Mechanistic studies on fluorocyclohexene conversion to fluorobenzene under Pd-catalyzed dehydrogenation

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ABSTRACT

The chemical reactivity and reaction mechanism of fluorobenzene formation by dehydrogenation of fluorocyclohexenes was investigated. 1-Fluorocyclohexene reacted with oxidants such as nitrobenzene and oxygen to give fluorobenzene in good yields under moderate conditions in the presence of a Pd catalyst. A detailed comparison of oxidative dehydrogenation with non-oxidative dehydrogenation proved that the oxidants effectively suppressed isomerization and disproportionation, and offered a selective synthesis of fluorobenzene.

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1. Introduction

Fluoroaromatics are widely used in the synthesis of pharmaceuticals [1], agrochemicals [2], functional organic materials [3], and high-performance polymers [4]. In particular, fluorobenzene is the most widely used fluoroaromatic as a starting material for commercial scale manufacturing processes. Among the reported synthetic methods [5], the most general method is the Schiemann reaction [6], which involves unstable diazonium salts. Nucleophilic displacement of aryl chloride by fluoride is known to generate chloride as waste, and requires a high temperature (450 °C) for unsubstituted benzene [7]. Direct fluorination of benzene using F_2 and some metal fluorides are limited in use because of their poor selectivity [7]. 1-Alkyl-4-fluoro-1,4-diazoniabicyclo [2.2.2]octane salts (Selectfluor[TM]) are more selective electrophilic fluorinating reagents, but only fluorinate activated aromatics [7,8]. Copper(II) fluoride also reacts directly with benzene and is regenerated after treating the copper metal with HF under molecular oxygen [9]. However, high reaction temperatures are necessary (fluorination: 450–550 °C; regeneration: 400 °C) and conversion is less than 30%.

Fluorocyclohexenes are alternative precursors in the synthesis of fluorobenzene and can be converted to fluorobenzenes by catalytic non-oxidative and oxidative dehydrogenation [10,11]. The fluorocyclohexenes are easily synthesized from gem-difluorocyclohexane [12], which can be obtained from cyclohexanone by various methods [13,14]. Although unsubstituted cyclohexene was reported to be catalytically disproportionated into benzene and cyclohexane or oxidatively dehydrogenated to benzene [15], fluorinated cyclohexenes were not discussed in detail. Herein, we report the chemical reactivity and reaction mechanism of the dehydrogenation of fluorocyclohexenes in the presence of catalyst at moderate temperature (ca. 100–200 °C). 1-Fluorocyclohexene yielded mainly benzene and cyclohexane via non-oxidative dehydrogenation, but gave fluorobenzene in good yields with oxidants, e.g., nitrobenzene and oxygen.
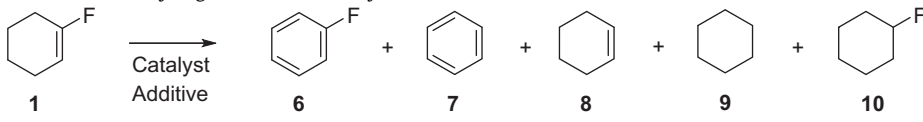
2. Experimental

2.1. General remarks

Unless otherwise noted, chemical reagents were commercial samples and used without further treatment. Catalysts were purchased from N.E. Chemcat Corporation. Quantitative analysis was carried on a gas chromatograph with a FID detector. The chemical structure of the product was identified by instrumental analysis. The metal analysis of the reaction mixtures was conducted using ICP-AES.

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Table 1
Non-oxidative dehydrogenation of 1-fluorocyclohexene **1**.[a]

Entry	Catalyst	Additive[b]	Temperature (°C)	Time (h)	Conversion[c] (%)	Selectivity[d] (%)					Catalyst activity[e] (mmol/m² h)
						6	7	8	9	10	
1	Pt-C	None	90	1	38	3	63	2	32	0	0.010
2	Ru-C	None	90	1	27	7	70	2	21	0	0.020
3	Pd-C	None	90	1	35	3	69	3	25	0	0.009
4	Pt-black	None	90	1	31	6	61	0	33	0	0.19
5	Ru-black	None	90	1	0	0	0	0	0	0	0.0
6	Pd-black	None	90	1	44	11	59	0	30	0	0.58
7	Pd-black	None	90	0.25	23	22	52	0	26	0	2.4
8	Pd-black	None	120	0.25	44	10	64	0	25	0	2.1
9	Pd-black	None	150	0.25	86	6	73	0	21	0	2.5
10	Pd-black	KF	150	0.25	77	12	76	0	9	2	4.4
11	Pd-black	PhNH₂	150	0.25	49	23	69	0	7	3	5.4
12	Pd-black	*tert*-BuOK	150	0.25	0	0	0	0	0	0	0.0

[a] Reaction was carried out with 30 mmol of **1** and 0.10 g of catalyst in a stainless steel closed reactor (volume: 10 mL) under N_2.
[b] 30 mmol was used.
[c] Determined by gas–liquid chromatography.
[d] Based on converted **1**.
[e] **6** yield per unit metal surface[f] area per hour.
[f] Pt-black 30 m²/g; Ru-black 90 m²/g; Pd-black 25 m²/g; Pt-C 30 m²/g; Ru-C 290 m²/g; Pd-C 350 m²/g.

2.2. Synthetic procedure

2.2.1. 1-Fluorocyclohexene **1** by dehydrofluorination of 1,1-difluorocyclohexane **2**

2 was synthesized from cyclohexanone via bis (trifluoroacetoxy)cyclohexane **3** according to literature procedures [14 g]: colorless liquid, bp 99–101 °C/760 mmHg (lit. [12a] 99–100 °C/760 mmHg). ^{1}H NMR (CDCl₃): δ 1.9–2.3 (m, 10H). MS (EI): m/z 120 (M⁺, 9%), 100 (63), 80 (12), 57 (98), 41 (100). Aluminium fluoride (2.5 g) was packed in a fixed bed flow reactor. To the reactor, N₂ gas was fed (200 mL/h). After the reactor was heated to 400–410 °C, gaseous **2** was fed to the reactor (7.5 g/h) for 10 h. All the reaction mixture was cooled and collected into a mixture of ice and saturated aq. NaHCO₃. The resulting mixture was extracted with diethyl ether. The combined extracts were washed with water, dried over MgSO₄, and the solvent was evaporated. The crude product was distilled under atmospheric pressure to give **1** [16b,17,18]: yield 60.1 g (96%). Colorless liquid, bp 95–96 °C/760 mmHg (lit. [17] 95–96 °C/760 mmHg). MS (EI): m/z 100 (M⁺, 47%). ^{1}H NMR (CCl₄): δ 1.7–2.0 (m, 4H), 2.1–2.4 (m, 4H), 5.1 (d, 1 H).

2.2.2. 3-Fluorocyclohexene **4** [19]

To diethylaminosulfur trifluoride (DAST, 0.05 mol) in a 50-mL polyethylene bottle cooled at −50 °C, 2-cyclohexen-1-ol (0.05 mol) was added slowly at −50 °C with stirring under nitrogen atmosphere, and the mixture was further stirred for 3 h while warming to room temperature. The reaction mixture was poured into a mixture of ice and saturated aq. NaHCO₃. The upper layer was separated, washed with ice water, and dried over MgSO₄ in a refrigerator to give crude **4**: 63% yield. ^{1}H NMR (CCl₄): δ 1.5–2.2 (m, 2 H), 4.9 (m, 1 H), 5.8 (m, 1 H), 6.0 (m, 1 H). The obtained product decomposed slowly at room temperature [19] to give HF[1] and 1,3-cyclohexadiene **5**, which was identified spectroscopically.
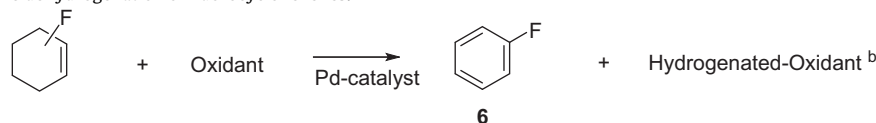
2.3. Catalytic reaction

2.3.1. Conversion of **1** to fluorobenzene **6** by non-oxidative dehydrogenation (Table 1)

In a closed stainless steel reactor (volume: 10 mL) equipped with pressure relief valve were placed **1** (30 mmol), catalyst (0.10 g), and additive (30 mmol) under nitrogen atmosphere. The reactor was shaken at 90–150 °C for 0.25–1 h. All the reaction mixtures were analyzed with toluene as an internal standard using gas–liquid chromatography. The yields of **6–10** were based on converted **1**. Products **6**, **7** and **9** were separated by preparative gas–liquid chromatography. All products **6–10** were characterized spectroscopically and showed identical MS and ^{1}H NMR spectra to the commercial reagents. The gas phase of the reaction mixture was analyzed using gas–liquid chromatography. Molecular hydrogen was detected in the gas phase of the reaction mixture (Entries 1–11). The Pd was not detected in reaction mixtures (Entries 1–11) by ICP-AES method (<0.1 ppm).

2.3.2. Conversion of **1** to fluorobenzene **6** by oxidative dehydrogenation (Table 2)

2.3.2.1. *Liquid phase reaction (Entries 1–6).* In a closed stainless steel reactor (volume: 10 mL) equipped with pressure relief valve were placed **1** (30 mmol), Pd-Black (0.10 g), and nitrobenzene (24 mmol) under nitrogen atmosphere. The reactor was shaken at 90–150 °C for 0.25–8 h. All the reaction mixtures were analyzed in the same manner as described above. The Pd was not detected in reaction mixtures (Entries 1–6) by ICP-AES method (<0.1 ppm). It was confirmed that aniline and H₂O were formed via reduction of nitrobenzene. A large-scale repetition of Entry 5 was carried out, increasing the quantity by 10. The reaction mixture was washed with saturated aq. NaHCO₃. The upper layer was separated, washed with water, and dried over MgSO₄ to give crude **4**, which was fractionated through a 60-cm spinning band column under atmospheric pressure to give fluorobenzene **6**: yield 26.2 g (91%). Purity 99.6%. Colorless liquid, bp 84–85 °C/760 mmHg. MS (EI): m/z 96 (M⁺, 100%), 70 (18), 50 (8). ^{1}H NMR (CDCl₃): δ 6.9–7.5 (m, 5H).

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[1] Caution: Since HF is corrosive, the reaction mixture containing HF should be handled in a well ventilated hood with protection.

Table 2
Oxidative dehydrogenation of fluorocyclohexenes.[a]

1-Fluorocyclohexene **1**
3-Fluorocyclohexene **4**

Entry	Substrate	Oxidant (equiv.)	Phase of reaction	Catalyst (weight ratio[c])	Temperature (°C)	Time[d] (h)	Conversion[e] (%)	Selectivity[f] (%)					Catalyst activity[g] (mmol/m² h)
								6	**7**	**8**	**9**	**10**	
1	**1**	PhNO₂ (1.2)	Liquid	Pd-Black (0.01)	90	0.25	6	98	0	0	0	0	9.4
2	**1**	PhNO₂ (1.2)	Liquid	Pd-Black (0.01)	120	0.25	10	99	0	0	0	0	15.8
3	**1**	PhNO₂ (1.2)	Liquid	Pd-Black (0.01)	150	0.25	32	99	0	0	0	0	50.7
4	**1**	PhNO₂ (1.2)	Liquid	Pd-Black (0.01)	150	2	76	99	0	0	0	0	15.0
5	**1**	PhNO₂ (1.5)	Liquid	Pd-Black (0.02)	150	8	97	99	0	0	0	0	4.8
6	**4**	PhNO₂ (1.2)	Liquid	Pd-Black (0.01)	150	0.25	100	0.6	99	0	0	0	1.0
7	**1**	O₂ (1.2)[i]	Gas	Pd–SiO₂ (0.05)	150	0.25	95	93	6	0.2	0.2	0	1.6
8	**1**	O₂ (1.2)[i]	Gas	Pd–SiO₂ (0.05)	150	0.5	97	88	11	0.3	0.4	0	0.40
9	**1**	O₂ (2.4)[i]	Gas	Pd–SiO₂ (0.05)	200	0.5	100	82	17	0.6	0.6	0	0.40

[a] Reaction was carried out with 30 mmol of **1** or **4** and catalyst in a 10-mL closed stainless steel reactor under N₂ (Entries 1–6); gaseous **1** was fed to a fixed bed flow reactor packed with catalyst (Entries 7–9).
[b] Aniline and H₂O were formed when PhNO₂ was used as oxidant; H₂O was formed when O₂ was used as oxidant.
[c] Catalyst to substrate weight ratio (Entries 1–6) or supported metal to carrier weight ratio (Entries 7–9).
[d] Reaction time (Entries 1–6) or residence time (Entries 7–10) calculated from a reciprocal of LHSV (Liquid Hourly Space Velocity).
[e] Determined by gas–liquid chromatography.
[f] Based on converted **1**.
[g] **6** yield per unit metal surface[h] area per hour.
[h] Pd-black 25 m²/g; Pd-SiO₂ 100 m²/g.
[i] Mixed gas [O₂/N₂ mol ratio: 10/90 (Entries 7 and 8) or 20/80 (Entry 9)] was used.

2.3.2.2. Gas phase reaction (Entries 7–9). The catalyst was packed in a fixed bed flow reactor. The weight ratio of supported metal to carrier was 0.01. To the reactor, mixed gas [O₂/N₂ mol ratio: 10/90 (Entries 7 and 8) or 20/80 (Entry 9)], which was used as carrier gas having oxidant, was fed. After the reactor was heated to 150–200 °C, gaseous **1** was fed to the reactor. Residence time calculated from a reciprocal of LHSV (Liquid Hourly Space Velocity) was 0.25–0.5 h. All the reaction mixtures were analyzed in the same manner as described above. Although H₂O₂ was not detected, H₂O was found in the oxidative dehydrogenation.

3. Results and discussion

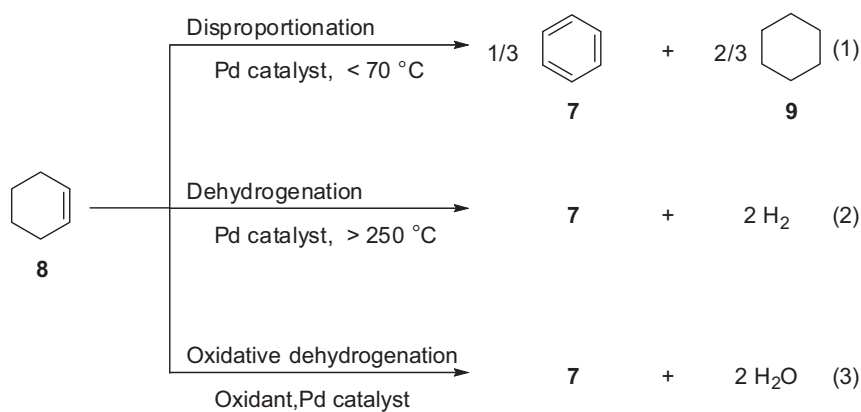### 3.1. Non-oxidative dehydrogenation of fluorocyclohexenes

We first characterized the catalytic non-oxidative dehydrogenation (disproportionation or simple dehydrogenation) of fluorocyclohexenes. 1-Fluorocyclohexene **1** was treated with heterogeneous Pd, Pt, and Ru catalysts, which were chosen from the viewpoint of easy separation and recovery. Reaction conditions and selected results are summarized in Table 1.

Comparing catalyst activities (yield of **6** per unit metal surface per hour), the Pd-black was the most active catalyst (0.58 mmol/m² h) among those studied in generating fluorobenzene **6** (Entries 1–6), but the major product was benzene **7**, followed by cyclohexane **9** (all entries). Examination of temperature dependency (Entries 7–9) showed that a relatively higher selectivity of **6** (22%) was observed at lower temperature, e.g., 90 °C (Entry 7). This differs from the results of unsubstituted cyclohexene **8** [15b]. As shown in Scheme 1, **8** was reported to be disproportionated into one-third equivalents of **7** and two-third equivalents of **9** at a temperature less than 70 °C (Eq. (1) in Scheme 1), and dehydrogenated with the evolution of hydrogen at a temperature greater than 250 °C (Eq. (2) of Scheme 1). The reported data (Fig. 7 in Ref. [14b]) indicated that disproportionation and dehydrogenation concurrently occurred at intermediate temperatures [15b], i.e., the

ratios of cyclohexane to benzene for Pd catalyst were estimated to be 2 at below 70 °C and 0 at over 250 °C. **8** was also oxidatively dehydrogenated to benzene **7** in the presence of oxidant (Eq. (3) in Scheme 1) [15a].

If the reaction of **1** to **6** similarly occurred in the absence of oxidant, the selectivity of **6** might range between 33% (via disproportionation: Eq. (1) in Scheme 1) and 100% (via dehydrogenation: Eq. (2) in Scheme 1). Since the yield obtained here was never more than 22% (Entry 7), dehydrofluorination and other side reactions must also occur.

Scheme 2 shows a possible reaction sequence including several dehydrogenation paths. The oxidative dehydrogenation path will be discussed later. When oxidant was not employed, molecular hydrogen was detected in the gas phase of the reaction mixture. This means that simple dehydrogenation (Eq. (2) in Scheme 1) actually proceeded, but the amount of the generated hydrogen was insufficient to ascribe to formation of **6**. Thus, **6** was formed by both simple dehydrogenation and disproportionation of **1**. Fluorocyclohexane **10** was not detected in Entries 1–9 in Table 1, but the intermediate **8** was formed in addition to **7** and **9** (Entries 1–3), suggesting that **10** was dehydrofluorinated to cyclohexene **8**. When **10** was independently synthesized and heated, it easily released HF in the absence of base and did not eliminate HF in the presence of base. This side reaction explains the higher yields of **7** and **9** but not the low selectivity of **6**. The isomerized 3-fluorocyclohexene **4** [20] was also confirmed to eliminate HF to yield 1,3-cyclohexadiene **5** besides being disproportionated to **6** and **10**. Dehydrofluorinated products **8** and **5** are subject to disproportionation and/or dehydrogenation to yield **7** and **9**. Another possible dehydrofluorinated product, cyclohexyne **11**, was not formed perhaps because **11** is highly strained [21]. Consequently, the selectivity of fluorobenzene **6** from **1** is lower than that of unsubstituted benzene **7** from **8**. Addition of base increased the selectivity of **6** in Entries 10 and 11 in comparison with Entry 9 (no additive), and fluorocyclohexane **10** appeared in the reaction mixture. Since the selectivity of **6** was less than 33%, dehydrofluorination must still occur. The addi-

Scheme 1. Reaction modes of unsubstituted cyclohexene.

tion of a weak base depressed autocatalytic HF elimination but a stronger base such as *tert*-BuOK terminated the reaction entirely (Entry 12). These results support the assumption of the existence of side reactions as described above.

3.2. Oxidative dehydrogenation of fluorocyclohexene

The oxidative dehydrogenation of fluorocyclohexenes was carried out with nitrobenzene **12** or molecular oxygen as an oxidant. Table 2 indicates that fluorobenzene **6** was obtained as the major product in 98–99% selectivity with nitrobenzene **12** (Entries 1–5) and 82–93% with molecular oxygen (Entries 7–9). Examination of temperature dependency (Entries 1–3) showed that selectivity of

6 was not temperature dependent (98–99%) and the activation energy Ea was low, $35 \, kJ \, mol^{-1}$ (calculated from catalyst activity of **6** formation). With longer reaction time, **6** was obtained almost quantitatively (Entry 5). In addition to the main product **6**, small amounts of **7** (6–17%), **8** (less than 1%), and **9** (less than 1%) were formed as by-products when molecular oxygen was used (Entries 7–9), but they were not detected at all in the presence of **12** (Entries 1–5). Catalyst activity of gas-phase reaction ($0.4 \, mmol \, m^{-2} \, h^{-1}$ in Entry 8) is lower than that of liquid-phase reaction ($4.8 \, mmol \, m^{-2} \, h^{-1}$ in Entry 5) even at same temperature. Both lower substrate concentration at gas-phase reaction and weaker oxidant than nitrobenzene, oxygen, would be responsible for this.
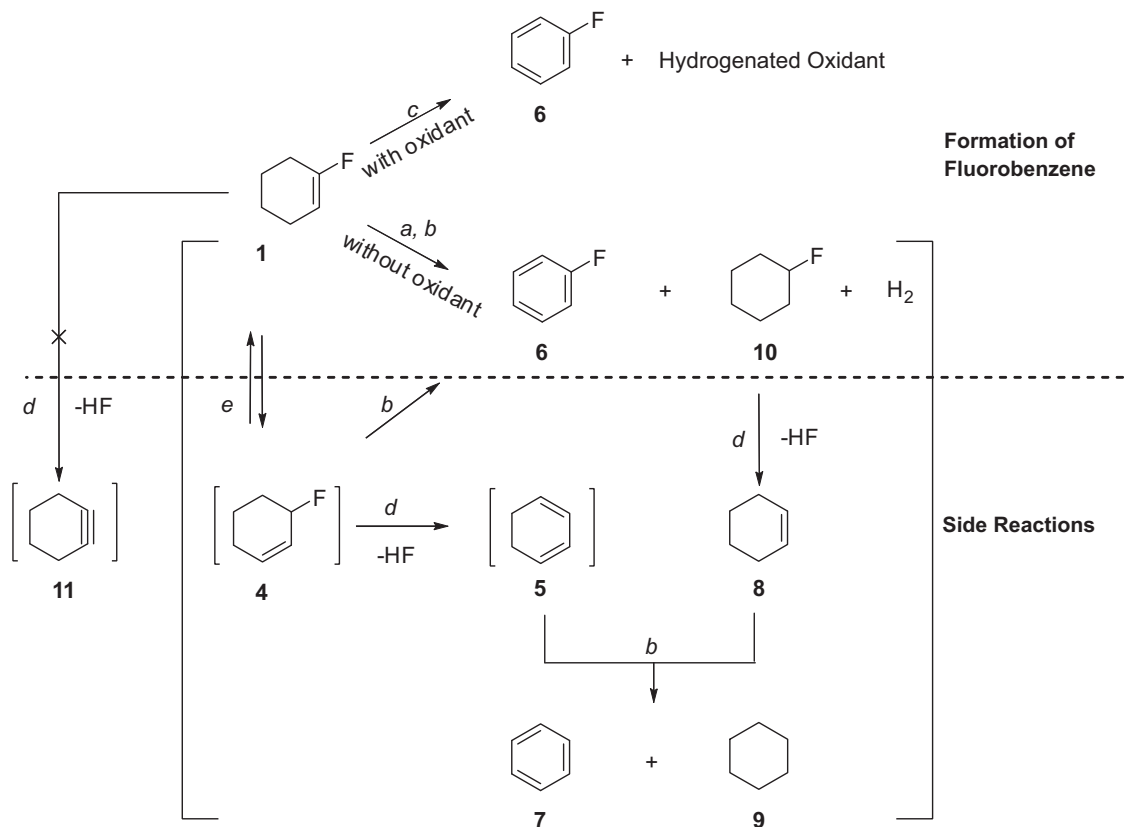
Scheme 2. Possible reaction sequence of fluorobenzene formation by dehydrogenation of **1**. [a] Simple dehydrogenation. [b] Disproportionation. [c] Oxidative dehydrogenation. [d] Dehydrofluorination. [e] Isomerization.
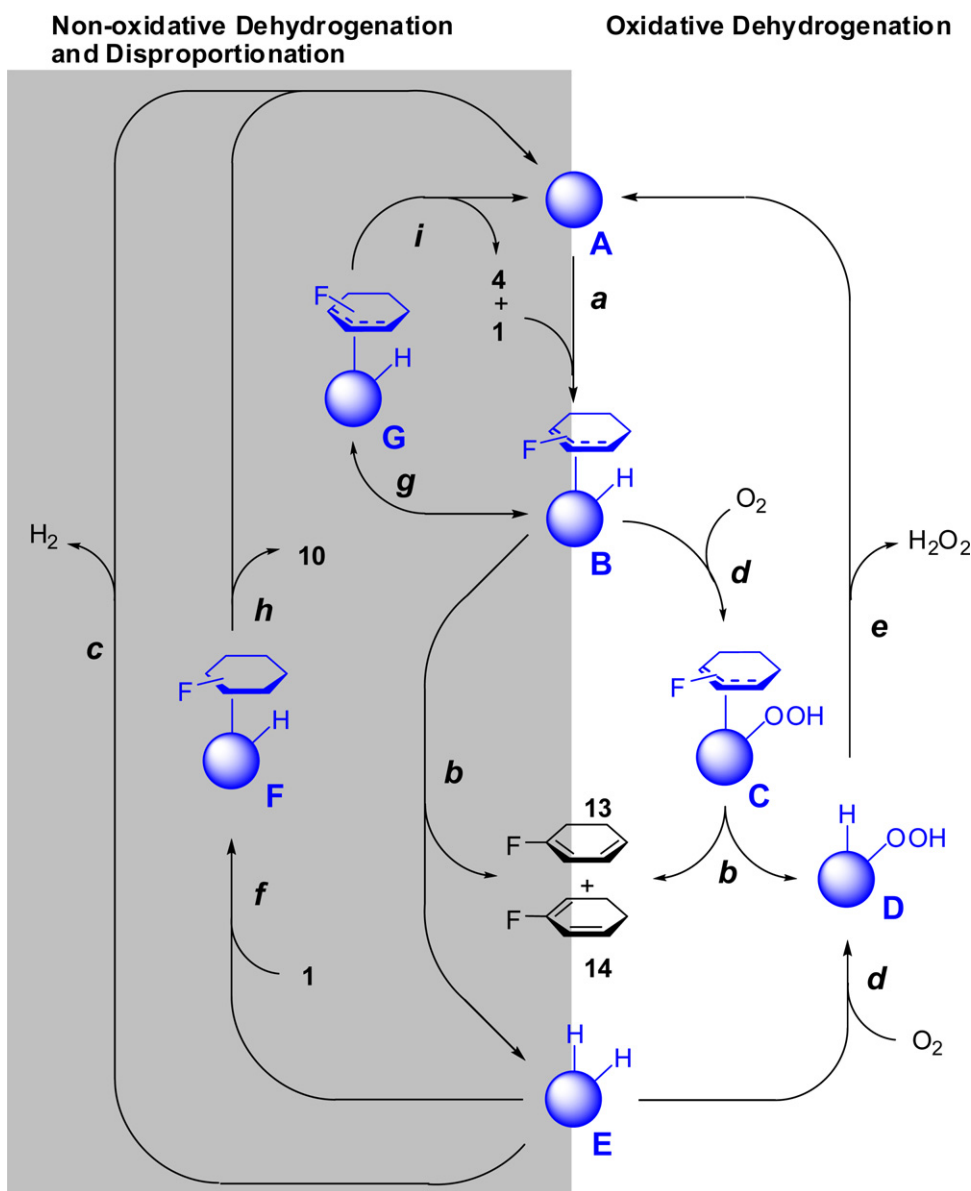
Scheme 3. Possible reaction mechanism of fluorobenzene formation. [a]Insertion of palladium metal (A) into the allylic C–H bond of **1** to form a π-allyl Pd-hydride (B). [b]β-Hydrogen elimination to give fluorocyclohexadienes (**13** and **14**) and Pd hydride species (D, E). [c]Reductive elimination of H_2. [d]Insertion of O_2 into the Pd–H bond producing a peroxy intermediate (C, D). [e]Reductive elimination of H_2O_2. [f]Migratory insertion to form an alkyl Pd-hydride species (F). [g]Isomerization of π-allyl Pd-hydride (B, G). [h]Reductive elimination of **10**. [i]Reductive elimination of **1** and **4**.

When non-oxidative dehydrogenation (Entry 7 in Table 1) and oxidative dehydrogenation (Entry 1 in Table 2) were compared, they showed comparable yields of **6** but marked differences in the selectivity of **6** [5% yield in the former (23% conversion and 22% selectivity) and 6% yield in the latter (6% conversion and 98% selectivity)]. The yields of by-products **7** and **9** of the latter is much less than those of the former, suggesting that the oxidant suppressed the isomerization and non-oxidative dehydrogenation (disproportionation and simple dehydrogenation in Scheme 2). Since molecular hydrogen was not detected in the gas phase of the latter reaction mixture, simple dehydrogenation was depressed. Independently synthesized **4** reacted with nitrobenzene to yield **7** almost quantitatively (Entry 6), showing that the isomerization of **4** was also depressed in the presence of oxidant. Fig. 1 shows time-courses of **6** formation in which nitrobenzene **12** was employed at a less than stoichiometric amount (8% based on **1**). The yields of **7** and **9** increased after **12** was consumed at ca. 0.1 h, confirming that

12 suppressed isomerization and disproportionation completely.

3.3. Mechanism for fluorobenzene formation

A possible reaction mechanism of **6** formation is shown in Scheme 3. The postulated steps for non-oxidative dehydrogenation are: insertion of palladium metal into the allylic C–H bond of **1** to form a π-allyl Pd-hydride (step a); β-hydrogen elimination to give fluorocyclohexadienes (**13** and **14**) and Pd-hydride species (step b); reductive elimination of H_2 (step c); migratory insertion to form an alkyl Pd-hydride species (step f); isomerization of π-allyl Pd-hydride (step g); reductive elimination of **10** (step h); and reductive elimination of **1** and **4** (step i). Formed 1-fluoro-1,3-cyclohexadiene **13** and 2-fluorocyclohexadiene **14** would react to give fluorobenzene **6** in a similar manner.

The postulated steps for oxidative dehydrogenation additionally include: insertion of O_2 into the Pd–H bond, producing a peroxy
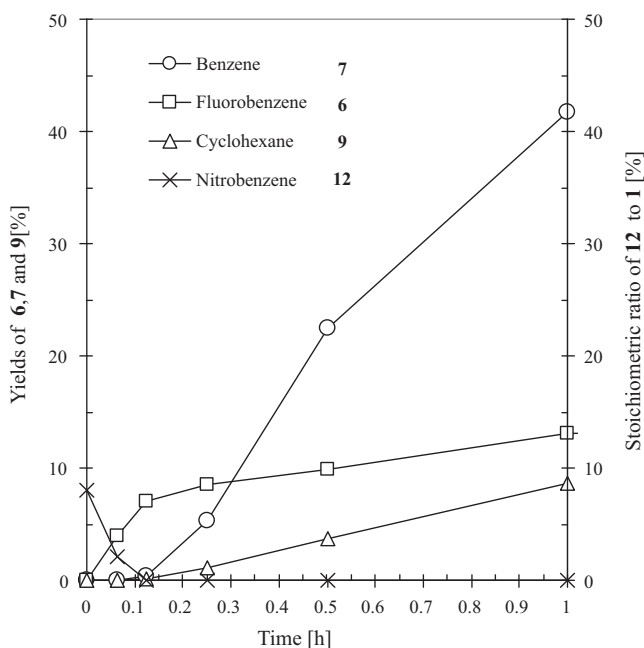
Fig. 1. Time-courses of oxidative dehydrogenation of 1-fluorocyclohexene **1**. Reaction was carried out with **1** (30 mmol), and Pd-Black (weight ratio Pd-Black to **1**: 0.01) and nitrobenzene **12** (1.6 mmol) in a 10-mL closed stainless steel reactor under N_2 at 150 °C.

intermediate (step d) and reductive elimination of H_2O_2 (step e). H_2O_2 was not observed, which was thought to be decomposed catalytically to molecular oxygen and H_2O under the employed conditions. Since the timing of β-hydrogen elimination of B (step b) versus O_2 insertion to B (step d) is mechanistically ambiguous, two paths can be drawn: via E and via C. Since our experimental results revealed that addition of oxidant suppressed the isomerization, the hydride of the π-allyl Pd-hydride species is consumed before it migrates into a π-allyl moiety and isomerizes. Thus, the oxidant was thought to immediately insert into the Pd-H bond of the π-allyl Pd-hydride species when it is formed. As a result of decreasing Pd-hydride concentration, succeeding reactions, such as isomerization, disproportionation, and hydrogen formation, are terminated. Similar mechanisms for several steps were reported previously, i.e., migratory insertion of hydrogen proposed by Alley et al. for olefin hydrogenation [22], C–H activation proposed by Trost et al. for the reaction of olefins [15c,15d] and by Bercaw et al. for a homogeneous system [15a], and oxidation of unsubstituted cyclohexene proposed by Bercaw et al. [15a].

Molecular oxygen showed less selectivity for **6** compared with nitrobenzene. Since nitrobenzene (redox potential E^0: 0.8 V [23a]) is a stronger oxidant than oxygen (E^0: 0.68 V [23b]), the Pd-hydride was more rapidly consumed by nitrobenzene than oxygen.

4. Conclusions

We described the chemical reactivity and reaction mechanism of fluorobenzene formation of fluorobenzene **6** by dehydrogenation of fluorocyclohexenes **1** and **4**. **1** reacted with nitrobenzene or oxygen oxidant to give fluorobenzene in good yields under moderate conditions in the presence of Pd catalyst. A detailed comparison of oxidative dehydrogenation with non-oxidative dehydrogenation proved that oxidants such as nitrobenzene and oxygen suppressed the isomerization and disproportionation of **1** and gave high selectivity of **6**.

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