^{++} but no Co(III).

Reaction with Co^{+++}.—A solution containing Co^{+++} was prepared by the method of Weiser.[3] This solution was added dropwise to a 0.02 *M* solution of the complex until 10% excess was added. Reaction takes place rapidly, a white precipitate forming and the red color of the solution fading. The precipitate was collected, washed, dried and titrated with standard alkali. Infrared examination showed the substance to be terephthalic acid, and the titration with base showed that it was recovered in 95% yield.

It is surprising that in an experiment made under similar conditions with Ce(IV) (perchlorate) as oxidizing agent, no reaction is observed in 3 days.

Discussion

The results obtained in the present study conform to those reported[2] on the oxidation of $(NH_3)_5CoC_2O_4H^{++}$. $2e^-$ oxidizing agents such as Cl_2 or H_2O_2 do not involve the Co(III) center in the oxidation of the ligand, but $1e^-$ oxidizing agents do. The net change for the second class of oxidizing agents may be represented as



As with the oxalato complex, the question as to whether the reduction of the Co(III) center takes place simultaneously with that of the external oxidizing agent or whether a radical ion of finite lifetime is formed is not settled by the experiments. But again such a radical ion, if it is formed, does not

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(1) D. K. Sebera, Ph.D. Dissertation, University of Chicago, 1960.

(2) P. Saffir and H. Taube, THIS JOURNAL, **82**, 13 (1960).

(3) D. W. Weiser, Ph.D. Dissertation, University of Chicago (1955).

last long enough to react with a second molecule of the oxidizing agent. If this reaction were to occur, it would preserve the oxidation state of the complexed Co(III).

These experiments also provide evidence for electron transport by the complex organic molecule. This conclusion follows whether it is assumed that the external oxidizing agent attacks the aldehyde end of the ligand or the carboxyl end. If the former, then the odd electron must flow from the aldehydo end through the molecule to the oxidizing agents; if the latter, two electrons must flow from the aldehydo end, through the molecule to the oxidizing centers. The question of where the attack occurs can perhaps be settled by tracer experiments with the H_2O_2–Mo(VI) oxidizing mixture but not as readily for the others.

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[CONTRIBUTION FROM THE NIEUWLAND LABORATORIES OF THE UNIVERSITY OF NOTRE DAME, NOTRE DAME, INDIANA]

Electric Moments of Some *p*-Amino- and *p*-Dimethylamino-β-styryl Derivatives[1]

BY ROBERT J. DOLTER AND COLUMBA CURRAN

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Electric moments have been determined for the *p*-amino derivatives of ethyl cinnamate, cinnamonitrile (*trans*) and benzalacetone in benzene and in dioxane, and for *cis-p*-aminocinnamonitrile and the *p*-dimethylamino derivatives of ethyl cinnamate, cinnamonitrile (*cis* and *trans*), benzalacetone, cinnamaldehyde and β-nitrostyrene in benzene. The introduction of the vinyl group between the benzene ring and the electron withdrawing groups results in appreciable increases in moments and in an increased solvent effect for the *p*-amino derivatives. Dielectric data indicate *s-cis* and *s-trans* conformations, respectively, for the ketones and aldehyde.

Electric moments, molar refractions and infrared and ultraviolet absorption spectra of *p*-amino and *p*-dimethylamino derivatives of some β-substituted styrenes have been determined to study the effect of increasing length of the conjugated chain on the resonance interaction between electron releasing and electron withdrawing groups and on the increase in π-electron delocalization in hydrogen bonding solvents. The electric moments and some of the refraction data in non-polar solvents are reported in this paper along with the ultraviolet absorption characteristics of *cis* and *trans* isomers.

Otto and Wenzke have reported[2] a moment of 0.37 Debye for styrene, opposite in direction to that of toluene; more recent measurements on styrene have indicated a value between 0.1 and 0.2 Debye. The moments of a series of monosubstituted styrenes determined by Sutton and co-workers[3] have led these authors to conclude that the vinyl group is electron withdrawing with respect to the benzene ring. The lower moment found for *trans*-benzalacetone as compared to the value for *trans*-cinnamaldehyde has been interpreted[4] as indicating an *s-cis* conformation for the ketone and an *s-trans* conformation for the aldehyde. These respective configurations are favored by steric factors.

Previous electric moment studies in this Laboratory[5] on *para*-substituted anilines in benzene and dioxane have indicated an appreciable stabilization of highly polar resonance structures for these compounds in dioxane by hydrogen bonding. The moments of the *p*-aminocinnamyl derivatives have been determined in these two solvents to compare the solvent on the moments of the disubstituted benzenes and β-styrenes. Two new compounds have been synthesized, *cis*- and *trans-p*-aminocinnamonitrile. The compounds other than the nitriles are all *trans*.

Experimental[6]

cis- **and** *trans-p*-**Dimethylaminocinnamonitrile** were prepared by a modification of the method of Ghosez.[7] Equimolar quantities of *p*-dimethylaminobenzaldehyde and cyanoacetic acid were condensed at 100° in dry pyridine containing 1 ml. of piperidine. The condensate was separated, crystallized from ethanol and decarboxylated by boiling for 36 hr. in pyridine containing a few crystals of $CuSO_4$. The solution was poured in water, the resulting precipitate treated with sodium carbonate and the *cis* and *trans* isomers separated by fractional crystallization from aqueous ethanol, m.p. *trans* 168–169°, *cis* 63°. These compounds were new when prepared, but they have since been reported by Coenen and Pestemer.[8]

Anal. Calcd. for $C_{11}H_{22}N_2$: C, 76.71; H, 7.02. Found: *trans* C, 76.9; H, 7.16; *cis* C, 76.8; H, 6.96.

cis- **and** *trans*-**Aminocinnamonitrile** were prepared by condensing *p*-nitrobenzaldehyde and cyanoacetic acid as above. The condensate forms within an hour at room temperature. Decarboxylation was complete in 5 hr. The *cis* and *trans* isomers of the nitro derivative were separated by fractional crystallization from 95% ethanol, m.p. 202° and 107°. These were reduced in boiling ammoniacal ferrous sulfate solution. The *trans* amino isomer was purified by recrystallization from aqueous ethanol, m.p. 109–110°, and the *cis* from water, m.p. 94°.

Anal. Calcd. for $C_9H_8N_2$: C, 74.97; H, 5.59. Found: *trans* C, 75.2; H, 5.80; *cis* C, 75.3; H, 5.59.

Ethyl ***p*-aminocinnamate** was prepared by condensing *p*-nitrobenzaldehyde with malonic acid, decarboxylating, esterifying with HCl and reducing in boiling ammoniacal ferrous sulfate solution. The product was crystallized from ethanol, m.p. 73.5°.

***p*-Aminobenzalacetone** was prepared by three procedures. (a) *p*-Nitrobenzaldehyde and acetone were condensed in alcoholic KOH, dehydrated with acetic anhydride and reduced as above. (b) Benzalacetone was nitrated and the *p*-isomer was reduced. (c) Polymeric *p*-aminobenzalde-

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(1) Presented at the 121st Meeting of the American Chemical Society, Milwaukee, Wis., April, 1952.

(2) M. M. Otto and H. H. Wenzke, THIS JOURNAL, **57**, 294 (1935).

(3) K. B. Everard, L. Kumar and L. E. Sutton, *J. Chem. Soc.*, 2815 (1951).

(4) J. B. Bently, K. B. Everard, R. J. B. Marsden and L. E. Sutton, *ibid.*, 2957 (1949).

(5) C. Curran and G. K. Estok, THIS JOURNAL, **72**, 4575 (1950).

(6) A more detailed description of the preparation of these compounds is given in the Ph.D. thesis of Rev. Robert J. Dolter, University of Notre Dame.

(7) J. Ghosez, *Bull. soc. Chim. Belg.*, **41**, 477 (1932).

(8) M. Coenen and M. Pestemer, *Z. Elektrochem.*, **57**, 785 (1953).