$$[H_2B(NH_3)_2][B_3H_8] + Na \longrightarrow H_2NBH_2 + NH_3 + NaB_3H_8 + 0.5H_2$$

4. The Reactions of $B_4H_{10}\cdot 2NH_3$ with HCl and HBr. The Formation of $[H_2B(NH_3)_2]Cl$ and $[H_2B(NH_3)_2]Br$.—In a typical run 1.84 mmoles of $B_4H_{10}\cdot 2NH_3$ was placed in a reaction tube and dissolved in about 2 ml. of diethyl ether. The solution was frozen with liquid nitrogen and an almost stoichiometric quantity (1.78 mmoles) of HCl was condensed into the tube. When the temperature was raised to −78°, 1.74 mmoles of hydrogen gas was evolved in 15 minutes and a white precipitate formed. The precipitate was separated in the vacuum line filtration assembly; the solid was washed through the filter disc with liquid ammonia and the solvent ammonia was distilled from the filtrate at −45°. A sample of $[H_2B(NH_3)_2]Cl$ weighing 119 mg. remained (yield was 79%). Analytical data showed B, 13.2; N, 33.9; hydridic H, 2.41; Cl^-, 42.7. The theoretical values for $[H_2B(NH_3)_2]Cl$ are: B, 13.1; N, 34.0; hydridic H, 2.43; Cl^-, 43.05. The molecular weight was determined by vapor pressure depression in liquid ammonia using standard methods.[4] The value obtained by extrapolation to infinite dilution was 95, which is in only fair agreement with the theoretical value of 82.3, but the deviation is in the range of uncertainty of the method for certain substances. The X-ray powder pattern was the same as that for $[H_2B(NH_3)_2]Cl$ made in an earlier study[6] and is identical with the powder pattern calculated from the single crystal data of Nordman and Peters.[10]

The compound $[H_2B(NH_3)_2]Br$ could be obtained by a similar procedure if HBr were substituted for HCl. Analysis of the bromide salt gave: B, 8.46; N, 22.15; Br^-, 62.5; hydridic H, 1.56. Values calculated for $[H_2B(NH_3)_2]Br$ are: B, 8.53; N, 22.10; Br^-, 63.02; hydridic hydrogen, 1.58. The molecular weight in liquid ammonia was about 120 as compared to a theoretical value of 127. Detailed data are available in dissertation form[3c]; the powder pattern is given elsewhere.[6]

When a large excess of the acid (4- to 6-fold excess) was used in this reaction, gas evolution proceeded very rapidly. One mole of hydrogen per mole of $B_4H_{10}\cdot 2NH_3$ was evolved in a few minutes; then the rate of gas evolution dropped almost to zero even when the temperature was raised to −63°. Yields of $[H_2B(NH_3)_2]Cl$ or $[H_2B(NH_3)_2]Br$ were unaffected by using a reasonable excess of acid.

5. The Preparation of $H_3NB_3H_7$ from $B_4H_{10}\cdot 2NH_3$.—The filtrate obtained from the reaction between $B_4H_{10}\cdot 2NH_3$ and HCl (see run described in previous section) was agitated constantly at −78° and a 1.44 mmole sample of ammonia gas was introduced slowly into the system. It was absorbed completely. The solvent ether was removed at room temperature and from the viscous liquid left in the tube, $H_3NB_3H_7$ was sublimed at 40 to 50° in the vacuum sublimation system. The yield was 36.5 mg. or 45% on the basis of ammonia added.

6. The System Ammonia–Tetraborane without Solvent.—The proportion obtained for the direct reaction of tetraborane and ammonia without solvent was strongly dependent upon experimental conditions. The two cases differentiated by Stock were: (a) reaction systems containing an excess of ammonia and (b) those containing an excess of tetraborane.

(a) **Excess Ammonia Present.**—A measured amount of B_4H_{10} was condensed with liquid nitrogen at the bottom of a reaction tube and a measured amount of ammonia condensed in a ring above it. The system was allowed to warm slowly to the reaction temperature. Data for a typical run are plotted in Fig. 3 and several runs under different conditions are summarized in Table III. Examination of runs 1 and 3 indicates that the formula approached by the resulting residue is strongly dependent upon the aging period provided at −78° and upon the temperature of the sample during removal of excess ammonia. The marked time dependence strongly suggests that the reaction mixture had not reached its equilibrium condition.

(b) **Excess Tetraborane Present.**—The reactants were frozen together as indicated previously. Excess B_4H_{10} was distilled from the mass. Typical data are shown in Table IV. In run 2 a small amount of solid, stable at room temperature, apppeared on the wall of the tube above the decomposing residue. The X-ray powder pattern of the solid was that of $B_4H_{10}\cdot 2NH_3$.

TABLE IV

THE ADDITION OF EXCESS B_4H_{10} TO AMMONIA

NH_3 (mmole)	B_4H_{10} (mmole)	Temp., (°C.)	Time at temp. listed (min.)	Ratio NH_3/B_4H_{10}	Remarks
1.62	5.53	−196 to			
		−126	20		Unstable at room temp.
		− 95	30	2.25	
		− 78	90		
2.46	8.37	−196 to			Mostly unstable at room temp. but some $B_4H_{10}\cdot 2NH_3$ isolated
		− 95	20 min.		
		− 78	30 min.	1.8	
		− 35	150 min.		

[CONTRIBUTION FROM RESEARCH AND ENGINEERING DIVISION, MONSANTO CHEMICAL CO., DAYTON, OHIO]

π-Complexes of the Transition Metals. XIII. Acetylenic Condensations on Nickel(II) and Chromium(II)[1]

BY M. TSUTSUI AND H. ZEISS

RECEIVED JUNE 29, 1960

The formation of dimesitylnickel(II) by the addition of mesitylmagnesium bromide to nickel(II) bromide in tetrahydrofuran is deduced from its reactions with diphenyl- and dimethylacetylene and the analogous formation and reactions of dimesitylchromium(II). The possibility of the existence of a π-complexed cyclobutadiene intermediate in the reaction between dimesitylnickel and tolane is considered and discussed within the framework of the cyclobutadiene problem.

The origin of the π-bis-arene concept in 1954 and the specific examples of the Hein compounds having two aromatic rings bound to chromium by π-bonds led to an extension of our structural proposals to nickel and its eight π-electron requirement for a stable krypton configuration.[2] On this basis the prediction of the eventual capture of cyclobutadiene in the form of a complex, such as biscyclobutadiene-nickel(0) or the nickel cation, was made. Reppe's synthesis of cycloöctatetraene from acetylene on a nickel catalyst[3] together with the Longuet-Higgins and Orgel molecular orbital treatment of the matter[4] permitted an optimistic view of this problem.

The low temperature, cyclic condensation of 2-butyne on triphenylchromium(III), yielding hexamethylbenzene and 1,2,3,4-tetramethylnaphthalene

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[1] A portion of this paper was presented in Chicago, Sept., 1958; Abstracts, 134th Meeting, Am. Chem. Soc., p. 59-P. Paper XII, THIS JOURNAL, **81**, 6090 (1959).

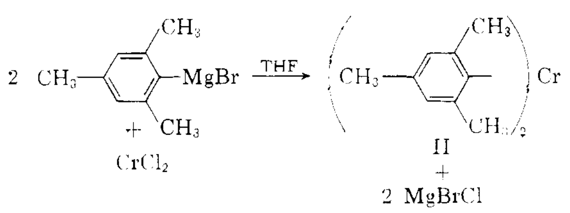
[2] H. Zeiss and M. Tsutsui, *ibid.*, **79**, 3062 (1957).

[3] See M. W. Bigelow and J. W. Copenhaver, "Acetylene and Carbon Monoxide Chemistry," Reinhold Publishing Co., New York, N. Y., 1949.

[4] H. C. Longuet-Higgins and L. E. Orgel, *J. Chem. Soc.*, 1969 (1956).

together with the formation of their π-complexes,[5] presented an interesting possibility for the preparation of tetramethylcyclobutadiene or at least the bis-tetramethylcyclobutadiene-nickel complex. Should the former substance prove too unstable for independent existence, as perhaps might be anticipated,[6] recourse could be had to diphenylacetylene (tolane) whose cyclic dimer, tetraphenylcyclobutadiene, should have higher thermal stability.

Prior to this attack on the cyclobutadiene problem we had found that, although triphenylchromium(III) was isolable in a tetrahydrofuran-coordinated form, diphenylchromium(II) collapsed even in tetrahydrofuran solution to π-complexes.[7] In contrast to triphenylchromium(III), trimesitylchromium(III) could not be rearranged to π-complex. Following this lead, dimesitylchromium(II) was prepared and isolated as a violet, crystalline compound admixed with magnesium salt. The stability of these mesityl-metal derivatives must be associated with the interference of the *ortho*-methyl groups in the aryl substituents bonded to chromium relative to the space required for internal oxidation–reduction rearrangement to the π-complexed structures.[7,8] These experimental observations provide support for the assignment of σ-bonding of aryl (and alkyl) groups to metal in these compounds, since small bond distances are needed to account for the space requirement during rearrangement of the aryl groups to the π-complexed structures.



The successful preparation and isolation of dimesitylchromium(II) from mesitylmagnesium bromide and chromium(II) chloride led then to the similar reaction of this Grignard reagent with nickel(II) chloride (or bromide). The yellow tetrahydrofuran solution of nickel(II) halide underwent a striking color change (a characteristic of these organometallic preparations) as mesitylmagnesium bromide was added, but the extreme solubility of the organonickel derivative in tetrahydrofuran precluded all attempts to isolate it. Dilution of the tetrahydrofuran solution with ether to induce precipitation or removal of the solvent tetrahydrofuran, for example, caused decomposition of the diarylnickel to bimesityl. However, its reactions with acetylenes provide evidence that dimesitylnickel(II) is a stable entity in tetrahydrofuran at temperatures below −10°.

In initial experiments with 2-butyne it was learned that, while dimesitylchromium(II) and also dimesityliron(II) were effective in cyclizing this acetylene to hexamethylbenzene and to its π-complex in yields of 70–80% and 20–30%, respectively, dimesitylnickel(II) produced only small amounts of this benzene together with large amounts of a major product which consisted of a nickel-containing amorphous material. Similiarly, when diphenylacetylene (tolane) was added to dimesitylnickel in tetrahydrofuran, meager yields of hexaphenylbenzene and a major amount of an orange, insoluble material having an approximate empirical formula $(C_6H_5C{\equiv}CC_6H_5)_4Ni$ were obtained. However, when the latter experiment was repeated with the order of addition reversed, that is, with mesitylmagnesium bromide being added to the mutually inert pair, nickel(II) bromide and tolane, the yield of hexaphenylbenzene rose steeply and no polymeric product was formed. An increase in the reacting ratio of tolane to nickel from 4:1 in these experiments caused corresponding increases in the hexaphenylbenzene from 11 to 85% at 8:1.[9] A greater ratio of 12:1 led to a small decrease in the yield of the benzene derivative (75%) and the reappearance of nickel polymer.

Our interpretation of this stoichiometric effect on product and product yield in these reactions between organonickel and tolane reinvokes the concept of an intermediate cyclobutadiene–nickel complex.[5] In the absence of excess tolane this expectedly reactive intermediate may condense in the Diels–Alder sense to form a nickel–tolane polymer which precipitates as reaction proceeds. Unfortunately, the extreme insolubility of this material did not permit a molecular weight determination and, although the nickel component of this material could be removed with hydrochloric acid, the organic residue remained intractable.

However, if tolane is present in excess of the four moles required to form the nickel complex, the Diels–Alder process between intermediate and tolane may lead to the theoretical yield of two moles of hexaphenylbenzene. The experimental limit of 1.7 moles obtained is in agreement with this value.

Inasmuch as arene complexes of nickel are not known and are not synthesized even under the very mild conditions used in this work, it is unlikely that hexaphenylbenzene is formed by way of an arene-nickel intermediate. However, bis-cyclopentadiene-nickel(0) has been prepared from cyclopentadiene and tetracarbonylnickel and is a stable, isolable substance,[10] as present knowledge of the metal complexes would require.

Dimesitylchromium(II) readily condensed 2-butyne to hexamethylbenzene and its π-complex as mentioned above without any insoluble metal-organic material precipitating. Its reaction with tolane gave hexaphenylbenzene, some stilbene, an unidentified, crystalline hydrocarbon, m.p. 253–255°, but no insoluble organometallic product.

The atomic number of nickel (28) seemed, as stated at the outset, to have given this element a

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[5] H. Zeiss and W. Herwig, THIS JOURNAL, **80**, 2913 (1958); W. Herwig, W. Metlesics and H. Zeiss, *ibid.*, **81**, 6203 (1959).

[6] See J. D. Roberts, A. Streitwieser and C. M. Regan, *ibid.*, **74**, 4579 (1952).

[7] M. Tsutsui and H. Zeiss, *ibid.*, **81**, 1367 (1959).

[8] W. Herwig and H. Zeiss, *ibid.*, **81**, 4798 (1959).

[9] These percentage yields are calculated on the basis of the ability of one atom of nickel (or one mole of dimesitylnickel) to form two moles of hexaphenylbenzene from six moles of tolane—see next paragraph.

[10] E. O. Fischer and H. Werner, *Chem. Ber.*, **92**, 1423 (1959).

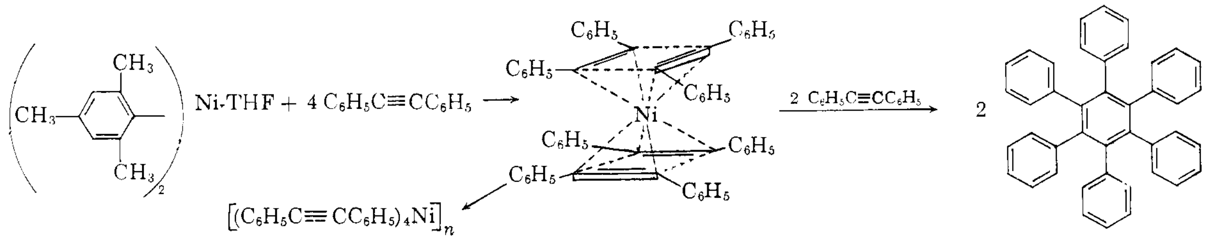

Fig. 1.

particular advantage over the other transition metals in serving as the metal nucleus for trapping the ephemeral cyclobutadiene. Concurrent work has involved this approach. But, in spite of what has appeared to be a promising lead, there is still no proof available of the *independent* existence of this four-membered "aromatic" ring.

Criegee and Schröder[11] describe a nickel(II) complex of tetramethylcyclobutadiene which they obtained by reduction of 1,2-dichloro-1,2,3,4-tetramethylcyclo-3-butene with tetracarbonylnickel. However, attempts to free the cyclobutadiene derivative by removal of nickel resulted in a dimer, octamethylcycloöctatetraene and a more complicated ring system. Nenitzescu and his co-workers[12] have claimed the capture of cyclobutadiene itself in the form of a silver nitrate complex. Confirmatory evidence, however, is not yet available. A palladium dichloride complex of tetraphenylcyclobutadiene is now also reported.[13]

It is well to remember in considering the organometallic approach to the cyclobutadiene problem that even though metal complexes of cyclobutadiene derivatives are available, the chemistry of cyclobutadiene or more sensibly substituted cyclobutadienes still remains obscure. In fact, the stability and reactions of these metal complexes now constitute a separate problem.

Experimental[14]

Preparation of Dimesitylchromium(II).—A 0.10 molar solution of mesitylmagnesium bromide in tetrahydrofuran (40 ml., 0.04 mole) was stirred magnetically under nitrogen in a Schlenk tube at −60° while 2.46 g. (0.02 mole) of anhydrous, powdered chromium(II) chloride was added in one portion. Reaction commenced at *ca.* −50°, the solution color becoming pink. After 2 hr. at −20° the reaction mixture had become violet in color and quite clear. Recooling to −80° produced a precipitation of white crystalline magnesium halide which was removed by filtration under nitrogen. The filtrate was now diluted with 100 ml. of ether and then recooled to −80°. These steps produced the precipitation of the violet crystalline dimesitylchromium compound admixed with magnesium salt which was collected on a filter and washed with 100 ml. of cold ether.

A sample of the solid dimesitylchromium admixed with magnesium salt was cleaved quantitatively with mercuric chloride in THF solution, as previously described for triphenylchromium(III),[8] to give 0.7351 g. (0.0020 mole) of mesitylmercuric chloride, m.p. 200–202°. Titration of the chromium ion remaining in solution gave a value of 0.06725 g. (0.0013 atom), or a ratio of 1 g. atom of chromium to 2 g. moles of mesitylmercuric chloride.

Preparation of Dimesitylnickel(II).—To 1.3 g. (0.01 mole) of nickel(II) chloride, stirred and cooled to −20° under nitrogen in 30 ml. of tetrahydrofuran (THF), 23 ml. (0.02 mole) of a 0.92 molar solution of mesitylmagnesium bromide in THF was added dropwise. Between −15 and −10° reaction commenced and the mixture turned to a red-brown color. After 4 hr. at −10° reaction was complete. On cooling the solution to −80° a precipitate of magnesium halide was obtained. On treating the solution with diethyl ether at this low temperature decomposition of the organonickel compound and precipitation of an amorphous, brown, unreactive solid resulted.

Reaction of Tolane and Dimesitylnickel. (a) **Mole Ratio of 8:1.**—A mixture of 7.12 g. (0.04 mole) of tolane and 1.08 g. (0.005 mole) of nickel(II) bromide in a Schlenk tube with 50 ml. of THF was cooled under nitrogen to −20° and then treated dropwise with 10.1 ml. of a 0.92 molar solution of mesitylmagnesium bromide in THF. At −13° the mixture began to show the characteristic reddish-brown color which persisted after 4 hr. at −10° and 2 hr. at 0°. During a stirring period of 4 days at room temperature this color gradually changed to brown-black. Finally the mixture was warmed to 50° for 2 hr. and then freed of the THF *in vacuo*. The residue was treated with 150 ml. of ether and then hydrolyzed with 50 ml. of water. An additional 30 ml. of ether and 200 ml. of ether was added, and then the ether layer was washed twice with water and filtered to remove flocculent material. The dried ether–water insoluble residue now was extracted in a Soxhlet apparatus with benzene from which 4.5 g. of hexaphenylbenzene was recovered, leaving 0.4 g. of a green powder, presumably nickel(II) hydroxide. The benzene derivative was characterized by analysis and by mixed m.p. and infrared and ultraviolet comparisons with an authentic sample prepared from 2,3,4,5-tetraphenylcyclopentadienone and tolane.[15]

The ether layer was dried over sodium sulfate, filtered and freed of solvent. The residue, 3.5 g., was fractionated at 0.04 mm. between 100 and 170°, but only 50 mg. of crystalline material, m.p. 155–158°, could be isolated, identity unknown.

(b) **Mole Ratio of 4:1.**—A solution of dimesitylnickel was prepared by the reaction of 1.08 g. (0.005 mole) of nickel(II) bromide and 10.1 ml. of 0.92 molar (THF) mesitylmagnesium bromide in 30 ml. of THF as described above. Tolane, 3.56 g. (0.02 mole), now was added to the solution at −20°, the mixture stirred for 2 hr. at 0° and then for 2 days at room temperature. The mixture next was hydrolyzed as described in the preceding experiment, but only 0.50 g. of hexaphenylbenzene could be extracted from the ether-insoluble material. The extraction thimble contained 2.7 g. of a deep orange-colored residue which proved to be completely insoluble in all solvents tried. Although the infrared spectrum of this solid clearly showed the presence of phenyl groups, no other structural details could be ascertained. This extreme insolubility precluded all attempts at molecular weight determination and chemical identification.

Anal. Calcd. for $(C_6H_5C\equiv CC_6H_5)_4Ni$: C, 87.1; H, 5.3; Ni, 7.6. Found: C, 79.3; H, 5.2; Ni, 7.4.

The ether layer contained 1.7 g. of a material which could be fractionally sublimed at 0.4 mm. Fraction 1, 0.4 g., collected at 120°, was separated by fractional crystallization into unreacted tolane and bimesityl. Fraction 2, 0.20 g., collected at 140°, was recrystallized from ethanol to give 20 mg. of needles, m.p. 146–148°, resolidifying to rhombic crystals, m.p. 165–167°, identity unknown.

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[11] R. Criegee and G. Schröder, *Ann.*, **623**, 1 (1959).

[12] C. D. Nenitzescu, M. Avram and E. Marica, *Chem. Ber.*, **92**, 1088 (1959).

[13] L. Malatesta, G. Santarella, L. Vallerino and F. Zingales, *Angew. Chem.*, **72**, 34 (1960).

[14] Analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside 77, N. Y. Melting points were determined on a Kofler hot stage. General Electric lamp grade nitrogen was used throughout.

[15] W. Dilthey and G. Hurtig, *Ber.*, **67**, 2004 (1934).

Anal. Found: C, 93.13; H, 6.96.

Fraction 3, 0.40 g., collected at 180°, also was recrystallized from ethanol to give 30 mg. of rhombs, m.p. 168–170°. A pot residue of 0.70 g. was discarded.

(c) Mole Ratio of 2:1.—This reaction was carried out in exactly the same way as the preceding experiment except that the amount of tolane used was reduced to 1.78 g. (0.01 mole). No hexaphenylbenzene was isolated from the ether-insoluble fraction but 1.52 g. of the orange polymer was obtained. The infrared spectrum of this material was the same as that of the insoluble product found above. No crystalline products were found in the ether-soluble fraction.

Reaction of Tolane and Dimesitylchromium (8:1).—A solution of 0.02 mole of mesitylmagnesium bromide in THF was added under nitrogen to 1.23 g. (0.01 mole) of chromium(II) chloride and 14.24 g. (0.08 mole) of tolane suspended in 100 ml. of THF at − 60°. The reaction mixture was gradually raised to room temperature over a period of 8 hr. and then refluxed for 0.5 hr. It was then hydrolyzed with iced water, and the solid reaction product collected on a filter and extracted with ether. The insoluble fraction remaining on the filter consisted of 0.20 g. of hexaphenylbenzene and a green chromium salt. The ether extract contained an organic fraction which on sublimation yielded 0.01 g. of *trans*-stilbene, m.p. 115–120°. The residue from the sublimation was crystallized from ethyl acetate to give 30 mg. of crystalline substance, m.p. 253–255°, identity unknown.

When the above reaction was performed using only 3.56 g. of tolane (0.02 mole) or a mole ratio of 2:1, no hexaphenylbenzene was found on the filter and the ether soluble fraction gave 0.2 g. of stilbene and 0.1 g. of a crystalline hydrocarbon, m.p. 300–302°, unidentified.

Anal. Found: C, 93.45; H, 6.36; mol. wt., 287.

Reaction of 2-Butyne and Dimesitylnickel.—A mixture of 1.08 g. (0.005 mole) of nickel(II) bromide and 7.12 g. (0.15 mole) of 2-butyne in 50 ml. of THF at −20° was treated under nitrogen with 11.0 ml. (0.01 mole) of a 0.92 molar solution of mesitylmagnesium bromide in THF. The mixture was stirred for 4 hr. at − 10°, for 2 hr. at 0° and then allowed to stand for 2 days at room temperature. Since the color of the mixture was still a deep reddish-brown, a large excess of 2-butyne (17.12 g.) was added after the mixture had been cooled to − 20°. It now was allowed to warm to room temperature and then to 60° for 2 hr. Solvent and excess butyne were removed *in vacuo* and the residue covered with 150 ml. of ether before hydrolyzing it with 0.5 *N* sulfuric acid. An additional 300 ml. of ether and 200 ml. of water was added, the ether layer separated and washed thoroughly with water. An insoluble white amorphous material (2.83 g.) was left which contained nickel but no halogen and which was completely insoluble in organic solvents.

The ether layer contained 6.40 g. of a brown solid after evaporation of solvent. This material yielded 1.66 g. of the picrate of hexamethylbenzene, m.p. 165–170°, which melted undepressed with and gave the same infrared spectrum as an authentic sample, m.p. 166–171°.

Reaction of 2-Butyne and Dimesitylchromium.—A violet solution of 0.01 mole of dimesitylchromium in 100 ml. of THF at − 20° was treated under nitrogen with 5.4 g. (0.1 mole) of 2-butyne. The reaction mixture was gradually brought to room temperature and then put aside to stand overnight. It was freed of THF *in vacuo* at room temperature and the dark brown residue remaining was triturated with water and ether. Elimination of solvent from the ether layer gave 6.24 g. of oily material from which 1.12 g. of the picrate of hexamethylbenzene, m.p. 170–171°, was isolated. No ether-water insoluble residue was observed.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE PENNSYLVANIA STATE UNIVERSITY, UNIVERSITY PARK, PENNSYLVANIA]

Stability Relationships Among the Rare Earth Acetylacetonates

BY INGMAR GRENTHE AND W. CONARD FERNELIUS

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Step-wise stoichiometric formation constants have been determined for the reaction between acetylacetone and the rare earths including yttrium. The measurements have been made at a temperature of 30° in 0.1 *M* aqueous perchlorate. A plot of the logarithm of the first formation constant against the ionic potential shows a linear relation from La to Eu with a change of 0.15 in log K_1 between consecutive elements. After Gd the stability remains nearly constant with a total change in log K_1 from Tb to Lu of 0.2. This relation between the ionic potential and log *K* has been compared with the same relation for other rare-earth complexes.

Introduction

Previous investigators[1] have studied complex formation between the acetylacetonate ion and the lighter rare-earth ions from La to Eu. The purpose of the present investigation was to extend these measurements to include all the rare earths. Since the earlier measurements were made in a medium of low but varying ionic strength, they were repeated at a constant ionic strength 0.1 *M* in order to find out the magnitude of the medium effect.

Experimental

Perchlorates of the rare earths and yttrium were obtained by repeated digestion of the corresponding nitrates with perchloric acid. The nitrates (Lindsay Light and Chemical Company, West Chicago, Illinois) were all of analytical grade. Stock solutions of the different metal perchlorates were prepared by dissolving the corresponding perchlorates in water. Their stoichiometric concentrations in the case of La, Ce, Pr, Nd and Sm were determined by precipitation of the oxalates and subsequent ignition of these to the corresponding oxides. The remaining rare earths were analyzed by running a fixed volume of the perchlorate solutions through a hydrogen-saturated ion-exchanger and then titrating the released hydrogen ions with standard sodium hydroxide. The analysis of the first five elements was also checked using this method; the agreement between the two methods was better than 0.5%. Excess perchloric acid in the stock solutions was determined by measuring the hydrogen ion concentration electrometrically. The hydrogen ion concentration in all cases except Ce was found to be less than 1% of the total metal-ion concentration; that is, the hydrogen ion concentration was negligible. Acetylacetone (Eastman Kodak Company) was purified by distillation. The boiling point (136°) and density (0.975 g./ml.) of the distillate agreed with the values reported in the literature for acetylacetone.

Standard sodium hydroxide solution was prepared by dissolving a concentrated carbonate-free sodium hydroxide solution in boiled distilled water. The solution was standardized against potassium hydrogen phthalate. Experimentally, *p*H measurements were made using a Beckman Model G *p*H meter equipped with calomel and glass electrodes. The general procedure in the titration was as follows: 100 ml. of a solution with a metal ion concentration, C_M, of about 2 m*M*, an acetylacetone concentration of 9.65 m*M*, a perchloric acid concentration of 3.40 m*M*

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[1] R. M. Izatt, *et al.*, *J Phys. Chem.*, **59**, 170 (1955).