COMMUNICATIONS TO THE EDITOR

ANION EXCHANGE STUDIES. XIX. ANION EXCHANGE PROPERTIES OF HYDROUS ZIRCONIUM OXIDE[1,2]

Sir:

In a search for inorganic materials which might exhibit anion exchange properties, investigation of hydrous zirconium oxide appeared particularly attractive. It is extremely insoluble and is expected to be insensitive to attack by acids, bases, oxidizing and reducing agents. Some adsorption properties of "zirconium hydroxide" have been described.[3] Anion exchange properties might be anticipated if one visualizes it to be formed from positively charged zirconium polymers, known to occur in solution,[4] which are partially cross-linked into a network during hydroxide precipitation or subsequent drying. Further, some hydroxides (or oxides) such as aluminum oxide or ferric hydroxide[5] have long been known to be good adsorbents for a number of materials.

"Zirconium hydroxide" was precipitated from recrystallized zirconium oxychloride with ammonia, centrifuged off, dried (room temperature to 800°), ground and sized. The materials, of indefinite composition, contained small amounts of water and chloride ions. They showed good adsorption in acidic solutions for negative ions, *e.g.*, Cl^-, Br^-, NO_3^-, and particularly sulfate and chromate and some, though small, selectivity for complex anions. At low drying temperatures they showed good uptake of negative ions from acidic solutions, *e.g.*, if dried at 32° apparent capacity for chromate was *ca.* 1.4 moles per kg. Though adsorptive capacity decreases with firing temperature, this does not become excessive below *ca.* 300°. Adsorption on the materials can be described in terms of ion exchange terminology. The materials show typical anion exchange displacement reactions and, at least at low loading, exchange is essentially ideal, *e.g.*, in tracer Br^-–NO_3^- exchange experiments the distribution coefficients D of Br^- (amount per kg. adsorber/amount per liter solution) were inversely proportional to M NO_3^-.

The materials should be classed as weak-base exchangers, since even in strongly acidic solutions apparent capacity is dependent on acidity. Although studies of rates of adsorption are not available, in adsorption–elution experiments the exchangers respond readily to changes in conditions, and elution bands showed at reasonable flow rates (*e.g.*, 1 cm. per minute) the expected Gaussian distributions. In view of their high chemical stability, high adsorptive capacities, rapid response, and reasonable selectivities, the hydrous zirconium oxides appear to be promising new materials for anion exchange applications.

Many insoluble "hydroxides" appear to have anion exchange properties. This was demonstrated, for example, for Sn(IV), Th(IV), Ti(IV), Cr(III), in addition to Fe(III) and Al(III). Precipitates of molybdic and tungstic acid, however, showed negligible anion exchange properties, even in strongly acidic solutions. Instead, they showed cation exchange properties. The hydrous zirconium oxides in basic solutions (*e.g.*, 0.01 or 1 M NaOH) lose their anion exchange properties but adsorb positive ions, *i.e.*, they become cation exchangers. Presumably the hydroxides and hydrous oxides in general may exhibit either anion exchange or cation exchange properties, depending on the acidity of the solutions and the tendency of the solids toward amphoteric character.

CHEMISTRY DIVISION
OAK RIDGE NATIONAL LABORATORY
OAK RIDGE, TENNESSEE
KURT A. KRAUS
HAROLD O. PHILLIPS

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[1] This document is based on work performed for the U. S. Atomic Energy Commission at the Oak Ridge National Laboratory.

[2] Previous paper: F. Nelson and K. A. Kraus, THIS JOURNAL, **77**, 4508 (1955).

[3] E. Wedekind and H. Wilke, *Kolloid-Z.*, **34**, 83, 283 (1924); **35**, 23 (1924).

[4] See, *e.g.*, J. S. Johnson and K. A. Kraus, *J. Am. Chem. Soc.*, in press.

[5] See *e.g.*, F. Nydahl and L. A. Gustafsson, *Acta Chem. Scand.*, **7**, 143 (1953).

CONTINUOUS RECORDING OF ELECTRON DENSITY IN A FUNCTIONING NICKEL CATALYST

Sir:

The decrease of magnetization occurring when supported nickel chemisorbs hydrogen[1] may be recorded by modifying standard gas adsorption apparatus.

The adsorption apparatus is the familiar purification train, gas buret, manometer, sample chamber, McLeod gage, and vacuum pumps.

Magnetization is determined by adapting an old method: the change of induced e.m.f. in a secondary coil surrounding the sample and energized by a primary solenoid producing about 1000 oersteds.[2] The secondary, of 50 turns, is connected in opposition through a similar, standard coil to a vacuum tube voltmeter. The primary, of 3100 turns, carries 1 ampere at 230 volts stabilized a.c. The output from the voltmeter amplifier circuit is isolated by a 1:1 transformer, then passed through a full-wave rectifier to a recorder.

A 7.66-g. sample of U.O.P. nickel hydrogenation catalyst, containing 52.8% nickel, was reduced for 12 hours at 350°, evacuated 2 hours at 350°, then cooled under vacuum to 25°. Hydrogen was then flushed on to the sample, up to atmospheric pressure. This caused an instantaneous decrease of magnetization, part of which was related to warming of the nickel by the heat of chemisorption. After 10 minutes the sample had cooled to a steady state in which the e.m.f. from the secondary before amplification was 0.40 millivolt less than initially, corresponding to a decrease in magnetization of 11.3%. The corrected volume of hydrogen ad-

[1] P. W. Selwood, S. Adler and T. R. Phillips, THIS JOURNAL, **77**, 1462 (1955).

[2] S. J. Barnett, *J. Applied Phys.*, **23**, 975 (1952).

sorbed was 68.4 cc., corresponding to an atom ratio, H/Ni, of 0.0886.

The change of magnetization as measured at room temperature is a rough measure of the change in saturation moment at absolute zero, and hence of the fractional change in unpaired, *d*-band electrons. If nickel metal has 0.6 unpaired electron per atom, then the adsorption of hydrogen caused the addition of approximately 0.068 electron per nickel atom.

At the end of the run the sample was evacuated, with rapid desorption of about one-third of the hydrogen and recovery of two-thirds of the magnetization.

If the hydrogen is first admitted to the sample slowly, rather than flushed on, the chemisorption is isothermal, with no excess diminution of magnetization. If a sample, once exposed to hydrogen, is evacuated at room temperature for an hour, then exposed to hydrogen again, the magnetization falls sharply but no thermal effect occurs.

This method provides a continuous record of electron density in the *d*-band of a functioning nickel catalyst, under widely varying conditions of pressure and temperature. The method also applies to any other gas capable of being chemisorbed on nickel, and to reactions, such as oxidation or reduction, under conditions identical with those encountered in actual catalytic practice.

The writer is indebted to Dr. L. N. Mulay and Mr. Edward L. Lee who first observed the thermal effect in this laboratory on other apparatus.

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DEPARTMENT OF CHEMISTRY
NORTHWESTERN UNIVERSITY P. W. SELWOOD
EVANSTON, ILLINOIS

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THE TOTAL SYNTHESIS OF *dl*-DEHYDROABIETIC ACID

Sir:

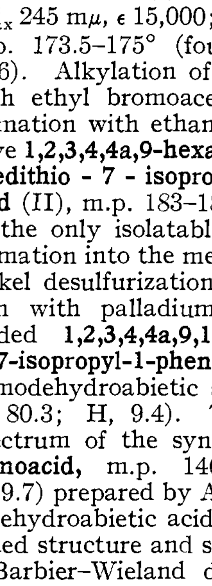
We would like to report the total synthesis of *dl*-dehydroabietic acid,[1] the first synthesis of a diterpenoid resin acid.

2-Isopropylnaphthalene[2] was sulfonated to the 6-sulfonic acid, isolated as its *sodium salt* (found: C, 57.3; H, 4.7); **sulfonamide,** m.p. 190–190.5° (found: C, 62.4; H, 5.9) which was transformed into **6-isopropyl-2-naphthol,** m.p. 111.5–112.5° (found: C, 83.8; H, 7.8), by fusion with potassium hydroxide. The structure of the naphthol was proved by independent synthesis of its **methyl ether,** m.p. 63.5–64.5° (found: C, 84.0; H, 8.1), from 6-methoxy-2-acetonaphthone[3] by reaction with ethyl chloroacetate in the presence of potassium *t*-butoxide to produce the **glycidic ester,** m.p. 107–108.5° (found: C, 71.4; H, 6.4), which was hydrolyzed and decarboxylated to α-methyl-6-methoxy-2-naphthaleneacetaldehyde; **semicarbazone,** m.p. 173–174.5° (found: C, 66.3; H, 6.2). Wolff–Kishner reduction of the aldehyde gave 2-isopropyl-6-methoxynaphthalene, identical with the product described above.

Reduction of 6-isopropyl-2-naphthol with sodium in liquid ammonia[4] gave 6-isopropyl-2-tetralone, b.p. 123–126° (0.6 mm.); *p*-**nitrophenylhydrazone,** m.p. 172.5–174.5° (found: C, 70.9; H, 6.7; N, 13.0). Monomethylation of this β-tetralone could be achieved satisfactorily only by the reaction of its pyrrolidine enamine with methyl iodide[5] to yield 6-isopropyl-1-methyl-2-tetralone, b.p. 120–123° (0.6 mm.); **2,4-dinitrophenylhydrazone,** m.p. 142.5–144° (found: C, 63.1; H, 5.8; N, 14.5).

Condensation with 1-diethylamino-3-pentanone methiodide[6] or ethyl vinyl ketone gave 4,4a,9,10-tetrahydro-1,4a-dimethyl-7-isopropyl-2(3H)-phenanthrone (I), b.p. 160–168° (0.25 mm.), $\lambda_{\max}^{\text{alc}}$ 245 mμ, ε 15,000; **2,4-dinitrophenylhydrazone,** m.p. 173.5–175° (found: C, 67.0; H, 6.3; N, 12.6). Alkylation of the α,β-unsaturated ketone with ethyl bromoacetate,[7] followed by thioketal formation with ethanedithiol and base hydrolysis gave **1,2,3,4,4a,9-hexahydro-1,4a-dimethyl-2-ethylenedithio-7-isopropyl-1-phenanthreneacetic acid** (II), m.p. 183–186° (found: C, 68.3; H, 7.5) as the only isolatable crystalline isomer. Transformation into the methyl ester, followed by Raney nickel desulfurization, hydrolysis, and hydrogenation with palladium-charcoal in acetic acid afforded **1,2,3,4,4a,9,10,10a-octahydro-1,4a-dimethyl-7-isopropyl-1-phenanthreneacetic acid** (III), (*dl*-homodehydroabietic acid), m.p. 173–174° (found: C, 80.3; H, 9.4). The identity of the infrared spectrum of the synthetic acid with that of the **homoacid,** m.p. 146–147.5° (found: C, 80.4; H, 9.7) prepared by Arndt–Eistert homologation of *d*-dehydroabietic acid served to confirm its anticipated structure and stereochemistry.

Barbier–Wieland degradation of the synthetic homoacid *via* the diphenylcarbinol and diphenylethylene gave *dl*-**dehydroabietic acid** (IV), m.p. 179.5–180.5° (found: C, 80.3; H, 9.3). The in-



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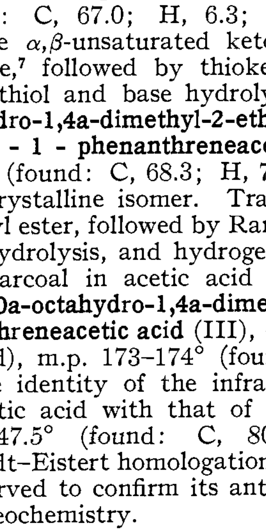

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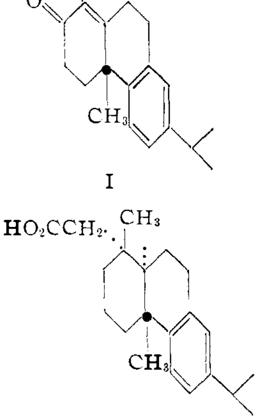

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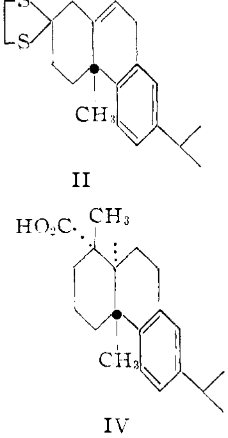

IV

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(1) The most recent experiments in this field are described by W. E. Parham, E. L. Wheeler and R. M. Dodson, THIS JOURNAL, **77**, 1166 (1955).

(2) F. Bergmann and A. Weizmann, *J. Org. Chem.*, **9**, 352 (1944).

(3) R. Robinson and H. N. Rydon, *J. Chem. Soc.*, 1934 (1939).

(4) *Cf.* A. J. Birch, *ibid.*, 430 (1944).

(5) G. Stork, R. Terrell and J. Szmuszkovicz, THIS JOURNAL, **76**, 2029 (1954).

(6) *Cf.* J. W. Cornforth and R. Robinson, *J. Chem. Soc.*, 1855 (1949).

(7) *Cf.* J. M. Conia, *Bull. soc. chim.*, 690; 943 (1954), for a discussion of related reactions.