



CARBON MONOXIDE RELATED REDUCTIONS

O. I. Afanasyev and D. Chusov

*Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
ul. Vavilova 28, Moscow, 119991 Russia*

Cite this: *INEOS OPEN*,
2020, 3 (4), 133–139
DOI: 10.32931/io2017r

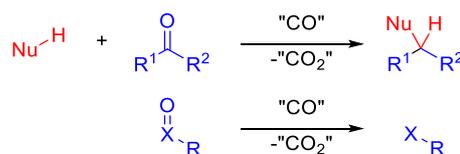
Received 28 April 2020,
Accepted 30 July 2020

<http://ineosopen.org>

Abstract

Carbon monoxide is a unique reducing agent that is only gaining popularity in organic chemistry. This review highlights the main approaches to the application of CO as a reducing agent, summarizes and critically analyzes the key trends in this field, and describes the current development prospects. Potentially the most selective and efficient route for the realization of these processes is demonstrated.

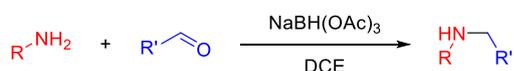
Key words: carbon monoxide, carbonyl complexes, Hieber base reaction, water-gas shift reaction, reductive addition.



Introduction

According to the main principles of green chemistry and atom economy formulated by B. Trost as early as 1991 [1], in an ideal chemical reaction, all the atoms included in reagents must be included, in the end, in the compositions of target products. It is important to take into account not only the conversion of starting compounds but also the use of auxiliary reagents and solvents as well as the whole chains of their production. A striking example of the reactions with a low atom economy is the reduction with boron hydrides. At first glance, a classical reaction of reductive amination is quite consistent with the principle of the atom economy. Almost all the atoms of the organic reactants end up in the reaction products (Scheme 1). However, considering that the reaction usually requires the use of two equivalents of a reducing agent (in this case, sodium triacetoxyborohydride) [2] and the isolation of products requires acid-base processing that affords the equimolar amounts of boron derivatives, each 1 kg of the product accounts minimum for the same amount of the boron-containing wastes which require special utilization. In addition, one should take into account the need for the preliminary synthesis of sodium triacetoxyborohydride, which includes at least four stages starting from the natural raw materials, in particular, the high-temperature conversion of methane to hydrogen. Given all the above-mentioned factors, the atom economy of the reduction with boron hydrides is out of question. This is not crucial for laboratory-scale syntheses but is essential to the potential implementation of these methods in large-scale production.

Therefore, development of efficient and selective reagents that would make a minimum contribution to the price formation



Scheme 1. Classical reductive amination.

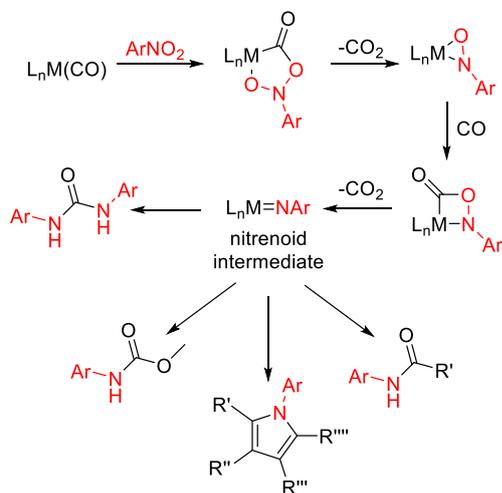
is of particular importance. Ideally, these reagents should not require separate production and should not lead to the formation of a great amount of wastes, which are difficult to utilize.

Carbon monoxide fully meets these criteria. It is a side product of many industrial processes. For example, it is the main component of a converter gas formed during the production of steel. The global steel production exceeds 1.5 billion tonnes per annum [3]. Therefore, the value of this reagent at an industrial scale is minimal. Nowadays, the main method for the utilization of carbon monoxide is its after-burning to carbon dioxide; the technologies for working with the latter are well established. It seems very attractive to use the reducing potential of CO in organic synthesis. The processes involving carbon monoxide must feature a high atom economy because this reagent does not require special production. This review analyzes the existing routes for the application of carbon monoxide as a reducing agent in organic synthesis with a particular emphasis on the reactions of reductive addition and outlines the main prospects of further development of this field. It is shown that CO can be used to accomplish these processes without an external hydrogen source, which enhances their selectivities.

Carbon monoxide as a selective reducing agent

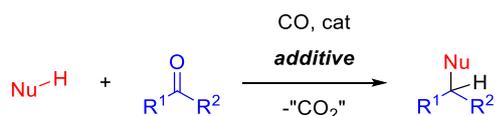
The current routes for the application of CO as a reducing agent in organic reactions could be divided into two large groups. The former includes multiple reactions of the reduction of a nitro group. An essential contribution to this research area was made by the group of Prof. F. Ragaini from the University of Milan [4–9]. A key to these transformations is the formation of a nitrenoid intermediate that results from the interaction of an aromatic nitro group with carbon monoxide (Scheme 2). This highly reactive particle can readily interact with nucleophiles (for example, amines and alcohols) and electrophiles (for

example, aldehydes and alkynes), being present in the system. Hence, this approach opens the way to the synthesis of ureas, carbamates, Schiff bases, amides, nitrogen-containing heterocycles, and other compounds (Scheme 2). These transformations amount to a wide class of chemical reactions that have been extensively reviewed [9]; therefore, their detailed analysis is beyond the scope of the current review.



Scheme 2. Selected possible synthetic approaches implying the reduction of an aromatic nitro group with carbon monoxide.

The second group of approaches to the application of carbon monoxide as a reducing agent encompasses the reactions of the reductive addition of various nucleophiles to carbonyl compounds (Scheme 3). They include, for example, reductive amination (amines as NH-nucleophiles), the reductive Knoevenagel condensation (CH-acids as CH-nucleophiles), reductive esterification (carboxylic acids as OH-nucleophiles), reductive amidation (amides as NH-nucleophiles), *etc.* In these reactions, the reducing potential of carbon monoxide can be used directly or indirectly.



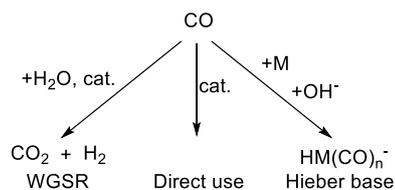
Scheme 3. Reductive addition.

The indirect use of carbon monoxide implies the introduction of some additive which gives rise to a true reducing agent, being active in the reaction. A series of transformations results in a target structure and carbon dioxide in the free or bound form. The examples of these transformations will be described below (Scheme 4).

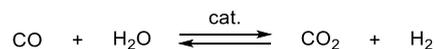
The following three concepts that utilize carbon monoxide in this type of reactions will be considered further: water-gas shift reaction (WGSR), application of the Hieber bases as reducing agents, and direct use of carbon monoxide in the reductive addition without an external hydrogen source (Scheme 4).

The water-gas shift reaction plays a key role in a range of industrial processes (Scheme 5). In particular, it is used in the production of hydrogen, ammonia, and many other compounds.

Harnessing the reducing properties of CO

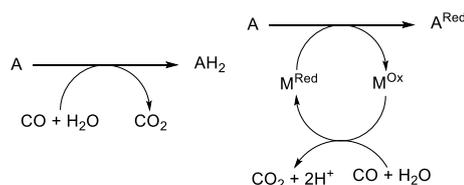


Scheme 4. Approaches to the application of CO as a reducing agent.



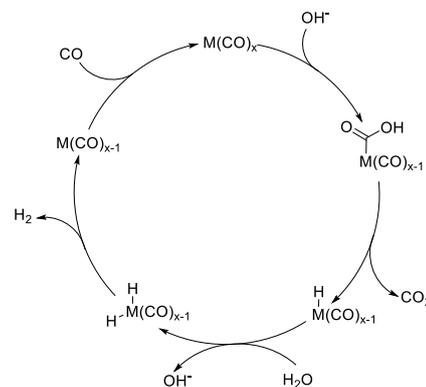
Scheme 5. Water-gas shift reaction.

Besides the large-scale fundamental industrial processes, WGSR finds application in fine organic synthesis. The latest review in this field was published by Prof. S. Denmark [10]. In these examples, a system CO + H₂O is used as a synthetic equivalent of hydrogen. This system can operate in two modes: in the first case, resulting hydrogen is directly inserted in the reaction product, while, in the second case, the reducing potential of the system is transferred to the reaction through a metal ion (Scheme 6) [10]. In the first case, the carbon monoxide/water system is used as a hydrogen source, whereas in the second case—directly as a reducing agent.



Scheme 6. Reduction modes using WGSR [10].

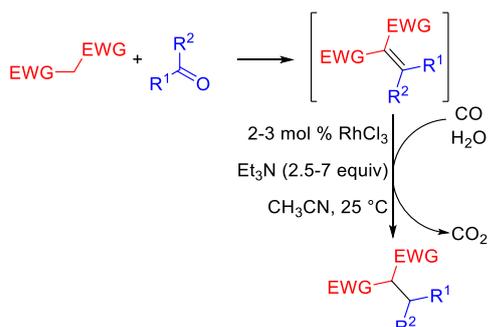
It is important to note that WGSR often requires a basic medium. Nowadays, the following mechanism is generally accepted (Scheme 7). A key step in this process is the nucleophilic activation of a CO molecule with a hydroxide ion followed by decarboxylation resulting in a metal carbonyl hydride. A catalytic cycle for this reaction under acidic conditions was described, and some variations of this mechanism under basic conditions were reported, but the essence remained the same: the attack of an oxygen-centered nucleophile at CO in the metal coordination sphere followed by



Scheme 7. Mechanism of WGSR under basic conditions.

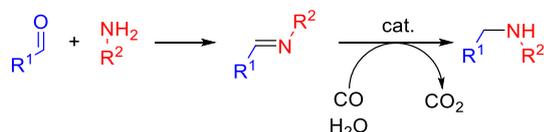
decarboxylation of this particle [10]. Under basic conditions, carbon dioxide is released in the form of a carbonate ion rather than in the free form.

A good illustration of the use of the reducing potential of WGSR is the reductive Knoevenagel condensation developed by the group of Prof. Denmark [11]. It was shown that carbon monoxide in a combination with water in the presence of triethylamine and rhodium chloride efficiently reduces a product of the Knoevenagel condensation even at room temperature (Scheme 8). Both water and triethylamine are likely to serve as hydrogen sources.



Scheme 8. Reductive Knoevenagel condensation.

Another example of the reductive addition harnessing the reducing potential of carbon monoxide is the reductive amination [12, 13]. The first step of this process is the formation of a Schiff base (or an iminium cation in the case of a secondary amine) which then undergoes hydrogenation under the action of hydrogen resulting from the interaction of water and carbon monoxide (Scheme 9).



Scheme 9. Reductive amination proceeding *via* WGSR.

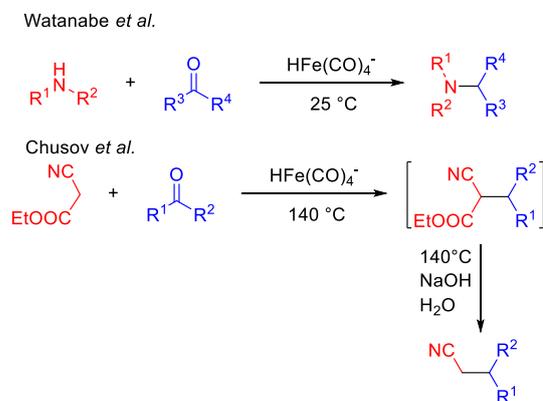
A related approach implies the use of the so-called Hieber bases, *i.e.*, carbonylhydridoferrates, as reducing agents. Their synthesis by the reactions of a strong base with a metal carbonyl was described by Hieber as early as 1932 (Scheme 10) [14]. The reaction essence is very close to that of the above-mentioned water-gas shift reaction. Analogously, a hydroxide anion attacks a CO molecule in the iron coordination sphere, then, a molecule of CO₂ is released with the concomitant formation of a hydride anionic complex. The latter is stable in an alkaline medium and possesses a good reducing potential. A key difference from WGSR is that, in this case, the carbonyl complex is used in stoichiometric amounts, whereas WGSR is a catalytic process.



Scheme 10. Formation of sodium tetracarbonylhydridoferrate.

This approach was used in the reductive amination [15–18] and the reductive Knoevenagel condensation [19]. The reductive amination developed by the group of Prof. Watanabe in the 1970–1980s proceeds at room temperature. The reductive

Knoevenagel condensation developed by our group requires the preliminary generation of tetracarbonylhydridoferrate and proceeds at a rather high temperature. Under these conditions, the ester group in an intermediate is unstable and undergoes hydrolysis and decarboxylation in the alkaline medium (Scheme 11). As a result, the reaction represents the formal reductive addition of acetonitrile to carbonyl compounds.

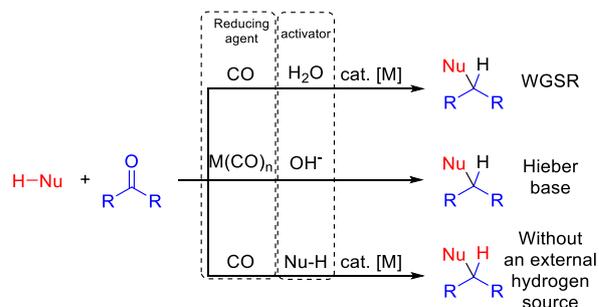


Scheme 11. Reductive addition using tetracarbonylhydridoferrate as a reducing agent.

The above-described water-gas shift reaction and reduction using the Hieber base refer to the indirect application of the reducing potential of carbon monoxide. The metal carbonyl complex interacts with a strong external hydrogen-containing nucleophile (water or hydroxide anion) resulting in the metal carbonyl hydride that serves as a true reducing agent. The presence of this external nucleophile is a key drawback of this approach.

In particular, a strongly basic medium is incompatible with a range of functional groups. Hydrogen, which results from the water-gas shift reaction, also leads to a reduction in the process selectivity. For example, cbz-protecting or nitro groups are principally incompatible with these conditions [11, 19].

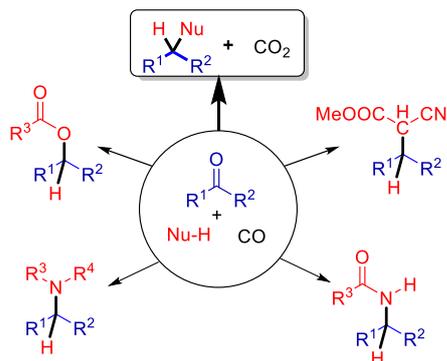
Nevertheless, this process can be considered from a wider perspective. Thus, both amines in the reductive amination and the compounds with active methylene components in the reductive Knoevenagel condensation are hydrogen-containing nucleophiles. This allows for concluding that they can activate the reducing potential of carbon monoxide in these reactions on their own (analogously to a hydroxide anion in the generation of tetracarbonylhydridoferrate) (Scheme 12).



Scheme 12. Reactions of reductive addition using CO.

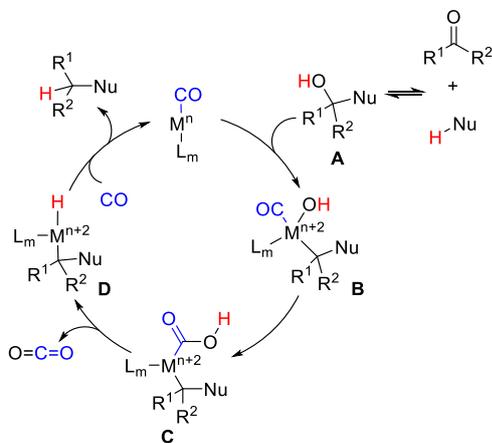
This approach was realized in the reactions of reductive addition without an external hydrogen source. Our group

developed the reactions of reductive amination [20–22], reductive amidation [23–25], reductive aldol condensation [26], and reductive esterification [27] (Scheme 13) [28].



Scheme 13. Main types of nucleophiles used in the reductive addition without an external hydrogen source.

The mechanistic studies performed by our research group for different types of nucleophiles [20, 26, 27] in a combination with quantum-chemical calculations [29] allowed us to suggest the following mechanism for this process (Scheme 14). At the first step, the attack of a nucleophile at a carbonyl compound gives rise to alcohol **A** (a hemiaminal in the case of the reductive amination). The insertion of the metal ion across the C–OH bond results in particle **B**, then the intrasphere oxidation of CO to COOH affords particle **C**, which undergoes the decarboxylation, affording hydride complex **D**. The reductive elimination of the latter yields the target product.

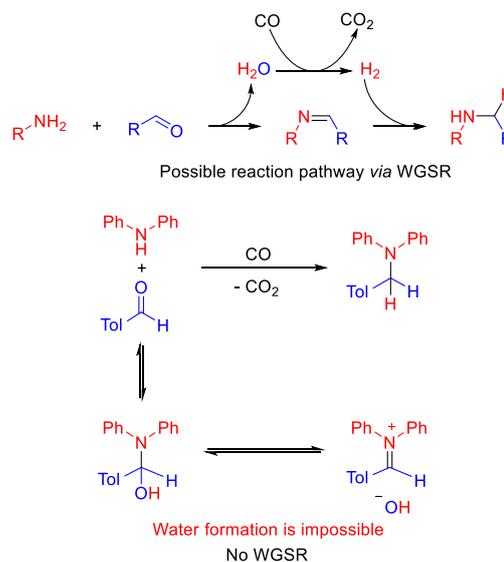


Scheme 14. Mechanism of the reductive addition without an external hydrogen source.

As can be seen from the mechanism presented, a key step, in this case, is the same as in the case of WGSR and the Hieber base reaction—the intrasphere oxidation of CO to COOH followed by the release of CO₂ with concomitant formation of a hydride complex. The main distinguishing feature of the reductive addition without an external hydrogen source is the fact that a hydrogen atom of the initial nucleophile Nu–H ends up in the reaction product, whereas in the case of the Hieber base or WGSR this hydrogen atom comes from external sources (Scheme 12).

Nevertheless, according to the general reactivity principles of organic compounds, another mechanism of the reaction

cannot be excluded (Scheme 15). In the case of the reductive amination, it can be assumed that an amine reacts with an aldehyde, resulting in a Schiff base and water. Water enters the water-gas shift reaction, affording hydrogen, which serves as a reducing agent of a Schiff base, yielding the target amine. In order to confirm or contradict this hypothesis, we performed the reductive amination between diphenylamine and 4-methylbenzaldehyde. As can be seen from the reaction material balance, the amount of hydrogen atoms in these molecules is insufficient for the release of water: the formation of a Schiff base or enamine is impossible. However, the reductive amination using CO proceeds in 74% yield at a gram scale, which contradicts the assumption about the occurrence of this process through WGSR [29].



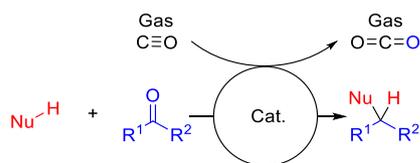
Scheme 15. Investigation of the possibility of occurrence of the reaction via a water-gas shift.

In general, the presence of water in the reaction mixture shows an ambiguous impact on reaction efficiency. Often it hampers the process; at the same time, in some cases it is an optimal solvent [30, 31]. However, under the reaction conditions, water can conduct the water-gas shift reaction, which results in the formation of hydrogen. Hydrogen, in turn, is capable of reducing carbonyl compounds to alcohols, which decreases the yield of a target product and makes impossible the production of a range of complex substrates. In some cases, the presence of water in the reaction mixture is crucial, whereas in the reductive aldol condensation or reductive amidation it is necessary to avoid even the traces of moisture in the reaction mixture [23, 26].

The absence of an external hydrogen source in the reductive addition is a very serious advantage. First of all, it provides very high reaction selectivity. In different reports our group showed that the process conditions tolerate aromatic nitro group, cbz and trifluoroacetamide protecting groups, Ar–Br and Ar–Cl bonds, *etc.* The comparison with common reducing agents revealed that carbon monoxide as a reducing agent in the reductive amination without an external hydrogen source exceeds in the efficiency and selectivity even the gold standards in this field such as sodium triacetoxyborohydride or cyanoborohydride [3].

Another key advantage of the reductive addition without an

external hydrogen source is its very high efficiency. In particular, this approach allows for the high-yielding synthesis of sterically hindered amines, including the reductive amination of camphor [3], which is impossible by other methods [32]. Finally, this approach features a very high atom economy. Taking into account that the reaction can be carried out without a solvent and using a very low catalyst loading, the efficiency of the reaction mass (the ratio of the product mass to the total mass of the starting compounds, reagents, solvents, catalysts, and so on [33]) reaches 80% [3]. This provides a high level of convenience for the reaction performance and isolation of products. The only reactant is gaseous carbon monoxide, and the only side product is gaseous carbon dioxide. Therefore, after the reaction completion, it is ideally enough to reduce the pressure and distill the product from the reaction mixture. This enables simple scaling up of the process (Scheme 16). Another unobvious advantage of this approach is the fact that consumed carbon monoxide immediately changes for an equivalent of carbon dioxide. This means that, unlike the reduction with hydrogen, the pressure in the reaction mixture is maintained at the constant level. This simplifies the hardware solution and process control.



Scheme 16. Advantage of the use of gaseous reagents.

Nevertheless, the reactions relating to the concept of reductive addition without an external hydrogen source have some drawbacks. For example, a principal limitation is the impossibility of synthesis of tertiary amines in which all carbon atoms at the α -positions are tertiary (Fig. 1).

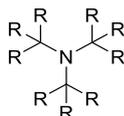
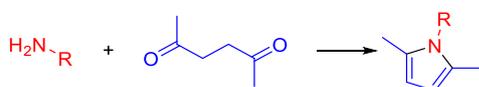


Figure 1. Tertiary amines that cannot be obtained by the reductive amination.

One more restriction is the problem of introduction of the substrates that react at room temperature irreversibly by another mechanism (or with a very high equilibrium constant). This factor makes impossible, for example, the synthesis of pyrrolidines from 1,4-dicarbonyl compounds (Scheme 17). As it follows from the mechanism (Scheme 14), the reaction requires the presence of alcohol **A**. In the case of 1,4-dicarbonyl compounds, the reaction irreversibly proceeds as the formation of aromatic pyrrole. As a result, the catalytic reduction cycle becomes impossible. Similar problems can appear in the case of

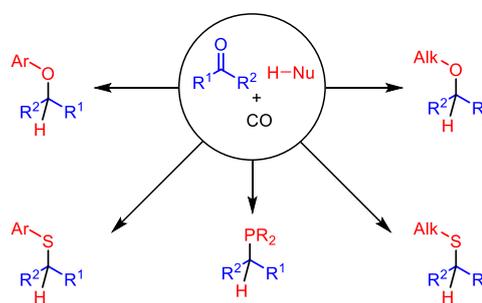


Scheme 17. Formation of pyrrole from a 1,4-dicarbonyl compound and an amine.

the very low solubility of a Schiff base, which would precipitate and leave the reaction medium, or in the case of the competing Michael reaction, Claisen rearrangement, *etc.*

Development prospects of the reductive addition without an external hydrogen source

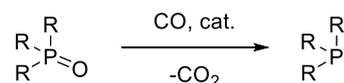
Based on our knowledge about the reactions relating to the concept of reductive addition without an external hydrogen source, the following prospects of further development in this field can be formulated. First of all, this is the extension of the approach to other nucleophiles (Scheme 18). Summarizing the data available at the present moment, it can be concluded that phenols, alcohols, thiols, and phosphines can also be used within this concept.



Scheme 18. Possible application of the concept of reductive addition without an external hydrogen source to other nucleophiles.

The described concept is based on the fact that CO can deoxygenize the molecules; therefore, a possible direction of further development of this field is the investigation of deoxygenation of phosphine oxides and other oxygen-containing compounds. The development of the methods for deoxygenation of phosphine oxides is of particular importance from the industrial point of view. Phosphines are key ligands in many large-scale processes. The deactivation of phosphines and, consequently, the whole process occurs due to their oxidation to phosphine oxides [34]. Taking into account the complexity of synthesis of these phosphines, a reliable method for their regeneration from phosphine oxides would be highly desirable (Scheme 19).

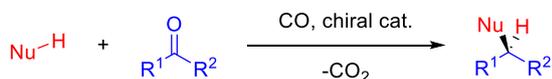
Another challenge is a search for more active catalysts for this type of processes. The high catalytic performance is demonstrated by rhodium, ruthenium, and iridium catalysts.



Scheme 19. Deoxygenation of phosphine oxides.

Nowadays, the lowest temperature which provides the reaction feasibility for iridium and ruthenium complexes is 120 °C, and that for rhodium is 40 °C in the case of the most active substrates. As the amine nucleophilicity reduces, the temperature must be elevated to 130–200 °C [32, 35]. Therefore, the development of active catalysts that would allow one to reduce the reaction temperature at least to the boiling points of common solvents is of particular importance.

A related task is the development of asymmetric modifications of the processes under consideration. An essential hindrance at this moment is the high temperature which hampers the achievement of high enantiomeric excesses. Therefore, a reduction in the process temperature will also enable the development of a chiral catalyst, which could provide an opportunity to synthesize enantiomerically pure products (Scheme 20).



Scheme 20. Realization of the reductive addition of a chiral catalyst.

On the one hand, the reductive addition offers a simple way to many classes of organic compounds and, on the other hand, proceeds smoothly and cleanly: it can be carried out without a solvent, using very low catalyst loadings, with a single reagent—carbon monoxide, and a single side product—carbon dioxide. Therefore, this approach can be used for the production of different materials: polyamines, polyamides, polyesters, *etc.*

One more global goal is switching from neat carbon monoxide to the gas mixtures on its base which are the side products in steel production. This refers, first of all, to a converter gas. Carbon monoxide is its main component; however, it can also contain admixtures that can inhibit the reaction. All this requires further detailed investigations and shows the great potential of this research field.

Conclusions

Nowadays, there are three routes for harnessing the reducing potential of carbon monoxide in the reactions of reductive addition of hydrogen-containing nucleophiles to carbonyl compounds: using the water-gas shift reaction, through the formation of a metal carbonyl hydride, or without the application of an external hydrogen source.

All three approaches have certain advantages and disadvantages. A key advantage of the reductive addition without an external hydrogen source is its high atom economy, selectivity, and simplicity of scaling up. Nevertheless, in most cases, it requires rather high temperatures and pressures. The use of water-gas shift reaction is possible under milder conditions; however, due to the presence of hydrogen in a reaction mixture, the selectivity reduces. The reductive addition using the Hieber base as a reducing agent is a convenient laboratory approach that does not require special equipment and rare reagents; however, this reaction requires stoichiometric amounts of the metal, which reduces its relevance to the industrial processes.

Owing to the high efficiency and atom economy, the reductive addition without an external hydrogen source is a highly attractive direction for further development. This approach has the lowest number of restrictions. To date, a possibility of the performance of this process in glassware at low pressures has already been shown for a range of examples, which opens new prospects for the laboratory application of this reaction. Owing to the absence of an external hydrogen source, different functional groups do not undergo hydrogenation, which makes this approach one of the most selective approaches

among the considered reactions. From the industrial point of view, of particular importance is a possibility to conduct the reaction using equimolar ratio of reagents. Moreover, it is important to reduce the catalyst loading to the level of several hundreds of ppm and, in many cases, to avoid the application of solvents. The achieved yields are often quantitative. A gas mixture formed as a side product can be readily utilized or transferred for the repeated use of carbon monoxide residues.

The main focus in this field must be extended to other nucleophiles, the development of more efficient catalysts to ensure milder reaction conditions, and the development of an asymmetric modification of this reaction. The successful solution of these problems would afford more efficient synthetic routes for many compounds which are used in different fields of science and industry. Furthermore, this would lead to the creation of polymeric materials which production was impossible earlier.

Acknowledgements

This work was supported by the Russian Foundation for Basic Research, project no. 18-03-00839, and the Council of the President of the Russian Federation, Grant for Young Scientists no. MK-1736.2019.3. Database studies were performed with the financial support from the Ministry of Science and Higher Education of the Russian Federation.

Corresponding author

* E-mail: chusov@ineos.ac.ru. Tel: +7(499)135-6212 (D. Chusov)

References

- (a) B. M. Trost, *Science*, **1991**, *254*, 1471–1477. DOI: 10.1126/science.1962206; (b) N. Z. Burns, P. S. Baran, R. W. Hoffmann, *Angew. Chem., Int. Ed.*, **2009**, *48*, 2854–2867. DOI: 10.1002/anie.200806086
- E. Podyacheva, O. I. Afanasyev, A. A. Tsygankov, M. Makarova, D. Chusov, *Synthesis*, **2019**, *51*, 2667–2677. DOI: 10.1055/s-0037-1611788
- <https://www.worldsteel.org/media-centre/press-releases/2020/Global-crude-steel-output-increases-by-3.4--in-2019.html#:~:text=Global%20crude%20steel%20production%20reached,Asia%20and%20the%20Middle%20East.&text=Asia%20produced%201%2C341.6%20Mt%20of,of%205.7%25%20compared%20to%202018>
- F. Ferretti, D. R. Ramadan, F. Ragaini, *ChemCatChem*, **2019**, *11*, 4450–4488. DOI: 10.1002/cctc.201901065
- F. Ferretti, D. Formenti, F. Ragaini, *Rend. Fis. Acc. Lincei*, **2017**, *28*, 97–115. DOI: 10.1007/s12210-017-0601-7
- F. Ragaini, S. Cenini, E. Gallo, A. Caselli, S. Fantauzzi, *Curr. Org. Chem.*, **2006**, *10*, 1479–1510. DOI: 10.2174/138527206778018249
- M. A. EL-Atawy, F. Ferretti, F. Ragaini, *Eur. J. Org. Chem.*, **2018**, 4818–4825. DOI: 10.1002/ejoc.201701814
- F. Ferretti, E. Barraco, C. Gatti, D. R. Ramadan, F. Ragaini, *J. Catal.*, **2019**, *369*, 257–266. DOI: 10.1016/j.jcat.2018.11.010
- A. M. Tafesh, J. Weiguny, *Chem. Rev.*, **1996**, *96*, 2035–2052. DOI: 10.1021/cr950083f
- A. Ambrosi, S. E. Denmark, *Angew. Chem., Int. Ed.*, **2016**, *55*, 12164–12189. DOI: 10.1002/anie.201601803

11. S. E. Denmark, M. Y. S. Ibrahim, A. Ambrosi, *ACS Catal.*, **2017**, *7*, 613–630. DOI: 10.1021/acscatal.6b03183
12. M.-M. Zhu, L. Tao, Q. Zhang, J. Dong, Y.-M. Liu, H.-Y. He, Y. Cao, *Green Chem.*, **2017**, *19*, 3880–3887. DOI: 10.1039/C7GC01579H
13. J. W. Park, Y. K. Chung, *ACS Catal.*, **2015**, *5*, 4846–4850. DOI: 10.1021/acscatal.5b01198
14. W. Hieber, F. Leutert, *Z. Anorg. Allg. Chem.*, **1932**, *204*, 145–164. DOI: 10.1002/zaac.19322040115
15. Y. Watanabe, S. C. Shim, T.-a. Mitsudo, M. Yamashita, Y. Takegami, *Bull. Chem. Soc. Jpn.*, **1976**, *49*, 2302–2305. DOI: 10.1246/bcsj.49.2302
16. S. C. Shim, K. T. Huh, W. H. Park, *Tetrahedron*, **1986**, *42*, 259–263. DOI: 10.1016/S0040-4020(01)87426-3
17. Y. Watanabe, M. Yamashita, T.-a. Mitsudo, M. Tanaka, Y. Takegami, *Tetrahedron Lett.*, **1974**, *15*, 1879–1880. DOI: 10.1016/S0040-4039(01)82583-1
18. Y. Watanabe, S. C. Shim, H. Uchida, T. Mitsudo, Y. Takegami, *Tetrahedron*, **1979**, *35*, 1433–1436. DOI: 10.1016/0040-4020(79)85039-5
19. O. I. Afanasyev, A. Zarochintsev, T. Petrushina, A. Cherkasova, G. Denisov, I. Cherkashchenko, O. Chusova, O. Jinho, C. Man-Seog, D. L. Usanov, S. E. Semenov, D. Chusov, *Eur. J. Org. Chem.*, **2019**, 32–35. DOI: 10.1002/ejoc.201801412
20. D. Chusov, B. List, *Angew. Chem., Int. Ed.*, **2014**, *53*, 5199–5201. DOI: 10.1002/anie.201400059
21. P. N. Kolesnikov, N. Z. Yagafarov, D. L. Usanov, V. I. Maleev, D. Chusov, *Org. Lett.*, **2015**, *17*, 173–175. DOI: 10.1021/ol503595m
22. O. I. Afanasyev, A. A. Tsygankov, D. L. Usanov, D. S. Perekalin, N. V. Shvydkiy, V. I. Maleev, A. R. Kudinov, D. Chusov, *ACS Catal.*, **2016**, *6*, 2043–2046. DOI: 10.1021/acscatal.5b02916
23. P. N. Kolesnikov, D. L. Usanov, K. M. Muratov, D. Chusov, *Org. Lett.*, **2017**, *19*, 5657–5660. DOI: 10.1021/acs.orglett.7b02821
24. N. Z. Yagafarov, K. M. Muratov, K. Biriukov, D. L. Usanov, O. Chusova, D. S. Perekalin, D. Chusov, *Eur. J. Org. Chem.*, **2018**, 557–563. DOI: 10.1002/ejoc.201701527
25. A. A. Tsygankov, M. Makarova, O. I. Afanasyev, A. S. Kashin, A. V. Naumkin, D. A. Loginov, D. Chusov, *ChemCatChem*, **2020**, *12*, 112–117. DOI: 10.1002/cctc.201901465
26. S. A. Runikhina, O. I. Afanasyev, K. Biriukov, D. S. Perekalin, M. Klussmann, D. Chusov, *Chem. Eur. J.*, **2019**, *25*, 16225–16229. DOI: 10.1002/chem.201904605
27. S. A. Runikhina, D. L. Usanov, A. O. Chizhov, D. Chusov, *Org. Lett.*, **2018**, *20*, 7856–7859. DOI: 10.1021/acs.orglett.8b03375
28. A. A. Tsygankov, M. Makarova, D. Chusov, *Mendeleev Commun.*, **2018**, *28*, 113–122. DOI: 10.1016/j.mencom.2018.03.001
29. O. I. Afanasyev, A. A. Tsygankov, D. L. Usanov, D. S. Perekalin, A. D. Samoylova, D. Chusov, *Synthesis*, **2017**, *49*, 2640–2651. DOI: 10.1055/s-0036-1588817
30. S. A. Runikhina, M. A. Arsenov, V. B. Kharitonov, E. R. Sovdagarova, O. Chusova, Y. V. Nelyubina, G. L. Denisov, D. L. Usanov, D. Chusov, D. A. Loginov, *J. Organomet. Chem.*, **2018**, *867*, 106–112. DOI: 10.1016/j.jorganchem.2017.11.003
31. K. Muratov, O. I. Afanasyev, E. Kuchuk, S. Runikhina, D. Chusov, *Eur. J. Org. Chem.*, **2019**, 6557–6560. DOI: 10.1002/ejoc.201901175
32. N. Z. Yagafarov, P. N. Kolesnikov, D. L. Usanov, V. V. Novikov, Y. V. Nelyubina, D. Chusov, *Chem. Commun.*, **2016**, *52*, 1397–1400. DOI: 10.1039/C5CC08577B
33. *Green Chemistry Metrics: Measuring and Monitoring Sustainable Processes*, A. Lapkin, D. J. C. Constable (Eds.), Blackwell Publ., Singapore, **2009**. DOI: 10.1002/9781444305432
34. E. Podyacheva, E. Kuchuk, D. Chusov, *Tetrahedron Lett.*, **2019**, *60*, 575–582. DOI: 10.1016/j.tetlet.2018.12.070
35. A. P. Moskovets, D. L. Usanov, O. I. Afanasyev, V. A. Fastovskiy, A. P. Molotkov, K. M. Muratov, G. L. Denisov, S. S. Zlotskii, A. F. Smol'yakov, D. A. Loginov, D. Chusov, *Org. Biomol. Chem.*, **2017**, *15*, 6384–6387. DOI: 10.1039/c7ob01005b