The determination of the heat capacity of the calorimeter containing 1500 ml. of 2 *N* hydrochloric acid was carried out at 25°. A potential of 14 volts was used for the solution heater circuit. The current passing into the heater was determined by the potential drop across a standardized one ohm resistance while the potential across the heater was measured by means of a shunt box. All measurements were made with a typical potentiometer circuit.

In the determination of the heat capacity, corrections for heat of stirring and heat losses were made by observing temperature changes over a long period of time before and after heat had been added to the solution. The temperature readings were plotted *versus* time; the resulting curves were extrapolated to obtain the corrected temperature. The determination of the heat capacity was made when the calorimeter contained 2 *N* hydrochloric acid alone and additional runs were made when the pyridinated complexes had been previously dissolved in the acid. The change in concentration when salt was added was so small that no measurable change in heat capacity was observed, nor did the added salt affect the heat of stirring.

Following the above procedure the heats of reaction of the simple salts, the pyridine and the pyridinated compounds with 2 *N* hydrochloric acid were determined, at 25°.

Results and Discussion

The results of our experimental work are summarized in Table I.

The heats of formation obtained show conclusively that the negative ion has considerably greater effect upon the heat of formation of the complex than does the metal. The simple interpretation of the data obtained previously[5] in regard to dissociation pressures and volume changes seems to be inadequate in light of the values reported here. The fact that the thiocyanates coordinating with four pyridines have higher heats of formation and lower volume changes than do the cyanates complexed with six pyridines seems anomalous. The need is indicated to obtain information concerning the crystal structures of the complexes. This work is in progress at the present time.

TABLE I

Substance	Metal,[a] % Calcd.	Found	Heat of solution, cal./mole[b] at 25°	Heat of formation, cal./mole at 25°
Pyridine	...	...	−7,860 (±25)	......
$Co(CNS)_2$	33.66	33.63	−340 (±10)	......
$Co(CNO)_2$	41.26	40.87	−34,900 (±100)	......
$Ni(CNS)_2$	33.59	33.50	1,140 (±10)	......
$Ni(CNO)_2$	41.13	41.70	−32,070 (±10)	......
$Co(CNS)_2 \cdot 4Py$	12.00	11.96	5,870 (±60)	−37,700
$Co(CNO)_2 \cdot 6Py$	9.55	9.52	−59,800 (±100)	−22,300
$Ni(CNS)_2 \cdot 4Py$	11.97	12.00	7,940 (±100)	−38,300
$Ni(CNO)_2 \cdot 6Py$	9.52	9.58	−60,700 (±200)	−18,500

[a] Nickel was determined by cyanide–silver titration; cobalt gravimetrically as the sulfate. [b] Averages obtained from 2 to 6 determinations on each compound.

CORVALLIS, OREGON

[CONTRIBUTION NO. 193 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE][1]

Thermochemistry of the Rare Earths. I. Cerium and Neodymium

BY F. H. SPEDDING AND CARL F. MILLER

RECEIVED DECEMBER 26, 1951

The heats of solution of the metals and chlorides in hydrochloric acid, the hydrated chlorides in water, and the heats of precipitation of the oxalates in oxalic acid of cerium and neodymium have been measured. The data have permitted a calculation of the standard heats of formations of these substances as well as an estimate of their free energies of formation. The electrode potentials have been calculated to be 2.335 volts for cerium metal and 2.246 volts for neodymium metal.

Introduction

Previous investigations on the thermal properties of rare earth solutions[2] have been extended, by means of calorimetric measurements, to include the basic thermal properties of a number of compounds of cerium and neodymium. In order to obtain precise calorimetric data, from which good values for the heats of formation and other thermodynamic properties of these compounds could be calculated, considerable care was exercised to maintain well-defined initial and final calorimetric systems. The present paper describes the experimental data from such systems and the thermodynamic properties derived therefrom. In addition, the heats of solution and dilution of oxalic acid hydrate, as well as a recalculation of its heat of formation, is presented.

Experimental

Preparation of Materials.—The purity and methods of preparation of the anhydrous chlorides of cerium and neodymium have been described.[3] The metals of cerium and neodymium were prepared by methods described by Spedding, *et al.*[4] The metals were cast in vacuum into large cylindrical billets which were then turned down on a lathe under oil. Fine turnings from the billets were washed free from oil with benzene and loaded into sample bulbs while submerged in the benzene. After the excess solvent was drained off, the bulb was evacuated and refilled with purified argon to nearly atmospheric pressure. The bulb was then sealed. Samples prepared in this manner retained their luster indefinitely. Both the cerium and neodymium metals were found, by spectrographic analysis, to be free of other rare earths and all common elements. The hydrated crystals of the chlorides were grown over a period of 14 months from solutions of the chlorides in 2–3 *N* hydrochloric acid. The crystal masses, in this period of time, grew to a height of about one inch in a 400-ml. beaker. The crystals were rinsed with a small amount of water several times and then with alcohol. After being crushed, they were stored in a dry-box. The *p*H values of solutions of the crystals, as measured with a Beckman model *p*H meter were from 6.3 to 6.6 (identical values were observed for solutions of the anhydrous chlorides) indicating that the crystals contained no hydrochloric acid. The solid crystals and their resulting solutions were both analyzed for composition by accepted gravimetric methods. Analytical grade oxalic acid was used; it was twice recrystallized from conductance water. The crystals were first air-dried and then placed in a dry-

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(1) Work was performed in the Ames Laboratory of the A.E.C.

(2) F. H. Spedding and Carl F. Miller, THIS JOURNAL, 74, 3158 (1952).

(3) F. H. Spedding, P. Porter and J. Wright, *ibid.*, 74, 2055 (1952).

(4) F. H. Spedding, H. A. Wilhelm, W. H. Keller, D. H. Ahmann, A. H. Daane, C. C. Hach and R. P. Ericson, *Ind. Eng. Chem.*, 44, 553 (1952).

box through which a slow stream of dry nitrogen was passed. The final solutions from all the experiments in which oxalic acid was used were analyzed for residual oxalate volumetrically. All were found to contain, within limits of experimental error, the calculated amount of oxalic acid.

The calorimetric apparatus has been described.[2] The only change in the calorimeter, when single-sample experiments were made, was the utilization of a glass tube with a tantalum foil basket fastened to one end with tantalum wire for holding the sample bulbs. The glass tube was fitted just to clear the inside of the hollow monel stirrer shaft. A blunt glass rod held up by a compression spring inside the glass tube served as a sample breaker.

Results

I. The Heats of Formation of the Anhydrous Chlorides of Cerium and Neodymium.—In order to determine the heats of formation of the chlorides by the use of the heat of solution calorimeter, the heat of reaction of the following reactions must be known or measured

$$\mathrm{Ce(s) + HCl(aq,}\ m_b\mathrm{) = 3/2H_2(g) + CeCl_3(aq,}\ m\mathrm{)\cdot HCl(aq,}\ m_f\mathrm{)} \qquad \mathrm{(I)}$$

$$\mathrm{CeCl_3(aq,}\ m\mathrm{)\cdot HCl(aq,}\ m_f\mathrm{) = HCl(aq,}\ m_f\mathrm{) + CeCl_3(s)} \qquad \mathrm{(II)}$$

$$\mathrm{3HCl(g) + HCl(aq,}\ m_f\mathrm{) = HCl(aq,}\ m_b\mathrm{)} \qquad \mathrm{(III)}$$

$$\mathrm{3/2\ H_2(g) + 3/2\ Cl_2(g) = 3HCl(g)} \qquad \mathrm{(IV)}$$

The sum of these reactions is

$$\mathrm{Ce(s) + 3/2\ Cl_2(g) = CeCl_3(s)} \qquad \mathrm{(V)}$$

Therefore, the sum of the changes in heat content for the four reactions is the heat of formation of cerium chloride. The heat of Reaction (I) has been measured by Sieverts and Gotta,[5] Neumann, Kroger and Kunz,[6] Biltz and Peiper[7] and by Bommer and Hohmann.[8] The last named investigators also measured the same reaction for neodymium. The values reported for cerium vary from −166.4 to −173.7 kcal./mole. The latter value, from Bommer and Hohmann, appears somewhat high, which was probably due to potassium inclusions and other impurities in their metals resulting in a rather obscure calorimetric reaction.

In the present work, the heats of reaction for Reactions (I) and (II) were determined in such a manner that the end concentrations for a given pair of reactions were very nearly the same. The data are given in Table I. The effect of hydrochloric acid on the heats of solution of the chlorides is to reduce the heats of solution to a greater amount than can be accounted for on the basis of ionic strength alone. In 0.2410 molal hydrochloric acid, the heats of solution of cerium chloride are reduced by about 850 cal./mole while those of neodymium chloride were reduced by about 1050 cal./mole. The thermal data for Reactions (III) and (IV) have been reported and reviewed by Rossini[9] and by Harned and Owen.[10] From the reported data and the results given in Table I, the standard heats of formation were found to be

TABLE I

HEATS OF SOLUTION OF CERIUM CHLORIDE, NEODYMIUM CHLORIDE, CERIUM AND NEODYMIUM IN HYDROCHLORIC ACID AT 25°

Material	$m^{1/2}$	$m_b^{1/2}$ (HCl)	$m_f^{1/2}$ (HCl)	$-\Delta C_p{}^a$	$-\Delta H$
$CeCl_3$	0.1327	0.6092	0.6091	238.3	32,261
	.1990	.6091	.6091	232.3	32,044
	.2475	.6091	.6091	227.9	31,892
	.1324	.4909	.4909	228.4	32,850
	.1505	.4909	.4909	226.8	32,663
$NdCl_3$	.1432	.4909	.4909	227.4	35,637
	.1885	.4909	.4909	223.4	35,433
Ce	.05280	.4964	.4879	143.4	167,155
	.06150	.4993	.4878	142.6	167,045
Nd	.06062	.5001	.4889	142.6	162,785
	.07315	.5069	.4907	141.5	162,385

[a] The ΔC_p values are smoothed. m_b and m_f are the initial and final hydrochloric acid concentrations.

$$\Delta H^0 = -252{,}840 \pm 20 \text{ cal./mole} \qquad (1)$$

for cerium chloride, and

$$\Delta H^0 = -245{,}615 \pm 20 \text{ cal./mole} \qquad (2)$$

for neodymium chloride.

II. The Heats of Formation of the Hydrated Chlorides of Cerium and Neodymium.—The heat of solution of cerium chloride hydrate ($CeCl_3\cdot 7H_2O$) has not been reported. Matignon[11] reported the heat of solution of neodymium hydrate ($NdCl_3\cdot 6H_2O$) to be −7.6 kcal./mole at 15°. The heats of solution and of hydration obtained in the present work are given in Table II. By the use of the value −68,313 cal./mole, for the heat of formation of water as given by Bichowsky and Rossini,[12] the standard heats of formation were calculated to be

$$\Delta H^0 = -758{,}460 \pm 25 \text{ cal./mole} \qquad (3)$$

for cerium chloride hydrate, and

$$\Delta H^0 = -683{,}580 \pm 45 \text{ cal./mole} \qquad (4)$$

for neodymium chloride hydrate.

TABLE II

THE HEATS OF SOLUTION AND HEATS OF HYDRATION OF THE HYDRATES OF CERIUM AND NEODYMIUM CHLORIDES AT 25°

Hydrate	$m^{1/2}$	$-\Delta C_p$	$-\Delta H$	$-H$ (hyd)
$CeCl_3\cdot 7H_2O$	0.09908	244.1	6370	27,452
	.2056	234.5	5934	27,405
			Average	27,428 ± 25
$NdCl_3\cdot 6H_2O$	.1659	236.9	8466	28,128
	.1435[a]	238.9	..	....
	.2490	229.4	8065	28,043
			Average	28,086 ± 45

[a] The second heat of solution was done with this initial concentration of neodymium chloride. The ΔC_p are smoothed values.

III. The Heats of Formation of the Ions of Cerium and Neodymium.—Combining the values for the heat of solution at infinite dilution for the two chlorides[2] and the heat of formation of the chloride ion,[9] the heat of formation of cerium ion is calculated as

$$\Delta H^0 = -167{,}430 \pm 20 \text{ cal./mole} \qquad (5)$$

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(5) A. Sieverts and A. Gotta, *Z. anorg. allgem. Chem.*, **172**, 1 (1929).

(6) B. Neumann, C. Kroger and H. Kunz, *ibid.*, **207**, 133 (1932).

(7) W. Biltz and H. Peiper, *ibid.*, **134**, 13 (1934).

(8) H. Bommer and E. Hohmann, *ibid.*, **248**, 357 (1941).

(9) F. D. Rossini, *J. Research Natl. Bur. Standards*, **9**, 679 (1932).

(10) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1950.

(11) C. A. Matignon, *Compt. rend.*, **133**, 289 (1901); **141**, 53 (1905).

(12) F. R. Bichowsky and F. D. Rossini, "Thermochemistry of Chemical Substances," Reinhold Publishing Corp., New York, N. Y., 1936.

and that for neodymium ion as

$$\Delta H^0 = -163{,}270 \pm 20 \text{ cal./mole} \qquad (6)$$

IV. The Heats of Formation and the Heats of Solution and Dilution of Oxalic Acid Hydrate.—

In order to determine the heat of formation of oxalic acid hydrate for use in subsequent calculations, the available information on anhydrous oxalic acid and the hydrated acid were correlated in the following manner. The heat of combustion of the anhydrous acid has been variously reported.[12] The Washburn correction[13] and heat capacity data[14] were applied to the data reported by Verkade, Hartman and Coops[15]; their value, when corrected to 25° under standard conditions, was found to be −59,690 ± 90 cal./mole. The heat of formation of the anhydrous acid was then calculated to be −197,030 cal./mole with respect to β-graphite.[12,16] Jorissen's[17] value for the heat of hydration of oxalic acid was calculated to be −6,360 cal./mole at 25°. Hence the heat of formation of the hydrated acid was found to be −340,020 cal./mole. The heat of combustion of the hydrated acid was reported by Jorissen and van de Stadt.[18] When their value was corrected to standard conditions at 25°, the heat of formation of the hydrated acid was found to be −340,000 cal./mole. The value −340,020 cal./mole for the heat of formation of oxalic acid was used in all subsequent calculations.

The data on the heats of solution and dilution of oxalic acid hydrate at 25°, obtained in the present work are given in Table III and are plotted in Fig. 1. The data are represented by the equations

$$\Delta H = 8{,}701 + 1{,}873m - 5{,}070m^2 \qquad (7)$$

and

$$\Delta C_p = 16.5 + 258m \qquad (8)$$

TABLE III

THE HEATS OF SOLUTION AND DILUTION OF OXALIC ACID HYDRATE AT 25°

m	ΔC_p[a]	ϕc_p	ΔH	ϕL[a]
0	(16.5)	(62.1)	(8701)	0
0.010403	19.2	64.8	8715	18
.026191	23.2	68.8	8745	45
.005511	17.8	63.4	8738	10
.012160	19.6	65.2	8711	21
.020409	21.7	67.3	8752	35
.032330	24.3	69.9	8756	55
.076228	36.2	81.8	8814	113
.12360	48.4	94.0	8855	154

[a] The ΔC_p and the ϕ_L values are smoothed.

These data, on the thermal properties of solutions of a weak electrolyte, have no counterpart in physical chemistry solution theory beyond that of thermodynamic treatment. Hence no particular significance can be put on the above coefficients.

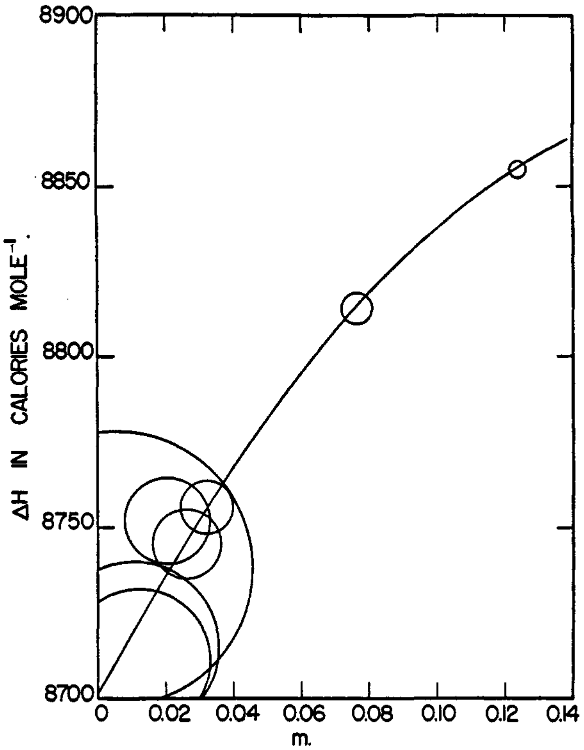

Fig. 1.—The heat of solution of oxalic acid dihydrate at 25°.

V. The Heats of Formation of the Hydrated Oxalates of Cerium and Neodymium.—

The heats of precipitation of the oxalates were measured in the calorimeter by dissolving the anhydrous chlorides in previously determined concentrations of oxalic acid so that the final oxalate concentrations would correspond to the oxalate concentrations which Crouthamel and Martin[19] give for the minimum solubility of the oxalates of cerium and neodymium. The experimental data obtained from the precipitation reactions are given in Table IV. By making corrections for the removal of the hydrochloric acid and the dilution of the oxalic acid, the heats of formation are calculated as

$$\Delta H^0 = -1{,}550{,}930 \pm 200 \text{ cal./mole} \qquad (9)$$

for $Ce_2(C_2O_4)_3 \cdot 9H_2O$, and as

$$\Delta H^0 = -1{,}611{,}620 \pm 150 \text{ cal./mole} \qquad (10)$$

for $Nd_2(C_2O_4)_3 \cdot 10H_2O$.

TABLE IV

THE HEATS OF PRECIPITATION OF THE OXALATES OF CERIUM AND NEODYMIUM AT 25°

m_b and m_f are the initial and final concentrations.

Compound	Mole	m_b (oxalic)	m_f (oxalic)	m_f (HCl)	$-\Delta C_p$	$-\Delta H$
$CeCl_3$	0.01212	0.03079	0.01264	0.03635	31.8	42,849
	.01409	.03376	.01264	.01264	38.4	42,885
$NdCl_3$	.01734	.03846	.01247	.05210	48.4	46,310
	.01928	.04155	.01264	.05795	53.7	46,298

The precision of the heat of precipitation reactions alone contributes only 10 calories to the above deviations. For the reaction

$$R_2(C_2O_4)_3 \cdot xH_2O(s) \rightleftarrows 2R^{+++} + 3C_2O_4^{=} + xH_2O(l) \qquad (VI)$$

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(13) E. W. Washburn, *J. Research Natl. Bur. Standards*, **10**, 525 (1933).

(14) L. L. Quill, "The Chemistry and Metallurgy of Miscellaneous Materials, Thermodynamics," McGraw-Hill Book Co., Inc., New York, N. Y., 1950.

(15) P. E. Verkade, H. Hartman and J. Coops, *Rec. trav. chim.*, **45**, 373 (1926).

(16) W. M. Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions," Prentice-Hall, Inc., New York, N. Y., 1938.

(17) W. J. Jorissen, *Z. physik. Chem.*, **74**, 308 (1910).

(18) W. J. Jorissen and van de Stadt, *J. prakt. Chem.*, **51**, 102 (1895).

(19) C. E. Crouthamel and D. S. Martin, Jr., THIS JOURNAL, **73**, 569 (1951).

Martin and Crouthamel[19] give $\Delta F^0 = 39,870$ cal./mole for cerium oxalate and $\Delta F^0 = 42,430$ cal./mole for neodymium oxalate. The combination of data gives $\Delta H^0 = 15,770$ cal./mole and $\Delta S^0 = -80.84$ e.u. for the solubility reaction of cerium oxalate, for neodymium oxalate $\Delta H^0 = 16,460$ cal./mole and $\Delta S^0 = -87.09$ e.u.

By the utilization of data presented by Latimer,[16,20] the entropies and entropies of formation of the solid compounds of cerium and neodymium have been calculated; these values permitted the evaluation of the entropies of the two ions. The results are given in Table V. From that information it is possible to calculate for

$$Ce(s) = Ce^{+++} + 3e^-, E^0 = 2.335 \quad (11)$$

and for

$$Nd(s) = Nd^{+++} + 3e^-, E^0 = 2.246 \quad (12)$$

Yost, Russell and Garner[21] estimate the E^0 values for cerium and neodymium to be 2.3 and 2.2 volts, respectively. The calculated standard electrode potentials are based on an empirical calculation of the entropies of the oxalates, these values would be subject to revision when more accurate determinations of the entropies are made. However, the $T\Delta S^0$ contribution to the standard free energy of the two rare earths ions is only about 4% of the value of the free energy so that it is possible that any revision would not change the values of E^0 appreciably.

TABLE V

THE FREE ENERGIES OF FORMATION; HEATS OF FORMATION; CALCULATED ENTROPIES; AND CALCULATED ENTROPIES OF FORMATION OF COMPOUNDS AND IONS OF CERIUM AND NEODYMIUM AT 25°

The values of $\Delta F°$ and $\Delta H°$ are in kcal./mole; $\Delta S°$ and $S°$ are in e.u.

Substance	ΔF^0	ΔH_0	ΔS^0	S^0
Ce	....	....	.....	13.8
Ne	....	....	.....	13.9
$CeCl_3$	−235.16	−252.84	−59.3	34.5
$NdCl_3$	−227.93	−245.61	−59.3	34.6
$CeCl_3 \cdot 7H_2O$	−644.26	−758.46	−383.0	101
$NdCl_3 \cdot 6H_2O$	−583.31	−683.58	−336.3	92
$Ce_2(C_2O_4)_3 \cdot 9H_2O$	−1349.08	−1550.93	−677	155
$Nd_2(C_2O_4)_3 \cdot 10H_2O$	−1396.05	−1661.62	−723	165
Ce^{+++}	−161.54	−167.43	−19.8	−52.8
Nd^{+++}	−155.40	−163.27	−26.4	−59.3

It might be added that the precipitation reactions in the calorimeter were very fast, clear-cut calorimetric processes. Shortly after the maximum temperature was reached, the temperature decreased for a few minutes before it settled to an equilibrium rating as determined previously from many calibrating runs. Hence, whether complete equilibrium had set in or not, the process was thermally complete as far as detection by the calorimetric apparatus was concerned. The slight cooling effect was attributed to the decrease of supersaturation and to orientation of the molecules in the crystals to an equilibrium state.

Acknowledgments.—The authors wish to thank Mr. J. P. Flynn for assistance in making the calorimetric observations, and Dr. C. V. Banks and Mr. A. S. Ayres for assistance in the analyses of many of the compounds and solutions.

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[20] W. M. Latimer, *ibid.*, **73**, 1480 (1951).

[21] D. M. Yost, H. Russell, and C. S. Garner, "The Rare-Earth Elements and Their Compounds," John Wiley and Sons, Inc., New York, 1947.

NOTES

Derivatives of Tetrahydroquinoline and Tetrahydroisoquinoline[1]

BY CARL TABB BAHNER, WILLIAM KENNETH EASLEY AND EMOGENE STEPHEN

RECEIVED MARCH 8, 1952

A previous paper[2] from this Laboratory has described the preparation of salts of substituted piperidines and pyrrolidines for use in the study of cancer chemotherapy. Derivatives of tetrahydroquinoline and tetrahydroisoquinoline have been prepared for comparison with the quaternary salts of quinoline and isoquinoline. 1,2,3,4-Tetrahydroquinoline and 1,2,3,4-tetrahydroisoquinoline, purchased from commercial sources, were used to prepare the tertiary amines listed in Table I by the method of Goode.[3] These pale yellow compounds were insoluble in water, but soluble in alcohol and ether.

The quaternary salts listed in Table II were prepared by reaction of the corresponding N-methyl tertiary amines with the appropriate phenacyl halides. They were crystalline solids, only slightly soluble in water.

TABLE I

1-(SUBSTITUTED PHENACYL)-1,2,3,4-TETRAHYDROQUINOLINES

Substituent	Empirical formula	M.p., °C.	Analyses, % Calcd. C	H	Found C	H
p-Methyl-	$C_{18}H_{19}NO$	90	81.52	7.16	81.20	7.12
p-Methoxy-	$C_{18}H_{19}NO_2$	114	76.84	6.81	76.80	6.98
p-Fluoro-	$C_{17}H_{16}FNO$	94	75.74	5.94	75.77	6.17
p-Chloro-	$C_{17}H_{16}ClNO$	103	71.45	5.64	71.15	6.02
p-Bromo-	$C_{17}H_{16}BrNO$	124	61.83	4.83	61.69	4.95
p-Iodo-	$C_{17}H_{16}INO$	160	53.92	4.23	54.06	4.26
m-Nitro-	$C_{17}H_{16}N_2O_3$	136[a]	68.90	5.44	68.78	5.51

[a] *Cf.* Kunckell, *Ber.*, **30**, 576 (1897).

2-Methyl-1,2,3,4-tetrahydroisoquinoline was obtained from a commercial source. 1-Methyl-1,2,3,4-tetrahydroquinoline and 2,3-dimethyl-1,2,3,4-tetrahydroisoquinoline were both prepared by hydrogenation of the corresponding

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[1] This research was supported in part by a research grant from the National Cancer Institute, of the National Institutes of Health, Public Health Service.

[2] C. T. Bahner, M. Fielden, L. M. Rives and M. D. Pickens, THIS JOURNAL, **73**, 4455 (1951).

[3] W. E. Goode, *ibid.*, **70**, 3946 (1948).