

Double bond migration, cyclohexadiene disproportionation and alkyne hydration by Dowex[®] 1–RhCl₃ ion pair catalysts

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Received 10 March 1997; accepted 9 May 1997

Abstract

Polystyrene-supported ion pairs, generated from RhCl₃ and Dowex[®] 1 anion exchangers were shown to be efficient, leach-proof and recyclable catalysts for double bond migration in allylic compounds, disproportionation of 1,3-cyclohexadiene and hydration of aromatic acetylenes. At 50–70°C the isomerization of allylbenzene in aqueous EtOH was found to be first order in the substrate, and for catalyst:substrate ratio > 1:40, pseudo-zero order in the catalyst. The reaction rate proved to be effected by the electronic nature of the allylic compound and by the structural properties of the polymeric support. The disproportionation of the diene in aqueous THF was found to follow the Michaelis–Menten rate equation. Addition of water was shown to be specific for aromatic alkynes. Aliphatic acetylenes proved to undergo, under the same conditions, catalytic oligomerization. While the rate of allylbenzene isomerization is mainly chemically controlled the disproportionation of 1,3-cyclohexadiene is governed chiefly by mass transfer processes. © 1997 Elsevier Science B.V.

Keywords: Immobilized-catalyst; Rhodium; Dowex[®] 1; Isomerization; Disproportionation; Hydration

1. Introduction

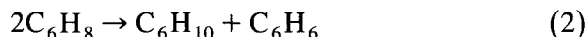
Under phase transfer conditions, the ion pairs generated from RhCl₃ · 3H₂O and quaternary ammonium salts are efficient and selective catalysts for a variety of organic processes [1–3]. In several cases the rhodium catalyst can be recovered in part as aqueous RhCl₄⁻ by treatment of the reaction mixture with a lipophilic anion [4–7]. In most processes, however, this method

of catalyst recovery is not applicable. In a short communication [8], we have reported some preliminary experiments in which we revealed that a polystyrene-supported ion pair, obtained from RhCl₃ and the commercially available Dowex[®] 1 ion exchanger, acts as a highly active and fully recyclable catalyst for several hydrogen transfer reactions.

We have now extended these experiments, in which we demonstrated the usefulness of this easily available immobilized catalyst in isomerization of allylarenes (Eq. (1)), in disproportionation of 1,3-cyclohexadiene (Eq. (2)), and in hydration of aromatic acetylenes (Eq. (3)), and

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elucidated some mechanistic features of these catalytic processes.



2. Experimental

2.1. General

^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 analyses were carried out with the aid of a Hewlett-Packard GC Model 7620A instrument equipped with a flame ionization detector and a 3.16×2000 mm copper column packed with 10% stabilized DEGS on Chromosorb W. Electronic spectra were recorded on a Hewlett-Packard spectrophotometer model 8454A. Nitrogen-BET surface area measurements were obtained by using a Micromeritics ASAP 2000 instrument. Atomic absorption spectrometry was performed on a Perkin-Elmer spectrophotometer model 403 using a Juniper rhodium cathode lamp.

2.2. Preparation of the catalyst

Typically, 1.5 g of commercially available Dowex[®] 1 \times 4 (i.e., polystyrene-bound trimethylbenzylammonium chloride crosslinked with 4% divinylbenzene) of 200–400 mesh containing 1.33 meq/g Cl^- , 150 mg (0.57 mmol) $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ and 5 ml of 95% EtOH were stirred under N_2 at room temperature for 24 h. The red resin was washed with EtOH until the washings were free of any Rh (checked by atomic absorption [9]). The rhodium content of the catalyst was obtained by subtraction of the

amount of metal in the washings from the initial quantity of rhodium used in the process. The effective surface area of the catalyst was determined by nitrogen-BET measurements [10].

2.3. Catalytic isomerization of allylbenzene

To a preheated mixture of the above immobilized catalyst (that contained 0.57 mmol Rh) and 5 ml of 92% aqueous EtOH, was added under N_2 atmosphere at 78°C , 1.5 ml (11.4 mmol) of allylbenzene. The mixture was stirred at that temperature at ca. 1000 rpm. Samples (1–2 μl) were withdrawn periodically from the reaction mixture and immediately frozen to await GC analysis. When the reaction mixture reached equilibrium of 0.3% of the starting material, and 7.7 and 92.0% of *cis*- and *trans*-3-propenylbenzene, respectively, the heating was discontinued, the liquid was decanted and analyzed by atomic absorption spectrometry for any leached rhodium. The residual solid resin was washed with 92% EtOH and recycled in a second run.

2.4. Disproportionation of 1,3-cyclohexadiene

To a preheated solution of 1 ml (10.5 mmol) of the diene in 8 ml of 90% aqueous THF was added at 50°C , 1.65 g of the immobilized catalyst which contained 0.57 mmol of Rh. The mixture was stirred under N_2 atmosphere at 1000 rpm for 2 h. Samples were withdrawn periodically from the reaction mixture and analyzed by GC. During the entire reaction period the ratio of the resulting benzene and cyclohexene proved to be 1:1. Upon completion of the reaction, the liquid was decanted, analyzed for leached metal, washed with THF and recycled in a second run.

2.5. Hydration of 4-bromophenylacetylene

A mixture of 2.06 g (11.4 mmol) 4-bromoacetylene, 8 ml of 92% aqueous EtOH and the immobilized catalyst that contained 0.57 mmol

Rh was stirred under N_2 at 50°C for 5 h. The liquid reaction mixture was decanted from the resin and distilled. There was obtained 2.20 g (97%) of 4-bromoacetophenone. The polymer-bound catalyst was washed with EtOH and recycled in a second run.

3. Results and discussion

Although RhCl_3 has been anchored to a basic ion exchanger already in 1976 [11], the resulting immobilized ion pair has never been applied as catalyst in its original ionic state. It has been employed in catalytic hydrogenation only after reduction to colloidal Rh(0). The product of Dowex 1 and the rhodium salt prepared in this study, which has been formulated as [polystyrene- $(\text{CH}_2\text{NMe}_3)_n$] $^{n+}$ [$\text{RhCl}_4(\text{H}_2\text{O})_m$] $^{n-}$ (**1**), has been used as a recyclable catalyst in hydrogen transfer processes without modification. The immobilized ion pair was shown to be air, insensitive and thermally stable below 100°C . However, upon prolonged stirring (> 3 d) with aqueous NaClO_4 it exchanged into NaRhCl_4 and polymer-bound trimethylammonium perchlorate [8] in a fashion similar to that of the non-supported catalyst $[(\text{C}_8\text{H}_{17})_3\text{NMe}]^+[\text{RhCl}_4(\text{H}_2\text{O})_2]^-$ (**2**) [4].

3.1. Catalytic double bond migration in allylic compounds

Under the conditions described in the Experimental section, **1** catalyzes the conversion of allylbenzene within 20 min into an equilibrium mixture of 0.3% of the starting material, 7.7% of *cis*- and 92.0% of *trans*-3-propenylbenzene in accordance with Eq. (1) ($\text{Ar} = \text{Ph}$). The process is preceded by a short, but distinguished, induction period. Thereafter, the reaction in which only one substrate is involved becomes first order in the substrate (as long as the concentration of the products does not exceed 1.48 M). Under these conditions the amount of the catalyst does not affect the rate. Actually, the

rate was found to depend on the amount of the rhodium only at molar catalyst:substrate ratio $\leq 1:80$. Analysis of the reaction mixture after completion of the catalytic process, revealed that absolutely no metal leaching had taken place during the isomerization. Therefore, no loss of activity had been observed upon recycling of the catalyst for seven consecutive runs, and the reaction profiles superimposed with that of the first cycle. Even the induction period was found to be unchanged. In order to investigate the cause for the induction period, we carried out isomerization experiments in which the dry catalyst had been pretreated for 24 h with either solvent-free allylbenzene, or with substrate free solvent. Since these experiments had only an insignificant effect on the induction period we concluded that it is neither associated with the formation of a substrate-catalyst adduct nor with slow generation of a rhodium hydride but with the swelling of the polymer support. We assume that swelling of the resinous catalyst takes place already during the induction period of the first run, the polystyrene backbone shrinks back to its original form during the washing and drying at the end of the cycle. Support in this assumption has been provided by experiments in which we isomerized allylbenzene in the presence of EtOH-pretreated catalyst till 70% of the starting compound has reacted. Thereafter, the reaction liquid has been decanted and the used catalyst recycled *without* washing and drying. In this experiment the induction period disappeared completely in the first as well as in all successive runs. It is notable that while the 'traditional' non-polar crosslinked polystyrene resins are swollen effectively by aromatic solvents, see e.g. Ref. [12], the polar polystyrene-supported ion pair is swollen best by aqueous carbinols rather than by aromatic hydrocarbons.

Unlike the smooth isomerization of allylbenzene under phase transfer conditions by the homogeneous catalyst **2**, hardly any reaction takes place by **1** in the two liquid phase systems: $\text{H}_2\text{O}/(\text{CHCl}_2)_2$, $\text{H}_2\text{O}/(\text{CH}_2\text{Cl})_2$, $\text{H}_2\text{O}/\text{PhH}$ and $\text{H}_2\text{O}/\text{PhMe}$. The catalysis pro-

ceeds, however, without difficulty in aqueous carbinols (EtOH, *n*-BuOH), fairly well in wet THF and slowly in moist DMF. The presence of water proved to be essential. In its absence no reaction occurs. The water molecules provided by the hydrated RhCl_3 and the 'Dowex 1' seems not to be sufficient, and ca. 8% of added water is required in order to obtain the maximum reaction rate. When the added water surpasses 12%, slow reduction and decomposition of the supported rhodium catalyst occurs, and consequently its efficiency decreases. Typical conversions of allylbenzene under the conditions given in the Experimental section were 0, 14, 64, 94 and 90% after 15 min respectively, for reactions with 0, 1, 5, 10 and 15% added H_2O .

The degree of crosslinking of the polystyrene support was shown to have a considerable effect on the reaction rate. The initial (maximum) rates of isomerization at 60°C by **1** on Dowex 1 crosslinked with 2, 4 and 8% divinylbenzene, were under comparable conditions, 4.25, 2.08 and $0.916 \times 10^{-4} \text{ mol l}^{-1} \text{ s}^{-1}$, respectively. It is notable that the different degree of crosslinking does not only alter the rigidity of the polymeric support but also affects its surface area. Thus, e.g., the average nitrogen BET values [10] for 40–80 μm RhCl_3 -bound Dowex 1 \times 2, Dowex 1 \times 4 and Dowex 1 \times 8 were found to be 0.90, 0.57 and 0.49 m^3/g , respectively. When Dowex 1 has been replaced by Dowex 11 (that resembles Dowex 1 except that its crosslinking is not defined) the initial rate was found to be similar to that of Dowex 1 \times 8. Although **1** on Dowex 1 \times 2 led to higher rates than **1** on Dowex 1 \times 4, we preferred in our standard experiments to use the latter catalyst because of its greater physical stability. While the more rigid resin never broke down, the catalyst with only 2% of divinylbenzene lasted usually only 5–6 runs.

The rate was found to depend also on the electronic nature of the substrate. Electron donating groups enhance the rate and visa versa the electron attracting chlorine atom. The same

Table 1
Substituent effect on the isomerization of allylbenzenes $\text{XC}_6\text{H}_4\text{CH}_2\text{CH}=\text{CH}_2$ by the supported RhCl_3 -Dowex 1 \times 4^a and by the soluble RhCl_3 -Aliquat[®] 336^b catalyst at 60°C

X	10^4 (initial rate) $\text{mol l}^{-1} \text{ s}^{-1}$ ^c		Ratio of rates catalyst 1:catalyst 2
	catalyst 1	catalyst 2	
4- CH_3O	4.46	1.65	2.70
4- CH_3	4.30	1.24	3.47
H	4.19	1.22	3.43
4-Cl	2.95	0.78	3.77

^a Reaction conditions: 12 mmol substrate, 0.57 mmol Rh, 8 ml 92% aqueous EtOH, stirring rate 1000 rpm.

^b Reaction conditions as described above except that the medium consisted of 8 ml H_2O and 8 ml toluene.

^c Under conditions where no induction period was observed.

trend was observed when the allylic compounds were isomerized by the soluble catalyst **2**. The results shown in Table 1 for catalyst **1** were expressed in terms of a Hammett plot from which $\rho = -1.05$ was obtained. This value suggests stabilization of positive charge on the rhodium atom during the rate determining step. The Table indicates that in all experiments the immobilized rhodium compound is a better catalyst than the RhCl_3 -Aliquat[®] 336 ion pair (**2**). Comparison between the activity of **1** and its soluble version $[\text{PhCH}_2\text{NMe}_3]^+ [\text{RhCl}_4(\text{H}_2\text{O})_n]^-$ (**3**) proved impossible because the latter readily undergoes under our experimental conditions, destructive reduction to the free metal.

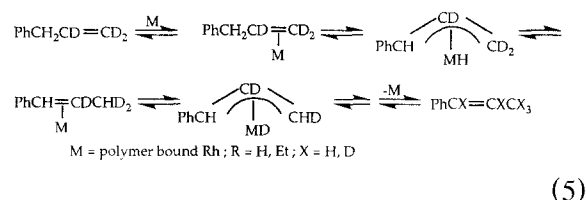
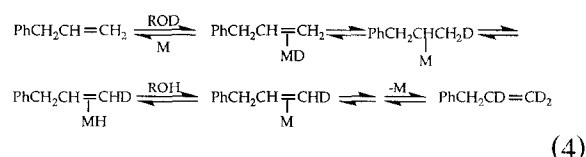
In the presence of **1**, Eq. (1) was found to take place in the temperature range between 55 and 70°C with essentially no change in selectivity. Initial rates were measured at 55, 58, 60, 65 and 70°C for several substrate concentrations between 0.65 M and 1.965 M. From plots of $\log C_0/C$ vs. time the reaction constants were calculated and from the corresponding Arrhenius plot the activation energy of $E_a(\text{hetero}) = 16.5 \text{ kcal mol}^{-1}$ was obtained. It is notable that in analogy with other catalyses by polystyrene-anchored catalyst, see e.g. Ref. [13], we could assume that Eq. (1) takes place within the pores of the polymeric catalyst particles rather than on

its surface. Thus, the units of the rate of the heterogeneous process are actually the same as those of homogeneous reactions and direct comparison between the thermodynamic constants in both systems is permissible. The value of $16.5 \text{ kcal mol}^{-1}$ indicates that the isomerization of allylbenzene by **1** is mainly, though not entirely, chemically controlled, see e.g. Ref. [14]. We recall that the activation energy for this isomerization by the soluble catalyst **2** under phase transfer conditions [4] is $E_a(\text{homo}) = 24.1 \text{ kcal mol}^{-1}$ [15].

Further indication that **1**-catalyzed Eq. (1) is chiefly governed by chemical factors has been deduced (a) from the fact that the rate of stirring between 120 and 1200 rpm has only an insignificant effect on the reaction rate, and (b) that the dependence on the particle size of catalyst is very small. The initial rates of allylbenzene isomerization by three samples of **1** (on Dowex 1×4) that differ only by their particle sizes were recorded under comparable conditions. For catalysts with diameters of $d(\text{i}) = 300\text{--}840$; $d(\text{ii}) = 150\text{--}300$ and $d(\text{iii}) = 40\text{--}80 \mu\text{m}$ (and N_2 -BET surface areas of 0.23, 0.46 and $0.57 \text{ m}^2/\text{g}$, respectively), the corresponding initial (maximum) rates were $r(\text{i}) = 1.61$, $r(\text{ii}) = 1.83$, and $r(\text{iii}) = 2.08 \text{ mol l}^{-1} \text{ s}^{-1}$. The ratios of $r(\text{ii})/r(\text{i}) = 1.83/1.61 = 1.13$ and $r(\text{iii})/r(\text{i}) = 2.08/1.61 = 1.29$ which are closer to unity than to the values of $d(\text{i})/d(\text{ii}) = 2.5$ and $d(\text{i})/d(\text{iii}) = 9.5$, are a convincing proof for the small part that intraparticle mass transfer plays in controlling the catalytic isomerization reaction [16].

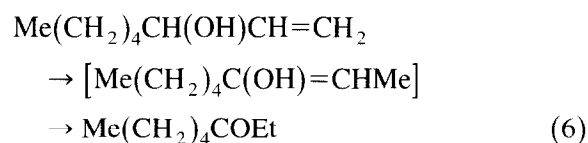
Valuable information on the mechanism of Eq. (1) has been obtained by labeling experiments. Upon substitution of the aqueous EtOH by a mixture of 92% $\text{C}_2\text{D}_5\text{OD}$ and 8% D_2O no kinetic isotope was observed. Deuterium however, has been incorporated in the products. Monitoring of the process by ^1H NMR and by mass spectrometry showed that H–D exchange took place both in the starting allylbenzene and in the products. When e.g., the reaction mixture was analyzed after conversion of 20% the recovered starting material was found to be

deuterated to an extent of 6% exclusively at the vinylic protons. In the isomerization products, *cis*- and *trans*-2-propenylbenzene, the α , β and γ protons were exchanged to an extent of 23, 56 and 86%, respectively. This result led us to the conclusion that at least part of the deuteration takes place in the starting allylbenzene by the route outlined in Eq. (4). Thus, the starting material for the deuterated *cis*- and *trans*-2-propenylbenzene (Eq. (5)) is allylbenzene enriched with $\text{PhCH}_2\text{CD}=\text{CD}_2$.



It should be noted that the process described in Eq. (4) requires a fast solvent-assisted reduction of some Rh(III) atoms in **1** to Rh(I) before the proton transfer and oxidative addition can take place. This indeed has been supported by XPS analysis of the catalyst (after exposure to the solvent at 50°C) that revealed the presence of both Rh(I) and Rh(III) species. The presence of these species as well as the absence of Rh(0) has been proven also after catalyst recycling. Analyses have been performed up to the sixth run.

In analogy to the isomerization of allylarenes the RhCl_3 -Dowex 1×4 catalyzes double bond migration also in allylic alcohols. E.g., at 80°C 1-octen-3-ol is transferred within 80 min in quantitative yield to 3-octanone (Eq. (6)).



Here too, the catalyst proved to be leach-proof and recyclable in numerous runs without loss in

activity, and to act more efficiently than the homogeneous ion pair **2** that operates under phase transfer conditions. It is remarkable however, that while in the presence of **2** allylbenzene reacts slower than 3-octen-1-ol [4], the supported catalyst **1** causes the rates to be *vis-à-vis*.

3.2. Disproportionation of 1,3-cyclohexadiene

1,3-Cyclohexadiene which has been shown to disproportionate to benzene and cyclohexane (Eq. (2)) both by soluble $[(C_8H_{17})_3NMe]^+[RhCl(H_2O)_2]^-$ (**2**) under phase transfer conditions [6], and by its sol-gel encapsulated version, in apolar aromatic solvents [17] has now been found to undergo the same reaction also by the Dowex 1-supported $RhCl_3$ (**1**) in 90% aqueous (but not in dry) THF at 50–80°C. In this solvent the catalyst proved leach-proof and recyclable in numerous runs (*vide infra*). Unlike the disproportionation by some soluble transition metal complexes [18,19], by palladium on carbon [20] or by silica supported dirhodium catalysts [21], the catalysis by **1** is not accompanied by dehydrogenation of the cyclohexadiene (Eq. (7)).

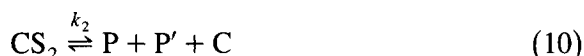


Benzene and cyclohexene are formed solely in equimolar quantities. Also the disproportionation by the *homogeneous* version of **1**, i.e. by $[PhCH_2NMe_3]^+[RhCl_4(H_2O)_n]^-$ has been found to be associated with substantial dehydrogenation, and to give cyclohexene and benzene in ratio 1:1.75.

Although the disproportionation of 1,3-cyclohexadiene takes place at a relatively low temperature, the reaction of α -terpinene, α -phellandrene and 1,2-dihydronaphthalene proved to react only above 100°C, at which the immobilized ion pair is partially reduced to metallic rhodium. Therefore, we chose Eq. (2) for kinetic studies. For substrate concentrations between 0.65 and 1.96 M, the disproportionation has been found to follow the Michaelis–Menten

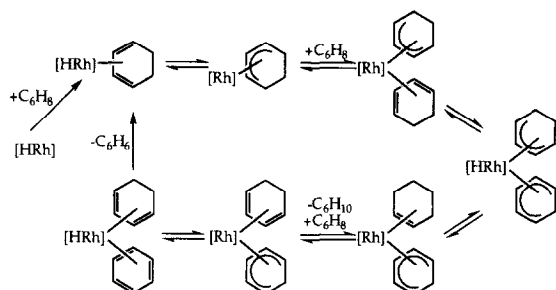
rate equation in numerous catalytic runs. Under the conditions of the Experimental section, in which the molar ratio catalyst:substrate is 1:18 the rate is practically independent on the amount of the catalyst. The rate dependence which is significant at low catalyst–substrate ratio levels off at ca. 1:35. Representative initial rates for the ratios of 1:150, 1:75, 1:37, 1:18 and 1:9 at 50°C are 0.75, 1.41, 1.70, 1.74 and 1.75×10^{-4} mol l⁻¹ s⁻¹, respectively.

In light of these kinetic measurements we assume that the catalytic cycle is composed of (i) fast interaction of the catalyst, C, with one molecule of the substrate, S, to give a catalyst–substrate adduct, CS (Eq. (8)); (ii) an equilibrium of this adduct, and a second molecule of substrate with the resulting complex CS₂ (Eq. (9)), and a final step (iii) which we believe to be rate limiting, is the decomposition of CS₂ into the two products, P and P', and the original catalyst C (Eq. (10)).



The rate equation for Eqs. (8)–(10) is in accordance with the classical Michaelis–Menten mechanism. For a typical set of experiments, the equilibrium and rate constants were found to be $K = 1.55 \pm 0.04$ M and $k_2 = 1.54 \pm 0.02 \times 10^{-3}$ s⁻¹.

This catalytic cycle is compatible with a mechanism similar to that proposed by Fischer et al. [19] shown in Scheme 1. The metal hydride is assumed to be generated by abstraction of a proton from the coordinated substrate and the chemical rate limiting step is believed to be the initial coordination of the starting compound to the rhodium nucleus. The catalysis is unlikely to follow the route suggested by Moseby and Maitlis [18] in which the rate determining step involves a species with two unsaturated cyclohexene residues, that would lead to second order kinetics in the substrate.



Scheme 1. Possible mechanism of **1**-catalyzed disproportionation of 1,3-cyclohexadiene.

Studies on the effect of the physical structure of the polystyrene backbone on the rates of Eq. (2), revealed that for supports crosslinked with 2–8% divinylbenzene, the more flexible resins are superior to the rigid ones. E.g., the initial rates of disproportionation of 1,3-cyclohexadiene by RhCl_3 on Dowex 1 \times 2, Dowex 1 \times 4 and Dowex 1 \times 8, were in the first cycle, under our experimental conditions, 2.02, 1.73 and $0.50 \times 10^{-4} \text{ mol l}^{-1} \text{ s}^{-1}$, respectively and the corresponding conversions after 2 h were 78, 72 and 25%. In successive runs (up to the fifth run) these figures increased. Typical rates and yields are listed in Table 2.

We attribute the increase in rate to slow swelling of the support by the THF solvent. Support in this assumption has been provided by an experiment in which the immobilized catalyst has been heated at 50°C in THF for 48 h (to ensure complete swelling) prior to the addition of the substrate. In this experiment the initial rate and yield were close to those ob-

Table 2
Disproportionation of 1,3-cyclohexadiene by the RhCl_3 -Dowex 1 \times 4 catalyst during six consecutive runs^a

Run No.	10^4 (initial rate) ($\text{mol l}^{-1} \text{ s}^{-1}$)	Yield after 2 h (%)
1	1.73	76
2	1.82	79
3	3.16	88
4	3.88	95
5	4.83	100
6	4.33	93

^a Reaction conditions as described in Section 2.

tained after 5 runs of 2 h ($4.50 \text{ mol l}^{-1} \text{ s}^{-1}$ and 98%, respectively) and in the consecutive runs the efficiency of the catalyst did not increase anymore. We have shown that after the five catalytic runs, as well as after the treatment of the catalyst for 48 h with the solvent, the N_2 -BET surface area of dried **1** (on 40–80 μm Dowex 1 \times 4) increased from 0.57 to 1.51 m^3/g . In the sixth run and in all further runs, slow retardation in rate was recorded. At the same time the mechanical properties of the resin changed. The hard beads became softer and finally turned into a cotton-like material.

The disproportionation of 1,3-cyclohexadiene by RhCl_3 -Dowex 1 \times 4 was found to take place in the temperature range of 50–70°C with no change in selectivity. Typical initial rates recorded at 50, 55, 60, 65 and 70°C were 1.73, 1.96, 2.54, 2.77 and $3.21 \times 10^{-4} \text{ mol l}^{-1} \text{ s}^{-1}$, respectively. When these data were expressed in terms of an Arrhenius plot of log initial rate vs. $1/T$ the apparent activation energy E_a (hetero) = 4.80 kcal mol^{-1} was obtained. This value indicates that under our experimental conditions, Eq. (2) is, unlike Eq. (1), largely diffusion controlled [14]. Further support to the fact that mass transfer is of prime importance in the **1**-catalyzed disproportionation, has been obtained from the observation that the rate is highly dependent on the stirring rate. Additional indication for the significant role of the mass transfer on the rate could be obtained by comparison of the rates of disproportionation by RhCl_3 -Dowex 1 \times 4 catalysts of different particle sizes. When **1** with particle diameters of $d(\text{i}) = 300\text{--}840$; $d(\text{ii}) = 150\text{--}300$ and $d(\text{iii}) = 40\text{--}80 \mu\text{m}$ were utilized, the respective initial rates were 1.08, 1.35 and $1.73 \times 10^{-4} \text{ mol l}^{-1} \text{ s}^{-1}$. Thus, the ratios $r(\text{ii})/r(\text{i})$ which are 1.25 and 1.60, respectively, do not fulfill the requirement for a purely chemically controlled reaction (in which $r(\text{ii})/r(\text{i}) = r(\text{iii})/r(\text{i}) = 1$) although they also do not match exactly the conditions for a purely diffusion controlled process (where $r(\text{ii})/r(\text{i}) = d(\text{i})/d(\text{ii})$ and $r(\text{iii})/r(\text{i}) = d(\text{i})/d(\text{iii})$) [16].

3.3. Hydration and oligomerization of alkynes

Under phase transfer conditions the soluble ion pair **2** was previously shown to catalyze cyclotrimerization of alkynes at 60–90°C [22], and to promote hydration of these compounds at 5–25°C [7]. The latter process proved to give in general rather low yield. The immobilized ion pair **1** has now been found to be by far a better catalyst than **2**, and to promote preferentially addition of H₂O to arylacetylenes even at 50°C. A particularly clean reaction was shown to take place when 4-bromophenylacetylene was used as substrate (Eq. (3), Ar = 4-BrC₆H₄). Since the water adds to the triple bond in accordance with Markownikoff's rule, 4-bromoacetophenone (free of any 4-bromophenylacetaldehyde) is the only product in this reaction. As in the isomerization and disproportionation reactions, the catalyst could be recycled in numerous runs without loss in activity. 4-Tolylacetylene and phenylacetylene itself, proved also to form acetophenone derivatives in high yields. The ketones were however, accompanied by the trimerization products, 1,2,4- and 1,3,5-triarylbenzene. The diyne 1-phenyl-1,4-pentadiyne, PhC≡CCH₂C≡CH formed, like the bromophenylacetylene, only hydration products. The water, added to the internal triple bond in

the two possible modes, but only in one way to the terminal ethynyl function. Thus, both PhCH₂COCH₂COMe and PhCOCH₂CH₂COMe have been obtained. The latter compound was found to undergo intramolecular cyclization by the well known pathway, see e.g. Ref. [23], to yield 2-methyl-5-phenylfuran. The ratio between the three products formed from 1-phenyl-1,4-pentadiyne, proved to depend on the reaction temperature. While the 1,4-diketone, the 2,4-diketone and the furan derivatives were formed at 50° in 11, 33 and 43%, respectively, at 70°C the entire 1-phenyl-1,4-pentadiyne was converted into 2-methyl-5-phenylfuran and consequently the reaction mixture consisted after 5 h, of 47% of the 2,4-diketone and 53% of the cyclized product.

Unlike the aromatic alkynes aliphatic acetylenes underwent in the presence of **1** only oligomerization. 1-Octyne e.g., formed at 50°C a ketone-free mixture of 1,2,4- and 1,3,5-tripentylbenzene as the major and minor products, respectively. Some other non-aromatic alkynes formed also dimers, but not hydration products. Ethyl propargylate e.g., gave in addition to the trimethyl esters of mellitic and trimesic acids, also the two dimers EtOCOC≡CC(CO₂Et)–CH₂ and *trans*-EtOCOC≡C(OH)=CHCO₂Et (c.f., Ref. [24]). Some representative results of

Table 3

Hydration and oligomerization of several alkynes in the presence of **1** under comparable conditions ^a

Alkyne	Hydration products (yield, %)	Oligomerization products (yield, %)
4-BrC ₆ H ₄ C≡CH	4-BrC ₆ H ₄ COMe (97)	
4-MeC ₆ H ₄ C≡CH	4-MeC ₆ H ₄ COMe (86)	1,2,4-C ₆ H ₃ (4-C ₆ H ₃ Me) ₃ (8) 1,3,5-C ₆ H ₃ (4-C ₆ H ₄ Me) ₃ (5)
PhC≡CH	PhCOMe (64)	1,2,4-C ₆ H ₃ Ph ₃ (20) 1,3,5-C ₆ H ₃ Ph ₃ (16)
PhC≡CCH ₂ C≡CH	PhCO(CH ₂) ₂ COMe (11) PhCH ₂ COCH ₂ COMe (33) PhC=CHCH=C(Me)O (43)	
Me(CH ₂) ₅ C≡CH		1,2,4-C ₆ H ₃ (C ₆ H ₁₃) ₃ (69) 1,3,5-C ₆ H ₃ (C ₆ H ₁₃) ₃ (10)
EtOCOC≡CH		1,2,4-C ₆ H ₃ (CO ₂ Et) ₃ (51) 1,3,5-C ₆ H ₃ (CO ₂ Et) ₃ (36) EtOCOC≡CC(CO ₂ Et)=CH ₂ (6) <i>t</i> -EtOCOC≡COH=CHCO ₂ Et (6)

^a Reaction conditions: 11.4 mmol alkyne, 0.57 mmol catalyst, 8 ml 92% aqueous EtOH, N₂ atmosphere, 5 h at 50°C.

the transformations of these alkynes are summarized in Table 3.

3.4. Activity of supported ion pair catalysts other than **1**

In addition to **1** we have studied the utilization of some of its analogs as recyclable catalysts. Double bond migration in allylic compounds has been the model catalysis in these studies. Polystyrene-bound onium salts other than Dowex 1 were obtained in two steps (i) by interaction of crosslinked chloromethylated polystyrene (Merrifield polymer), with the desired tertiary amine in a swelling solvent (e.g. benzene) at 65°C for 5 d [25]; (ii) by stirring of the resulting ammonium salt for 3 d at room temperature with RhCl_3 in EtOH. By this method we synthesized [polystyrene- $(\text{CH}_2\text{NR}^1\text{R}_2)_n$] $^{n+}$ [$\text{RhCl}_4(\text{H}_2\text{O})_m$] $^{n-}$ (**4**) where (a) $\text{R}^1 = \text{R}^2 = \text{Et}$; (b) $\text{R}^1 = \text{R}^2 = n\text{-Bu}$; (c) $\text{R}^1 = \text{R}^2 = \text{Me}(\text{CH}_2)_5$ and (d) $\text{R}^1 = \text{Me}(\text{CH}_2)_{11}$, $\text{R}^2 = \text{Me}$. Samples were prepared using resins crosslinked with 1, 2 and 4% divinylbenzene.

Allylbenzene isomerization by these catalysts was carried out best in butanol at 90°C. While **4a** proved to undergo rapid reduction (to colloidal $\text{Rh}(0)$), **4b** and **4d** reacted smoothly and the equilibrium mixture of allylbenzene, and *cis*- and *trans*-2-propenylbenzene (Eq. (1)) was obtained usually within less than 1 h. In moist diglyme and in butyl acetate the rates were about half of that recorded in butanol. Except for **4a**, these catalysts were leach-proof, and could be recycled with hardly any loss in activity for 3–5 runs. Thereafter, slow structural changes occurred that caused slow deterioration of these catalysts as well as reduction in rate. Ion pair **4c**, in which the rhodium atom is heavily shielded by the three large hexyl groups, has only a marginal catalytic activity for Eq. (1).

In analogy to the immobilized ammonium salts we synthesized also 1, 2 and 4% crosslinked polystyrene-bound tributylphosphonium chloride [25], which, in turn, was converted by

interaction with ethanolic RhCl_3 to [polystyrene- $(\text{CH}_2\text{PBu}_3)_n$] $^{n+}$ [$\text{RhCl}_4(\text{H}_2\text{O})_m$] $^{n-}$ (**5**). The phosphorus containing ion pair was leach-proof and catalyzed Eq. (1) in butanol at 90°C to the extent of 76% within 1 h. However, the polystyrene matrix turned rapidly into a sticky material of little activity. Typically, the conversions dropped from 76% in the first cycle to 18% and 4% in the second and third run, respectively.

Finally, we have substituted the rhodium in **1** by ruthenium and by iridium. The corresponding ion pairs **6** and **7** so formed, catalyzed isomerization processes in a rather selective manner. The ruthenium catalyst **6** promoted double bond migration in 1-octen-3-ol (Eq. (6)) but not in allylbenzene (Eq. (1)). Under conditions similar to those described for Eq. (1) by **1**, the conversion was 57% during 1 h. No change in reactivity was observed upon recycling for two further runs. Unlike **6**, the immobilized iridium containing ion pair **7**, catalyzed the isomerization of allylbenzene at 78°C (but not that of 1-octen-3-ol) to obtain the equilibrium mixture (Eq. (1)) within 70 min. The catalyst was found to be leach-proof and did not lose its activity in three successive runs. Both catalysts **6** and **7** were shown to be less sensitive than **1** to structural factors. Thus, hardly any differences in activity was observed when the ion pairs were supported on Dowex 1 × 2, Dowex 1 × 4 or Dowex 1 × 8.

Acknowledgements

We thank Claudio Rottman for his help in measuring the surface areas of the catalysts, and the Israel Science Foundation (administered by the Israel Academy of Sciences and Humanities) for financial support of this study.

References

- [1] J. Blum, Russ. Chem. Rev. 42 (1993) 1619.
- [2] Y. Badrieh, J. Blum, H. Schumann, J. Mol. Catal. 90 (1994) 231.

- [3] W. Baidossi, H. Schumann, J. Blum, *Tetrahedron* 52 (1996) 8349.
- [4] Y. Sasson, A. Zoran, J. Blum, *J. Mol. Catal.* 11 (1981) 293.
- [5] J. Blum, I. Pri-Bar, H. Alper, *J. Mol. Catal.* 37 (1986) 359.
- [6] I. Amer, V. Orshav, J. Blum, *J. Mol. Catal.* 45 (1988) 207.
- [7] J. Blum, H. Huminer, H. Alper, *J. Mol. Catal.* 75 (1992) 153.
- [8] M. Setty-Fichman, J. Blum, Y. Sasson, M. Eisen, *Tetrahedron Lett.* 35 (1994) 781.
- [9] G. Braca, R. Cioni, G. Sbrana, G. Scandiffio, *At. Absorpt. Newsl.* 14 (1975) 39.
- [10] S. Lowell, J.E. Shields (Eds.), *Powder Surface Area and Porosity*, 2nd ed., Chapman and Hall, New York, 1987.
- [11] J. Sabadie, G. Descotes, *Bull. Soc. Chim. Fr.* (1976) 911.
- [12] C.U. Pittman, in: G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), *Comprehensive Organometallic Chemistry*, vol. 8, Pergamon, Oxford, 1982, pp. 553–611.
- [13] J. Azran, O. Buchman, M. Orchin, J. Blum, *J. Org. Chem.* 49 (1984) 1327.
- [14] J. Smith, *Chemical Engineering Kinetics*, McGraw-Hill, New York, 1975, p. 297.
- [15] A. Zoran, Ph.D. Dissertation submitted to the Senate of the Hebrew University, Jerusalem, December, 1982.
- [16] O. Levenspiel, *Chemical Reaction Engineering*, 2nd ed., Wiley, New York, 1972, pp. 489–490.
- [17] A. Rosenfeld, J. Blum, D. Avnir, *J. Catal.* 164 (1996) 363.
- [18] K. Moseby, P.M. Maitlis, *J. Chem. Soc. (A)*, (1970) 2884.
- [19] M.B. Fischer, E.J. James, T.J. McNeese, S.C. Nyburg, S.C. Posin, W. Wong-Ng, S.S. Wreford, *J. Am. Chem. Soc.* 102 (1980) 4941.
- [20] N.D. Zelinsky, G.S. Pawlow, *Ber.* 66 (1933) 1420.
- [21] M. Eisen, T. Korpai, J. Blum, H. Schumann, *J. Mol. Catal.* 61 (1990) 19.
- [22] I. Amer, T. Bernstein, M. Eisen, J. Blum, K.P.C. Vollhardt, *J. Mol. Catal.* 60 (1990) 313.
- [23] D.M.X. Donnelly, M.J. Meegan, in: R.A. Katritzky, A.R. Rees (Eds.), *Comprehensive Heterocyclic Chemistry*, vol. 4, Pergamon, Oxford 1984, pp. 659, 660 and references cited therein.
- [24] K.A. Pollart, U.S. pat 3,383,403, May 14, 1968 (Chem. Abstr. 69 (1968) 35475k).
- [25] M. Tomoi, W.T. Ford, *J. Am. Chem. Soc.* 103 (1981) 3821.