nearly pure dibenzothiophene in three fractions melting within the range of 97–99°. Identity was established by the method of mixed melting points.

Run II.—A stirred suspension of 5.0 g. (0.025 mole) of dibenzothiophene-5-oxide in 250 ml. of dry ether was cooled in an acetone–Dry Ice-bath to $-10 \pm 5°$ (internal) while a total of 57.9 ml. of a 1.378 *M* ether solution of *n*-butyllithium (3.2 equivalents) was added over a period of 5.5 hours. The addition of the *n*-butyllithium was interrupted at predetermined intervals in order to follow the course of the reaction with color tests. A Color Test II was not positive until after 1.8 equivalents of *n*-butyllithium had been added. The mixture did not give a positive Color Test II after prolonged stirring until 3.2 equivalents of *n*-butyllithium were present. Color Test I was positive throughout. There was definite evidence of undissolved starting material until 2.0 equivalents of *n*-butyllithium had been added, at which point a finely divided precipitate began to form and the undissolved platelets of dibenzothiophene-5-oxide disappeared. Carbonation and hydrolysis were effected as in Run I. The ether and aqueous layers were easily separated as no insoluble material was present. Acidification of the aqueous layer yielded 3.1 g. (55.4%) of 4-dibenzothiophenecarboxylic acid; m.p. 232–246°. Recrystallization from dilute methanol yielded 2.0 g. of pure acid (35.7%) which melted at 256–256.5°. Infrared absorption measurements of this acid showed its spectrum to be identical with that of an authentic sample of 4-dibenzothiophenecarboxylic acid.[10a] From the ether layer there was isolated 0.5 g. (10.8%) of dibenzothiophene.

Run III.—The procedure for this run was exactly the same as that followed in Run II except that only 1.0 equivalent of *n*-butyllithium was added and that the mixture was stirred for seven hours. By working up the carbonated mixture as described in Run II there was obtained 0.2 g. (3.5%) of 4-dibenzothiophenecarboxylic acid, 2.8 g. (56.0%) of recovered dibenzothiophene-5-oxide and 0.2 g. (4.4%) of dibenzothiophene.

Metalation of Dibenzothiophene.—A solution of 4.6 g. (0.025 mole) of dibenzothiophene was treated at −10° with 1.4 equivalents of *n*-butyllithium in exactly the same manner as reported in Run II above. On working up the carbonated reaction mixture, no acidic material was found in the aqueous layer and the ether layer yielded 4.0 g. (89.4% recovery) of dibenzothiophene. Identical results were obtained in a check run with 89.3% of the starting material being recovered. When dibenzothiophene is treated with *n*-butyllithium for 24 hours at the temperature of refluxing ether, yields of 4-benzothiophenecarboxylic acid of 50–60% are obtained after carbonation.[8,10a,15]

A third run was made in which 0.5 g. (0.0025 mole) of dibenzothiophene-5-oxide was added to the initial solution of 4.6 g. (0.025 mole) of dibenzothiophene. Only a trace of acidic material was isolated and 91.3% of the starting dibenzothiophene was recovered.

The low-temperature metalation of sulfones, other sulfoxides and related types is being examined in order to determine the mechanism and scope of the reaction.

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Mechanism of Aquation of Carbonatopentaamminocobaltic Ion in Acid Solution

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The transformation of $[Co(NH_3)_5Co_3{}^+]$ to $[Co(NH_3)_5H_2O^{+++}]$ takes place rapidly in water, and even more rapidly when the solution is acidified.[1] The net change in acid solution is described by the equation

$$Co(NH_3)_5CO_3{}^+ + 2H^+ = Co(NH_3)_5H_2O^{+++} + H_2CO_3$$

Interest in this reaction developed out of research which is in progress on the mechanisms of substitution in hexacoördinated complex ions. We have performed some tracer experiments to learn whether the metal ion–oxygen bond or the carbon–oxygen bond breaks in the removal of carbonate from the complex ion. In the former event but not in the latter, the oxygen found in the resulting aquo ion will be derived from the solvent. The results obtained show that at least 99% of the change proceeds leaving the Co(III)–O bond intact. The mechanism is therefore of the type observed in the hydrolysis of certain esters.[2]

Kinetic experiments[1] have shown that the rate of aquation in acid is proportional to the concentration of the bicarbonato ion, $[Co(NH_3)_5Co_3H^{++}]$. This ion is analogous in structure to H_2CO_3, but has H^+ in the acid replaced by $Co(NH_3)_5{}^{+++}$. The tracer result shows that the mechanism of the aquation in acid is analogous to the change: $H_2CO_3 = H_2O + CO_2$, and a comparison of the specific rates of the two reactions is therefore of interest. From the work of Lamb and Mysels,[1] the specific rate of decomposition of $Co(NH_3)_5Co_3H^{++}$ at 0° is calculated as 0.19 min.$^{-1}$. Combining the value 0.0012 quoted by Faurholt[3] for the quotient $(H_2CO_3)/(CO_2)$ at equilibrium, with the specific rate measured by Mills and Urey[4] for the formation of H_2CO_3, the specific rate of decomposition of H_2CO_3 is calculated as 105 min.$^{-1}$. The higher value for H_2CO_3 as compared to $Co(NH_3)_5Co_3H^{++}$ is not unexpected in view of the greater acidity of H^+ as compared to $Co(NH_3)_5H_2O^{+++}$. ($Co(NH_3)_5H_2O^{+++}$ is a weak acid[5]—$K_{\text{diss.}} = 6 \times 10^{-7}$ at 15° and $\mu = 0.1$.)

The tracer result we have obtained demonstrates rather strikingly the inertia to substitution of the Co(III)–O bond in the complex ion. A mechanism similar in type to that established will come into question in other reactions involving replacement of a complex ligand from the central ion, for example in the aquation of acetatopentamminocobaltic ion. A system in which this type of mechanism probably operates is in the reaction of $Cr(H_2O)_6{}^{+++}$ with polymolybdates. Hall and Eyring[6] have shown the hexamolybdatochromic ion is formed rapidly. Substitutions on Cr(III) are in general slow, on Mo(VI) rapid. In the reaction therefore the Cr–O bond is probably preserved and the Mo–O bonds broken and re-established.

Experimental

The salt $[Co(NH_3)_5CO_3]NO_3 \cdot H_2O$ was prepared[7] following the method described by Lamb and Mysels.[1] A solution of the salt in water was found to give no precipitate of $CaCO_3$ initially when Ca^{++} was added but after a period of time a precipitate began to appear.

Two tracer experiments were performed. In one, 2 g. of salt was dissolved in 75 ml. of enriched water (mole fraction $O^{18} = N \simeq 8 \times 10^{-3}$) at room temperature. After a period of ten minutes the salt had dissolved, the solution was then cooled to 0° and *ca.* 1.5 ml. of concd. HCl was added. A few minutes later, the ion $Co(NH_3)_5H_2O^{+++}$ was precipitated as the salt $Co(NH_3)_5H_2OCl_3 \cdot HgCl_2$. This compound was filtered off, dried and heated to yield water. The iso-

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[1] A. B. Lamb and K. J. Mysels, THIS JOURNAL, **67**, 468 (1945).

[2] M. Polanyi and A. L. Szabo, *Trans. Faraday Soc.*, **30**, 508 (1934).

[3] C. Faurholt, *J. Chim. Phys.*, **21**, 400 (1924).

[4] G. A. Mills and H. C. Urey, THIS JOURNAL, **62**, 1019 (1940).

[5] J. N. Bronsted and K. Volquartz, *Z. physik. Chem.*, **134**, 97 (1928).

[6] H. T. Hall and H. Eyring, THIS JOURNAL, **72**, 782 (1950).

[7] We are indebted to Mr. John Below for preparing the compound.

topic composition of the water was established by equilibrating it with CO_2 and analyzing the CO_2 by means of a mass spectrometer. The second experiment differed only in that the reactant solution and the reagents needed to precipitate the double salt were not precooled before being added.

The results obtained are presented in Table I.

TABLE I

TRACER EXPERIMENTS ON THE AQUATION OF $Co(NH_3)_5CO_3^+$ IN ACID

	$N_{obsd.}$ in water from ion	$N_{calcd.}$ for H_2O from solvent
Experiment 1	2.197×10^{-3}	7.90×10^{-3}
Experiment 2	2.630×10^{-3}	7.52×10^{-3}
Blank; reaction in unenriched H_2O	2.158×10^{-3}	....

The result obtained in Expt. 1 is very close to that in the blank. The higher value in Expt. 2 can be attributed to the exchange[8] of $Co(NH_3)_5H_2O^{+++}$ with H_2O^* which took place when the solution warmed as the precipitating agents were added.

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[8] This exchange is at present under study (A. C. R. and H. T.). The method for isotopic sampling will be described in more detail when the data on the exchange are presented for publication.

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Spectrophotometry of Ferric Chloride Complexes with *m*-Cresol, Salicylaldehyde and Ethyl Acetoacetate

BY RALPH L. HERBST, JR., ROBERT H. CLOSE, FRANK J. MAZZACUA AND ROBERT F. DWYER

In 1934, the structure $Fe(OR)_6^{---}$, where OR represents the phenoxide or enolate ion, was postulated by Wesp and Brode[1] for the colored complex formed in the reaction of ferric chloride with phenols and enols. This postulation was based on the observation that the ferric chloride–phenol complexes gave absorption spectra similar to that found for the iron(III) ion–cyanate and monothiocyanate iron(III) ion complexes. At this time these latter complexes were described as $Fe(CN)_6^{---}$ and $Fe(CNS)_6^{---}$, respectively. More recent investigations by Bent and French,[2] Edmonds and Birnbaum,[3] and Vosburgh and associates[4] have shown the monothiocyanate iron(III) complex to be $Fe(SCN)^{++}$. These results prompted a study of the iron(III) ion–phenol and enol complexes by the method of continuous variations employed by Vosburgh.[4]

Experimental

Materials.—All the organic compounds were freshly distilled: *m*-cresol, b.p. 201°; salicylaldehyde, b.p. 196.5°; ethyl acetoacetate, b.p. 180°; reagent grade $FeCl_3 \cdot 6H_2O$ was used.

Method.—The experimental details have been described by Vssburgh.[4] For *m*-cresol and ethyl acetoacetate, the mixtures were made up by volume from a freshly prepared stock solution of 0.02003 *N* ferric chloride and a 0.02003 *M* stock solution of the organic compound. In the case of salicylaldehyde, it was necessary to use more dilute stock solutions of 0.0001 *M*. Optical densities were measured with a Beckman model B spectrophotometer within 10–15 minutes after the mixtures were prepared. Preliminary scanning of 1:1, 1:3 and 1:6 mixtures of ferric chloride–*m*-cresol, ferric chloride–salicylaldehyde, and ferric chloride–ethyl acetoacetate between 400 and 675 mμ showed that only one colored compound formed in each case since curves of the same shape resulted. Next a series of mixtures was measured at four arbitrarily selected wave lengths. The values of *y*, the difference between the optical density observed and the corresponding optical density calculated for no reaction, were plotted *versus* *x*, the volume of the phenol or ester solution added to the volume $(1 - x)$ of the ferric chloride solution. The data are plotted in Figs. 1 and 2; the *y* terms have been multiplied by constants for clarity in presentation. The optical density of the blank ferric chloride solution showed no change within the time the measurements were made.

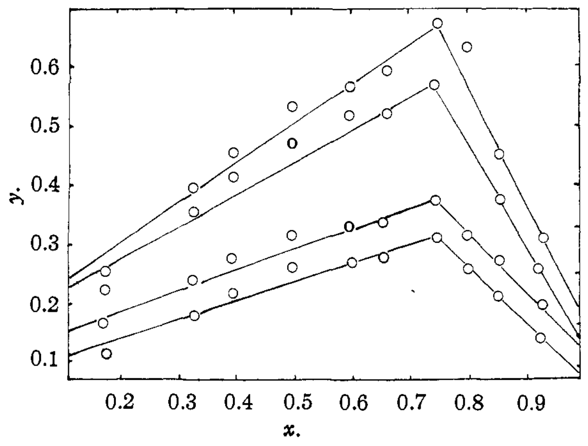

Fig. 1.—Ferric chloride-ethyl acetoacetate from top to bottom: 520, 475, 510, 490 mμ.

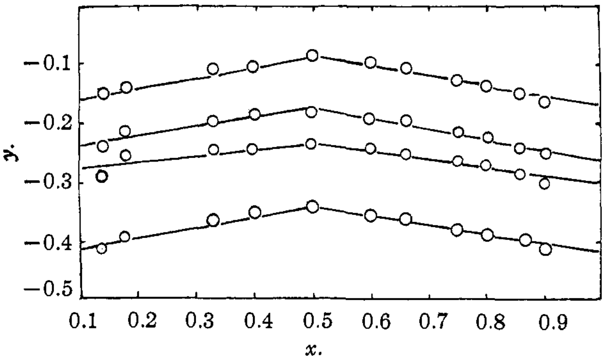

Fig. 2.—Ferric chloride–salicylaldehyde from top to bottom: 540, 520, 500, 560 mμ.

Results and Discussion

As shown in Figs. 1 and 2, the maxima for the colors occurred at 1 ferric chloride:3 ethyl acetoacetate and at a 1:1 ratio for ferric chloride–salicylaldehyde. A similar plot has also shown that the maximum occurs at 1 ferric chloride:3 *m*-cresol. At optical density readings of 0.704, 0.242 and 0.341 for ethyl acetoacetate, salicyladehyde and *m*-cresol, these maxima occurred at 510, 500 and 525 mμ, respectively Thus under the conditions used only one complex occurred for each pair of

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[1] E. F. Wesp and W. R. Brode, THIS JOURNAL, **56**, 1037 (1934).

[2] H. B. Bent and C. L. French, *ibid.*, **63**, 568 (1941).

[3] S. M. Edmonds and N. Birnbaum, *ibid.*, **63**, 1471 (1941).

[4] W. C. Vosburgh and G. R. Cooper, *ibid.*, **63**, 437 (1941); R. K. Gould and W. C. Vosburgh, *ibid.*, **64**, 1631 (1942).