

The Benefit of Leaving Your Synthetic Comfort Zone: Reactions in Uncommon Media

Cite This: *Inorg. Chem.* 2020, 59, 17823–17825

Read Online

ACCESS |



Metrics & More



Article Recommendations

The environment in the medium within which chemicals interact plays an important role in determining the rate, mechanism, and products of reactions. Processes that get along without the use of any reaction medium are carried out in the gas phase or as traditional high-temperature solid-state reactions, where the reactants are directly mixed and heated to the reaction temperature together. However, in contrast to reactions that include the reactants only, the addition of a reaction medium adds at least one more dimension to the reaction space, by reducing the influences of different melting or sublimation temperatures, enhancing the mixing of reactants, introducing templating effects, and diluting the reactants in order to control the reactivities and reaction rates or to manage an even reaction temperature. Because of these important effects, the choice of the most suitable and most effective reaction medium is a delicate task.

Water or organic liquids have been the most common reaction media in the history of chemical synthesis; the variety of organic solvents is enormous, thus enabling the dissolution of many different types of reactants. However, there are limits in solubility, especially of inorganic substances, and the accessible temperature is also restricted when using common liquids. Hence, there has been an interest in moving on to uncommon reaction media, thus allowing for the processing of virtually insoluble solids under moderate temperatures—and thereby in a more controlled fashion—and enabling alternative reaction pathways to be followed relative to conventional synthesis routes.

The development and use of nonclassical environments for chemical reactions may improve access to certain compounds or enable the fundamental study of the behavior of chemicals under unique conditions. In this Virtual Issue, “*Inorganic Synthesis in Uncommon Reaction Media*”, we highlight recent reports of reactions that take place in uncommon reaction media, selecting articles that feature a range of currently used systems. These reports include the descriptions of reactions in molten metals (metal flux), molten salts (nonmetal flux), ionic liquids (ionothermal if carried out under elevated temperatures), supercritical solvents (solvothormal), and liquefied gases.

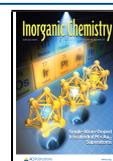
The latter, in particular, is one of the first used uncommon reaction media, developed as a result of the advent of cooling systems that would allow for the convenient (and safe) handling of liquefied gases, such as ammonia (NH_3). Not only have the excellent solvation properties of liquid NH_3 ¹ served to test and enhance the solubility of numerous organic and inorganic substances, but it also facilitated the identification of

new families of inorganic compounds and uncommon species, such as Zintl metalide polyanions. The application of liquid sulfur dioxide as a reaction medium became popular because of its excellent solvent properties and inertness to many chemicals and Lewis basic behavior, respectively, if desired.² More recently, anhydrous hydrogen fluoride (HF) has also joined the group of liquefied gases used as reaction media—on its own or in mixtures—that show superacidic behavior. Its specific fluorination and redox properties are the most important arguments for its use.³

For example, we note work by Mazej and Goreschnik on the photochemical reactions of a variety of oxides and fluorides in liquid anhydrous HF as a convenient way of producing dioxygenyl salts, which are generally difficult to obtain in pure form (DOI: [10.1021/acs.inorgchem.9b03518](https://doi.org/10.1021/acs.inorgchem.9b03518)). In addition, Schnick and coauthors describe the ammonothermal crystal growth of ATaN_2 ($A = \text{Na, K, Rb, Cs}$) as a valuable addition to the generation of nitrides (DOI: [10.1021/acs.cgd.9b00357](https://doi.org/10.1021/acs.cgd.9b00357)). Owing to the reactants' and products' usually high sensitivity to air and moisture, the preparation of this class of materials remains challenging, yet they are highly desirable because of their peculiar optical and electronic properties, especially in the context of light-emitting-diode phosphors.

The other end of the reaction temperature scale is characterized by solid-state reactions. However, because of the need for the application of high temperatures, these types of reactions often suffer from restrictions in reaction control and the inevitable ending with thermodynamically preferred. Hence, the search for more sophisticated ways of carrying out solid-state reactions under more moderate conditions has been an important research goal for solid-state and materials scientists. In this case, the application of supercritical liquids, such as water, alcohols, or amines, in so-called solvothormal reactions, has significantly broadened the product spectrum. While early work that dates back more than 150 years has mainly addressed oxidic materials,^{4,5} the field has been significantly extended toward other classes of compounds and by the use of more sophisticated technical methods, such as ultrafast heating under microwave irradiation.

Published: December 11, 2020



Applications of such new branches of solvothermal reactions include, for instance, a report by Hemmer and co-workers to access optically active materials for upconversion and downshifting for the synthesis of rare-earth-doped LiYF_4 micro-particles prepared by microwave-assisted solvothermal methods (DOI: [10.1021/acs.inorgchem.8b02697](https://doi.org/10.1021/acs.inorgchem.8b02697)). As discussed in the work by Albrecht-Schmitt and coauthors, hydrothermal conditions also serve to model the reactions of molten salts under hydrolysis conditions. This was shown for fluorido metalates of Th, U, Np, Zr, and Ce (as models for Pu and Am), which are relevant to the FLiBe molten salt reactor that is being discussed in the context of next-generation nuclear energy (DOI: [10.1021/acs.inorgchem.0c00360](https://doi.org/10.1021/acs.inorgchem.0c00360)).

Further recent developments include ionic liquids—low-melting salts that are often referred to as “designer solvents” for their highly variable and adjustable solvent properties. While the first “ionic liquid”, ethanolanmonium nitrate (mp 52 °C),⁶ and the first “room-temperature ionic liquid”, ethylammonium nitrate (mp 12 °C),⁷ were not initially used for chemical reactions, the field was reassessed in the second half of the last century and newly discovered more recently.⁸ Ionic liquids have shown an astonishing capability as reaction media: they not only serve as inert “solvents” for organic synthesis but also allow for solid-state-type transformations of a wide variety of typical inorganic compounds and nanomaterials under moderate temperatures of less than 200 °C. Depending on the composition of the reaction mixture, ionic liquids may be fully inert or reactive.⁹

An example for the involvement of an ionic liquid in a reaction was reported by Mudring and Rogers for transformations of lanthanide salts in dicyanamide-based compounds, which served to force the f-element ions into the rarely observed coordination by dicyanamide ligands, thus overcoming their distinct preference for O-donor ligands (DOI: [10.1021/acs.inorgchem.0c00667](https://doi.org/10.1021/acs.inorgchem.0c00667)). Furthermore, the specific design of reactive ionic liquids is a helpful tool for introducing specific properties into the target compounds. As an example, Bi^{3+} -containing ionic liquids were developed and applied for the synthesis of stimuli-responsive luminescent supramolecular assemblies by the groups of Huang and Hu (DOI: [10.1021/acs.inorgchem.9b00813](https://doi.org/10.1021/acs.inorgchem.9b00813)). Reactive ionic liquids were also helpful in the formation of phase-pure Bi_2E_3 (E = Se, Te) nanoparticles with high Seebeck coefficients, which readily formed from the combination of two reactive ionic liquids, $[\text{C}_4\text{C}_1\text{Im}]_3[\text{Bi}_3\text{I}_{12}]$ ($\text{C}_4\text{C}_1\text{Im}$ = 1-butyl-3-methylimidazolium) and $[\text{C}_4\text{C}_1\text{Pyr}][\text{ESiMe}_3]$ (E = Se, Te; $\text{C}_4\text{C}_1\text{Pyr}$ = 1-butyl-1-methylpyrrolidinium), free of metal oxide species. This is outlined in an article by Schierning and Schulz (DOI: [10.1021/acs.inorgchem.9b03060](https://doi.org/10.1021/acs.inorgchem.9b03060)).

Molten phases of common salts are used in so-called flux reactions, which serve to lower the temperatures in solid-state reactions by the formation of eutectic mixtures.¹⁰ In particular, “reactive flux” conditions allow for the deliberate introduction of (mostly anionic) components of the molten salts into the chemical composition of the products.

The publications that we selected for this Virtual Issue describe particularly exciting progress in this area. For instance, a synthetic route to tin(II) perovskite oxides that are highly desired as small-band-gap semiconductors and lead-free dielectrics has been discovered. Maggard and co-workers report that the syntheses of these compounds is complicated by their thermodynamic instability. Here, a low-melting $\text{SnCl}_2/\text{SnF}_2$ peritectic flux has been used to achieve a highly facile

exchange of Sn(II) by leveraging the exothermic formation of stable salts in order to form highly metastable perovskites (DOI: [10.1021/acs.chemmater.0c00044](https://doi.org/10.1021/acs.chemmater.0c00044)). A rather uncommon flux is formed by BaCN_2 , which enabled the growth of perovskite-type BaTaO_2N crystals by the Hosono and Masubuchi groups (DOI: [10.1021/acs.inorgchem.9b02917](https://doi.org/10.1021/acs.inorgchem.9b02917)). The synthesis allowed polarization measurements on the products, which led to the discovery of ferroelectricity with phase inversion on an oxynitride for the first time.

Since the use of an excess of one metal as a reaction medium in solid-state reactions was first described,¹¹ interest in employing this route is resurging. Examples include metals with an extremely low melting temperature, such as gallium (29.8 °C), or a moderately low melting temperature, such as bismuth (271.4 °C).¹² As expected—and desired in these cases—the flux metals may be incorporated in the reactions. Yet, it has also been shown that even nonprecious metals can stay inert without contributions to the (usually) intermetallic reaction products in spite of the generally high reactivity and reduction power of molten metals.

In our collection, we also highlight recent developments in this area, including reactions performed in the presence of an excess of one metal (Na, Sn, Bi) or a mixture of two metals. One example for the latter is the metal-flux growth of complex intermetallic phases, which are addressed for their fine tunability of the electronic and magnetic properties. By reactions of Ba, Y, and Si in a Mg-rich Mg–Al flux, the majority component of the flux was included in the products that crystallize as quaternary solids of different compositions at different temperatures from the flux, as reported by Lattner and coauthors (DOI: [10.1021/acs.inorgchem.9b00857](https://doi.org/10.1021/acs.inorgchem.9b00857)). While the combination of these very hard metals still requires relatively high temperatures (950 °C), the application of a Sn flux can be realized at a considerably lower temperature. For instance, Leddy, Gillan, and coauthors demonstrated that the Sn-flux-assisted synthesis of P-rich metal phosphides (without introduction of the flux metal), which took place at 500 °C, allowed for the formation of polymorphs that are not accessible by common high-temperature routes (DOI: [10.1021/acs.inorgchem.9b00032](https://doi.org/10.1021/acs.inorgchem.9b00032)).

The uncommon reaction media indicated above can be further varied by the application of unusual synthesis conditions, and we selected some recent publications relevant to this approach to feature. An example is the combustion synthesis, in contrast to ceramic or sol–gel methods, to prepare and isolate the α -polymorph of CuV_2O_6 . Rajeshwar and Macaluso groups showed that by controlling the pH of the solution, the synthesis of α - CuV_2O_6 free of other contaminants can be accomplished in a matter of minutes. The solution combustion synthesis product was then fabricated into a photoelectrode as part of a photoelectrochemical cell for splitting water into hydrogen and oxygen (DOI: [10.1021/acs.chemmater.0c02227](https://doi.org/10.1021/acs.chemmater.0c02227)). Another article reports on the synthesis of Co- and Ni-doped BaFe_2As_2 superconductors within 1 h by a novel synthetic method carried out in the Zaikina and Kauzlarich groups: BaH_2 and the respective elements Fe, Co/Ni, and As are heated in a sealed Nb container and spark-plasma-sintered at relatively low temperatures (873 °C) to form the target compound in record time (DOI: [10.1021/acs.chemmater.8b04039](https://doi.org/10.1021/acs.chemmater.8b04039)).

We trust that these and all other articles that are compiled to form this Virtual Issue on reactions in uncommon media serve to attract our readers' interest in synthesis methods that may

be characterized as “off the beaten track”. While some of the reported reactions are specifically aimed at solving a particular problem, many others may be of general interest and can be taken as an inspiration of how to vary your own reaction setup in order to move on to new pastures.

Julia Y. Chan, Guest Editor  orcid.org/0000-0003-4434-2160

Stefanie Dehnen, Associate Editor  orcid.org/0000-0002-1325-9228

■ AUTHOR INFORMATION

Complete contact information is available at:

<https://pubs.acs.org/10.1021/acs.inorgchem.0c03428>

Notes

Views expressed in this editorial are those of the authors and not necessarily the views of the ACS.

■ REFERENCES

- (1) Franklin, E. C. Reactions in Liquid Ammonia. *J. Am. Chem. Soc.* **1905**, *27*, 820–851.
- (2) Wickert, K.; Jander, G. Die Chemie in flüssigem Schwefeldioxyd, II. Mitteil.: Über substituierte Thionyl-diammonium-Verbindungen und über Thionyl-dichinolinium-Derivate. *Ber. Dtsch. Chem. Ges. B* **1937**, *70*, 251–257.
- (3) Olah, G. A. My Search for Carbocations and Their Importance in Chemistry (Nobel Lecture). *Angew. Chem.* **1995**, *107*, 1519–1532.
- (4) Flaschen, S. S. An Aqueous Synthesis of Barium Titanate. *J. Am. Chem. Soc.* **1955**, *77*, 6194–6194.
- (5) Peterson, J. H. Process for Producing Insoluble Titanates. U.S. Patent 2,218,655, 1940.
- (6) Gabriel, S.; Weiner, J. Ueber einige Abkömmlinge des Propylamins. *Ber. Dtsch. Chem. Ges.* **1888**, *21*, 2669–2679.
- (7) Walden, P. Molecular Weights and Electrical Conductivity of Several Fused Salts. *Bull. Acad. Imper. Sci. St. Petersburg* **1914**, *8*, 405–422.
- (8) Cooper, E. R.; Andrews, C. D.; Wheatley, P. S.; Webb, P. B.; Wormald, P.; Morris, R. E. Ionic liquids and Eutectic Mixtures as Solvent and Template in Synthesis of Zeolite Analogues. *Nature* **2004**, *430*, 1012–1016.
- (9) Santner, S.; Heine, J.; Dehnen, S. Synthesis of Crystalline Chalcogenides in Ionic Liquids. *Angew. Chem., Int. Ed.* **2016**, *55*, 876–893.
- (10) Sundermeyer, W. Fused Salts and Their Use as Reaction Media. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 222–238.
- (11) Fisk, Z.; Remeika, J. P. Growth of Single Crystals from Molten Metal Fluxes. In *Handbook on the Physics and Chemistry of Rare Earths*; Karl, A., Gschneidner, J., Eyring, L., Eds.; Elsevier, 1989; Vol. 12, Chapter 81, pp53–70.
- (12) Phelan, W. A.; Menard, M. C.; Kangas, M. J.; McCandless, G. T.; Drake, B. L.; Chan, J. Y. Adventures in Crystal Growth: Synthesis and Characterization of Single Crystals of Complex Intermetallic Compounds. *Chem. Mater.* **2012**, *24*, 409–420.