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Formic acid disproportionation into formaldehyde triggered by vanadium complexes with iridium catalysis under mild conditions in *N*-methylation[†]

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Formaldehyde (CH₂O) has been used as a key platform reagent in the chemical industry for many decades. Currently, the industrial production of CH₂O mainly depends on fossil resources, involving a highly energetic three-step process (200–1100 °C). Herein, we describe renewable formic acid (HCO₂H) disproportionation into CH₂O triggered by vanadium complexes with iridium catalysis under mild conditions at 30–50 °C in *N*-methylation. The gramscale application of *in situ* generated CH₂O by HCO₂H disproportionation is demonstrated.

Introduction

For many decades, formaldehyde (CH₂O) has been used as a key platform reagent in the chemical industry. It is commonly used in the preparation of many materials, including resins and plastics, with an annual global demand of over 30 megatons per year.¹ Currently, the industrial production of CH₂O mainly depends on a highly energetic three-step process consisting of steam reforming of natural gas to syngas (700–1100 °C), methanol synthesis (200–300 °C), and finally partial oxidation/dehydrogenation of methanol (300–400 °C).^{1–5} Selective CH₂O generation, by reduction of carbon monoxide^{6–12} or carbon dioxide^{13–27} and oxidation of methane, ^{28–39} is being developed.

Due to the dwindling supply of fossil resources, CH_2O production from renewable resources, such as renewable formic acid (HCO_2H) ,^{40–43} is highly desirable.¹ To date, only a few methods of CH_2O production by reduction of HCO_2H have been reported,^{44–46} probably due to the fact that the reduction potential is similar to that of HCO_2H reduction to methanol.⁴⁷

Gambarotta and co-workers reported an efficient reduction of HCO_2H to CH_2O at 350 °C with the consumption of a large amount of zinc as a reductant. This is the state of the art method for CH_2O production from HCO_2H .⁴⁶ In addition, utilization of HCO_2H for the synthesis of the formaldehyde surrogate dialkoxymethane was developed, *via* formate ester and methoxy methanol as the possible intermediates with the requirement of H_2 (80 bar) and methanol as the reactants at 80 °C.⁴⁸

Herein, we report the discovery of HCO₂H disproportionation into CH₂O triggered by vanadium complexes with iridium catalysis at 30–50 °C in *N*-methylation. Specifically, the active vanadium complexes are determined to be $[(VO)^{2+}(xH_2O)L]$. According to the control experiments, the ligand (L) should be the generated intermediates during renewable HCO₂H production by hydrolysis–oxidation of biomass,^{49–53} the analogues of glyoxal in aqueous solutions.⁵⁴ The vanadium complex may act as a Lewis acid to activate HCO₂H. As the feature of disproportionation, extra reductants can be avoided (Fig. 1).

Results and discussion

Recently, we demonstrated HCO_2H production in up to quantitative yield by hydrolysis–oxidation of various types of lignocellulosic biomass, including wheat straw, corn straw, rice straw, *etc* even in a near 10-gram-scale reaction.⁵⁵ In the trans-



Fig. 1 HCO₂H disproportionation into CH₂O triggered by vanadium complexes with iridium catalysis in the *N*-methylation. ^aL should be the analogues of glyoxal in the aqueous solution.

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formation, air/oxygen (3–5 MPa) was used as an oxidant and sodium metavanadate (NaVO₃, 3.5 mol%) was used as a catalyst precursor. The reaction was carried out in 0.7 wt% H_2SO_4 aqueous solution with 1 v% DMSO at 160 °C for 3 h.⁵⁵ Generally, the industrial production of HCO₂H mainly depends on CO as the starting material, which is normally produced in an unsustainable way from coal, oil or natural gas by gasification at high temperatures (>900 K), through a multistep process *via* methyl formate or formate as intermediates.⁵⁶

In comparison with industrial HCO_2H production, our method displayed some advantages, such as renewable starting materials, comparatively mild conditions, *etc.* The produced renewable HCO_2H was applied to the hydrogenation of nitroarenes by utilization of its hydrogen source.⁵⁷ Thus we envisioned the feasibility of utilization of the hydrogen source as well as the carbon source of the renewable HCO_2H^{58} for the *N*-methylation of quinolines to afford the corresponding *N*-methyl tetrahydroquinolines using tetrahydroquinolines as the intermediates.^{59–61}

Quinoline (1) was selected as a model substrate for *N*-methylation (Table S2[†]). Initially, the reaction was carried out using renewable HCO₂H (8 equiv.) contained in wheat straw hydrolysis–oxidation aqueous solution (HOAS).⁵⁵ *N*-Methyl tetrahydroquinoline **3** in 30% yield and tetrahydroquinoline **4** in 60% yield were obtained in the presence of iridium catalyst **2** (Table S2,[†] entry 1). As the comparatively easily available renewable HCO₂H from wheat straw, after a series of experiments, it was found that using renewable HCO₂H (30 equiv.) with **2** (1 mol%), **3** was obtained in 91% yield, by a total conversion of **4**, after 20 h at 50 °C (Fig. 2, eqn (1)), with the utilization rate of HCO₂H of 15% (Table S3[†]).



Fig. 2 Control experiments for the Eschweiler–Clarke reaction pathway of the *N*-methylation. ^a The renewable HCO_2H was prepared by the hydrolysis–oxidation of the wheat straw.⁵⁵ **1**, **4**, **5**, or **6** (0.25 mmol), **2** (1.0 mol%). Yields were determined by ¹H NMR using $Cl_2CHCHCl_2$ as an internal standard.

Meanwhile, the iridium complex, containing Cp* and 2,4dihydoxypyrimidine connected with an imidazoline moiety, which displayed the best efficiency for hydrogen production from the hydrolysis–oxidation solution of biomass,⁵⁵ only resulted in 40% yield of 3 (Table S4,† entry 1). Other catalysis systems of [RhCp*Cl₂]₂, rhodium complex containing Cp* and 4,4'-dihydroxy-2,2'-bipyridine, [RuCl₂(benzene)]₂/dppe, RuCl₃/ *m*-TPPTS, and Fe(BF₄)₂/(Ph₂PCH₂CH₂)₃P, which displayed lower efficiencies for the hydrogen production from the oxidation of glucose solution,⁵⁵ were also detected. No reactivity was observed (Table S4,† entries 2–6).

The influence of pH values on the transformation was also investigated (Table S5†). The results of control experiments demonstrated that there was no obvious influence on the catalytic activity during the change in pH value from 0.9 to 2.5 (Table S5,† entries 1–3). The catalytic activity was sharply decreased in the pH range from 3.0 to 3.5 (Table S5,† entries 4–6). The reaction activity was inhibited at the pH value of 4.0 (Table S5,† entry 7).

To gain insight into the reaction mechanism of the *N*-methylation, a series of experiments were conducted. As the reaction should involve the hydrogenation of quinoline followed by the *N*-methylation, sequential studies of the hydrogenation and the *N*-methylation were designed.

Firstly, hydrogenation of quinoline **1** in the presence of 2.5 equiv. of HCO_2H or the renewable HCO_2H contained in the wheat straw HOAS was studied (Fig. 2, eqn (2) and (3)). In both cases, the hydrogenation product **4** was obtained in excellent yields (90% and 89%, respectively). In addition, in comparison with the no *N*-methylation product **3** in the former case, 5% yield of **3** was detected in the latter case. These results suggest that the HCO_2H contained in the wheat straw HOAS is the major active component in the hydrogenation. For the *N*-methylation, there should be other factors contained in the wheat straw HOAS, besides HCO_2H .

Next, *N*-methylation was investigated using tetrahydroquinoline **4** with 2.5 equiv. of the renewable HCO_2H , and **3** was obtained in 25% yield (Fig. 2, eqn (4)). Furthermore, with 30 equiv. of the renewable HCO_2H , **3** was obtained in 88% yield (Fig. 2, eqn (5)). However, when using 30 equiv. of HCO_2H , **3** was not detected (Fig. 2, eqn (6)). These results further indicate that other factors contained in the wheat straw HOAS, besides HCO_2H , are essential for *N*-methylation.

Furthermore, possible intermediates of amide $5^{58,60,61}$ and urea 6^{62-65} for the *N*-methylation were tested under the optimized conditions (Fig. 2, eqn (7) and (8)), respectively. In both cases, **3** was not observed, which indicates that the *N*-methylation does not involve the pathways of the amide or the urea formation.

Then, the possibility of *N*-methylation *via* the Eschweiler– Clarke reaction pathway was tested with 4 (Fig. 2, eqn (9)–(11)). The Eschweiler–Clarke reaction pathway involves using CH₂O as the carbon source with HCO₂H as a reductant to afford the hydrogen source.^{66,67} In the presence of 1.1 equiv. of CH₂O and 1.5 equiv. of HCO₂H with 2 under similar conditions, 4 was converted to 3 in 46% yield (Fig. 2, eqn (9)). Increasing the amount of HCO_2H to 30 equiv., while keeping the amount of CH_2O constant, did not induce an obvious increase of the yield of 3 (49%, Fig. 2, eqn (10)). However, increasing the amount of CH_2O to 2 equiv., with 1.5 equiv. of HCO_2H , afforded 3 in 64% yield (Fig. 2, eqn (11)). Comparing these results with no observation of 3 in the presence of 30 equiv. of HCO_2H (Fig. 2, eqn (6)), we deduced the *in situ* CH_2O generation by HCO_2H disproportionation, triggered by the [V] complexes contained in the wheat straw HOAS, under optimized standard conditions (Fig. 2, eqn (1)).

To prove the deduction, the typical CH₂O capture experiment, in which ammonia and acetoacetic ester acted as capture reagents,⁶⁸ was conducted using renewable HCO₂H and normal HCO₂H under similar optimized conditions (Fig. 3, eqn (1) and (2)). In the transformation, the CH₂O capture rate, the ratio of *in situ* generated CH₂O to the consumed HCO₂H, was determined to be 41% or 21%, respectively. The captured product 7 was obtained in 77% or 23% yield, respectively. Notably, only in the presence of HCO₂H without the [V] complexes, 7 could not be obtained. These results demonstrate *in situ* CH₂O generation by HCO₂H disproportionation under optimized standard conditions.

As a supplementary specification, with an understanding of the Eschweiler–Clarke reaction pathway of *N*-methylation, we realized that the minor component $CH_2(OH)_2$ (3.4–3.6 mol%),⁵⁵ the major form of CH_2O in aqueous solution, with an accumulation of about 1.1 equiv. accompanied by 30 equiv. of HCO_2H in the wheat straw HOAS, should contribute to the transformation to some extent.

However, our experiments clearly proved the *in situ* CH₂O generation from HCO₂H under the standard conditions. First, 25% of **3** was obtained from **4** using 2.5 equiv. of renewable HCO₂H contained in the wheat straw HOAS, accompanied by no more than 0.09 equiv. of CH₂(OH)₂ (Fig. 2, eqn (4)). Production of **3** in 25% yield *via* the Eschweiler–Clarke



Fig. 3 CH₂O capture experiments. Reaction conditions of eqn (1): acetoacetic ester (2 mmol), renewable HCO₂H (8 mmol, 4.0 equiv.) contained in the wheat straw HOAS, NH₃ aqueous solution (16 mmol, 8.0 equiv.), 2 (1.0 mol%), 50 °C, 20 h. ^aThe renewable HCO₂H was prepared by the hydrolysis–oxidation of the wheat straw.⁵⁵ ^b Isolated yield is reported based on the average of two experiments. Reaction conditions of eqn (2): acetoacetic ester (2 mmol), HCO₂H (8 mmol, 4.0 equiv.), NH₃ aqueous solution (16 mmol, 8.0 equiv.), 2 (1.0 mol%), and the [V] solution prepared as shown in note c, 50 °C, 20 h. ^cThe wheat straw HOAS was extracted by EtOAc to remove HCO₂H and the other minor components to afford the [V] solution.

pathway required at least 0.25 equiv. of CH_2O or $CH_2(OH)_2$. Thus the lacking CH_2O should be *in situ* generated from HCO_2H . Second, a 41% capture rate of CH_2O was obtained under similar standard conditions with the deduction of the amount of $CH_2(OH)_2$ contained in the wheat straw HOAS (Fig. 3, eqn (1)).

The generation of MeOH during the transformation was also detected. There was about 3% MeOH in the renewable HCO_2H from the hydrolysis-oxidation of biomass, which is derived from the oxidation of DMSO.⁵⁵ After the reaction, the aqueous mixture was detected by crude ¹H NMR, the content of MeOH was still determined to be about 3% (Fig. S3†). Therefore, we deduce that further reduction of *in situ* generated CH_2O to MeOH is difficult in the aqueous reaction mixture. The reason should be the major form of *in situ* generated CH_2O as $CH_2(OH)_2$ in the aqueous reaction mixture.

After that, many experiments were performed using the [V] complexes related with the *in situ* CH₂O generation (Table 1). The amount of [V] complexes in the wheat straw HOAS used for the *N*-methylation was about 1.1 equiv., accompanied by 30 equiv. of renewable HCO₂H, as 3.5 mol% of NaVO₃ was used as the catalyst precursor for one mole of HCO₂H production.

The *N*-methylation was conducted in the presence of NaVO₃ (1.1 equiv.) or VOSO₄ (1.1 equiv.), both of which can be used as good catalyst precursors for the hydrolysis–oxidation of biomass into HCO_2H .⁵⁵ However, no observation of **3** using NaVO₃ or 7% yield of **3** using VOSO₄ was detected (Table 1, entries 2 and 3).

Meanwhile, the same amount of [V] complexes from wheat straw HOAS by removal of HCO_2H and other minor organic components, including HOAc, MeOH, 1,4-dioxane, DMSO, and $DMSO_2$,⁵⁵ was used for the *N*-methylation to give 3 in 45% yield (Table 1, entry 4). It was further proved that these minor organic components in wheat straw HOAS had no influence on the *in situ* CH₂O generation in the *N*-methylation (Table S6†).

Furthermore, it was found that 5 mol% of [V] complexes, simply prepared by a 10 minute procedure of hydrolysis–oxidation of glucose (0.24 equiv.), induced the *N*-methylation in 83% yield (Table 1, entry 5). To avoid some uncertain factors for the mechanism insight, herein, glucose was used instead of the wheat straw. When 10 mol% of [V] complexes was used, the yield of *N*-methylation reached 86% (Table 1, entry 6). Notably, with the lack of any one factor of the hydrolysis–oxidation procedure of glucose, the resulted [V] complexes could not afford product 3 (Table S7†).

In comparison with the standard reaction conditions to obtain 91% yield of 3 (Fig. 2, eqn (1)), these results suggest that the active [V] complexes should contain the vanadium element as well as the possible intermediates generated during the hydrolysis-oxidation of biomass.

First, the valence of the [V] complexes was detected. The [V] complexes from the wheat straw HOAS and the simply prepared [V] complexes by the hydrolysis–oxidation of glucose displayed the blue color of $[V^{4+}]$ in an aqueous solution.⁶⁹ These [V] complexes were further confirmed using the EPR spectrum (Fig. 4, 2b and 2c).⁵¹ It confirmed that $[V^{4+}]$ is contained in the

Table 1 Control experiments for in situ $\mathsf{CH}_2\mathsf{O}$ generation triggered by [V] complexes



1	HCO_2H (30 equiv.)	
2	HCO_2H (30 equiv.), NaVO ₃ (1.1 equiv.)	—
3	HCO_2H (30 equiv.), $VOSO_4$ (1.1 equiv.)	7
4	HCO_2H (30 equiv.), [V] (1.1 equiv.) from wheat	45
	straw HOAS with the removal of HCO ₂ H and other	
	minor organic components ^c	
5^d	HCO_2H (30 equiv.), prepared [V] (5 mol%) by a	83
	10 min hydrolysis-oxidation of glucose (0.24	
	equiv.) with NaVO ₃ as a catalyst precursor	
6 ^e	HCO_2H (30 equiv.), prepared [V] (10 mol%) by a	86
	10 min hydrolysis-oxidation of glucose (0.48	
	equiv.) with NaVO ₃ as a catalyst precursor	
7	HCO ₂ H (30 equiv.), VOSO ₄ (0.1 equiv.), 1,3-dihy-	7
	droxyacetone (0.1 equiv.)	
8	HCO ₂ H (30 equiv.), VOSO ₄ (0.1 equiv.), glyceralde-	13
	hyde (0.1 equiv.)	
9	HCO_2H (30 equiv.), $VOSO_4$ (0.1 equiv.), glycolalde-	—
	hyde $(0.1 \text{ equiv.})^f$	
10	HCO_2H (30 equiv.), $VOSO_4$ (0.1 equiv.), glyoxal (0.1	42
	equiv.) ^g	
11	HCO_2H (30 equiv.), $VOSO_4$ (0.1 equiv.), glycolic	12
	acid (0.1 equiv.)	
12	HCO_2H (30 equiv.), $NaVO_3$ (0.1 equiv.), glyoxal (0.1	35
,	equiv.) ^g	
13 ⁿ	HCO ₂ H (30 equiv.), Zn(OTf) ₂ (0.1 equiv.)	3
$14_{,}^{n}$	HCO ₂ H (30 equiv.), Zn(OTf) ₂ (1.1 equiv.)	5
15_{L}^{n}	HCO_2H (30 equiv.), $Cu(OTf)_2$ (0.1 equiv.)	5
16^n	HCO_2H (30 equiv.), $Cu(OTf)_2$ (1.1 equiv.)	10

^{*a*} Reaction conditions: 4 (0.25 mmol), 2 (1.0 mol%), reactants and additives, 50 °C, 20 h. Yields were determined by ¹H NMR using $Cl_2CHCHCl_2$ as an internal standard. ^{*b*} Herein, the experiment of eqn (6) in Fig. 2 was given for obvious comparison. ^{*c*} The [V] complexes were obtained from wheat straw HOAS by removal of HCO₂H and the other minor organic components by extraction with EtOAc. ^{*d*} The reaction was conducted at 30 °C, and the amount of $CH_2(OH)_2$ was determined to be less than 0.02 mmol from glucose HOAS. ^{*e*} The reaction was conducted at 30 °C, and the amount of $CH_2(OH)_2$ was determined to be less than 0.02 mmol from glucose HOAS. ^{*f*} The dimer of glycolal-dehyde was used. ^{*g*} Glyoxal aqueous solution was used, the major form of glyoxal aqueous solution was ethane-1,1,2,2-tetraol. ^{54 h} The reaction was conducted at 70 °C for 30 h.

[V] complexes besides $[V^{5+}]$, which was detected by ⁵¹V NMR (Fig. 4, 1b and 1c).⁵⁵ According to the influence of the pH values on the existing form of $[V^{4+}]$ complexes,⁶⁹⁻⁷² the $[V^{4+}]$ complexes should exist as $[VO^{2+}(xH_2O)]$ related complexes when the pH value of the reaction mixture was about 2.25. Next, the possible intermediates generated during the hydrolysis–oxidation of biomass contained in the active [V] complexes were investigated. VOSO₄ (10 mol%) aqueous solution with the possible intermediates (10 mol%) of hydrolysis–oxidation of biomass, including 1,3-dihydroxyacetone, glyceralde-hyde, glycolaldehyde, glyoxal, and glycolic acid,^{49–53} respectively, was stirred for 30 min at room temperature, and then the *N*-methylation was conducted (Table 1, entries 7–11). The



Fig. 4 The ⁵¹V NMR and EPR spectra of vanadium. (a) The same initial concentration of standard NaVO₃, pH 2.25 (the pH was adjusted by 0.7 wt% H₂SO₄ aqueous solution). (b) Wheat straw hydrolysis–oxidation aqueous solution, pH 2.25. (c) Glucose hydrolysis–oxidation aqueous solution, pH 2.25. (d) After the standard reaction of *N*-methylation, the reaction mixture was detected. (e) The same concentration of standard VOSO₄, pH 2.25 (the pH was adjusted by 0.7 wt% H₂SO₄ aqueous solution).

mixture of glyoxal with VOSO₄ induced 42% yield of 3 (Table 1, entry 10), which displayed an obvious higher efficiency than other possible intermediates (Table 1, entries 7–9, 11). These results indicate that the $[V^{4+}]$ or $[V^{5+}]$ complexes, with the analogues of glyoxal in aqueous solution, form the major active [V] complexes to trigger *in situ* CH₂O generation for the *N*-methylation.

In addition, the experiment of NaVO₃ instead of VOSO₄ with glyoxal gave 35% yield of 3 (Table 1, entry 12). During the procedure, after mixing glyoxal with the yellow aqueous solution of NaVO₃ for several minutes, the color of the reaction changed to blue due to $[VO_2^+(xH_2O)]$.^{69–72} Then mixing glyoxal with the aqueous solution of NaVO₃ was further detected using the *in situ* UV-visible absorption spectra. The initial spectra and the spectra within 3 min, 5 min and 30 min are shown in Fig. 5(a–d). They demonstrate that the UV-visible absorption spectra of mixing glyoxal with NaVO₃ are identical to those of mixing glyoxal with VOSO₄ within 30 min (Fig. 5e) and VOSO₄ in acidic aqueous solution.⁷¹ These results indicate that NaVO₃ is reduced to $[V^{4+}]$ as $[VO_2^+(xH_2O)]$ in the presence of glyoxal.

Furthermore, after the standard reaction of *N*-methylation, the reaction mixture was detected by EPR and ⁵¹V NMR again (Fig. 4, 1d and 2d). The results indicate that only the $[V^{4+}]$ complexes remained after the reaction.

Based on these experiments, the active vanadium complexes that triggered the HCO_2H disproportionation into CH_2O are determined to be [(VO)²⁺(xH_2O)L], in which the ligand (L) should be the analogues of glyoxal, generated during renewable HCO_2H production by hydrolysis–oxidation of biomass.

To further investigate the function of the active $[(VO)^{2+}(xH_2O)L]$ complexes, the transformation was conducted in the presence of typical Lewis acids, such as $Zn(OTf)_2$ or Cu $(OTf)_2$ both in 10 mol% or 1 equiv. (Table 1, entries 13–16).



Fig. 5 The *in situ* UV-visible absorption spectra of mixing glyoxal with the solution of NaVO₃. (a) The initial UV-visible absorption spectra of mixing glyoxal with NaVO₃ in 0.7 wt% H_2SO_4 aqueous solution under an Ar atmosphere. (b) The UV-visible absorption spectra of mixing glyoxal with NaVO₃ in 0.7 wt% H_2SO_4 aqueous solution under an Ar atmosphere over 3 min. (c) The UV-visible absorption spectra of mixing glyoxal with NaVO₃ in 0.7 wt% H_2SO_4 aqueous solution under an Ar atmosphere over 5 min. (d) The UV-visible absorption spectra of mixing glyoxal with NaVO₃ in 0.7 wt% H_2SO_4 aqueous solution under an Ar atmosphere over 5 min. (d) The UV-visible absorption spectra of mixing glyoxal with NaVO₃ in 0.7 wt% H_2SO_4 aqueous solution under an Ar atmosphere over 30 min. (e) The UV-visible absorption spectra of mixing glyoxal with VOSO₄ in 0.7 wt% H_2SO_4 aqueous solution under an Ar atmosphere. (f) The UV-visible absorption spectra of VOSO₄ in 0.7 wt% H_2SO_4 aqueous solution under an Ar atmosphere.

Product 3 was obtained in 3–10% yields. Based on these results, it was deduced that the active $[(VO)^{2+}(xH_2O)L]$ complexes may act as a Lewis acid to activate HCO_2H ,⁷¹ by coordination of the carbonyl group, during the *in situ* CH₂O generation.

Furthermore, in the standard mercury poisoning test,⁷³ 3 was obtained in a comparable yield of 87%, in comparison with 91% under standard conditions. This result indicates homogeneous catalysis for the *in situ* CH₂O generation in the *N*-methylation. The quantitative concentration of the vanadium complex is the same as the concentration of 0.02 M in the original wheat straw HOAS.

According to the results of these studies, the *in situ* CH₂O generation by disproportionation of HCO₂H during the *N*-methylation is proposed as shown in Fig. 6. The iridium catalyst precursor 2 releases H_3O^+ to afford the $[Cp^*L''IrH]^+$ complex (L'' = the anion of 4,4'-dihydroxy-2,2'-bipyridine), which is followed by coordination with formate (HCO₂⁻) and decarboxylation to generate the [Ir]-H complex of $[Cp^*L'' IrH]^+$.^{55,74,75} The active vanadium complexes, which were determined to be $[(VO)^{2+}(xH_2O)L]$ (L should be the analogues of glyoxal in the aqueous solution), promote the reduction of HCO₂H to CH₂(OH)₂ by the [Ir]-H complex by coordination of the carbonyl group. An equilibrium exists between CH₂(OH)₂ and CH₂O. Meanwhile, compound **1** is hydrogenated to **4** by the [Ir]-H complex. Condensation of **4** with CH₂O is followed



Fig. 6 Proposed *in situ* CH_2O generation by disproportionation of HCO_2H during the *N*-methylation. ^aL should be the analogues of glyoxal in aqueous solution.

by the hydrogenation of **7** with the [Ir]–H complex to afford the *N*-methylation product **3**.

Synthetic application

To make the transformation more applicable, the gram-scale reaction of *N*-methylation of quinoline **1** with HCO_2H in the presence of **2** (1 mol%), as well as the prepared [V] complexes (10 mol%), was conducted. 0.85 g of **3** was obtained in 75% yield at 30 °C. (Fig. 7, eqn (1)).

Furthermore, the gram-scale reaction of *N*-methylation of quinoline **1** with renewable HCO_2H , produced from 10.5 g of the wheat straw, was also conducted. **1.0** g of **3** was obtained in 91% yield with 0.5 mol% of catalyst **2** (Fig. 7, eqn (2)). Product **3** was obtained in 72% yield at 30 °C.

As 1.1 equiv. of [V] was contained by using renewable HCO_2H from the wheat straw HOAS in the *N*-methylation, the



Fig. 7 Gram-scale application of *in situ* generated CH₂O. ^a [V] (10 mol%) prepared by a 10 min hydrolysis–oxidation of glucose (0.24 equiv.) with NaVO₃ as a catalyst precursor. ^b [V] contained during the wheat straw HOAS. Reaction conditions of eqn (1): quinoline **1** (7.74 mmol, 1.0 g), **2** (0.0774 mmol, 1 mol%, 48.8 mg), 10 mol% [V] solution from glucose HOAS, HCO₂H (232.2 mmol, 30 equiv., 10.7 g, 8.8 mL), H₂O (250 mL), 30 °C, 65 h. Reaction conditions of eqn (2): quinoline **1** (7.74 mmol, 1.0 g), **2** (0.0387 mmol, 0.5 mol%, 24.4 mg), renewable HCO₂H (185.7 mmol, 24 equiv.) contained in the wheat straw HOAS (334.5 mL), 50 °C, 35 h. ^c 30 °C, 65 h.



Fig. 8 The recycling experiment of the $\left[V\right]$ species in the wheat straw HOAS for N-methylation.

recycling experiment of the [V] species in the wheat straw HOAS for the *N*-methylation was conducted furthermore. After the standard *N*-methylation of **1**, the reaction mixture was worked-up to give **3** in 91% yield as well as the aqueous phase contained the [V] species (Fig. 8, steps A and B). By applying the resulted aqueous phase without the addition of the catalyst precursor NaVO₃, the hydrolysis–oxidation of the wheat straw under standard conditions afforded the wheat straw HOAS contained HCO₂H in 66% yield (Fig. 8, steps C and D). The resulted wheat straw HOAS for the second *N*-methylation of **1** afforded **3** in 85% yield (Fig. 8, steps A' and B').

Conclusions

In summary, renewable HCO_2H disproportionation into CH_2O triggered by vanadium complexes with iridium catalysis under mild conditions is discovered. The gram-scale application of *in situ* generated CH_2O is demonstrated. These findings should provide motivation for further studies on energy-efficient CH_2O production by HCO_2H disproportionation under mild conditions and for various applications of *in situ* generated CH_2O from renewable resources.

Author contributions

C.-Z. Z. carried out the experimental and data-analysis work. Y.-R. Z., Y.-J. G., and Prof. P. Z. contributed to some experiments and the discussion. Y. L. designed the reaction and directed the project. Y. L. wrote the paper with the assistance of C.-Z. Z.

Conflicts of interest

There are no conflicts to declare.

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