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Reduction with 2-Propanol over Hydrous Tin(IV) Oxide

Kyoko TAKAHASHI,* Makoto SHIBAGAKI, Hideyuki KUNO, and Hajime MATSUSHITA
Life Science Research Laboratory, Japan Tobacco, Inc., 6-2 Umegaoka, Midori-ku, Yokohama, Kanagawa 227

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The reduction with 2-propanol as a hydrogen source over hydrous tin(IV) oxide has proved to be successful. Hydrous tin(IV) oxide was prepared from stannic(IV) chloride by precipitation with aqueous ammonia, followed by drying and calcination at 300 °C for 5 h. The specific surface area was 150 $m^2 g^{-1}$. The reductions were carried out in the vapor phase at temperatures of from 300 to 330 °C. The reduction of aliphatic carboxylic acids gives the corresponding alcohols. Aromatic carboxylic acids and their derivatives were further reduced, and the corresponding hydrocarbons were obtained. The reductions of aromatic ketones and the derivatives of benzyl alcohol also gave hydrocarbons. In the reaction of alkyl halides, reductive dehalogenation proceeded and the corresponding hydrocarbon was produced.

Hydrogen-transfer reactions have been studied by many researchers. In these reactions, the Meerwein–Ponndorf–Verley reduction is a well known reaction, the mechanism of which involves a hydride transfer from aluminum isopropoxide to the carbonyl carbon of the ketones. Kibby and Keithhall1) have reported on the hydrogen transfer reaction between alcohol and ketone over hydroxyapatite catalyst and proposed a mechanism that is similar to that of the Meerwein–Ponndorf–Verley reduction. This reaction can be carried out in a heterogeneous system. The use of heterogeneous catalysts such as zeolite,2) MgO,3,4) MgO–SiO_2,5) ZrO_2,6) CaO,7) and alumina8) has also been reported. These catalysts are used for the reduction of aldehydes or ketones with alcohol as a hydrogen donor to the corresponding alcohols.

We have reported that the hydrous zirconium(IV) oxide showed catalytic activity for the reduction of aldehydes or ketones.9) In addition, carboxylic acids and carboxylic acid derivatives10,11) can also be reduced over hydrous zirconium(IV) oxide by the use of 2-propanol as a hydrogen donor. These reductions gave the corresponding alcohols. Several heterogeneous catalysts such as Al_2O_3, SiO_2, and zeolite were investigated for the reduction of carboxylic acids and their derivatives. These catalysts did not show the activity.10) We newly found that hydrous tin(IV) oxide has the activity.

The hydrous tin(IV) oxide efficiently catalyzed the reduction of aliphatic carboxylic acid with 2-propanol to give the corresponding alcohols. In the case of aromatic acid, a further reduction was found to give the corresponding hydrocarbon by using hydrous tin(IV) oxide. Furthermore, aromatic ketones and the derivatives of benzyl alcohol were also reduced to the corresponding hydrocarbons. The reductive dehalogenation of alkyl halides also proceeded over hydrous tin(IV) oxide.

Generally, aromatic ketones are reduced to aromatic hydrocarbons by a Clemmensen reduction, a Wolf–Kishner reduction, organosilicon hydrides,12) lithium–ammonia–ammonium chloride,13) or catalytic hydrogenation using Raney-nickel.14) The derivatives of benzyl alcohol are readily reduced by catalytic hydrogenation.15) Reduction of the derivatives of benzyl alcohol was carried out by using $LiAlH_4$–$AlCl_3$,16) lithium–ammonia–ammonium chloride,17) Ni–Al alloy/alkali solution,18) or organosilicon hydrides;19) the corresponding hydrocarbon was obtained in good yield. The formation of hydrocarbons by the reduction of aromatic carboxylic acid is not well known; however, it can be reduced by reductive silylation using trichlorohydrosilane following cleavage by a basic reagent.20) The reductive dehalogenation of alkyl halide could proceed by various methods.

Tin(IV) oxide has been widely used for inorganic materials. For instance, it has been studied regarding its ion-exchange properties.21) Recently, there has been some interest in its properties as a semiconductor.22) Tin(IV) oxide was prepared by various methods, and its properties were dependent on the preparation conditions. For example, the effect of the calcination temperature on the specific surface area has been reported.23,24) In its use as a catalyst, tin(IV) oxide is often used in the form of a mixed oxide. In the presence of tin(IV) oxide catalyst alone, a few reactions are known,25) such as the oxidation of CO,23,26) the reduction of NO_x,27,28) the oxidation29) of olefin, and isomerization.30,31)

In this paper we report on the use of hydrous tin(IV) oxide in reductions of aromatic carboxylic acids, aromatic ketones, derivatives of benzyl alcohol, and alkyl halides to the corresponding hydrocarbons with 2-propanol as a hydrogen source.

Experimental

Materials. Commercial reagents were used for the reaction without any purification.

Hydrous Tin(IV) Oxide. This was prepared by the dropwise addition of aqueous ammonia solution (28%) to a vigorously stirred solution of $SnCl_4$ to a final pH of 7.0, followed by filtering, washing, and drying. The obtained gels were broken down by immersion in water. Calcination was carried out at 300 °C for 5 h. The hydrous tin(IV) oxide having a particle size of 24 to 60 mesh was used for the following reactions.

General Procedure for Reaction. Catalytic reduction was carried out in a glass-flow reactor (6.5 mm in diameter) with a fixed-bed catalyst. The flow rate of nitrogen gas was 60 $cm^3 min^{-1}$; 2.0 g of the catalyst was used, 24—60 mesh; and the reaction temperature was 300 °C. A mixture of a carboxylic acid, an alcohol, and a hydrocarbon as an internal standard was fed (5 $cm^3 h^{-1}$) into the reactor by means of a microfeeder. The conversion and yield of the reaction were determined after a steady state had been achieved. The products were then analyzed by gas chromatography (a capillary column DB WAX 30 m, or DB 1 30 m). The products were identified by a comparison of their retention times with those of authentic samples or by a GC-MS analysis.

Physical and Chemical Properties. The quantity of surface acidic or basic sites was measured by the butylamine- or benzoic acid-titration method, respectively, using various Hammett indicators.

The specific surface area was measured by the B.E.T. method using a BELSORP28 surface-area analyzer. The sample was outgassed under vacuum for 3 h at 150 °C prior to the measurement.

The X-ray photoelectron spectra were obtained using a Shimadzu ESCA-1000 spectrometer. Argon-ion etching for 5 min was carried out before the measurement.

An X-ray diffractogram was taken using a Mac Science MXP^{18} X-ray diffractometer with a copper target and a nickel filter at 40 kV.

Results and Discussion

Reduction of Carboxylic Acid or Carboxylic Acid Derivatives. The results of the reaction of carboxylic acids or carboxylic acid derivatives with 2-propanol over hydrous tin(IV) oxide are listed in Table 1.

The reduction of aliphatic carboxylic acids or ester has given the corresponding alcohol. It has been shown that hydrous tin(IV) oxide was a rare catalyst for the reduction of carboxylic acid to alcohol with 2-propanol used as a hydrogen source. The yields of the alcohols, however, were lower than those using hydrous zirconium(IV) oxide[10)] as a catalyst in each case.

In the case of aromatic carboxylic acids and their derivatives, they were further reduced to give the corresponding hydrocarbons. The catalytic activity was affected by the reaction temperature. The reduction of benzoic acid at 330 °C gave toluene in higher yield and selectivity than did that at 300 °C. In this reduction, a small amount of the corresponding isopropyl ester was observed as a by-product.

Ethyl benzoate was reduced to toluene as well as benzoic acid. The reductions of benzonitrile and 3-cyanopyridine gave the corresponding hydrocarbons; however, the yield of the hydrocarbon decreased with increasing reaction time. After 8 h, in the case of the reaction of the nitriles, the catalyst had been partly changed to metallic granules. Phthalic anhydride was reduced to *o*-xylene; toluene and phthalide were produced as by-products.

Reduction of Aldehyde or Ketones. The results of the reactions of aldehyde or ketones with 2-propanol over hydrous tin(IV) oxide are shown in Table 2. Benzaldehyde and benzophenone were reduced to the corresponding aromatic hydrocarbons in high yields. The reduction of acetophenone gave ethylbenzene and styrene which was produced by the dehydration of 1-phenylethanol as a half-reduction intermediate.

Reduction of Alcohols. The reductions of alcohols were carried out with 2-propanol over hydrous tin(IV) oxide; the results are listed in Table 3. The derivatives of benzyl alcohol were mainly reduced to the corresponding aromatic hydrocarbons. Benzyl alcohol and diphenylmethanol, which can not be dehydrated, were reduced to the corresponding hydrocarbons in high yields.

However, aliphatic alcohols were scarcely reduced to the corresponding hydrocarbon.

In order to investigate the dependence on the temperature, the reduction of benzyl alcohol was carried out at 250, 280, and 300 °C. Increasing the temperature tended to increase the yield of the product. In this reaction, a small amount of benzaldehyde was observed as a by-product. It was presumed that an Oppenauer-type oxidation of benzyl alcohol took place with acetone which was produced via the reaction. By raising the temperature to 300 °C, the selectivity of toluene was increased. The reductions of cinnamyl alcohol and 1-phenylethanol gave unsaturated hydrocarbons. When the reaction of styrene was carried out with 2-propanol over hydrous tin(IV) oxide under similar conditions, the yield of ethylbenzene was less than 5%. These results indicated that ethylbenzene was produced via a benzyl cation formed by the elimination of OH^-, without a reduction of the carbon–carbon double bond of styrene.

Although the reductions of aliphatic alcohols did not give the corresponding hydrocarbons, the derivatives of benzyl alcohol were reduced. It seems reasonable to assume that the stability of the benzyl cation affects the difference in the reactivity of the reductions.

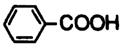
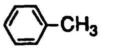
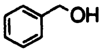
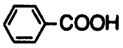
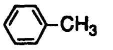
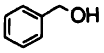
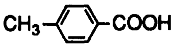
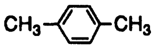
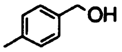
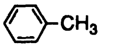
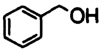
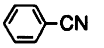
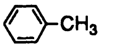
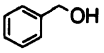
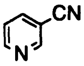
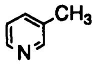
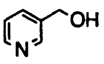
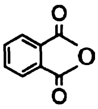
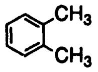
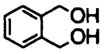
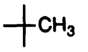
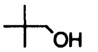
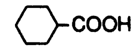
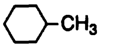
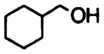
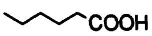
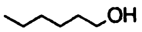
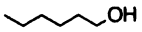
In the case of carboxylic acids or carbonyl compounds, benzyl compounds, such as benzoic acid or benzophenone, were also reduced to the corresponding hydrocarbons. Aliphatic compounds were not reduced to the corresponding hydrocarbons. Regarding the reason, it seems that the benzyl cation is more stable than the alkyl cation.

Reduction of Alkyl Halides. Table 4 shows the results of reductive dehalogenation.

Benzyl bromide was mainly reduced to toluene. The reductive dehalogenation of bromobenzene and 4-bromotoluene proceeded and gave the corresponding aromatic hydrocarbons in good yields. The reactivity of 4-chlorotoluene was low.

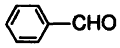
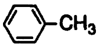
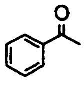
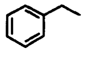
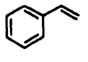
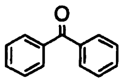
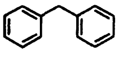
The reaction of 1-bromononane gave nonane and nonene. In order to confirm that nonane was not produced via nonene, the reduction of nonene was tried with 2-propanol over hydrous tin(IV) oxide. Nonene was converted to nonane in only 5% yield. This there-

Table 1. Reduction of Carboxylic Acid Derivatives over Hydrous Tin(IV) Oxide[a)]

	Reactant	Conv./%	Yield/%			
			Hydrocarbon		Alcohol	
1		100		65		16
2[b)]		100		98		1
3[b)]		100		93		7
4		99		56		15
5[c)]		60		20		4
6[c)]		88		35		5
7		100		58[d)]		0
8		100		Tr.		69
9		99		Tr.		65
10		100		Tr.		57
11		100		Tr.		51

a) Conditions: reaction temperature, 300 °C; reactant, 0.2 mmol cm^{-3} in 2-propanol; sample feed, 5 cm^3 h^{-1}; carrier gas, N_2 (60 cm^3 min^{-1}); catalyst, 2.0 g. b) Reaction temperature, 330 °C. c) Reaction time, 0.5 h. d) Yield, toluene 21% and phthalide 12%.

Table 2. Reduction of Aldehyde or ketones over Hydrous Tin(IV) Oxide[a)]

Entry	Reactant	Temp/°C	Conv./%	Product	Yield/%
1		300	99		91
2		330	98		48
					47
3		330	100		100

a) Conditions: catalyst, 2.0 g; reactant, 0.2 mmol cm^{-3} in 2-propanol; sample feed, 5 cm^3 h^{-1}; carrier gas, N_2 (60 cm^3 min^{-1}).

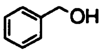
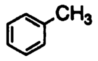
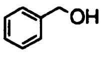
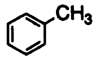
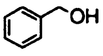
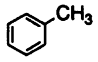
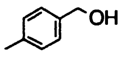
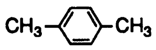
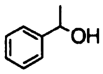
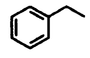
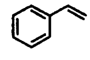
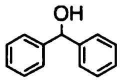
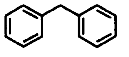
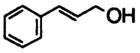
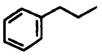
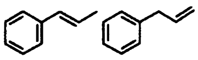
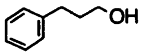
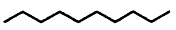
fore suggests that nonane was produced by a hydride attack on the nonyl cation, which was formed by dehalogenation of 1-bromononane.

However, in this reductive dehalogenation, the catalytic activity of hydrous tin(IV) oxide is lowered with the passage of time. The reason is presumed to be that the catayst is poisoned by bromide produced in the reaction.

Durability of Hydrous Tin(IV) Oxide. In order to estimate the durability of the hydrous tin(IV) oxide, the reduction of benzyl alcohol with 2-propanol was carried out at 300 °C over 1.0 g of hydrous tin(IV) oxide for 130 h. The results are shown in Fig. 1. Although the activity of the catalyst was maintained for a period of approximately 40 h, it gradually decreased with time.

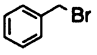
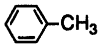
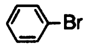
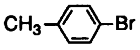
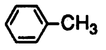
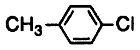
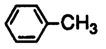
Physical and Chemical Property of Hydrous Tin(IV) Oxide. The acid or base amounts of the hy-

Table 3. Reduction of Alcohols over Hydrous Tin(IV) Oxide[a)]

Entry	Reactant	Temp/°C	Conv./%	Product	Yield/%
1		300	98		97
2		280	74		55
3		250	36		30
4		300	100		100
5		300	98		40
					19
6		300	100		100
7		300	99		Tr.
					79
					20
8		300	14		6

a) Conditions: catalyst, 2.0 g; reactant, 0.2 mmol cm^{-3} in 2-propanol; sample feed, 5 cm^3 h^{-1}; carrier gas, N_2 (60 cm^3 min^{-1}).

Table 4. Reduction of Alkyl Halides over Hydrous Tin(IV) Oxide[a)]

Entry	Reactant	Time/h	Conv./%	Yield/%	
1		4	99		57
2		0.5	68		45
3		0.5	84		71
4		1	Tr.		Tr.
5		2	80		30
					47

a) Conditions: catalyst, 2.0 g; reaction temperature, 330 °C; reactant, 0.2 mmol cm^{-3} in 2-propanol; sample feed, 5 cm^3 h^{-1}; carrier gas, N_2 (60 cm^3 min^{-1}).

Table 5. Acid or Base Amount of Hydrous Tin(IV) Oxide

Amount/mol g^{-1}						
$H_0 \leq -8.2$	$H_0 \leq -5.6$	$H_0 \leq -3.0$	$H_0 \leq +1.5$	$H_0 \leq +4.0$	$H_0 \leq +4.8$	$H_0 \geq +9.7$
0	0	0.5×10^{-4}	0.5×10^{-4}	1.3×10^{-3}	1.3×10^{-3}	0

drous tin(IV) oxide are given in Table 5. Neither strong acid sites nor strong basic sites were not found on hydrous tin(IV) oxide, and hydrous tin(IV) oxide have weak acid sites. These are similar to hydrous zirconium(IV) oxide.[32)]

The peaks of the X-ray diffractogram of hydrous

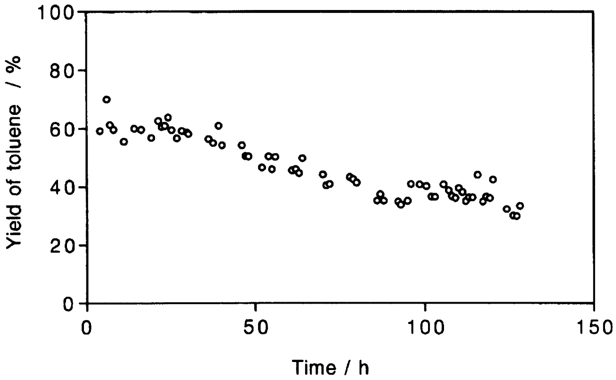


Fig. 1. Durability of hydrous tin(IV) oxide. Conditions: reaction temperature, 300 °C; catalyst, 1.0 g; reactant, benzyl alcohol (0.2 mmol cm^{-3} in 2-propanol); sample feed, 5 cm^3 h^{-1}; carrier gas, N$_2$ (60 cm^3 min^{-1}).

tin(IV) oxide were broadened. However, they corresponded to those of cassiterite (Sn^{IV}O$_2$). The hydrous tin(IV) oxide also had the same crystal structure as Sn^{IV}O$_2$.

The specific surface area of hydrous tin(IV) oxide was 150 m^2 g^{-1}.

Tin oxides are produced by various methods. The preparation of hydrous tin(IV) oxide was similar to that of the so-called α-stannic acid. The effect of the calcination temperature on the specific surface area of SnO$_2$ gel had been previously studied by Fuller et al.[23,24] The specific surface areas of SnO$_2$ gel calcined at 300 °C were nearly equal to that of the hydrous tin(IV) oxide; the results of an X-ray diffractogram have shown that the oxide was cassiterite. Hydrous tin(IV) oxide might be analogous to the oxide.

In order to investigate the valence charge of tin in the reaction, hydrous tin(IV) oxides before a reaction, after a reaction for 130 h with benzyl alcohol, and after a reaction for 8 h with 3-cyanopyridine, acetophenone, *p*-methyl benzoic acid, or bromobenzene were measured by XPS. The results showed that only the Sn(IV) species was detected in the oxide before the reaction. In the case of the oxides after the reaction, the peaks assigned as Sn(0) were observed together with those of Sn(IV), except for the oxide after the reaction with bromobenzene. In the oxide after the reaction of bromobenzene, only the Sn(IV) species was detected. The time-course of the reactions of these reactants is shown in Fig. 2.

The activity of the reduction of 3-cyanopyridine has been markedly decreased over hydrous tin(IV) oxide. It seemed that the reason was the reduction of Sn(IV) to Sn(0) or poisoning with products. The activity of the reduction of *p*-methyl benzoic acid, acetophenone, or benzyl alcohol over hydrous tin(IV) oxide was maintained for more than 8 h. These facts suggested that the decrease in the activity was affected by the reactant.

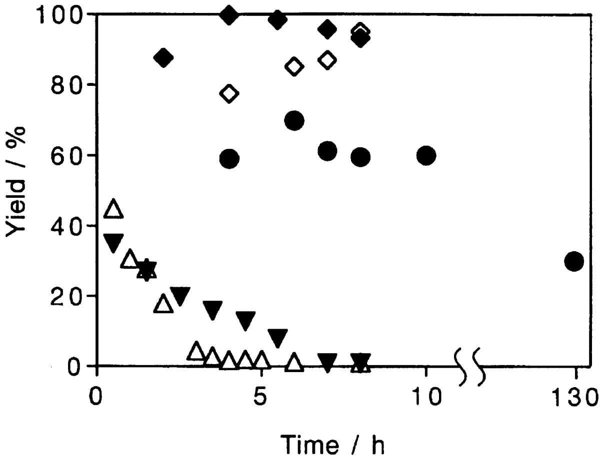


Fig. 2. Time-course of the yield by reduction over hydrous tin(IV) oxide. The yield of *p*-xylene produced from *p*-methyl benzoic acid (◆), The yield of ethyl benzene and styrene produced from acetophenone (◇), The yield of 3-picoline produced from 3-cyanopyridine[a] (▼), The yield of benzene produced from bromobenzene (△), The yield of toluene produced from benzyl alcohol[a,b] (●). Conditions: reaction temperature, 330 °C; catalyst, 2.0 g; reactant, 0.2 mmol cm^{-3} in 2-propanol; sample feed, 5 cm^3 h^{-1}; carrier gas, N$_2$ (60 cm^3 min^{-1}). a) Reaction temperature, 300 °C. b) Catalyst, 1.0 g.

The peaks assigned as Sn(0) were observed together with those of Sn(IV) in the case of the oxide after a reaction for 130 h with benzyl alcohol. The reduction of Sn(IV) to Sn(0) might be one of the reasons why a lowering of the activity was brought about.

These properties in which the specific surface area was large and the acidity and basicity were not strong on the hydrous tin(IV) oxide are similar to those of hydrous zirconium(IV) oxide. Further, both hydrous tin(IV) oxide and hydrous zirconium(IV) oxide have catalytic activities for the reduction of carboxylic acids with 2-propanol used as a hydrogen source. It seems that hydrous tin(IV) oxide is analogous to hydrous zirconium(IV) oxide regarding its characteristic reactivity. On the other hand, although the reduction gave the corresponding alcohol over hydrous zirconium(IV) oxide, benzyl compounds could be reduced to the corresponding hydrocarbons by using hydrous tin(IV) oxide. It was found that hydrous tin(IV) oxide has the ability to reduce benzyl compounds to hydrocarbons.

Conclusion

The reduction with 2-propanol as a hydrogen source over hydrous tin(IV) oxide has proved to be successful. The reduction of aliphatic carboxylic acids gives the corresponding alcohols. Aromatic carboxylic acids and their derivatives were further reduced to the corresponding hydrocarbons. The reductions of aromatic ketones and the derivatives of benzyl alcohol also gave hydrocarbons. In the reaction of alkyl halides, reductive dehalogenation was found to proceed.

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