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# Transfer hydrodehalogenation of aryl halides accelerated by saturated sodium acetate aqueous solution

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Zhimin Xue,<sup>a</sup>\* Xinhui Zhao,<sup>b</sup> Jinfang Wang,<sup>b</sup>and Tiancheng Mu<sup>b</sup>\*

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Development of catalytic hydrodehalogenation of halogenated organic compounds is an important topic from the viewpoint of environment protection. Herein, we conducted the first work on the utilization of saturated aqueous solution of sodium acetate (CH<sub>3</sub>COONa) as efficient and environmentally-friendly reaction media for transfer hydrodehalogenation of various aryl halides using Pd/C as the catalyst. It was found that the transfer hydrodehalogenation could be accelerated significantly by the saturated CH<sub>3</sub>COONa aqueous solution due to the surfactantsimilar effect of CH<sub>3</sub>COONa and the activation of C-Cl bond by the dissolved solvated ions.

Halogenated organic compounds are important chemicals applied in synthetic chemistry and industrial processes.<sup>1</sup> However, most of these compounds show high toxicity and generally are unfriendly to the environment, and thereby have been classified as persistent organic pollutants.<sup>2</sup> Therefore, it is necessary and urgent to develop efficient methods and techniques to dispose them from the viewpoint of environment protection. Currently, several processes have been explored for the disposal of halogenated organic compounds, such as incineration,<sup>3</sup> microbial or photochemical degradation,<sup>4</sup> and catalytic hydrodehalogenation,<sup>5</sup> etc. Among these methods, catalytic hydrodehalogenation has been recognized as an environmentally friendly and cost-saving procedure with non-destructive treatment. Various catalysts, including supported metal catalysts (e.g., Pd,<sup>6</sup> Rh,<sup>7</sup> Au,<sup>8</sup> Ru,<sup>9</sup> Pt,<sup>10</sup> and Ni<sup>11</sup>) and transition metal complexes,<sup>12</sup> have been designed and used for the catalytic hydrodehalogenation of halogenated organic compounds with H<sub>2</sub>,<sup>13</sup> NaBH<sub>4</sub>,<sup>14</sup> formic acid or formic salts,<sup>15</sup> or alcohols<sup>16</sup> as the hydrogen resource. Although good results have been achieved, it is highly desirable to develop more environmentally friendly routes to

overcome some drawbacks of the use of organic solvents and the low activity.

Simple inorganic (e.g., sodium chloride, sodium bromide, sodium sulfate, and sodium nitrate) and organic (sodium acetate) salts are abundant, non-toxic, and cheap. Their solutions have been found to be able to accelerate some organic reactions (i.e., Diels-Alder cycloadditions,<sup>17</sup> Baylis-Hillman reaction,<sup>18</sup> Wittig reaction,<sup>19</sup> nucleophilic substitution reactions,<sup>20</sup> dehydration of fructose and cellulose depolymerization<sup>21</sup>) due to its influence of solvent pressure, hydrogen bond, hydrophobic hydration, and saltingout/salting-in effects.<sup>22</sup> It has been reported that catalytic hydrodehalogenation of halogenated organic compounds can be conducted in water,<sup>23</sup> but the efficiency need to be further improved. Delighted by the enhancement effect of salts on organic reactions, we think that the aqueous solutions of sodium salts may be applied as an efficient media for the hydrodehalogenation reactions.

Herein, catalytic transfer hydrodehalogenation of various aryl halides was conducted using sodium formate (HCOONa) as the hydrogen resource in saturated aqueous solutions of several sodium salts. It was demonstrated that the saturated salts aqueous solutions could affect the activity significantly, and sodium acetate (CH<sub>3</sub>COONa) showed the best performance. To the best of our knowledge, this is the first work on the use of saturated salts aqueous solutions as the reaction media in the catalytic transfer hydrodehalogenation.

Initial experiments were carried out to evaluate the influence of concentrated or saturated aqueous solutions of sodium salts on transfer hydrodehalogenation of aryl halides with HCOONa as the hydrogen resource, and chlorobenzene was used as the model reactant. All experiments were carried out at 100 °C by using commercial Pd/C as the catalyst in a 50 ml round bottom flask, and the results were summarized in Table 1. It is obvious that the effect of the used salts varied from different salts. Compared with the control experiment conducted under salt-free conditions (Table 1, entry 1), saturated aqueous solutions of CH<sub>3</sub>COONa or sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>) could improve the transfer hydrodehalogenation of

<sup>&</sup>lt;sup>a.</sup> Beijing Key Laboratory of Lignocellulosic Chemistry, College of Materials Science and Technology, Beijing Forestry University, Beijing 100083, China. Email: zmxue@bjfu.edu.cn.

<sup>&</sup>lt;sup>b</sup> Department of Chemistry, Renmin University of China, Beijing 100872, China. Tel: 86-10-62514925, Email: tcmu@ruc.edu.cn

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chlorobenzene (Table 1, entries 2 and 3). However, salts like sodium chloride (NaCl), sodium bromide (NaBr), sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) and sodium nitrate (NaNO<sub>3</sub>) showed negative effect on the reaction (Table 1, entries 4-7). Especially for sodium iodide (Nal, Table 1, entry 8), the reaction hardly happened under the same reaction conditions due to the high poison of I on the Pd/C catalyst.<sup>24</sup> For example, when a chlorobenzene conversion of 36.9% was achieved without any salts (Table 1, entry 1), a quantitative conversion would be produced in saturated aqueous solution of CH<sub>3</sub>COONa (Table 1, entry 2) while the chlorobenzene conversion was only 4.8% in Nal aqueous solution (Table 1, entry 8). These results indicated that CH<sub>3</sub>COONa showed the highest improvement effect to transfer hydrodehalogenation of chlorobenzene, and the reason will be discussed in detail in the following sections. Therefore, we chose the saturated aqueous solutions of CH<sub>3</sub>COONa for further experiments.

**Table 1.** Effect of saturated aqueous solutions of varioussodiumsaltsontransferhydrodehalogenationofchlorobenzene.<sup>a</sup>

Entry	Salt (saturated	Percentage	Yield of
	in water)	conversion (%) <sup>b</sup>	benzene (%) <sup>b</sup>
1	none	37.6	35.3
2	CH₃COONa	>99	98.2
3	Na <sub>2</sub> SO <sub>4</sub>	67.8	67.4
4	NaCl	36.9	35.6
5	NaBr	26.1	25.1
6	Na <sub>2</sub> CO <sub>3</sub>	25.4	23.8
7	NaNO <sub>3</sub>	15.3	13.9
8	Nal	4.8	2.7

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<sup>a</sup>Reaction conditions: chlorobenzene, 5 mmol; HCOONa, 10 mmol; sodium hydroxide, 1 g; water, 5 g; Pd/C (5 wt%), 50 mg; salt, saturated amount; reaction temperature, 100  $^{\circ}$ C. <sup>b</sup>The conversion of chlorobenzene and the yield of benzene were determined by GC using toluene as the internal standard.

reaction As an important parameter, reaction temperature could affect the reaction significantly. We subsequently examined the influence of reaction temperature on the transfer hydrodehalogenation of chlorobenzene in saturated aqueous solution of CH<sub>3</sub>COONa with a reaction time of 2 h. Considering the boiling point of water, herein, we examined the influence of reaction temperature in the scale of not higher than the boiling point of water, and the results were showed in Fig. 1. It was found that the conversion of chlorobenzene decreased drastically from 99.4% to 9.7% when temperature changed from 100  $^{\circ}$ C to 40  $^{\circ}$ C. Therefore, 100  $^{\circ}$ C was chosen as reaction temperature in our following experiments. Here, we should point out that the quality of CH<sub>3</sub>COONa in each saturated solution was different because the solubility of sodium acetate changed with the temperatures, and the effect of CH<sub>3</sub>COONa amount would be discussed in the following section.

As shown in Table 1,  $CH_3COONa$  had an important impact on the transfer hydrodehalogenation of chlorobenzene. Therefore, the influence of the  $CH_3COONa$  amount was examined (Fig. 2). The conversion of chlorobenzene increased dramatically before the aqueous solution of  $CH_3COONa^4$  was saturated. When the solution got the saturated point (8.5 g in 5g water), further increase of CH<sub>3</sub>COONa resulted in the decrease of the conversion of chlorobenzene and the yield of benzene. This may be caused by that the solid CH<sub>3</sub>COONa particles after the saturated point mixed with Pd/C, and thus some catalytic active center was embedded by the CH<sub>3</sub>COONa particles, which could decrease the interaction opportunity between chlorobenzene and Pd/C. Therefore, the activity decreased after the solution was saturated.



**Fig. 1.** Influence of reaction temperature. Reaction conditions: chlorobenzene, 5 mmol; HCOONa, 10 mmol; sodium hydroxide, 1 g; water, 5 g; Pd/C (5 wt%), 50 mg; CH<sub>3</sub>COONa, saturated amount.



**Fig. 2.** Effect of CH<sub>3</sub>COONa amount. Reaction conditions: chlorobenzene, 5 mmol; HCOONa, 10 mmol; sodium hydroxide, 1 g; water, 5 g; Pd/C (5 wt%), 50 mg; reaction temperature,  $100^{\circ}$ C.

Delighted by the excellent performance of saturated solution CH<sub>3</sub>COONa for aqueous of transfer hydrodehalogenation of chlorobenzene, we conducted transfer hydrodehalogenation of other aryl chlorides in this novel reaction media at 100 °C (Table 2). It was obvious that the results for all the examined aryl chlorides were much better in saturated aqueous solution of CH<sub>3</sub>COONa than in pure water, indicating the important role in the transfer hydrodehalogenation of aryl chlorides. In all experiments, the aryl chlorides were completely converted into benzene without by-products generated (Table 2, entries 1-8). More surprising, there was no 1-phenylethyl alcohol produced when

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using 3'-chloroacetophenone as the reactant in CH<sub>3</sub>COONa solution, while 1-phenylethyl alcohol could be detected in pure water (Table 2, entry 9). This may be caused by the inhibiting effect of CH<sub>3</sub>COONa on the transfer hydrogenation of carbonyl groups. In order to prove this, we conducted the control experiments of transfer hydrogenation of acetatebenzene in CH<sub>3</sub>COONa solution and pure water. It was found that the reaction did not happen in the CH<sub>3</sub>COONa solution (Table 2, entry 10), suggesting the inhibiting effect of CH<sub>3</sub>COONa. Compared with phase-transfer agents (such as TBAB)<sup>25</sup> on the hydrodehalogenation reaction, the saturated aqueous solution of CH<sub>3</sub>COONa showed much better selectivity to product (quantitative to benzene) and avoided the use of organic solvent (CH<sub>3</sub>OH).

Additionally, we found that transfer hydrodehalogenation of fluorobenzene, bromobenzene and iodobenzene could also be conducted more efficiently in saturated CH<sub>3</sub>COONa solution than in water. However, fluorobenzene (Table 2, entry 11) showed much lower activity due to the high bond energy of C-F, while bromobenzene (Table 2, entry 12) and iodobenzene (Table 2, entry 13) would generate biphenyl as the by-product resulting from the high reactivity of bromobenzene and iodobenzene. It was also found that iodobenzene (Table 2, entry 13) need longer reaction time (3 h) to complete the reaction due to the poison effect of the *in-situ* formed I<sup>°</sup> on Pd/C.

**Table 2.** Transfer hydrodehalogenation of various aryl chlorides in saturated aqueous solution of  $CH_3COONa$  or in pure water.<sup>a</sup>

Entry	Substrate (mmol)	Prod. <sup>b</sup>	t <sup>b</sup> - (h)	Yield(%)	
				With	Without
				CH₃COONa	CH <sub>3</sub> COON
1	(5)	$\bigcirc$	2	98.2	35.3
2		$\bigcirc$	6	100	21.4
3		$\bigcirc$	3	86.9	22.5
4		$\bigcirc$	3	100	44.9
5	CI (2.5)	$\bigcirc$	3	100	37.1
6 <sup>c</sup>	CI (5)	$\bigcirc$	6	100	15.9
7		NH <sub>2</sub>	2	100	12.9

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<sup>a</sup>Reaction conditions: HCOONa, 10 mmol; sodium hydroxide, 1 g; water, 5 g; Pd/C (5 wt%), 50 mg; CH<sub>3</sub>COONa, 8.5 g; reaction temperature, 100 °C. <sup>b</sup>The yield of benzene was determined by GC using toluene as the internal standard. Prod. = Product. t = Time. <sup>c</sup>The internal standard was *n*-dodecane.

discussed above, saturated CH<sub>3</sub>COONa solution As transfer showed excellent promotion for the hydrodehalogenation. There may be three reasons for this enhancement of CH<sub>3</sub>COONa solution. Firstly, the basicity may attribute to the improvement effect because the solution of CH<sub>3</sub>COONa was basic. To confirm whether the improvement effect was caused by basicity or not, we conducted a control experiment with 5 g sodium hydroxide added to get a high basic environment. However, the reaction was inhibited with a benzene yield of only 4.2% generated in the presence of more sodium hydroxide. This control experiment excluded the effect of basicity on the transfer hydrodehalogenation. Secondly, the dissolved CH<sub>3</sub>COONa may play some similar role of surfactants. In saturated solution of CH<sub>3</sub>COONa, part of CH<sub>3</sub>COONa molecules located at the interface of substrate and water phase (Fig. 3). The non-polar tail of acetate anion in the substrate phase may enrich the concentration of the substrate, while the polar part of acetate anion in the water phase may facilitate the transport of hydrogen chloride from the interface to the bulk water phase, which accelerated its neutralization with sodium hydroxide in bulk water phase. These above two effects were beneficial for the reaction. It was also found that the reaction in saturated solution of sodium propionate

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(CH<sub>3</sub>CH<sub>2</sub>COONa) showed a faster reaction rate than in saturated solution of CH<sub>3</sub>COONa. Additionally, the solution of 1-propanesulfonic acid sodium (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>SO<sub>3</sub>Na, 96.2%) showed better chlorobenzen conversion than the solution of methanesulfonic acid sodium (CH<sub>3</sub>SO<sub>3</sub>Na, 83.7%), which were both higher than the solution of NaSO<sub>4</sub> (67.8%). These results proved that longer side chain in the salts was beneficial for the transfer hydrodehalogenation of chlorobenzen. Therefore, we concluded that CH<sub>3</sub>COONa indeed played similar role as surfactants to some extent. Thirdly, the dissolution of CH<sub>3</sub>COONa in water could increase the ionic strength of the solutions, which was beneficial for activating the C-Cl bond in chlorobenzene through the interaction between chlorobenzene and solvated ions, and thus enhancing the transfer hydrodehalogenation. Through these discussions, we assumed that the improvement effect of the CH<sub>3</sub>COONa solution on the transfer hydrodehalogenation may be resulted from the surfactant-similar effect of CH<sub>3</sub>COONa and the activation of C-Cl bond by the dissolved solvated ions.



Fig. 3. Structure of acetate at the interface of oil phase and water phase.

# Conclusions

In summary, saturated aqueous solution of CH<sub>3</sub>COONa was found to be an efficient and environmentally-friendly reaction media for transfer hydrodehalogenation of aryl halides using Pd/C as the catalyst. For various aryl chlorides, there was only hydrodehalogenation reaction happened in the presence of other unsaturated groups in the CH<sub>3</sub>COONa solution. Meanwhile, the CH<sub>3</sub>COONa solution could even improve the reaction of fluorobenzene, which could not be conducted in pure water. Additionally, bromobenzene and iodobenzene could generate biphenyl as by-product due to the high reactivity of C-Br and C-I bonds. Detail discussion revealed that the improvement effect of the CH3COONa solution on the transfer hydrodehalogenation was resulted from the surfactant-similar effect of CH<sub>3</sub>COONa and the activation of C-Cl bond by the dissolved solvated ions. We believed that saturated aqueous solution of CH<sub>3</sub>COONa could be applied as a novel and efficient media in more other organic reactions.

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## Notes and references

- (a) C. Amorim, G. Yuan, P. M. Patterson and M.A. Keane, J. Catal., 2005, 234, 268; (b) X. Ma, S. Liup Y1d in 3@CGuA24059C. Xia, Sci. Rep., 2016, 6, 25068.
- 2 (a) R. Baumgartner, G. K. Stieger and K. McNeill, Environ. Sci. Technol., 2013, 47, 6545; (b) E. L. Teuten and C. M. Reddy, Environ. Pollut., 2007, 145, 668.; (c) J. Luo, J. Hu, X. Wei, L. Fu and L. Li, Chemosphere, 2015, 131, 17.
- B. R. Stanmore, Combust. Flame, 2004, 136, 398.
- (a) H. I. Gomes, C. Dias-Ferreira and A. B. Ribeiro, Sci. Total Environ., 2013, 445-446, 237; (b) X. Chen, W. Ma, J. Li, Z. Wang, C. Chen, H. Ji and J. Zhao, J. Phys. Chem. C, 2011, 115, 4089.
- 5 (a) F. Alonso, I. P. Beletskaya and M. Yus, Chem. Rev., 2002, 102, 4009; (b) R. Navon, S. Eldad, K. Mackenzie and F.-D. Kopinke, Appl. Catal. B: Environ., 2012, 119-120, 241.
- 6 (a) M. A. Aramendía, V. Boráu, I. M. García, C. Jiménez, A. Marinas, J. M. Marinas and F. J. Urbano, Appl. Catal. B: Environ., 2003, 43, 71; (b) C. Xia, J. Xu, W. Wu and X. Liang, Catal. Commun., 2004, 5, 383.
- Y. L. Ren, G. Y. Fan and C. Y. Wang, J. Hazard. Mater., 2014, 274.32.
- 8 S. Gómez-Quero, F. Cárdenas-Lizana and M. A. Keane, J. Catal., 2013, 303, 41.
- 9 T. Yoneda, T. Takido and K. Konuma, Appl. Catal. B: Environ., 2008, 84, 667.
- 10 C. B. Molina, A. H. Pizarro, J. A. Casas and J. J. Rodriguez, Appl. Catal. B: Environ., 2014, 148-149, 330.
- 11 X. Ma, S. Zhou, C. Yang, S. Liu, S. Liu, X. Bi and C. Xia, Catal. Commun., 2010, 12, 282.
- 12 (a) Y. Deng, B. Yang, G. Yu, Q. Zhu, S. Deng and H. Zhang, Prog. Chem., 2016, 28, 564; (b) R. Garrido, P. S. Hernández-Montes, Á. Gordillo, P. Gómez-Sal, C. López-Mardomingo and E. de Jesús, Organometallics, 2015, 34, 1855; (c) H. Tsurugi, A. Hayakawa, S. Kando, Y. Sugino and K. Mashima, Chem. Sci., 2015, 6, 3434.
- 13 (a) G. V. Lowry and M. Reinhard, Environ. Sci. Technol., 1999, 33, 1905; (b) L. Hizartzidis, P. J. Cossar, M. J. Robertson, M. I. Simone, K. A. Young, A. McCluskey and C. P. Gordon, RSC Adv., 2014, 4, 56743.
- 14 G. Chelucci and S. Figus, J. Mol. Catal. A: Chem., 2014, 393, 191.
- 15 A. C. Bényei, S. Lehel and F. Joó, J. Mol. Catal. A: Chem., 1997, 116. 349.
- 16 (a) S. Akzinnay, F. Bisaro and C. S. J. Cazin, Chem. Commun., 2009, 5752; (b) R. Abazari, F. Heshmatpour and S. Balalaie, ACS Catal., 2013, 3, 139.
- 17 P. A. Grieco, J. J. Nunes and M. D. Gaul, J. Am. Chem. Soc., 1990, 112, 4595.
- 18 A. Kumar and S. S. Pawar, Tetrahedron, 2003, 59, 5019.
- 19 S. Tiwari and A. Kumar, Chem. Commun., 2008, 4445.
- 20 (a) K. C. Westaway, Y. Gao and Y.-R. Fang, J. Org. Chem., 2003, 68, 3084; (b) M. J. Pregel and E. Buncel, J. Chem. Soc.,
- 21 (a) Z. Xue, B. Cao, W. Zhao, J. Wang, T. Yu, T. Mu, RSC Adv., 2016, 6, 64338. (b) T. vom Stein, P. Grande, F. Sibilla, U. Commandeur, R. Fischer, W. Leitner and P. D. de María, Green Chem., 2010, 12, 1844.
- 22 (a) A. Kumar, Chem. Rev., 2001, 101, 1; (b) C. Yan, T. Mu, Phys. Chem. Chem. Phys., 2015, 17, 3241; (c) C. Yan, Z. Xue, W. Zhao, J. Wang, T. Mu, ChemPhysChem, 2016, 17, 3309.
- 23 K. Mackenzie, H. Frenzel and F.-D. Kopinke, Appl. Catal. B: Environ., 2006, 63, 161.
- 24 V. R. Choudhary and C. Samanta, J. Catal., 2006, 238, 28.
- 25 S. Mukhopadhyay, S. Ratner, A. Spernat, N. Qafisheh and Y. Sasson, Org. Process Res. Dev., 2002, 6, 297.

Perkin Trans. 2, 1991, 307.

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# **Graphical abstract**

Saturated sodium acetate aqueous solution could be applied as efficient and environmentally-friendly reaction media to accelerate transfer hydrodehalogenation of various aryl halides.

