Chemoselective Hydrogenolysis of Urethanes to Formamides and Alcohols in the Presence of More Electrophilic Carbonyl Compounds

Takanori Iwasaki,[†,*] Yuto Yamada,[†] Naoki Naito,[†,‡] Kyoko Nozaki[†,*]

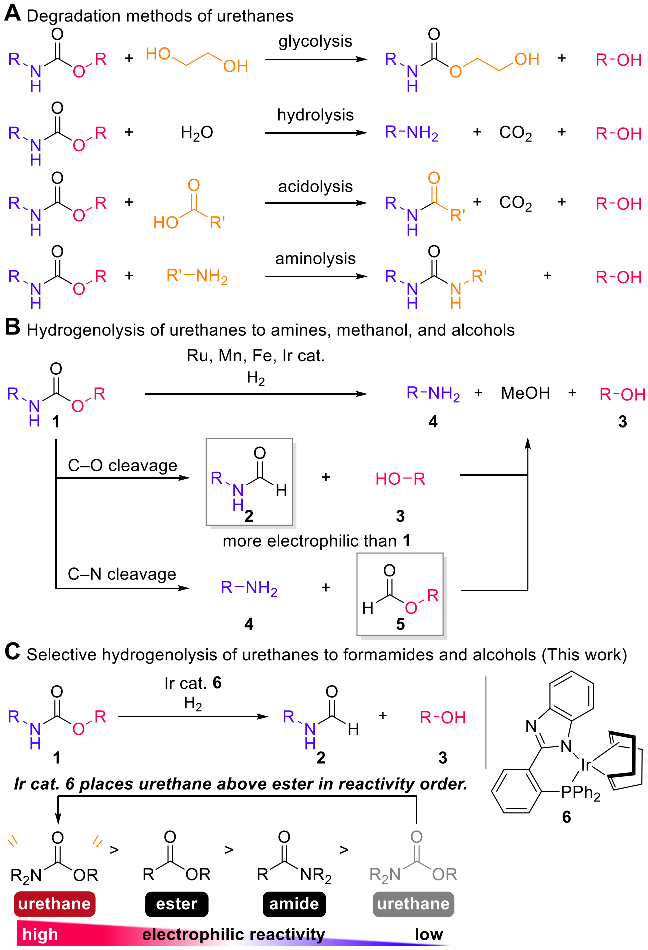
[†]Department of Chemistry and Biotechnology, Graduate School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

ABSTRACT: The development of methods for the chemical recycling of polyurethanes is recognized as an urgent issue. Herein, we report the Ir-catalyzed hydrogenolysis of the urethane C–O bond to produce formamides and alcohols, where both formamides and ester and amide functionalities are tolerated. The chemoselectivity observed is counterintuitive to the generally accepted electrophilicity order of carbonyl compounds. Hydrogenolysis of urea and isocyanurate, potential byproducts in the polycondensation process of polyurethanes, is achieved alongside the selective degradation of polyurethanes themselves, which affords diformamides and diols. The present catalysis offers a novel method for the recycling of polyurethane-containing polymer waste.

Polyurethanes are the sixth most commonly used polymers approximately 28 megatons are produced per year, accounting for almost 8% of the annually produced plastic materials.[1] Commercial polyurethane materials, such as flexible and rigid polyurethane foams, are produced from the reaction of aromatic diisocyanates with polyols,[2] and are utilized in a wide variety of applications from household necessities to building insulation materials.[3] To realize a circular carbon economy and sustainable society, a methodology to cleave the urethane bond for the chemical recycling of polyurethanes must be urgently developed.[1,4–6] Various methods for polyurethane degradation, including glycolysis,[7–11] hydrolysis,[12,13] acidolysis,[14–19] and aminolysis,[20,21] have been developed (Scheme 1A). However, these methods have drawbacks. For example, glycolysis and related C–O bond exchange reactions with alcohols require harsh conditions, and the carbamoyl moieties are converted to the urethane of glycol, which is difficult to utilize for chemical recycling.[7–11] Hydrolysis and acidolysis waste the carbonyl moiety as CO_2.[12–19] Aminolysis forms ureas, which are difficult to utilize as chemical feedstock because of their stability toward nucleophilic substitution reactions.[20,21] Overall, these methods successfully recover polyol fragments in polyurethanes, but the remaining fragments delivered from diisocyanates are converted to recalcitrant product(s), which makes the application of polyurethane degradation still difficult.

Since the pioneering work by Milstein in 2011,[22] the catalytic hydrogenolysis of urethanes to amines, methanol, and alcohols is considered to be a promising method for cleaving the urethane functionality.[23–28] To this end, various catalysts have been developed using Ru,[22,29–34] Mn,[33,35–39] Fe,[33] and Ir[33] complexes (Scheme 1B). In the hydrogenolysis of urethane **1**, formamide **2** and formate ester **5** would be generated by the C–O and C–N bond cleavage, respectively. Because esters and amides are more electrophilic than urethanes,[40,41] intermediates **2** and **5** readily undergo further hydrogenolysis to afford amine **4**, methanol, and alcohol **3**. We note that multiple carbonyl functionalities often coexist in practical polymeric material, with one or more different polymers combined or blended with polyurethanes to achieve the required performance. For example, polyester-diols are often used as the co-monomers of polyurethane. Thus, the selective cleavage of urethane over these carbonyl functionalities is highly desirable for the chemical recycling of polymeric materials. However, the chemoselective transformation of the less reactive carbonyl compounds against the generally accepted reactivity order remains an inherent issue in state-of-the-art organic synthesis.[42–44] Indeed, the tolerance of more electrophilic carbonyl compounds, such as esters and amides, has never been achieved in the hydrogenolysis of urethanes; furthermore, this is believed to be unfeasible.[22,29–38] The polyurethane degradation methods using nucleophilic reagents (Scheme 1A) also face the obstacle of chemoselective urethanes degradation because of the facile nucleophilic substitution of esters and amides compared to urethane.[4–6]

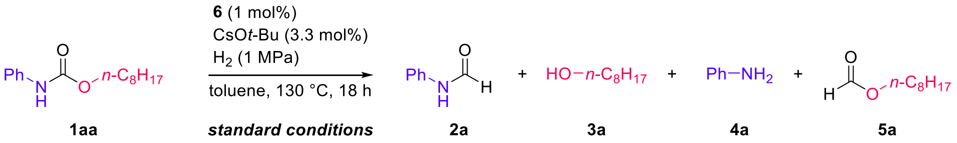
Scheme 1. Chemical Degradation of Urethanes



While the semi-hydrogenolysis of urethanes has not been reported, the hydrogenolysis of ureas to formamides and amines has been achieved using a Ru-triphos catalyst.[45-47] In this transformation, the least electrophilic ureas are selectively reduced over formamide intermediates. Recently, Li et al. utilized the semi-hydrogenolysis of ureas for the conversion of CO_2 to value-added chemicals, such as formamides and *N*-methylamines.[46,47] We have also reported that an Ir complex bearing a bidentate ligand with phosphino and pyrrolido coordinating sites catalyzed the semi-hydrogenolysis of ureas to formamides and amines[48] and showed unique chemoselectivity that tolerated ester, amide, and urethane functionalities, in contrast to the generally accepted electrophilicity order of these carbonyl compounds.[48]

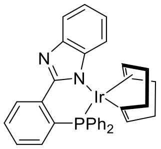
This prompted an investigation into the selective hydrogenolysis of urethanes to obtain products that retain the carbonyl moiety. The challenges associated with the selective hydrogenolysis of urethanes are as follows: (1) preventing over-reduction of formamide/formate ester intermediates and to preserve the carbonyl group in the product via the semi-hydrogenolysis of urethanes, (2) achieving regioselectivity between C–O and C–N bond cleavage, and (3) chemoselectively reducing urethanes in the presence of more electrophilic carbonyl compounds such as esters and amides. Herein, we report the selective hydrogenolysis of urethanes to formamides and alcohols using Ir complex **6**, which possesses a PN bidentate ligand consisting of benzimidazole (Scheme 1C). Under the reaction conditions, ester and amide functionalities were well tolerated; therefore, the Ir catalyst placed urethane above ester and amide in the reactivity order, in sharp contrast to the generally accepted reactivity order of carbonyl compounds.[40,41,44]

Table 1. Hydrogenolysis of urethane 1aa[a]



Entry	Variation from standard conditions	**2a** (%)	**3a** (%)	**4a** (%)	**5a** (%)	Selectivity (%)[b]
1	none	71	77	14	5	79
2	KO*t*-Bu instead of CsO*t*-Bu	55	61	13	7	77
3	NaO*t*-Bu instead of CsO*t*-Bu	30	25	8	1	73
4	LiO*t*-Bu instead of CsO*t*-Bu	28	36	8	5	74
5	without CsO*t*-Bu	<1	<1	<1	<1	–
6	at 150 °C	64	70	33	13	65
7	in THF	82	78	6	3	93
8	Ir cat. **7** instead of **6** in THF	82	86	12	1	93
9	Ir cat. **8** instead of **6** in THF	43	84	56	<1	43
10	Mn cat. **9** instead of **6** in THF	<1	89	85	<1	0
11	$[IrCl(cod)]_2$ instead of **6** in THF	<1	6	2	<1	0
12	Without catalyst **6** in THF	<1	6	3	<1	0

[a] Reaction conditions: Urethane **1aa** (0.5 mmol), Ir catalyst **6** (1 mol%), CsO*t*-Bu (3.3 mol%), and H_2 (1 MPa) in toluene (3 mL) at 130 °C for 18 h. Conversion and yields were determined by ^1H NMR using dibromomethane as an internal standard. [b] Selectivity = yield of **2a** / conversion of **1aa** × 100 (%). cod: cycloocta-1,5-diene.



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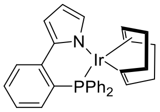

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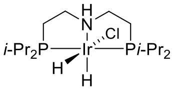

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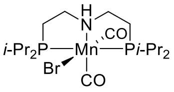

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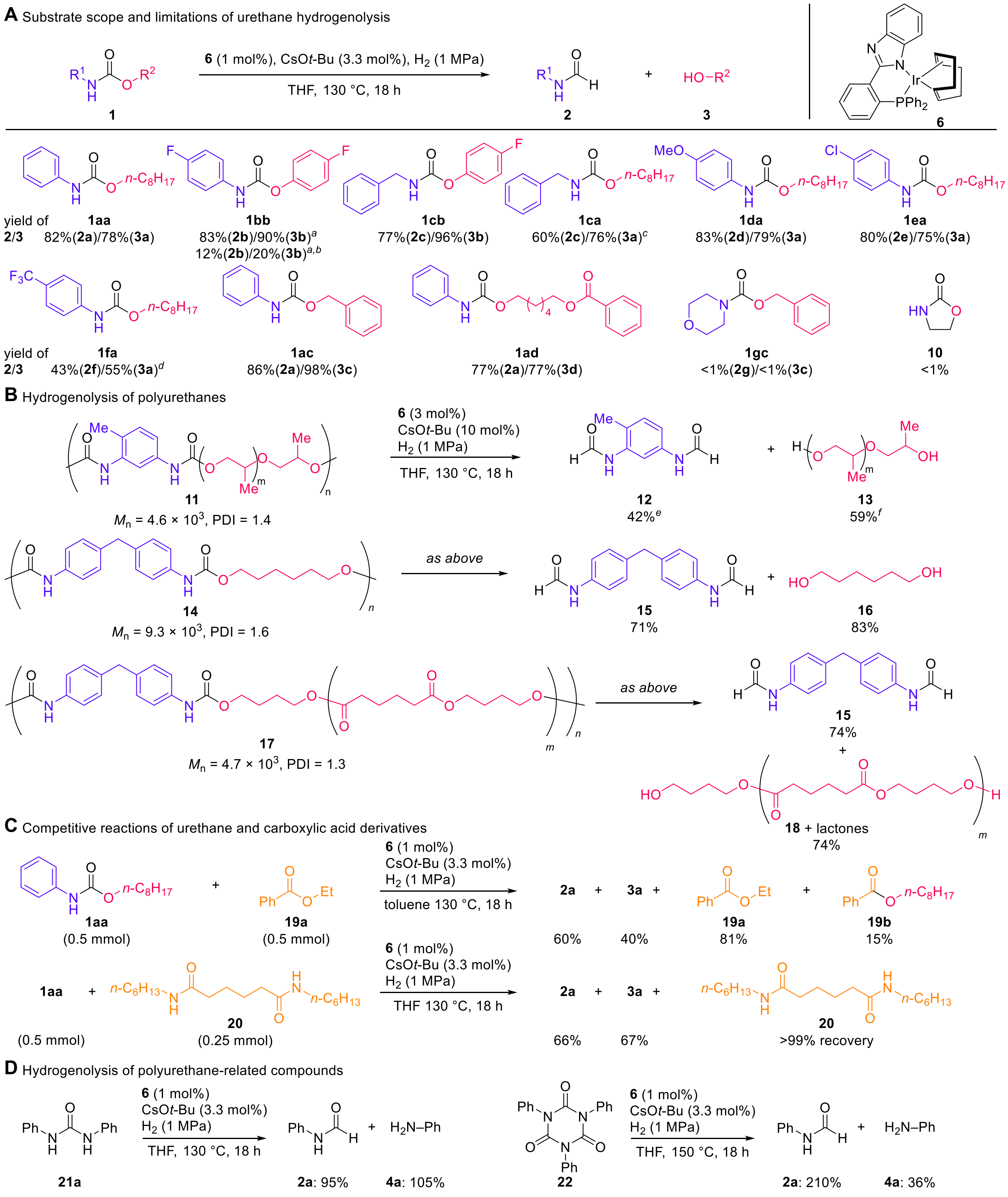
The optimal conditions for the hydrogenolysis of ureas using Ir complex **7** were not suitable for *n*-octyl *N*-phenylcarbamate (**1aa**).[48] Therefore, we used urethane **1aa** as a representative substrate with Ir complex **6** (Figure S1) supported by a phosphine-benzimidazole bidentate ligand (Table 1, also see Table S1). When **1aa** was treated with Ir complex **6** (1 mol%), CsO*t*-Bu (3.3 mol%), and H_2 (1 MPa) in toluene at 130 °C for 18 h, formanilide (**2a**) and *n*-octanol (**3a**) were obtained in 71% and 77% yields, respectively, via the regioselective cleavage of the C–O bond along with a small amount of aniline (**4a**) (14%) and *n*-octyl formate (**5a**) (5%) (entry 1). The selectivity of formanilide against the over-reduction to aniline was 79%. As an additive of the reaction, CsO*t*-Bu played a crucial role in hydrogenolysis. The reaction efficiency decreased when harder alkali metal alkoxides were used; however, the alkali metal cation did not affect the selectivity (entries 2–4). No reaction occurred in the absence of base (entry 5). Increasing the reaction temperature to 150 °C resulted in the over-reduction of **2a** to **4a** and decreased the selectivity to 65% (entry 6). When hydrogenolysis was conducted in THF, the yields of **2a** and **3a** as well as the selectivity increased (entry 7). Next, we screened catalysts in THF. Iridium complex **7** with a pyrrolido moiety showed comparable yields and selectivity (entry 8), but lower catalytic activity for other urethane substrates (vide infra). Combinations of MACHO with Ir and Mn, which have been previously employed in the hydrogenolysis of urethanes to amines, alcohols, and methanol,[33] were also tested (entries 9 and 10). Ir complex **8** catalyzed the hydrogenolysis with significantly low selectivity and afforded **2a** (43%), **3a** (84%), and **4a** (56%) as the products. Mn complex **9** preferentially reduced the

Scheme 2. Hydrogenolysis of Urethanes to Formamides and Alcohols



[a] Without CsO*t*-Bu in toluene for 4 h. [b] Ir catalyst **7** instead of **6**. [c] Reaction was conducted at 150 °C. [d] **4f** (53%) and **5a** (40%) were also obtained. Except for **1fa**, amine **4** and formate **5** were obtained in a trace amount (See SI for details). [e] Along with 19% of monoformamides. [f] Isolated yield.

formanilide intermediate to give **3a** and **4a**. The PN bidentate ligands were essential to achieve the hydrogenolysis of **1aa**, as the reaction did not progress to a notable extent when $[IrCl(cod)]_2$ was used as the catalyst, similar to the reaction in the absence of an Ir complex (entries 11 and 12).

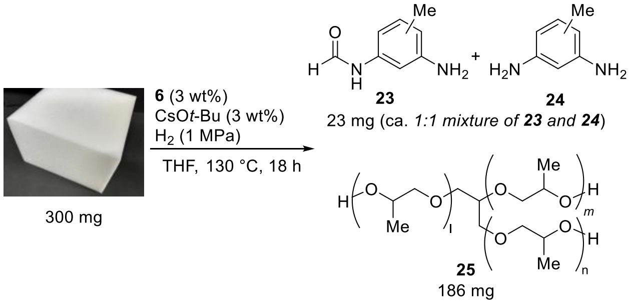
Various urethane derivatives were tested under the optimized conditions (Scheme 2A). Urethane **1bb**, consisting of aniline and phenol, was highly reactive, and the reaction was completed within 4 h to give formanilide **2b** and phenol **3b** in 83% and 90% yields, respectively. Notably, good yields of these products were obtained even in the absence of CsO*t*-Bu, whereas Ir complex **7** showed lower catalytic activity under the same conditions. Urethane **1cb**, consisting of aliphatic amine and phenol, was smoothly reduced to **2c** and **3b**, while the hydrogenolysis of **1ca** with aliphatic amine and alcohol required an elevated temperature. These results indicate that conjugation stabilization by both O and N atoms reduced the reactivity of urethanes. The electron-donating methoxy and electron-withdrawing chloro groups on the aniline moiety had insignificant effects on the reaction efficiency, and urethanes **1da** and **1ea** participated in the hydrogenolysis to give formanilides **2d** and **2e** and *n*-octanol (**3a**) in good yields. Interestingly, the stronger electron-withdrawing CF_3 group did not afford regioselectivity, instead yielding a mixture of **2f** (43%), **3a** (55%), **4f** (53%), and **5a** (40%). The benzyloxycarbonyl (Cbz) group is often used to protect amino groups and can be removed by catalytic hydrogenation using Pd/C, where Cbz is converted to toluene and CO_2 via the cleavage of the benzylic C–O bond.[49] In contrast, the carbonyl C–O bond of **1ac** was selectively cleaved to give **2a** and benzyl alcohol **3c**. Notably, when the substrate was urethane **1ad** with a benzoyl ester moiety, Ir complex **6** reacted selectively with the urethane moiety to give monoester **3d** in 77% yield. Conversely, *N*,*N*-disubstituted urethane **1gc** and cyclic urethane **10** were unsuitable substrates for this catalysis.

Next, we focused on the chemical degradation of polyurethanes (Scheme 2B). Polyurethane **11**, prepared by the polycondensation of toluene diisocyanate (TDI) with polypropylene glycol, was subjected to hydrogenolysis to recover diformamide **12** and diol **13**. 4,4'-Diphenylmethane diisocyanate (MDI)-based polyurethanes **14** and **17** readily underwent hydrogenolysis to afford diformamide **15** and diols **16** and **18** in good yields. Because the present catalyst showed tolerance to the ester moiety, diol **18** was obtained in 74% yield without the loss of the ester functionality (Scheme 2B). Transesterification[50] occurred slightly, broadening the molecular weight distribution of **18** and forming lactones (See SI for details). We further investigated the compatibility of carbonyl compounds often encountered in polymer materials for the selective chemical degradation of polyurethanes in a mixture of plastic waste (Schemes 2C and S1, Table S2). Notably, the models of polyethylene terephthalate and 6,6-nylon were not reduced under these reaction conditions. When a mixture of urethane **1aa** and ester **19a** was subjected to hydrogenolysis, formanilide **2a** and *n*-octanol **3a** were obtained in 60% and 40% yields, respectively. Additionally, **19a** and *n*-octyl benzoate (**19b**) were generated by transesterification,[50] but 96% of the ester was retained. A similar reaction using amide **20** resulted in the selectively reduction of **1aa** to **2a** and **3a** without significant loss of catalytic activity and with completely recovery of amide **20** (Scheme 2C). In contrast, 1,3-diarylurea exhibited reactivity comparable to that of urethane **1aa** under these reaction conditions (Scheme S1). Therefore, when the reaction utilizes catalyst **6**, urethane and urea are ranked above the ester and amide in the order of reactivity.

In the preparation of polyurethane foam, urea and the cyclic oligomers of isocyanate, such as six-membered isocyanurate, are formed via trimerization.[2] Therefore, we tested the hydrogenolysis of these relevant units in commercial polyurethanes (Scheme 2D). Urea **21a** underwent semi-hydrogenolysis to give formanilide (**2a**) and aniline (**4a**) in 95% and 105% yields, respectively (based on moles of **21a**, 200% in maximum). This result was consistent with that of our previous study on **7**; however, the efficiently and selectively were higher (Scheme S2).[48] The hydrogenolysis of isocyanurate **22** proceeded smoothly to give formanilide and aniline in 210% and 36% yields, respectively (based on moles of **22**, 300% in maximum). These results confirmed the usefulness of the present catalyst for the chemical degradation of technical-grade polyurethanes.

Finally, we performed the hydrogenolysis of the technical-grade polyurethane samples (Scheme 3). Finely cut polyurethane foam (300 mg) was subjected to hydrogenolysis to obtain a yellow suspension, which was acidified by HCl aq. and extracted with CH_2Cl_2 to obtain 186 mg of polyol **25**. In addition, a 1:1 mixture of diaminotoluenes **23** and their monoformamides **24** (23 mg) was recovered from the aqueous phase.

Scheme 3. Hydrogenolysis of Technical-Grade Polyurethanes



In conclusion, we demonstrated that the combined use of an Ir complex supported by a phosphine-benzimidazole bidentate ligand and CsO*t*-Bu catalyzed the hydrogenolysis of urethanes to formamides and alcohols via the regioselective cleavage of the C–O bond. Counterintuitively, formamides, which are classified as more electrophilic than urethanes, were obtained in good-to-excellent yields. Moreover, the present catalyst tolerated esters and amides well, contrary to the hierarchy of electrophilicity order of carbonyl compounds. This is the first example of the chemoselective hydrogenolysis of urethanes over esters and amides. We successfully demonstrated the chemical degradation of polyurethanes with a diol-containing ester in the main chain and technical-grade polyurethane foam. The carbonyl group was maintained in the formamide product, in sharp contrast to products afforded from conventional urethane hydrogenolysis catalysts[22–39] and other methods.[4–6] The chemoselective conversion of urethane to formamide and alcohol offers a novel method for the chemical recycling of polyurethanes through H_2 transfer by combining dehydrogenative coupling between formamide and alcohol.[51,52] In addition, the unique chemoselectivity of the present catalyst enables the selective degradation of thermoset polyurethanes and recovery of thermoplastic polyesters and polyamides, providing a new avenue for the chemical recycling of combined or blended polymer materials for a sustainable society.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Detailed condition screening, functional group tolerance toward carbonyl compounds, X-ray crystallographic data, experimental details, experimental procedures, and spectroscopic data (PDF)

Accession Codes

CCDC 2351707 (**6**) contains the supplementary crystallographic data for this paper. This data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Author

Takanori Iwasaki – Department of Chemistry and Biotechnology, Graduate School of Engineering, The University of Tokyo, Bunkyo-ku, Tokyo 113-8656, Japan; ORCID: 0000-0002-6663-3826; Email: iwasaki@chembio.t.u-tokyo.ac.jp

Kyoko Nozaki – Department of Chemistry and Biotechnology, Graduate School of Engineering, The University of Tokyo, Bunkyo-ku, Tokyo 113-8656, Japan; ORCID: 0000-0002-0321-5299; Email: nozaki@chembio.t.u-tokyo.ac.jp

Author

Yuto Yamada – Department of Chemistry and Biotechnology, Graduate School of Engineering, The University of Tokyo, Bunkyo-ku, Tokyo 113-8656, Japan
Naoki Naito – Department of Chemistry and Biotechnology, Graduate School of Engineering, The University of Tokyo, Bunkyo-ku, Tokyo 113-8656, Japan; ORCID: 0000-0001-8492-120X

Present Addresses

‡Department of Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts, 02138, United States

Notes

A Japan patent application on this work has been filed (Japan Patent Application No. 2022-020544), where K.N., T.I., and N.N. are listed as inventors.

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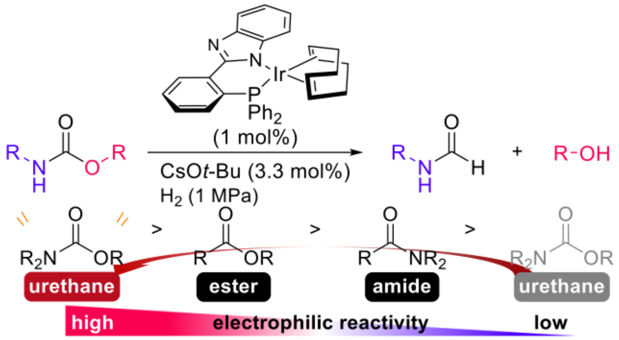
(1 mol%)
CsO*t*-Bu (3.3 mol%)
H_2 (1 MPa)
R-OH
urethane
ester
amide
urethane
high
electrophilic reactivity
low