BuOO-*t*-Bu). However, intermediate peroxides (diacyl peroxides and peresters) could only be qualitatively differentiated from either of the other two types. For reactions where appropriate, the aqueous and organic layers were separated and titrated for peroxide separately. When the reaction was judged complete, usually by cessation of gas evolution and/or complete disappearance of the yellow superoxide color, water or dilute HCl was injected into the mixture and any additional gas evolution noted. For reactions which seemed likely to produce gas other than oxygen, gas samples from the gas buret were withdrawn by syringe and analyzed by gas chromatography. It was found that suspensions of superoxide in benzene/crown ether prepared in this way were quite stable over the time periods studied in this work; less than 10% of the original superoxide had disappeared after 24 h. Because of the relative volumes of the apparatus, gas solubility, etc., gas evolution measurements are believed to be accurate to no better than 10–15%. Some specific experimental procedures are described below as typical examples.

Reaction of Superoxide with H_2O_2. To a stirred suspension of 1.96 mmol of KO_2 in 10 mL of 0.1 M 18-crown-6 ether in benzene was added 2.02 mmol of "98%" H_2O_2 in 1 mL of dioxane over a 10-min period. At the end of this time, gas evolution slowed and the mixture was white. Over the next 45 min, the rate of O_2 evolution increased, and the mixture turned yellow and then faded back to white as gas evolution ceased completely. Total O_2 yield was 2.21 mmol and titration showed that no peroxidic material remained.

Reaction of Superoxide with *t*-BuOOH. A solution containing 4.0 mmol of *t*-BuOOH in benzene was added over 20 min to a mixture of 2.07 mmol of KO_2 in benzene containing 18-crown-6. After 20 min of stirring, the mixture was white, 1.31 mmol of O_2 had been evolved, and titration showed 3.96 mmol of total peroxidic material.

Reaction of Superoxide with Benzoyl Peroxide in the Presence of Cyclohexene. A mixture containing 2.0 mmol of KO_2, 1 mL of cyclohexene, and 6 mL of 0.1 M 18-crown-6 ether in benzene was stirred vigorously, and then 2.0 mmol of benzoyl peroxide in 3 mL of 0.1 M 18-crown-6 ether in benzene was added by syringe. Gas evolution began immediately and was complete within 20 min, whereupon 1.3 mmol of O_2 had been evolved. Gas chromatographic analysis of the final solution showed the presence of 0.28 mmol of cyclohexene oxide.

Reaction of Superoxide and Acetic Anhydride with Tetramethylethylene. Acetic anhydride (2.0 mmol) was injected into a mixture containing 4.0 mmol of KO_2, 9 mL of 0.1 M 18-crown-6 in benzene, and 1 mL of tetramethylethylene. Gas evolution began immediately; after 15 min, 0.75 mmol of O_2 had been evolved, and GC analysis showed the formation of 0.98 mmol of tetramethylethylene oxide. After 1 h, 1 mmol of O_2 and 1.15 mmol of epoxide were observed and after 2 h the reaction was apparently complete with the evolution of 1.25 mmol of O_2 and the formation of 1.37 mmol of epoxide. A trace of acetone was also detected by GC.

Registry No. KO_2, 12030-88-5; H_2O_2, 7722-84-1; *t*-BuOOH, 75-91-2; $(PhCO_2)_2$, 110-22-5; AcOAc, 108-24-7; H_2O, 7732-18-5; CH_3CO_3H, 79-21-0; $(PhCO)_2O$, 93-97-0; LPO, 2388-12-7; cyclohexene, 110-83-8; TME, 563-79-1; styrene, 100-42-5; 1-octene, 111-66-0; 1,2-dimethylcyclohexene, 1674-10-8; TME epoxide, 5076-20-0; cyclohexene epoxide, 286-20-4; styrene epoxide, 96-09-3; 1-octene epoxide, 2984-50-1; 1,2-dimethylcyclohexene epoxide, 17612-36-1; KOH, 1310-58-3; O_2, 7782-44-7; CH_3CONH_2, 60-35-5; *t*-BuOH, 75-65-0.

Hydrogenation with Anthranilic Acid Anchored, Polymer-Bound Nickel Catalysts

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A Ni^{II} polymer-bound catalyst was prepared by anchoring anthranilic acid to chloromethylated, highly crosslinked polystyrene beads and then equilibrating with $NiCl_2 \cdot 6H_2O$. By treating this catalyst with sodium borohydride, a second catalyst was prepared. Both nickel catalysts are active in the hydrogenation of alkenes and dienes and in the reduction of nitrobenzene. The structures of the catalysts were probed by XPS studies.

The literature of hydrogenation with homogeneous nickel complexes, in contrast to that of second row group 8 metal complexes, is relatively limited and reflects the modest hydrogenation activity of all first-row transition-metal complexes. The nickel complexes receiving attention may be grouped into rather general categories: Ni^{II} complexes activated with an alkylaluminum (Ziegler),[1] Ni^{II} complexes,[2] borohydride-activated species,[3] $Ni_2(CN)_6^{4-}$,[4] and the nickel phthalocyanines.[5] Alkenes, dienes, alkynes,

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Table I. Hydrogenation with Nickel(II) and Nickel-Borohydride Catalysts at 100 °C

substrate (amt, mmol)	amt Ni, mmol	t, h	pressure, psig	products (% yield)
1-hexene (100)	0.015	20	1000	hexane (10), 2-hexene (20)
1-hexene (100)	0.20	3	1000	hexane (77), 2-hexene (11)
cyclohexene (100)	0.015	20	1000	cyclohexane (2)
cyclohexene (100)	0.20	15	1000	cyclohexane (70)
1,5-cyclooctadiene (100)	0.030	15	1000	cyclooctane (trace), cyclooctene (48), 1,3-cyclooctadiene (36), 1,4-cyclooctadiene (8)
1,5-cyclooctadiene (100)[a]	0.030	12	1000	cyclooctane (56), cyclooctene (44)
isoprene (100)	0.030	15	1000	70% monomeric products: isopentane (40), 2-methyl-2-butene (55), 2-methyl-1-butene (15); 30% oligomers: 60% at bp 80-190 °C (2 mm), 40% residue
isoprene (100)[a]	0.030	15	1000	95% monomers: isopentane (90), methylbutenes (10)
benzene (100)	0.030	30	2000	no hydrogenation
benzene (100)[a]	0.030	30	2000	no hydrogenation
corn oil (10 g)	0.030	3	1000	21% hydrogenation
nitrobenzene (250)	0.20	14	1000	see text
nitrobenzene (250)[a]	0.20	14	1000	see text

[a] "Reduced nickel" catalyst.

and vegetable oils have been hydrogenated.

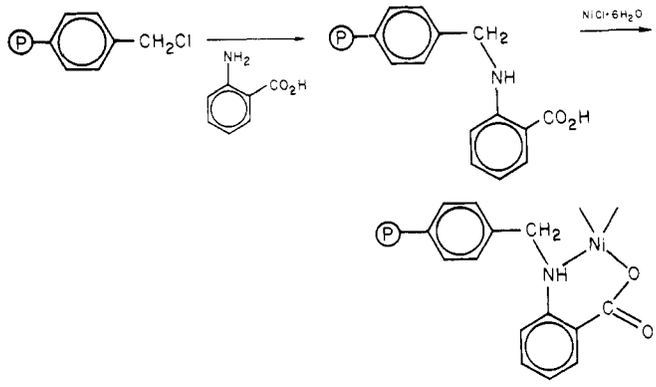
Hydrogenation studies using polymer-bound nickel catalysts are even more limited than those of homogeneous nickel catalysts. Catalysts are prepared by treating a supported nickel complex with borohydride[6] or an alkylaluminum.[7] The only report in which Ni^{II} was used without an activating agent involved anchoring $NiCl_2$ to calcined polyacrylonitrile, but this catalyst was then heated to 300 °C in the presence of hydrogen, conditions favoring formation of metal.[8] Hydrogenation studies with these catalysts have been limited to alkenes and alkynes.

Previously, these laboratories have been concerned with an investigation of the characteristics of anthranilic acid anchored, polystyrene (Rohm and Haas, XAD-4) catalysts, using rhodium and palladium.[9] The high activity of the palladium catalyst suggested that the analogous nickel polymer might demonstrate reasonable activity, and because of the lower cost of nickel and its lesser tendency in homogeneous catalysts to cause olefin isomerization, it was considered that polymer-bound nickel merited examination.

Experimental Section

The polystyrene beads (Amberlite XAD-4) were a gift of the Rohm and Haas Co. They are hard, insoluble 20–50-mesh macroreticular spheres (crosslinking > 50%, exact degree proprietary) and were cleaned by a procedure described by Frechét:[10] the cleaning is necessary to avoid fragmentation of the beads either during the anchoring of anthranilic acid or the hydrogenation. Chloromethylation was carried out for 0.5 h according to the procedure of Pepper et al;[11] the chlorine content was 1.90% (0.54 mequiv/g). Anthranilic acid was anchored to the beads by refluxing 10.0 g of the chloromethylated beads with 5.0 g of anthranilic acid in 50 mL of ethanol for 20 h, filtering, and washing with several portions of ethanol. The beads were stirred with 10% aqueous KOH for 1 h, filtered, washed with water, triturated several times with water, and finally filtered and washed with water and ethanol. Anal.: Cl, 0.60 (0.17 mequiv/g); N, 0.46 (0.33 mequiv/g). The beads were stirred with 2.50 g (10.5 mmol) of $NiCl_2 \cdot 6H_2O$ for 24 h in 50 mL of ethanol, filtered, washed with ethanol and water, triturated with water and ethanol, filtered, and air-dried for 2 days. Anal.: Ni, 1.36 (0.23 mequiv/g); N, 0.30 (0.28 mequiv/g); Cl, 1.16 (0.33 mequiv/g).

Scheme I



Except for isoprene and 1,5-cyclooctadiene, which were distilled immediately prior to use, reagent-grade chemicals were employed in the hydrogenations without purification. For the hydrogenations, the neat reactants were added to the 300-mL reaction vessel of an Aminco shaking assembly (catalogue no. 44-13106), the reaction vessel was flushed four times with hydrogen, and the reactor was partially pressurized and then heated, with shaking, to the desired temperature. The pressure was then adjusted to the desired level. The reactions were not considered to have begun until the system was at the desired temperature and pressure, and all reaction times were measured from this point. The products were analyzed on a 6 ft × $^1/_4$ in., 10% Carbowax column and/or isolated by distillation and identified by IR and ^{1}H NMR.

The "reduced" nickel catalyst was prepared by stirring a portion of the Ni^{II} catalyst with an excess of $NaBH_4$ in ethanol for 1 h, filtering, and washing thoroughly with ethanol. Anal.: Ni, 1.50 (0.26 mequiv/g); N, 0.42 (0.30 mequiv/g); Cl, 1.25 (0.35 mequiv/g); B, 0.32 (0.30 mequiv/g).

Results and Discussion

Bead Preparation. We have observed that if the beads are fragmented either during the course of anchoring the catalyst or during the hydrogenation, the catalytic activity is diminished or even terminated. This problem is avoided if the beads are cleaned prior to chloromethylation. Otherwise, the procedure for anchoring the nickel catalyst is similar to those we have reported previously and involves chloromethylation, anchoring of anthranilic acid and then Ni^{II} (Scheme I). In the following discussion catalyst 1 shall

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Table II. XPS Study of the Unused Ni^{II} Catalyst

	etch time,[a] min			
	0	2	4	15
Ni	857.0	853.4	853.6	853.5
Cl	200.0	199.6	199.5	198.8
N	400.4	399.8	400.0	~399.5
O	532.3	532.3	532.6	532.0
C	285.0		285.0	285.0

[a] Etching energy = 1 keV. Energies in eV.

be referred to as the "Ni^{II} catalyst".

Our studies have also dealt with a second catalyst, one derived from the Ni^{II} catalyst. This is a "reduced" nickel catalyst that is prepared by treating the Ni^{II} catalyst with an excess of sodium borohydride. Upon addition of borohydride, the beads immediately turn black.

Hydrogenation Studies. In Table I are summarized the results of the hydrogenation of a variety of compounds. Both the Ni^{II} and "reduced" catalysts are effective, with the functionalities typically hydrogenated by homogeneous nickel complexes. Neither catalyst is exceptionally active, and both require some heating and reasonably high pressure for catalysis. It is also clear that each catalyst differs somewhat in its activity. These differences are most evident with isoprene. The Ni^{II} catalyst effects oligomerization, hydrogenation, and isomerization. The "reduced" nickel catalyst forms little oligomer. Also, the reduced nickel catalyst is more active toward simple olefins, as illustrated by the high degree of conversion of 1,5-cyclooctadiene to cyclooctane, while the Ni^{II} catalyst produces almost no saturated alkane; this is the major product with the reduced catalyst.

The data in Table I demonstrate that neither catalyst displays activity with benzene. Nitrobenzene is not cleanly reduced to aniline. Hydrogenation of nitrobenzene with the Ni^{II} catalyst produces water and a sticky amorphous solid which was partially soluble in acetone and, by GLC, contained a low percentage of aniline. By TLC several products were evident, though there was no indication that either azo- or azoxybenzene were among them. The reduced nickel catalyst gave the same gross analysis, a low yield of aniline, many products, and no azo- or azoxybenzene, but differed to the extent that the products were liquid.

Longevity. The lifetime of the catalyst is rather short, compared to others we have investigated and to many phosphine catalysts. The activity after 900 turnovers in the 1-hexene hydrogenation was approximately 10% of the original.

Elemental analysis revealed that the nickel content had fallen by 36% (from 1.36 to 0.87%), and the chlorine content had dropped 92% (from 1.16 to 0.09%). Thus, the falloff in activity more closely parallels the loss of chloride than nickel. Mechanistically one cannot draw firm conclusions from this, however, because it could be a coincidental relationship.

XPS Studies. Examination of the Ni^{II} catalyst by X-ray photoelectron spectroscopy reveals that the oxidation state of the nickel at the surface of the beads is +2. This is not surprising since Ni^{II} was placed on the beads under conditions in which reduction would be extremely unlikely. The signal after argon etching looks markedly different and occurs at 853.6 eV, or approximately between the energies of Ni^{2+} (~855) and nickel metal (852.8).[12] It is possible that this represents Ni^{1+} or Ni^0. It is considered that the Ni^0 oxidation state is more likely because the Ni spectrum observed is stable under repeated etchings (Table II). This behavior would appear to be unlikely for the normally unstable Ni^{1+}. The shift of Ni^0 to a higher binding energy position would suggest the presence of small nickel particles which would reduce the nickel interatomic relaxation energy.[13] In view of the aforementioned mild conditions for introduction of the metal, the etching process itself is considered responsible for the reduced metal. Low ionicity peaks are indicated for Cl, N, and O.

A sample of once-used catalyst was also examined, and this material behaved very much like the unused catalyst. The nickel at the surface was clearly in the Ni^{2+} state.

In the "reduced" catalyst it was not possible to make a clear distinction between nickel(I) and metallic nickel. The boron in the sample appears to be highly charged.

Registry No. 1-hexene, 592-41-6; cyclohexene, 110-83-8; 1,5-cyclooctadiene, 111-78-4; isoprene, 78-79-5; benzene, 71-43-2; nitrobenzene, 98-95-3; hexane, 110-54-3; 2-hexene, 592-43-8; cyclohexane, 110-82-7; cyclooctane, 292-64-8; cyclooctene, 931-88-4; 1,3-cyclooctadiene, 1700-10-3; 1,4-cyclooctadiene, 1073-07-0; isopentane, 107-83-5; 2-methyl-2-butene, 513-35-9; 2-methyl-1-butene, 563-46-2; anthranilic acid, 118-92-3; Ni^{II}, 14701-22-5.

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