

Notes

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BROOKLYN COLLEGE OF THE CITY UNIVERSITY
OF NEW YORK, BROOKLYN, NEW YORK

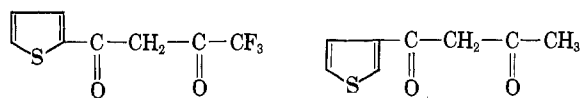
Formation Constants of Complexes of 2-Thenoyltrifluoroacetone and 3-Thenoylacetone¹

By JOSEPH L. ROSENSTREICH AND DAVID E. GOLDBERG

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2-Thenoyltrifluoroacetone is an excellent agent for extracting metal ions from relatively acidic solutions into nonaqueous solution.² The present study was initiated to determine if the ligand might be terdentate in nature, a fact which might account for its exceptional ability.

Average formation constants for the first and second coordination steps have been determined for the ligand with copper(II) and nickel(II) ions. Use of the standard technique³ involves too great an initial coordination to make it possible to determine the stepwise constants for the reactions. Thus adapted techniques were used to determine the stepwise formation constants with several bivalent cations. Constants were also determined for 3-thenoylacetone for comparison to the data for 2-thenoyltrifluoroacetone.



2-Thenoyltrifluoroacetone

3-Thenoylacetone

Experimental

Reagents.—2-Thenoyltrifluoroacetone (Fisher Scientific Co., New York, N. Y.), m.p. 44°, reported⁴ 44°, was reported⁵ at least 99% pure. An infrared spectrum showed no detectable impurities, and the compound was used without further purification.

3-Thenoylacetone (Chemical Procurement Laboratories, Inc., New York, N. Y.) boiled at 112–113° (3 mm.), reported⁶ 129–131° (8 mm.). This reagent was reported to be at least 99% pure. An infrared spectrum showed no detectable impurities, and the compound was used without further purification.

Fresh samples of spectral grade dioxane were used for each run without further purification. Other reagents were reagent grade and were used without purification. Standard analytical methods were used to standardize all reagents.

Titration Procedure.—The titration procedure was essentially that described by Goldberg.⁷ The procedure was modified by

(1) (a) A portion of a thesis presented by Joseph L. Rosenstreich for the degree of Master of Arts, Jan. 1964. (b) Partially supported by the Research Corporation, and aided by the Data Processing Center of Brooklyn College.

(2) A. M. Poskanzer and B. M. Forman, Jr., *J. Inorg. Nucl. Chem.*, **16**, 323 (1961).

(3) L. G. Van Uitert, W. C. Fernelius, and B. E. Douglas, *J. Am. Chem. Soc.*, **75**, 457 (1953).

(4) H. Cook and R. W. Taft, Jr., *ibid.*, **74**, 6103 (1952).

(5) Fisher Scientific Co., Control Laboratory, private communication.

(6) Chemical Procurement Laboratories, private communication.

(7) D. E. Goldberg, *J. Chem. Educ.*, **40**, 341 (1963).

use of more dilute systems and by addition of perchloric acid in some cases.

The initial molar concentrations of reagents for Cu²⁺, Ni²⁺, Co²⁺, and UO₂²⁺ with TTA and for Cu²⁺ and UO₂²⁺ with 3TA were cation, 1 × 10⁻⁴; ligand, 4 × 10⁻⁴; HClO₄, 4 × 10⁻⁴; with 1 × 10⁻² M (CH₃)₄NOH. For Zn²⁺ with TTA and for Ni²⁺, Zn²⁺, and Co²⁺ with 3TA, the initial molar concentrations were cation, 5 × 10⁻⁴; ligand, 2 × 10⁻³; with 3 × 10⁻² M (CH₃)₄NOH.

Calculation Method.—The calculation method was described previously.⁷ It was necessary to add a term corresponding to the added perchloric acid in the cases where acid was added. Equation 20 was changed to read $\log K_1 = \log q_1 + 4 \log 1/\gamma_{\pm}$ and $\log K_2 = \log q_2 + 2 \log 1/\gamma_{\pm}$. Calculations were performed on an I.B.M. 1620 computer using a modified AFIT Fortran program. The only change in the calculation procedure from manual calculation was the linear interpolation of molarity data in order to determine the activity coefficient function; 95% confidence intervals were determined by the method of Youden.⁸

Results

Logarithms of formation constants are reported in Table I; 95% confidence intervals are reported with the constants.

TABLE I
LOGARITHMS OF FORMATION CONSTANTS^a

Ion	Log K ₁	Log K ₂	No. of points	— \bar{n} ranges used—	
2-Thenoyltrifluoroacetone					
H ⁺	8.64 ± 0.02		12	0.29–0.56	
Cu ²⁺	8.23 ± 0.18	8.08 ± 0.21	12	0.29–0.78	1.27–1.76
Ni ²⁺	7.93 ± 0.07	7.33 ± 0.16	6	0.45–0.62	1.27–1.68
Co ²⁺	7.81 ± 0.01	7.09 ± 0.22	6	0.44–0.65	1.35–1.68
Zn ²⁺	7.75 ± 0.03	6.32 ± 0.12	10	0.38–0.61	1.24–1.71
UO ₂ ²⁺	8.71 ± 0.11	7.92 ± 0.04	8	0.53–0.72	1.30–1.70
3-Thenoylacetone					
H ⁺	12.41 ± 0.01		20	0.33–0.77	
Cu ²⁺	12.43 ± 0.10	10.08 ± 0.33	12	0.53–0.77	1.33–1.78
Ni ²⁺	10.73 ± 0.07	8.48 ± 0.12	10	0.36–0.63	1.24–1.69
Co ²⁺	10.29 ± 0.05	8.10 ± 0.01	12	0.37–0.61	1.25–1.80
Zn ²⁺	10.02 ± 0.16	7.99 ± 0.17	12	0.35–0.69	1.20–1.75
UO ₂ ²⁺	12.25 ± 0.14	10.32 ± 0.04	6	0.44–0.57	1.29–1.62

^a 30°; I → 0; 75 vol. % dioxane.

Discussion

2-Thenoyltrifluoroacetone is a bidentate ligand, at least in its coordination with copper(II) ion. If three donor atoms were bonded to the copper ion, which has only four stable coordination sites, the second ligand would have greater difficulty being bound than is shown by the results. The formation curve shows no sign of a shoulder at $\bar{n} = 1$, while in a similar investigation Hoyer⁹ found a broad plateau at $\bar{n} = 1$ for a terdentate ligand. Also, K_1 and K_2 are essentially equal. If the first ligand were bonded by three bonds, K_1 would be expected to exceed K_2 greatly. Thirdly, $\log K_{\text{formation}}/\log K_{\text{protonation}}$ is approximately the same for 2-thenoyltrifluoroacetone as for 3-thenoylacetone. This fact indicates a similarity in the type of bonding.¹⁰

(8) W. J. Youden, "Statistical Methods for Chemists," D. Van Nostrand Co., Inc., New York, N. Y., 1953, p. 512.

(9) E. Hoyer, *Ber.*, **93**, 2475 (1960).

(10) D. E. Goldberg and W. C. Fernelius, *J. Phys. Chem.*, **63**, 1246 (1959).

The sulfur atom of the 3-substituted compound is sterically incapable of coordination to the same metal atom that the oxygen coordinates. Thus, it is likely that the sulfur of 2-thenoyltrifluoroacetone does not coordinate.

Van Uitert³ reported a value of 9.1 for the logarithm of the protonation constant for 2-thenoyltrifluoroacetone at 30° in 75 vol. % dioxane. He reported values of 9.5 and 8.0 for the average logarithm of the formation constants for both steps of the coordination reactions of copper(II) and nickel(II), respectively. The values reported in this study are lower in each case. In his pioneering work, Van Uitert based his calculations on only one point in each titration. He titrated with aqueous NaOH, using concentrated solutions of titrant so as not to deviate excessively from 75 vol. % dioxane. He could not determine the stepwise constants at the concentrations of reagents that he used, for the initial coordination in each formation constant titration was greater than $\bar{n} = 1$ before addition of any titrant.

In this work, many points were used in each titration to determine average values for each tabulated quantity. The titrant, tetramethylammonium hydroxide, was dissolved in 75 vol. % dioxane, so as not to change the solvent system during the titration. Use of dilute reagents and addition of perchloric acid together retarded the initial coordination enough to allow determination of stepwise formation constants.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF TEXAS, AUSTIN, TEXAS

The Reaction of Iron Pentacarbonyl with Acetylacetone

By J. W. FITCH, III, AND J. J. LAGOWSKI

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It has recently been reported that acetylacetone and iron pentacarbonyl react to form ferric acetylacetonate in low yield (8.5% based on iron pentacarbonyl).¹ The reaction was performed in the absence of a solvent and the isolation of the product involved its precipitation from acetone by the addition of water followed by subsequent recrystallization from benzene.

We have observed that iron pentacarbonyl reacts with acetylacetone in refluxing di-*n*-butyl ether to form, primarily, ferrous acetylacetonate (52% yield based on acetylacetone used), all manipulations being conducted in a nitrogen atmosphere. Isolation of the reaction product in air gives only ferric acetylacetonate in low yield.

Experimental

In a typical experiment acetylacetone (14.64 g., 0.1464 mole) and iron pentacarbonyl (28.60 g., 0.1460 mole) were dissolved

(1) T. G. Dunne and F. A. Cotton, *Inorg. Chem.*, **2**, 263 (1963).

together, under nitrogen, in 200 ml. of di-*n*-butyl ether. The mixture was refluxed for 15 hr. in the dark at 140°, after which time an orange precipitate had formed and the solution had turned dark red-brown. As the solution cooled under a slow stream of prepurified nitrogen more orange precipitate formed. The precipitate was filtered and washed twice with small portions of anhydrous diethyl ether and stored in a helium-filled drybox. The yield was 9.78 g. (52% based on acetylacetone used).

Anal. Calcd. for FeC₁₀H₄O₄: Fe, 21.98. Found: Fe, 22.07.

The magnetic susceptibility of the compound was determined with a Cheneveau balance and, after applying the diamagnetic correction, was found to correspond to 4.88 B.M. The spin-only moment for iron(II) is 4.90 B.M.²

The compound sinters at 177° and melts at 200–201° in an evacuated sealed capillary. Ferrous acetylacetonate is reported to sinter at 177° and to melt at 201°.³ When determined in air, the compound melted at 178–181°, indicating that it had been converted into ferric acetylacetonate. Ferrous acetylacetonate is reported to be easily oxidized, especially when moist, to ferric acetylacetonate.³

Acknowledgment.—We wish to express our appreciation to the Robert A. Welch Foundation for supporting this investigation and to NASA for a fellowship (to J. W. F.).

(2) B. N. Figgis and J. Lewis, "The Magneto-chemistry of Complex Compounds," in J. Lewis and R. G. Wilkins, Ed., "Modern Coordination Chemistry," Interscience Publishers Inc., New York, N. Y., 1960, p. 406.

(3) B. Emmert and R. Jarczynski, *Ber.*, **64**, 1072 (1931).

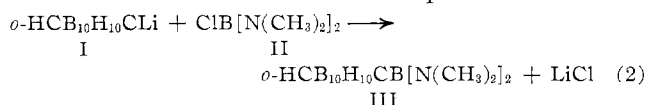
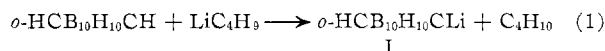
CONTRIBUTION FROM THE U. S. BORAX RESEARCH CORPORATION, ANAHEIM, CALIFORNIA

o-Carboranyl Derivatives of Boron Compounds

By J. L. BOONE, R. J. BROTHERTON, AND L. L. PETTERSON

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The synthesis of many carborane derivatives has been accomplished by reaction of metallocarboranes with halo compounds.^{1–3} In the present work, monolithio-*o*-carborane (I) was prepared from *o*-carborane and butyllithium in ether (eq. 1) and added to chlorobis(dimethylamino)borane (II) at 0° (eq. 2). The precipitate contained 84% of the theoretical amount of lithium chloride. Vacuum distillation of the solvent and recrystallization of the residue gave a 45% yield of the desired product, bis(dimethylamino)-*o*-carboranylborane (III). This compound



melted at $46 \pm 2^\circ$ and slowly distilled under vacuum at 100° in a molecular still. The infrared spectrum of

(1) For nomenclature consult R. Adams, *Inorg. Chem.*, **2**, 1087 (1963).

(2) T. L. Heying, J. W. Ager, Jr., S. L. Clark, R. P. Alexander, S. Papetti, J. A. Reid, and S. I. Trotz, *ibid.*, **2**, 1097 (1963).

(3) D. Grafstein, J. Bobinski, J. Dvorak, H. Smith, N. Schwartz, M. S. Cohen, and M. M. Fein, *ibid.*, **2**, 1120 (1963).