

On the promoting effect by quaternary ammonium salts in the multiphase hydrodechlorination with hydrogen gas on Raney nickel catalyst

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Received 14 December 2006; received in revised form 28 March 2007; accepted 31 March 2007

Available online 13 April 2007

Abstract

Hydrodechlorination of 1,3,5-trichlorobenzene with hydrogen gas on Raney nickel catalyst in the biphasic system composed of isooctane, aqueous KOH, and a quaternary ammonium compound as a promoter at 70 °C and atmospheric pressure was studied. The promoter increased the rate of reaction above two orders of magnitude. Several quaternary chloride salts were studied, such as Aliquat 336, trioctylmethylammonium, tridodecylmethylammonium, cetyltrimethylammonium, tetrabutylammonium and tetraethylammonium. The relationship of the reaction rate with adsorption, micelle formation, and the structural properties of the promoter are discussed.

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Keywords: Hydrodechlorination; Quaternary ammonium; Raney nickel; Multiphase; Promoter

1. Introduction

The effects of quaternary ammonium salts quats as promoters in liquid phase hydrodechlorination over heterogeneous catalysts, such as Pd/C and Raney nickel has been studied in our laboratory for more than 10 years with the focus on a variety of substrates and catalytic systems [1–4]. However, the mechanism of the promoting action of the quaternary salt remains undisclosed. Based on our previous data, it appeared that the promoting action may be influenced by several properties of the quaternary salt, such as phase-transfer of OH[−] or another species, solvent effects arising from an ionic liquid supported on the catalyst surface, or a micellar phenomenon. In our previous studies we demonstrated that amongst several of the examined quaternary salts, Aliquat 336 (tricaprylmethylammonium chloride) showed the best performance as a promoter for hydrodechlorination, whilst no reaction was observed in the presence of benzyl or pyridinium substituted quats [1,5]. Phosphonium salts generally showed lower activity while chloride and bromide counter ions of the salt were preferred. The promoting effect was mainly noted in the

multiphase systems, whereby isooctane and aqueous KOH constituted the organic and aqueous phases, which additionally contained the solid catalyst and substrate while being bubbled with hydrogen at atmospheric pressure at a moderate temperature (50 °C).

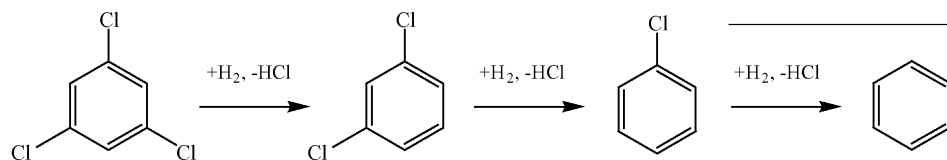
On one hand, it is well known that the quaternary salts, such as Aliquat 336 or cetyltrimethylammonium chloride (CTAC), can form reverse micelles in the isooctane–aqueous system or similar. Such reverse micelles are used for extraction of bioactive compounds [6,7], and more recently for synthesis of metal nanoparticles in microemulsions [8–10]. On the other hand, colloidal nanoparticles of Pd can also be stabilized in solution by the quaternary salts (ionic liquids), resulting in an efficient catalytic system, for example, as used in C–C bond forming reactions [11]. Coordination of Pd(0) by quaternary ammonium or amine functions has also been used for the preparation of supported Pd on polymers and zeolites [12,13].

In order to obtain a preliminary insight for the mechanism of the promoting action by quaternary salts in the multiphase hydrodechlorination system, we studied the reaction of 1,3,5-trichlorobenzene (TCB) on Raney nickel with hydrogen gas in the biphasic isooctane/aqueous medium (1). We have previously reported some of our data for the same system [14]. Reaction of 1,3,5-TCB is a simple scheme with only two intermediates and imitates well the general reactivity of

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polychlorinated aromatics. In this case, Raney nickel is interesting owing to the more pronounced effect that is induced by the quaternary salt, compared with the Pd/C system [1,14].



This investigation explores the relationship between the structure, properties, and related phenomena of several quaternary ammonium compounds amongst other substrates, and the activity of Raney nickel catalyst in the hydrodechlorination system.

2. Experimental

All the reagents and solvents were used as purchased without further purification. Raney-Ni (50% slurry in water) Actimet MTM (Ni 93% and Al 7%, particle size distribution of 0–80 μm , surface area of 70–80 m^2/g) was a gift from Engelhard. Trioctylmethylammonium chloride was synthesized according to the procedure reported in [15]. GC analyses were performed on a Varian 3400 using a fused silica capillary column “Chrompack CPSil 24 CB lowbleed/MS” (30 $\text{m} \times$ 0.25 mm , film thickness 0.25 μm). GC/MS analyses were performed on an Agilent 5973 mass detector coupled to an Agilent 6890N GC with an HP-5MS capillary column (30 $\text{m} \times$ 0.25 mm , film thickness 0.25 μm). Water content was determined by Karl Fischer titration using a Metrohm 736 GP Titrimo apparatus.

A 25 mL three-necked round-bottomed reactor thermostated in a silicone bath at 70 $^\circ\text{C}$ and supplied with a condenser, was loaded with a 10 mL isooctane solution containing 0.059 g of

n-dodecane (GC internal standard), 0.25 g of the Raney nickel slurry in water (*ca.* 2.3 mmol Ni as experimentally determined) and the required amount of the additive (see Table 1). After pretreating the mixture for 10 min with hydrogen, bubbled through the solution at *ca.* 10 mL/min, a 5 mL aliquot of aqueous KOH solution was added to the mixture followed by 0.127 g (0.7 mmol) of 1,3,5-trichlorobenzene. Each reaction was then stirred magnetically at 1000 rpm, thermostated, and bubbled with hydrogen.

Samples were periodically collected from the organic phase, and analysed by GC and/or GC/MS. Approximately 0.20 mL was removed for each sample which was subsequently diluted in ethyl ether with a total volume made to 1–2 mL. The relative concentrations of reaction components were obtained by reference of their respective GC peak areas with that of the internal standard or from the percent ratio of the respective areas of MS total ion peaks.

3. Results and discussion

Hydrodechlorination experiments were run in the biphasic isooctane–aqueous base system which was heated at 70 $^\circ\text{C}$, and

Table 1
Hydrodechlorination of 1,3,5-TCB in the presence of different additives^a

No.	Additive	Amount (mmol)	Additive localization	KOH (%)	Initial rate $\times 10^5$ ($\text{mol}_{\text{sub}}/\text{mol}_{\text{cat}} \text{ s}$)
1.	None	–	–	4	0.23
2.	Aliquat 336	0.260	Micelles in isooctane	4	35.0
3.	(i) TOMAC	0.280	Micelles in isooctane	4	10.0
	(ii) 1-Octanol	0.320			
4.	TOMAC	0.280	Third liquid phase	4	25.0
5.	TDMAC	0.260	Third liquid phase	4	17.0
6.	CTAC	0.280	Aqueous phase	4	7.60
7.	TBAC	0.260	Aqueous phase	4	1.20
8.	TBAC	0.360	Third liquid phase	20	1.60
9.	TEAC	0.260	Aqueous phase	4	0.42
10.	TMAC	0.260	Aqueous phase	4	0.52
11.	NH ₃	3.400	Aqueous phase	–/4	0.00
12.	(i) NH ₄ Cl	3.740	Aqueous phase	–	0.00
	(ii) NH ₃	72.00			
13.	(i) Aliquat 336	0.260	Aqueous phase	–	7.00
	(ii) NH ₃	72.00			
14.	MBIC	0.260	Aqueous phase	4	0.00
15.	AOT	0.260	Aqueous phase	4	0.00
16.	SDS	0.260	Aqueous phase	4	0.51
17.	Triton-X 100	0.260	Aqueous phase	4	0.14

^a 0.7 mmol substrate, 0.25 g Raney nickel slurry (2.3 mmol Ni), 10 mL isooctane – 5 mL aqueous KOH solution, hydrogen flow *ca.* 10 mL/min, atmospheric pressure, 70 $^\circ\text{C}$, 1000 rpm stirring.

contained the Raney nickel slurry, substrate and additive, while being bubbled with hydrogen – the standard procedure used in our previous studies [14]. The results are summarized in Table 1. The reported initial rates refer to TCB decay (zero order in most cases). The rate values were obtained by fitting the data points lying on the initial linear part of the profile or within the faster initial part of the kinetic curve and within the conversion of 30%, in cases where this was achieved.

Similar with our previous study [14], a difference of two orders of magnitude was observed in the rate of reaction between the system without additive (entry 1) and the system which included 0.26 mmol of Aliquat 336 (entry 2). As previously suggested, the higher rate of reaction observed in the presence of Aliquat 336 could be attributed to its adsorption on the catalyst surface. Additionally, it was noted by visual observation that the presence of Aliquat 336 in the system generally improved catalyst dispersion. This could be associated with the formation of micelles or lipophilization of the catalyst surface by the adsorbed Aliquat 336.

Technical grade Aliquat 336 contains a minimum of 85% of tricaprilmethyl ammonium chloride, in which the capryl component comprises a mixture of C7–C9, which is predominately C8. Typical impurities of Aliquat 336 are C7–C9 alcohols, which are known to be co-surfactants. Due to the presence of such impurities, Aliquat 336, which also contains *ca.* 5% water, is apparently soluble in isooctane. At a higher value of water content, or in the biphasic isooctane–water system, Aliquat 336 precipitates as a separate liquid phase which is immiscible in water and isooctane [1]. This phase which is composed of Aliquat 336, water, and isooctane resides at the organic aqueous interphase and disappears in the presence of aqueous KOH above 3%, since the formation of reverse micelles by Aliquat 336 requires a basic pH [7]. For example, pure trioctylmethyl ammonium chloride (TOMAC) is not soluble in water. However, with the addition of 20% of 1-octanol to the isooctane–aqueous KOH system containing TOMAC, complete dissolution of the TOMAC occurs in the isooctane phase. In the reaction system (isooctane–aqueous KOH 4%) containing Aliquat 336, a water content of *ca.* 0.3% was measured for the organic phase. In contrast, only 0.006% H₂O was measured for the same system without Aliquat 336 or *ca.* 0.01% H₂O for a system with an equimolar amount of TOMAC. Additionally, in the presence of TOMAC/1-octanol (5:1) for the same system, the water content in the organic phase was found to be 0.2% H₂O.

In principle, the emulsification processes associated with the presence of Aliquat 336 may influence the reaction by the development of the liquid–liquid interphase and consequently increase the accessibility of hydroxide ion and Raney nickel by the substrate from the organic phase. Nevertheless, this effect seems to be negligible since efficient dechlorination also occurred in the system that included an equimolar amount of TOMAC in place of Aliquat 336, either solely or within a mixture with 1-octanol. In the former case (entry 4), emulsification did not occur and the TOMAC layer resided at the interphase; while in the latter case (entry 3), TOMAC was emulsified in isooctane. Another quaternary salt of similar

structure, tridodecylmethylammonium chloride (TDMAC) also exerted a pronounced promoting influence on the rate of hydrodechlorination, despite being completely insoluble in the reaction medium (entry 5). Furthermore, no effect was observed for the rate of reaction in the presence of other types of surfactants, namely anionic ones, such as sodium bis-(2-ethylhexyl)sulfosuccinate (AOT) and sodium dodecylsulfate (SDS), and the non-ionic Triton-X 100 (polyethylene glycol *p*-(1,1,3,3-tetramethylbutyl)-phenyl ether) (entries 15–17). This data suggested that rate promoting effects arising from the development of a liquid–liquid interphase are unlikely to be significant.

It was noted by visual observation that addition of Raney nickel to the isooctane–aqueous system which contained TOMAC or TDMAC, led to complete adherence of the liquid film of the latter to the surface of the catalyst, bringing it to the liquid–liquid interphase and creating an ionic liquid environment on its surface. This could be considered a solvent effect, similar to that of ionic liquids as observed in several catalytic reactions; however, the reaction did not proceed at all where pure Aliquat 336 was used as the organic phase. Previously, we also suggested that the exact action of the quaternary salt in this system was attributed only to a partial amount of Aliquat 336 covering the metal sites [14]. A sharp saturation of the rate dependencies occurred at 0.2–0.3 mmol of the quaternary salt; however, this amount is considerably higher than that necessary to form a monolayer on the surface of Raney nickel (*ca.* 8–9 m² for 0.125 g of dry Raney nickel). For the present analogous system using TOMAC, the hydrodechlorination rate dependence on the content of TOMAC also showed a break (see Fig. 1). In this case, the break occurred at *ca.* 0.05 mmol of TOMAC, which agreed more consistently with the calculated surface area of Raney nickel present in the system. Assuming that the ionic radius of a TOMAC molecule is near 100 Å, and considering that only an approximation can be made, an amount of 0.05 mmol should cover an area of nearly 30 m² which is close to the surface area of Raney nickel in the system (*ca.* 10 m²) [14].

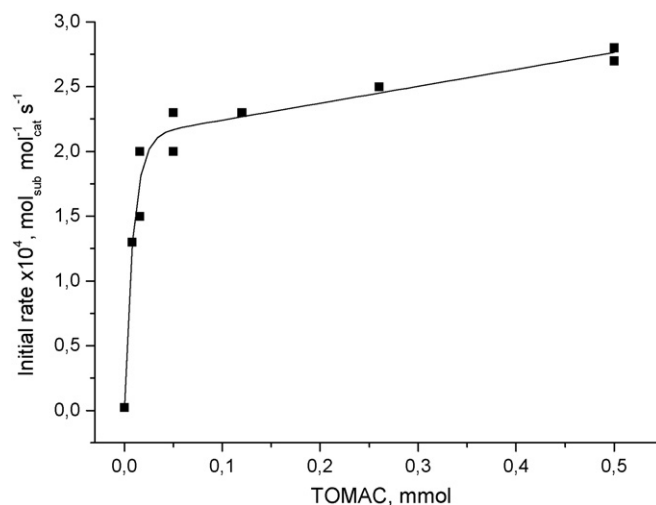


Fig. 1. Dependence on the initial rate of reaction for TCB over Raney nickel (for conditions see Table 1) by the amount of TOMAC in the system.

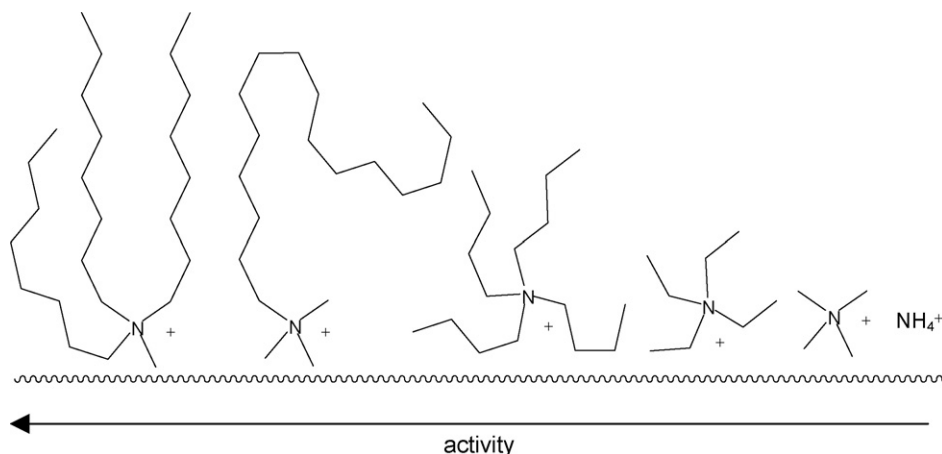


Fig. 2. Relative correlation between the structure of quaternary cations and their activity as promoters in hydrodechlorination over Raney nickel.

Several water soluble quaternary salts, such as cetyltrimethylammonium chloride (CTAC) and tetrabutylammonium chloride (TBAC) also showed a promoting effect on the rate of the reaction (entries 6–8), however, a less pronounced effect than that exhibited by TOMAC, TDMAC, or Aliquat 336. Under certain conditions (e.g. at KOH concentrations greater than 17%), TBAC also formed an immiscible liquid phase which was rich with the quaternary salt (entry 8). Nevertheless, a noticeable difference was absent in comparison to the system where TBAC was dissolved in aqueous KOH (entry 7).

More hydrophilic quaternary salts, such as tetraethylammonium chloride (TEAC) and tetramethylammonium chloride (TMAC) also influenced the rate of the reaction (see entries 9 and 10), with the rates being close to that of the blank system (entry 1). Ammonia solutions or ammonium salts only caused inhibition (see entries 11, 12). The reaction occurred in the presence of ammonia which was used as a base in the presence of Aliquat 336 (entry 13), however, it ceased when the extent of conversion reached 60%. This data suggested that ammonium chloride acts rather as an inhibitor than a promoter. A negative effect was also produced by 1-methyl-3-butylimidazolium chloride (MBIC) (entry 14), a well known ionic liquid which alternatively provides a solvent medium for numerous polar reactions.

4. Conclusions

From the data obtained we can conclude that the promoting effect by quaternary salts in the examined hydrodechlorination system is unlikely to be related to a micellar phenomena, that would favour mass transfer through the liquid–liquid interphase. Nor does it appear to be influenced by solvent effects constituted by a new ionic liquid phase composed of the quaternary salt. The observed effect on rate is likely to be attributed to the physical interaction of the charged nitrogen on the quaternary cation (quat) with the nickel sites. This effect seems to be limited only to the quat molecules which are in direct contact with the surface. Nevertheless, micellar processes and phase-transfer phenomena can also incur changes in reaction behaviour. For example, octanol and additional alcohol impurities of commercial Aliquat

336, known to favour micelle formation, render it less efficient than pure TOMAC at low concentrations. Therefore, attention should be paid to the purity of the substrates that participate in adsorption processes.

The data also point out that the structure of the quat is firmly linked to its activity as a promoter. In particular, quats with amphiphilic structures are more active i.e., those possessing at least one long and one short alkyl chain. On one hand, hydrophilic properties of the quat favour stronger adsorption on the catalyst surface (in competition with water); on the other hand, lipophilic properties support access of the organic substrate to the catalyst. Therefore, it is not important whether the quaternary salt i.e., potential promoter is water or organic soluble, nor if it forms a separate phase or leads to micelle formation. Among the quats studied, asymmetric examples such as TOMAC and CTAC gave enhanced performance, whereas symmetric examples such as TMAC and TEAC did not produce a notable effect. In the case of the moderately lipophilic TBAC, only a negligible effect was observed. The tendency of quats to act as promoters and the relationship with their structural composition is depicted in Fig. 2.

Acknowledgements

We acknowledge support from the Italian Ministry of Foreign Affairs (Directorate General for Cultural Promotion and Co-operation – Office V) and thank Dr. Alvis Perosa for a gift of TOMAC.

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