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Disproportionation of Dihydroarenes by Sol–Gel Entrapped $RhCl_3$-Quaternary Ammonium Ion Pair Catalysts

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The ion pairs generated from $RhCl_3 \cdot 3H_2O$ and the quaternary ammonium salts $[(C_8H_{17})_3NMe]Cl$ (Aliquat 336) and $[Me_3N(CH_2)_3Si(OMe)_3]Cl$ were physically and chemically entrapped, respectively, in SiO_2 sol–gel matrices under mild conditions. The resulting immobilized ion pairs proved to be stable, leach-proof, and recyclable catalysts for disproportionation of 1,3-cyclohexadiene and several other *vic*-dihydroarenes. In these reactions, equimolar quantities of the respective tetrahydro- and fully aromatic compounds were obtained. The entrapped catalysts, in most cases, proved to be more efficient and more selective than their homogeneous analogues. The reaction rates and conversions were shown to depend strongly on steric effects of substituents and on the bulkiness of the substrate skeleton. The recorded first order kinetics in the substrates (organic reactants) suggests that the mechanism involves stepwise addition of two molecules of the dihydroarenes to the rhodium nucleus, and that the addition of the first substrate molecule is rate limiting.

INTRODUCTION

The sol–gel methodology has so far been used in catalysis in the context of inorganic catalysts, as part of the matrix (1, 2), as supports for dispersed metal particles (3) and for copolymerization with suitable silicon-containing ligands (4), but, to the best of our knowledge, not for low temperature direct entrapment of metal catalysts that carry organic moieties as reported briefly in our recent publications (5, 6). The success of this approach in enzymatic catalysis and in photocatalysis, respectively, has also been described (7, 8). According to this methodology, the dopant molecules are simply added to tetraalkoxysilane during its hydrolytic polymerization (9). The resulting immobilized catalysts proved to exhibit either similar or superior catalytic activity as compared with the nonentrapped metal complexes (6). The immobilized catalysts were found to be stable under ambient conditions, leach-proof, and recyclable in numerous runs.

We now report the utilization of the SiO_2 sol–gel encapsulated ion pair $[(C_8H_{17})_3NMe]^+[RhCl_4 \cdot n(H_2O)]^-$ (10) (catalyst SG-1) as catalyst for the disproportionation of 1,3-cyclohexadiene and of various *vic*-dihydroarenes to the corresponding fully aromatic and tetrahydroaromatic compounds. For comparison, we applied also an entrapped rhodium catalyst generated from $RhCl_3$, $[Me_3N(CH_2)_3Si(OMe)_3]Cl$ and $Si(OMe)_4$, in which the ion pair had been bound *chemically* to the skeleton of the sol–gel matrix (catalyst SG-2).

METHODS

Chemicals. 1,3-Cyclohexadiene, 1,4-cyclohexadiene, tetramethoxysilane, methyltricaprylammonium chloride (Aliquat 336), and rhodium trichloride trihydrate were purchased from Aldrich Chemical Co., Inc. *N*-Trimethoxysilylpropyl-*N*,*N*,*N*-trimethylammonium chloride (50% in MeOH) was purchased from ABCR GmbH & Co. The substrates 1,2-dihydronaphthalene (IV, $R = H$) (11), 1,2-dihydro-4-methylnaphthalene (IV, $R = Me$) (12), 4-ethyl-1,2-dihydronaphthalene (IV, $R = Et$) (13), 1,2-dihydro-4-phenylnaphthalene (IV, $R = Ph$) (13), 4-carbo ethoxy-1,2-dihydronaphthalene (IV, $R = COOEt$) (14), 1,2-dihydro-8-methoxynaphthalene (VII) (12), 3,4-dihydro phenanthrene (X) (15), 1,2-dihydrophenanthrene (XI) (15), 10,11-dihydrobenz[*a*]anthracene (XIV) (16), and 9,10-dihydrobenzo[a]pyrene (XVII) (15) were prepared as described in the literature.

Instruments. ^1H and ^{13}C NMR spectra were recorded on a Bruker AMX-400 instrument. MS measurements were performed on a Hewlett–Packard Model 4989A mass spectrometer equipped with an HP gas chromatograph model 5890 series II. Gas chromatographic separations and analyses were carried out with the aid of a Hewlett–Packard CG model 417 equipped with a 2 m long column packed with 10% DEGS on Chromosorb W and operated at 120°C. Electronic spectra were recorded on a Hewlett–Packard spectrophotometer model 8454A. Nitrogen Langmuir surface area and average pore diameters of the sol–gel matrices

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were measured using a Micromeritics ASAP 2000 instrument. Atomic absorption spectrometry was carried out on a Perkin–Elmer spectrophotometer model 403 using a Juniper rhodium cathode lamp.

Preparation of the entrapped ion pair catalysts SG-1 and SG-2. A mixture of 20 mg (7.59×10^{-2} mmol) of $RhCl_3 \cdot 3H_2O$ and an equimolar amount of the appropriate quaternary ammonium salt ($[(C_8H_{17})_3NMe]Cl$ for SG-1 and $[Me_3N(CH_2)_3Si(OMe)_3]Cl$ for SG-2) in 2.4 ml of triply distilled water was stirred in a cylindrical vial (diameter 2 cm) at 25°C for 10 min. Methanol (3.5 ml) was added and the stirring was continued for 30 min. Tetramethoxysilane (2.5 ml) was added (molar ratio silane : water = 1 : 8) and the stirring was continued for an additional 30 min. The mixture was then left to stand at 25°C for 3–4 days until gelation was completed. The gel was heated to 45°C until a constant weight was achieved. The resulting catalyst granules were washed with 20 ml of boiling CH_2Cl_2 and sonicated for 30 min in the same solvent in order to remove any rhodium compound that adhered onto the outer surface of the matrix. The catalyst was then dried for 3 h at 1 mm, washed with 20 ml of boiling triply distilled water and dried again at 25°C at 1 mm for 20 h before use. The rhodium content within SG-1 and SG-2 was shown to be practically the same as in the $RhCl_3 \cdot 3H_2O$ employed. Atomic absorption measurements (17) revealed that the rhodium content in the washings was usually <1 ppm and in no case exceeded 5 ppm. To ensure the existence of the entrapped catalysts in the state of ion pairs, electronic spectra of the sol–gel glasses were recorded [cf., e.g., (18)].

General procedure for the disproportionation experiments. A reaction flask equipped with a reflux condenser, a magnetic bar, and a rubber sealed side arm was charged, under argon atmosphere, with the catalyst material and 2 ml of toluene. The vessel was placed in an oil bath thermostated at the desired temperature. After temperature equilibration, 2 mmol of the substrate was either injected or introduced with the aid of a Tygon tube into the flask. Samples of ca. 2 μl were withdrawn periodically. The products were analyzed either by direct comparison with authentic samples or by comparison of their spectral data (UV, ^{1}H NMR, ^{13}C NMR, GC-MS, or LC-MS) with those reported in the literature. Typical results are summarized in Table 1. Upon achievement of the desired conversion, the liquid reaction mixture was decanted and analyzed for leached rhodium by atomic absorption. The catalyst was refluxed in 20 ml of CH_2Cl_2, sonicated for 30 min, washed again with the same amount of solvent, and dried for 3 h at 1 mm. The dried catalyst was used in a subsequent run.

Kinetic measurements were carried out in modified pressure tubes with sampling devices.

TABLE 1

Disproportionation of Some *vic*-Dihydroarenes by SG-1 and SG-2 at 107°C[a]

			Yields after 40 min (%)	
Expt.	Substrate	Products	SG-1	SG-2
1	I	II; III	97	96
2	IV, $R = H$	V, $R = H$; VI, $R = H$	83	99
3	IV, $R = Me$	V, $R = Me$; VI, $R = Me$	58	41
4	IV, $R = Et$	V, $R = Et$; VI, $R = Et$	16	17
5	VII	VIII; IX (26)	52	87
6	X	XII; XIII (27)	28	73
7	XI	XII; XIII (27)	20	50
8	XIV	XV; XVI (28)	8	23
9	XVII	no products	—	—

[a] Reaction conditions as specified in the Experimental section.

RESULTS AND DISCUSSION

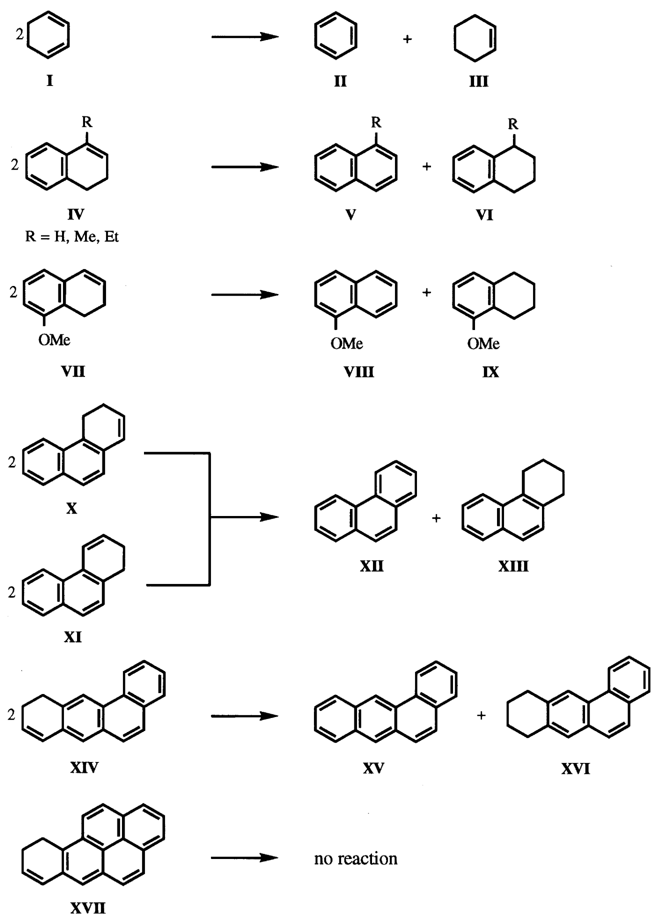
Encapsulation of the ion pair $[(C_8H_{17})_3NMe]^+ \cdot [RhCl_4 \cdot nH_2O]^-$ in a SiO_2 sol–gel matrix has been accomplished by addition of equimolar quantities of $RhCl_3 \cdot 3H_2O$ and Aliquat 336 at room temperature to the reaction mixture of $Si(OMe)_4$, MeOH, and water. After the gel was dried at 45°C the doped xerogel was activated by refluxing in CH_2Cl_2, sonication, washing with boiling water, and drying under reduced pressure. The electronic spectrum of the immobilized catalyst which consisted of a strong absorption band at 510 nm was found to resemble that of the soluble ion pair $[(C_8H_{17})_3NMe]^+[RhCl_4 \cdot nH_2O]^-$ (19) ($\lambda_{max} = 507$ nm), but shifted slightly to a higher wavelength. A similar bathochromic shift (from 474 to 480 nm) (18) was observed during the entrapment of the ammonium ion-free $RhCl_3 \cdot 3H_2O$ in a xerogel matrix.

When the Aliquat 336 in the above process had been replaced by $[Me_3N(CH_2)_3Si(OMe)_3]Cl$ the resulting homogeneous ion pair copolymerized with the $Si(OMe)_4$ forming SG-2, in which the ligand is bound chemically to the sol–gel matrix.

Both the physically encapsulated and the chemically bound catalysts were shown to be microporous materials, with a narrow pore size distribution, centered around 15 and 20 Å for SG-1 and SG-2, respectively. Their corresponding N_2-Langmuir surface area was found to be 722 and 832 m^2/g.

The entrapped ion pairs, SG-1 and SG-2, catalyzed the disproportionation of 1,3-cyclohexadiene (I) equally well. They promoted the formation of equal molar quantities of benzene (II) and cyclohexene (III) in 96–97% yield within 40 min.

Although both immobilized catalysts have been shown to promote double bond migration in allylbenzene (6), they failed, in contrast to other disproportionation catalysts



SCHEME 1. Disproportionation of dihydroarenes.

(20–22), to convert 1,4-cyclohexadiene into the 1,3-isomer, i.e., the nonconjugated diene could not be converted into II and III under the above reaction conditions. The *vic*-dihydroarenes IV ($R = \mathrm{H}$, Me, Et), VII, X, XI and XIV, which can formally be regarded as higher benzologues of I, were found to undergo catalytic disproportionation to form the corresponding tetrahydro-, and fully aromatic compounds (see Scheme 1). Dihydronaphthalenes IV ($R = \mathrm{H}$, Me, and Et) yielded the respective naphthalene and tetralin derivatives V and VI, and the methoxy-compound VII gave VIII and IX. Both 3,4- and 1,2-dihydrophenanthrene (X and XI, respectively) were transformed to phenanthrene (XII) and 1,2,3,4-tetrahydrophenanthrene (XIII), and 10,11-dihydrobenz[*a*]anthracene (XIV) yielded the aromatic benz[*a*]anthracene XV and the 8,9,10,11-tetrahydro-derivative XVI. Representative results are shown in Table 1. The disproportionation of I and IV ($R = \mathrm{H}$) by SG-1 was found to proceed faster than that by the homogeneous ion pair (23). Typical reaction profiles for the disproportionation of IV ($R = \mathrm{H}$) by SG-1 and SG-2 are presented in Fig. 1. We assume that the enhanced rates obtained by the immobilized catalysts are associated with the limited space available within the narrow pores that permits the presence of only few solvent molecules, which forces the catalyst to exist as contact ion pairs. Under homogeneous conditions the catalyst may exist as heavily solvated solvent-separated ion pairs in which the metal nucleus is less accessible by the substrate than in the entrapped catalysts. The porous nature of the sol–gel structure seems to be responsible also for the strong dependence of the rate on the bulkiness and steric effects of the substrates. Table 1 indicates that the tricyclic dihydrophenanthrenes, X and XI react more slowly than the small 1,3-cyclohexadiene (I) and the unsubstituted 1,2-dihydronaphthalene (IV, $R = \mathrm{H}$). The tetracyclic 10,11-dihydrobenz[*a*]anthracene (XIV) disproportionates even more slowly, and the pentacyclic 9,10-dihydrobenzo[*a*]pyrene (XVII) seems not to be able to penetrate the matrix pores, and does not react at all. The rate was also strongly affected by substituents that extend steric effects on the reaction site. Table 1 reveals that introduction of a methyl group in position 1 of IV reduces the rate considerably. An ethyl group inhibits the disproportionation to an even larger extent, and 4-carboethoxy-1,2-dihydronaphthalene (IV, $R = \mathrm{COOEt}$) as well as 1,2-dihydro-4-phenylnaphthalene (IV, $R = \mathrm{Ph}$) fail to disproportionate at all under our experimental conditions. Substituents at a more remote position from the reaction site, such as in 1,2-dihydro-8-methoxynaphthalene, proved to hardly affect the reaction rate. Because of steric reasons 3,4-dihydrophenanthrene (X) reacts faster than the 1,2-dihydro-isomer, XI, in which the reacting double bond

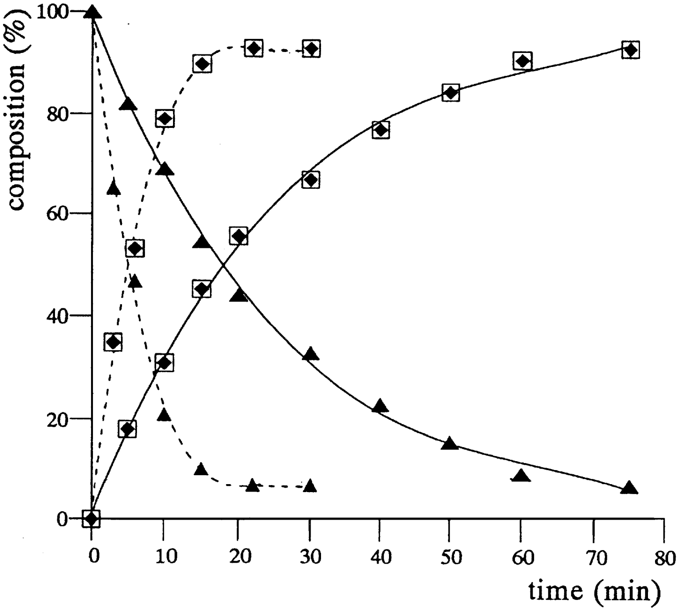


FIG. 1. Concentration-time profiles for the reactant and products in SG-1 (—) and SG-2 (– – –) catalyzed disproportionation of 1,2-dihydronaphthalene (▲) to naphthalene (□) and tetralin (◆) (obtained always in a 1 : 1 ratio).

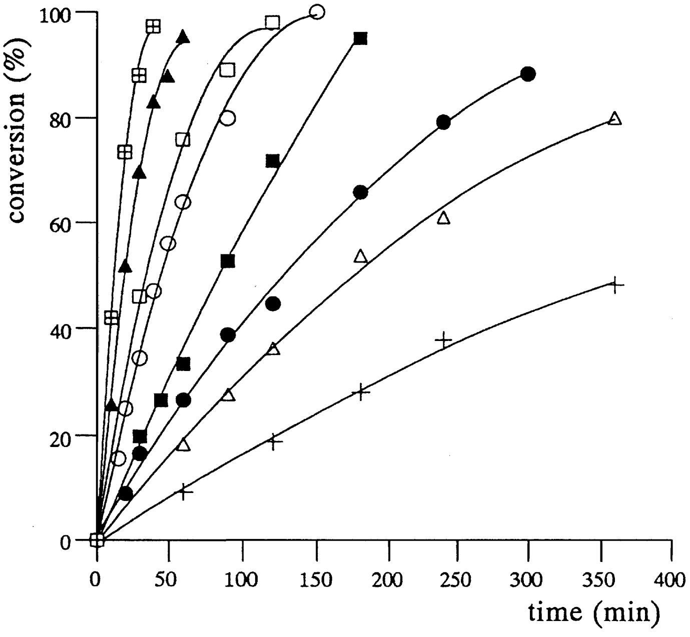


FIG. 2. Conversion-time profiles for SG-1-catalyzed disproportionation of I (⊞), IV, $R = \mathrm{H}$ (▲), IV, $R = \mathrm{Me}$ (○), IV, $R = \mathrm{Et}$ (△), VII (□), X (■), XI (●), and XIV (+), under the conditions of Table 1.

is shielded by the "bay-region" hydrogen atoms H4 and H5. The relative activities of the various substrates can be deduced from the conversion-time profiles shown in Fig. 2 and Fig. 3. These figures reveal some differences in the order of the activities of SG-1 and SG-2-catalyzed disproportionations. This observation can be rationalized by the difference between the inter-matrix construction of the physically encapsulated and chemically bound catalysts. The structural differences and particularly the larger pore diameter and surface area of SG-2 (20 Å as compared to 15 Å for SG-1), may explain also why both entrapped catalysts promote almost equally well the disproportionation of small substrates, but that SG-2 is superior to SG-1 for the disproportionation of the large polycyclic dihydroarenes (see Table 1).

Since the disproportionation of 1,3-cyclohexadiene and 1,2-dihydronaphthalene derivatives by soluble complexes (20, 21), by palladium on carbon (22) and by silica-supported catalysts (24) is generally accompanied by dehydrogenation processes, it is remarkable that SG-1 and SG-2-catalyzed disproportionations give in all cases only equimolar quantities of the aromatic and tetrahydroaromatic products. Previous experiments revealed that under phase transfer conditions, in a toluene/H_2O system, $[(C_8H_{17})_3NMe]^+[RhCl_4 \cdot nH_2O]^-$ (23) converts the dihydroaromatic substrates IV ($R = \mathrm{H}$), X, XI, and XIV into mixtures of products in which the fully aromatic compounds prevail. Similar results have now been obtained under homogeneous conditions in water-free toluene. The results of some representative experiments are summarized in Table 2. It is notable that none of the 1,2-dihydronaphthalene derivatives IV that have a substitutent at the reaction site (i.e., on C4) could be disproportionated by the homogeneous ion-pair catalyst.

The most important feature of the sol–gel entrapped catalysts is obviously their ability to be recycled in numerous runs. We recall that in 1,3-cyclohexadiene disproportionation, the soluble $RhCl_3$-Aliquat 336 catalyst could be recycled for a few runs, but the rates dropped after each run by more than 30% (23). Both the physically encapsulated catalyst, SG-1, and the chemically bound SG-2 have been shown to be perfectly leachproof and their catalytic activity has hardly changed upon recycling. It is necessary,

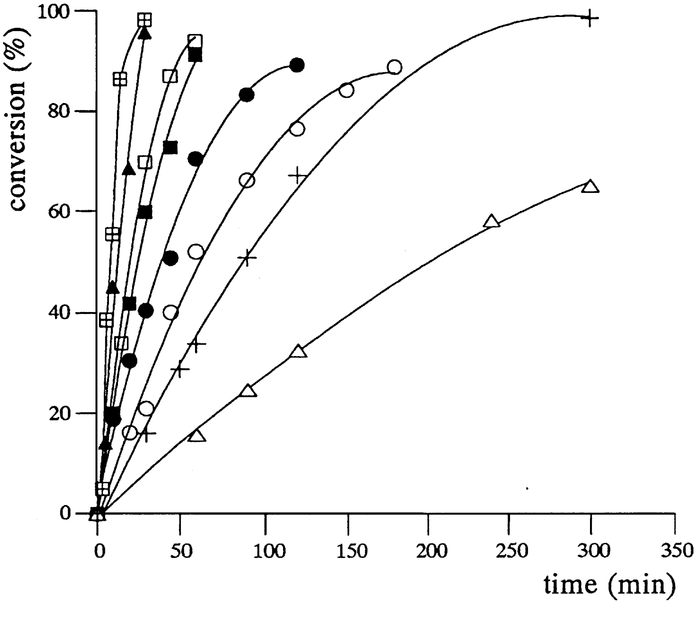


FIG. 3. Conversion-time profiles for SG-2-catalyzed disproportionation of I (⊞), IV, $R = \mathrm{H}$ (▲), IV, $R = \mathrm{Me}$ (○), IV, $R = \mathrm{Et}$ (△), VII (□), X (■), XI (●), and XIV (+), under the conditions of Table 1.

TABLE 2

Disproportionation and Dehydrogenation of some Dihydroarenes by $[(C_8H_{17})_3NMe]^+[RhCl_4 \cdot nH_2O]^-$ under Homogeneous Conditions at 104°C[a]

Substrate	Reaction time (h)	Conversion (%)	Tetrahydroaromatic: aromatic product ratio
I	2	70	1 : 1[b]
IV, $R = \mathrm{H}$	1	90	1 : 1.9
X	0.5	100	1 : 4.3
XI	1	81	1 : 5
XIV	1	100	1 : 4

[a] Reaction conditions: ion pair generated from 7.59×10^{-2} mmol of $RhCl_3 \cdot 3H_2O$ and 7.59×10^{-2} mmol of Aliquat 336, 2 ml H_2O, and 2 ml toluene; aqueous layer removal; 2 mmol substrate; Ar atmosphere.

[b] In $(CH_2Cl)_2$ the ratio was 1 : 2 [cf. (22)].

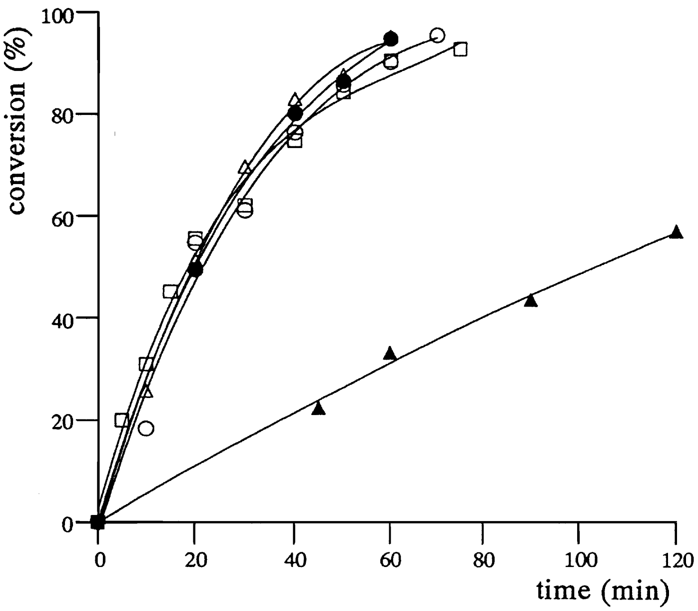


FIG. 4. Conversion-time profiles for SG-1-catalyzed disproportionation of 1,2-dihydronaphthalene under the conditions of Table 1. First run (▲) (catalyst was not activated with boiling water); second run (△); third run (●); fourth run (□); fifth run (○).

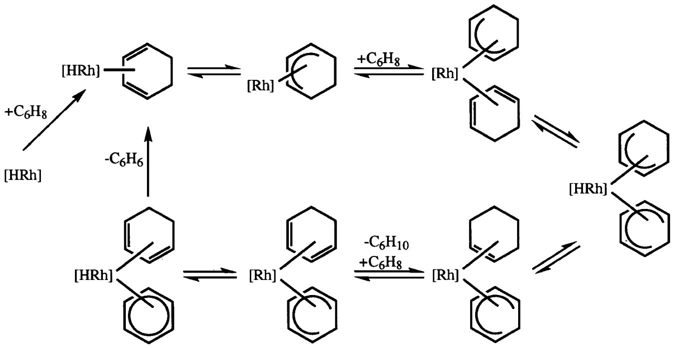
however, to prevent any pore clogging between the cycles by washing the doped material with an organic solvent (followed by sonication) and eventually with boiling water. The latter breaks the Si–O–Si bonds and opens somewhat the pore network. Figure 4 presents a typical set of conversion-time plots for SG-1-catalyzed disproportionation of 1,2-dihydronaphthalene (IV, $R = \mathrm{H}$) in the first five runs (SG-2 gave similar profiles). In this set of experiments the catalyst had not been treated with boiling water prior to the first run. Consequently, the rate of the first run was lower than those of the subsequent cycles for which the ceramic material had been reactivated. The rates for all subsequent runs were almost identical (Fig. 4).

Under phase transfer conditions the nature of the quaternary ammonium salt was shown to have only a small effect on the rate of disproportionation of dihydroarenes (23). The encapsulated catalyst proved however to be strongly affected by the size of the ammonium ion. When ions with relative short alkyl chains were employed, the resulting ion-pairs leached gradually from the sol–gel matrix. For example, replacement of the Aliquat 336 in SG-1 with $[\mathrm{Bu_4N}]\mathrm{Br}$ resulted in the formation of a catalyst which, in contrast to SG-1, lost part of its activity due to leaching. In a typical set of experiments of disproportionations of I by the $\mathrm{RhCl_3}$–$[\mathrm{Bu_4N}]\mathrm{Br}$ catalyst (initial rhodium content, 7.8 mg) metal leaching extended during each of the first four runs (of 90 min at 107°C) to 0.8 mg. Varying additional amounts of rhodium were eluted during the washings between the cycles. ^{1}H NMR measurements of the reaction mixtures showed that together with the rhodium, equivalent amounts of the quaternary ammonium salt had been eluted.

The disproportionation of I by $[(\mathrm{C_8H_{17}})_3\mathrm{NMe}]^+ \cdot [\mathrm{RhCl_4} \cdot n\mathrm{H_2O}]^-$ (23) as well as by some silica-supported dirhodium catalysts (24) could be explained best in terms of the mechanism of Moseby and Maitlis (20) in which the rate determining step involves a species with two unsaturated cyclohexane residues, leading to second order in the substrate. However, the data recorded for SG-1- and SG-2-catalyzed disproportionation of I and of IV, $R = \mathrm{H}$, proved incompatible with such a mechanism. Kinetic measurements at 107°C for 0.25–0.75 *M* solutions of 1,2-dihydronaphthalene (IV, $R = \mathrm{H}$) in toluene revealed that under the conditions given in the Experimental section, the disproportionation is pseudo zero order in the rhodium and apparent first order in the substrate [$k_{\mathrm{obs}}(\text{SG-1}) = 4.34 \pm 0.08 \times 10^{-4}\,\mathrm{s^{-1}}$; $k_{\mathrm{obs}}(\text{SG-2}) = 2.73 \pm 0.07 \times 10^{-3}\,\mathrm{s^{-1}}$].

In contrast to the homogeneous processes (23, 24) in which deuteriated solvents caused deuterium labeling of the tetrahydroaromatics, the application of toluene-d_8 to our systems did not lead to incorporation of deuterium in the products. Likewise, sol–gel matrices that had been prepared by hydrolysis of $\mathrm{Si(OMe)_4}$ in $\mathrm{D_2O}$ and methanol-d_4 did not promote deuterium transfer to V or VI, nor to the unreacted starting material IV. These observations can be interpreted in the light of a mechanism similar to that of Fischer *et al.* (21), shown in Scheme 2, in which the metal hydride is generated by abstraction of a proton from the coordinated substrate rather than from the medium, and the rate limiting step is the initial coordination of the starting dihydro compound to the rhodium nucleus.

The catalytic disproportionation of IV, $R = \mathrm{H}$, proved to have the same reaction patterns between 100 and 120°C. Therefore, we could express the initial rates measured at 101, 110, 113, 115, and 120°C in terms of Arrhenius plots (Fig. 5). It should be noted that it was not at all obvious that the Arrhenius equation could be applied to



SCHEME 2. Possible mechanism of SG-1- and SG-2-catalyzed disproportionation of 1,3-cyclohexadiene and similar compounds.

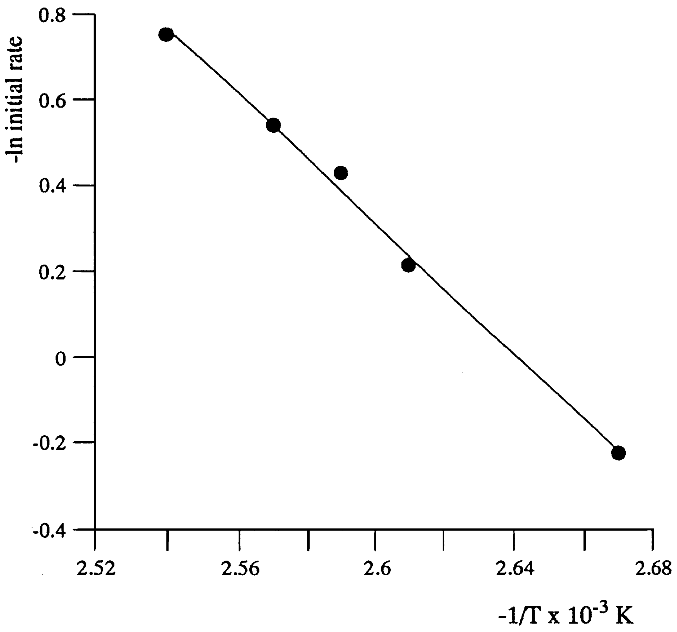


FIG. 5. Arrhenius plot of disproportionation of IV, $R = H$ at 101–120°C.

this type of disordered matrices. The resulting values of $E_a = 15.0$ kcal mol^{-1} and $\Delta H^{\#}(115°C) = 14.0$ kcal mol^{-1}, which are lower than those of typical chemically controlled reactions, but higher than those of purely diffusion-controlled reactions (25), suggest, as one could expect, that both processes contribute to the progress of the catalysis.

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