

A Novel Production of γ -Butyrolactone Catalyzed by Ruthenium Complexes

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γ -Butyrolactone (hereafter abbreviated GBL) is produced by the two-stage hydrogenation of maleic anhydride (MAH) in the liquid phase: the hydrogenation of MAH to succinic anhydride (SAH) in the first stage and the subsequent hydrogenation of SAH to GBL in the second stage. The latter hydrogenation has been studied using a homogenous catalyst. A novel ruthenium catalyst system consisting of Ru(acac)₃, P(octyl)₃, and *p*-toluenesulfonic acid (*p*-TsOH) was developed for hydrogenating the SAH, which exhibited excellent catalytic performance, exceeding 95% selectivity for GBL and higher activity than that reported in the literature. It was found that *p*-TsOH plays an important role not only in enhancing the reaction rate, but also in improving selectivity. *p*-TsOH induces a structural change in the Ru complexes, leading to the cationic change which shows higher catalyst activity. It also prevents the undesired side reaction catalyzed by free P(octyl)₃ thus resulting in high selectivity for GBL. A process to produce GBL was investigated. Some novel features of this process include the external preparation method of the Ru complex, the coupling reaction, and the separation to remove H₂O, a product of hydrogenation of SAH, to increase the reaction rate. A catalyst recovery system was also developed to recover over 90% of the catalyst. © 2000 Academic Press

Key Words: hydrogenation; succinic anhydride; γ -butyrolactone production; homogeneous ruthenium catalyst.

INTRODUCTION

The demand for GBL is steadily growing because of its major use as an important intermediate and its direct use as a dielectric material or a solvent. According to Morgan (1), more than 70,000 tons of GBL was manufactured in 1995, roughly 50% of which was used for the production of *N*-methylpyrrolidone. The majority of the remaining amount was 2-pyrrolidone. The world demand for GBL is predicted to be 120,000 tons by the year 2005. In the United States and Europe, a major portion of GBL is currently being produced via the dehydrogenation of 1,4-butanediol, which is manufactured by the classical Reppe process based on

acetylene and formaldehyde. GBL can also be produced based on the hydrogenation of MAH, which is the way it is manufactured in Japan. Butane-based MAH is now available in sufficient amounts at reasonable prices because of the construction of a large-scale fluid-bed MAH plant; the hydrogenation of MAH is the direct method of production of GBL, which is believed to proceed via SAH and does not require the use of hazardous materials (such as in the Reppe process).

Various reasearch projects have carried out extensive studies of the hydrogenation of MAH over different noble metals and Cu catalysts both in the gas phase and in the liquid phase. For example, Castiglioni *et al.* (2) showed that GBL can be obtained by the vapor phase hydrogenation of MAH if copper catalysts with promoted Zinc oxide are used. Also, some patents disclose the liquid phase hydrogenation of MAH in the presence of a supported Pd–Re catalyst (3) and Ni–Co oxide catalyst (4).

However, generally, heterogenous catalysts do not always exhibit satisfactory selectivity for GBL due to the formation of many different and less valuable by-products like *n*-butanol and butyric acid caused by hydrogenolysis and the overhydrogenation reaction. On the other hand, Lyons (5) first pointed out in 1975 that Ru complexes, such as RuCl₂(PPh₃)₃, could catalyze the hydrogenation of SAH to give GBL under mild conditions. Later, various types of Ru catalysts have been proposed. Yoshikawa *et al.* (6) reported that the unsymmetrically substituted succinic anhydride catalyzed by Ru₂Cl₄(dppb)₂ (wherein dppb represents diphenylphosphinobutane) produced the corresponding two isomeric lactones. Moreover, Bianch (7) has described that some cyclic carboxylic anhydrides were hydrogenated in the homogeneous phase using Ru₄H₄(CO)₈(PBu₃)₄ as a catalyst to afford the lactones which did not undergo further hydrogenation.

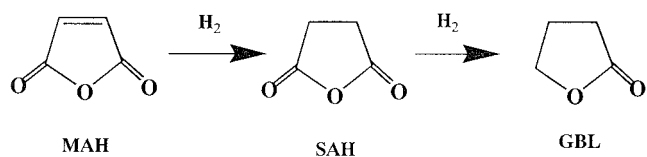
Though these Ru complex catalysts gave much higher selectivity for GBL compared to the heterogenous catalysts, they had some problems from a technological viewpoint. The catalytic activity of RuCl₂(PPh₃)₃ reported in the literature (5) was low, having a TOF (turnover

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frequency-product mol/Ru g · atom h) for SAH hydrogenation of up to 26. Also, most of the proposed Ru complexes contain unfavorable halogen ligands in them, which might cause corrosion of the reaction vessel.

In the course of our studies on the hydrogenation of SAH, a novel catalyst system consisting of Ru salt, alkyl phosphine, and acid promoter useful in producing GBL was developed. A process to maximize the catalyst performance and stability to produce GBL was also investigated.

In our process, GBL is produced by the two-stage hydrogenation of MAH in the liquid phase; MAH is hydrogenated to SAH in the first stage, which is followed by conversion into GBL during the second stage:



The first reaction is to hydrogenate the C=C bond of MAH, which proceeds almost quantitatively in the presence of a supported Pd catalyst under the pressure of 0.5 MPa. The technical barrier to overcome exists in the latter stage, for example, which requires a catalyst with a high performance. Accordingly, we focused on the hydrogenation of SAH to produce GBL.

This article describes the catalyst system developed for GBL production and some features of the process to produce GBL using a novel catalyst.

EXPERIMENTAL

All solvents and reagents were used without further purification from commercial products. Ru(acac)₃ was purchased from the N.E. Chemical Corp. RuCl₂(PPh₃)₃, RuHCl(PPh₃)₃, and H₂Ru(PPh₃)₄ were prepared according to the published procedure (8). NMR spectra were recorded on a Varian UNITY-300 spectrometer using TMS and H₃PO₄ as internal standards. Assignments of the Ru complexes from the NMR measurements were also reported elsewhere (9).

Catalyst Tests

The catalytic tests were carried out in a glass vessel with a H₂ gas inlet, thermocouple, and a cooler connected with a receiver, operating at atmospheric pressure in the 100–200°C temperature range.

In a typical experiment, a catalyst, SAH, and solvent are charged into the vessel and then the vessel is immersed in an oil bath while hydrogen gas is supplied under normal pressure. The reaction begins when the prescribed temperature is reached.

For the gas flow reaction in the presence of RuCl₂(PPh₃)₃, 0.2 mmol of RuCl₂(PPh₃)₃ and 20 ml of TGM were charged into the vessel. Further, 20.0 g (200 mmol) of SAH was charged as a starting material for the reaction. While introducing hydrogen gas under a normal pressure at a rate of 2 l/h, the mixture was heated at 170°C for reaction. The reaction was conducted for 15 h, starting material was added intermittently at 7.5 g every two hours as it decreased by consumption or by evaporation.

Hydrogenation

Gas flow reactions under pressure were performed using the apparatus. A schematic representation of the gas flow reaction is depicted in Fig. 1. The apparatus contained an autoclave and various supporting subsystems for introducing the hydrogen gas at controlled flow rates, condensing the product vapor, separating the condensed product effluent into gas and liquid streams, controlling the reaction pressure, and measuring the off-gas flow rate.

In a batchwise operation, the reactions were conducted under constant pressure without gas flow. The catalyst components and solvent were charged into an autoclave with an inductive type stirring in an argon atmosphere. After flushing with H₂, they were pretreated under a hydrogen pressure of 1 MPa at 200°C for 2 h. After the components and solvent were cooled to room temperature, SAH was then introduced into the autoclave. The temperature was raised to 200°C under hydrogen atmosphere. When the temperature reached 200°C, the hydrogen was pressurized to 1 MPa and the reaction was started. Hydrogen was fed into the reactor at a constant flow rate. After the reaction, the reaction solutions were removed from the reactor and the gas-liquid separator and both samples were combined.

The resultant reaction mixture was measured by titration and gas chromatography. Conversion was calculated from an alkali titration, and the reaction products were analyzed using a gas chromatograph equipped with a FID and two columns (3.2 mm × 2.0 m) filled with Poropak Q. Under normal conditions, by-products of the hydrogenation other than GBL were only trace amounts. In the absence of

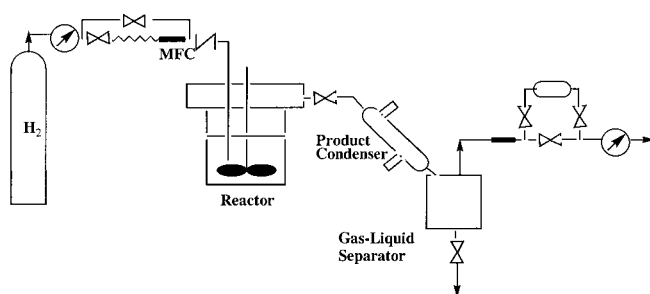


FIG. 1. High pressure apparatus used for GBL hydrogenation experiments.

p-TsOH, spirodilactone can be detected by gas chromatography, which was identified using a GC-MS spectrometer.

The conversion of SAH and selectivity for GBL were defined as follows.

$$\text{SAH conversion (mol\%)} = \frac{\text{amount of acid consumed}}{\text{amount of acid added}}$$

$$\text{GBL selectivity (mol\%)} = \frac{\text{amount of GBL formed}}{\text{amount of acid consumed}}$$

RESULTS AND DISCUSSION

Development of Ru Catalyst System

First, we examined $\text{RuCl}_2(\text{PPh}_3)_3$, which is a known catalyst for the hydrogenation of SAH. Figure 2 shows the catalytic activity and selectivity to GBL as a function of time on stream for the gas flow hydrogenation of SAH. $\text{RuCl}_2(\text{PPh}_3)_3$ displays a very high selectivity to GBL over the whole range of the reaction time. The activity is 80 as the TOF during the initial stage but gradually drops with time, finally leveling off at a value of 22. The result means that $\text{RuCl}_2(\text{PPh}_3)_3$ is not stable and does not retain its efficiency during the reaction. The spectroscopic studies revealed that this phenomenon was associated with the transformation of $\text{RuCl}_2(\text{PPh}_3)_3$, in which the Cl ion is replaced by a carboxylate ion derived from SAH and released from the system. In

contrast, we verified that the gradual addition of LiCl into the reactor allowed the initial activity to be maintained over the course of the hydrogenation.

Thus, ruthenium complexes like $\text{RuCl}_2(\text{PPh}_3)_3$ have problems of the catalytic stability and the Cl ion seems to be indispensable for maintaining the catalytic activity during the reaction. In addition, for the hydrogenolysis of SAH to GBL, an equivalent amount of H_2O is always formed as a by-product which hinders the reaction because of converting SAH into the less reactive succinic acid. In fact, the reaction rate dropped by about 1/3 when succinic acid was used instead of SAH. Therefore, the reaction must operate at temperatures at least higher than 100°C in order to remove the H_2O formed in the reaction mixture. However, PPh_3 , which is a component of the catalyst, is so thermally unstable and likely to decompose at higher temperature that the reactions are obliged to be performed in a limited temperature range (10).

The characteristics of $\text{RuCl}_2(\text{PPh}_3)_3$ determined in our studies are summarized as follows:

- (1) $\text{RuCl}_2(\text{PPh}_3)_3$ affords GBL with selectivities above 95%.
- (2) The catalyst is not active enough for a technological catalyst.
- (3) Deactivation is observed as the reaction proceeds.
- (4) Initial catalytic activity is maintained by adding Cl ion.

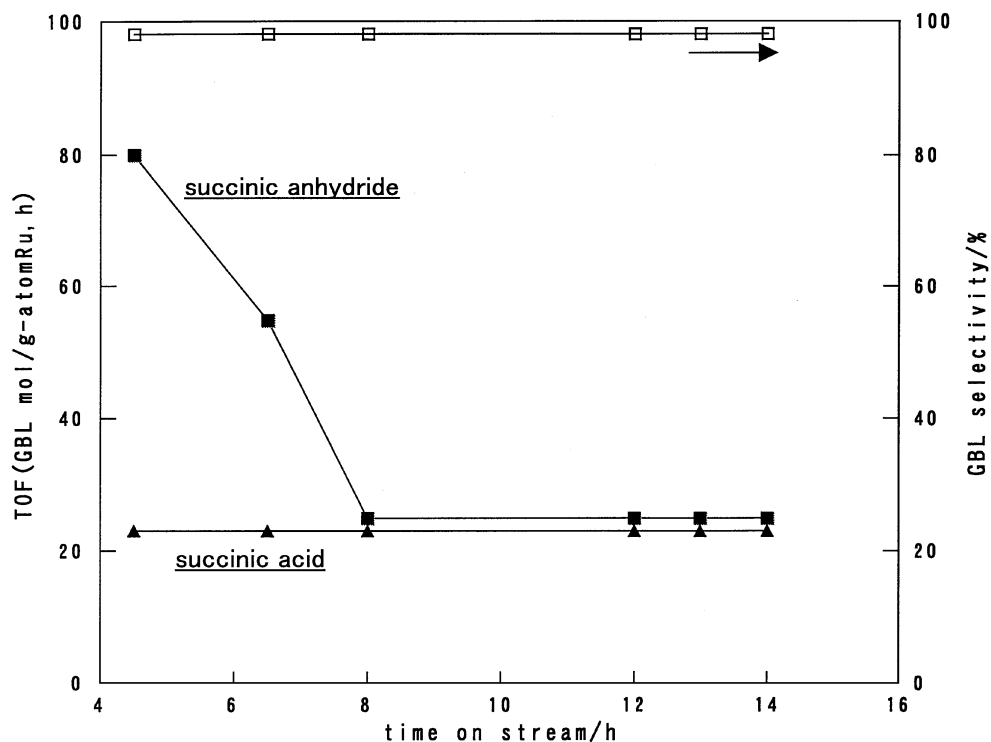
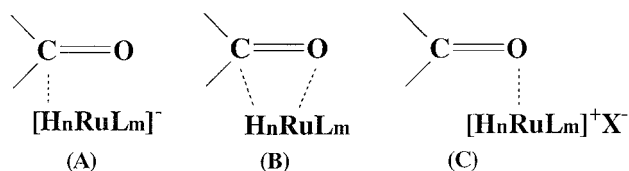


FIG. 2. Time course of GBL production rate in the presence of $\text{RuCl}_2(\text{PPh}_3)_3$. Gas flow reaction. ($\text{RuCl}_2(\text{PPh}_3)_3$, 0.2 mmol; SAH, 200 mmol; TGM, 20 ml; H_2 0.1 MPa, GHSV = 500 h^{-1} , 170°C).

(5) Decomposition of PPh_3 become significant above 180°C .

Thus, $\text{RuCl}_2(\text{PPh}_3)_3$ has the advantage over the conventional heterogeneous catalyst in selectivity for GBL but has some drawbacks with respect to activity and stability.

To solve problems (2)–(5), we got started by systematically designing a new type of catalyst system. Three different types of ruthenium complexes, that is, anionic (11), neutral (12), and cationic complexes (13) are known in the field of ruthenium complex chemistry so far. The strategy of designing this new type of catalyst was to strengthen the interaction between substrate and catalyst.



We expected a cationic complex would make the carbonyl group of the substrate more accessible to the Ru metal, which might lead to boosting the catalytic activity. On the basis of $\text{RuHCl}(\text{PPh}_3)_3$, which had been reported to be the most active for the hydrogenation of aldehydes (14), we attempted the preparation of Ru complexes with a ligand more acidic than Cl, with the aim of creating Type C complex.

The results of SAH hydrogenation when using $\text{RuHX}(\text{PPh}_3)_3$ are shown in Table 1, which was prepared *in situ* by treating $\text{RuHCl}(\text{PPh}_3)_3$ with the corresponding AgX . We thought that Cl played an important role in improving the activity from studies of $\text{RuCl}_2(\text{PPh}_3)_3$. However, it turned out that it was not a crucial factor, and the Ru complexes containing weakly coordinating anion like OTs and PF_6 gave activity higher than $\text{RuHCl}(\text{PPh}_3)_3$. Based

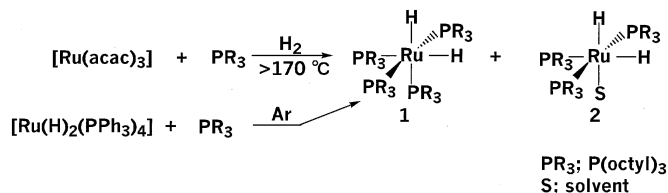
TABLE 1

Effect of X in $[\text{Ru}(\text{H})\text{X}(\text{PPh}_3)_3]$ for Hydrogenation^a

X in $[\text{Ru}(\text{H})\text{X}(\text{PPh}_3)_3]$	Activity ^b
OTs	46
PF_6	42
SO_3CF_3	36
NO_3	34
Cl	21
OAc	17
SO_4	13
$\text{OC}(\text{O})\text{Ph}$	9

^a Ru complex 0.2 mmol, succinic anhydride 100 mmol, tetraglyme 20 ml, H_2 0.1 MPa, 170°C .

^b γ -Butyrolactone mol/mol Ru, h.

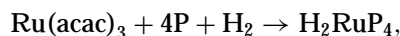


1: ¹H NMR(dioxane-*d*₈, δ); -12(m)
³¹P{¹H}NMR(TGM, δ); 24.3(t,cis to H, 21 Hz), 14.3(t,trans to H, 21 Hz)
 FD-MS; m/z=1584
 2: ¹H NMR(dioxane-*d*₈, δ); -8.6(qd,cis to P, J_{H-P}=24 Hz, J_{H-H}=5 Hz)
 -10.2(dtd,trans to P, J_{H-P(trans)}=74 Hz, J_{H-P(cis)}=29 Hz, J_{H-H}=5 Hz)
³¹P{¹H}NMR(TGM, δ); 31.8(d,cis to H, 20 Hz), 19.8(t,trans to H, 20 Hz)
 TGM; tetraglyme

FIG. 3. Characterization of Ru complexes prepared from $\text{Ru}(\text{acac})_3$ and $\text{P}(\text{octyl})_3$.

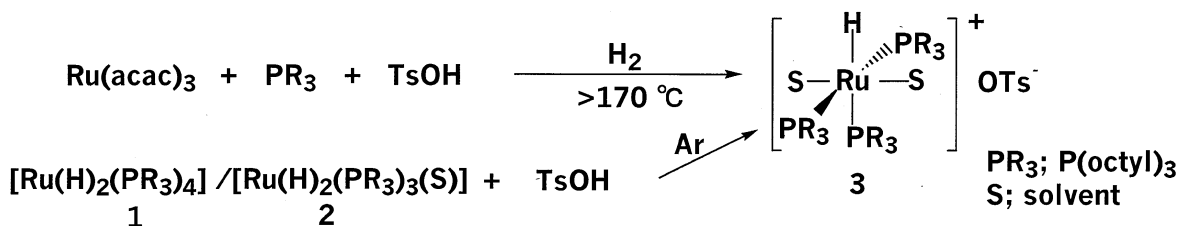
on these fundamental findings, we then examined how the Type C complex should be technologically generated.

Various methods for preparing the Type C complex are shown below.



where P donates organic phosphine.

The first two methods are already known in the literatures (15, 16), but both of them must use a large amount of expensive reagents such as silver salts and carbenium salts. Method [3], in which a Brønsted acid reacts with a dihydride Ru complex was investigated. It was found that the dihydride Ru complex could be obtained by treating a mixture of Ru salt and organic phosphine under a hydrogen atmosphere above 170°C when the Ru salt had soft anion like acetylacetonate. Figure 3 shows the structure of Ru complexes assigned from the NMR spectra data. A solution of $\text{Ru}(\text{acac})_3$ and $\text{P}(\text{octyl})_3$ in dioxane-*d*₈ was carried out under hydrogen (3 MPa) at 200°C for 3 h. The reaction gave a clear yellow solution. The same NMR spectra were also obtained by a simple ligand exchange reaction of $\text{H}_2\text{Ru}(\text{PPh}_3)_4$ and $\text{P}(\text{octyl})_3$ under Argon at room temperature. Two types of neutral dihydridoruthenium complexes, 1 and 2, were formed. Complex 2 seems to be an unsaturated Ru complex that a part of phosphine ligand trans to a hydride in complex 1 to dissociate in the solution. Though both of these Ru complexes could not be isolated, $\text{H}_2\text{Ru}(\text{PMe}_3)_4$ was prepared and isolated as a white solid in the same way by using PMe_3 in place of $\text{P}(\text{octyl})_3$. ³¹P NMR and ¹H NMR spectra of the reaction mixture obtained by adding 1 equivalent of *p*-TsOH into the mixture solution of complex 1 and 2 at room temperature are shown in Fig. 4.



3: ¹H NMR(dioxane-d₈, δ); -7.8(dt, J_{H-P(trans)})

=114 Hz, J_{H-P(cis)}=25 Hz)

³¹P{¹H} NMR(dioxane-d₈, δ); 19.5(d, cis to H,

J_{P-P}=20 Hz), 0.6(t, trans to H)

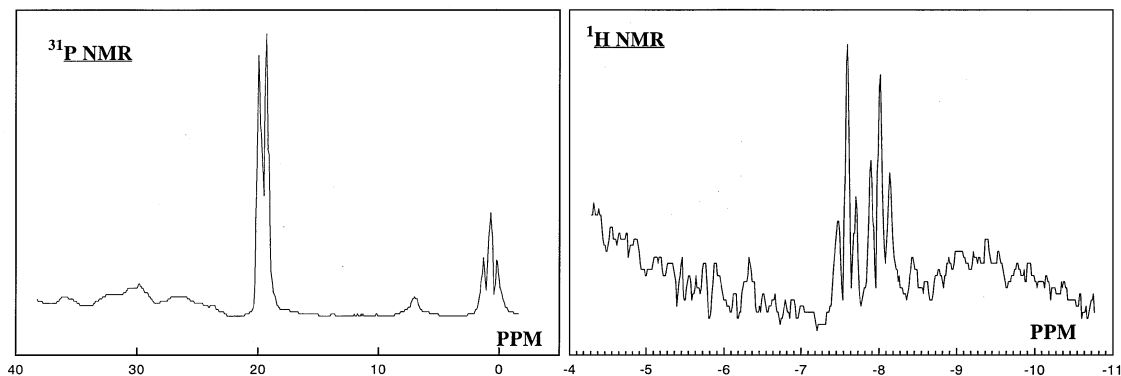


FIG. 4. Characterization of Ru complex prepared from Ru(acac)₃, P(octyl)₃ and *p*-TsOH.

The structure of the complex formed was spectroscopically characterized and assigned to be the cationic monohydride complex, 3, that is, the Type C complex. The reaction of Ru(acac)₃, P(octyl)₃, and *p*-TsOH in dioxane-*d*₈ under hydrogen (3 MPa) at 200°C for 3 h also gave the same NMR spectra. That is to say, it is possible to generate the type C complex by reducing the mixture of Ru salt, organic phosphine, and Brønsted acid with H₂ at one time. The cationic monohydride complex 3 could not be isolated in a pure form as well as complexes 1 and 2. However, Yamamoto *et al.* (17) reported that [RuH{(PMe)₃]₅]⁺ PF₆⁻ could be prepared from the reaction of H₂Ru(PMe₃)₄ and NH₄PF₆ and isolated in a pure form. Thus, it is thought that the treatment of dihydride Ru complex with Brønsted acid is the general method to generate monohydride cationic Ru complex.

We also confirmed that the complex prepared in this way was spectroscopically consistent with that obtained by alternative methods of [1] and [2]. As a result, we decided to prepare the Type C complex according to method [3] because it is the most economical procedure. The complex was also checked to determine if it had a similar catalytic activity as that prepared in other ways. A comparison of the activity for various types of catalyst systems is shown in Table 2. As can be seen, all catalyst systems gave almost the same catalytic performance. Thus, after building up the basic framework

of the catalyst system, the subsequent step to be done is to choose the specific organic phosphine and Brønsted acid suitable for the reaction. The effects of organic phosphines are listed in Table 3. Linear trialkyl phosphines like PBu₃ or P(octyl)₃ were the most active among the various types of organic phosphines examined and fortunately, have been known to be thermally stable (10).

PPh₃ was observed to decompose under these reaction conditions since benzene derived from PPh₃ was detected in the reaction mixture. That is why PPh₃ exhibited low catalytic activity. Of the linear trialkyl phosphines, P(octyl)₃ was selected because it is readily separated from the reaction

TABLE 2

Catalytic Activities of Various Catalyst Systems^a

Catalyst system	Activity ^b
[RuCl(H)(PPh ₃) ₃]/AgOTs	46
[Ru(H) ₂ (PPh ₃) ₄]/TsOH	51
[Ru(acac) ₃]/PPh ₃ /TsOH	44

^a Ru complex 0.2 mmol, succinic anhydride 100 mmol, tetraglyme 20 ml, H₂ 0.1 MPa, 170°C.

^b GBL mol/mol Ru, h.

TABLE 3

Effect of Phosphine for Succinic Anhydride Hydrogenation ^a	
Phosphine	Activity ^b
PBu ₃	132
P(octyl) ₃	120
P(cyclohexyl) ₃	40
PPh ₃	5
P(OC ₈ H ₁₇) ₃	0

^a[Ru(acac)₃] 0.05 mmol, phosphine 0.5 mmol, succinic anhydride 40 mmol, H₂ 3 MPa, 200°C.

^bGBL-mol/mol Ru, h.

products. The influence of P(octyl)₃ on the reaction rate is shown in Fig. 5. The mole ratio of P(octyl)₃ to Ru(acac)₃ was the most suitable in the range from 5 to 10 for the reaction. So we tested various type of Brønsted acids at the constant molar ratio (P(octyl)₃/Ru(acac)₃ = 10). The effect of Brønsted acids likewise examined are listed in Table 4.

Various kinds of Brønsted acids were effective for the reaction including the solid acids. First, it must be pointed out that Brønsted acids not only enhanced the catalytic activity but improved the selectivity for GBL. For instance, the addition of H₃BO₃ to the solution accelerated the reaction rate by about 2 times and achieved improved selectivity up to 98% compared with the system in the absence of the acid. *p*-TsOH as an acid was chosen because of its solubility, resistance to reduction, and low price.

As already mentioned, Brønsted acids induce a structural change in the Ru complexes, leading to the cationic complexes, which increase the catalytic activity. It should be noted that the acids also played another important role in

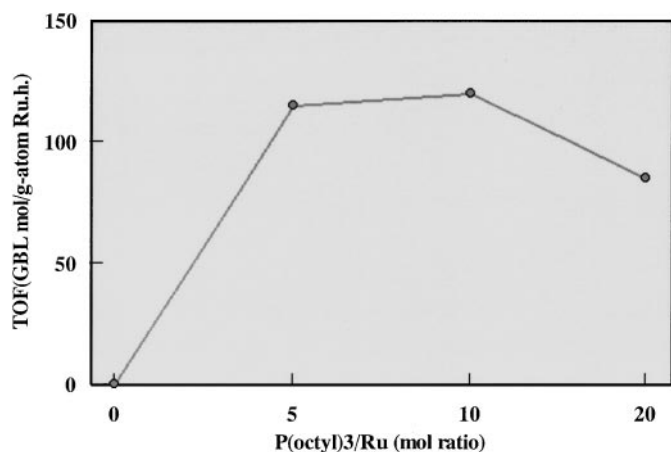


FIG. 5. Influence of the P(octyl)₃/Ru(acac)₃ ratio on the reaction rate. Batchwise reaction. (Ru(acac)₃, 0.05 mmol; SAH, 40 mmol; TGM, 16 ml, H₂ 3 MPa, 200°C).

TABLE 4

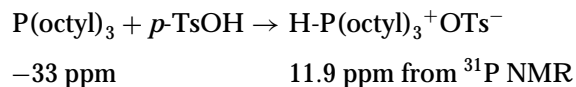
Effect of Acids for Succinic Anhydride Hydrogenation ^a		
HX	Activity ^b	GBL sel. %
None	120	50
H ₄ SiW ₁₂ O ₄₀	258	99
H ₃ BO ₃	241	98
(NH ₄) ₂ B ₄ O ₇	204	83
<i>p</i> -TsOH	257	95
PhSO ₃ H	264	99
MeSO ₃ H	242	87
CF ₃ SO ₃ H	141	51

^aRu(acac)₃ 0.05 mmol, P(octyl)₃ 0.5 mmol, HX 0.4 mmol, succinic anhydride 40 mmol, tetraglyme 20 ml, H₂ 3 MPa, 200°C.

^bGBL mol/mol Ru, h.

improving the selectivity toward GBL. Trialkyl phosphines are known not only to function to stabilize the ruthenium metal as a ligand, but to serve as a strong base. When SAH was hydrogenated using Ru(acac)₃ coupled with P(octyl)₃, a large amount of spirodilactone and its derivatives were formed and the selectivity for GBL was only around 50% (see Scheme 3). The formation of spirodilactone has been reported to take place by condensation reaction of SAH catalyzed by a strong base like KOH (18). However, by adding *p*-TsOH to a mixture of Ru(acac)₃ and P(octyl)₃, selectivity for GBL was drastically improved and side reactions of this kind were actually reduced.

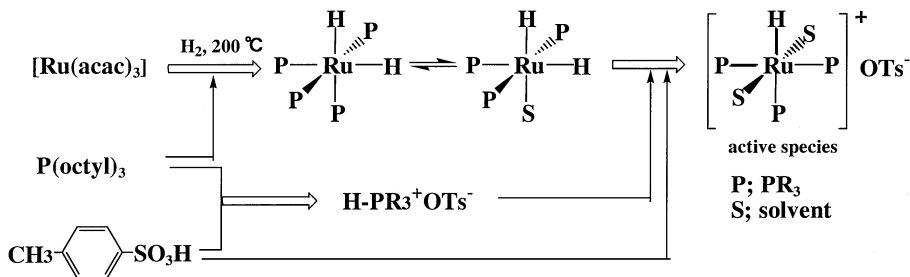
In a controlled experiment, it was recognized that free P(octyl)₃ catalyzed the condensation reaction of SAH similar to KOH. But all of the free P(octyl)₃ that existed in the solution disappeared with the addition of *p*-TsOH and was transformed into a phosphonium salt consisting of P(octyl)₃ and *p*-TsOH. The evidence obtained from the ³¹P NMR measurement is in complete agreement with the formulation shown below.



Thus, *p*-TsOH transforms free P(octyl)₃, which could cause unfavorable side reactions, into phosphonium salt, consequently, affording high selectivity for GBL.

The overall reaction scheme of the catalyst system consisting of Ru(acac)₃, P(octyl)₃ and *p*-TsOH is illustrated in Scheme 1.

[RuHP₃]⁺X⁻ type complex is formed via the dihydride Ru complex from three components by reducing them under a hydrogen atmosphere. The remaining *p*-TsOH converts free P(octyl)₃ into a phosphonium salt which could be provided to the Ru complex as a ligand. No other species except [RuHP₃(S)₂]⁺OTs⁻ (P denotes organic phosphine and S is solvent) and HPR₃⁺OTs⁻ could be spectroscopically



SCHEME 1. Reaction scheme for catalyst formation.

detected after activating these three components. Even when Ru(acac)₃ was treated in the same way after complexing P(octyl)₃ with *p*-TsOH in advance, no significant change was observed in the spectroscopic measurement and catalytic performance. Thus, Brønsted acids such as *p*-TsOH play an important role in our catalyst system, that is, they enhance the reaction rate and improve the selectivity for the desired product.

Solvent Effect

Succinic anhydride is a solid having a melting point of 120°C. In selecting the solvent, some points must be taken into consideration, that is, for example, good solubility, easy separability, thermal stability, and resistance to reduction. In preliminary experiments, we tested various kinds of solvent in the batchwise reaction. The results of solvent effect are shown in Table 5. MIBK was hydrogenated under the reaction condition employed. Of the solvent examined, TGM (tetraglyme), Dodecyl benzene, and Sulfolane afforded GBL in relatively high yield. But Dodecyl benzene and Sulfolane have little solubility toward SAH. We eventually chose TGM as the candidate of solvent from the points cited above; finally, we compared it with GBL, which is the reaction product used as a solvent. It seems that GBL is the

most ideal solvent from the viewpoint of building a simple system. The comparison between TGM and GBL as a solvent is demonstrated in Table 6. It can be seen that GBL selectivity (when GBL is used as a solvent) is significantly inferior to that of TGM, at around 87%. That fact can be explained that GBL itself undergoes further hydrogenation to 1,4-butanediol. In fact, high boiling products were detected in substantial quantity from the G.P.C. measurement when using GBL as a solvent. Since 1,4-butanediol can be detected from the alkali hydrolysis products of the residue after removing GBL from the reaction mixture carried out in GBL solvent, ester oligomers from 1,4-butanediol and succinic acid could be formed during the reaction. The formation of esters has also been reported to take place even in the gas phase (19). Finally, TGM was selected as the solvent for the reaction.

Reaction Mechanism

In Scheme 2 is illustrated the possible mechanism for the hydrogenation of SAH. The 3-formylpropionato Ru complex intermediate could be involved via the hydride transfer and C–O bond cleavage of SAH after RuHP₃ coordinates to the carbonyl group of SAH.

Yoshikawa *et al.* (20) reported that the Ru complex of this kind could be prepared from the reaction of RuH₂(PPh₃)₄ with SAH and could be isolated as crystals in high yields, which released GBL upon contact with hydrogen at elevated pressure, thus indicating 3-formylpropionato Ru complex as key intermediate. Though there is no experimental evidence, the analogous intermediate may

TABLE 5
Solvent Effect for SAH Hydrogenation

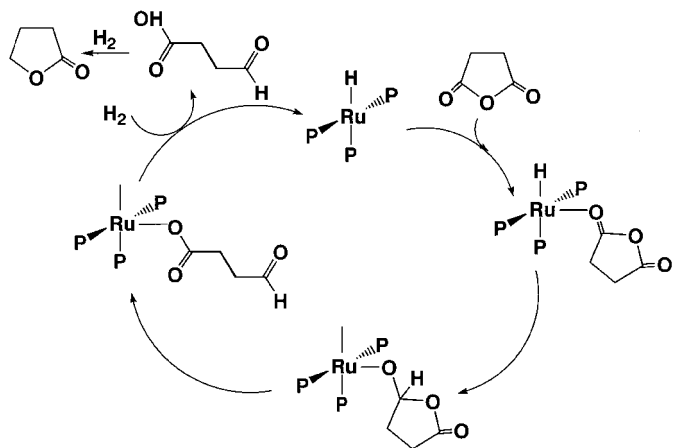
Solvent	GBL yield (%)
TGM	72
MIBK	35
DMF	6
NMP	53
AcOH	47
Sulfolane	61
Adiponitrile	3
Dimethyl phthalate	32
Dodecyl benzene	70

Note. Ru(acac)₃ 0.05 mmol, P(octyl)₃ 0.5 mmol, *p*-TsOH 0.4 mmol, succinic anhydride 40 mmol, solvent 16 ml, H₂ 3 MPa, 200°C, 2 h.

TABLE 6
Comparison between TGM and GBL as Solvents^a

Solvent	SAH conv./%	GBL sel./%
TGM	97.8	94.5
GBL	96.5	87.0

^aGas flow reaction. Reaction conditions: Ru 500 ppm, SAH/Ru = 1000 (mol-R) GHSV; 500 h⁻¹, H₂ 1 MPa, 200°C.



SCHEME 2. Presumed reaction mechanism.

possibly take part in our catalyst cycle. The contact of the 3-formylpropionate Ru complex with H_2 forms $RuHP_3$ and 3-formylpropionic acid, which is followed by the reduction of the formyl group, subsequent to ring closure to form GBL. Among various classes of carbonyl compounds, aldehydes is known to be much more readily hydrogenated than acid anhydrides (21). The formation of GBL from γ -hydroxybutyric acid completes rapidly at elevated temperatures (22). Therefore, 3-formylpropionic acid can be reduced and cycled to GBL rapidly and nearly quantitatively under the reaction conditions.

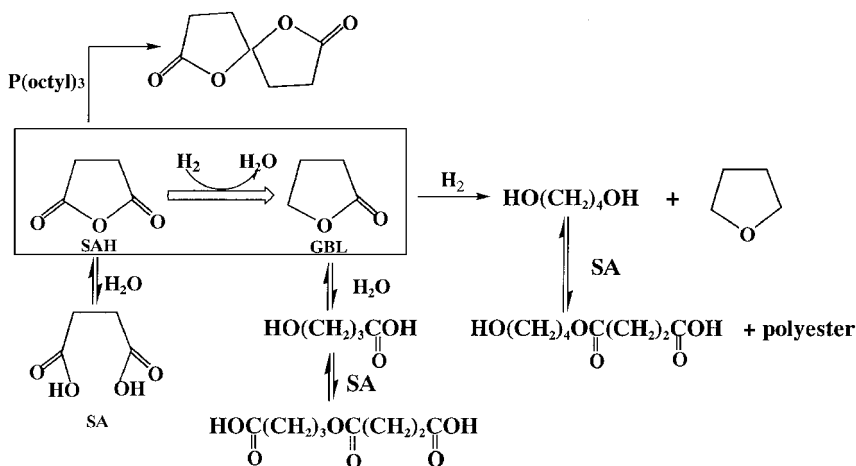
Reaction Profile and Reaction Performance

The entire profile of the SAH hydrogenation is illustrated in Scheme 3. As described in a previous section, free $P(octyl)_3$ induces an undesired side reaction, that is, the condensation reaction of SAH. In order to suppress by-product formation of this kind, it is necessary to com-

pletely convert $P(octyl)_3$ into the phosphonium salt before contacting with SAH. Accordingly, the catalyst components are pretreated with H_2 in advance before the reactions are conducted.

In this process, the external preparation method of the Ru complex is employed for this reason. For this reaction, an equivalent amount of H_2O is always produced along with GBL. When H_2O is accumulated in the reaction zone, the reaction rate drops because of converting SAH into the less reactive succinic acid. We stated that the activity fell by one-third using succinic acid as the reactant instead of SAH in the case of $RuCl_2(PPh_3)_3$. Moreover, H_2O could give rise to various kinds of side reactions. For example, 3-hydroxyvaleric acid formed by the hydrolysis of GBL could react with succinic acid leading to ester oligomers. Thus, formed H_2O must be constantly removed from the reaction system. Also, decreasing H_2O in the reaction zone favors the transformation of SAH from succinic acid since they are in equilibrium with each other. A protocol to avoid the influence of H_2O can be solved with stripping which controls the concentration of H_2O in the reactor by adjusting the H_2 gas flow rate. GBL has one carbonyl group which is still reducible and can be regarded as an intermediate in the pathway for SAH hydrogenation. As mentioned in a previous section, GBL is not suitable as a solvent because it undergoes further partial hydrogenation resulting in lower GBL selectivity. Overhydrogenation to 1,4-butanediol cannot be perfectly controlled though the high yield in GBL observed may be mostly attributed to the capacity of the catalyst itself. We are forced to cope with the reaction conditions to minimize the overhydrogenation by optimizing the operating parameters such as substrate concentration, hydrogen pressure, and residence time.

Table 7 shows the results of SAH hydrogenation under optimized conditions. It can be seen that high selectivity



SCHEME 3. Reaction scheme for GBL production. SAH: succinic anhydride, SA: succinic acid.

TABLE 7

Reaction Performance on Ru Complex Catalyst

Succinic anhydride conc. (wt%)	Conv. (%)	GBL sel. (%)
10	96.9	98.4
19	95.3	97.5
29	89.2	97.1

Note. Gas flow reaction (Ru 500 ppm, Ru(acac)₃/P(octyl)₃/p-TsOH = 1/10/8 mol-R, H₂ 1 MPa, GHSV 800 h⁻¹, 200°C, 1.6 h.

toward GBL exceeding 97% is achieved as long as the reactions are performed with a SAH concentration up to 30 wt%.

Entire GBL Production Process

The process for manufacturing GBL was developed based on these fundamental findings. The entire flow diagram of GBL production is shown in Fig. 6. MAH is hydrogenated in the first reactor to SAH, which is fed to the second reactor, where SAH is converted into GBL. During the second hydrogenation stage, the reaction protocol that combines the overflow reaction with stripping is actually adopted for the constant removal of H₂O. The effluent from the second reactor, after going through catalyst separation, is sent to the purification section. After distillation, GBL can be obtained in a pure form. Regarding catalyst flow, the catalyst is introduced into the hydrogenation reactor after being activated in advance before feeding. Though a large portion of the catalyst is recycled into the reactor by catalyst separation, a part of it is discarded together with high-boiling by-products. An attempt to recover the catalyst from high-boiler products containing catalyst was made. The procedure for Ru catalyst recovery is illustrated in Fig. 7. Aqueous NaOH solution and heptane are added to the high-boiler waste. After mixing, the resulting solution is observed to be separated into three phases. It turned

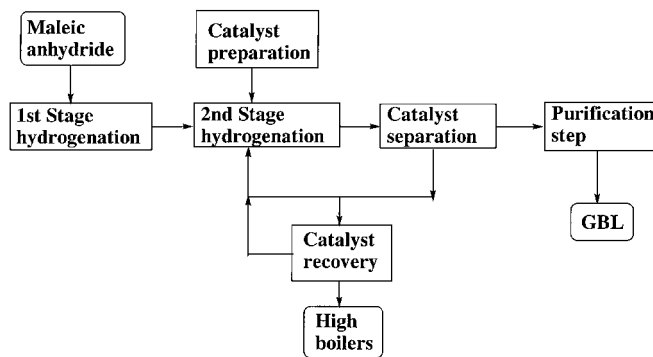


FIG. 6. Entire flow diagram for GBL process.

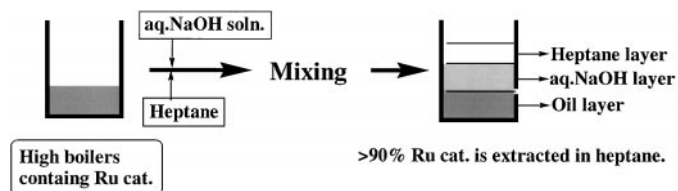


FIG. 7. Ru catalyst recovery by extraction.

out that more than 90% of the Ru complexes could be extracted in the heptane layer in the active form. By recycling the recovered catalyst into the reactor, it is possible to operate under conditions of higher catalyst concentration than would be possible without catalyst recycling from the viewpoint of cost. The high catalyst concentration makes it possible to lower the hydrogen pressure and achieve the same productivity. The process on this reaction will be published in detail elsewhere.

CONCLUSIONS

A new process for producing GBL involves a two-stage hydrogenation in the liquid phase, that is, the hydrogenation of MAH to SAH in the first stage and a further hydrogenation of SAH to GBL in the second stage. The second reaction is more difficult to realize due to hydrogenolysis of the C=O bond. A catalyst with high activity and high selectivity is required to accomplish the hydrogenation of SAH. The latter hydrogenation was examined using a homogeneous catalyst. A novel ruthenium catalyst system consisting of Ru(acac)₃, P(octyl)₃, and p-TsOH was developed to meet the requirements; the selectivity of the reaction toward GBL is realized as high as 97%.

A process to maximize the catalyst performance and the stability to produce GBL was also examined. Some novel features of this process include the external preparation method of the Ru complex, the coupling of reaction and separation to remove water, a product of the hydrogenation of SAH, in order to increase the reaction rate. A catalyst recovery system was also developed to recover over 90% of the catalyst. The successful recovery of the catalyst allows an increase of the catalyst concentration in the reactor possible leading to a lower hydrogen pressure down for the same reactivity.

As a result of that, the operating pressure of this novel GBL process is the lowest among all the GBL production units using the MAH route.

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