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The Racemization and Reduction of Optically Active 1,1′-Binaphthyl by Raney Nickel Catalysts

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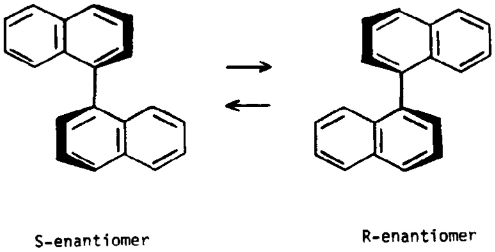
Raney nickel catalyzes the racemization of (*R*)- or (*S*)-1,1′-binaphthyl in heptane at 25°C and reduces it, via three successive intermediates, to 5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl. Treatment of catalyst preparations with relatively small amounts of sulfur or dodecanethiol poisons the reduction reaction; increasingly larger amounts stop the racemization and finally prevent adsorption of binaphthyl on the Raney nickel. After an initial period of slow adsorption, which can be eliminated by pretreatment with optically inactive binaphthyl, the racemization is first order in binaphthyl. Unfortunately, variations arising from preparation, transfer, and poisoning of catalyst preparations prevented systematic comparisons of rate constants. It is suggested that two different sites are responsible for the two different types of reaction (racemization and reduction) observed. Electron donor sites on Raney nickel, rather than hydrogen atom donor sites, are likely involved in the catalytic racemization reaction.

INTRODUCTION

The interconversion of the two enantiomeric forms of binaphthyl occurs by rotation around the central 1–1′ bond joining the two aromatic units. This sterically hindered process is slow in homogeneous solutions but can be rapid when catalyzed by various carbon blacks (*1*). The reaction presents an unusual example of heterogeneous catalysis of bond rotation with no further change in the molecule occurring.



Some kinetic characteristics of the catalyzed reaction, especially the effects of substituents in the 4 and 4′ positions, as well as observed catalysis by potassium-graphite compounds and by solvated electrons, indicate that a reversible electron donation from the surface of the carbon catalyst to adsorbed binaphthyl occurs in the racemization process (*2*). Metallic hydrogenation catalysts, such as Raney nickel, are normally associated only with a process of overall hydrogen atom donation rather than solely with electron transfer. However, electron transfer, as well as hydrogen atom transfer capabilities, might be present with some heterogeneous hydrogenation catalysts.

It was therefore of interest to investigate the possibility that Raney nickel could catalyze the racemization of optically active 1,1′-binaphthyl. When catalytic racemization as well as reduction was observed, it was of concern to determine, by poisoning experiments, whether or not the racemization capability is distinctly separate from the well-known capability of Raney nickel to reduce aromatic hydrocarbons.

EXPERIMENTAL

1,1′-Binaphthyl was synthesized by the method of Sakellarios and Kyrimis (*3*) and resolved by the solid-state method (*4*).

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Gas–liquid chromatographic (GLC) analyses of binaphthyl concentrations were carried out using a Hewlett–Packard 5803A flame ionization chromatograph with a 3% OV-17 on Chromosorb WAW-DMCS, 80/100 mesh, column. Changes in concentrations were measured by the method of internal standards. A fresh solution of 4,4′-dimethyl-1,1′-binaphthyl (DMB) was made up at a concentration approximately equal to the initial concentration of 1,1′-binaphthyl. DMB has a retention time sufficiently different to permit resolution of the response peaks. Filtered reaction solutions were mixed 1:1 with 100 μl of the DMB solution using a 100-μl Eppendorf pipet. Following GLC analysis, relative concentration changes were determined as changes in the ratio of peak area of the compound to DMB peak area. Optical rotations were determined on either a Perkin–Elmer 141 or 241 MC polarimeter using a 1-dm or 1-cm quartz-faced jacketted cell. Proton nuclear magnetic resonance spectra were recorded on a Bruker 270-MHz FT spectrometer; mass spectra on an Atlas CH-46 spectrometer.

Raney nickel catalyst was prepared by the widely used method given by Fieser and Fieser (*5*). Sodium hydroxide (20 g) was added to 75 ml of distilled water in a 250-ml beaker. The solution was stirred with a magnetic stirrer and maintained at 75°C. Nickel–aluminum alloy powder (15 g, Alfa Inorganics) was added over 30 min. A vigorous reaction ensued with each addition of alloy powder and the temperature was maintained between 70 and 90°C by use of a cold water bath. After all the alloy had been added, the suspension was allowed to cool to room temperature with stirring (45 min). The nickel was allowed to settle out, the milky aqueous phase decanted, and the nickel was rinsed to neutrality with distilled H_2O (8 to 20 liters). It was then rinsed three times with 100 ml EtOH and three times with 100 ml *n*-heptane, and stored in a sealed bottle under *n*-heptane. Batches of Raney nickel were used within 6 weeks of preparation. Sensitivity of this catalyst was shown, for example, when washing the catalyst with tap water rather than distilled water poisoned it for racemization and reduction, but not for adsorption.

For each batch of Raney nickel prepared, it had to be determined first whether that batch of catalyst was active toward reduction, racemization, and adsorption and second, what amount of poison was necessary to stop the individual processes. In the former case, 1.3 g of fresh Raney nickel slurry (total volume of 1 ml) was added to a pear-shaped flask fitted with an overhead bladed stirrer and nitrogen inlet. This was followed by 4 ml 5.0×10^{-3} *M* optically active binaphthyl ($[\alpha]_{589} = -132$). Stirring was begun and 10 sec later the $t = 0$ sample removed with a Pasteur pipet and filtered through a Swinny syringe filter. The solution was analyzed for optical activity and binaphthyl concentration. Other samples were removed periodically and analyzed in a similar fashion. GLC analysis showed the appearance of reduction products and a decrease in binaphthyl concentration. Polarimetric analysis showed a decrease in optical activity.

The amount of poison necessary to poison the individual processes was determined by trial and error. In general either dodecanethiol (Aldrich) or elemental sulfur (0.014 *M* in *n*-heptane) could be used as a poison. However, at high concentrations the thiol turned the reaction solution light brown and made polarimetric readings difficult. For this reason sulfur was used as poison whenever polarimetric analyses were to be performed.

For kinetic studies of racemization or adsorption the Raney nickel, in a stirred heptane slurry, was transferred with a wide-mouth Pasteur pipet into a three-neck pear-shaped or Morton (*6*) flask equipped with an overhead blade-type stirrer. All reactions were carried out under N_2 or Ar. In a typical adsorption study, 5.0 g of Raney nickel slurry (total volume = 4 ml) was rinsed into a 100-ml flask with 25 ml *n*-

heptane. The suspension was equilibrated at 7.0°C for ½ hr. Stirring was started and 65 μl of 5.0×10^{-3} M dodecanethiol in *n*-heptane was added dropwise over 2 min. The poisoned catalyst was used immediately by addition of 75 ml of a freshly prepared solution of binaphthyl. Poisoning the catalyst for a kinetic run was done in an identical manner but using the appropriate amount of poison required to only stop the reduction reaction.

Preparation of 5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl. Racemic binaphthyl (2.0 g) was dissolved in 250 ml spectrograde *n*-heptane and stirred under N_2. Approximately 10 g Raney nickel was added and the reaction was stirred under reflux for 2 weeks. During this time the binaphthyl was cleanly reduced through three intermediates (GLC analysis at 190°C) to give a final fourth product. The solution was then filtered, treated once with decolorizing Norit, and evaporated to dryness to give a clear oil. After 1 hr in an ice bath, crystals began to appear. They were recrystallized once from 100% EtOH to give 0.60 g (29%) clear prisms: mp 91.0–91.5; $[\alpha]_{365}^{23} = 0$; ir ($CHCl_3$) 2900 (C–H); mass spectrum parent peak *m/e* 262.

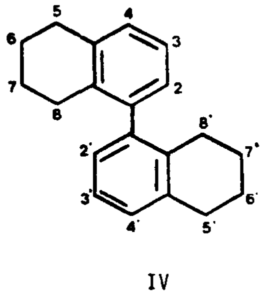
Anal. Calcd for $C_{20}H_{22}$: C, 91.55; H, 8.45. Found: C, 91.40; H, 8.65.

The proton-NMR spectrum of this compound in deuterochloroform showed protons for C2(2′), doublet (J = 7.5 Hz) at 6.88δ; C3(3′), two unresolved doublets (J = 7.5 and 7.5 Hz) at 7.11δ; C4(4′), doublet (J = 7.5 Hz) at 7.06δ; C5(5′), multiplet at 2.82δ; C6(6′) and C7(7′), broad multiplet 7.3δ. Because of a dihedral angle less than 180° at carbons 1 and 1′, and close proximity to the opposed aromatic rings, different chemical shifts occur for the two protons on C8(8′); these appeared as C8(8′)a two triplets (J = 18 Hz, J = 7.0 Hz) at 2.41δ and C8(8′)b as two triplets (J = 18 Hz, J = 7.0 Hz) at 2.18δ.

RESULTS

After addition of an optically active solution of binaphthyl to a stirred suspension of Raney nickel in *n*-heptane at 25°C the course of the reaction was periodically followed by polarimetry (decrease in optical activity) and by gas–liquid chromatography (decrease in concentration of binaphthyl and increase in reduction products). For example, with 0.025 M binaphthyl and a Raney nickel catalyst at 100 mg/ml, 95% of the initial optical rotation was lost in 115 min. At that time GLC analysis showed that 65% of the binaphthyl had disappeared and about 30% of this had been transformed to reduced products. Although adsorption and reduction of binaphthyl is therefore extensive at this high catalyst concentration, the loss in optical activity can not be accounted for by these processes alone. Since optical rotations of such solutions smoothly reach a final value of zero, the direct reduction of binaphthyl to an optically active product can also not account for rapid and complete loss of optical activity.

The actual sequence of product formation could be followed by GLC and is as shown in Fig. 1. Three transient intermediates, labeled **I, II,** and **III,** rise and fall in concentration. These were not isolated but the final product, compound **IV**, is an octahydro compound which was separately produced in a larger-scale reaction (see Experimental). The intermediates, **I, II,** and **III,** are very likely compounds corresponding to addition of 1, 2, or 3 mol of H_2 to the outer aromatic rings of binaphthyl as it is successively hydrogenated to yield **IV.** However, the sequential structures of these intermediates was not established.



IV

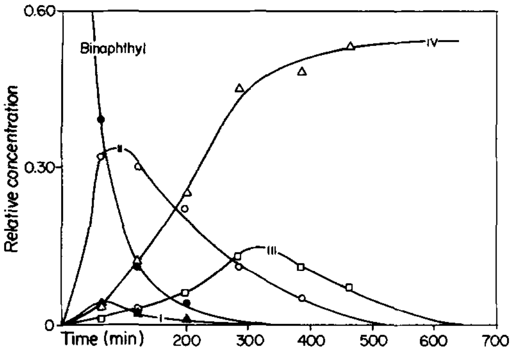


FIG. 1. Product distribution curves for the intermediates in the Raney nickel reduction of 1,1′-binaphthyl.

Since adsorption, racemization, and reduction of binaphthyl all occur on a Raney nickel catalyst, the question which arises is to what extent are these three types of surface effects related. One possibility is that a single type of site is responsible. On the other hand, the surface may have separate sites for reduction, racemization, and additional adsorption. This was investigated by poisoning experiments with elemental sulfur or dodecanethiol. For example, with 0.002 *M* binaphthyl and 50 mg/ml of catalyst in heptane at 25°C, a ratio of 6×10^{-3} mg of sulfur to 1 mg of catalyst completely eliminated the reduction reaction. However, a 68% loss of optical activity still occurred in 20 min. At a ratio of 19×10^{-3} only an 8% loss of rotation occurred in 20 min; a ratio of 25×10^{-3} prevented any observable adsorption as well as racemization. These ratios of sulfur to nickel are not the specific values required to achieve the effects given. Because of difficulties in preparing and handling the nickel suspension, it was not possible to reproduce the same catalytic activity in each new batch of nickel, nor even to obtain the same activity of catalyst in successive experiments. This was apparently due to uncontrolled but critical variations in the preparation, transfer, aging, and/or poisoning of the catalyst. Such features of heterogeneous catalysis are common, and Raney nickel perhaps especially variable (*5*, *7*), and made quantitative comparison of nickel catalysis impossible. Nevertheless, the sequence of poisoning effects was first on the reduction, then on the racemization, and finally on the adsorption. This was always the same sequence with various batches of catalyst.

The selective poisoning of the reduction reaction made it possible to kinetically study the racemization without interference from loss of binaphthyl through hydrogenation reactions. For an individual batch of Raney nickel, a trial and error determination (see Experimental) of the amount of sulfur necessary to stop the reduction was made. A kinetic run could then be carried out with poisoned catalyst, and at constant binaphthyl concentration, simply by analysis of the optical activity in filtered samples. Unfortunately, the difficulties mentioned above made it impossible to reproduce the same rate of racemization in any two runs. However, a number of generalizations concerning the kinetic results are still possible since over 30 runs showed the same qualitative features.

Figure 2 shows typical first-order kinetic plots for loss of optical rotation (α) in the presence of poisoned catalyst. Following an initial curved portion, the reaction shows first-order kinetic behavior. In some runs rate constants obtained from the straight line portion of the graph showed

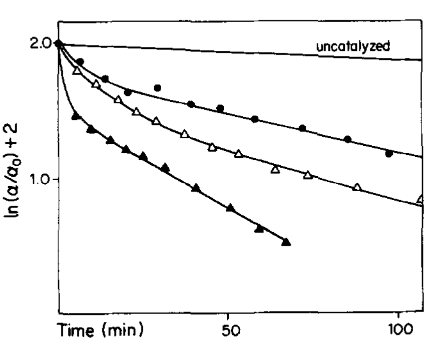


FIG. 2. First-order kinetic plots for the poisoned Raney nickel catalyzed racemization of binaphthyl in *n*-heptane at 25.0°C. Binaphthyl concentration 0.050 *M*. Relative concentration of Raney nickel 0.40 (●), 0.35 (△), and 0.30 (▲) in terms of milliliters of an initial catalyst preparation per milliliter of total volume.

rate enhancements of more than 10-fold over the uncatalyzed rate.

The initial curved portion of the kinetic plot is explained by reference to Fig. 3. Here the fraction of the total amount adsorbed (right axis, determined by GLC) is plotted along with the first-order kinetic data (left axis, determined by polarimetry). The curvature in the racemization plot stops at the same time that adsorption equilibrium is reached. In conjunction with these results, a suspension of catalyst which was pretreated with racemic binaphthyl before being used for a kinetic run with optically active binaphthyl gave a good first-order plot throughout the course of the run (see Fig. 4). In spite of attempts to carefully control the preparation, transfer, and treatment of the Raney nickel catalyst, the slopes of kinetic plots such as in Figs. 2–4 were erratic and even consecutively irreproducible. This unfortunately prevented investigation of how first-order rate constants varied with temperature, various additives or poisons, and concentration of substrate and catalyst.

Adsorption of binaphthyl on Raney nickel poisoned by dodecanethiol was also studied. As shown in Fig. 5 the rate of adsorption was measurably slow but subject to the same difficulties of irreproducibility. The character of the curves and the points in a run were reasonably consistent; the specific curves themselves were not. (For example, curves *a* and *b*, which are from otherwise identical runs, differ in both rate of adsorption and total amount of adsorption.) Again the problem seemed due to frustrating problems in preparing, handling, and poisoning the nickel catalyst.

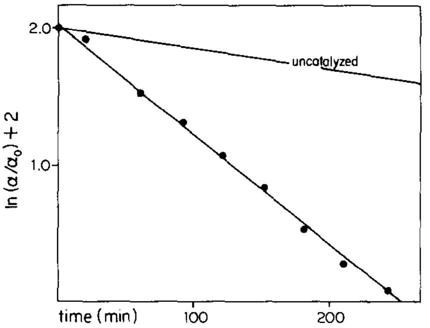


FIG. 4. The effect on the first-order kinetic plot of pretreating poisoned Raney nickel with binaphthyl [Binaphthyl] = 0.0025 *M*; [Ni] = 37.7 (mg/ml), temperature: 25.0°C.

DISCUSSION

Although quantitative kinetic studies of the adsorption, racemization, and reduction of binaphthyl were not possible, the qualitative aspects such as maxima in amount adsorbed (Fig. 5), first-order kinetic character in binaphthyl (Figs. 3 and 4), and sensitivity to additives such as sulfur or dodecanthiol, are consistent with an adsorption–desorption mechanism for racemization on active sites of the catalyst.

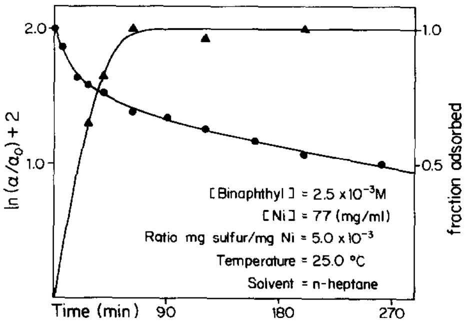


FIG. 3. First-order kinetic plot (left and ●) and fraction adsorbed (right and ▲) for the poisoned Raney nickel catalyzed racemization of binaphthyl.

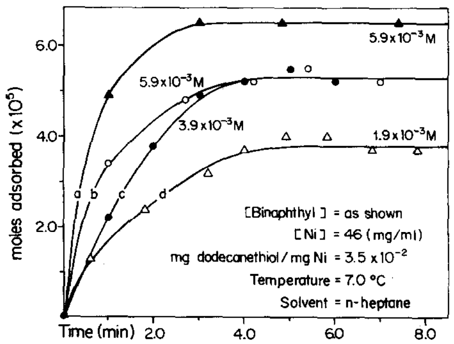


FIG. 5. Moles adsorbed versus times for the adsorption of binaphthyl on poisoned Raney nickel.

The initial adsorption observed (see Figs. 2 and 3) is relatively more difficult to poison than the reduction or racemization. This adsorption may actually be due to adsorption on aluminium oxides or other residues (*8*) which always accompany Raney nickel, rather than on the nickel surface itself (*9*). But since racemization of binaphthyl is not promoted by acids or bases (and not by alumina alone) the catalytic racemization, like the reduction, occurs on the nickel surface.

With regard to multiplicity of active sites, the progressive poisoning of reduction and then racemization, through pretreatment with increasing amounts of sulfur, could be ascribed to modification of the activity of a single type of site on the nickel surface. In principle at least, although difficult to visualize in practice, reaction with differing amounts of sulfur could modify the reactive ability of the single site.

On the other hand, the effects of sulfur may be ascribed to selective poisoning of two functionally different types of surface sites. Since racemization of binaphthyl seems to involve electron transfer (*2, 10*), one site would be an electron donor type; the other site would have hydrogen atom donor capabilities responsible for the reduction of binaphthyl to the octahydro compound **IV**.

It can be further suggested that the general hydrogenation ability of Raney nickel is due to the activity of both types of sites. The electron donor site would give the equivalent of hydrogen atom transfer, after a proton is subsequently transferred. In any case, toward binaphthyl as substrate, both types of activity seem indicated, with the hydrogen atom donating properties of nickel more easily poisoned than the electron donor properties. Following the patterns of some other studies of poisoning effects on catalytic activity (*11*), it seems mechanistically simpler to ascribe the observed effects of sulfur to more selective poisoning of two different sites on nickel rather than to modification of only one site. Multiple types of surface sites, with separate adsorption sites for different compounds, or different adsorption sites for a single compound are well established on metallic surfaces (*12*). Separate sites with different reactivities toward the same compound (as suggested here for binaphthyl on Raney nickel) seem less commonly observed (*13*).

Aside from the question of site multiplicity, the fact that catalytic racemization is found at all on a nickel catalyst requires a modification of an initially suggested mechanism for racemization of binaphthyl on active carbon surfaces (*14*). The prominence of large graphite-like planes in these catalytic carbons suggested that adsorption could result in a flattened (and therefore achiral) intermediate state on the surface. Large planar areas do not exist on a Raney nickel surface. Such a planar adsorbed state for binaphthyl on nickel is therefore not a possible intermediate even if nickel is a much less effective catalyst than certain types of carbon. The common characteristics of both surfaces would seem to be their electron donor capabilities. Complete transfer of an electron to form the binaphthyl radical ion results in very rapid racemization (*10*); reversible electron transfer via a nonstereospecific and loosely adsorbed state on nickel, as well as on carbon (*2*), seems to give a reasonable mechanistic picture for heterogeneous catalytic racemization of binaphthyl.

ACKNOWLEDGMENT

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