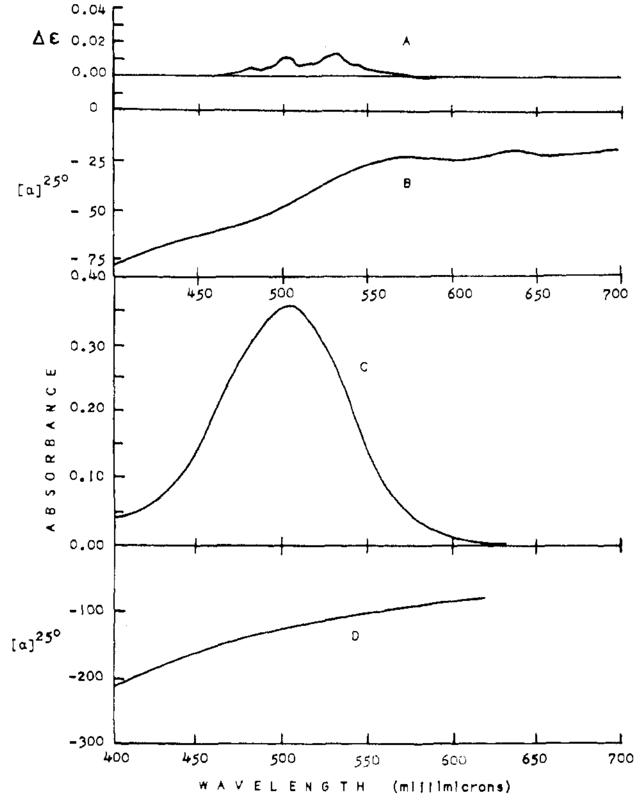

Figure 1.—A: circular dichroic absorption. B: optical rotatory dispersion of [Co(NH$_3$)$_5$(*l*-menac)](NO$_3$)$_2$ (I) in water at 25° (c = 0.12 g/100 ml, 10-cm cell). C: absorption spectrum of I in water at 25° (c = 0.24 g/100 ml, 1-cm cell). D: optical rotatory dispersion of sodium *l*-menthoxyacetate in 50% ethanol–water at 25° (c = 0.12 g/100 ml, 10-cm cell).

natopentaamminecobalt(III) nitrate, [Co(NH$_3$)$_5$CO$_3$]NO$_3$ (0.0036 mole), were added to the solution. The mixture was refluxed for 5 hr with stirring and was then cooled to room temperature. The product was filtered and washed with 50 ml of absolute ethanol (the washings were added to the filtrate). The product was then washed with diethyl ether and dried at 50°; yield 0.67 g (37%), sample 1. To the filtrate was added 3.0 g of ammonium nitrate and the mixture was refluxed with stirring for 1 hr, after which it was cooled and treated as above. Additional yield 0.48 g (27%), sample 2; over-all yield 64%. *Anal.* Calcd for [Co(NH$_3$)$_5$(*l*-C$_{12}$H$_{21}$O$_3$)](NO$_3$)$_2$: C, 29.94; H, 7.54; N, 20.37. Found, sample 1: C, 30.12; H, 7.76; N, 20.52; sample 2: C, 30.08, H, 7.76; N, 20.44. These two samples had identical spectral properties.

Microanalyses.—These were performed by the Alfred Bernhardt Microanalytical Laboratory, Mulheim, Germany.

Optical and Spectral Measurements.—The visible absorption spectrum of the complex was determined on a Cary Model 14 spectrophotometer (c = 0.24 g/100 ml of water) at 25°. The optical rotatory dispersion of the complex was determined on a Cary Model 60 spectropolarimeter (1-dm sample tube; c = 0.12 g/100 ml of water) at 25°. The optical circular dichroism was determined on a Jasco ORD–CD instrument (1-dm sample tube; c = 0.12 g/100 ml of water) at 25°. The ordinate of the curve for circular dichroism is $\Delta\epsilon$, the circular dichroic absorption,[10] and is equal to $\Delta D/cd$, where ΔD is the circular dichroic optical density ($D_l - D_r$), c is the concentration in moles/liter, and d is the path length in centimeters. Because the circular dichroic absorption ($\Delta\epsilon$) is relatively small, it was also determined on another instrument (Roussel–Jouan Dichrograph) with substantially identical results. The authors are not prepared at this time to interpret the various peaks in Figure 1A, the important aspect in this work being to demonstrate that the sample is circularly dichroic in this region. The optical rotatory dispersion of the complex was also determined on the Jasco instrument, and it gave exactly the same shape of curve as that obtained with the Cary instrument. The optical rotatory dispersion of the sodium salt of the ligand was determined at 25° on a Perkin-Elmer Model 141 photoelectric polarimeter (1-dm sample tube; c = 0.12 g/100 ml of 50% ethanol–water) using a Bausch and Lomb high-intensity monochromator in place of the filters which are normally used with this polarimeter.

Conclusions

It is now clear that it is possible for the Cotton effect to be induced and measured in the vicinity of the d–d transition absorption band of a complex containing an optically active ligand inside the coordination sphere, even if the ligand has no absorption in this region. Further, it is possible to measure the Cotton effect for some complexes of this type whether the ligand is monodentate or polydentate and whether the ligand has several asymmetric centers or only one. Consequently, the appearance of a Cotton effect under such circumstances may be utilized as an indication of the coordination of an optically active ligand as proposed earlier[5] although the nonappearance of such an effect cannot be considered confirmatory of noncoordination of such a ligand. The work of Mason,[7] mentioned earlier, indicates that additional work is necessary on the circular dichroism induced by outer-sphere coordination of optically active ligands, in order to determine the effects of concentration and other factors on the induction of Cotton effects in the d–d transition regions of optically inactive complex ions.

Acknowledgments.—The authors wish to express their sincere appreciation to the National Science Foundation for a research grant (GP-5399) which contributed significantly to the progress of this investigation, to Drs. Elsie Gulyas and Leonard Katzin of the Argonne National Laboratory for their assistance and for the use of the Jasco ORD–CD instrument, to Professor Bodie Douglas of the University of Pittsburgh for his assistance and that of his students and for the use of the Roussel–Jouan Dichrograph, to Mr. G. Kincaid of the Applied Physics Corp. for his assistance and for the use of the Cary spectropolarimeter, and to Mr. Kenneth Magnell of Wayne State University for his help with sample and curve preparation.

[10] L. Velluz, "Optical Circular Dichroism," Academic Press Inc., New York, N. Y., 1965, p 73.

CONTRIBUTION FROM THE ETHYL CORPORATION,
BATON ROUGE, LOUISIANA

The Direct Synthesis of Na$_3$AlH$_6$

BY E. C. ASHBY[1a] AND P. KOBETZ[1b]

Received February 21, 1966

Recently, Zakharkin and Gavrilenko reported the preparation of Na$_3$AlH$_6$ by the reaction of NaH and NaAlH$_4$ at 160° in heptane.[2] Due to the insolubility

---

[1] (a) Sloan Fellow, 1965–1967. (b) Requests for reprints should be addressed to this author.

[2] L. I. Zakharkin and V. V. Gavrilenko, *Dokl. Akad. Nauk SSSR*, **145**, 145, 793 (1962).

of the product in all solvents tested, it could not be

$$2NaH + NaAlH_4 \longrightarrow Na_3AlH_6 \qquad (1)$$

purified. Proof for the formation of Na_3AlH_6 was based on two observations: (1) extraction of the product with tetrahydrofuran did not result in the extraction of $NaAlH_4$, and (2) reaction of the product with diisobutylaluminum hydride resulted in the formation of $NaAlH_4$ and sodium diisobutylaluminum hydride according to the equation

$$Na_3AlH_6 + 2(i\text{-}C_4H_9)_2AlH \longrightarrow NaAlH_4 + 2NaAl(i\text{-}C_4H_9)_2H_2 \qquad (2)$$

More recently Ehrlich and co-workers[3] reported the preparation of Li_3AlH_6 by the reaction of $LiAlH_4$ and *n*-butyllithium. The existence of this compound appears to be well authenticated by both infrared and X-ray diffraction data. The preparation of Li_3AlH_6 by this method requires a large excess of $LiAlH_4$ and is somewhat plagued by the appearance of butyl groups in the product. We are prompted by the work of both Zakharkin[2] and Ehrlich[3] to report a convenient and high-yield method for the preparation of Na_3AlH_6 in approximately 95% purity.

Discussion

Since our original disclosure of the direct synthesis of $NaAlH_4$,[4] we have continued to investigate the Al–H_2 system as a route to simple and complex metal hydrides.[5] Subsequent studies on the effect of reaction parameters on the rate of formation of $NaAlH_4$ from Na, Al, and H_2 show that a plot of hydrogen pressure *vs.* time reveals at least two inflection points in the curve, indicating a change in reaction rate. In order to pursue this observation further, we examined the reaction products obtained when the reaction is stopped short of completion. Particularly we have found that by allowing the reaction to proceed to about 80% completion (based on hydrogen uptake) the major product obtained exhibits an X-ray powder diffraction pattern different from those of NaH, Al, or $NaAlH_4$. Only a small amount of $NaAlH_4$ is obtained under these conditions, as demonstrated by extraction with Dimethyl Carbitol.

This same compound was prepared directly in 98% yield by the reaction of sodium and aluminum in 3:1 ratio in toluene at 165° and 5000 psi hydrogen pressure. The product was insoluble in Dimethyl Carbitol ($NaAlH_4$ is very soluble), decomposed at 260–280° ($NaAlH_4$ decomposes rapidly at 185°), exhibited an X-ray powder diffraction pattern which was completely different from those of NaH, Al, and $NaAlH_4$ and which was similar to that of cryolite (Na_3AlF_6), and by elemental analyses showed a Na:Al:H ratio of 3:1:6. The product is thus shown to be Na_3AlH_6 prepared according to eq 3.

$$3Na + Al + 3H_2 \longrightarrow Na_3AlH_6 \qquad (3)$$

In addition, Na_3AlH_6 can be made to react further with aluminum and hydrogen, under conditions comparable to its preparation, to produce $NaAlH_4$.

$$Na_3AlH_6 + 2Al + 3H_2 \longrightarrow 3NaAlH_4 \qquad (4)$$

Decomposition of $MAlH_4$ compounds was thought for a long time[6] to proceed according to eq 5 until Garner and Haycock[7] studied the decomposition of

$$MAlH_4 \longrightarrow MH + Al + {}^3/_2H_2 \qquad (5)$$

$LiAlH_4$ and $LiBH_4$ in more detail. They concluded from decomposition studies that $MAlH_2$ is formed, since a plot of hydrogen evolution *vs.* time at 100° leveled off at 50% total hydrogen evolution. It is clear now that these results can also be explained by a decomposition according to eq 6.

$$3NaAlH_4 \longrightarrow Na_3AlH_6 + 2Al + 3H_2 \qquad (6)$$

We have found that indeed Na_3AlH_6 is produced by the controlled thermal decomposition of $NaAlH_4$. Thus by heating $NaAlH_4$ under a nitrogen atmosphere at 220° for 3 hr a solid residue was obtained whose X-ray pattern was identical with that of Na_3AlH_6 in admixture with aluminum metal.

Unlike $NaAlH_4$, the hexahydride is insoluble in Dimethyl Carbitol and tetrahydrofuran as well as other common organic solvents. It is decomposed by water and alcohols with vigorous evolution of hydrogen.

Experimental Section

Preparation of Na_3AlH_6.—Sodium (21.0 g, 0.91 g-atom), activated aluminum powder (8.0 g, 0.30 g-atom), triethylaluminum (2.0 ml, 0.014 mole), and toluene (100 ml) were heated at 165° and 5000 psi of H_2 for 10 hr, at which time the hydrogen uptake appeared to level off. The solids were removed from the toluene by filtration and extracted with five 50-ml portions of Dimethyl Carbitol to extract any $NaAlH_4$ present. The residue was dried under vacuum. The product weight was reduced by 0.004 g from its original 30.06 g.

X-Ray Powder Data.—A Norelco Philips X-ray instrument with a copper source, a nickel filter, and a 114.6-cm camera was used to obtain the X-ray data. The intensities were visually estimated.

X-Ray analyses showed the solid material to be similar to Na_3AlF_6 and to contain traces of Al and NaH. The results are shown in Table I.

Anal. Calcd for Na_3AlH_6: Al, 26.45; Na, 67.65; H, 5.88. Found: Al, 24.7; Na, 64.3; H, 5.55; Al:Na:H, 1.00:2.98:5.90.

Preparation of $NaAlH_4$.—Sodium aluminum hexahydride (12 g, 0.12 mole), activated aluminum powder (6.3 g, 0.234 g-atom), triethylaluminum (0.6 ml, 0.004 mole), and 125 ml of toluene were heated at 160–165° and 5000 psi of H_2. Approximately 4 hr was required to initiate the reaction. Hydrogen uptake was slow. At the end of 8 hr approximately 80% of the theoretical amount of H_2 was taken up. X-Ray analyses showed $NaAlH_4$ to be the major component.

A 3-g sample of the reaction solids was extracted with 50 ml of Dimethyl Carbitol. All but 0.4 g was solubilized in the Dimethyl Carbitol.

Decomposition of $NaAlH_4$.—Sodium aluminum hydride (5 g, 0.093 mole) was heated in a flask under nitrogen at 210–220° for 3 hr. Hydrogen was evolved during the heating period. X-Ray analyses of the residue established the product to be a mixture of Na_3AlH_6 and Al.

---

(3) R. Ehrlich, A. R. Young, G. Rice, J. Dvorak, P. Shapiro, H. F. Smith, and S. I. Morrow, presented before the Second International Symposium on Organometallic Chemistry, Madison, Wis., Aug 31, 1965.

(4) E. C. Ashby, French Patent 1,235,689 (1960).

(5) (a) E. C. Ashby, *J. Am. Chem. Soc.*, **86**, 1882 (1964); (b) E. C. Ashby and W. E. Foster, *ibid.*, **84**, 3407 (1962).

(6) T. R. P. Gibb, Jr., *J. Chem. Educ.*, **25**, 577 (1948).

(7) W. E. Garner and E. W. Haycock, *Proc. Roy. Soc.* (London), **A211**, 335 (1952).

TABLE I
X-RAY POWDER DATA

Na_3AlH_6		Na_3AlF_6	
d value	Rel intensity	*d* value	Rel intensity
11.2	w	. . .	. . .
8.7	w	. . .	. . .
7.8	vw	. . .	. . .
4.45	w	4.51	mw
3.83	w	3.88	mw
3.44	mw	3.49	vw
3.03	mw	3.33	vw
2.72	vs	2.75	s
2.58	w	. . .	. . .
2.42	m–mw	2.42	w
2.32	vvw	2.33	ms
	mw	2.22	vw
2.13	mw	2.15	m–mw
. . .	. . .	2.18	mw
1.93	s	1.94	vs
1.865	mw	1.89	w
1.72	mw	1.72	mw
1.68	mw	1.68	mw–w
1.58	s–ms	1.60	m
1.555	s–ms	1.57	ms
. . .	. . .	1.49	w–vw
1.46	vw	1.454	vw
1.435	vw	1.425	vw
. . .	. . .	1.388	vvw
1.362	m	1.375	w
1.340	w	1.350	w
1.220	m	1.229	w

[a] w, weak; v, very; m, medium; s, strong.

Acknowledgments.—The authors are grateful to Mr. Julius Chidester and Dr. L. N. Niebylski for the X-ray analyses and to Mr. R. A. Ashby for the chemical analyses.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
MARSHALL UNIVERSITY, HUNTINGTON, WEST VIRGINIA

Kinetics of Exchange of Iron(II) and Iron(III) 8-Quinolinol Complexes[1,2]

BY M. R. CHAKRABARTY, J. F. STEPHENS, AND E. S. HANRAHAN

Received March 1, 1966

The electron exchange reactions between Fe(II) and Fe(III) have received considerable attention from many investigators.[3] Although a considerable amount of reliable data is available for the Fe(II)–Fe(III) system where the latter is complexed with various 1,10-phenanthrolines,[4,5] reactions involving other complicated organic ligands coordinated to Fe(III) have not been extensively studied. The stability constants of the 1:1 and 1:2 Fe(III) complexes of 8-quinolinol have been measured at 25° and an ionic strength of 0.5 *M*.[6] It was, therefore, decided to study the influence of 8-quinolinol as a ligand on the rate of the electron exchange between Fe(II) and Fe(III).

Experimental Section

Reagents.—Fe^{59} was obtained from the Abbott Laboratories, and Fe^{55} was supplied by the Nuclear Science and Engineering Co. Both of the tracer solutions were received as ferric chloride dissolved in hydrochloric acid and were converted to ferric perchlorate by evaporating to dryness with perchloric acid. Hydrogen peroxide (30%) was added to the tracer solutions before evaporation in order to convert any Fe(II) to Fe(III). None of the tracer solutions showed any positive tests of the probable impurities, such as Co and Mn. Inactive ferric perchlorate and ferrous perchlorate were obtained from the G. F. Smith Chemical Co. and were recrystallized twice from 8 *F* perchloric acid.

Iron(II) was determined by titrating the original solution with the standard ceric sulfate solution. Iron(III) in the stock solutions was determined by reducing it in a Jones reductor and titrating it with a standard ceric sulfate solution. The analytical concentrations of perchloric acid in Fe(II) and Fe(III) stock solutions were determined by passing aliquots of the iron solutions through a column of Dowex 50 cation-exchange resin and titrating the resulting metal ion free acid solutions with a standard sodium hydroxide solution. Knowing the concentrations of Fe(III) and Fe(II) in these solutions, the concentrations of perchloric acid were calculated.

Sodium perchlorate solutions were prepared by neutralizing Baker and Adamson reagent grade sodium carbonate with Baker Analyzed Reagent perchloric acid.

8-Quinolinol (mp 73–74°) was supplied by Eastman Organic Chemicals Co.

All of the solutions were made by using freshly boiled, double-distilled, deionized water and were kept under a nitrogen atmosphere.

The hydrogen ion concentrations were measured by using a Leeds and Northrup No. 7405 pH meter, which was standardized against a potassium acid phthalate buffer. The meter was then calibrated by titrating a 0.5 *M* sodium perchlorate solution with a standard perchloric acid solution (ionic strength 0.5 *M*).

Electron-Exchange Measurements.—An exchange apparatus similar to that described by Sheppard and Wahl[7] was used. The electronic timers employed in this study have been described in a previous paper.[8] The reaction mixtures were quenched with bipyridine obtained from Matheson Coleman and Bell Chemical Co. Iron(III) was precipitated from the quenched solutions by adding a saturated solution of 8-quinolinol. The specific activity of the precipitate was determined by using a Baird Atomic X-ray counter tube for Fe^{55} and a Picker scintillation counter for Fe^{59}. A Picker solid-state scaler was used in all the measurements.

Results and Discussion

The rate, *R*, of the electron-exchange reaction was calculated using the McKay equation. Figure 1 shows representative plots of log $[(y_0 - y_\infty)/y - y_\infty)]$ *vs.* *t*, where y_0, y, and y_∞ are the specific activities of the initially active species at zero time, at time *t*, and at infinite time, respectively. Using the following relationship, the apparent second-order rate constant *k* was calculated

$$R = kab \qquad (1)$$

where *a* and *b* are the analytical concentrations of ferrous and ferric iron, respectively.

---

[1] Presented at the Southeast–Southwest Regional Meeting of the American Chemical Society, Memphis, Tenn., Dec 1965.

[2] Taken in part from the M.S. Thesis of J. F. Stephens, Marshall University, Huntington, W. Va., 1965.

[3] For a review of this topic see: (a) N. Sutin, *Ann. Rev. Nucl. Sci.*, **12**, 285 (1962); (b) J. Halpern, *Quart. Rev.* (London), **15**, 207 (1961); (c) B. J. Zwolinski, R. J. Marcus, and H. Eyring, *Chem. Rev.*, **55**, 157 (1955); (d) H. Strehlow, *Ann. Rev. Phys. Chem.*, **16**, 167 (1965).

[4] N. Sutin and B. M. Gordon, *J. Am. Chem. Soc.*, **83**, 70 (1961).

[5] M. H. Ford-Smith and N. Sutin, *ibid.*, **83**, 1830 (1961).

[6] M. R. Chakrabarty, Ph.D. Thesis, University of Toronto, Toronto, Canada, 1962.

[7] J. C. Sheppard and A. C. Wahl, *J. Am. Chem. Soc.*, **79**, 1020 (1957).

[8] J. F. Stephens and M. R. Chakrabarty, *J. Chem. Educ.*, **42**, 562 (1965)