Harnessing the Unique Properties of Iridium

ATTRACTIVE CATALYST FOR HYDROGENATION

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With the exception of osmium, iridium is the least abundant of the six platinum group metals. It is of crucial importance in a number of high technology applications and, at least in the past, has been regarded as a strategic material and stockpiled by major governments. In recent years it has become more readily available, prompting renewed interest by researchers, including those seeking to develop improved catalysts. In this paper we discuss the results of our investigations on the use of iridium as an hydrogenation catalyst. Data are presented on the characteristics of an iridium-based catalyst developed here for the effective and selective synthesis of substituted N-aryl-hydroxylamines and chloro-substituted anilines, symmetric and asymmetric azoxybenzenes, and unsaturated alcohols. These demonstrate that iridium is unique among the platinum metals.

Historically, the interest of researchers in the use of iridium as a catalyst for the hydrogenation of organic compounds has been intermittent. One recent period of activity occurred in the late 1960s to early 1970s when the characteristics and properties of various iridium-based catalysts were investigated. Russian scientists were involved in these researches; in particular, a new procedure to prepare a boron-promoted iridium-based catalyst, containing 0.5 to 20 wt.% iridium and 0.002 to 0.45 wt.% boron based on the weight of carrier, and a carrier which is inert towards various chemicals was developed by E. N. Bakhanova, M. L. Khidekel and colleagues at the Institute of Chemical Physics in Chernogolovka of the Russian Academy of Sciences (ICPC RAS) (1). This enabled the iridium-based catalyst to be produced on an industrial scale and to be used for the selective synthesis of 3,4-dichloroaniline by the hydrogenation of 3,4-dichloronitrobenzene, with more than 700 tonnes of high quality amino product being manufactured from this reaction.

However, at that time the availability of iridium for use by the chemicals industry could not be assured. Supplies were limited and used mainly for military purposes. More recently, with the easing of tension between the major powers and the reduction of their armed forces, the strategic importance of iridium has been downgraded, resulting in major changes in its availability and cost.

Thus, through the late 1980s and early 1990s the reduced strategic demand for iridium was matched by a decrease in its price, see Figure 1 (2). The lower prices offered opportunities for further economic use to be made of iridium and some increased demand has occurred in the 1990s. Even now, with supply and demand governed by normal commercial considerations price variations are always possible.
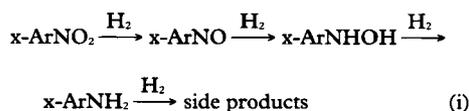
Iridium Catalyst Development

Over the years, research into hydrogenation has continued at ICPC RAS. It has been established that the iridium-based catalyst developed here has specific characteristics which are especially advantageous during the hydrogenation of various substances. In particular, in our research an iridium catalyst of the following composition was used: 4.7 to 4.9 weight per cent iridium and 0.08 to 0.1 weight per cent boron based on the weight of carrier, with an

activated carbon used as an inert carrier. Some of the reactions that may be facilitated by this unique catalyst are presented here.

Selective Synthesis of Substituted N-Arylhydroxylamines

The useful properties of our iridium-based catalyst were determined during liquid-phase hydrogenations of substituted nitrobenzenes. This reaction typically proceeds in the presence of platinum group metals, in a neutral medium, according to the following scheme:

$$x\text{-}ArNO_2 \xrightarrow{H_2} x\text{-}ArNO \xrightarrow{H_2} x\text{-}ArNHOH \xrightarrow{H_2}$$

$$x\text{-}ArNH_2 \xrightarrow{H_2} \text{side products} \qquad (i)$$

where $x\text{-}ArNO_2$, $x\text{-}ArNO$, $x\text{-}ArNHOH$ and $x\text{-}ArNH_2$ are substituted nitrobenzene, nitrozobenzene, N-arylhydroxylamine and aniline, respectively, and x is a substituent, such as -H, -Cl, -Br, -I, -F, -COOH, -CHO, -OH, -NH₂, -OCH₃, -COOCH₃, -OC₂H₅, -NHCOCH₃, etc.

The side products of the reaction are formed during transformation of the final $x\text{-}ArNH_2$ via hydrogenation of the benzene ring or elimination of one or several functional groups at a high volume of conversion (more than 95 to 98 per cent) of the initial $x\text{-}ArNO_2$. The nitrozo compound does not get into the solution, due to its extremely high adsorption on the catalytic surface, where it reacts immediately to give $x\text{-}ArNHOH$.

We investigated the hydrogenation of a number of nitro compounds in the presence of iridium-, platinum- and palladium-based catalysts, see Table I. A comparison of the hydrogenation rates indicates the relative similarities of the specific activities of the catalysts under consideration. It must be noted, however, that the iridium catalyst is less suitable for the hydrogenation of nitro compounds with electron-donating substituents, especially by comparison with the palladium catalyst. At the same time, in the presence of the iridium-based catalyst, the hydrogenation of halogen-substituted nitro compounds proceeds at a high rate. Due to the very high halogen ion elimination rate, the palladium
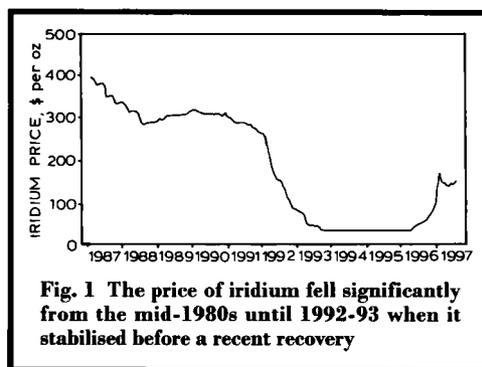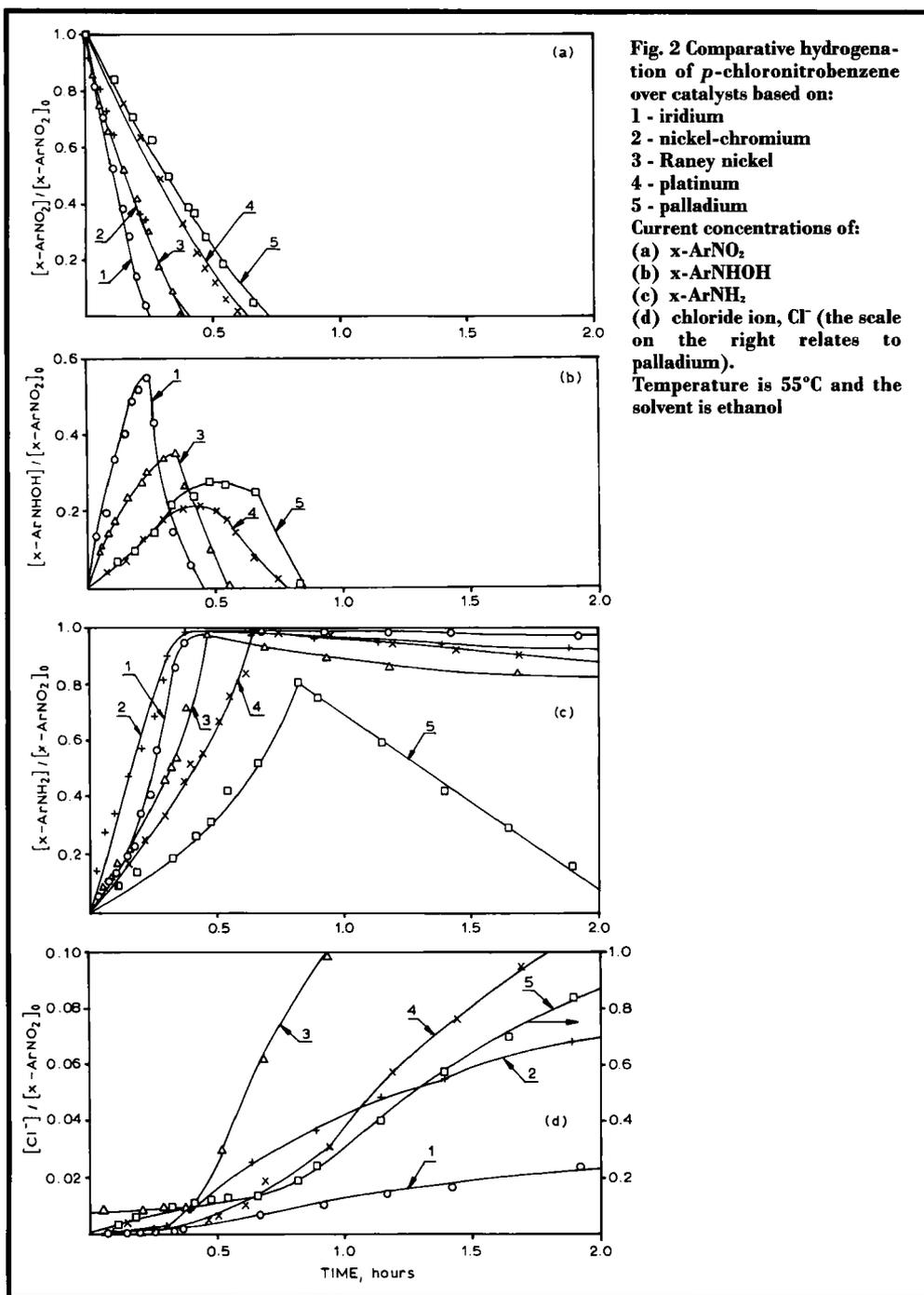

Fig. 1 The price of iridium fell significantly from the mid-1980s until 1992-93 when it stabilised before a recent recovery

catalyst was found to be totally unsuitable for this reaction.

Comparing the hydrogenation rates over iridium- and platinum-containing catalysts shows their similarities. However, a significant difference in the distribution of products, compared with the platinum catalysts, is clearly observed during the iridium-catalysed hydrogenation. In particular, much higher concentrations of the intermediate, N-arylhydroxylamine, have been noted and it has a lower rate of transformation into the amino product.

Our researches show that the regularities of the product distribution during hydrogenation of substituted nitrobenzenes over various catalysts are similar. Data on the product distribution in the course of hydrogenations of p-chloronitrobenzenes in the presence of a number of catalysts are given in Figure 2. The product distribution curves are similar in appearance. The concentration of the initial nitro product, see Figure 2(a), falls in direct proportion to the reaction time, up to a high volume of conversion, that is, the reaction is zero order with respect to the starting nitro compound.

At first the concentration of the intermediate N-arylhydroxylamine increases linearly, reaches a maximum, then decreases, roughly proportional to the reaction time after the initial nitro compound is used up in the reaction mixture, see Figure 2(b). It must be noted that in some cases the catalytic hydrogenation of aromatic nitro compounds can proceed without the visible accumulation of N-arylhydroxylamine in the reaction mixture. For example, during

Fig. 2 Comparative hydrogenation of p-chloronitrobenzene over catalysts based on:
1 - iridium
2 - nickel-chromium
3 - Raney nickel
4 - platinum
5 - palladium
Current concentrations of:
(a) x-ArNO$_2$
(b) x-ArNHOH
(c) x-ArNH$_2$
(d) chloride ion, Cl$^-$ (the scale on the right relates to palladium).
Temperature is 55°C and the solvent is ethanol

hydrogenation of o- and p-nitroanisoles, p-nitro-phenetole and p-nitrophenol. Figure 2(c) shows that p-chloroaniline is formed continuously during the period when the concentrations of the initial and intermediate products change.

The rate of the side dehalogenation reaction

Table I

Apparent Rate Constants for Hydrogenations of Nitroaromatic Compounds over Iridium-, Platinum- and Palladium-Based Catalysts

Nitro compound	Apparent rate constants, k_a, mol h^{-1}/kg of catalyst		
	Iridium	Platinum	Palladium
p-Chloronitrobenzene	83.2	103.3	153.4
Nitrobenzene	73.4	106.7	200.2
p-Nitrotoluene	69.8	106.5	190.2
p-Nitrophenetol	46.8	86.8	190.0
p-Nitroanisole	50.0	86.9	173.2
p-Nitrophenol	26.6	43.2	233.3
3,4-Dichloronitrobenzene	116.6	116.6	143.3
m-Nitrobenzofluoride	126.7	123.5	216.7
o-Nitroanisole	53.3	106.6	193.3
m-Nitrotoluene	66.6	199.9	190.1
2,4-Dinitrotoluene	63.4	93.2	156.6

Reaction conditions: hydrogen pressure is 0.1 MPa; reaction temperature is 50°C and solvent is isopropyl alcohol

is very slow when the nitro compound and N-arylhydroxylamine are present in the reaction mixture, see Figure 2(d); it increases only after complete transformation of the N-arylhydroxyl-amine into the amino product. However, as previously reported, during hydrogenation over the iridium-based catalyst a much higher concentration of the intermediate N-arylhydroxylamine was observed, as was its slow rate of transformation into amino products. Moreover, an increase in the hydrogen pressure over the range 0.1 to 1.0 MPa leads to proportional increases in the rate of hydrogenation of the nitro compound into N-arylhydroxylamine, see Figure 3(a), but at the same time does not affect the rate of transformation of the latter into the amino product, see Figure 3(b).

The peculiarities determined from these reactions allow the production of a number of substituted N-arylhydroxylamines by hydrogenation of the corresponding nitro compound over iridium-based catalyst at temperatures in the range from −10 to 0°C and at a pressure of about 1.0 MPa. Thus, production of m-tolylhydroxyl-amine, p-chlorophenylhydroxylamine and 3,4-dichlorophenylhydroxylamine has been achieved in high yield at a pilot plant at ICPC RAS.

As we have previously reported (3–5), the above mentioned peculiarities during the hydrogenation of aromatic nitro compounds over iridium-containing catalyst and opportunities for the production of various substituted N-arylhydroxylamines in its presence are caused by a change in the reaction mechanism in the transformation of x-ArNHOH into x-ArNH$_2$. Over iridium, this transformation mainly occurs not by hydrogenation but by disproportionation of x-ArNHOH:

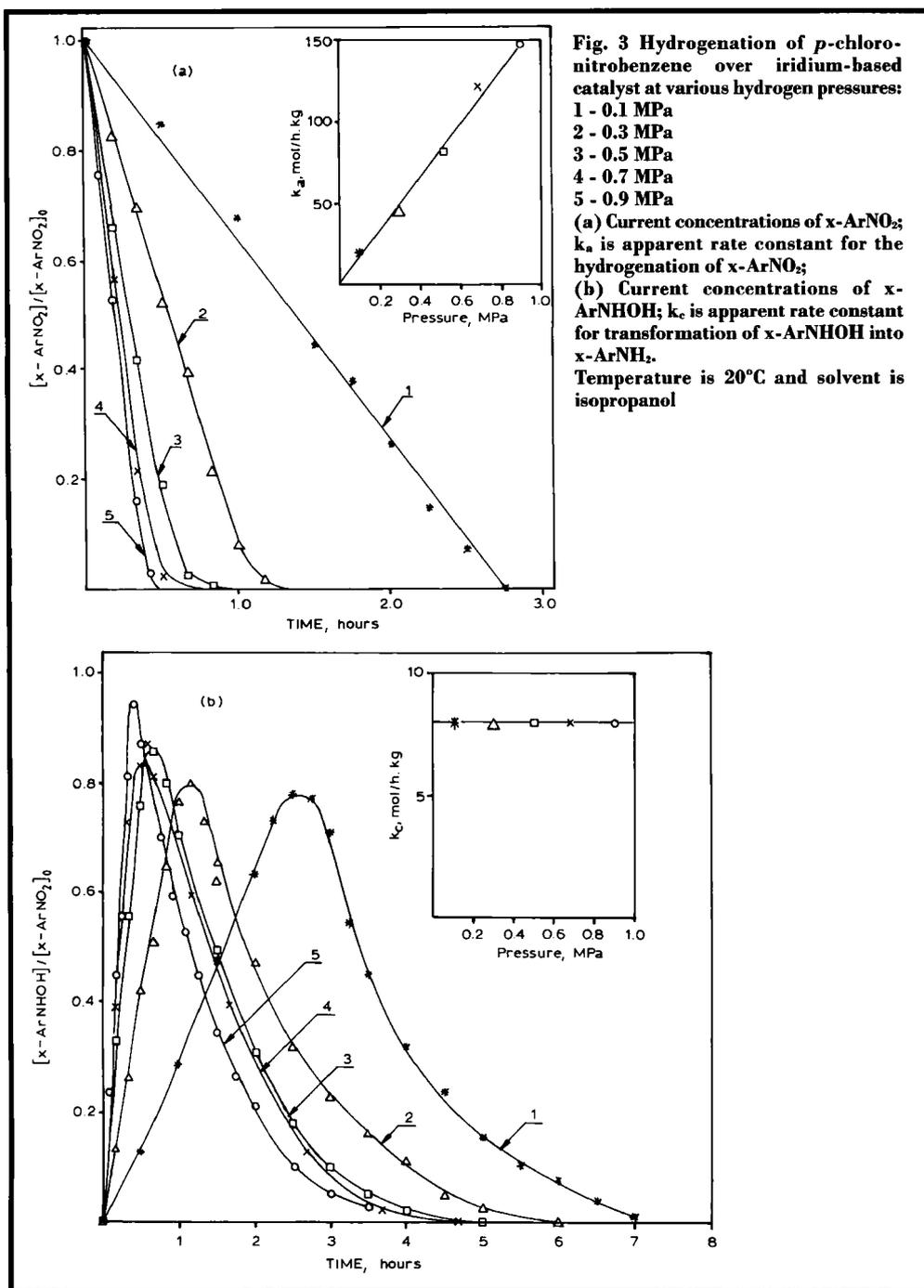$$2 \text{ x-ArNHOH} \rightarrow \text{x-ArNO} + \text{x-ArNH}_2 \qquad \text{(ii)}$$

This step is slower than hydrogenation over palladium, and accounts for the lower conversion to x-ArNH$_2$, especially at high hydrogen pressures. Hydrogen pressure does not affect the disproportionation rate.

Synthesis of Symmetric and Asymmetric Substituted Azoxybenzenes*

It is known from the literature that when x-ArNO and x-ArNHOH are simultaneously present in a reaction medium they interact to form substituted azoxybenzenes (6). The results of our investigation show that platinum group metals are able to catalyse this reaction. In particular it was discovered that symmetric azoxybenzenes could be produced directly from aromatic nitro compounds in a two-step process, in the presence of an iridium catalyst. Direct

Fig. 3 Hydrogenation of p-chloro-nitrobenzene over iridium-based catalyst at various hydrogen pressures:
1 - 0.1 MPa
2 - 0.3 MPa
3 - 0.5 MPa
4 - 0.7 MPa
5 - 0.9 MPa
(a) Current concentrations of x-ArNO$_2$; k$_a$ is apparent rate constant for the hydrogenation of x-ArNO$_2$;
(b) Current concentrations of x-ArNHOH; k$_c$ is apparent rate constant for transformation of x-ArNHOH into x-ArNH$_2$.
Temperature is 20°C and solvent is isopropanol

synthesis is ensured by the selective hydrogenation of x-ArNO$_2$ into the corresponding x-ArNHOH in the first step, Equation (iii), followed by the disproportionation of x-ArNHOH in the second step, see Equation (iv), and its interaction with the x-ArNO which

is thus formed, in the absence of hydrogen, Equation (v):

$$x\text{-ArNO}_2 \xrightarrow{\text{H}_2} x\text{-ArNHOH} + \text{H}_2\text{O} \qquad \text{(iii)}$$

$$x\text{-ArNHOH} \longrightarrow x\text{-ArNO} + x\text{-ArNH}_2 \qquad \text{(iv)}$$

The simultaneous presence of x-ArNHOH and x-ArNO in the reaction mixture during the second step, Equation (iv), leads to the formation of symmetric azoxybenzenes, as in (6):

$$x\text{-ArNO} + x\text{-ArNHOH} \rightarrow x\text{-Ar-}\overset{\overset{\text{O}}{\uparrow}}{\text{N}}\text{=N-Ar-x} \qquad \text{(v)}$$
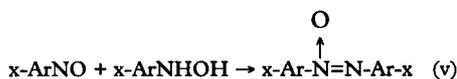
In accordance with the above method, 4,4'-dichloroazoxybenzene, 3,3'-dimethylazoxybenzene, 3,3',4,4'-tetrachloroazoxybenzene and other symmetric azoxy compounds have been synthesised in high yields of 88 to 99 per cent.

It is interesting to note that for the simultaneous hydrogenation of two nitro compounds with different substituents on the benzene ring, an opportunity also occurs for the synthesis of asymmetric azoxybenzenes. Such a simple and effective technique for the production of asymmetric azoxybenzenes provides a viable alternative to complex and multistep conventional methods.

Thus, during the simultaneous hydrogenation of 3,4-dichloronitrobenzene and 4-chloronitrobenzene, in the ratio of 3:1, we were able to successfully produce asymmetric 3,3',4-trichloroazoxybenzene in an approximately 44 per cent yield. At the same time, symmetric 3,3',4,4'-tetrachloroazoxybenzene and 4,4'-dichloroazoxybenzene were formed.

Production of Halogenated Anilines

Taking into consideration the demand for halogenated anilines by the chemical industry, it is necessary to find a method to increase the selectivity of the hydrogenation reaction of the corresponding halogenated nitro compounds, because there are side reactions involving the elimination of a halide ion. Examination of the literature demonstrates that conventional hydrogenation catalysts based on copper, nickel and some platinum group metals, in particular palladium and to a lesser degree platinum, possess significant dehalogenation activities.

We have found that iridium also has unique catalytic properties for the above mentioned process. As shown previously, the iridium-catalysed hydrogenation of substituted nitrobenzenes is characterised by a very low rate of side dehalogenation, see Figure 2(d). It has been shown that the ratio of the reaction rates of hydrogenation to dehalogenation over iridium-based

Table II
Comparative Hydrogenation of 3,4-Dichloronitrobenzene under Non-gradient Flow Conditions

Catalyst	Contact load, mol kg^{-1} h^{-1}	Ratio [x-ArNO$_2$]: [x-ArNO$_2$]$_0$ $\times$ 10^4	Ratio [x-ArNHOH]: [x-ArNO$_2$]$_0$ $\times$ 10^2	Ratio [Cl$^-$]: [x-ArNO$_2$]$_0$ $\times$ 10^2	Yield of amino product, per cent
Iridium	2.4	0.1	0.35	1.5	98.0
	4.1	0.2	0.72	1.1	98.8
	5.2	0.4	1.45	0.9	97.3
	6.4	0.6	2.20	0.8	97.5
	9.5	1.5	4.85	0.7	94.6
Platinum	4.5	0.65	0.15	9.3	95.0
	6.6	0.9	0.20	7.5	96.1
	10.1	2.0	0.50	5.4	97.0
	14.0	4.0	0.90	4.8	96.5
	19.2	7.0	1.60	4.0	96.2

[x-ArNO$_2$]$_0$ is the initial concentration of 3,4-dichloronitrobenzene; [x-ArNO$_2$], [x-ArNHOH] and [Cl$^-$] are the current concentrations of 3,4-dichloronitrobenzene, 3,4-dichlorophenylhydroxylamine and chloride ion, respectively. Temperature is 50°C

Table III				
Characteristics of the Hydrogenation of Unsaturated Aldehydes over Iridium-Based Catalyst in Ethanol			
Unsaturated aldehyde	Half-life, min	Reaction product	Yield, mol per cent
Crotonaldehyde	60	Crotyl alcohol	96
Cinnamaldehyde	60	Cinnamyl alcohol	100
Furylacrolein	70	Furylallyl alcohol	100
Citral	70	Geraniol	100

catalyst at a temperature of 50°C is 240, while that for platinum-based catalyst is 7 to 10 times lower. Thus, with the iridium catalyst having such low dehalogenation activity, it becomes possible to perform the selective synthesis of halogenated anilines via hydrogenation of the corresponding nitrobenzenes.

Data for the hydrogenation of 3,4-dichloronitrobenzene in the presence of iridium and platinum catalysts are compared in Table II under non-gradient flow conditions. It can be seen that the highest yield of 3,4-dichloroaniline over platinum-based catalyst is achieved at contact loads of about 10 mol $kg^{-1}h^{-1}$ and at loads of about 4 mol $kg^{-1}h^{-1}$ for iridium.

It should also be noted that the 3,4-dichloroaniline is obtained in an almost quantitative yield in the presence of the iridium-based catalyst, while for the platinum-catalysed hydrogenation, additional efforts are needed to increase the final product yield. Decreasing or increasing the contact loads outside these ranges results in a decrease in amino product yield because of the side reactions in the first case, and the accumulation of unreacted intermediate N-arylhydroxylamine and initial nitro compounds in the second case, respectively. As stated above, owing to its high selectivity the iridium-based catalyst has been used in Russia for full-scale production of 3,4-dichloroaniline (7).

Selective Hydrogenation of Unsaturated Aldehydes

Our iridium-based catalyst was also found to possess selectivity in the hydrogenation of α,β-unsaturated aldehydes to unsaturated alcohols.
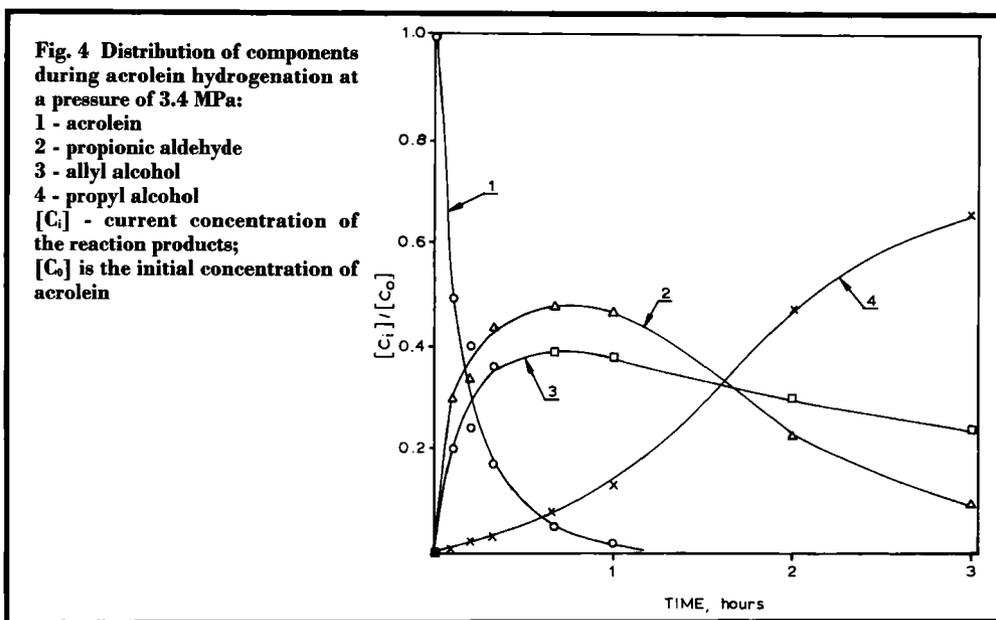
In Table III data on the hydrogenation of crotonaldehyde, cinnamaldehyde, furylacrolein and citral are given, which demonstrate the opportunity for high yield production of the corresponding alcohols over this iridium catalyst (8).

However, it must be stated that the hydrogenation of acrolein proceeds with lower selectivity. The distribution of products from acrolein hydrogenation in the presence of iridium-based catalyst at a hydrogen pressure of 3.4 MPa is given in Figure 4. From this it can be seen that allyl alcohol and propionic aldehyde are formed in approximately equal amounts. After conversion of 80 to 90 per cent of the acrolein, the products obtained are hydrogenated to propyl alcohol. The fact that the rate of allyl alcohol hydrogenation is slower than that of propionic aldehyde allows allyl alcohol to be synthesised in yields of up to 50 per cent.

Regeneration of Spent Catalyst

Another remarkable feature of this iridium catalyst is that its catalytic activity can be almost completely regenerated by treatment with concentrated nitric acid without dissolving the iridium. At the same time many of the iridium catalyst poisons are removed from the catalyst surface. The nitric acid treatment can be repeated many times and this allows the service life of the iridium catalyst to be significantly increased, and decreases its contribution to the total cost of the end products. Of course, such treatment with concentrated nitric acid is impossible for the other platinum group metals because they dissolve in it. Iridium can, like other platinum metals, be extracted from spent catalyst by refining, and used again for new syntheses. Commercial use of our iridium-based catalyst

Fig. 4 Distribution of components during acrolein hydrogenation at a pressure of 3.4 MPa:
1 - acrolein
2 - propionic aldehyde
3 - allyl alcohol
4 - propyl alcohol
[C_i] - current concentration of the reaction products;
[C_0] is the initial concentration of acrolein

for the production of 3,4-dichloroaniline has shown that its service life after refining three or four times is over 10,000 hours and that only 5 to 7 g of iridium are needed to produce 1 tonne of final product; this ignores the refining process which recovers about 90 to 95 per cent of the iridium and returns it to the process.

Conclusions

Investigations on the behaviour of our iridium-based catalyst in some hydrogenation reactions have revealed that it possesses a number of features which make it superior to other platinum metals catalysts and testify to its unique hydrogenation characteristics. We believe that this may open up opportunities for the use of iridium in full-scale processes in the chemical industry.

References

1 E. N. Bakhanova, M. L. Khidekel, V. I. Savchenko et al., *British Patent* 1,453,966; 1976
2 New York Dealer low price figures from *Platt's Metals Week*
3 I. A. Makaryan, V. I. Savchenko and Kh. M. Brikenshtein, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1981, **30**, (5), Part 1, 745
4 I. A. Makaryan and V. I. Savchenko, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1988, **37**, (12), Part 2, 2567
5 I. A. Makaryan and V. I. Savchenko, "New Frontiers in Catalysis", Proc. 10th International Congress on Catalysis, Budapest, 1992, Part C, pp. 2439–2442
6 E. Bamberger, *Ber.*, 1900, **33**, 3600
7 V. I. Savchenko and Kh. M. Brikenshtein, *Khim Promysh.*, 1989, (1), 11
8 E. N. Bakhanova, A. S. Astakhova, Kh. A. Brikenshtein, V. G. Dorokhov, V. I. Savchenko and M. L. Khidekel, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1972, (9), 1993

Ruthenium Sensitisers in Solar Cells

Highly efficient nanocrystalline photovoltaic devices, based on Ru and Os sensitisers have been reported previously (1). The most efficient and stable sensitisers known at present are carboxylated Ru(II) polypyridyl complexes.

Now, researchers from Switzerland (2) have developed a series of new Ru(II) complexes with 2,6-bis(1-methyl-benzimidazol-2-yl)pyridine (bmipy), and tested them by structural variations of NCS and 4,4'-dcbpy in prototype K[Ru(II)(bmipy)(4,4'-dcbpy)(NCS)] (4,4'-dcbpy = 2,2'-bipyrdine-4,4'-dicarboxylate), for their performance as charge transfer sensitisers for nanocrystalline TiO$_2$. A phosphonate group, substituted for carboxyl, was a useful alternative as an anchoring unit, as the Ru complex did not desorb on exposure to water.

References

1 M. Grätzel, *Platinum Metals Rev.*, 1994, **38**, (4), 151
2 S. Ruile, O. Kohle, P. Péchy and M. Grätzel, *Inorg. Chim. Acta*, 1997, **261**, (2), 129