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Scope and reaction mechanism of an aerobic oxidative alkyne homocoupling catalyzed by a di-copper-substituted silicotungstate

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ABSTRACT

The di-copper-substituted γ-Keggin-type silicotungstate $TBA_4[\gamma\text{-}H_2SiW_{10}O_{36}Cu_2(\mu\text{-}1,1\text{-}N_3)_2]$ (**I**, TBA = tetra-*n*-butylammonium) could act as an efficient reusable homogeneous catalyst for the aerobic oxidative alkyne homocoupling. Various kinds of structurally diverse terminal alkynes including aromatic, heteroaromatic, aliphatic, double bond-containing, silylacetylene, propargylic alcohol, and propargylic amine derivatives could selectively be converted into the corresponding diynes in the presence of **I**. The catalytic activity of **I** was much higher than those of the mono-copper-substituted silicotungstate, monomeric copper complexes, and simple copper salts, showing that the di-copper core in **I** plays an important role in the present alkyne homocoupling. The reaction mechanism involving the formation of the di-copper(II)-alkynyl intermediate, reductive elimination of a diyne, and re-oxidation of reduced copper species by O_2 has been proposed.

1. Introduction

Diyne derivatives are a very important class of compounds and have been used as key structural elements for natural product synthesis, polymer chemistry, supramolecular chemistry, and material science [1]. Therefore, much attention has been paid to the development of efficient synthetic procedures for the diyne derivatives. An alkyne homocoupling is one of the most widely used procedures for the synthesis of symmetrical diyne derivatives. Classically, stoichiometric amounts of copper salts have been used for the alkyne homocoupling (Glaser coupling) [2]. In Hay's [3] and Campbell and Eglinton's [4] systems, catalytic amounts of copper salts or complexes with appropriate nitrogen bases (as ligands or solvents) and O_2 (as an oxidant of reduced copper species) have been utilized [5–8]. Although the Hay's and Eglinton's systems show high catalytic performance for the homocoupling of aromatic alkynes, yields of aliphatic diynes are generally still low to moderate for aliphatic alkynes [3–8]. Palladium salts and complexes have been reported to be active for the homocoupling of aliphatic alkynes. However, these systems have disadvantages of the use of expensive palladium catalysts and the need for bases and copper co-catalysts [9,10].

Bohlmann and co-workers proposed that the copper(II)-catalyzed alkyne homocoupling proceeds through the formation of the di-copper(II)-alkynyl intermediate, i.e., $\{Cu_2(\mu\text{-}C{\equiv}CR)_2\}$, which collapses directly to the diyne products with the formation of copper(I) species [11]. The reduced copper species can be re-oxidized by O_2. The reaction mechanism proposed by Bohlmann and co-workers has widely been accepted [1]. Although it is expected that the alkyne homocoupling should efficiently be promoted by the presence of catalysts with di-copper(II) sites on the basis of Bohlmann's mechanism, an alkyne homocoupling catalyzed by complexes with di-copper(II) sites has been as yet unknown.

Very recently, we have successfully synthesized the silicotungstate **I** with the di-copper core and used it for the aerobic oxidative alkyne homocoupling [12,13]. As we expected, various kinds of alkynes could be converted into the corresponding diynes in high yields in the presence of **I** and the catalytic activity of **I** was much higher than those of the mono-copper-substituted silicotungstate, monomeric copper complexes, and simple copper salts [12,13]. In this paper, we extend the scope of the previously reported **I**-catalyzed alkyne homocoupling (Fig. 1) and discuss the reaction mechanism in more detail on the basis of the catalyst effects, spectroscopic analyses, kinetics, and DFT calculations. In addition, the applicability of **I** to the 1,3-dipolar cycloaddition reactions is also mentioned.

2. Experimental

2.1. General

Copper salts and complexes were obtained from Wako, Kanto, or Alfa Aesar (reagent grade) and used as received. Sol-

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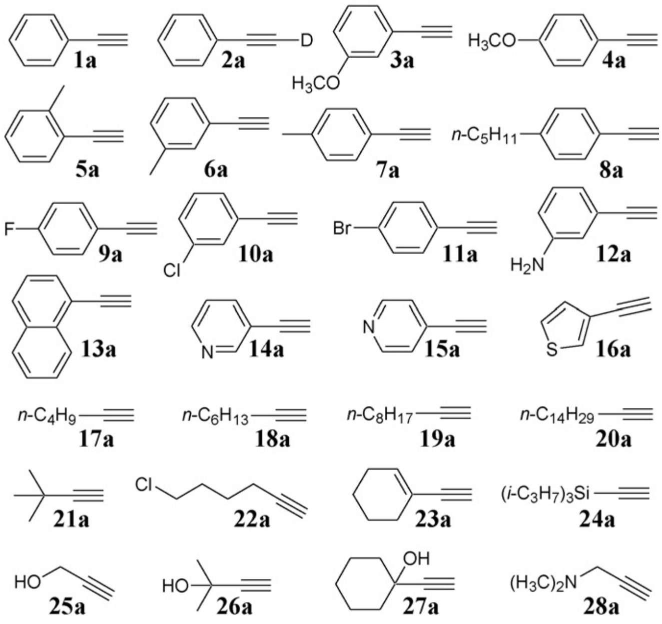

Fig. 1. Various kinds of alkynes used.

vents and alkynes were obtained from Tokyo Kasei or Aldrich (reagent grade) and purified prior to the use [14]. The di-copper-substituted silicotungstate **I**, mono-copper-substituted silicotungstate $TBA_4[\alpha\text{-}H_2SiW_{11}CuO_{39}]$ (**II**), and lacunary silicotungstate $TBA_4[\gamma\text{-}SiW_{10}O_{34}(H_2O)_2]$ (**III**) were synthesized according to the previously reported procedures [12,13,15].

2.2. Procedures for the catalytic reactions

The alkyne homocoupling was carried out as follows. Into a glass tube reactor were successively placed **I** (2.2 mol%), alkyne (1 mmol), and benzonitrile (1 mL). The reaction mixture was stirred at 100 °C under O_2 atmosphere. After the reaction was completed, diethyl ether (20 mL) was added to the solution. The precipitated catalyst was recovered by filtration (ca. 95% recovery), washed with diethyl ether (ca. 50 mL), and dried in vacuo prior to the recycling experiments. The isolation of diyne products were carried out by column chromatography on silica gel using *n*-hexane as an eluent. The 1,3-dipolar cycloaddition reactions were carried out according to the similar procedures to those under Ar atmosphere.

2.3. Density functional theory (DFT) calculations

The DFT calculations were carried out at the B3LYP level theory [16] with 6-31G* basis sets for H, C, N, O, and Si atoms, and the double-ξ quality basis sets with effective core potentials proposed by Hay and Wadt [17] for Cu and W atoms. The entire structure of the **I** anion was used as a model for the calculations. Methylacetylene was used as a model alkyne substrate for the calculation. In order to minimize the differences in the solvent effect among the intermediates and transition states, protons were added to the polyanion framework and the total charge of the system was kept −4 throughout the calculations. Transition state structures were searched by numerically estimating the matrix of second-order energy derivatives at every optimization step and by requiring exactly one eigenvalue of this matrix to be negative. For the transition states, the frequency analysis was conducted at the same level at the final geometry. The zero-point vibrational energies were not included. All calculations were performed with the Gaussian03 program package [18].

3. Results and discussion

3.1. Effects of solvents, additives, and catalysts on the alkyne homocoupling

The effects of solvents on the **I**-catalyzed oxidative homocoupling of phenylacetylene (**1a**) to 1,4-diphenyl-1,3-butadiyne (**1b**) were investigated (Table 1). Among the solvents examined without any additives, benzonitrile gave the highest yield of **1b** (entry 1). Non-polar and protic polar solvents such as 1,2-dichloroethane, toluene, 2-propanol, and acetic acid gave low yields of **1b** (entries 10–14). The present homocoupling was strongly inhibited by the presence of water (entry 5 vs. entry 2). In the case of benzonitrile, equimolar amounts of benzamide (formed through the hydration of benzonitrile) with respect to the corresponding diyne **1b** (water produced) were formed as a co-product. When the homocoupling of **1a** in DMF was carried out in the presence of benzonitrile, 88% yield of **1b** was obtained (entry 4). In contrast, 63% yield of **1b** was obtained without benzonitrile (entry 3). These results suggest that benzonitrile can act as a water scavenger in the present **I**-catalyzed homocoupling. Furthermore, the homocoupling in DMF and DMSO with Molecular Sieve 4A (MS 4A) pretreated at 150 °C gave **1b** in high yields (entries 6 and 8). Therefore, benzonitrile is not a special solvent and various solvents can be used for the **I**-catalyzed homocoupling reaction with appropriate water scavengers.

Next, the homocoupling of **1a** in benzonitrile was carried out with various catalysts (Table 1). In the absence of catalysts, or the presence of copper salts and complexes, the reaction hardly proceeded (entries 18–23). The mono-copper-substituted silicotungstate **II** (entry 15), the non-copper-substituted lacunary silicotungstate **III** (entry 16), and a mixture of catalyst precursors **III** and $CuCl_2$ (entry 17) were almost inactive, suggesting that the di-copper(II) core $\{Cu_2(\mu\text{-}1,1\text{-}N_3)_2\}$ in **I** plays an important role in the present alkyne homocoupling (see Section 3.3).

3.2. Scope and limitation of the *I*-catalyzed reactions

The scope of the present **I**-catalyzed oxidative homocoupling was examined (Table 2). The homocoupling reactions of aromatic alkynes with electron-donating as well as -withdrawing substituents on phenyl rings efficiently proceeded to afford the corresponding diphenylbutadiyne derivatives (entries 1–13). The position of substituents on phenyl rings did not affect the reaction; the reaction rates of 2-, 3-, and 4-methylphenylacetylenes were almost the same (entries 5–7), for example. The reaction of the nitrogen- and sulfur-containing heteroaromatic alkynes also smoothly proceeded to give the corresponding diynes (entries 14–16). Notably, less reactive aliphatic C6–C16 alkynes were effectively converted into the corresponding aliphatic diynes (entries 17–21). The reaction of the double bond-containing alkyne also smoothly proceeded to give the corresponding enyne product (entry 23). The present system could be applied to the homocoupling of the silylacetylene derivative, giving the corresponding silyl diyne (entry 24). Interestingly, propargylic alcohols and amine also gave the corresponding hydroxy and amino group-containing diynes, respectively (entries 25–28). Although the homocoupling of terminal alkynes efficiently proceeded, no reactions of internal alkynes such as 2-octyne and diphenylacetylene proceeded in the presence of **I**. This suggests that the copper species in **I** is terminally bound to an alkyne (see Section 3.3).

After the reaction was completed, the catalyst could easily be recovered by addition of an excess of diethyl ether (ca. 95% recov-

Table 1
Effects of solvents, additives, and catalysts on the oxidative homocoupling of **1a**[a].

Entry	Catalyst	Solvent	Additive	Time (h)	Yield (%)[b]
1	**I**	Benzonitrile	–	3	91
2	**I**	DMF	–	3	39
3	**I**	DMF	–	24	63
4	**I**	DMF	Benzonitrile (0.5 mmol)	24	88
5	**I**	DMF	Water (1 mmol)	3	9
6	**I**	DMF	MS 4A (200 mg)	3	90
7	**I**	DMSO	–	3	39
8	**I**	DMSO	MS 4A (200 mg)	3	86
9	**I**	Acetonitrile	–	3	15
10	**I**	1,2-Dichloroethane	–	3	4
11	**I**	Nitrobenzene	–	3	3
12	**I**	Toluene	–	3	2
13	**I**	2-Propanol	–	3	2
14	**I**	Acetic acid	–	3	2
15	**II**	Benzonitrile	–	3	2
16[c]	**III**	Benzonitrile	–	3	<1
17[d]	**III** + $CuCl_2$	Benzonitrile	–	3	5
18	$Cu(OAc)_2$	Benzonitrile	–	3	10
19	$CuCl_2$	Benzonitrile	–	3	4
20	CuCl	Benzonitrile	–	3	7
21	CuI	Benzonitrile	–	3	2
22	$[Cu(CH_3CN)_4]PF_6$	Benzonitrile	–	3	<1
23	$[Cu(I)(C{\equiv}CPh)]_n$	Benzonitrile	–	3	<1
24	None	Benzonitrile	–	3	<1

[a] *Reaction conditions*: Catalyst (Cu: 4.4 mol% with respect to **1a**), **1a** (1 mmol), solvent (1 mL), 100 °C, O_2 (1 atm).
[b] Yields were determined by GC using naphthalene as an internal standard.
[c] 2.2 mol%.
[d] A mixture of **III** (2.2 mol%) and $CuCl_2$ (4.4 mol%) was used as a catalyst.

ery, precipitation method, see Section 2.2). The recovered catalyst could be recycled at least five times without significant loss of the catalytic activity; 94, 82, 88, 80, and 78% yields of **1b** for the first, second, third, forth, and fifth recycling experiments, respectively. In a larger-scale reaction of **1a** (reaction conditions: **I** (0.2 mol%), **1a** (20 mmol), benzonitrile (20 mL), O_2 (1 atm), 100 °C, 18 h), the turnover number (TON = amounts of **1a** consumed/amounts of **I**) reached up to 468. This value was about one order of magnitude higher than those reported for the copper-based oxidative alkyne homocoupling reactions (TON: 1–50) [2–10].

As above-mentioned, an alkyne was converted into the corresponding diyne in the presence of **I**. In other words, an alkyne itself can act as a reducing agent to produce copper(I) species (see Section 3.3). Therefore, it is expected that the cycloadditions of 1,3-dipolar compounds with alkynes, in which copper(I) species is reported to be active [19,20], can be promoted with **I** in the absence of O_2 (anaerobic conditions). Indeed, the 1,3-dipolar cycloadditions of an organic azide (**1c**) to an alkyne (**1a**) (Fig. 2(a)) [21] and an azomethine imine (**1e**) to an alkyne (**29a**) (Fig. 2(b)) efficiently proceeded to afford the corresponding 1,2,3-triazole (**1d**) and five-membered heterocyclic compound (**1f**), respectively.

3.3. *Mechanistic studies*

The reaction profiles for the **I**-catalyzed homocoupling of **1a** showed an induction period (approximately 5 min under the conditions described in Table 2). The length of the induction period depended on the concentrations of **I** and **1a** and the decrease of the concentrations of **I** and **1a** resulted in a prolongation of the induction period. The induction period disappeared upon pretreatment of **I** with **1a** under Ar atmosphere at 100 °C. These results suggest that the induction period is caused by the reaction of **I** with an alkyne to form the catalytically active species.

Compound **1a** (50 equivalents with respect to **I**) was added to the benzonitrile solution of **I** (4 mM, 1 mL) and the resulting solution was heated to 100 °C under Ar atmosphere. Then, the UV–vis spectra of the solution and the production of **1b** were monitored. An approximately 50 min-induction period was observed for the

Table 2
Scope of the **I**-catalyzed oxidative homocoupling[a].

Entry	Alkyne	Time (h)	Yield (%)[b]	Entry	Alkyne	Time (h)	Yield (%)[b]
1	**1a**	3	91(88)	15	**15a**	2	83
2	**2a**	3	87	16	**16a**	4	92
3	**3a**	3	91(90)	17	**17a**	5	91(80)
4	**4a**	3	97(82)	18	**18a**	5	91(86)
5	**5a**	3	95	19	**19a**	7	92(89)
6	**6a**	3	97(93)	20	**20a**	8	76
7	**7a**	3	95(97)	21	**21a**	5	90
8	**8a**	3	96(64)	22	**22a**	7	76
9	**9a**	3	96(89)	23	**23a**	6	94
10	**10a**	3.5	90(93)	24	**24a**	4	84
11	**11a**	4.5	94(90)	25	**25a**	18	85
12	**12a**	5	90	26	**26a**	2	>99(99)
13	**13a**	4	93	27	**27a**	4	90(82)
14	**14a**	2	95(82)	28	**28a**	4	91

[a] *Reaction conditions*: **I** (2.2 mol% with respect to an alkyne), alkyne (1 mmol), benzonitrile (1 mL), 100 °C, O_2 (1 atm).
[b] Yields were determined by GC using naphthalene as an internal standard. The values in the parentheses were the isolated yields.

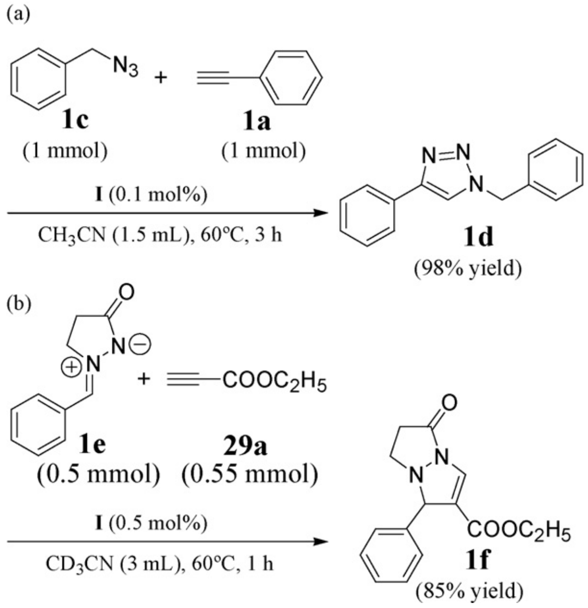

Fig. 2. The **I**-catalyzed 1,3-dipolar cycloaddition reactions.

formation of **1b** (Fig. 3(a)). During the induction period, the intensity of the absorption band at around 360 nm assignable to the $N_3^- \rightarrow Cu(II)$ ligand to metal charge transfer (LMCT) [22,23] of **I** was gradually decreased and the LMCT band almost disappeared after approximately 50 min (Fig. 2(b)). As mentioned in Section 3.1, the dicopper core in **I** plays an important role in the present alkyne homocoupling. Thus, it is likely that the present homocoupling proceeds through the formation of the di-copper(II)-alkynyl species [1,11] formed by the ligand exchange between the N_3^- ligands in **I** and alkynyl groups and that the induction period corresponds to the formation of the catalytically active di-copper(II)-alkynyl species (step 1 in Fig. 4).[1] The formation of the di-copper species during the catalysis is supported by the fact that the reaction is first-order dependent on the concentration of **I**.

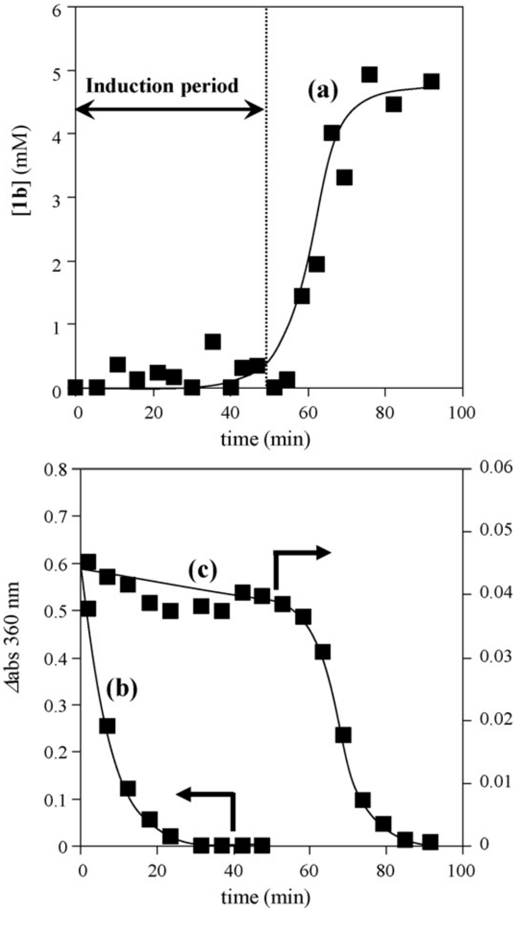

Fig. 3. Reaction profiles for the formation of **1b** under Ar atmosphere (a), and the profiles of the absorbance at 360 nm (b) and 700 nm (c). *Reaction conditions*: **I** (4 mM), **1a** (200 mM), benzonitrile (1 mL), 100 °C, Ar (1 atm).

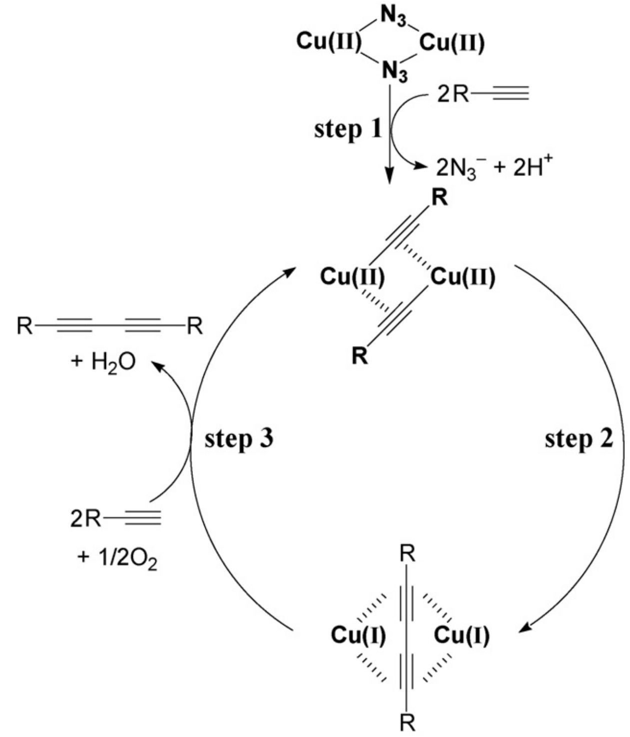

Fig. 4. A possible reaction mechanism for the present **I**-catalyzed alkyne homocoupling. Polyoxotungstate frameworks of $[\gamma\text{-}H_2SiW_{10}O_{36}]^{6-}$ are omitted for clarity.

After the induction period, almost equimolar amounts of **1a** (8.8 ± 1.0 mM) with respect to the copper(II) species in **I** (8.0 mM) was converted into the corresponding diyne **1b** with a simultaneous decrease in the absorption band at around 700 nm assignable to the d–d transition of the copper(II) species in **I** (Fig. 3(c)) [24]. These results suggest that the copper(II) species in **I** is reduced to copper(I) species (step 2 in Fig. 4). The d–d transition band of the copper(II) species again appeared by the introduction of O_2 (1 atm) to the solution, indicating that the reduced copper(I) species in **I** can be re-oxidized to copper(II) species by O_2 (step 3 in Fig. 4).

On the basis of the above-mentioned experimental results, we here proposed the possible reaction mechanism for the present **I**-catalyzed alkyne homocoupling, as shown in Fig. 4. The step 1 corresponds to the induction period for the present homocoupling. Monitoring the formation of water (in this case the formation of benzamide, see Section 3.1) for the **I**-catalyzed homocoupling of **1a** revealed that the amount of water produced was the same as that of **1b**. The measurement of O_2 uptake during the homocoupling of **1a** was also carried out and the amount of O_2 consumed was half that of **1b** produced. These respective 1:1 (water formed:diyne formed)

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[1] While it has been reported that the absorption bands of copper alkynyl species are observed around 370 nm, the absorption band could not be detected because of the overlap with the very intense absorption bands of **I**, solvent, and products.

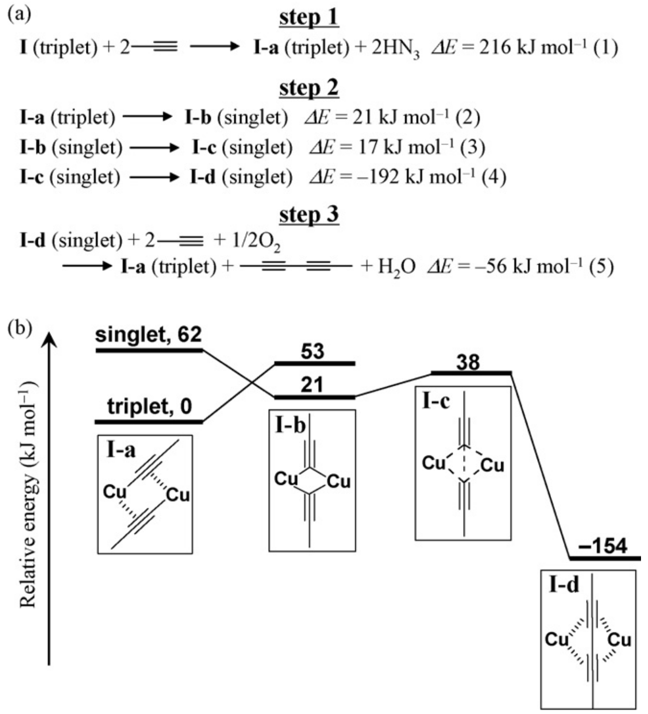

Fig. 5. (a) The calculated energy changes for each step and (b) detailed energy diagram in the step 2 (Eqs. (2)–(5)) for the oxidative homocoupling of **30a** in the gas phase. Polyoxotungstate frameworks of $[\gamma\text{-}H_2SiW_{10}O_{36}]^{6-}$ are omitted for clarity.

and 1:2 (O_2 consumed:diyne formed) stoichiometries support the overall catalytic cycle in Fig. 4.

The reaction rate for the homocoupling of **1a** showed the first-order dependence on the concentration of **I** and was almost independent of both the concentration of **1a** and the partial pressure of O_2. The kinetic isotope effect was not observed for the oxidative homocoupling of **1a** and **2a** ($k_H/k_D = 1.0$). All these results show that the formation of a diyne from the alkynyl species (electron transfer from the alkynyl species to copper species, step 2 in Fig. 4) is the rate-determining step in the catalytic cycle.

The DFT calculations were carried out to confirm the possible cooperative involvement of two copper centers in catalyzing the present alkyne homocoupling. Methylacetylene (**30a**) was used as a model substrate for the DFT calculations. The energies of the reaction steps were calculated according to the proposed reaction mechanism (Fig. 4) and the results are summarized in Fig. 5. First, the di-copper(II) intermediate with two σ,π-bridging acetylide units (**I-a**) was formed by the reaction of **I** with **30a** (step 1, Eq. (1) in Fig. 5). This step corresponds to the induction period for the present homocoupling. The triplet state of **I-a** was calculated to be more stable by 62 kJ mol^{-1} than the singlet state. Next, the di-copper(II) intermediate with two σ-bridging acetylide units (**I-b**) was formed and the energies of **I-b** in the triplet and singlet states referenced to the triplet state of **I-a** were calculated to be 53 and 21 kJ mol^{-1}, respectively. Thus, the spin interconversion between the triplet and singlet potential energy surfaces would proceed during the transformation from **I-a** to **I-b**. The activation energy from di-copper(II) intermediate **I-a** to di-copper(I) species (**I-d**) via the transition state **I-c** was calculated to be 38 kJ mol^{-1}. The re-oxidation of **I-d** with O_2 (step 3, Eq. (5) in Fig. 5) was a downhill reaction and calculated to be exothermic by 56 kJ mol^{-1}. These results are consistent with the experimental ones that the formation of a diyne from the di-copper(II)-alkynyl species is the rate-determining step.

4. Conclusions

The di-copper(II)-substituted silicotungstate **I** exhibited high catalytic activity for the aerobic oxidative homocoupling. In addition, the 1,3-dipolar cycloaddition reactions efficiently proceeded with **I**. The catalyst effect, spectroscopic analyses, kinetics, and DFT calculations show that the di-copper(II) core on **I** is the active site for the present oxidative homocoupling.

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