

Hydrogenation catalysts from used nickel metal hydride batteries

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Supporting material

General

Linalool and sodium borohydride were supplied by Aldrich. Nickel chloride was supplied by Merck. All other chemicals were supplied by Acros or Fisher. 3,3,5-Trimethylcyclohexanone was prepared by the hydrogenation of an ethanol solution of isophorone using 5% Pd on carbon as the catalyst, after two distillations this compound was used. The octene was formed *in situ* by the reduction of the octyne. ^1H and $^{13}\text{C}\{-^1\text{H}\}$ NMR spectra were obtained using a Varian Unity 500 machine. GCMS results were obtained using helium as the carrier gas, an initial oven temperature of 70 °C, a solvent delay of 2 minutes, a heating rate of 5 °C min⁻¹, and a Hewlett-Packard G1800A GCD system (Electron impact ionization) which is fitted with a Supelco SP-2330 (15 m) column. Injections of 1 to 2 µl were made with the injection port operating in the splitless mode, and the mass of the analyte was approximately 90 ng.

Metal analysis

The metal content of aqueous solutions was determined by ICPOES (Inductively Coupled Plasma Optical Emission Spectroscopy) using a Thermo iCAP6500 machine using a pure argon plasma using nitric acid (1M) as the matrix for both samples and standards. Solid compounds were dissolved in nitric acid (1M) to enable their examination by ICPOES.

Confirmation of the identities of the organic products.

The ethanol solution of the product of linalool hydrogenation was filtered through a 0.45 µm syringe filter before being placed in a round bottomed flask. The majority of the ethanol was then removed using a rotary evaporator before part of the oily residue was dissolved in deuterated chloroform for ^1H and ^{13}C NMR spectroscopy. The ^1H NMR spectrum concurred with the hypothesis that the product would be 3,7-dimethyl-oct-6-en-3-ol, and the shifts in the ^{13}C NMR spectrum are a close match to those reported for 3,7-dimethyloct-6-en-3-ol.¹

The ethanol solution of the product of octyne hydrogenation was filtered through a 0.45 µm syringe filter. Part of this solution was placed in a NMR tube, after the addition of deuterated chloroform the mixture was examined by ^1H and ^{13}C NMR. By ^1H NMR the octene was found to be present as a single isomer rather than as a mixture of the *cis* and *trans* forms, while the shifts in the ^{13}C spectrum a close match to those reported for *cis*-oct-4-ene.²

Table 1. ^{13}C NMR chemical shifts observed for the *cis*-oct-4-ene formed in the experiment.

Identity of a carbon atom	Chemical shift (ppm)
Alkene	129.51
Allylic	28.98
Methylene	22.58
Methyl	13.41

¹ Y. Imada, H. Iida, and T. Naota, *J. Am. Chem. Soc.*, 2005, **127**, 14544.

² R.G.F. Giles, V.R. Lee Son and M.V. Sargent, *Aust. J. Chem.*, 1990, **43**, 777.

N.B. An initial attempt was made to examine the product using the same method as was used for the isolation of 3,7-dimethyl-oct-6-en-3-ol but no organic product was detected by NMR, it is thought that the oct-4-ene was lost by evaporation as a result of forming an azeotrope with the ethanol.

The ethanol solution of the products of isopronone hydrogenation was filtered through a 0.45 μm syringe filter and diluted to render it suitable for examination by GCMS. It was found that only 3,3,5-trimethylcyclohexanone could be detected in this sample. The retention times of the different compounds are listed in the following table, *N.B.* no attempt has been made to determine which isomer is responsible for each of the two peaks due to the 3,3,5-trimethylcyclohexanols.

Table 2. Results from the gas chromatography- mass spectroscopy experiments.

Compound	Retention time (minutes)	Mass spectrum (m/z in amu)
Isopronone	6.80	138, 123, 110, 95, 82
3,5,5-Trimethylcyclohex-2-enol	4.56	140, 125, 107, 91, 84
3,3,5-Trimethylcyclohexanol	3.91	141, 124, 110, 109, 95, 83
3,3,5-Trimethylcyclohexanone	3.42	140, 125, 112, 97, 83
3,3,5-Trimethylcyclohexanol	3.06	140, 124, 109, 96, 83

Preparation of a mixed *cis*-3,3,5-trimethylcyclohexanol, *trans*-3,3,5-trimethylcyclohexanol and 3,5,5-trimethylcyclohex-2-enol standard.

Isopronone (140 mg) was placed in a test tube; to this was added ethanol (1 ml) and sodium borohydride (120 mg). The resulting mixture was occasionally shaken during the next twenty hours before the addition of water (8 ml). The mixture was extracted twice with dichloromethane (10 ml). The combined dichloromethane extracts were dried (Na_2SO_4) before decanting into a 100 ml round bottomed flask. After removal of the solvents by rotary evaporation a heavy oil (144 mg) remained. This oil was used without further purification or characterisation as the sample of the alcohols for the determination of the retention times of the three alcohols.

Recycling method

A whole nickel hydride electrical cell (120 grams) was cut to remove the terminals; the electrodes were separated and cut with hand shears before being placed in a beaker. To this was added water (100 ml) and acetic acid (100 ml). When the initial production of gas had subsided concentrated hydrochloric acid (30 ml) was added. The resulting mixture was allowed to stand for sixty hours. The semi-solid mixture was twice extracted with water (2 x 100 ml), then with a 1:1 mixture of water and acetic acid (100 ml). The solid residue was further extracted with water until all the soluble salts had redissolved in water. The liquid extracts were combined and diluted with water to 2 L. The acetic acid insoluble residue was treated with concentrated hydrochloric acid (400 ml), after being allowed to stand for one week. The liquid was decanted away from the solid; the solid was washed with water to recover the remaining metal chlorides. The combined chloride extracts were diluted with water to 2 L.

A portion of the sea green crude acetic acid extract (**AL1**, 263 g) was heated and stirred in an open beaker until it the volume was *circa* 100 ml, this was then filtered while hot through celite to form a new green solution (**AL2**). This evaporation and filtration was repeated to furnish *circa* 20 ml of a dark green solution (**AL3**) which was allowed to stand until crystals formed. These crystals (**RN1**) were collected on a paper filter, washed with a small volume of cold water and dried in air.

Recycled nickel (1.01 grams of **RN1**) was dissolved in a small volume of water, to this was added a solution of potassium fluoride (40.3 mg) in water (2 ml). The resulting mixture was filtered and diluted to a volume of 10 ml with water to create a new acetate liquor (**AL4'**). Then **AL4'** (7.5 ml) was treated with potassium fluoride (74 mg dissolved in 0.5 ml water), after allowing the mixture to stand (90 minutes) the mixture was filtered to create a lanthanum free acetate liquor (**AL4**).

A portion of the green crude hydrochloric acid extract (**CL1**, 302 g) was heated and stirred in an open beaker until only a small volume remained; this was then allowed to stand at room temperature until crystals formed. The solid (**RN2**) was collected on a paper filter and washed with a 1:1 mixture of water and ethanol before being dried in air.

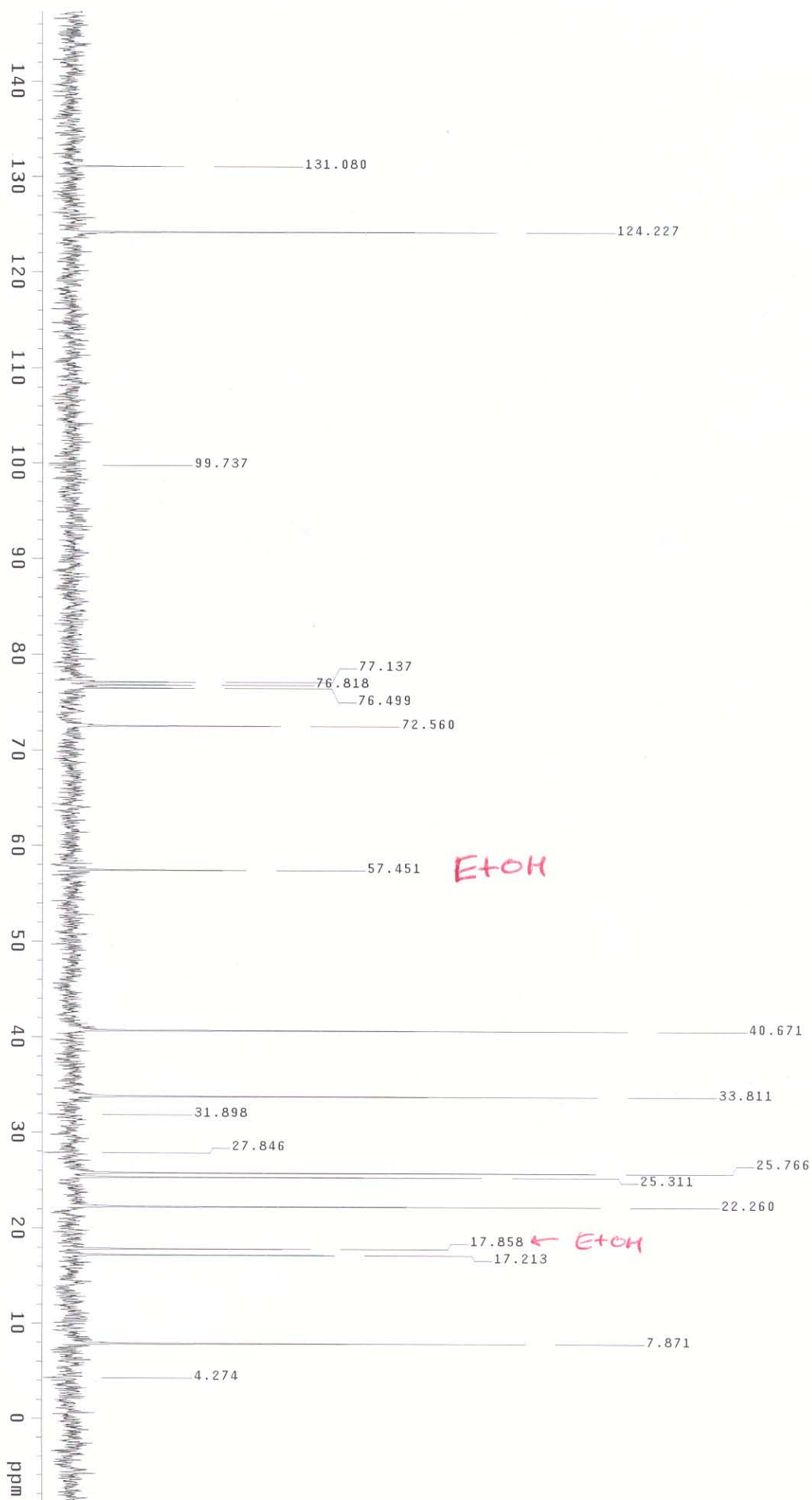
Attempted production of a catalyst from a mixture of nickel, cobalt and lanthanum salts.

$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (220 mg), $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (21.4 mg) and $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (17 mg) were dissolved in 2 ml water which was treated with NaBH_4 (236 mg) in 2 ml 0.2 M KOH according to the normal method. This formed a black solid which on treatment with water formed a black slurry.

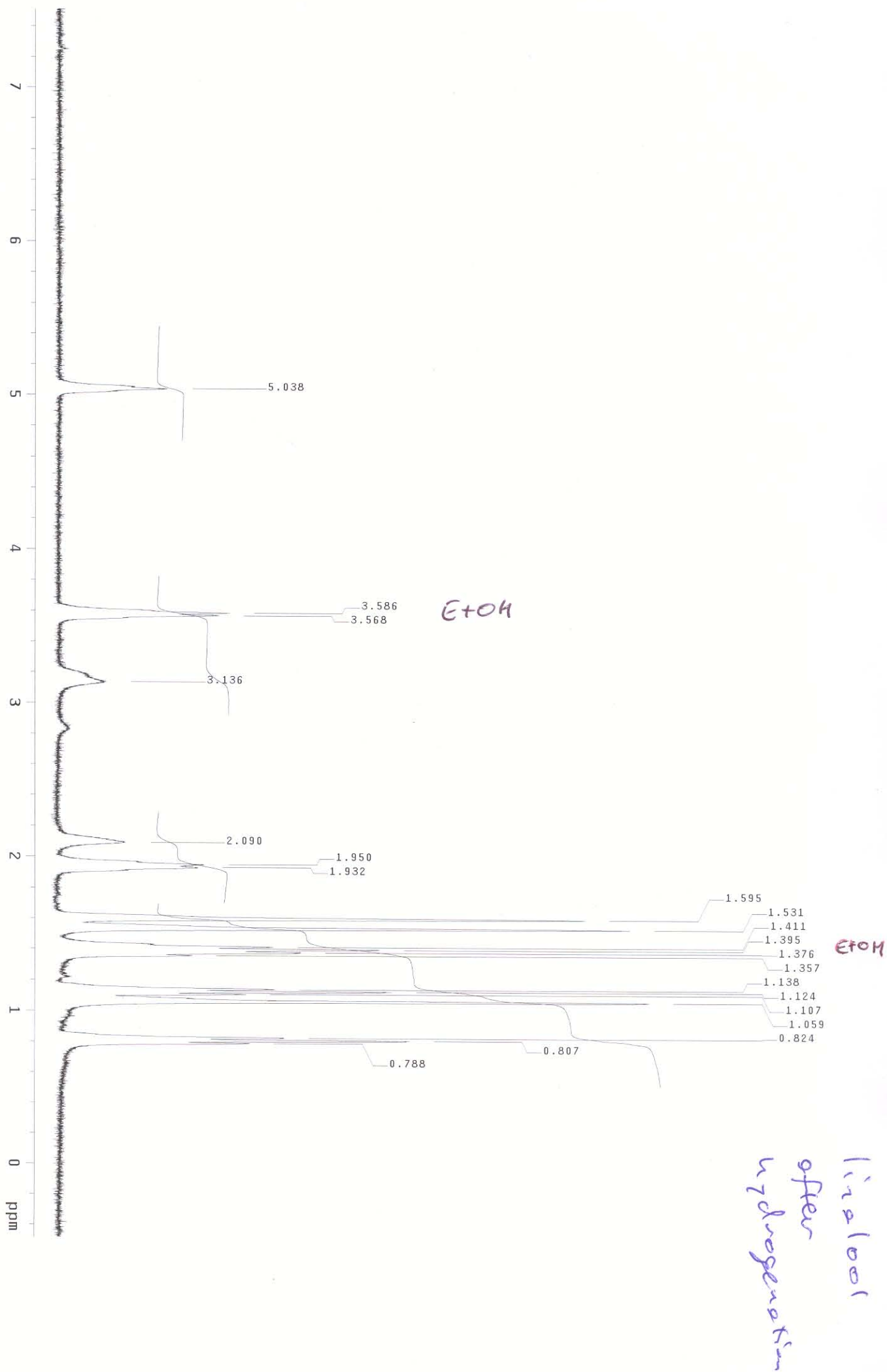
Hydrogenation equipment and materials

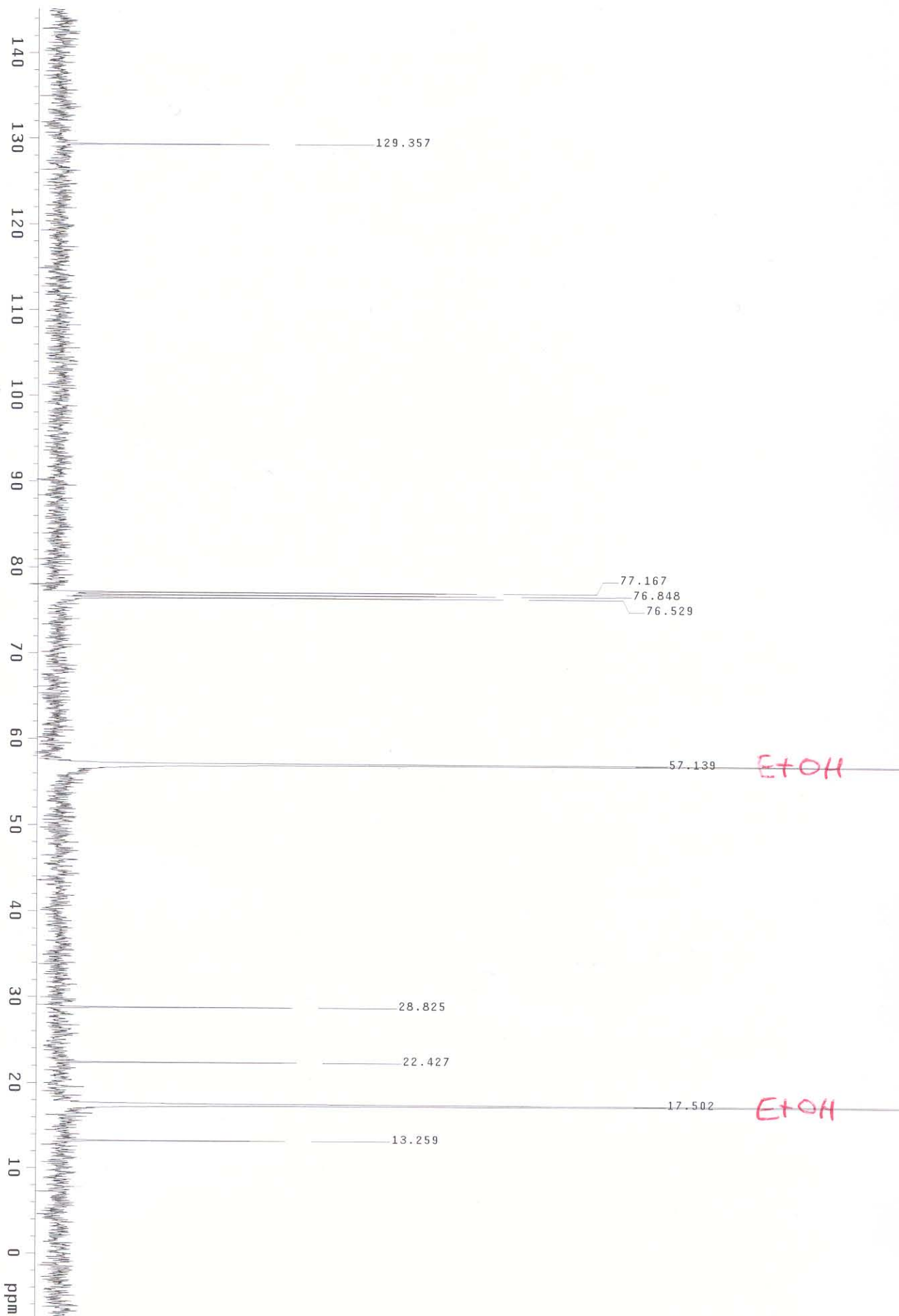
The ethanol used was absolute ethanol and was used as supplied. The hydrogen gas was instrument grade and was used as supplied by AGA. The gas burette on the hydrogenation apparatus was a 100 ml burette fitted with a greased tap originally made for volumetric analysis. The burette was connected *via* PVC tubing to a glass manifold bearing three greased taps, one for vacuum, one for hydrogen and one to allow air to enter the equipment. A hose barb without a tap was connected to the reaction vessel via a short length of PVC tubing. The hydrogen hose was equipped with a rubber balloon to allow short term (< 5 minutes) storage of hydrogen gas, care was taken to remove any air from the hydrogen by repeated evacuation of the balloon and hose followed by refilling of the balloon before the hydrogen gas was introduced into the reaction flask. The reaction mixtures in all hydrogenation runs were stirred (750 rpm) using an egg shaped magnetic stir bar (34 mm long and *circa* 15 mm diameter) and were performed in 100 ml round bottomed flasks. An initial test was made using 5% palladium on carbon black showed that under these conditions (with a total ethanol volume of 5, 10, 15 or 20 ml) in the flask that the transfer of hydrogen gas is such that the mixture could absorb at least 6.6 ml per minute. For the kinetic runs the uptake of hydrogen was always 2.3 ml min⁻¹ or less and it is assumed that the rate of hydrogen uptake was limited by the rate of the chemical processes at the surface of the metal particles. After disposal of the bulk of the catalyst the flask and the stir bar were soaked (at least overnight) in aqua regia to remove any traces of metal. After this acid soaking these items were washed with water and then dried.

Volume data was entered into Microsoft Excel, and normally the initial rate of each hydrogenation was estimated by fitting a linear trend line to the experimental data, the rate of adsorption in the experiment (expressed in moles of hydrogen per hour) was then divided by the mass of number of moles of the metal (Ni, Co and Fe) present in the sample to give a rate expressed as a turnover rate for the catalyst.



Hydrogenated
linoleol





1024 scans
octene from
octyne hydrazide.