Analytical

The cobalt targets were dissolved in the minimum amount of concentrated nitric acid and known milligram quantities of inert carriers added. It was necessary to use yttrium as the carrier for radioscandium. Separations were carried out from this solution by the procedures[8] indicated below, with extensive use being made of holdback carriers and scavengers to ensure purity. These chemical procedures were adapted to fit the particular order of removal of the various ions from the solutions of the different target samples. Chemical yields were determined by quantitative methods, usually gravimetric.

Chlorine was distilled as Cl_2 while the target, to which carrier had been added, was being dissolved in concentrated nitric acid and precipitated as AgCl. Potassium was precipitated as $KClO_4$ and as K_2PtCl_6. Calcium was precipitated as CaC_2O_4. Scandium was carried by precipitated YF_3 and $Y(OH)_3$. Vanadium was separated by the Berkeley procedures. Chromium as peroxychromic acid was extracted into ethyl ether following removal of insoluble hydroxides with sodium hydroxide and hydrogen peroxide. Manganese was precipitated as MnO_2 from acid solution on addition of bromate. Iron was extracted into ethyl ether as $FeCl_3$ and precipitated as $Fe(OH)_3$ with aqueous ammonia. Cobalt was precipitated as $K_3Co(NO_2)_6$ after separation as the sulfide from aqueous ammonia. Nickel was precipitated with dimethylglyoxime from neutral solution.

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(8) A. A. Noyes and W. C. Bray, "A System of Qualitative Analysis for the Rare Elements," The Macmillan Co., New York, N. Y., 1948; W. W. Meinke, "Chemical Procedures Used in Bombardment Work at Berkeley," AECD-2738 (UCRL-432), Technical Information Division, Oak Ridge, Tenn., 1949.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF ROCHESTER
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The Composition of W-6 Raney Nickel[1]

BY GEORGE W. WATT AND SIDNEY G. PARKER[2]

In a recent note, Ipatieff and Pines[3] published data on the composition of W-6 Raney nickel that differ markedly from results given earlier by Adkins and Billica[4] and from data obtained by the present authors prior to the appearance of the note by Ipatieff and Pines. The latter authors *assumed* that a nitric acid-insoluble residue obtained during the preparation of samples for analysis consisted of aluminum(III) oxide and that sodium was present as a sodium aluminate. Of the total aluminum found, one fraction was calculated as sodium aluminate on the basis of sodium found by analysis, another small fraction was attributed to elemental aluminum, while the major portion was interpreted as being present as aluminum(III) oxide, presumably in order that the sum of the various constituents be made exactly equal to 100%. No consideration was given to the presence of minor constituents other than sodium, and Ipatieff and Pines concluded that the aluminum(III) oxide is present in the catalyst formed by the method of Adkins and Billica[4] and influences the activity of the catalyst.

Following publication of the note by Ipatieff and Pines, we repeated most of our experiments and confirmed the results obtained earlier. The catalysts used in our work were prepared exactly as described by Adkins and Billica; with one exception, the method of preparation of samples for analysis and the analytical procedures for the determination of nickel and aluminum were identical with those specified by Ipatieff and Pines. In contrast to the work of the latter authors, however, the nitric acid-insoluble residue was separated by filtration, washed with water, dried, and weighed; the filtrates were analyzed for aluminum.[5] Whereas Ipatieff and Pines describe the nitric acid-insoluble residue as a dense white solid, we found a grayish-white residue sufficient only to impart a pronounced turbidity to the nitric acid solution. Data relative to the aluminum content of these catalysts are given in Table I; the identity of the nitric acid-insoluble residue as $Al_2O_3 \cdot 3H_2O$ is established by the X-ray diffraction data given in Table II.

TABLE I

ALUMINUM CONTENT OF W-6 RANEY NICKEL

[a]HNO_3, %	$Al_2O_3 \cdot 3H_2O$, %	Al, %
5	1.0	12.2
10	1.0	12.5
30	0.4	12.9
60	0.5	13.0

[a] Concentration of acid used to dissolve samples for analysis.

TABLE II

X-RAY DIFFRACTION DATA FOR ALUMINUM(III) OXIDE 3-HYDRATE[a]

[b]HNO_3-insol. residue		[c]α-$Al_2O_3 \cdot 3H_2O$	
D, Å.	I/I_1	*D*, Å.	I/I_1
4.73	0.9	4.85	1.00
4.40	.7	4.37	.84
3.22	.5	..	..
..	..	2.46	.59
2.07	1.0	2.38	.59
..	0.2	2.05	.41
1.71	.7	1.75	.41
1.60	.2	1.69	.41
1.45	.2	1.46	.41
1.39	.2	1.41	.31

[a] Although more complete data are available, only the ten most intense diffraction maxima are included here. [b] Data obtained using Cu K_α radiation, Ni filter, 2–3 hr. exposure at 30 kv. and 15 ma.; samples mounted in cellulose acetate capillary tubes. [c] Data from A.S.T.M. Index of X-Ray Diffraction Patterns.

Spectrographic analysis of nitric acid solutions of independent samples of W-6 Raney nickel[6] for minor constituents gave the following results (in per cent.): Na (0.5); Fe, Cu (0.2); Ca (0.1); Mg (0.005); <2: Ce, Hg; <0.2: Ba, Cd, Co, Cr, In, La, Li, Mn, Pb, Sr, Ti, Zn, Zr. Elements not detected include Ag, As, Au, Bi, Ga, K, Mo, P, Pt, Sb, Sn, Th, Tl, U, V, and W; C was not detected owing to interference.[7] The elements detected spectrographically, together with hydrogen and oxygen, presumably account for that fraction

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(2) Field Research Laboratories, Magnolia Petroleum Company, Dallas, Texas.

(3) V. N. Ipatieff and H. Pines, THIS JOURNAL, **72**, 5320 (1950).

(4) H. Adkins and H. R. Billica, *ibid.*, **70**, 695 (1948).

(5) The nickel content of these particular catalyst samples was 80.2%. In other cases, nickel contents as low as 70–75%, with correspondingly high aluminum content (11-15%) were found depending upon the conditions employed in the preparation of the catalysts.

(6) The writers are indebted to Dr. W. W. Marshall through whose coöperation these data were obtained.

(7) The following data (in per cent.) were obtained for independent samples of commercial Raney alloy: Ni (49.5); Al (49.8); <0.2: As, Ce, Cu, Hg, U; <0.1: Ba, In, Pb, Sb, Th, Zn; <0.05: Cd, Fe, Sn; <0.01: Bi, Ca, Co, Cr, La, Li, Mg, Mn, Na, Nb, Sr, Ti, V, Zr.

of the catalyst not represented by nickel and aluminum. The spectrographic analysis for sodium is in good agreement with results of chemical analyses; this element may be present as sodium aluminate[3] or as sodium hydroxide not removed despite extensive washing.

The data given in Table I show that the maximum alumina formed is 1% rather than 21% as reported by Ipatieff and Pines. Since aluminum (III) oxide is insoluble in hot 60% nitric acid, the small but measurable difference in the quantity of alumina found using concentrated and dilute acid cannot be attributed to solubility. Furthermore it is significant that the decrease in the quantity of alumina found when concentrated nitric acid is used to dissolve the catalyst samples parallels qualitatively the trend in oxidation potential of nitric acid as a function of concentration. This clearly indicates that alumina is not a constituent of W-6 Raney nickel prepared by the method of Adkins and Billica but rather that alumina is formed during dissolution of the samples taken for analysis. This conclusion is further supported by X-ray diffraction studies on Raney nickel carried out both in this laboratory and in connection with work described by Taylor and Weiss.[3] In both instances, no diffraction maxima attributable to any of the known forms of aluminum(III) oxide or its hydrates were observed. Finally, it should be recognized that the type of specific composition data proposed by Ipatieff and Pines is also unwarranted on the grounds that, even with respect to the two major components, the composition of W-6 Raney nickel catalysts is not rigorously reproducible and varies over an appreciable range owing to unavoidable variation in the conditions that prevail during the leaching of the nickel-aluminum alloy.

(8) A. Taylor and J. Weiss, *Nature*, **141**, 1055 (1938).

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Benzylamine as a Reagent for the Characterization of Isothiocyanates[1,2,3]

BY LOWELL E. WELLER, CHARLES D. BALL AND HAROLD M. SELL

In an investigation concerning the occurrence of mustard oils in plants it became necessary to identify minute quantities of isothiocyanates. Since a suitable derivative was not available, work was directed toward obtaining solid derivatives of some of the more common isothiocyanates which have been obtained from plants. The substituted benzylthioureas formed by treating benzylamine with the aliphatic and aromatic isothiocyanates herein reported are crystalline compounds with convenient melting points. The reaction of the basic benzylamine with the acidic isothiocyanates proceeds spontaneously without the addition of heat to give nearly quantitative yields of the substituted benzylthioureas.

Experimental

Materials Used.—Ethyl, allyl and phenyl isothiocyanate as well as benzylamine were commercial products of Eastman Kodak Company. These were distilled under reduced pressure before they were used. Benzyl, 2-methylthioethyl, 2-methoxyethyl and β-phenylethyl isothiocyanate were synthesized by the method described by Slotta, *et al.*[4] Crotonic isothiocyanate was prepared from the corresponding thiocyanate according to the general procedure of Gerlich.[5] The remaining isothiocyanates listed were prepared in 50–70% yields according to the method as given by Delépine.[6]

Preparation of Substituted Benzylthioureas.—A mixture of 0.01 mole of the isothiocyanate in 5 ml. of 95% ethanol and an equimolar amount of benzylamine dissolved in the same solvent (5 ml.) was boiled gently for five minutes. Water was added until the hot solution appeared cloudy, then enough ethanol was added to clear the hot solution. If upon cooling an oil separates out it can usually be caused to crystallize readily by scratching the sides of the vessel. However, a better procedure at this point was to redissolve the oil in the hot solvent and then increase the ethanol content of the solution. Upon slow cooling the product will usually crystallize out. Skelly B[7] was used for the first recrystallization of *n*-butyl, crotonic and isoamyl benzylthiourea since these did not crystallize readily from their aqueous ethanolic solutions. If benzylamine was added to the isothiocyanate in the absence of a solvent the reaction proceeded spontaneously with the evolution of heat. Aqueous ethanol (60–70%) was then added for recrystallizing the product. Usually two recrystallizations were sufficient for purification. The yields of the recrystallized products were approximately 60–70%. The nitrogen values reported were the averages of two Kjeldahl determinations.[8]

TABLE I

DERIVATIVES OF ISOTHIOCYANATES

Isothiocyanate	Formula	Substituted M.p., °C.	benzyl thioureas Nitrogen, % Found	Calcd.
Methyl	$C_9H_{12}N_2S$	78	15.6	15.5
Ethyl	$C_{10}H_{14}N_2S$	103	14.2	14.4
Allyl	$C_{11}H_{14}N_2S$	94.5	13.6	13.6
n-Propyl	$C_{11}H_{16}N_2S$	88	13.3	13.4
Isopropyl	$C_{11}H_{16}N_2S$	126	13.4	13.4
n-Butyl	$C_{12}H_{18}N_2S$	50	12.8	12.6
s-Butyl	$C_{12}H_{18}N_2S$	78	12.4	12.6
Isobutyl	$C_{12}H_{18}N_2S$	112	12.7	12.6
Crotonic	$C_{12}H_{16}N_2S$	49.5	12.7	12.7
n-Amyl	$C_{13}H_{20}N_2S$	62	12.0	11.8
Isoamyl	$C_{13}H_{20}N_2S$	54	11.8	11.8
2-Methoxyethyl[a]	$C_{11}H_{16}ON_2S$	71	12.5	12.5
3-Methoxy propyl[a]	$C_{12}H_{18}ON_2S$	51	11.7	11.8
2-Methylthioethyl[a]	$C_{11}H_{16}N_2S_2$	58	11.7	11.7
Phenyl	$C_{14}H_{14}N_2S$	153	11.4	11.6
Benzyl	$C_{15}H_{16}N_2S$	148	11.0	10.9
2-Phenylethyl	$C_{16}H_{18}N_2S$	118	10.5	10.4
1-Naphthyl	$C_{18}H_{16}N_2S$	173[b]	9.7	9.6

[a] Preparation and properties not reported in the literature. [b] Previously reported as 171–172°, C. M. Suter and E. W. Moffett, THIS JOURNAL, 55, 2497 (1933).

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[2] From the Master's thesis of Lowell E. Weller, Michigan State College.

[3] This research was supported by the Horace H. Rackham Research Endowment.

[4] K. H. Slotta and H. Dresseler, *Ber.*, **63**, 888 (1930).

[5] G. Gerlich, *Ann.*, **178**, 80 (1875).

[6] M. M. Delépine, *Compt. rend.*, **144**, 1126 (1907); *Bull. soc. chim.*, [4] **3**, 642 (1908).

[7] A petroleum ether, b.p. 62–67°, marketed by the Skelly Oil Company, Chicago, Ill.

[8] J. B. Niederl and V. Niederl, "Organic Quantitative Microanalysis," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1942, p. 72.