ABSTRACTS
of current literature on the platinum metals and their alloys

PROPERTIES
On the Temperature Dependence of the Atom Susceptibility of Ruthenium, Rhodium and Palladium as well as Osmium, Iridium and Platinum between 80 and 1850 K
Specific magnetic susceptibilities of the Pt metals were determined at 80–1850 K by a modified Faraday technique. The temperature dependence of the susceptibility of Pd above its m.p. was also observed. Results for Rh, Pd and Pt are compared with those of M. SHIMIZU et al. but no earlier work on Ir, Ru and Os was known.

Kinetics of Quenched-in Vacancies in Pure Platinum
Isothermal annealing curves of pure Pt quenched in H2O show the characteristic “S” shape indicative of second order kinetics which is explained, together with the low values of effective energy of migration obtained, by assuming the existence of a thermal equilibrium between single vacancies and di-vacancies at temperatures >260°C. The binding energy of a single vacancy is estimated as (0.18±0.05)eV and the difference in the energies of migration of single and di-vacancies is (0.34±0.05)eV.

Thermal Diffusivity of Platinum from 300° to 1200° K
Thermal diffusivity measurements on five Pt samples with R4.2/R4.1 of 12, 34, 100, 900 and 5000 at 300–1200°K suggest that pure Pt would be suitable for a thermal conductivity standard but that measurements by other absolute methods are desirable also. Only the least pure sample (R4.173/R4.172 =12) showed more than 3% deviation from the average thermal diffusivity of the two purest samples. Comparison with previous work agrees well at room temperature but agreement is poor at high temperatures.

Uniform Microcrystals of Platinum and Gold
To study physical properties dependent on crystal size, three methods for preparing Pt hydrosols were used and two for Au hydrosols. Optimum conditions of preparation were established for uniform sized crystals and sizes from 40 to 500Å were obtained.

The Lattice Thermal Conductivity of Some Palladium and Platinum Alloys
R. FLETCHER and D. GREIG, Phil. Mag., 1967, 16, (130), 303–315
Measurements on some Pd-Ag, Pt-Ir alloys at 2–120°C showed that the lattice thermal conductivity below ~30°CK is an order of magnitude less than in noble metal alloys of similar concentrations. This is explained by strong electron-phonon scattering but at present it cannot be decided whether the electronic transitions are s to d or d to d. At higher temperatures measurements are largely independent of solute concentration. At 100°C, lattice resistance is mainly due to phonon-phonon U-processes.

Growth of Modulated Structure in Gold-Platinum Alloys
X-ray studies of the growth of structural modulations during early stages of precipitation in 20, 40 and 60% Au-Pt alloys at 500–600°C indicated a nearly constant modulation wavelength for short ageing times with a uniform increase to a maximum value upon further ageing. 40% Au-Pt has a smaller maximum wavelength than the other alloys, caused by a maximum in elastic strain energy due to coherency strains.

Experimental Investigation on Exchange Interaction in Platinum-Iron Alloys
Measuring using the Mössbauer effect of the temperature dependence of the hyperfine magnetic field H1 at Fe nuclei and of the concentration dependence of the transition temperature Tc was carried out on 1–15 at. % Fe-Pt alloys and showed that, when T < Tc, H1 is nearly the same at each Fe nucleus but that as T increases, the Mössbauer spectral lines broaden, due perhaps to a wide range of H1 values.

Ordered Pt3-Co Alloy Studied in the Field-ion Microscope
Images of the {111} planes of ordered Pt3-Co confirmed the invisibility of the Co atom species. Layer by layer field evaporation confirmed that the composition of the {110} and {100} planes alternates in subsequent layers of pure Pt and...
partially ordered state between the ordered and disordered phases.

The Ageing Mechanism of the Cold Work Peak of Hydrogen in Palladium

The cold work peak of β-PdH occurs at ~150°K and decreases considerably after ageing at room temperature and above. Its behaviour is related to the pinning of dislocations by interstitial impurities.

Reactions with Hydrogen of the Alloy Pd-40 wt.% Ag

Unlike ≤20 wt.% Ag-Pd alloys, 40 wt.% Ag-Pd does not become deformed during heating and cooling cycles in H2. This is due in part to formation of β-Pd-Ag-H. The permeability of 40 wt.% Ag-Pd for H2 is nearly equal to that of pure Pd but is less than that of 18.5 wt.% Ag-Pd.

The Transformations in the Solid Chromium-Palladium Alloys

Studies of the phase diagram at low temperatures on 10–49 at.% Cr-Pd alloys show that an ordered L12 structure exists at 24–46 at.% Cr-Pd and a tetragonal L10 structure at ~50 at.% Cr-Pd. The L12 phase is formed by a peritectoid transformation at ~505°C.

The Constitution of Cerium-Palladium Alloys Containing 50–100% Palladium

Metallographic and X-ray studies of 48–100 at.% Pd–Ce alloys between 800°C and the melting points indicated four intermetallic compounds, which were compared with Th-Pd alloys. Solubility of Ce in Pd at 800 and 1050°C is 13±1%. CePd and CePd2 crystallise directly from the melt at 1137±12 and 1437±12°C respectively; compounds containing 57±1 and 62.5±1 at.% Pd form peritectically at 1137±12 and 1037±12°C respectively. Eutectics occur at 987±12°C and 1075±12°C.

On the Effects of Cold-working and Annealing, and of Cycles of Absorption and Desorption of Hydrogen, on the Electrical Resistance of Some Palladium-Boron Alloys

The electrical resistance of work-hardened 16 at.% B-Pd wire falls rapidly above 80°C and there are irregularities in the curve indicating that thermally activated changes occur at higher temperatures. The variation of resistance during thermal cycling indicates that a metallurgical equilibrium does not exist although there is no evidence for phase changes. Isothermal cycles of charge and discharge of H2 at 25°C have little effect on the annealed resistance value.

Concentration Dependence of Electrical Resistance of Liquid Alloys Pd-Ag, Pd-Cr, Pd-Si, Ag-Si

A correlation between the variation of specific electrical resistance with composition and the composition diagram is shown for Pd-Ag, Pd-Si, Pd-Cr and Ag-Si at temperatures up to 1600°C, e.g. the maximum on the Pd-Si isotherm corresponds to the formation of the compound PdSi. Minimal superheating above the liquidus shows a correspondence between the character of the isotherm of ρ and the alloy composition Z represented by the equation.

\[ \Delta \rho = A + B (Z_\alpha - Z)^2 \]

where A and B are constants, c is the at.% addition of Zn to the major alloy constituent Z.

Crystal Lattice Parameters and Structural Deformation in Fe-Rh Alloys during Phase Conversions

The antiferromagnetic-ferromagnetic transformation of Fe-Rh alloys occurs at 353–440°C. Both the initial cubic phase and the new crystal formed are deformed during the process, depending on the initial composition of the alloy, and hysteresis for direct and reverse transformation may amount to from 3 to 14°C.

The Preparation and Some Properties of Tungsten-Rhenium-Osmium Alloys

W-Re-Os alloys were fabricated by powder metallurgical techniques and were studied to learn the effect of Os in thermocouples of Re-W alloy. 5% Re-5.25% Os-W alloys contain a single-phase α solid solution. 26% Re-8.13% Os-W alloys contain α up to ~1.67% Os, and both α and brittle γ phase at greater Os content. Alloys of ~26% Re-W with ~0.69–4.5% Os are very prone to deformation twinning, especially at ~1.67% Os.

Thermionic Work Function of Polycrystalline Ruthenium

Measurements in variable spacing, relatively
large electrode area thermionic converters showed that the thermionic electron work function of Ru under high vacuum is \( \Phi_{\text{Ru}} = 4.55 \pm 0.05 \) eV. Measurements in a Cs vapour environment corresponded to \( \Phi_{\text{Ru}} = 4.57 \pm 0.05 \) eV. The process of applying Ru powder to achieve large and dense area electrode coatings is detailed.

### CHEMICAL COMPOUNDS

**π-Allyl Complexes of the Transition Metals**


The structure of π-allyl complexes of the transition metals, including Rh, Ru, Ir, Pd and Pt, were studied by NMR, IR, UV and dipole moment measurements. The preparation and properties of the complexes are discussed together with their use in a wide range of synthetic organic reactions. (318 references.)

**Olefin Coordination Compounds of Rhodium (I)**

V. The Relative Stabilities and Rates of Exchange of Olefin Complexes of Rhodium (I)


Comparisons of stabilities of various olefin complexes of Rh(I) show that alkyl substituents on olefin Cs destabilise Rh(I) complexes much more than the corresponding Ag compounds but that coordination is enhanced by electronegative substituents due to stronger π- or back-bonding. Strongly-coordinating CsF displaces CsH4 from Rh(I) far more slowly than do CsH2 or CsH30, which coordinate weakly, which suggests that a-bond formation plays little part in development of the transition state for nucleophilic olefin exchange.

**X-ray, Infrared, and Magnetic Studies of α- and β-Ruthenium Trichloride**


X-ray, magnetic susceptibility, IR and neutron diffraction measurements of α- and β-RuCl3 indicate that the former has a distorted octahedral structure and belongs to the space group \( P3_1212 (D_3d) \), and the latter contains linear chains in a trigonal structure belonging to the space group \( P3c_1 (C_6v) \).

**New Transition Metal Tetrafluorides**


PuF4, RhF4 and IrF4 have been prepared and possess low-spin electron configuration. PuF4 has undistorted UCl4-structure and IrF4 and PtF4 are monoclinic relatives of its tetragonal cell. Each Pd atom is coordinated to four F atoms. RuF4, IrF4 and PtF4 are more similar to NbF4, where each metal atom is six-coordinated by F ligands.

**Carbonyl Halide Complexes of Platinum Group Metals**


Careful control of reaction conditions and reactants enabled eleven new carbonyl halide salts of Os, Ru and Ir to be isolated and these are tabulated. See also *Platinum Metals Rev.*, 1967, 11, (4), 148–149.

### ELECTROCHEMISTRY

**Instability of Supported-platinum Surface Area in the Presence of Electrolytes**


A study of the growth of supported Pt crystallites at <200°C in electrolytes indicated that the growth rate depended on the support type, the solution, the Pt concentration, and the initial crystallite size. High support areas and low conductivity solutions reduced growth rates but the best dispersions showed Pt area loss rates up to 90% because their small initial crystallites possessed a high tendency to recrystallise. Electrorecrystallisation is a possible mechanism of the results, with cells formed between large and small Pt crystallites and the small acting as anodes because their surface energies are higher.

**The Kinetics of Propane Adsorption on Platinum in Hydrofluoric Acid**


The rate of adsorption of C3H8 on smooth Pt at 90°C in 37 mole % HF was studied by single linear voltage sweep techniques in all-PTFE apparatus with surface coverage of C3H8 measured as a function of adsorption time and potential. Steady-state coverage reached a maximum at 0.2 V and the amount of the most electrochemically active species was highest at 0.3 V. Rate constants were measured at these values.

**Oxygen Reduction at Pt-Au and Pd-Au Alloy Electrodes in Acid Solution**


Kinetic studies of O2-reduction in 0.1 M HClO4
at room temperature showed that at Pt, Pd, Pt-rich Pt-Au, and Pd-rich Pd-Au electrodes, Tafel relationships with $8V/\beta \log 100 - RT/F$ occur at $10^{-4}$ to $10^{-3} A/cm^2$, while at Au and Au-rich alloys the slope is close to $-2RT/F$.

The change of slope from $-RT/F$ to $-2RT/F$, which occurs at $>50$ at.% Au, is related to the electronic structure of the alloys, for at $\sim 60$ at.% Au there are no longer unpaired d-electrons and the $O_2$-reduction mechanism changes. Exchange current density for Pt- and Pd-rich alloys changes exponentially with alloy composition; it decreases as Au % increases. At a given potential the linear change in log(activity) with Au % in Pd-rich Pd-Au is due to the change of heat adsorption of reaction intermediates with alloy composition.

Oxygen Reduction on Gold Alloys of Platinum, Palladium and Silver

10-90% Au alloys of Pt, Pd and Ag were used as rotating electrodes in the cathodic reduction of $O_2$ in 2 N KOH at 25°C. Activity of Au-Ag decreased with increasing Ag content; Au-Pt alloys possessed almost constant activity; Au-Pd alloys showed a maximum activity greater than that of Au-Pt for 20-70% Au-Pd. Order of activity of pure metals at low polarisation was Pd>Pt=Au>Pd-Ag. Results at 75°C were similar to those at 25°C.

Preparation and Characterisation of Pt-black for Anodic Hydrocarbon Oxidation

J. GINER, J. M. PARRY and S. M. SMITH, Ibid., L18
Pt-black was prepared by reduction of $H_2PtCl_6$ with HCHO in a basic medium under various nucleation and growth conditions. They were characterised by surface area, pore size, etc., and their activity for anodic oxidation of $C_2H_4$ at 150°C in 85% $H_2PO_4$ was measured using a Pt-Teflon structure. Effects of conditions of preparation on the physical characteristics and activity of the blacks were determined.

ELECTRODEPOSITION AND SURFACE COATINGS

Radioisotope Powered Cardiac Pacemaker Project. Platinum Plating on Component Parts

A. RECHIA, USAEC Rept NUMEC 37314, 57-1, 1967, (Mar.), 13 pp
Pt was successfully plated on Hastelloy “C” either with or without a prior Ni flash plating and a good mechanical bond was shown to exist in both cases. Hardnesses of the Pt plated surface and of the Pt anode were compared. Post-plating treatment at 200°C expelled gases and moisture trapped in the plating. Thermal shock tests caused micro-blisters to form between Pt and Hastelloy “C” but not between Pt and the Ni-flashed alloy. Barrel plating was shown to be suitable for this work.

The Electrolytic Deposition of Platinum and Platinum Alloys with Respect to the Increase of Hardness

G. HÄNSEL, Metaloberfläche, 1967, 21, (8), 238-242
Pt and 5% Re-Pt, deposited electrolytically from sulphamic or fluorboric acid electrolytes containing complex Pt, and Pt and Re salts, have a hardness approaching that of thermally melted metals and alloys. The hardness of 5% Re-Pt is similar to that of Pt-Ir which is used in the manufacture of laboratory apparatus.

Investigation of Processes of Electrochemical Deposition of Silver-Palladium Alloys in Cyanide Electrolytes

N. P. FEDOT’EV, P. M. VYACHESLAVOV, B. SH. KRAMER and V. V. IVANOVA, Zh. prikladnoi Khim., 1967, 40, (7), 1474-1478
X-ray analysis and physico-chemical studies showed that electrodeposited Ag-Pd alloys form a continuous series of solid solutions. Increases in specific electrical resistance and microhardness occur as the Pd content increases. When deposition occurs from cyanide electrolytes, Ag is deposited with overpolarisation but Pd with depolarisation.

LABORATORY APPARATUS AND TECHNIQUE

An Investigation into the Use of Platinum Ware for Silicate Analysis

Tests to determine the amount of Pt that dissolves from crucibles used for fusing samples in silicate analysis showed that alkaline fluxes dissolve more Pt than do acid fluxes and that, if the sample contains ferrous iron, considerable amounts may be absorbed by the Pt. The preferred technique is sintering at 440°C with a mixture of Na$_2$O$_2$ and NaOH. Where Fe is to be determined an acid flux should be used and separate crucibles should be reserved for this purpose. Alternate ignitions and pyrosulphate fusions can be used to remove Fe from contaminated crucibles. Pt crucibles are attacked least when they possess a fine crystal structure. 5% Au-Pt crucibles, whilst at least as resistant to attack and to Fe absorption, are less deformable than Pt. The interference of dissolved Pt on the subsequent determinations of SiO$_2$, Al$_2$O$_3$, Fe, Ti, Ca, and Mg was investigated.
HETEROGENEOUS CATALYSIS

The Mechanism of Isomerisation of Aliphatic Hydrocarbons at a Platinum Surface

A model for C4 and C6 alkane isomerisation on Pt provides more detailed interpretation of C18-labelled n-butane results by proposing that the surface precursor is 1,3-diadsorbed with a double bond to the surface of a C atom and that isomerisation occurs by its transformation to a bridged structure. Energy considerations show that isomerisation will occur when there is partial electron transfer from the hydrocarbon residue to the surface metal atom.

On the Activation Energy of Adsorption Catalysts
Pt atoms in Pt black have 130 times the activity of those on Al2O3 and 140 times the activity of those on SiO2. Active centres on SiO2 are 22 Å apart and Pt atoms therefore transmit energy rather better during highly exothermic reactions. Active centres on Al2O3 are 51 Å apart, energy transmission is weaker and the activity of Pt on it is less. When only small amounts of Pt are present on the supports, their specific activities are similar because the active centres are far apart.

Deuterium Exchange between n-Hydrocarbons on a Pt/Al2O3 Catalyst
D. GELBIN and E. WILDE, Chem. Tech., 1967, 19, (8), 480-483
Rapid deuteration of n-C4H10 and n-C6H13 occurs on Pt/Al2O3 at 60°C but no exchange occurs between deuterated and non-deuterated hydrocarbons at this temperature. Exchange is apparent between deuterated butane and both n-C4H10 and n-C6H13 at 300°C. The rate of exchange increases with the pressure of hydrocarbon. γ-Al2O3 alone cannot activate the exchange under these conditions. The dissociative adsorption model of the exchange reaction is confirmed.

The Dehydrogenation of Decalin. Effect of Reaction Variables on Selectivity and Catalyst Stability
Good stability of Pt/Al2O3 catalyst in the vapour phase dehydrogenation of decalin was favoured by high pressure, high conversion and low temperature. Practical grade decalin gave better stability than pure grade. The two-stage process had tetralin as an intermediate product. Selectivity for naphthalene occurred at high temperature, high conversion and low pressure. cis-Decalin was more reactive than the trans species and cis→trans isomerisation occurred during dehydrogenation, but no trans→cis conversion.

Isomerisation and Transmethylation over Platinum-on-Silica Catalyst
Isomerisation of 1-methyl-2-ethylbenzene and n-C6H13 over Pt/SiO2 proceeded via cyclic intermediates to give n-propylbenzene and 3-methylhexane respectively. A new type of transmethylation equivalent to the reverse of hydrogenolysis formed small amounts of dimethylbenzenes, cymenes, methyl-n-propylbenzenes, and diethylbenzenes from methyl-ethylbenzene.

The Structure and Activity of Supported Metal Catalysts. II. Crystallite Size and CO Chemisorption on Platinum/Silica Catalysts
X-ray and micrographic measurements on the structure of Pt/SiO2 catalysts gave results for crystallite size and proportionality of Pt area to (weight Pt) 2/3 which suggest that a fixed number of crystallites increase in size with Pt content—this number depending on the pore structure of the SiO2. Ratios of (Pt atoms exposed)/(CO molecules adsorbed) vary from ~1 to ~2. CO coverage of Pt depends on crystallite size and the number of CO molecules adsorbed, calculated from Pt crystallite size distribution, agrees with experiment.

Modification of Raney Nickel Catalysts by Additions of the Transition Metals. VII. Electrooxidation of Hydrogen and Catalytic Hydrogenation on Raney Nickel-Palladium Alloys
Raney catalysts were prepared from Ni-Pd-Al alloys containing 50 wt.% Al. Isothermal annealing of the original alloys increased the activity of the catalysts and altered the relation of the reaction rate to the promoter content. Changes of the composition and kinetics of the catalysts indicated that Pd increased their lattice parameters. The effect of electron structure on catalytic activity was studied for the Ni-Pd alloys.

The Parahydrogen Conversion on Palladium-Silver Alloy Films
Studies of the para-ortho H2 conversion on evaporated films of 50, 70, 80 and 100% Ag-Pd at 273-413 K indicated that activation energy for the process increased with Ag content, especially between the 50 and 70% Ag-Pd alloys.

Platinum Metals Rev., 1968, 12, (1)
The Oxidation of Ethylene over Evaporated Palladium-Silver Alloy Films. I. Film Structure and Stability under Reaction Conditions
Electron micrographs of evaporated Ag-Pd films showed extensive coalescence of crystallites in Ag-rich films but a compact mass of small crystallites in Pd-rich films. After use in C,H4 oxidation, Ag-rich films remained homogeneous but Pd-rich films behaved like Pd-Ag-H alloys with α and β phases apparently present. The deviation of the lattice constant from expected values then correlated with the O2 used from the reaction mixture. Pure Pd films always gave the bulk lattice constant but films with less than 1% Ag were apparently well charged with H2 after reaction. At 250°C, O2 can cause some separation of the alloy into its component metals.

Active Centres in Cyclohexene Disproportionation on Supported Palladium
Kinetic studies of the disproportionation of cyclohexene to C6H6 and C7H8 at 50–50°C by feeding cyclohexene in He over samples of highly dispersed Pd on Al2O3 showed that catalyst activity maxima correspond to particular values of %Pd on the support. Statistics on Pd atom distribution on the catalyst surface indicate that these maxima are related to the probability of formation of particular atomic clusters as active centres.

The Low Temperature Oxidation of Ammonia over a Supported Ruthenium Catalyst
Oxidation kinetics of NH3 and O2 over 0.5 wt.% Ru/Al2O3 as 0.318 cm pellets were studied in a stirred flow reactor at 246–365°C, 176–280 cm Hg. Rates of formation of N2 and NO depend on PNH3, PO2, and PH2O but are independent of PNH3 and P2O5. Equations are developed for both these rates and the stages of reaction are discussed.

Polyethylene Synthesis from Carbon Monoxide and Hydrogen on Ruthenium Catalysts. Part 10. On the Importance of Catalyst Pretreatment and Carbonyl Formation for the Conversions
The sizes of polymeric paraffins are greater when the synthesis temperature is lower, but at low temperature and high pressure, besides the alkylruthenium carboxyls, which have possible importance as reaction intermediates, both volatile and heavier Ru carbonyls are formed, which deactivate the RuO4 catalyst for reduction. To reduce Ru carbonyl formation and improve catalyst activity, reduction by H2 is recommended. The Ru carbonyls were isolated and identified as containing Ru3(CO)12, Ru carbonyl hydrate and alkylruthenium carbonyl.

The Oxidation of Cyclobutanals and Aromatic Rings with Ruthenium Tetroxide
The first oxidations by RuO4 of cyclobutanals to cyclobutanones and of benzene rings to carbonylic acid groups are reported. 3-Phenylcyclobutane-carboxylic acid was oxidised to cis-1,3-cyclobutanedicarboxylic acid, and cis-2-phenylcyclobutane-carboxylic acid to cis-1,2-cyclobutanedicarboxylic acid. Ethyl 3-hydroxycyclobutane-carboxylate was oxidised to ethyl 3-ketocyclobutane-carboxylate with 78% yield. p-tert-Butylphenol was oxidised to pivalic acid, and phenylcyclohexane to cyclohexanecarboxylic acid.

Interaction of Hydrogen and Carbon Monoxide on Platinum Group Metals
Studies of CO-H2 mixtures on unsupported metals at 100–200°C showed that CO is adsorbed on Pt and that the chemisorbed CO could not be removed completely by reduction and evacuation at 150°C. On Rh or Ir the gases interacted somewhat and some CH4 was detected at 200°C. On Ru, chemisorbed CO was removed completely by reduction and evacuation at 150°C, H2 adsorption was enhanced by CO, and CH4 formed appreciably above 250°C; activation energies for reactions between CO and H2 or D2 were ~9 kcal/mole. Higher specificity of Ru for the methanation reaction is due to its lower affinity for CO.

Catalytic Hydrogenolysis of Ethane over the Noble Metals of Group VIII
Kinetic studies of hydrogenolysis of C2H6 over 5–10 wt.% Ru, Rh, Pd, and Ir on SiO2 show that the order of catalytic activities is Ru>Rh>Ir>Pd. The rate of hydrogenolysis decreased strongly with increasing H2 pressure. Extensive dissociation of C-H bonds in the C2H6 molecule occurs during the initial chemisorption step. Catalytic activities are compared with those of Fe, Co, and Ni.

The Role of Hydrogen in the Configurational Isomerisation of Dialkylecycloalkanes in the Presence of the Noble Group VIII Metals
Configurational isomerisation of 1,2-dialkyl-
cyclopentanes and of 1,3-dimethylcyclohexanes on C-supported Pt metals does not proceed without free H₂. The activity of Pt/C and Pd/C decreases steadily in He-H₂ mixtures up to high He concentrations; only C₂H₂, C₃H₆, C₄H₈ and Ru/C lose considerable activity even at low He concentrations. Activity is restored only after heating in a stream of H₂.


The reactions of Si-H bonds with nonhydroxyl compounds containing active H were studied over Pd/AI₂O₃, Rh/Al₂O₃, Pd/C, Pt/C, Rh/C, Ru/C and Raney Ni, and provide quick, convenient preparations of silylamines, silanethiols and halosilanes.

**HOMOGENEOUS CATALYSIS**

Homogeneous Catalysis by Noble Metal Salts. II. Isomerisation of 1-Pentene by a Platinum(II) – Tin(II) Complex


In the presence of H₂ and a Pt(II) – Sn(II) complex at room temperature, 1-C₅H₁₀ isomerises to a 2-C₅H₁₀ mixture containing 85% trans isomer and more at lower temperature. The slow rate of hydrogenation is proportional to 1-C₅H₁₀ concentration; virtually no hydrogenation occurs with cis-2-C₅H₁₀. Styrene is hydrogenated slowly. Isomerisation and hydrogenation rates are maximum when Sn:Pt is ~1.2. The mechanism is 1-C₅H₁₀ addition to a hydride formed from H₂ and trans-[Pt(SnCl₃)₂Cl₂].

Homogeneous Hydrogenation Using Platinum-Tin Complexes

H. VAN BEKKUM, J. VAN GOGH and G. VAN MINNEN-PATHUS, Ibid., 1967, 32, (8), 292-294

Complexes prepared from H₂PtCl₆ and SnCl₂ are efficient catalysts for the hydrogenation of cyclohexene provided that the Sn:Pt ratio is right, that extra Cl or Br is added, and that solvents other than CH₃OH are applied. Results are tabulated and discussed.

Homogeneous Hydrogenation with Platinum-Tin Chloride Complexes as Catalysts

L. F. VAN'T HOF and B. G. LINSEN, Ibid., 1967, 32, (8), 295-297

In solvents other than CH₃OH or its homologues, the complex of H₂PtCl₆·6H₂O and SnCl₂·2H₂O catalyses homogeneous hydrogenations at atm. pressure and room temperature. Aliphatic carboxylic acids and their esters are suitable solvents, e.g. 1-hexene is hydrogenated in glacial CH₃COOH. The effects of reaction temperature, Sn:Pt ratio, and substrate and catalyst concentrations have been studied. Unsaturated edible oils can also be hydrogenated with this catalyst system, e.g. soya bean oil has been hydrogenated in CH₃COOH and shows preferential hydrogenation of linoleic acid.

Homogeneous Catalysis in the Reactions of Olefinic Substances. IX. Homogeneous Catalysis of Specific Hydrogenation of Polyolefins by Some Platinum and Palladium Complexes


The mechanism of hydrogenation of nonaromatic polyolefins catalysed by [MX(QPh₂)] or [PrX₆(O)] (where M = Pt or Pd, X = halide, Q = P or As when n = 3 and S or Se when n = 2, Ph = phenyl, Ol = bidentate diene), is described. The double bonds migrate stepwise to conjugation, the conjugated diene is then hydrogenated to the monoene, and the monoene when catalysed causes isomerisation by double bond migration. Reaction intermediates are reported. Effects of solvent, nature of the olefin and the catalysts, and other related effects were studied.

Oxidation of Olefins by Palladium(II). III. Oxidation of Olefins by a Combination of Palladium(II) Chloride and Copper(II) Chloride in Acetic Acid

P. M. HENRY, J. org. Chem., 1967, 32, (8), 2575-2580

PdCl₂-CuCl₂ in CH₃COOH oxidises olefins to acetate esters of glycol and chloride alcohols. C₃H₆ oxidised in solutions with high Cu(II) content forms 2-chloroethyl acetate, and ethylene glycol mono- and di-acetates, rather than vinyl acetate. Distributions of products of C₅H₁₀ and 1- and 2-C₅H₁₀ are reported. Oxypalladation adducts act as intermediates in these reactions and decompose by reaction with CuCl₂. Product distribution is explained by isomerisation of the oxypalladation adduct before reacting with Cu(II).

Oxidation of Cyclohexene by a Mixture of PdCl₂ and CuCl₂ in Acetic Acid


Experiments showed that saturated disubstituted cyclohexanes (esters) were formed by oxidation only when both PdCl₂ and CuCl₂ were present in the reaction mixture; 2- and 3-cyclohexenyl-1-acetate were found in the absence of Cu(II). Saturated esters were mainly 1,2 isomers, chloroacetates were both cis and trans isomers, 1,2 and 1,3 diacetates were the cis isomers. The mechanism involves an oxypalladation adduct as intermediate which eliminates Pt(II) hydride to give unsaturated esters and which reacts with CuCl₂ to give saturated esters. Isomerisation of the intermediate leads to the product isomers.
A Catalyst for the Homogeneous Hydrogenation of Aldehydes under Mild Conditions
Whereas RhCl(PPh3)3 is deactivated by aldehydes, IrH2(PPh3)3 catalyses homogeneous hydrogenation of aldehydes and some olefins at 50°C, 1 atm, e.g. n-butyraldehyde to n-butanol, in CH2COOH solution. Ir hydrido-acetates are assumed to be the true catalysts in this reaction.

The Decomposition of Formic Acid Catalysed by Soluble Metal Complexes
Ibid., 923-924
Many phosphine-stabilised complexes of transition metals, particularly of Ir and Ru, are excellent homogeneous catalysts for decomposition of HCOOH to H2 and CO, and functional groups can also be reduced. Results for six catalysts are tabulated and discussed.

GLASS TECHNOLOGY
Wetting Behaviour of Glasses on Pt and Pt Alloys
R. KATZSCHMANN, Silikat Tech., 1967, 18, (7), 211-214
Dynamic methods were used to study the wetting behaviour of Pt, 5% Au-Pt, 5% Ir-Pt, 5% Rh-Pt, and a Be-Pt alloy at 400–1400°C with a heating rate of 10°C/min, on five types of glass. Contact angles are plotted and the results are discussed.

NEW PATENTS
METALS AND ALLOYS
Iridium Alloys
INTERNATIONAL NICKEL LTD.
British Patent 1,082,078
The addition of 0.1–2% Nb to an Ir of commercial purity produces easily workable alloys.

CHEMICAL COMPOUNDS
Metalloccenyl Organopolysiloxanes
GENERAL ELECTRIC CO. (NEW YORK)
U.S. Patent 3,324,157
Highly stabilised organopolysiloxanes are produced by the usual cohydrolysis method where one hydrolysable monomer is a metalloccenyl silane, where “metalloccenyl” is a residue of a cyclopentadienyl derivative of a transition metal. The Pt group metals are specifically mentioned.

TEMPERATURE MEASUREMENT
Platinum Resistance Thermometry below 10°K
An assessment of Pt resistance thermometers at 2–10°K, based on sensitivity, stability and ease of calibration, concludes that their overall accuracy in this range is 0.03–0.05°K, when used in a fairly convenient manner, and 0.01°K, when great care is taken.

Birdcage Resistance Thermometer
A Pt resistance thermometer of “birdcage” construction was tested as a possible instrument for defining the IPTS scale and measured the gold point (1063°C) to ±0.001°C.

High-temperature High-vacuum Thermocouple Drift Tests
Stability of ±10°C for 1000h at 10^-6–10^-8 torr, 1200–1450°C was found for Pt : 10% Rh-Pt, 6% Rh-Pt : 30% Rh-Pt, W : 26% Re-W and 5% Re-W : 26% Re-W thermocouples but at 1200°C severe thermal emf changes occurred with Pt : 10% Rh-Pt in Ta and Nb.

ELECTROCHEMISTRY
Anodes and Electrolytic Cells having Such Anodes
IMPERIAL METAL INDUSTRIES (KYNOC) LTD.
British Patent 1,076,973
A coated anode is formed from a plurality of Ti members placed side-by-side with each member coated with a Pt metal. The members are connected together by at least one transverse rib.