

Organic Carbonates as Solvents in Synthesis and Catalysis

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Contents

1. Introduction	4554	6. Catalysis in Organic Carbonates	4569
2. Synthesis of Organic Carbonates	4556	6.1. Product Isolation and Catalyst	4569
2.1. Outline	4556	6.1.1. Recovery	4569
2.2. Recent Trends in Synthesis	4556	6.2. Catalysis in Organic Carbonates	4570
2.2.1. Strategies	4556	6.2.1. Homogeneous Catalysis	4570
3. Physico-Chemical Properties	4559	7. Other Applications as Solvent or Agent	4574
3.1. Thermodynamic Properties	4559	7.1. Organic Synthesis	4574
3.1.1. Further Property Studies	4560	7.2. Synthesis of Ionic Liquids	4575
3.1.2. First-Principles Calculations	4560	7.3. Cosmetic Applications	4575
3.2. Mixtures with Other Fluids or Gases	4560	7.4. Cleaning Cosolvents	4575
3.2.1. Gas–Liquid Phase Equilibria and Activity Coefficients in Carbonate-Containing Mixtures	4561	7.5. Oil Processing Industry	4575
3.2.2. Static Method Measurements	4561	7.6. Lacquer Applications	4575
3.2.3. Dynamic Method: Isobaric Measurements	4561	7.7. Others	4576
3.2.4. Dynamic Measurements: Isothermal Methods	4561	8. Summary	4576
3.2.5. Liquid–Liquid Equilibrium (LLE) of Mixtures Containing Organic Carbonates	4561	9. List of Abbreviations	4576
3.2.6. Solid–Liquid Phase Equilibria (SLE) of the Mixtures Containing Carbonates	4562	10. Acknowledgments	4576
3.2.7. Prediction of the Fluid-Phase Equilibria of the Mixtures Containing Carbonates	4562	11. References	4576
3.2.8. Molecular Dynamic Simulations of Carbonates and Their Mixtures	4562		
4. Handling	4562		
5. Organic Carbonates as Solvent	4563		
5.1. Li-Ion Battery Research	4564		
5.2. Electroanalytics	4565		
5.3. Polymerization	4565		
5.3.1. Electropolymerization	4565		
5.3.2. Radical and Ionic Polymerizations of Organic Carbonates in Neat Solutions	4568		

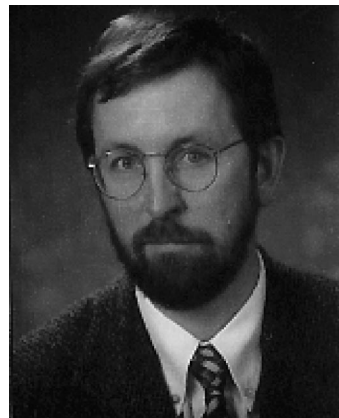
1. Introduction

A solvent is one key component in a chemical transformation. As a reaction medium it controls the interactions between reaction partners through heat transfer and intermolecular forces (stability of transition states and intermediates) and forms a solvate shell around the solute. Its interaction with the solute plays a pivotal role for achieving conversion and selectivity.¹ However, history has revealed that new solvent innovations must be critically analyzed. Today a new solvent must introduce advantages to a reaction as well as being environmentally acceptable.² This acceptance of new or alternative solvents is determined by the 12 principles, which form the background of green chemistry.³ The summarized aims of the principles are the reduction of toxic auxiliaries and reagents or solvents, prevention of waste production, and use of energy-efficient processes. One aspect of this field is research in alternative or so-called “green” solvents⁴ like ionic liquids (ILs) and their enhanced application in industrial processes.^{5,6} In addition to ionic liquids,

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supercritical fluids like supercritical carbon dioxide^{7–9} ($T_C = 31.0\text{ }^\circ\text{C}$; $p_C = 73.8\text{ bar}$) have become popular alternative solvents. Under ambient conditions water,^{10–13} fluorinated solvents,^{14–17} and polyethers^{18–20} are well established as alternative solvents in synthesis and catalysis. One aim of using such solvents is to reduce solvent volatility and toxic byproduct or waste following the reaction. Due to their commonly higher boiling and flash points alternative solvents are ideally suited to replace toxic and easy-flammable volatile organic compounds (VOC) as solvents. In addition, an environmentally benign reaction medium provides a platform for further reaction development (e.g., enhance the rate of reaction or solubility of gases within the medium, allow catalyst recycling). Unfortunately, most of the listed alternative solvents are only available in limited quantities and are expensive in comparison to VOCs. Therefore, they are in most cases only suitable for smaller industrial applications with high-priced products like pharmaceuticals or fine chemicals.^{21,22}

It is important to note that definitions of sustainable, alternative, and so-called “green” solvents can be different. A commonly used VOC can be the most sustainable solvent



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for a process or reaction if the sum of its use minimizes the used energy for the synthesis and disposal of this solvent as well as the amount of waste produced in the process. Alternative solvents often replace existent solvents (often VOCs) in processes without diminishing the efficiency of the process. Thus, often publications deal only with a narrow view of the exemplified process without dealing with the overall life cycle of these solvents in a process. Finally, the term “green” solvents is often used to characterize their low toxicity, low vapor pressure, or biodegradability. For example, fluorinated solvents offer a broad spectrum of applications as nonpolar solvents but are not biodegradable.^{23–26} With the huge number of possible combinations,



Figure 1. Equilibrium between carbonic acid with water and carbon dioxide.

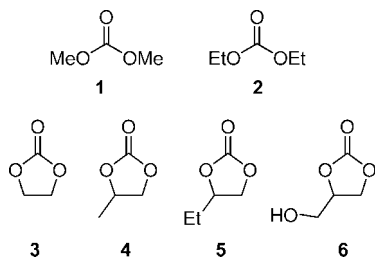


Figure 2. Organic carbonates representatives that have been used as solvent: (1) dimethyl carbonate (DMC), (2) diethyl carbonate (DEC), (3) ethylene carbonate (EC), (4) propylene carbonate (PC), (5) butylene carbonate (BC), (6) glycerol carbonate (GyC).

ILs offer a large variety of different characteristics. Although all ILs possess negligible vapor pressures and are inflammable, the mostly unknown toxicity is a striking problem for using them as “green” solvents.²⁷ Additionally, the biodegradability of an IL depends strongly on the combination of cation and anion.²⁸

Alternatively, new solvents can be derived from feedstock with a lower environmental footprint.²⁹ One impressive example is γ -valerolactone from nonedible carbohydrates.³⁰ Organic solvents with a reduced environmental footprint are of great interest for industrial and pharmaceutical applications (first-generation green solvents).³¹ They can replace VOC in existing processes without having a significant impact on the reaction. Environmental, health, and safety (EHS)³² and life-cycle assessment (LCA)³³ tools have been developed in recent years to search for solvent alternatives.³⁴ In many instances it is possible to find suitable alternatives for VOCs (e.g., recently Pfizer published an internal list of solvents as substitutes for toxic or flammable solvents³⁵). Although progress could be made by prevention of halogenated solvents or highly flammable solvents like diethyl ether there is still a demand to replace polar, nonprotic solvents like *N,N*-dimethylformamide (DMF) or *N*-methylpyrrolidin-2-one.³⁶ In addition to their toxicity, these solvents cause problems in water-intensive workup and possible NO_x formation.

Organic carbonates represent an alternative for these solvents. This interesting class of molecular organic solvents has been known since the 1950s. In contrast to carbonic acid, which is in an equilibrium with water and CO_2 (Figure 1),³⁷ organic carbonates are stable under ambient conditions (carbonic acid is only stable in the absence of water and at low temperature³⁸).

They offer various advantages as solvents. (1) They are available in large amounts and at low prices (in 2007 carbonates reached a worldwide production of about 1 megaton).³⁹ (2) As polar solvents they offer a suitable liquid temperature range (e.g., for propylene carbonate, mp = -49 °C, bp = 243 °C). (3) They display only low (eco)toxicity and are completely biodegradable. Despite their advantages it is remarkable that organic carbonates are known primarily as solvents for electrochemical and extractive applications. In recent years, however, they were spotlighted as possible alternatives to replace VOCs. Six carbonates which have been identified to be especially suitable as solvents are shown in Figure 2.

Reviews covering the production of organic carbonates from carbon to 2007⁴⁰ and reviews of their use as synthetic

building blocks to 1996³⁷ can be found in the literature. In addition, their use in lithium batteries was published in a review in 2004.⁴¹ To date, their use as polar, aprotic solvents has not been reviewed. Therefore, the present review gives a compendium of organic carbonates as alternative or so-called “green” solvents. We will focus on the representatives in Figure 2 and their use in reactions focusing on catalysis. Transition information about the physicochemical properties should help to select the right organic carbonate as solvent in reactions and, especially, larger processes. In addition, sections 2, 5, and 7 highlight recent research in their syntheses and application as a solvent in electrochemical applications of Li batteries, electropolymerizations, cleaning processes, and analytics. Together with formerly published reviews on the synthesis and use of organic carbonates as reagents this work will fill in the gaps to get the overall picture. Since organic carbonates are already used as solvents on an industrial scale, this review also includes a large number of patents.

2. Synthesis of Organic Carbonates

2.1. Outline

Today organic carbonates are produced in multiton scale from various companies. Major products like dimethyl, propylene, or ethylene carbonate are available for about \$2500/ton.⁴² Two general pathways have been established to obtain cyclic and linear carbonates. It should be noted that although organic carbonates are “green” solvents, this does not hold for their syntheses. The industrial routes to linear carbonates mainly use phosgene as a starting material, while cyclic carbonates are synthesized from propylene oxide. Both compounds are classified as highly toxic chemicals. Therefore, a great deal of research has focused on a more direct synthesis using alcohols directly for the synthesis.⁴⁰ A general overview is given in Figure 3.

2.2. Recent Trends in Synthesis

2.2.1. Strategies

The synthesis of noncyclic carbonates is mainly carried out by reaction of phosgene with 2 equiv of methanol (Figure 4).³⁷ In addition to phosgene as starting material, another major drawback in this reaction is the formation of corrosive HCl, which has to be recycled or trapped as a salt (e.g., with pyridine).⁴³

Ideally, carbonates would be produced directly from alcohols by condensation with CO_2 . However, this procedure

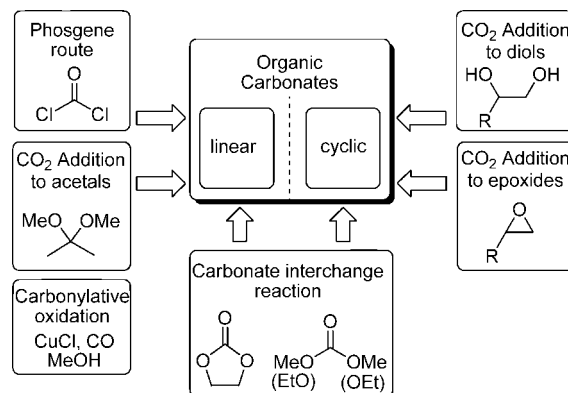


Figure 3. Commonly used building blocks in the synthesis and modification of organic carbonates.

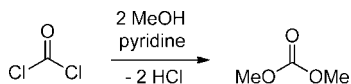


Figure 4. Synthesis of dimethyl carbonate using phosgene.

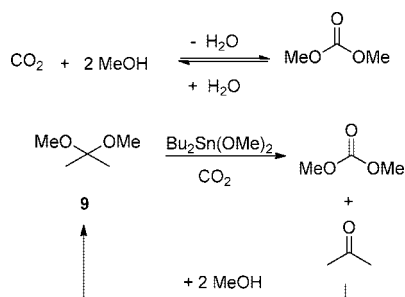


Figure 5. Synthesis of dimethyl carbonate using acetals.

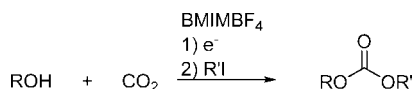


Figure 6. Electrochemical synthesis of alkyl carbonates.

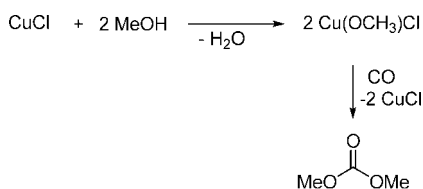


Figure 7. Oxidative carbonylation using copper(I) chloride as catalyst.

suffers from the formation of water as part of the equilibrium. To overcome this drawback, the use of acetals, e.g., **9**, in supercritical carbon dioxide (scCO₂) has been suggested for the synthesis of dimethyl carbonate.⁴⁴ In the presence of tin catalysts yields up to 88% have been achieved (Figure 5). The byproduct acetone can be recycled with 2 equiv of methanol to give acetal **9**. A study on the influence of carbon dioxide pressure and reaction temperature was published by the group of Sakakura.⁴⁵

Electrochemical synthesis of dialkyl carbonates with CO₂ and the corresponding alcohol in the presence of an excess of methyl or ethyl iodide as an alkylating agent was published by Lu and co-workers (Figure 6).⁴⁶ When 1-butyl-3-methylimidazolium tetrafluoroborate (BMIMBF₄) was used as an ionic liquid to activate CO₂ they obtained yields up to 74% dimethyl carbonate (DMC) and 67% for diethyl carbonate (DEC) through formation of the anionic formation of a CO₂^{•-} radical.

Another method for the synthesis of DMC is the oxidative carbonylation of methanol in the presence of copper(I) chloride and carbon monoxide (Figure 7). In contrast to other popular metals, such as mercury and palladium, copper is directly reoxidized during the reactions.⁴⁷ The use of ionic liquids (IL) has a promoting effect on the formation of dimethyl carbonate in the presence of copper(I) chloride.⁴⁸ Without the use of ionic liquids a conversion of only 9% was obtained. However, in the presence of [BPy]BF₄ the yield was increased to 17%.

Carbonate synthesis through the carbonylation reaction can be also performed with a Cu-exchanged zeolite Y catalyst. The mechanism of this reaction has been studied by Bell et al.⁴⁹ In another approach, the group of Li used a zeolite-encapsulated Co-Schiff base complex which could be

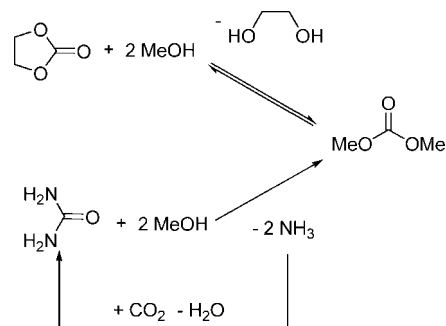


Figure 8. Carbonate interchange reaction in the synthesis of DMC.

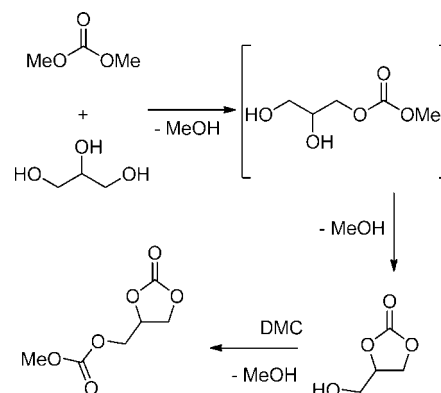


Figure 9. Synthesis of glycerol carbonate via transesterification with DMC.

recycled up to five times without losing chemoselectivity in the formation of DMC.⁵⁰

Another synthetic pathway to organic carbonates involves transesterification of ethylene carbonate using a base (e.g., hydroxides, alkoxides, hydrides, alcoholate amides) in the presence of aliphatic or aromatic alcohols.⁵¹ Since the formation of ethylene and propylene carbonate from epoxides and carbon dioxide is well established, the transesterification is a suitable synthetic pathway to dimethyl carbonate (Figure 8) without using phosgene. An alternative pathway leading to DMC began from urea.^{52–57} Interestingly, the ammonia formed during the reaction could be used to regenerate urea provided that water could be removed efficiently.⁵⁸

Several different catalysts have been found to accelerate this reaction. Activated dawsonites,⁵⁹ homogeneous zirconium, titanium, and tin catalysts,⁶⁰ titanium silicate molecular sieves,⁶¹ Mg–Al–hydrotalcite materials,⁶² smectite systems with Mg or Ni content,⁶³ and CaO and MgO as catalysts⁶⁴ gave the desired linear carbonate under mild conditions in good to excellent yields.

The carbonate interchange reaction can also be applied to obtain diphenyl carbonate, which is a valuable monomer for the synthesis of polycarbonates.^{65,66} Furthermore, the transesterification is up to date the commonly used route to glycerol carbonate (GyC).⁶⁷ The reaction with dimethyl, diethyl,⁶⁸ or propylene carbonate and glycerol is catalyzed by an immobilized lipase from *Candida antarctica* (Figure 9) and yields glycerol carbonate in low enantiomeric excess (13% ee) in nearly quantitative yield.⁶⁹ However, care must be taken to avoid an overreaction to glycerol carbonate ester. It can be suppressed with an appropriate ratio of DMC and glycerol by exactly 1:1.

Dimeric tin catalysts bearing organic moieties are also suitable in the transesterification of diethyl carbonate to

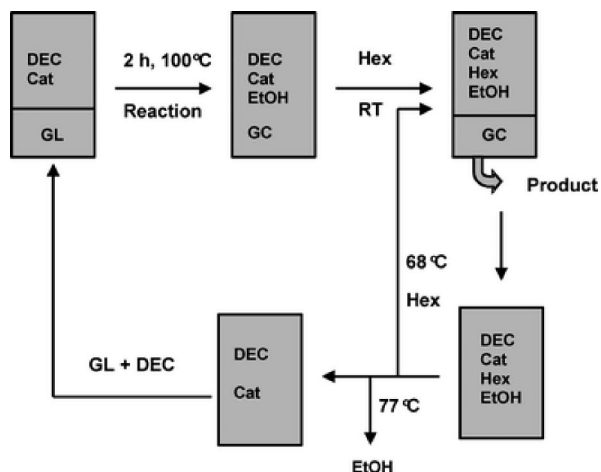


Figure 10. Continuous GyC synthesis using the transesterification with DEC. Reprinted with permission from ref 70. Copyright 2009 Royal Chemical Society.

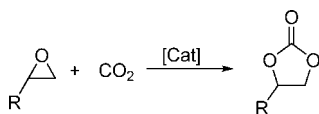


Figure 11. Synthesis of cyclic carbonates through cyclization with carbon dioxide.

glycerol carbonate. The process can be applied in a continuous manner for up to five cycles in nearly quantitative yields (Figure 10).⁷⁰

The addition of carbon dioxide to epoxides (e.g., ethylene, propylene, and butylene oxide) is an important industrial process for the synthesis of cyclic carbonates and has been applied with carbon dioxide pressures between 5 and 150 bar (Figure 11).⁴⁰ Several recent improvements in the synthesis of these epoxides have been published. In particular, propylene oxide can be synthesized today from propene using hydrogen peroxide as the sole oxidant.⁷¹ Thus, a one-pot synthesis from propene to propylene carbonate has been realized.⁷²

Although the reaction of ethylene and propylene oxide and CO₂ is run on an industrial scale, there is still an ongoing search for more active catalysts (e.g., cyclodextrines,⁷³ new salen complexes,⁷⁴ and magnetic iron nanoparticles supported on an ionic liquid catalyst⁷⁵). This synthetic pathway is not limited to simple alkyl groups at the epoxide. Thus, it can be also used for epoxides fixed in large molecular structures, such as lipids.^{76,77} In general, this reaction can be accomplished in supercritical carbon dioxide, which simplifies the workup due to the fact that most carbonates have only a low solubility in scCO₂.⁷⁸ Recently, the synthesis of several organic carbonates was accomplished in water using PPh₃BuI as catalyst.⁷⁹ Alternatively, carbon dioxide has been used under atmospheric pressure to obtain the desired carbonate (EC and PC) from the corresponding epoxide.⁸⁰ Most recently, the group of North published the use of ‘waste carbon dioxide’ in the presence of aluminum–salen catalysts. The optimized catalyst achieved turnovers of 26 h⁻¹ and converted 66% of the waste carbon dioxide to the carbonate at a temperature of 150 °C.⁸¹ Interestingly, the catalyst could be reactivated and reused over 31 cycles.

The direct enantioselective synthesis of cyclic carbonates, especially propylene carbonate, is difficult. Recent results using cobalt–salen complexes gave PC with moderate enantioselectivities of up to 56% (Figure 12).^{82,83} A modified

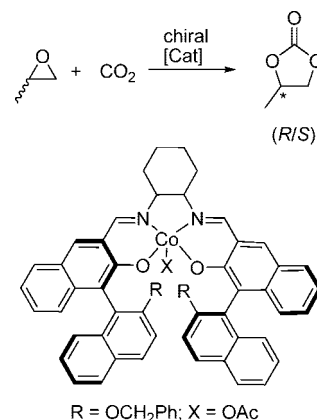


Figure 12. Asymmetric synthesis of propylene carbonate with a chiral Co–salen complex.

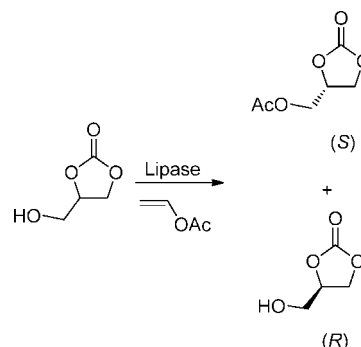


Figure 13. Lipase-catalyzed resolution of glycerol carbonate with vinyl acetate.

cobalt–salen complex, bound on a chiral polymer, has been used efficiently and obtained the carbonate with 73% ee.⁸⁴ The polymeric catalyst could be recycled 10 times without loss of enantioselectivity. The use of a bifunctional chiral cobalt–salen catalyst could increase the enantioselectivity up to 78% in the synthesis of PC. Unfortunately, the activity of the catalyst is low, and only 23.5% of PC was observed after 48 h reaction time.⁸⁵

Alternatively, a lipase-catalyzed kinetic resolution of organic carbonates with vinyl acetate is possible, providing up to 90% ee of the recovered starting material and up to 65% ee for the acetate.⁸⁶ In this case, however it is necessary that the carbonate contains additional functional groups at the side chain, like glycerol carbonate (Figure 13). Finally, enantiopure cyclic carbonates can be obtained by enzyme-mediated stereoselective hydrolysis from racemic mixtures.^{87,88} Good enantioselectivities (up to 80%) could be achieved for the cyclic carbonate. However, those hydrolyses are limited to cyclic carbonates with longer side chains.

As mentioned for linear carbonates, the direct synthesis of organic carbonates from the corresponding alcohol is difficult because the equilibrium favors the starting materials. Recently, pathways to cyclic carbonates starting from 1,2-diols have been investigated. In particular, the direct synthesis of glycerol carbonate would provide a more direct synthesis, since the current methods rely on carbonate interchange reactions (Figure 14).³⁷ An initial study using molecular sieves and a tin catalyst (Sn(OCH₃)₂) gave only a low yield of glycerol carbonate.⁸⁹ Better results were obtained in the presence of zeolites and ion-exchange resins in supercritical carbon dioxide.⁹⁰ Under these conditions, the yield could be enhanced to 32%.

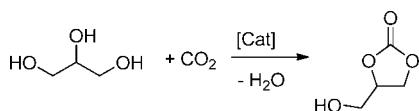


Figure 14. Addition of carbon dioxide to glycerol.

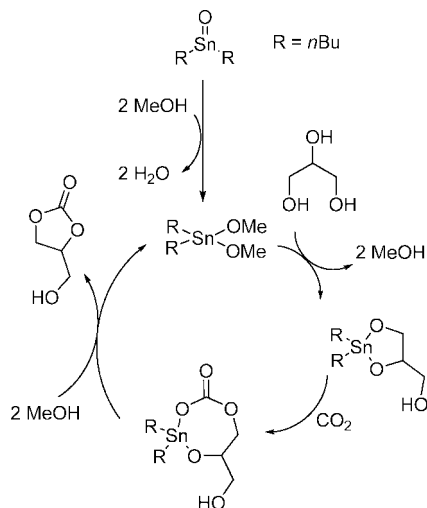


Figure 15. Proposed reaction mechanism for the Sn-catalyzed addition of CO₂ to glycerol in the presence of methanol.

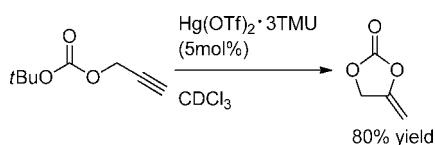


Figure 16. Hg-catalyzed synthesis of cyclic enol carbonates, with TMU = *N*-(4-methoxybenzyl)-*N'*-(5-nitro-1,3-thiazol-2-yl)urea.

An interesting approach is the reaction of glycerol in methanol in the presence of Bu₂SnO and zeolites as catalyst.⁹¹ A yield of 35% of glycerol carbonate could be isolated after 4 h. The reaction pathway is shown in Figure 15.

The formation of propylene carbonate directly from 1,2-propylene glycol is also difficult to effect. High chemoselectivities are possible in this reaction, but the yield of propylene carbonate suffers from the low catalyst activity.^{92–98} Improved results were obtained with 3-chloropropanol. Thereby, Xi et al. achieved propylene carbonate with 95% selectivity and 98% conversion for 3-chloropropanol in the presence of organic or inorganic bases.⁹⁹

Finally, only a few examples address formation of simpler organic carbonates through transition-metal-catalyzed ring-closure reactions. Since the starting material for those reactions are rather expensive or not easy available, the reactions have been only applied for special carbonates. One example, the mercury-catalyzed ring formation of *tert*-butyl propargyl carbonate to exomethene ethylene carbonate is depicted in Figure 16.¹⁰⁰

The current 'state-of-the-art' for large-scale production of organic carbonates involves either epoxides or phosgene.⁴⁰ As a result, it is difficult to consider organic carbonates as environmentally benign solvents. Currently, the oxidative carbonylation of methanol is the most promising method for the industrial syntheses of linear carbonates. Other pathways, especially the syntheses from 1,2-diols, will require additional development prior to industrial implementation. The use of dehydrating agents, like orthoesters, may prove essential for using environmentally benign alcohols in the synthesis of

Table 1. Transport and Thermodynamic Properties

organic carbonate	bp [K]	<i>d</i> (293 K) [g/cm ³]	viscosity (298 K) [cP]
DMC	363 ^b	1.07 ^b	0.590 ^b
DEC	399 ^b	0.98 ^b	0.753 ^c
EC	521 ^d	1.34 ^{a,d}	2.56 ^{a,d}
PC	515 ^d	1.20 ^d	2.50 ^d
BC	524 ^d	1.14 ^d	3.14 ^c

^a For the undercooled liquid state. ^b Reference 104. ^c Reference 100. ^d Reference 105.

organic carbonates. Since they are expensive agents, it is necessary to find an efficient recycling process for the organic dehydrating agents.¹⁰¹ Progress in this field during recent years is encouraging, especially regarding the fact that linear carbonates are potential fuel additives. However, for this application a daily amount of 5000–10 000 barrels is estimated.¹⁰²

3. Physico-Chemical Properties

3.1. Thermodynamic Properties

With their increased use, the physical-chemical properties and phase behavior of organic carbonates are receiving more attention, since they are critically important for their applications as solvents.

The industrially important dialkyl carbonates are all colorless liquids. Ethylene carbonate is a low melting solid with a melting point of 36.4 °C. Densities of organic alkyl carbonates are very close to those of water. For example, the density of DMC at room temperature is 1.07 g/cm³ (see Table 1). However, densities of cyclic carbonates (EC, PC, BC) are larger than 1.0 g/cm³. With a density of 1.34 g/cm³, undercooled EC provide the most dense carbonate at 293 K.

Transport properties play an important role in chemical reactions and separations. Of particular importance are the viscosity coefficients. According to the data presented in Table 1, alkyl carbonates possess acceptable viscosities. For example, viscosities of the open-chained alkyl carbonates such as dimethyl carbonate or diethyl carbonate are higher than the viscosity of acetone (0.320 cP) but lower than the viscosity of water (0.891 cP) at 298 K. Viscosities of the cyclic carbonates (EC, PC, BC) are somewhat higher (2.5–3.1 cP), but they are on the level of commonly used solvents such as *n*-butanol (2.99 cP).¹⁰³

In several investigations the transpiration method has been used to extend the range of vapor pressure data down to ambient temperature, where the data are especially relevant for the assessment of their fate and behavior in the environment.¹⁰⁶ The experimental saturated vapor pressures of the carbonates were correlated with the temperature-dependent equation

$$R \cdot \ln p_i^{\text{sat}} = a + \frac{b}{T} + \Delta_f^{\text{g}} C_p \cdot \ln \left(\frac{T}{T_0} \right) \quad (1)$$

where *a* and *b* are adjustable parameters and Δ_f^g C_p is the difference between the molar heat capacity of the gaseous and the liquid phase. T₀ is an arbitrarily chosen reference temperature (T₀ = 298.15 K in this work). Taking into account the very good agreement between vapor pressure data reported in our work and the literature the experimental data were regressed together to develop correlations ac-

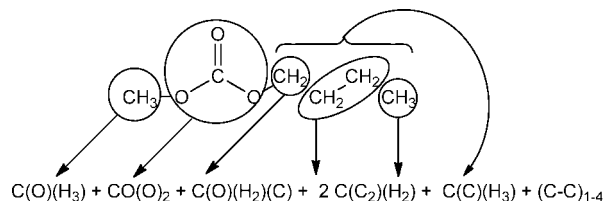


Figure 17. Group-additivity theory for butyl methyl carbonate.

curately describing the vapor pressure of alkylene carbonates over a temperature range from ambient temperature to the normal boiling point.¹⁰⁷ The coefficients of the vapor pressure correlation (eq 1) for alkylene carbonates as well as the recommended molar enthalpies of vaporization values were presented in several publications.¹⁰⁸ Furthermore, summaries of the consistent and reliable vaporization enthalpies, $\Delta_f^g H_m$, of linear and cyclic alkylene carbonates derived from vapor pressure or calorimetric measurements were given by Ver-evkin and co-workers.¹⁰⁹ Experimental data on the critical temperature and critical pressure of alkyl carbonates are very limited. These data were measured only for propylene carbonate by a flow method with ultralow residence times.¹¹⁰

The enthalpy of formation in the gaseous phase of any compound is made up of two contributions: $\Delta_f H_m^g = \Delta_f^g H_m + \Delta_f H_m^l$, where $\Delta_f^g H_m$ is the enthalpy of vaporization and $\Delta_f H_m^l$ is the enthalpy of formation in the liquid state. An isoperibol bomb calorimeter is usually used to measure the energy of combustion and to obtain the enthalpy of formation, $\Delta_f H_m^l$, of dialkyl carbonates. The detailed experimental procedure has been described in the literature.^{111,112} A detailed, critical analysis of the literature data on enthalpies of formation together with consistency tests has also been reported in these two studies.

3.1.1. Further Property Studies

The group-additivity methods serve as a valuable tool for many scientists and engineers whose research involves thermodynamic characterization of elementary and overall reaction processes. New experimental thermochemical results for alkylene carbonates have been determined.^{111,112} Benson's group-additivity method seems to have the most widespread acceptance at present and the overall best record for reliability of estimation techniques.¹¹³ A group is defined by Benson¹¹³ as "a polyvalent atom (ligancy ≥ 2) in a molecule together with all of its ligands."

The group-additivity values (GAV) which are specific for alkanes [$C(C)(H_3)$, $C(C_2)(H_2)$, $C(C_3)(H)$, $C(C_4)$] and correction for 1–4 C–C interactions ($(C-C)_{1-4}$) and those values specific for carbonates [$(CO)(O)_2$, $C-(C)(H)_2(O)$, $C-(C)_2(H)(O)$, $C-(C)_3(O)$] have been calculated (Figure 17).^{111,112} For example, for the prediction of the enthalpy of formation of methyl butyl carbonate the contributions in Figure 17 should be accounted for.

Original work by Benson¹¹³ does not provide group-additivity values for calculation of vaporization enthalpies, $\Delta_f^g H_m$, at 298 K. The same definition of groups as those for enthalpies of formation were applied for prediction of vaporization enthalpies of carbonates.^{108a} Comparison of predicted and experimental data has revealed that the accuracy of the predicted vaporization enthalpies of carbonates is on average within 1 kJ mol^{-1} of data from the experiments.

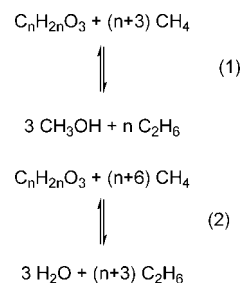


Figure 18. Reactions of carbonates for the calculation of enthalpies.

3.1.2. First-Principles Calculations

Use of the modern first-principle calculations allowed the validation of the mutual consistency of the experimental data. The remarkable ability of the ab initio methods to predict gaseous enthalpies of organic carbonates accurately has been recently demonstrated.^{111,112} The enthalpies of formation of dialkyl carbonates have been calculated with the help of the standard atomization reactions (Figure 18) as well as using two bond separation reactions.

A comparison of the calculated and experimental data is given in the literature.^{111,112} Enthalpies of formation of dialkyl carbonates derived with the help of the atomization procedure and both of the bond separation reactions (reactions 1 and 2) are practically indistinguishable and in excellent agreement with the experimental data. Due to high time consumption for ab initio calculations, an alternative group-additivity procedure (Figure 17) still remains helpful for predicting thermochemical properties of alkylcarbonates.

Nowadays, quantum-mechanical calculations are widely used for theoretical studies of reaction mechanisms, e.g., for the reduction of ethylene carbonate¹¹⁴ or to elucidate the conformational behavior of carbonates.¹¹⁵ Self- and cross-associations of cyclic as well as linear carbonates such as ethylene carbonate, propylene carbonate, and dimethyl carbonate were investigated with ab initio and DFT methods.¹¹⁶ In order to develop an ab initio force field for polycarbonates, extensive quantum-mechanical calculations were carried out on several model compounds: carbonic acid and methyl and dimethyl carbonate.¹¹⁷ Combination of the modern first-principle calculations together with the experimental thermochemical methods makes it possible to understand the interrelations of structure and energetics of organic carbonates and predict the thermochemical properties of a broad range of organic compounds containing a carbonate moiety.

3.2. Mixtures with Other Fluids or Gases

Recently, the group of Börner published their work on homogeneous asymmetric hydrogenation.¹¹⁸ They compared the results in PC with other solvents like methanol, tetrahydrofuran, and methylene chloride and obtained superior results in the organic carbonate. The solubility of the reaction gas in the phase of the reaction is central for development and design of such processes. The solubility of hydrogen in BC was determined at 283.3, 298.2, and 323.1 K with a high-pressure view-cell technique based on the synthetic method up to a maximum pressure of 9.3 MPa. The solubility increases with increasing temperatures, as the gas molarity at $p = 6.0 \text{ MPa}$ increases to $0.070 \text{ mol} \cdot \text{kg}^{-1}$ at 283.3 K and $0.093 \text{ mol} \cdot \text{kg}^{-1}$ at 323.1 K. An extended modification of Henry's law was employed to correlate the solubility

pressure, and the final results for the Henry's constant (at zero pressure) of hydrogen in BC was correlated. A literature survey revealed that the hydrogen solubility in BC is considerably higher than in PC.¹¹⁹ The solubility of carbon dioxide in propylene carbonate, ethylene carbonate, dimethyl carbonate, diethyl carbonate, and mixtures of these components has been measured at temperatures from 275 to 333 K at atmospheric pressure. The Henry's law constants for the dissolution of CO₂ in these solvents have been deduced from the solubility data. The value of the Henry's law constants increases in the following order: DEC < DMC < PC < EC, which is identical to the order of the Hildebrand parameters of the corresponding solvents.¹²⁰ Trejo et al. studied solubilities of carbon dioxide and hydrogen sulfide in propylene carbonate at several temperatures and pressures. Values of the Henry's law constant and heat of solution were derived from the solubility data. The experimental results have been correlated with the Soave–Redlich–Kwong equation of state using a binary interaction parameter.¹²¹

3.2.1. Gas–Liquid Phase Equilibria and Activity Coefficients in Carbonate-Containing Mixtures

Thermodynamic activity coefficients are a measurement for the deviation of ideal behavior in liquid mixtures. Values of activity coefficients and molar excess Gibbs energies are required for the calculation of the thermodynamic equilibrium constants of chemical reactions as well as for modeling of separation processes. As a rule, activity coefficients are obtained from the vapor pressure measurements of binary or ternary mixtures. There are two kinds of vapor pressure measurements: static and dynamic.

3.2.2. Static Method Measurements

Extended experimental studies of mixtures containing carbonates have been performed by Jose and co-workers using the static apparatus.¹²² The vapor pressures of binary mixtures of DMC with alkynes, alkanes, and aromatics were measured. The data were correlated with the Antoine equation. Molar excess Gibbs energies were calculated, and activity coefficients for several constant temperatures were fitted to a fourth-order Redlich–Kister equation. The equimolar molar excess Gibbs energy values calculated from the vapor pressure data of the mixtures containing saturated hydrocarbons are the highest ca. 1200 J mol⁻¹ for heptane and ca. 1170 J mol⁻¹ for cyclohexane; the molar excess Gibbs energies value decreases to ca. 895 J mol⁻¹ for hex-1-ene, ca. 520 J mol⁻¹ for hex-3-yne, and ca. 460 J mol⁻¹ for hex-2-yne. The mixture containing hex-1-yne has a much smaller molar excess Gibbs energy, ca. 290 J mol⁻¹ (all molar excess Gibbs energies values are given at 303.15 K). The molar excess enthalpies, estimated from the temperature dependence of the molar excess Gibbs energy, follow the same trend. These results reflect the existence of fairly strong interactions between the polar O(C=O)O group of DMC and the carbon–carbon double or triple bonds of the unsaturated hydrocarbons.

Isothermal vapor–liquid equilibria (VLE) data at 333.15 K are measured for the ternary system dimethyl carbonate with ethanol and 2,2,4-trimethylpentane and DMC with 1-propanol, 1-butanol, or methanol. The experimentally obtained binary and ternary vapor–liquid equilibrium data were correlated with different activity coefficient models.

These data were correlated with the Redlich–Kister equation for the binary systems.¹²³

3.2.3. Dynamic Method: Isobaric Measurements

Using the dynamic method, isobaric vapor–liquid equilibria (VLE) have been experimentally measured for binary systems of DMC with methanol or ethanol and DEC with ethanol or DMC. Interaction parameters related to the carbonate group (–OC(O)O–) in the UNIFAC model have been determined using the VLE data, implying a strong nonideality of the systems involving alkanes and alkyl carbonates.¹²⁴ Isoobaric VLE have been studied for the binary systems containing DMC and DEC with 2-propanol, 2-butanol, acetone, 2-butanone, 2-pentanone, methanol, ethanol, 1-propanol, 1-butanol, 1-pentanol, and methylcyclohexane at 101.3 kPa. The activity coefficients were calculated to be thermodynamically consistent and correlated with the Wilson, NRTL, and UNIQUAC equations. ASOG and UNIFAC group contribution methods were developed to predict these binary systems.¹²⁵

Isoobaric VLE have been determined for the binary systems of dimethyl carbonate and various other solvents under ambient pressure in Ellis equilibrium. The data have been correlated by means of both the Wilson equation and the NRTL equation. The experimental results demonstrated that the systems of DMC with ethanol and DMC with propylene glycol show strong positive deviations from ideality and that the systems of DMC/DEC and DMC/PC are close to ideality.¹²⁶ Furthermore, several boiling temperatures and activity coefficients have been investigated for the binary mixtures,^{127–129} which are also useful in the synthesis of DMC by transesterification.¹³⁰

3.2.4. Dynamic Measurements: Isothermal Methods

The vapor–liquid equilibrium (P , T , x) of water with ethylene carbonate was measured by the ebulliometry method. The results were correlated with a NRTL model,¹³¹ while isothermal VLE were measured to obtain the molar excess Gibbs energies and activity coefficients¹³² or have been correlated by the Wilson equation.¹³³

3.2.5. Liquid–Liquid Equilibrium (LLE) of Mixtures Containing Organic Carbonates

To use carbonates as solvents, it is necessary to be able to predict their behavior in extraction processes in terms of their miscibility with other solvents. In addition, it is important to know how products of reactions will be distributed in the solvent. Ethylene carbonate is infinitely soluble in water. Propylene carbonate is soluble in water only to the extent of 25.0 g of propylene carbonate/100 g of water (at 25 °C). Butylene carbonate is less soluble, as only 7.0 g of butylene carbonate will dissolve in 100 g of water (at 25 °C). Dimethyl carbonate and diethyl carbonate are only sparingly soluble in water. They are soluble in many organic solvents, particularly polar solvents, such as esters, ketones, ethers, alcohols, and aromatic hydrocarbons. The lower molecular weight aliphatic carbonates form azeotropic mixtures with several organic solvents.³⁷ Recently, LLE of water/propylene carbonate and water/butylene carbonate systems were carefully measured and the results were correlated with a NRTL model.¹³¹ The same working group determined basic physicochemical properties and Hildebrand

and Hansen solubility parameters.¹³⁴ Furthermore, several LLE parameters are available in the literature from the extraction of aromatics and phenols.¹³⁵ In the past decade the number of publications in the field of physicochemical properties of binary and ternary mixtures using suitable fitting equations (UNIFAC, UNIQUAC, Redlich–Kister, and Cibulka equations) has increased steadily and offer today a comprehensive overview.^{136,137}

3.2.6. Solid–Liquid Phase Equilibria (SLE) of the Mixtures Containing Carbonates

Temperature–composition values of liquid–solid equilibrium were measured calorimetrically and tabulated for 10 binary solutions of EC, PC, DMC, and DEC.¹³⁸ Furthermore, heat capacity (C_p), temperature (T_m), and enthalpy of fusion ($\Delta_{\text{fus}}H$) were measured for the five carbonates, with the C_p values fitted with polynomial functions. On the basis of these T_m and $\Delta_{\text{fus}}H$ values and polynomial functions of C_p , the binary phase diagrams were fitted with thermodynamic nonideal solution models for an evaluation of the model parameters. The results of the evaluation were tabulated and discussed as an indication of the nature and strength of the molecular interactions between different carbonates. These interactions were shown to determine many of the important features of the binary phase diagrams.

3.2.7. Prediction of the Fluid-Phase Equilibria of the Mixtures Containing Carbonates

Since it is impossible to measure all of the possible combinations of systems containing carbonates, it is necessary to make measurements on selective systems to provide results that can be used to develop correlations and test predictive methods. There are a number of techniques used to predict LLE and the mutual solubility of conventional organic solvents. For example, the DISQUAC interaction parameters for the linear organic carbonate–alkane, carbonate–cyclohexane, carbonate–benzene or –toluene, and carbonate– CCl_4 contacts were revised on the basis of new experimentally obtained data of vapor–liquid equilibrium for DMC or DEC with n -alkane mixtures.¹³⁹ The quasi-chemical interchange coefficients for carbonate–alkane or –cyclohexane contacts and the purely dispersive interchange coefficients for carbonate–benzene or –toluene and carbonate– CCl_4 contacts show a relatively weak steric effect. The model provides a fairly consistent description of the low-pressure fluid-phase equilibrium (VLE, LLE, and SLE) and related excess functions (Gibbs energy and enthalpy) using the same set of parameters. Literature data on enthalpies of mixing and the vapor–liquid equilibrium of organic linear carbonates + n -alkanes mixtures was examined on the basis of the UNIFAC model.¹⁴⁰ The predictions were achieved with mean deviations of 4.4% for the excess Gibbs energies and 2.3% for the excess enthalpies. Further experimental data have been achieved using the following equations: Soave–Redlich–Kwong (SRK), Peng–Robinson (PR), Patel–Teja (PT), and Dohrn–Prausnitz (DP).¹⁴¹

3.2.8. Molecular Dynamic Simulations of Carbonates and Their Mixtures

One of the modern principal tools in the theoretical study of molecules is the method of molecular dynamics simulations (MD). This computational method calculates the time-

dependent behavior of a molecular system. MD simulations are able to provide detailed information on the fluctuations and conformational changes in pure compounds and their mixtures.

Monte Carlo simulations have been used to investigate molecular association in pure liquid EC and PC.¹⁴² Standard force fields have been developed in order to reproduce accurately experimental pure liquid properties. The resultant force fields yielded average errors of 1–2% in computed densities and heats of vaporization. A thorough characterization of the liquid structures was performed with radial distribution functions, energy distributions, and dipole–dipole correlations. The electrostatic interactions in condensed phase cause the neighboring molecules to have a preferential head to tail alignment of the dipoles. In contrast, the most energetically favored configuration for the EC and PC dimers in the gas phase exhibited antiparallel dipoles. Furthermore, experiments and simulations were carried out in PC, DMC, EC, and DEC in the liquid state at various temperatures and gave reasonable results.¹⁴³

In summary, the knowledge gap between physicochemical properties of organic carbonates in the pure state and as mixtures with gases, other liquids, and solids and their use as solvents has been closed by intensive thermodynamic studies. Today, simulations allow a fair prediction of unknown organic carbonate mixtures, while various mixtures have been measured using the whole spectra of existing methods. They form the base for further investigation and the use of organic carbonates as alternative solvents.

4. Handling

For all-day usage of a solvent in the laboratory or on the industrial scale it is necessary that the solvent meets several specifications. First, purification must be possible using standard purification methods without the need of special equipment. Unfortunately, the high boiling points of environmentally benign solvents require harsh conditions for distillation (high temperature and vacuum) or in the case of the ionic liquids alternative purification methods. Stability at ambient conditions is also an important factor for the use of a solvent in large amounts. It has to be noncorrosive and air and moisture stable and should be stable toward irradiation, acids, and bases.

Organic carbonates are stable under ambient conditions, can be stored under an air atmosphere, and are not affected by moisture. Unfortunately, until now only calculated data for the photodegradation of propylene carbonate exist in the literature with a half time of 4 days if hydroxyl radicals are used as a sensitizer.¹⁴⁴ The decomposition of PC via an aqueous acidic medium was investigated by the group of Novák.¹⁴⁵ The decomposition of PC and the rate of formation of allylic alcohol and propane-1,2-diol was increased many times by addition of aqueous solutions of LiClO_4 or HClO_4 (Figure 19). Furthermore, the pyrolytic behavior of organic carbonates was determined by Williams et al.¹⁴⁶

Precise boiling and melting points of organic carbonates have been determined, allowing standard purification (e.g., vacuum distillation). However, the rate of decomposition under distillation conditions is increased by the amount of

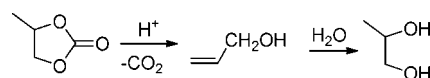


Figure 19. Acid-catalyzed decomposition of PC.

water of the solvent. A trace amount of water can be removed by treatment of the organic carbonate with calcium hydride.^{147,148} Unlike the cyclic carbonates, the linear carbonates, DMC and DEC, generally possess lower boiling points. They are generally distilled at ambient pressure and can be removed by a standard rotary evaporator.

As technical samples, propylene carbonate can contain impurities such as propylene glycol, propylene oxide, allyl alcohol, and water, which can be detected by GC or HPLC methods.^{149,150} The purity of propylene carbonate can be verified indirectly by analyzing the impurities and decomposition products.^{151–154} Furthermore, Mouloungui and co-worker used GC and HPLC methods to determine glycerol carbonate from a carbonate interchange reaction of ethylene carbonate with glycerol.¹⁵⁵

Next to physical data, (eco)toxicological data of a solvent receive more and more attention. Thus, a full set of toxicological, ecotoxicological, and stability data exists only for propylene carbonate. For other carbonates only incomplete data are found. Table 2 gives an overview of existing data for organic carbonates in comparison to standard organic solvents. The data was collected from MSDS data of several chemical suppliers.

All organic carbonates show an ecologically benign behavior and a very low toxicity. However, the decomposition products of organic carbonates can show different effects. DMC liberates methanol during the biodegradation.

Investigations revealed that ethylene glycol (LD₅₀ 8.0–13.0 (rat) and 8.0–15.3 g/kg (mice)) can be formed in vivo rapidly from ethylene carbonate and result in a higher health risk than ethylene carbonate itself.¹⁵⁶ However, in all studies, propylene carbonate showed only a low (eco)toxicity.¹⁵⁷ Thus, like other chemicals, release to the environment should be avoided in all cases.

5. Organic Carbonates as Solvent

With respect to their polarity, organic carbonates belong to a class of aprotic highly dipolar solvents (AHD) like DMSO or DMF.¹ In contrast to these solvents, most organic carbonates show only limited or no miscibility with water.¹⁵⁸ One possibility to compare solvents is determination of the polarity using solvatochromic dyes. The solvent properties of organic carbonates are rather unique and only met by few other solvents (Figure 20).¹⁵⁹ Interestingly, the polarity and hydrogen-bond acceptor properties (basicity β) of PC (0.39) match perfectly those of acetonitrile (AN) (0.38).¹⁶⁰ However, displaying the same basicities, the noncyclic carbonates like DMC and DEC possess lower polarities which resemble methylene chloride and THF.¹⁶¹ Unfortunately, only scant data are available for organic carbonates. Prediction of those parameters by modeling is a powerful tool to overcome this limitation.^{162–166}

Organic carbonates can be further characterized by their high dipole moment and high dielectric constant. Thus, PC has a dipole moment of $\mu = 16.5 \times 10^{-30}$ Cm and an outstanding dielectric constant of $\epsilon_r = 64.92$ (for comparison, ϵ_r (H₂O) = 78.36 and ϵ_r (DMSO) = 46.45). This makes PC particularly well-suited for anhydrous, electrochemical applications.

The use of organic carbonates as a solvent in chemistry should lead to an exclusive benefit (higher selectivities, rates, yields) in the reaction or process next to their “green” solvent properties. In organic synthesis and catalysis it is especially necessary to solve the question of product separation. Due

Table 2. (Eco)Toxicological Data for Representative Organic Carbonates in Comparison to Commonly Used Organic Solvents

	DMC	DEC	EC	PC	BC	GyC	CH ₂ Cl ₂	THF	MeOH	DMF	DMSO	toluene
biodegradability [d ⁻¹]	88% (28)	75%	readily	94%/29 ^a , 97%/4 ^b	readily	readily	5–26% (28) ^c	39% (28)	76% (5) ^e	90% (28) ^d	3.1% (14)	n.a.
LC ₅₀ (fish) [mg/L] (96 h) <i>L. idus</i>	1000	n.a.	>1000	~5300 ^c –2200 ^d	480 ^e	>1040 ^f	310 ^g	2160 ^h	15 400 ⁱ	6300 (96 h) ^j	33 500 (48 h) ^k	13 ^m
EC ₅₀ (invertebrates) [mg/L] <i>Daphnia magna</i>	n.a.	n.a.	>100 (48 h)	>1000 ^e (48 h)	>1000 (48 h)	n.a.	1682 (48 h)	382 (24 h) ^e	>10 000 (48 h) ^e	15 700 (48 h)	n.a.	11.5 (48 h)
EC ₅₀ (bacterial) [mg/L] <i>P. putida</i>	n.a.	n.a.	>10 000 (17 h)	>10 000 ^e (17 h)	>100 ^b (3 h)	n.a.	1000–880 (15 min) ⁿ	580 (16 h)	6600 (16 h)	20 000 (5 min) ⁿ	n.a.	20 (0.5 h) ^r
IC ₅₀ (aquatic plants) [mg/L] <i>Desmodium subspicatus</i>	n.a.	n.a.	n.a.	>900 ^e (72 h)	>100 ⁱ	n.a.	>660 (96 h) ^o	3700 (ppm) (8d) ^{cr}	8000 (8d) ^o	>500 (96 h)	n.a.	12 (72 h) ^o
Bioaccumulation potential	0.23 ^e	1.21	–0.34 ^e	–0.48 ^e	–0.00533	–1.6 ^e	1.3	0.45	–0.77	–0.85	–1.35	2.65
Log p(o/w)												
LC ₅₀ (inhalation) (rat) [mg/L]	>140 (4 h)	n.a.	n.a.	n.a.	n.a.	n.a.	88 (0.5 h)	53.9 (4 h)	64 000 (ppm) (4 h)	9–15 (4 h)	n.a.	49 (4 h)
LD ₅₀ (oral) (rat) [mg/kg]	9000	>4900	>5000	34920	>5000	>5000	1600, 357 ^q	1650	5628, 143 ^r	2800	14 500	636
LD ₅₀ (dermal) (rabbit) [mg/kg]	>5000	n.a.	>2000	>20 000	>2000	>2000	n.a.	n.a.	n.a.	1500	40 000	12124
bacterial mutagenicity	–	– ^s	–	–	–	–	+	–	–	–	–	–
solubility with water [g/L] (20 °C)	139	insoluble	214	240	1–10	10–100	20	soluble	soluble	soluble	soluble	0.52 (15 °C)

^a OECD 301 E. ^b OECD 302 B. ^c IUCLID. ^d L. idus NOEC IUCLID. ^e Calculated. ^f Ames test. ^g *Salmonella typhimurium*. ^h Sewage sludge. ⁱ *Selenastrum* sp. ^j MITI test. ^k *Pimephales promelas*. ^l *Lepomis macrochirus*. ^m *Carassius auratus*. ⁿ *Selenastrum capricornutum*. ^o *Selenastrum quadricauda*. ^p Human. ^q *Selenastrum quadricauda*. ^r Test in sealed bottle IUCLID; n.a. = not available.

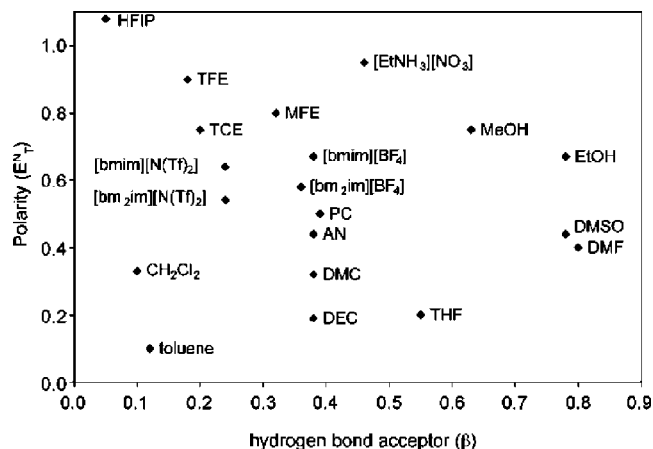


Figure 20. Polarities and basicity of several organic carbonates in comparison to other VOC and ionic liquids: bmim = 1-butyl-3-methylimidazolium, bm₂im = 1-butyl-2,3-dimethylimidazolium, N(Tf)₂ = bis(trifluoromethylsulfonyl)imide, HFIP = hexafluoroisopropanol, TFE = trifluoroethanol, MFE = monofluoroethanol, TCE = trichloroethanol. Reprinted with permission from ref 159. Copyright 2008 Wiley-VCH Verlag GmbH & Co. KGaA.

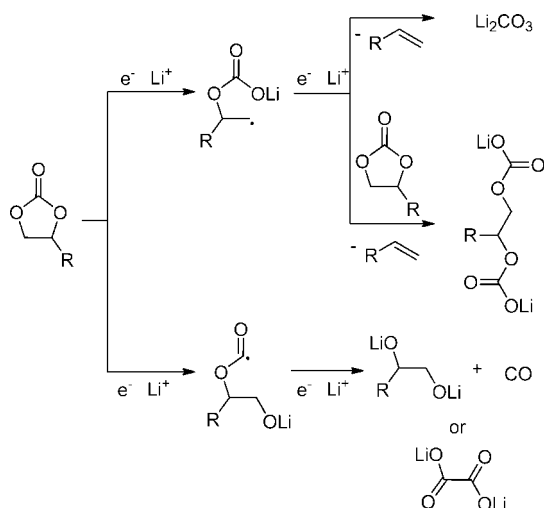


Figure 21. Reaction of an organic carbonate at a lithium surface.

to the fact that cyclic organic carbonates have a high boiling point, distillative removal of the solvent is nearly impossible. In some polymer applications it is possible as the polymer precipitates out of the solvent (section 5.3.2).

5.1. Li-Ion Battery Research

The use of organic carbonates as solvents for electrochemical applications, especially as a nonaqueous electrolyte, is well established.⁴¹ Since the early 1960s, ethylene and propylene carbonate have been used as solvents for lithium batteries.^{167–169} By virtue of their high dielectric constants, they are able to solvate lithium salts. To reduce the viscosity of both carbonates (ethylene carbonate is solid at room temperature) an electrolyte includes dimethyl carbonate, diethyl carbonate, or dimethoxy ethane. One major problem for the use of propylene carbonate is its susceptibility to reduction by single electron transfer from lithium. This side reaction reduces the cycling efficiency of the system. A simplified expression of this reduction is depicted in Figure 21. The decomposition products form a passivation film which also forms dendrites (Figure 22). Remarkably, EC possess the unique ability to reverse the lithium-ion inter-

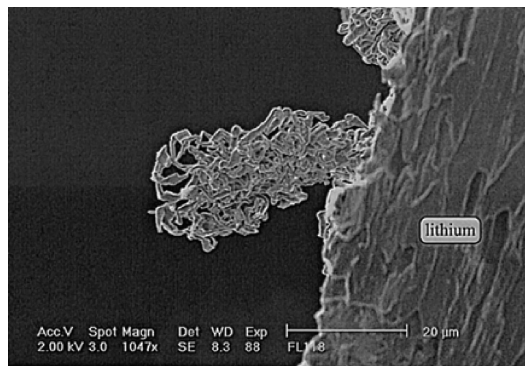


Figure 22. Dendrite formation after one charge at 2.2 mA/cm².¹⁷⁹ Reprinted with permission from ref 179. Copyright 1998 Elsevier.

calation/deintercalation process at graphite electrodes. EC alone forms an efficient protection layer (solid electrolyte interphases, SEI) on the surface of the anode. Currently, a sufficient explanation for the efficiency of this SEI with EC is unknown.¹⁷⁰ However, it is believed that EC undergoes a similar reduction at the graphite electrode as shown for PC in Figure 21 and the differences in the interphasial chemistry arise from different bulk properties of the reduction products.¹⁷¹ There remains intensive research in this field to determine this mechanism for ethylene carbonate. Several spectroscopic techniques (Fourier transform infrared spectroscopy (FTIR), photoelectron spectroscopy (PES, XPS)) and soft X-ray (XAS and XES) have been utilized to get a better understanding.^{172–178}

In order to improve the thermal properties of the SEI, Profatilova et al. added fluoroethylene carbonate to a classical electrolyte mixture of EC and ethyl methyl carbonate.¹⁸⁰ Yang and co-workers achieved a better cathode performance for ethylene carbonate by adding vinyl ethylene carbonate,¹⁸¹ which is a stable alternative to vinyl carbonate and a well-known compound for SEI formation.^{182–184} Both are able to form stable SEI films to improve the cyclic performance of lithium cells. Recent results have shown that SEI formation can be facilitated by coating the graphite electrode with an organic film like the above-mentioned additives vinyl carbonate, vinyl ethylene carbonate, or fluoroethylene carbonate. A comprehensive summary of organic additives was given by Zhang.¹⁸⁵ In addition, surface-modified graphite electrodes could be used with propylene carbonate without exfoliation. Polymers¹⁸⁶ (Figure 23) or surface-fluorinated graphite¹⁸⁷ are usually applied in this context.

Furthermore, SEI formation is not only limited to carbon electrodes. The group of Cui analyzed the SEI morphology of a silicon nanowire lithium-ion battery containing an EC/DEC electrolyte.¹⁸⁸ Additionally, Dedryvère and co-workers investigated the use of Ni₃Sn₄ electrodes in a 1 EC/1 PC/3 DMC electrolyte solution with formation of a Li–Sn alloy.¹⁸⁹

SEI formation is not the only focus of the research with electrolytes. General investigations on the conductivity of organic electrolyte solutions were published by Petrowsky et al. (Figure 24).¹⁹⁰ They showed that ion mobility does not depend in a quantitative manner on the solvent viscosity or size of the solvated charge carrier. However, an increase of viscosity decreases the molar conductivity as predicted by Walden's rule.

The mass transport and conductivity in organic carbonate electrolytes (PC, EC, and DEC and mixture thereof) were determined by Schneider and co-workers for LiClO₄¹⁹¹ and

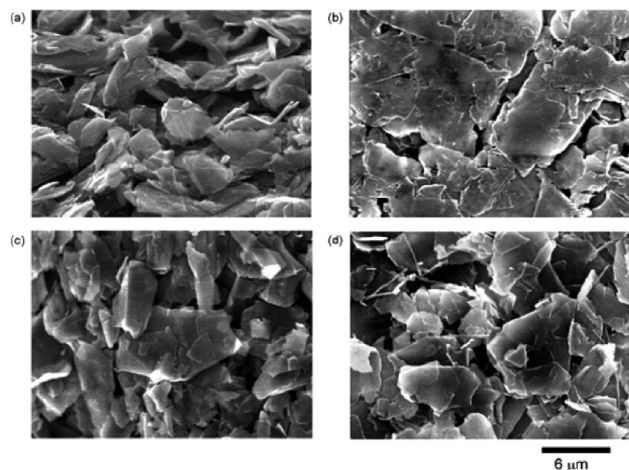


Figure 23. Graphite electrodes with (a) conventional polyvinylidene fluoride binder, (b) poly(acrylic acid), (c) polymetracrylic acid, and (d) polyvinyl alcohol as binder (SEM images). Reprinted with permission from ref 186a. Copyright 2009 Elsevier.

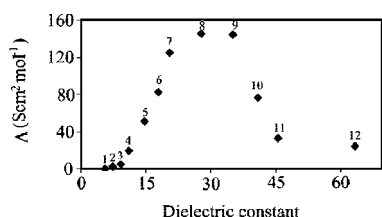


Figure 24. Molar conductivity vs dielectric constant, 0.0055 M tetrabutylammonium triflate in various solvents (25 °C): (1) propyl acetate, (2) tetrahydrofuran, (3) 2-nonanone, (4) 65% 2-pentanone + 35% propyl acetate (vol %), (5) 2-pentanone, (6) 2-butanone, (7) acetone, (8) 50% acetone + 50% acetonitrile (vol%), (9) acetonitrile, (10) 50% DMSO + 50% acetonitrile (vol %), (11) DMSO, (12) PC. Reprinted with permission from ref 190. Copyright 2008 American Chemical Society.

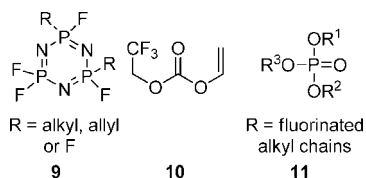


Figure 25. Flame retardants for organic carbonate electrolytes.

by Barthel et al. for LiBr in mixtures with acetonitrile.¹⁹² If not applicable as single-electrolyte solvents, organic carbonates can be used in mixtures with γ -butyrolactone. Whereas EC and PC do not suppress the decomposition of the lactone, vinylene and vinyl ethyl carbonate efficiently suppress this process by formation of a polymeric SEI on the electrode surface (LiCoO₂/graphite cell).¹⁹³ Despite these disadvantages, ethylene and propylene carbonate and their mixtures are still standard for the evaluation of new salts and electrochemical systems.^{194–197}

One major problem for all organic solvent electrolytes is flammability. This problem can be overcome by adding allyl tris(2,2,2-trifluoroethyl) carbonate (**10**),¹⁹⁸ phosphazenes **9**,¹⁹⁹ or phosphoric acid esters with fluorinated alkyl moieties **11**²⁰⁰ to the electrolyte (Figure 25). However, these flame retardants affect the viscosity and capacity ratio during discharge. Therefore, it is necessary to choose a flame retardant wisely while minimizing the effect on the Li-cell efficiency.

In recent years, gel polymer electrolytes (GPE) have attracted increased attention. Due to their advantageous properties, it is possible to avoid some drawbacks of solid

polymer electrolytes (SPE) like low ionic conductivity at room temperature and poor contact between electrode and electrolyte in comparison to liquid electrolytes. Furthermore, SPE possesses poor mechanical properties and is a safety hazard in the case of an internal short.²⁰¹ Most GPEs use organic carbonates in combination with Li salts to obtain high conductivity and high cohesion and adhesion.²⁰² An effective lithium–air GPE system could be applied with a 50% epoxidized natural rubber polymer with 35% LiCF₃SO₃ and 10% PC as plasticizer. With other mixtures of EC or PC lower conductivities were observed.²⁰³ In contrast to a liquid electrolyte system of 1 M LiClO₄/PC, the polymer electrolyte is more stable against corrosion.²⁰⁴ A polyacrylonitrile (PAN) system using a 42/36/7 mol % EC/PC/LiCF₃SO₃ mixture was developed by Dissanayake and co-workers and has obtained a maximum conductivity of $1.2 \times 10^{-3} \text{ S} \cdot \text{cm}^{-1}$.²⁰⁵ Furthermore, they investigated cells of the form Li/PAN-EC-PC-LiCF₃SO₃/polypyrrole-alkylsulfonate. Proton-conducting polymer electrolytes derived from methacrylates were developed by Reiter et al. and gave a conductivity of $6.7 \times 10^{-5} \text{ S} \cdot \text{cm}^{-1}$ in a GPE system of polyethyl methacrylate-PC-H₃PO₄ (31/42/27 mol %).²⁰⁶ However, the conductivity obtained in the GPE system was one magnitude lower than with the liquid electrolyte (PC-H₃PO₄ = 59/41 mol %; $5.2 \times 10^{-4} \text{ S} \cdot \text{cm}^{-1}$) and increased with the concentration of H₃PO₄. The same group investigated GPE systems based on poly(2-ethoxyethyl methacrylate) (PEOEMA) with PC-LiClO₄²⁰⁷ (PEOEMA-PC-LiClO₄ = 48/41/6 mol %; $1.8 \times 10^{-4} \text{ S} \cdot \text{cm}^{-1}$) or with mixtures of the weakly coordinating bis(oxalato)borate anion (BOB⁻) (PEOEMA-PC-LiBOB = 34/62/4 mol %; $4.6 \times 10^{-4} \text{ S} \cdot \text{cm}^{-1}$).²⁰⁸ The polymers exhibited higher electrochemical and thermal stability compared to conventional liquid electrolytes. A GPE film based on various polymer mixtures of poly(ethylene-*co*-acrylic acid) and poly(ethylene glycol) monomethyl ether achieved ion conductivities of $1.4 \times 10^{-3} \text{ S} \cdot \text{cm}^{-1}$ in 1.0 M solutions of LiBF₄ in PC/EC 1:1 and EC/DMC 1:2.²⁰⁹

5.2. Electroanalytics

With their excellent electrochemical properties (especially the high dielectric constant) organic carbonates can be used for sensors. A propylene carbonate-based ammonia sensor was developed in the groups of Mishima²¹⁰ and Compton.²¹¹ Furthermore, PC was an excellent solvent for capillary electrophoresis for the investigation of mobility and ionization constants of various aliphatic amines.²¹² Detection of thallium(III) and other inorganic salts has been accomplished by polarographic methods in propylene carbonate in extractive mixtures with water²¹³ for ‘salting-out’ extractions.²¹⁴ Neutral substances like phenanthrene could be separated by nonaqueous capillary electrophoresis using cationic additives in propylene carbonate.²¹⁵

5.3. Polymerization

5.3.1. Electropolymerization

Closely related (but not limited) to electrochemical applications in lithium batteries is the use of propylene carbonate as an ideal solvent for electropolymerization. This method provides several conducting polymers by polymerization at the surface of an electrode. The advantage of this approach in comparison with chemical polymerization is the

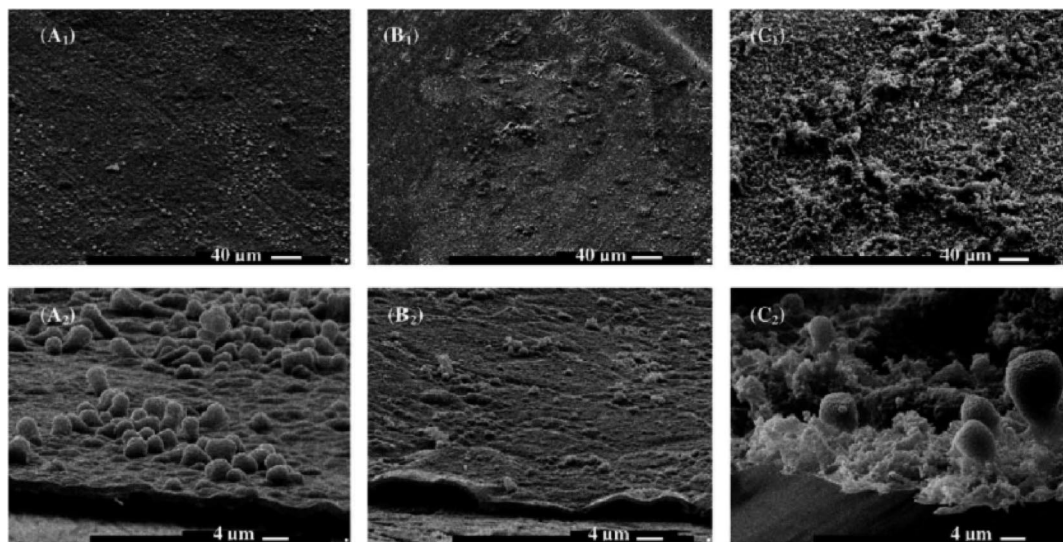


Figure 26. SEM images of polypyrrole films on zinc alloy electrodes in PC (A), acetonitrile (B), and nitrobenzene (C). The potential was scanned 18 times between -0.8 and 1.3 V vs ECS with a 100 mV s^{-1} scan rate. Reprinted with permission from ref 218. Copyright 2002 Elsevier.

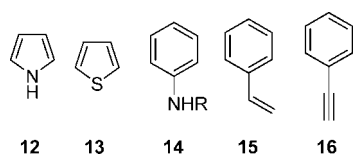


Figure 27. Monomers for electropolymerization.

simple, clean, and efficient synthesis of polymers. Those polymers can be used for batteries, conductive textiles and fabrics, antistatic coatings, supercapacitors, and special sensors. The choice of solvent is particularly important. It must provide an ionic conducting medium and must be stable at the oxidation potential of the monomer.²¹⁶ Furthermore, it affects the electrochemical activity, conductivity, and morphology of the resulting polymer.²¹⁷ Finally, it has to be noted that an organic solvent has to dissolve many electrolytes for incorporation to the polymers. The differences between polymers derived from polymerization in propylene carbonate (A1, A2), acetonitrile (B1, B2), and nitrobenzene (C1, C2) are depicted in Figure 26.²¹⁸

Electropolymerization in propylene carbonate is mainly utilized for monomers like pyrrole, thiophene, and aniline derivatives, but some applications can also be found for styrene and acetylenes (Figure 27). One of PC's main advantages is its high relative permittivity and relatively neutral character (the acid, basic, or neutral character of a solvent derives from the ability of this solvent to release a proton which was bound by the molecule before).

Pyrroles. Polypyrrole (PPy) is the most intensively studied conducting polymer. This can be explained with the easy oxidation of the monomer and good environmental stability of the polymer as well as good redox properties and a high electronic conductivity.²¹⁹ There are several proposed mechanisms for polymerization of pyrrole.²²⁰ In most cases, electropolymerization of pyrrole in PC provided polymers with mechanical properties and conductivities superior to acetonitrile.^{221,222} PPy synthesis in acetonitrile normally needs a small amount of water,²²³ which has been explained by the decreased electrostatic repulsion of pyrrole in the presence of water. Kupila et al. achieved good conductivities for PC without adding water.²²⁴ In contrast to acetonitrile, addition of water gives no benefit to polymerization. Martins

and co-workers investigated the solvent effect in the electropolymerization of pyrrole on a zinc–lead–silver alloy electrode.²¹⁸ On untreated zinc alloys, PPy films were only obtained in acetonitrile. Nevertheless, high quality and thick coatings on the pretreated Zn alloy were only obtained in PC. A reason for this could be the neutral character of PC in comparison to acetonitrile and nitrobenzene. The choice of propylene carbonate as solvent for pyrrole polymerization was affirmed by Lacaze and co-workers.²²⁵ They studied electropolymerization on zinc electrodes in acetonitrile, PC, methanol, and water, but PPy was only formed in PC in the presence of *p*-toluene sulfonate ammonium salts. When iron was used as the material for the electrode it was necessary to prevent oxidation.²²⁶ This is only possible in basic solvents like THF ($\text{p}K_{\text{BH}} = -2.1$, all values from ref 226 for a solution with 0.1 M NBu_4PF_6) or MeOH ($\text{p}K_{\text{BH}} = -2.4$) and neutral solvents like PC ($\text{p}K_{\text{BH}} = \text{n.a.}$). In acetonitrile ($\text{p}K_{\text{BH}} = -10.0$), oxidation of iron is favored in relation to PPy film formation. A detailed description of poly(*N*-phenylpyrrole) films synthesized in acetonitrile or propylene carbonate clarified that the solvent transport behavior is determined by the solvent which was used for film preparation and not by the solvent used for the following redox reaction.²²⁷ Finally, electropolymerization of pyrrole is not limited to homopolymers. Copolymers with bithiophenes could be obtained in a PC/ LiClO_4 system.²²⁸ One advantage of this system is the absence of nitrogen and sulfur in the solvent. Because of trapping solvent molecules in the polymer, analysis of the copolymer would be more complicated.²²⁹ 3-Substituted ‘graft’ polypyrroles can be obtained in a stepwise fashion from 3-carboxy-pyrrole by reduction with lithium aluminum hydride followed by electropolymerization of the pyrrole (Figure 28).²³⁰ In contrast to normal graft polymers, the side chain was fixed on the monomer ($m = 5-20$) before polymerization was carried out in propylene carbonate.

Thiophenes. Similar to pyrrole, formation of polythiophene (PT) needs a careful choice of solvent. Several derivatives of thiophene and bithiophenes have been used for electropolymerization in propylene carbonate (Figure 29).

Therefore, the poly-EDOT system (PEDOT) is of special interest because it possesses high stability in the conducting

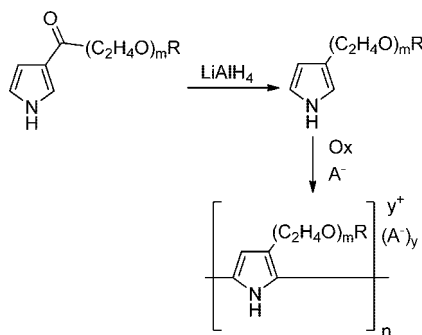


Figure 28. Synthesis of 3-substituted PPy.

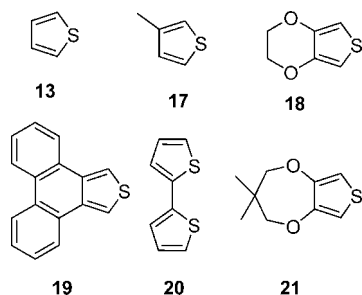


Figure 29. Monomers for polymerization in organic carbonates: thiophene (**13**), 3-methyl thiophene (**17**), 3,4-ethylenedioxythiophene (EDOT) (**18**), phenanthro(9,10-*c*)thiophene (**19**), 2,2'-bithienyl (**20**), and 3,3-dimethyl propylene dioxythiophene (ProDOT-Me₂) (**21**).

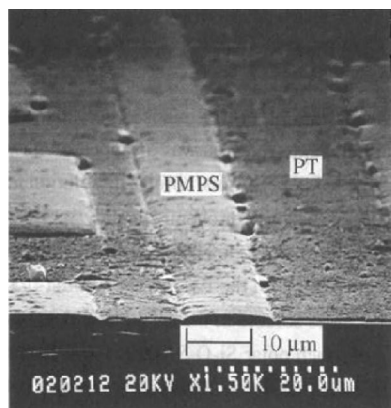


Figure 30. SEM image of thiophene which polymerized only in the UV-exposed area of the polysilane. Reprinted with permission from ref 234. Copyright 1994 The Chemical Society of Japan.

state and a high degree of visible light transitivity. It can also be used as a cathodic material in batteries.^{231,232} Furthermore, poly terthiophene-appended uranyl–salen compounds²³³ and polythiophene pattern in an organopolysilane film²³⁴ could be realized by polymerization in PC. Yokoyama and co-workers achieved a fine line pattern of 10 μm width after electropolymerization of dissolved UV-exposed polysilanes (Figure 30). Next to thiophene, which required a high voltage (>+ 2.1 V vs saturated calomel electrode), 2,2'-bithiophene was polymerized at a lower voltage of +1.1 V. PC was especially suitable because a solubility difference between the UV-exposed and unexposed polysilanes was achieved (UV-exposed films are soluble in solvents with $E_{\text{T}}^{\text{N}} < 0.79$; unexposed films only in solvents with $E_{\text{T}}^{\text{N}} < 0.355$, Table 3).

Further electropolymerization of 2,2'-bithienyl (**20**) is of importance due to its lower oxidation potential. A systematic study on this system at several different electrodes using PC

Table 3. Electrochemistry Parameters and Dissociation Constants of Various Solvents

	H ₂ O	DMF	PC	AN	ref
DN	33.0	26.6	15.1	14.1	1
E_{T}^{N}	1.0	0.39	0.49	0.46	1
conductivity (S cm ⁻¹) 10 ⁻⁸	6	6	1	0.06	243
viscosity (cP)	0.89	0.80	2.53	0.34	243
acid/base					
H ₂ SO ₄					
p <i>K</i> _{a1}	S ^a	3.1	8.4	7.8	243
p <i>K</i> _{a2}	1.96	17.2	n.a. ^b	25.9	243
MSA ^c	S ^a	3.0	8.3	10.0	243
HClO ₄	S ^a	S ^a	1.3	2.1	246

^a S = strong acid. ^b n.a. = not available. ^c MSA = methane sulfonic acid.

or AN as solvent revealed that the electropolymerization is thermodynamically and kinetically favored in AN but the resulting polymer films have a more compact structure. Finer morphologies and better mechanical stabilities have been obtained in PC.²³⁵ Only polymerization of **19** failed in PC at a Pt electrode and seems to require a more acidic solvent like acetonitrile,²³⁶ whereas formation of (PEDOT) films occurred without problems on tin²³⁷ or platinum electrodes.²³⁸ The morphology of poly(3-methylthiophene) formation in PC could be controlled by the arrangement of the electrodes.²³⁹ ProDOT monomers could be successfully deposited on tin oxide electrodes using cyclic voltammetry (+0.8 to -1.0 V, scanning rate 20 mV/s; 10 cycles).²⁴⁰

In contrast to formation of PPy, it turned out that an acidic solvent like methylene chloride (DN = 4) is favored over PC if the galvanostatic mode is used.²⁴¹ Thus, very high current densities were necessary to initiate polymerization in PC. A basic solvent like THF totally failed in this reaction. Graphitized carbonaceous materials could be protected by a film of PT as an alternative to SEI formation with vinylene carbonate.²⁴² The subsequent phase-transfer kinetics of the lithium ion in the resulting graphite electrode was not affected by the PT film.

Anilines. In the group of aromatic amines aniline and methyl aniline are suitable for electropolymerization. A proposed mechanism published by Kvarnström and co-workers revealed a strong solvent effect.²⁴³ Next to the DN of the solvent, the proton concentration of the added acid is an important parameter. However, best results were obtained in water and DMF, while film formation was less effective in PC and acetonitrile due to lower donor numbers (Table 3).²⁴⁴ A highly acidic media is favored due to the fact that it hinders formation of N–N coupling.²⁴⁵ An improvement could be achieved when propylene carbonate was used in mixtures with water (80% water:10–20% PC, Figure 31). Furthermore, a more narrow molar weight distribution was achieved, which resulted in higher electrical conductivities.²⁴⁶

In addition, PC can also be used as a solvent for nonaqueous electropolymerization without using an acid as a proton donor.²⁴⁷ Nevertheless, polymerization under these conditions needed more cycles in PC to complete than in 1,2-dichloroethane, and it turned out that some polymer particles are dissolved in PC. A possible growth mechanism for nonaqueous electropolymerization (TFA/LiClO₄/PC) was described by Hwang et al.²⁴⁸ The effect of different anilinium ions in the electropolymerization was investigated, and it has been shown that there is a strong difference in the morphology of the polymers between polymerization in aqueous and nonaqueous solutions.^{249–251} The method of choice for

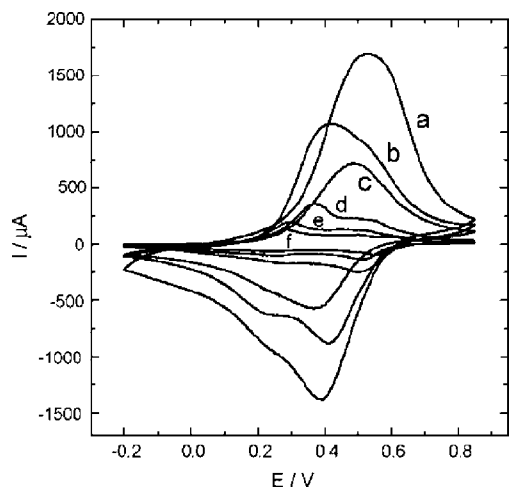


Figure 31. Characterization of poly-*N*-methyl aniline films in HClO₄ (1.0 M; fifth cycle, $v = 50$ mV/s); preparation in water with (a) acetonitrile, (b) PC, (c) THF, (d) no organic solvent, (e) DMF, and (f) DMSO. Reprinted with permission from ref 246. Copyright 2006 Elsevier.

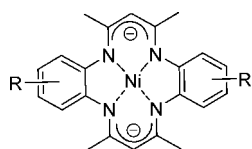


Figure 32. Ni[Me₄(RBzO)₂]¹⁴tetraeneN₄ complex with R = Me, H, Cl, CO₂Me, CO₂Et, NO₂.

evaluation of the electrochemical properties is impedance measurements.²⁵² Thus, it is possible to estimate further battery performances of the polymers. The solvent has a strong impact on the discharge and charge characteristics of polyanilines. In particular, for use in batteries, for polyanilines containing 1.0 mol dm⁻³ aniline tetrafluoroborate a better performance was noted in AN as opposed to PC or γ -butyrolactone.²⁵³

Other Monomers. Next to isothianaphthenes²⁵⁴ for charge-storage devices and styrene²⁵⁵ in particular, electropolymerization of phenylacetylene was investigated systematically in propylene carbonate.²⁵⁶ Another field of application is the modification of electrodes by deposition of complexes. A nickel-tetraene complex was successfully formed on gold, platinum, glassy-carbon, and SnO₂ surfaces by cyclic voltammetry in PC (Figure 32).²⁵⁷

5.3.2. Radical and Ionic Polymerizations of Organic Carbonates in Neat Solutions

Several publications have dealt with the use of organic carbonates as monomers for the formation of polycarbonates. Phosgene-free synthetic pathways using dimethyl or diphenyl carbonate are of particular importance.²⁵⁸

Ring-opening polymerizations using propylene or ethylene carbonate are usually carried out in neat solutions. In these reactions the organic carbonates act simultaneously as monomer and solvent. To obtain solutions with low viscosity it is necessary to run the reactions at elevated temperatures. Polymerizations of ethylene carbonate are carried out generally at temperatures above 100 °C (Figure 33).²⁵⁹ Best results were achieved at 175 °C with Al(acac)₃ and a reaction time of 128 h with 46% conversion and a high selectivity for the obtained polymer.²⁶⁰ Comparable results were obtained with Zn(acac)₂ at 160 °C for propylene carbonate.

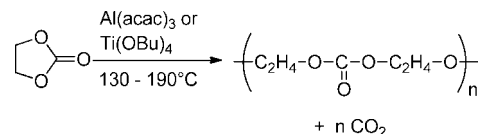


Figure 33. Polymerization with EC as solvent and monomer.

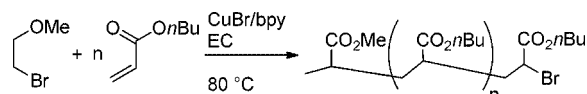


Figure 34. ATRP of *n*-butyl acrylate in ethylene carbonate.

Recently, the group of Zsuga investigated the ring-opening polymerization by employment of the matrix-assisted laser desorption/ionization mass spectrometry (MALDI-TOF MS) technique to determine the composition of the polycarbonate.²⁶¹ A systematic study for the polymerization of ethylene carbonate without further solvents was accomplished by Lee et al.²⁶² One problem in these polymerizations is the increasing viscosity during the reaction. The use of an appropriate reactor had a strong influence on the properties of the polycarbonate. An extensive study on the graft polymerization of wood sawdust and peat in ethylene carbonate was accomplished in a batch-stirred, semicontinuous-stirred, and continuous vapor-phase tubular reactor.²⁶³ Hydroxyalkylations of urea²⁶⁴ and oxamic acid²⁶⁵ in propylene carbonate lead to a complex polymer network through decarboxylation of the carbonate.

Organic carbonates can also be used as controlling solvent for polymerization. Synthesis of polysuccinimide is favored in organic carbonates because it dissolves the monomer (aspartic acid) as well as the polymer.²⁶⁶ In addition, ethylene, propylene, and butylene carbonate are inert under the used conditions and their boiling point is high enough to initiate polymerization at 150 °C. The isolated polymer can be obtained by diluting the mixture in organic solvents like acetone. Yields between 40% and up to 100% of polymers (3000 < MW < 50 000) with purities between 70% and 100% were achieved by this method. Ethylene carbonate is especially suitable for the atom-transfer radical polymerization (ATRP) of *n*-butyl acrylates (Figure 34).²⁶⁷ High selectivities for polydispersity and molecular weight are achieved in ethylene carbonate. Another copper-catalyzed polymerization is the single electron transfer living radical polymerization (SET-LRP), which allows good control of the molecular weight and good retention of chain-end functionality. Since this polymerization involves a disproportionation of the Cu(I)X salt into Cu(0) and Cu(II)X₂, the polymerization parameter depends on the used solvents (which can act as solvent ligand). The influence of different solvents was investigated by Percec et al., and the results indicate that polymerization can be accomplished efficiently in ethylene and propylene carbonate. Furthermore, the group found that addition of 5–10% of water in EC can improve the molecular weight distribution.²⁶⁸

Figure 35 presents the dependency of the polydispersity on solvent and conversion in the ATRP of *n*-butyl acrylate. In PC and EC the polydispersity is around 1 and stable also at higher conversions. Acrylates and methacrylates were successfully subjected to ATRP in ethylene carbonate and polymers.²⁶⁹

Besides their use as monomers in polymerization, they are also valuable plasticizer,²⁷⁰ additives for the synthesis of polyisocyanates,²⁷¹ or assistants to coalesce nitrile copoly-

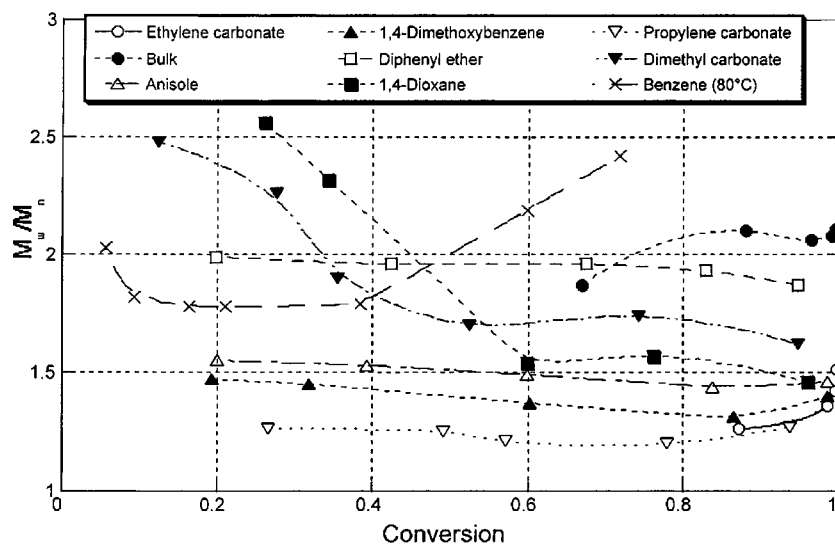


Figure 35. Dependence of polydispersity (M_w/M_n) on monomer conversion and the used solvent in the ATRP of *n*-butyl acrylate initiated by 1-phenylethylbromide. Reprinted with permission from ref 267. Copyright 1998 American Chemical Society.

mers.²⁷² During these processes organic carbonates are only used at low percentages (up to 20%) and do not act as solvent.

6. Catalysis in Organic Carbonates

6.1. Product Isolation and Catalyst

6.1.1. Recovery

As mentioned in earlier sections, the high boiling points of organic carbonates can be a drawback during product isolation. In contrast to polymers, well-soluble compounds are more difficult to isolate from the carbonate reaction medium. Moreover, one must carefully consider the reaction workup if organic carbonates are to be classified as green solvents. For example, the amount of VOC required during workup is not included in the classification of the carbonate as a “green” alternative.

Possible workup procedures are summarized in Figure 36. In the case of catalyst recycling, three pathways are employed. The most effective workup consists of a simple separation using a stripper (Figure 36A). This workup does not require a second solvent, which has to be recycled in a further workup step. However, this pathway is only possible for products like fatty acids, which can be easily separated

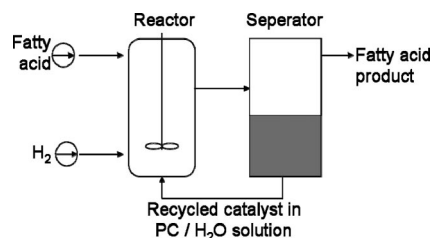


Figure 37. Separation of fatty acids from a catalyst solution.

from organic carbonates.²⁷³ In this reaction the polarity of the organic carbonate was initially increased by the addition of water to simplify the separation of the product (Figure 37). Heterogeneous catalysts can be recycled by nanofiltration (Figure 36B). However, another separation step is necessary to obtain the isolated product from solution. This step normally consists of a distillation which can result in loss of solvent to the environment.

Homogeneous catalysts can be nanofiltrated if they possess high molecular weights. Catalysts with molecular weights of 627 and 2195 g mol^{-1} were successfully filtered off from the product/dimethyl carbonate mixture (Figure 38).²⁷⁴ An alternative for high-boiling carbonates could retain a product from PC in order to obtain product-enriched solutions. However, such products should possess molecular weights higher than 300.

Most research activities in this field are focused on extractive methods for catalyst recovery (Figure 36C). The catalyst is retained in the polar organic carbonate phase, while the product is extracted with a nonpolar volatile organic compound (VOC). It has to be noted that these solvents have to be removed in order to isolate the product.

Nevertheless, because of its convenient process, extractive methods seem to be the most favored workup procedure for organic carbonates. For example, an Ir catalyst used for the asymmetric hydrogenation of nonfunctionalized olefins was successfully recycled 6 times using a 3:1 mixture of *n*-hexane and toluene.¹¹⁸

Temperature-dependent multicomponent solvent (TMS) systems offer efficient catalyst recycling and product separation from cyclic organic carbonates.²⁷⁵ The methodology is based on solvents with different polarities (Figure 39). The polar solvent (e.g., PC) is used to retain the catalyst in the

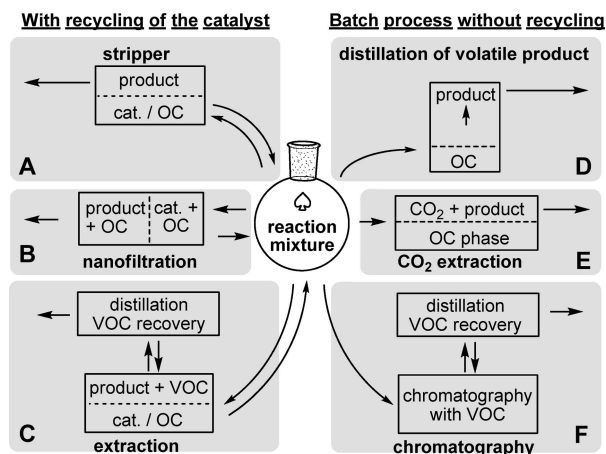


Figure 36. Several workup procedures for the use of organic carbonates as solvents in catalysis.

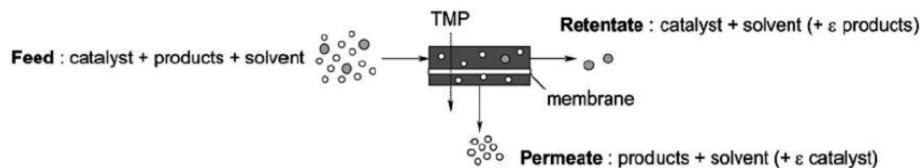


Figure 38. Principle of the cross-flow nanofiltration in Ru metathesis with enlarged catalysts. Reprinted with permission from ref 272. Copyright 2008 Wiley-VCH Verlag GmbH & Co. KGaA.

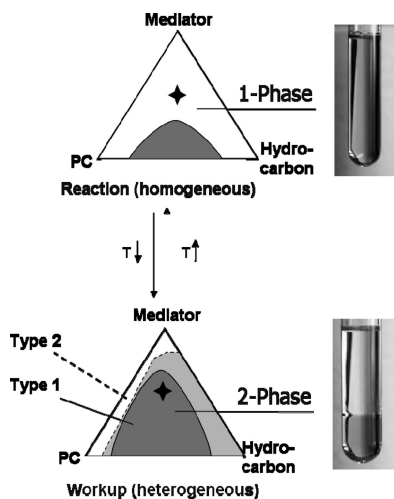


Figure 39. Principle of catalyst recycling using a TMS system. The workup is based on a TMS system with a closed miscibility gap (type 1, dark gray) and an open miscibility gap (type 2, light gray); the star symbolizes the operating point.

reaction phase, while the product is dissolved in a second solvent with low polarity (e.g., hydrocarbons like *n*-dodecane). A crucial additive is the mediator which acts as a third solvent. Its polarity should be between the polar and the nonpolar solvent. At elevated temperature the miscibility gap between the three solvents is small, which leads to a homogeneous solution. These principles are explained by the Hansen model of solubility parameters,²⁷⁶ which in turn is derived from the theory from Hildebrand and Scott.²⁷⁷ The TMS system type 1 (dark gray) in Figure 39 is a classical system with a closed miscibility gap, which means that the catalyst layer as well as the product layer consists of all three solvents in different ratios.²⁷⁸ Accordingly, the catalyst is not completely immobilized and can be found in the product layer as well as in the organic carbonate layer. Superior results could be obtained in a TMS system with an open miscibility gap (Figure 39, type 2, light gray).²⁷⁹

In contrast to type 1, the product layer contains exclusively the extracting solvent and the mediator whereby only negligible amounts of the catalyst or the ligand can be found in the product phase. With proper polarity, the starting material can also act as a mediator. Behr and co-workers recently published a simplified type 3 TMS system which contained only two solvents.²⁸⁰ Until now it has only been tested in DMF or *N*-methyl pyrrolidone with a nonpolar solvent.

Alternative methods can be used for catalyst recycling if the catalyst is robust enough. For instance, direct distillation (Figure 36D) gives the pure product without the assistance of any other solvent. However, this approach is only applicable for high-boiling cyclic carbonates in combination with low-boiling products like lactic acid esters.¹⁵⁹ In order to obtain complete separation, a temperature difference between 60 and 70 °C is necessary for the use of a slit

tube column under industrially relevant temperature and pressure (7.5 mbar, 92 °C). For catalysis at elevated temperature with more robust catalysts (e.g., hydroformylations) it should be possible to recycle the catalyst.

Due to the incomplete solubility of supercritical carbon dioxide in propylene carbonate, it can be used as an extraction solvent (Figure 36F). The advantage of using PC in this process is in the more selective dissolving of the natural compound artemisinin than with the more frequently used hydrocarbons. To obtain the isolated compound, extractions with scCO₂ or liquid–liquid extractions have been applied.²⁸¹

If silica gel chromatography is required for product separation, use of organic carbonates is less efficient (Figure 36E). Due to their high polarity, cyclic carbonates are retained on silica columns if an eluent mixture with a ratio higher than 9:1 (cyclohexane:ethyl acetate) is chosen.²⁸²

In all cases it might be necessary to purify the used organic carbonate prior to reuse in another catalytic reaction. Nageshwer et al. published a procedure to remove water and high-boiling waste materials from organic carbonates without saponification.²⁸³ Furthermore, specialized membranes (mixtures of poly(acrylic acid) and poly(vinylalcohol) could be employed for the separation of dimethyl carbonate from methanol by pervaporation (purification of liquid mixtures) or extractive distillation.²⁸⁴ A problem with methanol is the formation of azeotropic mixtures. This can be used as a purification method, where DMC is subsequently crystallized out at –70 °C.²⁸⁵

6.2. Catalysis in Organic Carbonates

6.2.1. Homogeneous Catalysis

Two organic carbonates have been well established as viable solvents for homogeneous catalysis. For low-temperature processes dimethyl carbonate is commonly used. However, it possesses a lower polarity than the cyclic carbonates, and some catalysts (especially rhodium hydrogenation catalysts) show only low solubility in this solvent. In contrast, the second-generation Grubbs and Hoveyda catalysts are soluble in DMC and have been successfully used for ring closing and cross metathesis (Figure 40).²⁸⁶ In the ring-closing metathesis yields up to 98% were reported in dimethyl carbonate and 99% in methylene chloride.

Enlarged Ru catalysts could be used in a similar metathesis reaction with up to 5 cycles in DMC (Figure 41). However, the reaction time increased with every cycle from 10 to 384 min.

Recently, the same group used diethyl carbonate as an alternative solvent for Ru-catalyzed sp²-C–H bond functionalization. The products were obtained with yields up to 97% based on [RuCl₂(*p*-cymene)]₂ as a catalyst.²⁸⁷

Oxidations of olefins were investigated with oxone, NaIO₄, and bleach as oxidants.²⁸⁸ Furthermore, several aromatic compounds and phenols have been oxidized by hydrogen

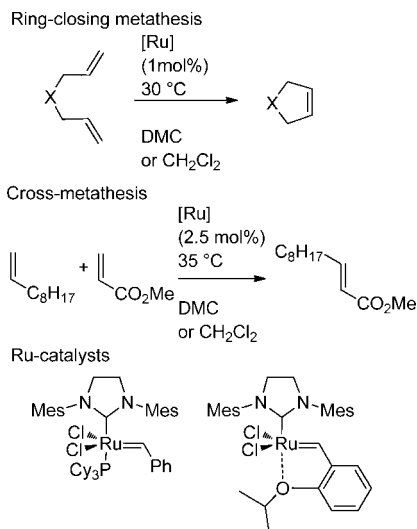


Figure 40. Metathesis reactions in methylene chloride and DMC with second-generation Grubbs and Hoveyda catalysts.

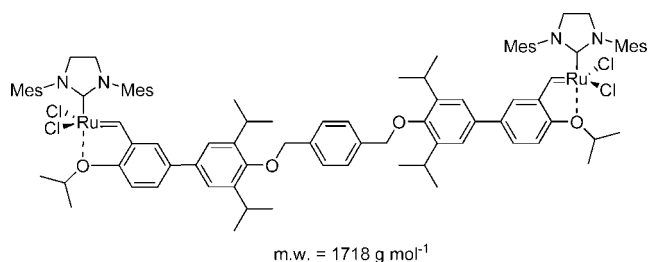


Figure 41. Enlarged Ru catalyst for ring-closing metathesis and subsequent cross-flow nanofiltration.

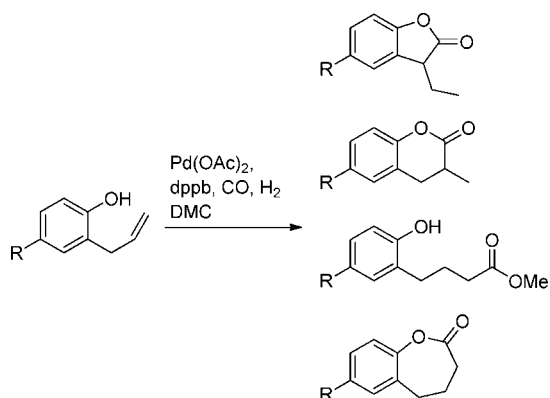


Figure 42. Pd-catalyzed cyclocarbonylations in dimethyl carbonate.

peroxide methyltrioxorhenium ($\text{H}_2\text{O}_2/\text{CH}_3\text{ReO}_3$) in DMC (98% yield).²⁸⁹ Vasapollo et al. investigated the Pd-catalyzed cyclocarbonylation in DMC (Figure 42). Allylphenols were converted into a mixture of different lactones.²⁹⁰ Under normal conditions (100 °C, 24 h) formation of the oxepinone is preferred. After prolonged reaction times or higher temperatures (120 °C, 48 h), allyl alcohols did not react to the corresponding lactone but furnished noncyclic carboxylic acids.

A sophisticated, Pd-catalyzed phosgene-free process has been developed for the oxidative carbonylation of bisphenol A to provide polycarbonate (Figure 43).²⁹¹ As ligands for the homogeneous Pd-catalysts, 2,2'-bipyridines or 2,2'-bithienyl structures were employed. The polycarbonate was precipitated from the reaction mixture by adding an excess of methanol.

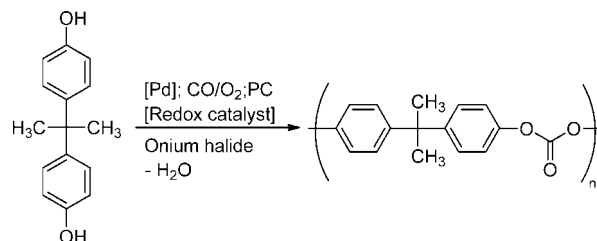


Figure 43. Pd-catalyzed phosgene-free synthesis of polycarbonates in propylene carbonate.

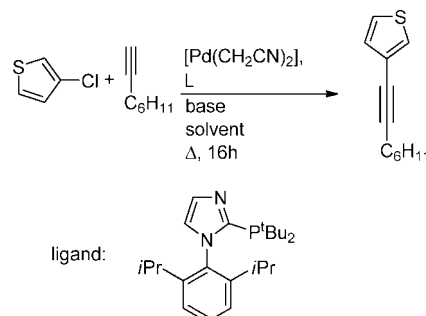


Figure 44. Copper-free Sonogashira reaction of chloro-thiophenes and hexyl acetylenes.

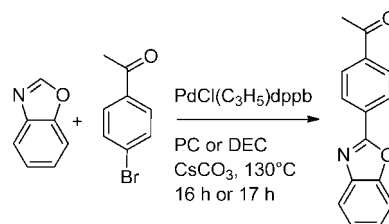


Figure 45. Pd-catalyzed 2-arylation of benzoxazole.

Since it is known that some chemo-physical properties of propylene carbonate are similar to those of acetonitrile, this solvent has been successfully substituted in the copper-free Sonogashira reaction (Figure 44).²⁹² With an imidazole-based ligand, which was originally used in Pd-catalyzed hydroxylation reactions,²⁹³ the coupling product was carried out in PC to give yields up to 76%.

When diethyl carbonate was used for Pd-catalyzed 2-arylation of oxazole derivatives, less byproduct was produced in organic carbonates compared to DMF.²⁹⁴ Next to diethyl carbonate, propylene carbonate was an efficient solvent for reaction of benzoxazole with aryl bromides (Figure 45; DEC = 91% vs PC = 78%).

Moreover, stereoselective palladium-catalyzed reactions like the asymmetric allylic alkylation can be accomplished in organic carbonates. Besides propylene and butylene carbonate, also aliphatic carbonates like diethyl carbonate could be used. Due to their lower polarities, dialkyl carbonates are not suitable for reactions with highly charged metal catalysts (e.g., cationic Rh hydrogenation catalysts are only partly soluble in noncyclic carbonates). Schäffner et al. tested several chiral ligands in the Pd-catalyzed asymmetric alkylation with *rac*-1,3-diphenylallyl acetate and observed enantioselectivities up to 93% in PC (Figure 46).²⁸² In addition, new chiral monophosphites from easily available building blocks were tested in methylene chloride as well as in propylene carbonate.²⁹⁵ Unfortunately, PC was not necessarily the best solvent choice. In addition, enantiopure propylene carbonate was also used instead of the racemic solvent; however, no stereodifferentiation was observed.²⁸²

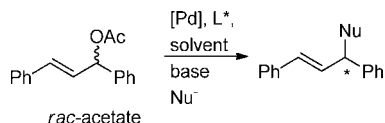


Figure 46. Asymmetric allylic substitution with *rac*-1,3-diphenylallyl acetate.

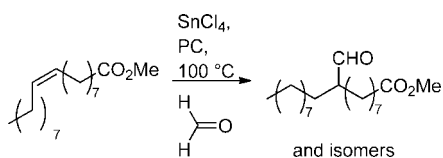


Figure 47. Tin-catalyzed reaction of formaldehyde with oleic acid.

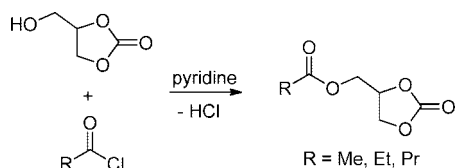


Figure 48. Synthesis of high-boiling carbonates from glycerol carbonate.

This result is in contrast to the use of enantiopure ionic liquids (ILs), which probably establish stronger interactions with the catalyst and substrate.²⁹⁶

The use of TMS systems is especially suitable for nonpolar compounds like hydrocarbons, fatty acids, or aldehydes. Behr et al. used PC as the solvent in the reaction of formaldehyde with unsaturated fatty acid esters in the presence of SnCl_4 and other Lewis acids as catalysts (Figure 47).²⁹⁷ The use of PC reduced the sublimation of *p*-formaldehyde significantly and increased the yield from 52% in 1,4-dioxane to 74%. As products methyl 9-formyloctadecanoate, isomers and byproduct were obtained.

Propylene carbonate was especially suitable for reactions using long-chain fatty acids. Platinum-catalyzed hydrosilylations of unsaturated fatty acids gave the silylated products with yields by up to 88% within 4 h reaction time.²⁹⁸

High-boiling carbonates are useful solvents for reactions under fine vacuum conditions at elevated temperature. They are available from glycerol carbonate with carboxylic acid chlorides (Figure 48).²⁹⁹ Similar to glycerol, these high-boiling carbonates are very viscous at room temperature.

These particular solvents were applied in the telomerization of butadiene with carbon dioxide to form δ -lactones, which are valuable intermediates for a large variety of reactions (Figure 49).³⁰⁰ The possible impact of this particular reaction for more atom-efficient chemistry was presented by Trost.³⁰¹ The reaction control toward the desired lactones is difficult due to several side reactions: dimerization to octa-1,3,7-triene, acid formation, and formation of esters.³⁰² In cyclic carbonates like ethylene, propylene and butylene carbonate δ -lactones were formed in good yields and selectivities (in BC with selectivities up to 70%). However, the boiling points of these carbonates are too low for use in a continuous reactor. Thus, the use of glycerol carbonate esters has been developed. Unfortunately, glycerol carbonate butyrate (with $\text{R} = \text{Pr}$) furnished only low conversion of 46% and yielded the δ -lactones in 23% yield with a selectivity of 49%. Yet, the use of high-boiling carbonates could be attractive on a semitechnical scale, where δ -lactones can be removed by distillation.

Application of temperature-dependent multicomponent solvent systems (TMS) (Figure 39) based on propylene

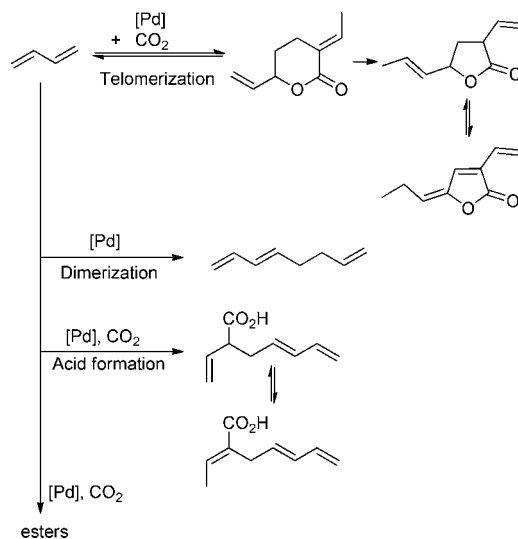


Figure 49. Telomerization of butadiene with carbon dioxide in organic carbonates.

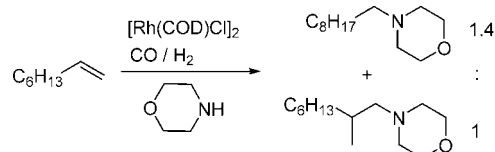


Figure 50. Rhodium-catalyzed hydroaminomethylations of 1-octene.

carbonate was pioneered by Behr for several Rh-catalyzed reactions.³⁰³ Thus, very low catalyst leaching was noted in the hydroaminomethylation (Figure 50).³⁰⁴ A suitable ternary mixture for this reaction was found with a ratio of PC/*n*-hexane/dioxane = 1/0.55/1.3. In these conditions 1-octene was converted to the targeted amines with a selectivity of 96% and a ratio of 1.4/1. In the Rh-catalyzed hydroformylation reaction the best results were obtained at an operating point of 22.5 wt % PC, 19.5 wt % dodecane, and 58 wt % *p*-xylene.³⁰⁵ PC has been identified as a promoter to obtain better selectivities toward linear aldehydes.³⁰⁶ Excellent catalytic activities with high turnover frequencies (TOF) were obtained in the isomerizing hydroformylation with rhodium phosphite complexes.³⁰⁷ The TOF increased from 4064 h^{-1} in toluene to 6750 h^{-1} in propylene carbonate. A similar effect is known for other polar solvents.³⁰⁸

Next to the use of solvatochromic dyes, the use of self-assembling ligands is a good method to investigate the character of a solvent. Formation of a pseudo-bidentate ligand (Figure 51, right down) is only possible in aprotic solvents with low hydrogen-bond acceptor properties (β) (Figure 20).³⁰⁹

Unfortunately, the high selectivity of self-assembling ligands is accompanied by low catalytic activities if they are used with benchmark substrates in the Rh-catalyzed hydrogenation (Figure 52). High reactivities but low ee's were only achieved in the protic solvent methanol. Nevertheless, it could be shown by the group of Börner that hydrogenations in propylene carbonate combine the high enantioselectivity of aprotic solvents with the increased reactivity of the rhodium complex in methanol.³¹⁰

To evaluate the ability of organic carbonates to serve as aprotic, highly dipolar solvents (AHD), several experiments with various AHD solvents were investigated with standard benchmark substrates in Rh-catalyzed hydrogenations using

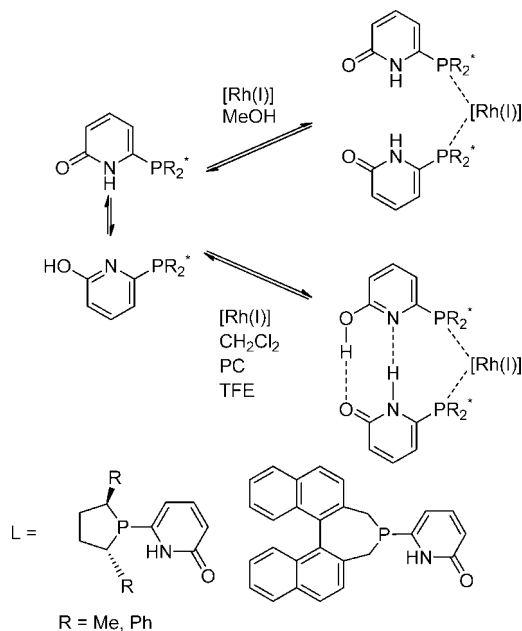


Figure 51. Solvent-dependent self-assembling Rh catalysts for asymmetric hydrogenations.

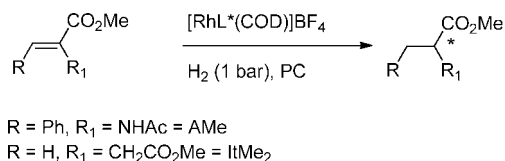


Figure 52. Asymmetric hydrogenation with benchmark substrates.

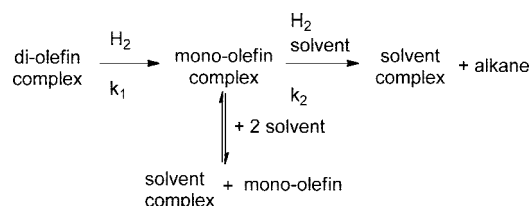


Figure 53. Formation of the solvent complex from a diolefin complex.

commercially available ligands (Figure 52).^{311,312} In DMSO, hydrogenation products were obtained with low stereoselectivity. Better results were observed with DMF. Propylene and butylene carbonate provided excellent results in this hydrogenation, and interestingly, BC provided higher enantioselectivities while PC provided faster reaction rates.³¹³ Previously, investigations have been published where the transformation of Rh precatalysts into active solvent complexes were studied in PC (Figure 53).³¹⁴ The rates in PC were comparable to those determined for typical hydrogenation solvents like methanol, THF, or methylene chloride.

Furthermore, the advantage of a biphasic workup for asymmetric hydrogenations was shown in an isomerization/hydrogenation network approach. Methylene-1,2,3,4-tetrahydronaphthalene isomerizes quickly to the internal olefin in standard hydrogenation solvents like methylene chloride (Figure 54).¹¹⁸ Nevertheless, isomerization was slowed down in PC and resulted in higher enantioselectivities due to the favored formation of the (*R*)-enantiomer instead of (*S*)-enantiomer. In contrast to methylene chloride, where the highest ee was 26% (*S*) with the dicyclohexyl phosphine ligand and 17% (*R*) with the diphenyl phosphine ligand,

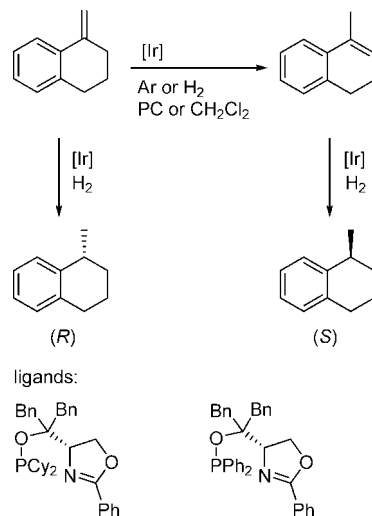


Figure 54. Isomerization–hydrogenation network in the Ir-catalyzed hydrogenation of methylene-1,2,3,4-tetrahydronaphthalene.

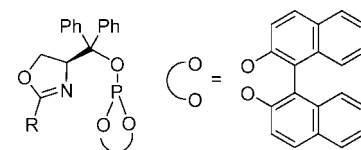


Figure 55. Chiral ligand for the Ir-catalyzed hydrogenation of nonfunctionalized olefins.

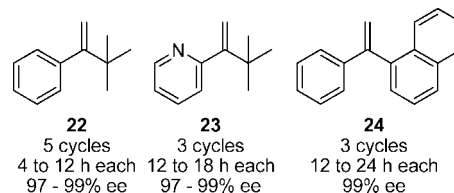


Figure 56. Ir-catalyzed hydrogenation of nonfunctionalized olefins in PC.

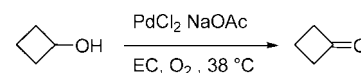


Figure 57. Cyclobutanol oxidation in EC using a PdCl₂/NaOAc system.

enantioselectivities increased in PC to 82% (*S*) with the diphenyl phosphine ligand. The best results were obtained at hydrogen pressures of 50 and 100 bar. Finally, recycling experiments using *n*-hexane for extraction of the product showed that 6 cycles could be accomplished without losing reactivity or stereoselectivity.

By analogy to these results, Pamies and Diéguez achieved 87% ee with an Ir catalyst based on the ligand depicted in Figure 55 in propylene carbonate at 99% conversion after 10 h at 40 °C.³¹⁵ In accordance to the accelerating effect of the solvent for this hydrogenation the same experiment in methylene chloride gave only 25% ee.

Subsequent recycling experiments with several substrates were performed in PC.³¹⁴ Nearly constant enantioselectivities were observed with the nonfunctionalized substrates **22**, **23**, and **24**, while the activities decreased with progressing cycle numbers (Figures 56 and 57).

Alcohol oxidations using a catalytic system of PdCl₂/NaOAc have been conducted in ethylene carbonate at 38 °C.³¹⁶ Noteworthy, compound cyclobutanone was also accessible with this procedure (Figure 56). After addition of

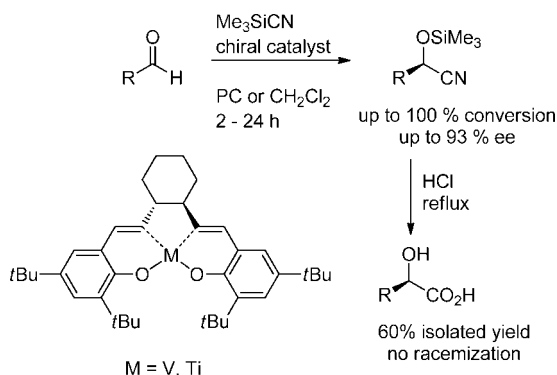


Figure 58. Asymmetric cyanohydrin synthesis in propylene carbonate.

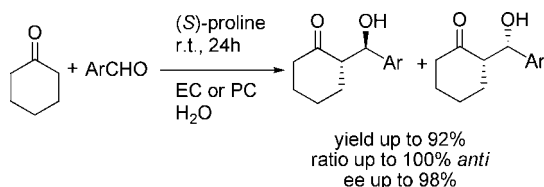


Figure 59. Proline-catalyzed asymmetric Aldol reaction in PC and EC.

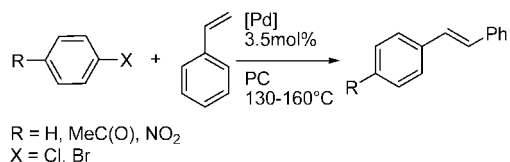


Figure 60. Heck reaction with PC-stabilized Pd clusters.

30% acetone the reaction could also be accomplished at room temperature.

The asymmetric cyanohydrin synthesis in propylene carbonate as solvent was accomplished by the group of North (Figure 58).³¹⁷ Similar results were obtained using dichloromethane as the solvent. With chiral vanadium or titanium salen catalysts enantioselectivities could be obtained up to 93%. However, isolation of the cyanohydrins from PC was difficult to achieve due to their low stability during the chromatographic purification. Therefore, the products were directly converted into the desired mandelic acid using concentrated hydrochloric acid. The acid could be isolated through crystallization from ether/hexane.

In mixtures with water, in propylene and ethylene carbonate excellent results for the (*S*)-proline-catalyzed aldol reaction were obtained by North et al. (Figure 59).³¹⁸

Colloids, Heterogeneous, and Biocatalysis

Propylene carbonate is a suitable solvent for colloid-based-catalyzed reactions. It displays good phase-separating properties and donor abilities and may therefore stabilize colloids. In addition to propylene carbonate, DMF is known to assist in the formation of nanostructures. Electrochemically generated Pd clusters were successfully stabilized by PC and used for the Heck reaction with aryl halides and styrene (Figure 60).³¹⁹

Furthermore, dienes, alkynes, and diolefinic fatty acids have been selectively hydrogenated in propylene carbonate with a Pd–colloid catalyst. The selective hydrogenation has been accomplished at room temperature and ambient hydrogen pressure.³²⁰ The Pd catalyst is stabilized by propylene carbonate. This stabilizing effect is illustrated in Figure 61.

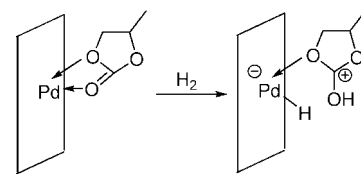


Figure 61. Reaction of the Pd–solvent catalyst with hydrogen.

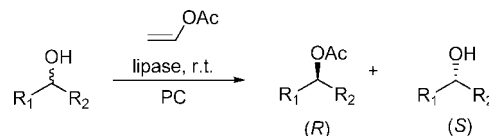


Figure 62. Lipase-catalyzed kinetic resolution in propylene carbonate.

In the experiments, the highest catalyst activities were observed with cyclic carbonates, while noncyclic carbonates were less effective.³²¹ As with homogeneous catalysts, propylene carbonate could be used for heterogeneous Pd-catalyzed carbonylations to form polycarbonates of bisphenol A.³²² Furthermore, with the combination of $\text{Co}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ as an oxidative cocatalyst and a polymer-supported Pd catalyst, a recyclable carbonylation catalyst was obtained.³²³ A study on the kinetics of heterogeneous, enantioselective hydrogenations with platinum on alumina ($\text{Pt}/\text{Al}_2\text{O}_3$) and a chiral dihydrocinchonidine was conducted by Gamez et al.³²⁴ The rates of the reactions were compared by running the transformations in nonpolar (toluene), polar protic (EtOH), and polar, aprotic solvents (PC).

To date, biocatalysis has not been extensively investigated in organic carbonates. Many enzymes need a mixture of water with an organic solvent in which the pH value can be easily adjusted. Thus, hydrolysis of cyclic carbonates may occur during enzymatic reactions. Recently, the group of Xia presented a lipase-catalyzed kinetic resolution of several chiral alcohols with vinyl acetate in propylene carbonate (Figure 62).³²⁵

A combination of electrochemical chemistry and catalysis has been used for the electrochemical reduction of halogen alkanes at silver plates.³²⁶ Similarly, hydroformylations were electrochemically performed with a PtCl_2 catalyst in PC.³²⁷

7. Other Applications as Solvent or Agent

7.1. Organic Synthesis

Classical organic transitions in organic carbonates as solvent are not well established. One rare example for organic synthesis in organic carbonates is the bromination of toluene and derivatives with *N*-bromosuccinimide in propylene carbonate.³²⁸ Furthermore, the quaternizations of pyridine and 4-picoline were investigated in propylene carbonate.³²⁹ Formation of cation–ligand complexes with $\text{N}(\text{Bu})_3\text{H}^+$ and several carbonates were studied by Gilkerson and co-worker.³³⁰ It was assumed that PC does not strongly interact with ions in comparison to other strongly polar solvents.³³¹ Indeed, it was shown that solvation is similar to that found in acetone, keeping in mind that PC possesses a 3-fold higher dielectric constant. Organic carbonates could also be used in the synthesis of acyloxy–boron compounds³³² and in the synthesis of trialkoxy–stannates.³³³

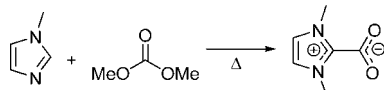


Figure 63. Formation of 1,3-dimethylimidazolium-4-carboxylate from DMC and 1-methylimidazol.

7.2. Synthesis of Ionic Liquids

Carbonate-based syntheses of ionic liquids (CBILS) can be used as a convenient method for various molten salts. The problem of acidic or salt waste production during the synthesis of ILs can be avoided with dimethyl carbonate as reagent. Formation of quaternary carbonate salts with DMC has been published by Jansen,³³⁴ Ue,³³⁵ and Takehara.³³⁶ The CBILS proceeds via a carboxylate intermediate (Figure 63), which could be subsequently converted into the final IL under release of carbon dioxide.³³⁷ Nevertheless, organic carbonates have been chosen as solvents to dissolve organic salts like sulfonium salts.³³⁸

7.3. Cosmetic Applications

In many cosmetic applications organic carbonates (especially PC) are allowed to act as a cosolvent or solubilizer³³⁹ with up to 20 mass %. The use of PC is regulated by the cosmetic ingredient review (CIR); PC was introduced in 1987.³⁴⁰ Despite increasingly strict regulations during the last two decades, PC was again granted as a cosolvent for cosmetics in 2004 in a new cosmetic ingredient review. It is used to regulate the viscosity of mixtures.³⁴¹ Furthermore, propylene and ethylene carbonate have been added to nail polish to obtain high flexibilities during the drying process combined with their low toxicity.³⁴²

7.4. Cleaning Cosolvents

Due to their low toxicity, organic carbonates have been turned out to be excellent cosolvents for cleaning and depainting products. For cleaning of carpets, rugs, and fabrics PC can be used as a sequestering agent.³⁴³ It has been added as cosolvent up to 5%. PC can also be applied in higher concentrations (up to 25%) as solvent for cleaning processes which involve human contact.³⁴⁴ With its softening and swelling effect on paint, PC turned out to be an appropriate solvent in aqueous mixtures for the removal of paints from skin. In this application it has been added as cosolvent in up to 40%.³⁴⁵ In addition, the U.S. Environmental Protection Agency evaluated the use of PC as solvent in depainting operations in air logistics centers.³⁴⁶ Furthermore, alkylene carbonates can be used to reduce the odor of amine-containing compounds like urine. An advantage is the high biodegradability of organic carbonates. Therefore, odor-reducing agents containing ethylene, propylene, or butylene carbonate can be applied in environmental open places like zoos, wool plants, and fish canneries.³⁴⁷ The reduction of odor is achieved by reaction of the respective carbonate with the amine. Furthermore, carbonates like glycerol carbonate are starting materials to synthesize nonionic tensides which can be used in cleaning products.³⁴⁸

7.5. Oil Processing Industry

The FLUOR process is one of the oldest industrial applications of organic carbonates (especially propylene carbonate). This process was invented by the FLUOR Company in 1960 for the removal of carbon dioxide from

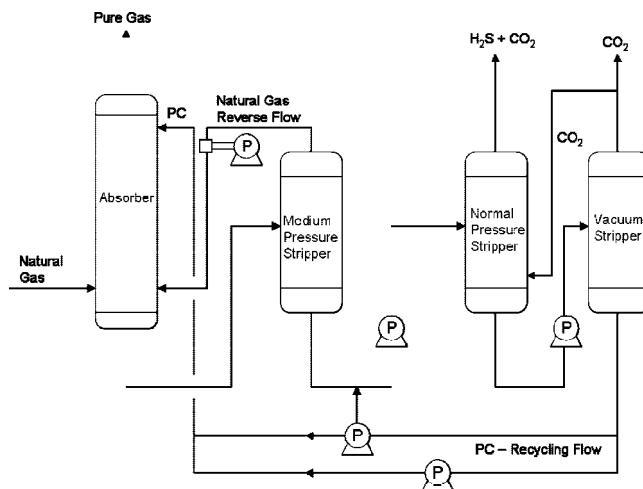


Figure 64. Fluor process for the removal of carbon dioxide from natural gas streams.

natural gas streams.³⁴⁹ To act as a physical absorption solvent PC has an equilibrium capacity for absorbing carbon dioxide several times higher than water and does not absorb high amounts of natural gas and hydrogen. With its low viscosity, low vapor pressure, and noncorrosive behavior it is an excellent choice as an absorbing solvent.³⁵⁰ The operating conditions with propylene carbonate in the modern FLUOR process have been adjusted at 3.1–6.9 MPa and run below ambient temperature. Today the process is especially used on drilling platforms but is in general not limited to carbon dioxide removal from natural gas. A general scheme of the process is given in Figure 64.

Another example for the use of organic carbonates in the oil-processing industry is given by Huntsman Petrochemical Corp.³⁵¹ Organic carbonates can be utilized in combination with carbon dioxide to recover oil from maturing reservoirs. In contrast to other known methods (e.g., the application of toluene) the use of organic carbonates is environmentally friendly and highly efficient. Furthermore, it offers a simple recovery method for asphaltenes from the reservoirs.

7.6. Lacquer Applications

Organic carbonates can be used for nonaqueous liquid pigment dispersions without safety problems due to their high boiling and flash points.³⁵² Many coloring processes use toxic or flammable organic solvents like toluene or cresol. Thus, large amounts of organic waste are produced during this process. In detail, 50–75 mass % of the chemicals in the lacquer wire-coating process are organic solvents. In particular, thin wires need a high amount of organic solvents. In 1999 82.506 t of lacquer-isolated wires and 5200 t of organic waste solvents were produced in Germany.³⁵³ During the lacquering process the solvent is evaporated and the solvent containing air is burned. However, in many cases the contaminated air is leaked partly to the production area. Recently, BASF replaced cresol by propylene carbonate after comparison of the complete life cycle of both solvents including production, application, and waste removal in the copper wire-coating process.³⁵⁴ It could be shown that both ecological and economical aims are maximized to obtain the best results for the production process of coated copper wires.

7.7. Others

The development of liquid crystal devices has received increased attention in the past decade in order to produce light and long-living electronics. With its polarity, propylene carbonate is suitable to act as a solvent in the formation process of alignment films. Furthermore, it is necessary that the solvent can be modified by a second solvent to control the surface tension during the process.³⁵⁵ It turned out that PC can be used in both functions. However, best results were obtained in combination with glycol ethers.

8. Summary

Since the 1960s applications of organic carbonates as solvents have spread to nearly every field of chemistry. In particular, the use in lithium batteries and other electrochemical applications like the electropolymerization are well established. The high solubility of ions, dielectric constants, and dipole moments are basic properties for the success of organic carbonates in these research areas. Furthermore, the low toxicities and environmentally benign properties make them acceptable alternatives for standard organic solvents and valuable candidates to substitute NMP, DMF, and other polar, aprotic solvents.

Not mentioned in this review is the extensive use of organic carbonates as environmentally friendly building blocks for classical organic transformations, where they can be used as methylation agents or in methoxycarbonylations.^{356–358} Furthermore, it has to be noted that synthesis and application of organic carbonates is often connected with the synthesis of polycarbonates.³⁵⁹ These processes are already highlighted in separate reviews with regard to the special properties of various polycarbonates.^{360,40}

The synthesis of organic carbonates is still the bottleneck in their use as real “green” solvents. Today numerous applications have been published with these polar solvents especially in research of homogeneous catalysis. However, due to the high boiling point, from an ecological point of view an advantage, product separation will be the major challenge for the future. An alternative for this could be the use of noncyclic carbonates, which can be evaporated more easily. The results of carbonylations, metathesis reactions, and hydrogenations show clearly that organic carbonates are not magic solvents which are able to replace every other solvent. However, their use should always be taken into consideration in a solvent screen for new reactions and catalysts. In particular, the weak interactions between catalysts and the organic carbonates could be of interest to stabilize nanocluster or even homogeneous catalysts in order to develop more efficient recycling processes. The numerous publications on the synthesis and use of organic carbonates each year reveal that this field is of major interest to the chemical community, and the authors hope that this review will stimulate further work.

9. List of Abbreviations

AHD	aprotic highly dipolar (solvent)
AN	acetonitrile
β	hydrogen-bond acceptor/basicity
BC	butylene carbonate
bp	boiling point
CBILS	carbonate-based ionic liquid synthesis
d	density
DEC	diethyl carbonate

DMC	dimethyl carbonate
DMF	<i>N,N</i> -dimethyl formamide
DN	donor number
EC	ethylene carbonate
E^N_T	Reichardt's solvent polarity values
GAV	group-additivity values
EC ₅₀	effective concentration (50)
EHS	Environmental Health and Safety
GPE	gel polymer electrolyte
GyC	glycerol carbonate
IL	ionic liquid
IC ₅₀	inhibitory concentration (50)
LCA	life cycle assessment
LC	lethal concentration (50)
LD ₅₀	lethal dose (50)
LLE	liquid–liquid equilibria
OC	organic carbonate
PC	propylene carbonate
PPy	polypyrrole
PT	polythiophene
sc	supercritical
SEI	solid electrolyte interphase
SEM	single-electron microscope
SLE	solid–liquid equilibria
SPE	solid polymer electrolyte
TMS	temperature-dependent multicomponent solvent
VLE	vapor–liquid equilibria
VOC	volatile organic compound

10. Acknowledgments

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11. References

- Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*, 3rd ed.; Wiley-VCH: Weinheim, 2003.
- Adams, D. J.; Dyson, P. J.; Tavener, S. J. *Chemistry in Alternative Reaction Media*; Wiley & Sons: Chichester, 2004.
- Anastas, P. T.; Warner, J. C. *Green Chemistry: Theory and Practice*; Oxford University Press: New York, 1998; p 30.
- Anastas, P. T.; Kirchoff, M. M. *Acc. Chem. Res.* **2002**, *35*, 686.
- Welton, T. *Chem. Rev.* **1999**, *99*, 2071.
- Wasserscheid, P.; Welton, T. *Ionic Liquids in Synthesis*; Wiley-VCH: Weinheim, 2003.
- Lide, D. R.; Frederiks, H. P. R. *CRC Handbook of Chemistry and Physics*; CRC Press: Boca Raton, 1994.
- Cole-Hamilton, D. J. *Adv. Synth. Catal.* **2006**, *348*, 1341.
- Leitner, W. *Acc. Chem. Res.* **2002**, *35*, 746.
- Starks, C. M.; Liotta, C. L.; Halpern, M. *Phase Transfer Catalysis: Fundamentals, Applications and Industrial Perspectives*; Chapman and Hall: London, 1994.
- Kuntz, E. G. *Chem. Abstr.* **1977**, *87*, 101944. FR Patent 2314910, 1975.
- Bonilla, R. J.; James, B. R.; Jessop, P. G. *Chem. Commun.* **2000**, 941.
- Bhanage, B. M.; Ikushima, Y.; Shirai, M.; Arai, M. *Chem. Commun.* **1999**, 1277.
- Horváth, I. T. *Acc. Chem. Res.* **1998**, *31*, 641.
- For a review, see: Shuklov, I. A.; Dubrovina, N. V.; Börner, A. *Synthesis* **2007**, 2925.
- Horváth, I. T.; Rábai, J. *Science* **1994**, *266*, 72.
- In *Handbook of Fluorous Chemistry*; Gladysz, J. A., Curran, D. P., Horváth, I. T., Eds.; Wiley & Sons: New York, 2005.
- Heldebrant, D. J.; Jessop, P. G. *J. Am. Chem. Soc.* **2003**, *125*, 5600.
- Chen, J.; Spear, S. K.; Huddleston, J. G.; Rogers, R. D. *Green Chem.* **2005**, *7*, 64.

- (20) Zhou, H.-F.; Fan, Q.-H.; Tang, W.-J.; Xu, L.-J.; He, Y.-M.; Deng, G.-J.; Zaho, L.-W.; Gu, L.-Q.; Chan, A. S. C. *Adv. Synth. Catal.* **2006**, *348*, 2172.
- (21) Adam, D. *Nature* **2000**, *407*, 938.
- (22) Behr, A. *Angewandte Homogene Katalyse*; Wiley-VCH: Weinheim, 2006.
- (23) Betzemeier, B.; Knochel, P. *Top. Curr. Chem.* **1999**, *206*, 60.
- (24) Riess, J. G.; Krafft, M. P. *Biomaterials* **1998**, *19*, 1529.
- (25) Jiao, H.; Le Stang, S.; Soós, T.; Meier, R.; Kowski, K.; Rademacher, P.; Jafarpour, L.; Hamard, J.; Nolan, S. P.; Gladysz, J. A. *J. Am. Chem. Soc.* **2002**, *124*, 1516.
- (26) Luo, Z.; Zhang, Q.; Oderaotoshi, Y.; Curran, D. P. *Science* **2001**, *291*, 1766.
- (27) Ranke, J.; Stolte, S.; Störmann, R.; Arning, J.; Jastoff, B. *Chem. Rev.* **2007**, *107*, 2183–2206.
- (28) Harjani, J. R.; Farrell, J.; Garcia, M. T.; Singer, R. D.; Scammells, P. J. *Green Chem.* **2009**, *11*, 821.
- (29) Horváth, I. T.; Anastas, P. T. *Chem. Rev.* **2007**, *107*, 2869.
- (30) Horváth, I. T.; Mehdi, H.; Boda, L.; Mika, L. T. *Green Chem.* **2008**, *10*, 238.
- (31) Leitner, W. *Green Chem.* **2009**, *11*, 603.
- (32) Koller, G.; Fischer, U.; Hungerbühler, K. *Ind. Eng. Chem. Res.* **2000**, *39*, 960.
- (33) EN ISO 14040, *European Committee for Standardisation*, Brussels, Belgium, 1997.
- (34) Capello, C.; Fischer, U.; Hungerbühler, K. *Green Chem.* **2007**, *9*, 917.
- (35) Alfonsi, K.; Colberg, J.; Dunn, P. J.; Fevig, T.; Jennings, S.; Johnson, T. A.; Kleine, H. P.; Knight, C.; Nagy, M. A.; Perry, D. A.; Stefaniak, M. *Green Chem.* **2008**, *10*, 31.
- (36) Constable, D. J. C.; Dunn, P. J.; Hayler, J. D.; Humphrey, G. R.; Leazer, J. L., Jr.; Linderman, R. J.; Lorenz, K.; Manley, J.; Pearlman, B. A.; Wells, A.; Zaks, A.; Zhang, T. Y. *Green Chem.* **2007**, *9*, 411.
- (37) Shaikh, A.-A.; Sivaram, S. *Chem. Rev.* **1996**, *96*, 951.
- (38) Andrei, H. S.; Nizkorodov, S. A.; Dopfer, O. *Angew. Chem., Int. Ed.* **2007**, *46*, 4754.
- (39) Schäffner, B.; Verevkin, S. P.; Börner, A. *Chem. Unserer Zeit* **2009**, *43*, 12.
- (40) Sakakura, T.; Choi, J.-C.; Yasuda, H. *Chem. Rev.* **2007**, *107*, 2365.
- (41) Xu, K. *Chem. Rev.* **2004**, *104*, 4303.
- (42) *JEFFSOL PC*; Huntsman: Conroe, TX, 2008.
- (43) (a) Patent DE 109933 (Chemische Fabrik von Heyden), 1900; 1901, 5; *Chem. Abstr.* **1906**, 210695. (b) DE 116386 (Chemische Fabrik von Heyden), 1900; 1904, 6, 1160. *Chem. Abstr.* **1906**, 213476.
- (44) (a) Tanaka, Y.; Sawamura, N.; Iwamoto, M. *Tetrahedron Lett.* **1998**, *39*, 9457. (b) Sakakura, T.; Choi, J.-C.; Saito, Y.; Masuda, T.; Sako, T.; Oriyama, T. *J. Org. Chem.* **1999**, *64*, 4506.
- (45) Kohno, K.; Choi, J.-C.; Ohshima, Y.; Yili, A.; Yasuda, H.; Sakakura, T. *J. Organomet. Chem.* **2008**, *693*, 1389.
- (46) Zhang, L.; Niu, D.; Zhang, K.; Zhang, G.; Luo, Y.; Lu, J. *Green Chem.* **2008**, *10*, 202.
- (47) (a) Drake, I. J.; Fajdala, K. L.; Bell, A. T.; Tilley, T. D. *J. Catal.* **2005**, *230*, 14. (b) Dunn, B. C.; Guenneau, C.; Hilton, S. A.; Pahnke, J.; Eyring, E. M. *Energy Fuels* **2002**, *16*, 177.
- (48) Dong, W.-S.; Zhou, X.; Xin, C.; Liu, C.; Liu, Z. *Appl. Catal. A: Gen.* **2008**, *334*, 100.
- (49) Zhang, Y.; Bell, A. T. *J. Catal.* **2008**, *255*, 153.
- (50) Zhu, D.; Mei, F.; Chen, L.; Li, T.; Mo, W.; Li, G. *Energy Fuels* **2009**, *23*, 2359.
- (51) (a) Krimm, H.; Buysch, H. J.; Ruldolph, H. *Chem. Abstr.* **1979**, *90*, 168058g. Bayer AG Ger. Offen. 2,740,242, 1979. (b) Buysch, H.-J.; Klausener, A.; Langer, R.; Mais, F. J. *Chem. Abstr.* **1993**, *118*, 254406. Bayer AG Ger. Offen. 4,129,316, 1993. (c) Frevel, L. K.; Gilpin, J. A. *Chem. Abstr.* **1972**, *76*, 99140. Dow Chemical Co. U.S. Patent 3,642,858, 1972.
- (52) Zhao, X.; Jia, Z.; Wang, Y. *J. Chem. Technol. Biotechnol.* **2006**, *81*, 794.
- (53) Yutaka, K.; Takashi, O.; Masahayu, D.; Kenichi, K. I.; Atsushi, O. *Chem. Abstr.* **1994**, *120*, 245070. EP 0581131, 1993.
- (54) Zhao, X. Q.; Zhang, Y.; Wang, Y. *J. Ind. Eng. Chem. Res.* **2004**, *43*, 4038.
- (55) Bhanage, B. M.; Fujita, S.; Ikushima, Y.; Arai, M. *Green Chem.* **2003**, *5*, 429.
- (56) Wang, M.; Zhao, N.; Wei, W.; Sun, Y. *Stud. Surf. Sci. Catal.* **2004**, *153*, 197.
- (57) Behr, A.; Eilting, J.; Irawadi, K.; Leschinski, J.; Lindner, F. *Green Chem.* **2008**, *10*, 13.
- (58) Wang, M.; Zhao, N.; Wei, W.; Sun, Y. *Ind. Eng. Chem. Res.* **2005**, *44*, 7596.
- (59) Stoica, G.; Abelló, S.; Pérez-Ramírez, J. *ChemSusChem* **2009**, *2*, 301.
- (60) Knifton, J. F.; Duranleau, R. G. *J. Mol. Catal.* **1991**, *67*, 389.
- (61) Tatsumi, T.; Watanabe, Y.; Koyano, K. A. *Chem. Commun.* **1996**, 2281.
- (62) Watanabe, Y.; Tatsumi, T. *Microporous Mesoporous Mater.* **1998**, *22*, 399.
- (63) Bhanage, B. M.; Fujita, S.; He, Y.; Ikushima, Y.; Shirai, M.; Torii, K.; Arai, M. *Catal. Lett.* **2002**, *83*, 137.
- (64) Wei, T.; Wang, M.; Wei, W.; Sun, Y.; Zhong, B. *Fuel Process. Technol.* **2003**, *83*, 137.
- (65) Li, Z.; Cheng, B.; Su, K.; Gu, Y.; Xi, P.; Guo, M. *J. Mol. Catal. A: Gen.* **2008**, *289*, 100.
- (66) Luo, S.; Chi, Y.; Sun, L.; Wang, Q.; Hu, C. *Catal. Commun.* **2008**, *9*, 2560.
- (67) (a) Pagliaro, M.; Ciriminna, R.; Kimura, H.; Rossi, M.; Della Pina, C. *Angew. Chem., Int. Ed.* **2007**, *46*, 4434. (b) Naik, P. U.; Petitjean, L.; Refes, K.; Picquet, M.; Plasseraud, L. *Adv. Synth. Catal.* **2009**, *351*, 1753.
- (68) Kenar, J. A.; Knothe, G.; Copes, A. L. *J. Am. Oil Chem. Soc.* **2004**, *81*, 285.
- (69) (a) With DMC: Kim, S. C.; Kim, Y. H.; Lee, H.; Yoon, D. Y.; Song, B. K. *J. Mol. Catal. B: Enz.* **2007**, *49*, 75. (b) With PC: Jung, K. S.; Kim, J. H.; Cho, J. H.; Kim, D. K. *Chem. Abstr.* **2009**, *150*, 356052. WO 2009/035269, 2009.
- (70) Patel, Y.; George, J.; Pillai, S. M.; Munshi, P. *Green Chem.* **2009**, *11*, 1056.
- (71) (a) Tullo, A. H.; Short, P. L. *Chem. Eng. News* **2006**, *84*, 22. (b) For further information see: Meiers, R.; Dingerdissen, U.; Hölderich, W. F. *J. Catal.* **1998**, *176*, 376. (c) Jenzer, G.; Mallat, T.; Maciejewski, M.; Eigenmann, F.; Baiker, A. *Appl. Catal., A* **2001**, *218*, 31. (d) Chen, Q.; Beckmann, E. J. *Green Chem.* **2007**, *9*, 802.
- (72) (a) Chen, Q.; Beckmann, E. J. *Green Chem.* **2008**, *10*, 934. (b) Sheldon, R. A. *Chem. Commun.* **2008**, 3352.
- (73) Song, J.; Zhang, Z.; Han, B.; Hu, S.; Li, W.; Xie, Y. *Green Chem.* **2008**, *10*, 1337.
- (74) Zhang, X.; Jia, Y.-B.; Lu, X.-B.; Li, B.; Wang, H.; Sun, L.-C. *Tetrahedron Lett.* **2008**, *49*, 6589.
- (75) Zheng, X.; Luo, S.; Zhang, L.; Cheng, J.-P. *Green Chem.* **2009**, *11*, 455.
- (76) Gomes, C. R.; Ferreira, D. M.; Leopoldo Constantino, C. J.; Pérez González, E. R. *Tetrahedron Lett.* **2008**, *49*, 6879.
- (77) Doll, K. M.; Erhan, S. Z. *Green Chem.* **2005**, *7*, 849.
- (78) He, L. N.; Yasuda, H.; Sakakura, T. *Green Chem.* **2003**, *5*, 92.
- (79) Sun, J.; Ren, J.; Zhang, S.; Cheng, W. *Tetrahedron Lett.* **2009**, *50*, 423.
- (80) (a) Meléndez, J.; North, M.; Pasquale, R. *Eur. J. Inorg. Chem.* **2007**, 3323. (b) North, M.; Pasquale, R. *Angew. Chem., Int. Ed.* **2009**, *48*, 2946. (c) Meléndez, J.; North, M.; Villuendas, P. *Chem. Commun.* **2009**, 2577.
- (81) North, M.; Villuendas, P.; Young, C. *Chem. Eur. J.* **2009**, *15*, 11454.
- (82) Jin, L.; Huang, Y.; Jing, H.; Chang, T.; Yan, P. *Tetrahedron: Asymmetry* **2008**, *19*, 1947.
- (83) Chen, S.-W.; Kawthekar, R. B.; Kim, G.-J. *Tetrahedron Lett.* **2007**, *48*, 297.
- (84) Yan, P.; Jing, H. *Adv. Synth. Catal.* **2009**, *351*, 1325.
- (85) Chang, T.; Jin, L.; Jing, H. *ChemCatChem* **2009**, *1*, 379.
- (86) Pallavicini, M.; Valoti, E.; Villa, L.; Piccolo, O. *J. Org. Chem.* **1994**, *59*, 1751.
- (87) Matsumoto, K.; Fuwa, S.; Kitajima, H. *Tetrahedron Lett.* **1995**, *36*, 6499.
- (88) Shimojo, M.; Matsumoto, K.; Hatanaka, M. *Tetrahedron* **2000**, *56*, 9281.
- (89) Aresta, M.; Dibenedetto, A.; Nocito, F.; Pastore, C. *J. Mol. Catal. A: Chem.* **2006**, *257*, 149.
- (90) Vieville, C.; Yoo, J. W.; Mouloungui, Z. *Catal. Lett.* **1998**, *56*, 245.
- (91) George, J.; Patel, Y.; Pillai, S. M.; Munshi, P. *J. Mol. Catal. A: Chem.* **2009**, *304*, 1.
- (92) Huang, S.; Ma, J.; Li, J.; Zhao, N.; Wei, W.; Sun, Y. *Catal. Commun.* **2008**, *9*, 276.
- (93) Tomishige, K.; Yasuda, H.; Yoshida, Y.; Nurunnabi, M.; Li, B. T.; Kunimori, K. *Green Chem.* **2004**, *6*, 206.
- (94) Tomishige, K.; Yasuda, H.; Yoshida, Y.; Nurunnabi, M.; Li, B. T.; Kunimori, K. *Catal. Lett.* **2004**, *95*, 45.
- (95) Du, Y.; Kong, D. L.; Wang, H. Y.; Cai, F.; Tian, H. S.; Wang, J. Q.; He, L. N. *J. Mol. Catal. A: Chem.* **2005**, *241*, 233.
- (96) Zhao, X.; Sun, N.; Wang, S.; Li, F.; Wang, Y. *Ind. Eng. Chem. Res.* **2008**, *47*, 1365.
- (97) Huang, S.; Liu, S.; Li, J.; Zhao, N.; Wei, W.; Sun, Y. *Catal. Lett.* **2007**, *118*, 290.
- (98) Du, Y.; He, L.-N.; Kong, D.-L. *Catal. Commun.* **2008**, *9*, 1754.
- (99) Zhou, X.; Yang, X.; Chen, T.; Zhang, Y.; Wang, G. *Chin. J. Catal.* **2009**, *30*, 7.
- (100) Yamamoto, H.; Nishiyama, M.; Imagawa, H.; Nishizawa, M. *Tetrahedron Lett.* **2006**, *47*, 8369.
- (101) Sakakura, T.; Kohno, K. *Chem. Commun.* **2009**, 1312.
- (102) Pacheco, M. A.; Marshall, C. L. *Energy Fuels* **1997**, *11*, 2–29.

- (103) Gonzalez, B.; Dominguez, A.; Tojo, J. *J. Chem. Thermodyn.* **2004**, *36*, 267.
- (104) See <http://www.huntsman.com>.
- (105) Wachter, P.; Schweiger, H.-G.; Wudy, F.; Gores, H. *J. Chem. Thermodyn.* **2008**, *40*, 1542.
- (106) Verevkin, S. P.; Emel'yanenko, V. N. *Fluid Phase Equilib.* **2008**, *266*, 64.
- (107) Chernyak, Y.; Clements, J. H. *J. Chem. Eng. Data* **2004**, *49*, 1180.
- (108) (a) Kozlova, S. A.; Emel'yanenko, V. N.; Georgieva, M.; Verevkin, S. P.; Chernyak, Y.; Schäffner, B.; Börner, A. *J. Chem. Thermodyn.* **2008**, *40*, 1136–1140. (b) Steele, W. V.; Chirico, R. D.; Knipmeyer, S. E.; Nguyen, A.; Smith, N. K. *J. Chem. Eng. Data* **1997**, *42*, 1037. (c) Mansson, M. *J. Chem. Thermodyn.* **1972**, *4*, 865–871. (d) Kusano, K. *Thermochim. Acta* **1985**, *88*, 109. (e) Chickos, J. S.; Acree, W. E., Jr.; Liebman, J. F. *J. Phys. Chem. Ref. Data* **1999**, *28*, 1535. (f) Chickos, J. S.; Webb, P.; Nichols, C. *J. Chem. Thermodyn.* **2002**, *34*, 1195. (g) Kiparisova, E. G.; Rabinovich, I. B. *Dokl. Phys. Chem. (Engl. Transl.)* **1971**, *199*, 675. (h) Friestad, G. K.; Marie, J. C.; Suh, Y. S.; Qin, J. *J. Org. Chem.* **2006**, *71*, 7016.
- (109) Verevkin, S. P.; Toktonov, A. V.; Chernyak, Y.; Schäffner, B.; Börner, A. *Fluid Phase Equilib.* **2008**, *268*, 1.
- (110) Wilson, G. M.; Von Niederhausern, D. M.; Giles, N. F. *J. Chem. Eng. Data* **2002**, *47*, 761.
- (111) Verevkin, S. P.; Emel'yanenko, V. N.; Kozlova, S. A. *J. Phys. Chem. A* **2008**, *112*, 10667.
- (112) Verevkin, S. P.; Emel'yanenko, V. N.; Toktonov, A. V.; Chernyak, Y.; Schäffner, B.; Börner, A. *J. Chem. Thermodyn.* **2008**, *40*, 1428.
- (113) Benson, S. W. *Thermochemical Kinetics*; Wiley: New York, 1976.
- (114) Li, T.; Balbuena, P. B. *Chem. Phys. Lett.* **2000**, *317*, 421.
- (115) Bohets, H.; van der Veken, B. *J. Phys. Chem. Chem. Phys.* **1999**, *1*, 1817.
- (116) Wang, Y.; Balbuena, P. B. *J. Phys. Chem. A* **2001**, *105*, 9972.
- (117) Sun, H.; Mumby, S. J.; Maple, J. R.; Hagler, A. T. *J. Phys. Chem.* **1995**, *99*, 5873.
- (118) Bayardon, J.; Holz, J.; Schäffner, B.; Andrushko, V.; Verevkin, S.; Preetz, A.; Börner, A. *Angew. Chem., Int. Ed.* **2007**, *46*, 5971.
- (119) Kumelan, J.; Tuma, D.; Verevkin, S. P.; Maurer, G. *J. Chem. Eng. Data* **2008**, *53*, 2844. (a) Blanchard, F.; Carre, B.; Bonhomme, F.; Biensan, P.; Lemordant, D. *Can. J. Chem.* **2003**, *81*, 385.
- (120) (b) Jihoon, I.; Myungyoum, K.; Jaewon, L.; Hwayong, K. *J. Chem. Eng. Data* **2004**, *49*, 243.
- (121) Murrieta-Guevara, F.; Romero-Martinez, A.; Trejo, A. *Fluid Phase Equilib.* **1988**, *44*, 105.
- (122) (a) Negadi, L.; Delepine, H.; Ait-Kaci, A.; Jose, J. *ELDATA: Int. Electron. J. Phys. Chem. Data* **1999**, *5*, 197. (b) Negadi, L.; Ghanem, G.; Ait-Kaci, A.; Jose, J. *ELDATA: Int. Electron. J. Phys. Chem. Data* **1997**, *3*, 53.
- (123) (a) Oh, J.-H.; Hwang, I.-C.; Park, S.-J. *Fluid Phase Equilib.* **2009**, *276*, 142. (b) Oh, J.-H.; Han, K.-J.; Park, S.-J. *J. Chem. Eng. Data* **2006**, *51*, 1852. (c) Han, K.-J.; Park, S.-J. *Hwahak Konghak* **2005**, *43*, 387. *Chem. Abstr.* **2005**, *139*, 394123.
- (124) Luo, H.-P.; Xiao, W.-D.; Zhu, K.-H. *Fluid Phase Equilib.* **2000**, *175*, 91.
- (125) (a) Pereira, A. B.; Rodriguez, A.; Canosa, J.; Tojo, J. *J. Chem. Thermodyn.* **2005**, *37*, 249. (b) Pereira, A. B.; Rodriguez, A.; Canosa, J.; Tojo, J. *Fluid Phase Equilib.* **2005**, *235*, 83. (c) Rodriguez, A.; Canosa, J.; Dominguez, A.; Tojo, J. *J. Chem. Eng. Data* **2003**, *48*, 86. (d) Rodriguez, A.; Canosa, J.; Dominguez, A.; Tojo, J. *Fluid Phase Equilib.* **2002**, *201*, 187.
- (126) Luo, H.-P.; Zhou, J.-H.; Xiao, W.-D.; Zhu, K.-H. *J. Chem. Eng. Data* **2001**, *46*, 842.
- (127) Prasad Viital, T. E.; Banerjee, S.; Kishore Babu, J.; Prasad, D. H. L. *Fluid Phase Equilib.* **2004**, *218*, 291.
- (128) Annesini, M. C.; Capparucci, C.; Marrelli, L.; Vergara, A. M. *Fluid Phase Equilib.* **1985**, *23*, 293.
- (129) Resa, J. M.; Gonzalez, C.; Ortiz de Landaluce, S.; Goenaga, J. M. *J. Chem. Eng. Data* **2005**, *50*, 1212.
- (130) Fang, Y.-J.; Qian, J.-M. *J. Chem. Eng. Data* **2005**, *50*, 340.
- (131) Chernyak, Y. *J. Chem. Eng. Data* **2008**, *53*, 603.
- (132) Cocero, M. J.; Garcia, I.; Gonzalez, J. A.; Cobos, J. C. *Fluid Phase Equilib.* **1991**, *68*, 151.
- (133) (a) Comelli, F.; Francesconi, R. *J. Chem. Eng. Data* **1994**, *39*, 560. (b) Francesconi, R.; Comelli, F. *J. Chem. Eng. Data* **1997**, *42*, 697. (c) Comelli, F.; Francesconi, R. *J. Chem. Eng. Data* **1997**, *42*, 705. (d) Francesconi, R.; Comelli, F. *J. Chem. Eng. Data* **1996**, *41*, 736. (e) Comelli, F.; Francesconi, R.; Ottani, S. *J. Chem. Eng. Data* **1996**, *41*, 534. (f) Sporzynski, A.; Szurgocinska, M.; Domanska, U.; Gonzalez, J. A. *Ind. Eng. Chem. Res.* **2003**, *42*, 4382.
- (134) Chernyak, Y. *J. Chem. Eng. Data* **2006**, *51*, 416.
- (135) (a) Ali, S. H.; Lababidi, H. M. S.; Merchant, S. Q.; Fahim, M. A. *Fluid Phase Equilib.* **2003**, *214*, 25. (b) Lababidi, H. M. S.; Ali, S. H.; Fahim, M. A. *Ind. Eng. Chem. Res.* **2006**, *45*, 5086. (c) Olejniczak, J.; Staniewski, J.; Szymanowski, J. *Anal. Chim. Acta* **2005**, *535*, 251.
- (136) (a) Jain, P.; Singh, M. *J. Chem. Eng. Data* **2004**, *49*, 1214. (b) Comelli, F.; Francesconi, R. *J. Chem. Eng. Data* **2005**, *50*, 191. (c) Rodriguez, A.; Canosa, J.; Tojo, J. *J. Chem. Eng. Data* **2001**, *46*, 184. (d) Comelli, F.; Francesconi, R.; Bigi, A.; Rubini, K. *J. Chem. Eng. Data* **2006**, *51*, 665. (e) Castellari, C.; Vitalini, D.; Comelli, F.; Francesconi, R. *Thermochim. Acta* **2004**, *412*, 125. (f) Castellari, C.; Comelli, F.; Francesconi, R. *Thermochim. Acta* **2004**, *413*, 249. (g) Comelli, F.; Francesconi, R.; Castellari, C. *J. Chem. Eng. Data* **2001**, *46*, 63. (h) Francesconi, R.; Comelli, F.; Castellari, C. *J. Chem. Eng. Data* **2000**, *45*, 544. (i) Francesconi, R.; Castellari, C.; Comelli, F. *J. Chem. Eng. Data* **1999**, *44*, 1373. (j) Comelli, F.; Francesconi, R.; Castellari, C. *J. Chem. Eng. Data* **1999**, *44*, 739. (k) Francesconi, R.; Comelli, F.; Castellari, C. *Thermochim. Acta* **1999**, *327*, 145. (l) Comelli, F.; Francesconi, R.; Castellari, C. *J. Chem. Eng. Data* **1999**, *44*, 144. (m) Francesconi, R.; Comelli, F. *J. Chem. Eng. Data* **1999**, *44*, 44. (n) Comelli, F.; Francesconi, R.; Ottani, S. *J. Chem. Eng. Data* **1998**, *43*, 333. (o) Francesconi, R.; Castellari, C.; Comelli, F. *Thermochim. Acta* **1997**, *306*, 99. (p) Comelli, F.; Righetti, M. C.; Francesconi, R. *Thermochim. Acta* **1997**, *306*, 37. (q) Comelli, F.; Ottani, S.; Francesconi, R. *J. Chem. Eng. Data* **1997**, *42*, 1208. (r) Righetti, M. C.; Comelli, F.; Francesconi, R. *Thermochim. Acta* **1997**, *294*, 179. (s) Francesconi, R.; Comelli, F.; Ottani, S. *J. Chem. Eng. Data* **1997**, *42*, 702. (t) Francesconi, R.; Comelli, F. *J. Chem. Eng. Data* **1997**, *42*, 45. (u) Francesconi, R.; Comelli, F. *J. Chem. Eng. Data* **1996**, *41*, 1397. (v) Francesconi, R.; Comelli, F.; Ottani, S. *Thermochim. Acta* **1996**, *277*, 121. (w) Francesconi, R.; Comelli, F. *Thermochim. Acta* **1995**, *264*, 95. (x) Comelli, F.; Francesconi, R. *J. Chem. Eng. Data* **1995**, *40*, 1184. (y) Comelli, F.; Francesconi, R. *J. Chem. Eng. Data* **1995**, *40*, 25. (z) Francesconi, R.; Comelli, F. *J. Chem. Eng. Data* **1995**, *40*, 811.
- (137) (a) Comelli, F.; Francesconi, R. *J. Chem. Eng. Data* **1995**, *40*, 808. (b) Comelli, F.; Francesconi, R. *J. Chem. Eng. Data* **1995**, *40*, 805. (c) Francesconi, R.; Comelli, F. *J. Chem. Eng. Data* **1995**, *40*, 512. (d) Comelli, F.; Francesconi, R. *J. Chem. Eng. Data* **1995**, *40*, 509. (e) Francesconi, R.; Comelli, F. *J. Chem. Eng. Data* **1995**, *40*, 31. (f) Comelli, F.; Francesconi, R. *J. Chem. Eng. Data* **1995**, *40*, 28. (g) Francesconi, R.; Comelli, F. *J. Chem. Eng. Data* **1994**, *39*, 106. (i) Comelli, F.; Francesconi, R. *J. Chem. Eng. Data* **1994**, *39*, 108. (j) Negadi, L.; Blondel, A.; Mokbel, I.; Ait-Kaci, A.; Jose, J. *Int. DATA Ser., Selected Data on Mixtures, Ser. A* **1993**, *21*, 177. (k) Negadi, L.; Blondel, A.; Mokbel, I.; Ait-Kaci, A.; Jose, J. *Int. DATA Ser., Selected Data on Mixtures, Ser. A* **1993**, *21*, 189. (l) Negadi, L.; Blondel, A.; Mokbel, I.; Ait-Kaci, A.; Jose, J. *Int. DATA Ser., Selected Data on Mixtures, Ser. A* **1993**, *21*, 183. (m) Negadi, L.; Blondel, A.; Mokbel, I.; Ait-Kaci, A.; Jose, J. *Int. DATA Ser., Selected Data on Mixtures, Ser. A* **1993**, *21*, 171. (n) Negadi, L.; Blondel, A.; Mokbel, I.; Ait-Kaci, A.; Jose, J. *Int. DATA Ser., Selected Data on Mixtures, Ser. A* **1993**, *21*, 193. (p) Moreiras, A. F.; Garcia, J.; Lugo, L.; Comunas, M. J. P.; Lopez, E. R.; Fernandez, J. *Fluid Phase Equilib.* **2003**, *204*, 233. (q) Baylaucq, A.; Comunas, M. J. P.; Boned, C.; Allal, A.; Fernandez, J. *Fluid Phase Equilib.* **2002**, *199*, 249. (r) Lugo, L.; Comunas, M. J. P.; Lopez, E. R.; Fernandez, J. *Fluid Phase Equilib.* **2002**, *199*, 135. (s) Comunas, M. J. P.; Baylaucq, A.; Boned, C.; Fernandez, J. *Int. J. Thermophys.* **2001**, *22*, 749. (t) Lugo, L.; Comunas, M. J. P.; Lopez, E. R.; Fernandez, J. *Fluid Phase Equilib.* **2001**, *186*, 235. (u) Lopez, E. R.; Lugo, L.; Comunas, M. J. P.; Garcia, J.; Fernandez, J. *J. Chem. Thermodyn.* **2000**, *32*, 743. (v) Gonzalez, J. A.; Mozo, I.; Villa, S.; Riesco, N.; Fuente, I. G.; Cobos, J. C. *J. Solution Chem.* **2006**, *35*, 787.
- (138) Ding, M. S. *J. Chem. Eng. Data* **2004**, *49*, 276.
- (139) (a) Kehiaian, H. V.; Gonzalez, J. A.; Garcia, I.; Cobos, J. C.; Casanova, C.; Cocero, M. J. *Fluid Phase Equilib.* **1991**, *64*, 1. (b) Kehiaian, H. V.; Gonzalez, J. A.; Garcia, I.; Cobos, J. C.; Casanova, C.; Cocero, M. J. *Fluid Phase Equilib.* **1991**, *69*, 81. (c) Gonzalez, J. A.; Garcia, I.; Cobos, J. C.; Casanova, C.; Kehiaian, H. V. *Thermochim. Acta* **1993**, *217*, 57.
- (140) Garcia, J.; Lopez, E. R.; Fernandez, J.; Legido, J. L. *Thermochim. Acta* **1996**, *286*, 321.
- (141) (a) Lugo, L.; Garcia, J.; Comunas, M. J. P.; Fernandez, J. *Fluid Phase Equilib.* **2003**, *212*, 111. (b) Lugo, L.; Luna, V.; Garcia, J.; Lopez, E. R.; Comunas, M. J. P.; Fernandez, J. *Fluid Phase Equilib.* **2004**, *217*, 165.
- (142) Silva, L. B.; Freitas, L. C. G. *J. Mol. Struct. Theochem.* **2007**, *806*, 23.
- (143) Soetens, J.-C.; Millot, C.; Maignet, B.; Bakó, I. *J. Mol. Liq.* **2001**, *92*, 201.
- (144) Meylan, W. M.; Howard, P. H. *Chemosphere* **1993**, *26*, 2293.
- (145) Hlavatý, J.; Novák, P. *Electrochim. Acta* **1992**, *37*, 2595.
- (146) Williams, J. L. R.; Dunham, K. R.; Laakso, T. M. *J. Org. Chem.* **1958**, *23*, 676.

- (147) Armarego, W. L. F.; Perrin, D. D. *Purification of Laboratory Chemicals*, 4th ed.; Butterworth-Heinemann: Oxford, 1996.
- (148) In *Recommended Methods for Purification of Solvents and Tests for Impurities*; Coetzee, J. F., Ed.; Pergamon Press: Oxford, 1982. (b) Coetzee, J. F. *Pure Appl. Chem.* **1985**, *57*, 634.
- (149) Method No. ST-11.1-81; Texaco Chemical Co.: Austin, TX, 1981.
- (150) Fujinaga, T.; Izutsu, K. *Pure Appl. Chem.* **1971**, *27*, 275.
- (151) Jasinski, R. J.; Kirkland, S. *Anal. Chem.* **1967**, *39*, 1663.
- (152) Cheng, H.; Gadde, R. R. *J. Pharm. Sci.* **1985**, *74*, 695.
- (153) Shepot'ko, N. B. *Neftepererab Neftekhim (Moscow)* **1973**, *5*, 51. *Chem. Abstr.* 1979, *79*, 61269.
- (154) Teruya, K.; Matsuo, I.; Hayashida, H.; Nakamoni, I. *Bunseki Kagaku* **1972**, *21*, 1385. *Chem. Abstr.* **1973**, *78*, 52381.
- (155) Pelet, S.; Yoo, J. W.; Mouloungui, Z. *J. High Resolut. Chromatogr.* **1999**, *22*, 276.
- (156) Yang, Y.-L.; Ramaswamy, S. G.; Jakoby, W. B. *J. Biol. Chem.* **1998**, *273*, 7814.
- (157) A full study about the toxicological behavior of propylene carbonate was accomplished in the US.EPA HPV challenge program. For results see: <http://www.epa.gov/chemrtk/pubs/summaries/prplcarb/c13688tc.htm>.
- (158) Itoh, H.; Shinbori, Y. *Bunseki Kagaku* **1977**, *26*, 134. *Chem. Abstr.* **1977**, *87*, 77968.
- (159) Schäffner, B.; Andrushko, V.; Holz, J.; Verevkin, S. P.; Börner, A. *ChemSusChem* **2008**, *1*, 934–940.
- (160) Ritzoulis, G. *Can. J. Chem.* **1989**, *67*, 1105.
- (161) (a) Reichardt, C. *Chem. Rev.* **1994**, *94*, 2319. (b) Reichardt, C. *Pure Appl. Chem.* **2008**, *80*, 1415. (c) Reichardt, C.; Harbusch-Görnert, E. *Liebigs Ann. Chem.* **1983**, 721. (d) Wu, M.; Wu, F.; Luan, H.-L.; Chen, R.-J. *Acta Chim. Sinica* **2005**, *63*, 787.
- (162) For further information on Kamlet-Taft values see: Kamlet, M. J.; Abboud, J. L. M.; Abraham, M. H.; Taft, R. W. *J. Org. Chem.* **1983**, *48*, 2877.
- (163) Schwöbel, J.; Ebert, R.-U.; Kühne, R.; Schüürmann, G. *J. Chem. Inf. Model.* **2009**, *49*, 956.
- (164) Klamt, A. *Chemosphere* **1993**, *26*, 1273.
- (165) Klamt, A. *Chemosphere* **1995**, *32*, 717.
- (166) Schwöbel, J.; Ebert, R.-U.; Kühne, R.; Schüürmann, G. *J. Comput. Chem.* **2009**, *30*, 1454.
- (167) Jasinski, R. *J. Electroanal. Chem.* **1967**, *15*, 89.
- (168) Nelson, R. F.; Adam, R. N. *J. Electroanal. Chem.* **1967**, *15*, 184.
- (169) Elliott, W. Report No. 1, Contract NAS 3-6015 (N65-11518), Sept 1964.
- (170) (a) Tarascon, J.-M.; Armand, M. *Nature* **2001**, *414*, 359. (b) Aurbach, D.; Daroux, M. L.; Faguy, P. W.; Yeager, E. *J. Electrochem. Soc.* **1987**, *134*, 1611. (c) Aurbach, D.; Teller, H.; Levi, E. *J. Electrochem. Soc.* **2002**, *149*, A1255. (d) Zhuang, G. V.; Yang, H.; Bližanac, B.; Ross, P. N. *Electrochem. Solid-State Lett.* **2005**, *8*, A441.
- (171) Xu, K. *J. Electrochem. Soc.* **2009**, *156*, A751.
- (172) Edström, K.; Herstedt, M.; Abraham, D. P. *J. Power Sources* **2006**, *153*, 380.
- (173) Andersson, A. M.; Edström, K. *J. Electrochem. Soc.* **2001**, *148*, A1100.
- (174) Andersson, A. M.; Herstedt, M.; Bishop, A.; Edström, K. *Electrochim. Acta* **2002**, *47*, 1885.
- (175) Zhuang, G. R., Jr. *Electrochem. Solid-State Lett.* **2003**, *6*, A136.
- (176) Herstedt, M.; Abraham, D.; Kerr, J. B.; Edström, K. *Electrochim. Acta* **2004**, *49*, 5097.
- (177) Andersson, A. M.; Henningsson, A.; Siegbahn, H.; Jansson, U.; Edström, K. *J. Power Sources* **2003**, *119–121*, 522.
- (178) Augustsson, A.; Herstedt, M.; Guo, J.-H.; Edström, K.; Zhuang, G. V.; Ross, P. N.; Rubensson, J.-E.; Nordgren, J. *Phys. Chem. Chem. Phys.* **2004**, *6*, 4185.
- (179) Orsini, F.; Du Pasquier, A.; Beaudoin, B.; Tarascon, J. M.; Trentin, M.; Langenhuizen, N.; De Beer, E.; Notten, P. *J. Power Sources* **1998**, *76*, 19.
- (180) Profatilova, I.; Kim, S.-S.; Choi, N.-S. *Electrochim. Acta* **2009**, *54*, 4445.
- (181) Li, J.; Yao, W.; Meng, Y. S.; Yang, Y. *J. Phys. Chem. C* **2008**, *112*, 12550.
- (182) Ota, H.; Sakata, Y.; Inoue, A.; Yamaguchi, S. *J. Electrochem. Soc.* **2004**, *151*, A1659.
- (183) Aurbach, D.; Gamolsky, K.; Markovsky, B.; Gofer, Y.; Schmidt, M.; Heider, U. *Electrochim. Acta* **2003**, *47*, 1423.
- (184) Guerfi, A.; Dontigny, M.; Charest, P.; Peticlerc, M.; Lagacé, M.; Vijh, A.; Zaghbi, K. *J. Power Sources* **2009**, *195*, 845.
- (185) Zhang, S. S. *J. Power Sources* **2006**, *162*, 1379.
- (186) (a) Komaba, S.; Ozeki, T.; Okushi, K. *J. Power Sources* **2009**, *189*, 197. (b) Mikami, F.; Watanabe, M.; Komaba, S.; Yashiro, H.; Kumagai, N. *46th Battery Symp. (Jpn.)* **2005**, 494. (c) Ui, K.; Kikuchi, S.; Mikami, F.; Kadoma, Y.; Kumagai, N. *J. Power Sources* **2007**, *173*, 518. (d) Komaba, S.; Okushi, K.; Groult, H. *ECS Trans.* **2008**, *11*, 63.
- (187) Nakajima, T.; Achiha, T.; Ohzawa, Y.; Panich, A. M.; Shames, A. I. *J. Phys. Chem. Sol.* **2008**, *69*, 1292.
- (188) Chan, C. K.; Ruffo, R.; Hong, S. S.; Cui, Y. *J. Power Sources* **2009**, *189*, 1132.
- (189) Ehinon, K. K. D.; Naille, S.; Dedryvère, R.; Lippens, P.-E.; Jumas, J.-C.; Gonbeau, D. *Chem. Mater.* **2008**, *20*, 5388.
- (190) Petrowsky, M.; Frech, R. *J. Phys. Chem. B* **2008**, *112*, 8285.
- (191) Verbrugge, M. W.; Koch, B. J.; Schneider, E. W. *J. Appl. Electrochem.* **2000**, *30*, 269.
- (192) Barthel, J.; Neueder, R.; Rawtytsch, P.; Roch, H. *J. Electroanal. Chem.* **1999**, *471*, 78.
- (193) Kinoshita, S.; Kotato, M.; Sakata, Y.; Ue, M.; Watanabe, Y.; Morimoto, H.; Tobishima, S. *J. Power Sources* **2008**, *183*, 755.
- (194) Choi, N.-S.; Ryu, S.-W.; Park, J.-K. *Electrochim. Acta* **2008**, *53*, 6575.
- (195) Li, L. F.; Lee, H. S.; Li, H.; Yang, X. Q.; Nam, K. W.; Yoon, W. S.; McBreen, J.; Huang, X. J. *J. Power Sources* **2008**, *184*, 517.
- (196) Abouimrane, A.; Ding, J.; Davidson, I. J. *J. Power Sources* **2009**, *189*, 693.
- (197) Fu, M. H.; Huang, K. L.; Liu, S. Q.; Liu, J. S.; Li, Y. K. *J. Power Sources* **2009**, *195*, 862.
- (198) Chen, S.; Wang, Z.; Zhao, H.; Qiao, H.; Luan, H.; Chen, L. *J. Power Sources* **2009**, *187*, 229.
- (199) Tsujikawa, T.; Yabuta, K.; Matsushita, T.; Matsushima, T.; Hayashi, K.; Arakawa, M. *J. Power Sources* **2009**, *189*, 429.
- (200) Jow, T. R.; Xu, K.; Zhang, S.; Ding, M. S. *Chem. Abstr.* **2005**, *143*, 29545. U.S. Patent 6,924,061, 2005.
- (201) Pasquier, A. D.; Disma, F.; Bowmer, T.; Gozdz, A. S.; Amatucci, G.; Tarascon, J. M. *J. Electrochem. Soc.* **1998**, *145*, 472.
- (202) Meisel, T.; Kränzler, T.; Scherber, W. *Chem. Abstr.* **1993**, *118*, 31282. EP 0499115, 1992.
- (203) Mohamed, S. N.; Johari, N. A.; Ali, A. M. M.; Harun, M. K.; Yahaya, M. Z. A. *J. Power Sources* **2008**, *183*, 351.
- (204) Kuboki, T.; Okuyama, T.; Ohsaki, T.; Takami, N. *J. Power Sources* **2005**, *146*, 766.
- (205) Perera, K. S.; Dissanayake, M. A. K. L.; Skaarup, S.; West, K. *J. Solid State Electrochem.* **2008**, *12*, 873.
- (206) Reiter, J.; Velická, J.; Míka, M. *Electrochim. Acta* **2008**, *53*, 7769.
- (207) Reiter, J.; Vondrák, J.; Mièka, Z. *Solid State Ionics* **2007**, *177*, 3501.
- (208) Reiter, J.; Dominko, R.; Nádherná, M.; Jakubec, I. *J. Power Sources* **2009**, *189*, 133.
- (209) Oyama, N.; Fujimoto, Y.; Hatozaki, O.; Nakano, K.; Maruyama, K.; Yamaguchi, K.; Iwase, Y.; Kutsuwa, Y. *J. Power Sources* **2009**, *189*, 315.
- (210) López de Mishima, B. A.; Mishima, H. T. *Sens. Actuators B* **2008**, *131*, 236.
- (211) Ji, X.; Banks, C. E.; Silvester, D. S.; Wain, A. J.; Compton, R. G. *J. Phys. Chem. C* **2007**, *111*, 1496.
- (212) Muzikar, J.; van de Goor, T.; Gas, B.; Kenndler, E. *Anal. Chem.* **2002**, *74*, 428.
- (213) Nagaosa, Y.; Horita, K. *Mikrochim. Acta* **1992**, *108*, 151.
- (214) Nagaosa, Y.; Yoshida, N.; Maegawa, Y.; Fuwa, T. *Microchim. Acta* **1984**, *2*, 39.
- (215) Tjørnelund, J.; Hansen, S. H. *J. Chromatogr. A* **1997**, *792*, 475.
- (216) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods, Fundamentals and Applications*; John Wiley & Sons: New York, 1980.
- (217) Imisides, M. D.; John, R.; Riley, P. J.; Wallace, G. G. *Electroanalysis* **1991**, *3*, 879.
- (218) Bazzouai, M.; Bazzouai, E. A.; Martins, L.; Martins, J. I. *Synth. Met.* **2002**, *130*, 73.
- (219) (a) Wise, D. L.; Winek, G. E.; Trantolo, D. J.; Cooper, T. M.; Gresser, J. D. *Electrical and Optical Polymer Systems*; Marcel Dekker Inc.: New York, 1998; Vol. 17. (b) Rodríguez, J.; Grande, H. J.; Otero, T. F. In *Handbook of Organic Conductive Molecules and Polymers*; Nalwa, H. S., Ed.; John Wiley & Sons: New York, 1997; p 415. (c) Simonet, J.; Berthelot, J. R. *Prog. Solid State Chem.* **1991**, *21*, 1.
- (220) Sadki, S.; Schottland, P.; Brodie, N.; Sabouraud, G. *Chem. Soc. Rev.* **2000**, *29*, 283.
- (221) (a) Cvetko, B. F.; Brungs, M. P.; Burford, R. P.; Skyllas-Kazacos, M. *J. Mat. Sci.* **1988**, *23*, 2102. (b) Cvetko, B. F.; Brungs, M. P.; Burford, R. P.; Skyllas-Kazacos, M. *J. Appl. Electrochem.* **1987**, *17*, 1198.
- (222) Sun, B.; Jones, J. J.; Burford, R. P.; Skyllas-Kazacos, M. *J. Electrochem. Soc.* **1989**, *136*, 698.
- (223) (a) Beck, F.; Oberst, M.; Jansen, R. *Electrochim. Acta* **1990**, *35*, 1841. (b) Beck, F. *Electrochim. Acta* **1988**, *33*, 839.
- (224) Kupila, E.-L.; Kankare, J. *Synth. Met.* **1996**, *82*, 89.
- (225) Zaid, B.; Aeiyaeh, S.; Lacaze, P. C. *Synth. Met.* **1994**, *65*, 27.
- (226) Ferreira, C. A.; Aeiyaeh, S.; Delamar, M.; Lacaze, P. C. *J. Electroanal. Chem.* **1990**, *284*, 351.
- (227) Lee, H.; Yang, H.; Kwak, J. *J. Phys. Chem. B* **1999**, *103*, 6030.
- (228) Peters, E. M.; van Dyke, D. *J. Polym. Sci. A: Polym. Chem.* **1991**, *29*, 1379.

- (229) Peters, E. M. M.Sc. Thesis, Simon Fraser University, Burnaby, Vancouver, Canada, May 1987.
- (230) Delabouglise, D.; Lemaire, M.; Roncali, J.; Garnier, F. *Chem. Abstr.* **1991**, *114*, 144286. Nippon Oil Co. U.S. Patent 5,059,694, 1991.
- (231) Tran-Van, F.; Garrean, S.; Louarn, G.; Froyer, G.; Chevrot, C. *J. Mater. Chem.* **2001**, *11*, 1378.
- (232) Chang, C.-C.; Her, L.-J.; Hong, J.-L. *Electrochim. Acta* **2005**, *50*, 4461.
- (233) Kim, J.; Kang, D. M.; Shin, S. C.; Choi, M. Y.; Kim, J.; Lee, S. S.; Kim, J. S. *Anal. Chim. Acta* **2008**, *614*, 85.
- (234) Tachibana, Y.; Sakurai, Y.; Yokoyama, M. *Chem. Lett.* **1994**, 1119.
- (235) Zhang, W.; Plieth, W.; Kofmehl, G. *Electrochim. Acta* **1997**, *42*, 1653.
- (236) Kathirgamanathan, P.; Shepherd, M. K. *J. Electroanal. Chem.* **1993**, *354*, 305.
- (237) Wang, X. J.; Wong, K. Y. *Thin Solid Films* **2006**, *515*, 1573.
- (238) Blanchard, F.; Pagès, H.; Bonhomme, F.; Biensan, P.; Lemordant, D. *J. New Mater. Electrochem. Systems* **2003**, *6*, 245.
- (239) Cahalane, W.; Labes, M. M. *Mol. Cryst. Liq. Cryst.* **1992**, *211*, 331.
- (240) Xu, C.; Liu, L.; Taya, M. *Chem. Abstr.* **2007**, *147*, 288340. U.S. Patent 7,450,290, 2008.
- (241) Aeiych, S.; Bazzaoui, E. A.; Lacaze, P.-C. *J. Electroanal. Chem.* **1997**, *434*, 153.
- (242) Doi, T.; Takeda, K.; Fukutsuka, T.; Iriyama, Y.; Abe, T.; Ogumi, Z. *Carbon* **2005**, *43*, 2352.
- (243) Wei, D.; Kvarnström, C.; Lindfors, T.; Kronberg, L.; Sjöholm, R.; Ivaska, A. *Synth. Met.* **2006**, *156*, 541.
- (244) Izutsu, K. *Electrochemistry in Nonaqueous Solutions*; Wiley-VCH: Weinheim, 2002; pp 2–22.
- (245) Comisso, N.; Dahlio, S.; Mengoli, G.; Salmaso, R.; Zecchin, S.; Zotti, G. *J. Electroanal. Chem.* **1988**, *25*, 97.
- (246) Blomquist, M.; Lindfors, T.; Vähäsalo, L.; Pivrikas, A.; Ivaska, A. *Synth. Met.* **2006**, *156*, 549.
- (247) Yamada, K.; Teshima, K.; Kobayashi, N.; Hirohashi, R. *J. Electroanal. Chem.* **1995**, *394*, 71.
- (248) Hwang, B.-J.; Santhanam, R.; Wu, C.-R.; Tsai, Y.-W. *J. Solid State Electrochem.* **2003**, *7*, 678.
- (249) Osaka, T.; Ogano, S.; Naoi, K. *J. Electrochem. Soc.* **1988**, *135*, 539.
- (250) Takehara, Z.; Kanamura, K.; Yonezawa, S. *J. Electrochem. Soc.* **1989**, *136*, 2767.
- (251) Kanamura, K.; Yonezawa, S.; Kawai, Y.; Takehara, Z.-I. *J. Electroanal. Chem.* **1991**, *301*, 291.
- (252) Osaka, T.; Momma, T. *Electrochim. Acta* **1993**, *38*, 2011.
- (253) Yonezawa, S.; Kanamura, K.; Takehara, Z.-I. *J. Electrochem. Soc.* **1995**, *142*, 3309.
- (254) Sivakkumar, S. R.; Saraswathi, R. *J. Power Sources* **2004**, *137*, 322.
- (255) Pistoia, G. *J. Polym. Sci. B: Polym. Lett. Ed.* **1972**, *10*, 787.
- (256) (a) García-Cañadas, J.; Lafuente, A.; Rodríguez, G.; Marcos, M. L.; Velasco, J. G. *J. Electroanal. Chem.* **2004**, *565*, 57. (b) García-Cañadas, J.; Lafuente, A.; Rodríguez, G.; Marcos, M. L.; Velasco, J. G. *Port. Electrochim. Acta* **2004**, *22*, 411.
- (257) Bailey, C. L.; Bereman, R. D.; Rillema, D. P.; Nowak, R. *Inorg. Chem.* **1986**, *25*, 933.
- (258) (a) Kim, W. B.; Joshi, U. A.; Lee, J. S. *Ind. Eng. Chem. Res.* **2004**, *43*, 1897. (b) Ono, Y. *Catal. Today* **1997**, *35*, 15. (c) Sweileh, B. A.; A-Hiari, Y. M.; Aiedeh, K. M. *J. Appl. Polym. Sci.* **2008**, *110*, 2278.
- (259) Soga, K.; Hosada, S.; Tazuke, Y.; Ikeda, S. *J. Polym. Sci. B: Polym. Lett. Ed.* **1976**, *14*, 161.
- (260) Soga, K.; Tazuke, Y.; Hosoda, S.; Ikeda, S. *J. Polym. Sci.: Polym. Chem. Ed.* **1977**, *15*, 219.
- (261) Kéki, S.; Török, J.; Deák, G.; Zsuga, M. *Macromolecules* **2001**, *34*, 6850.
- (262) Lee, J.-C.; Litt, M. H. *Macromolecules* **2000**, *33*, 1618.
- (263) Hernández-Meléndez, O.; Peydecastaing, J.; Bárzana, E.; Vaca-García, C.; Hernández-Luna, M.; Borredon, M. E. *Bioresour. Technol.* **2009**, *100*, 737.
- (264) Zarzyka-Niemiec, I. *J. Appl. Polym. Sci.* **2008**, *110*, 3917.
- (265) Zarzyka-Niemiec, I. *J. Appl. Polym. Sci.* **2008**, *110*, 66.
- (266) Mazo, G. Y.; Batzel, D. A.; Kneller, J. F.; Mazo, J. *Chem. Abstr.* **1998**, *129*, 28372. U.S. Patent 5,756,595, 1998.
- (267) Matyjaszewski, K.; Nakagawa, Y.; Jasieczek, C. B. *Macromolecules* **1998**, *31*, 1535.
- (268) Nguyen, N.; Rosen, B. M.; Jiang, X.; Fleischmann, S.; Percec, V. *J. Polym. Sci. A: Polym. Chem.* **2009**, *47*, 5577.
- (269) Pilgram, P. Dissertation, RWTH Aachen, Germany, 2002; URN:nbn:de:hbz:82-opus-4172.
- (270) (a) Smutny, E. J.; Kivovsky, T. E. *Chem. Abstr.* **1989**, *111*, 40590. U.S. Patent 4,775,708, 1988. (b) Vinson, K. D.; Coffaro, P. *J. Chem. Abstr.* **2004**, *141*, 8759. WO 2004/048694, 2004.
- (271) (a) Hunter, F. R.; Lincoln, J. F. L.; Park, D. W. *Chem. Abstr.* **1991**, *115*, 52134. U.S. Patent 5,140,086, 1992. (b) Barker, M. C.; Brown, J. P.; Cunningham, A.; Randall, D. *Chem. Abstr.* **1991**, *114*, 63485. U.S. Patent 5,112,877, 1992.
- (272) Samuels, K. E.; Wiggins, W. T. *Chem. Abstr.* **1982**, *97*, 164642. U.S. Patent 4,379,875, 1983.
- (273) Behr, A.; Westfechtel, A.; Pérez Gomes, J. *Chem. Eng. Technol.* **2008**, *31*, 700.
- (274) Keraani, A.; Renouard, T.; Fischmeister, C.; Bruneau, C.; Rabiller-Baudry, M. *ChemSusChem* **2008**, *1*, 927–933.
- (275) Behr, A.; Roll, R. *Chem. Ing. Tech.* **2005**, *77*, 748. Behr, A.; Fängewisch, C. *Chem. Eng. Technol.* **2002**, *25*, 143.
- (276) (a) Hansen, C. M. *J. Paint Technol.* **1967**, *39*, 505. (b) Hansen, C. M. *Hansen Solubility Parameters: A User's Handbook*; CRC Press: Boca Raton, 2000.
- (277) (a) Hildebrand, J.; Scott, R. L. *The Solubility of Nonelectrolytes*, 3rd ed.; Reinhold: New York, 1950. (b) Hildebrand, J.; Scott, R. L. *Regular Solutions*; Prentice-Hall Inc.: Englewood Cliffs, 1962.
- (278) Behr, A.; Henze, G.; Schomäcker, R. *Adv. Synth. Catal.* **2006**, *348*, 1485.
- (279) Behr, A.; Fängewisch, C. *Chem. Eng. Technol.* **2002**, *25*, 143.
- (280) Behr, A.; Henze, G.; Johnen, L.; Awungacha, C. *J. Mol. Catal. A: Chem.* **2008**, *285*, 20.
- (281) Lapkin, A. A.; Peters, M.; Greiner, L.; Chemat, S.; Leonhard, K.; Liauw, M. A.; Leitner, W. *Green Chem.* Submitted for publication.
- (282) Schäffner, B.; Holz, J.; Verevkin, S. P.; Börner, A. *ChemSusChem* **2008**, *1*, 249.
- (283) Bantu, N. R.; Bhatt, A. C.; Papatthomas, K.; Sinclair, T. D.; Wagner, J. J. *Chem. Abstr.* **1994**, *120*, 273520. U.S. Patent 5,281,723, 1994.
- (284) (a) Wang, L.; Li, J.; Lin, Y.; Chen, C. *J. Membr. Sci.* **2005**, *305*, 238. (b) Won, W.; Feng, X.; Lawless, D. *J. Membr. Sci.* **2002**, *209*, 493. (c) Won, W.; Feng, X.; Lawless, D. *Sep. Purif. Technol.* **2003**, *31*, 129. (d) Walter, H.; Fischer, K.; Kaibel, G.; Schneider, K.; Irnich, R. *Chem. Abstr.* **1979**, *90*, 5903. DE 2,706,684, 1979. (e) Passoni, G. A. *Chem. Abstr.* **1975**, *83*, 96445. DE 2,450,856, 1973. (f) Romano, U. *Chem. Abstr.* **1976**, *85*, 159462. DE 2,607,003, 1976. (g) Janisch, I.; Landscheidt, H.; Struver, W.; Klausener, A. *Chem. Abstr.* **1995**, *123*, 344112. U.S. Patent 5,455,368, 1994.
- (285) Gilpin, J. A.; Emmons, A. H. *Chem. Abstr.* **1974**, *80*, 145452. U.S. Patent 3,803,201, 1977.
- (286) Miao, X.; Fischmeister, C.; Bruneau, C.; Dixneuf, P. H. *ChemSusChem* **2008**, *1*, 813.
- (287) Arockiam, P.; Poirier, V.; Fischmeister, C.; Bruneau, C.; Dixneuf, P. H. *Green Chem.* **2009**, *11*, 1871.
- (288) Cornely, J.; Su Ham, L. M.; Meade, D. E.; Dragojlovic, V. *Green Chem.* **2003**, *5*, 34.
- (289) Bernini, R.; Mincione, E.; Barontini, M.; Crisante, F.; Fabrizi, G.; Gambacorta, A. *Tetrahedron* **2007**, *63*, 6895.
- (290) Vasapollo, G.; Mele, G.; Maffei, A.; Del Sole, R. *Appl. Organomet. Chem.* **2003**, *17*, 835.
- (291) (a) Okamoto, M.; Ishii, H.; Sugiyama, J.-I. *J. Appl. Polym. Sci.* **2008**, *109*, 758. (b) Okamoto, M.; Sugiyama, J.; Takeuchi, K. *J. Appl. Polym. Sci.* **2007**, *106*, 2840.
- (292) Torborg, C.; Huang, J.; Schulz, T.; Schäffner, B.; Zapf, A.; Spannenberg, A.; Börner, A.; Beller, M. *Chem.—Eur. J.* **2009**, *15*, 1329.
- (293) Schulz, T.; Torborg, C.; Schäffner, B.; Huang, J.; Zapf, A.; Kadyrov, R.; Börner, A.; Beller, M. *Angew. Chem., Int. Ed.* **2009**, *48*, 918.
- (294) Roger, J.; Verrier, C.; Le Goff, R.; Hoarau, C.; Doucet, H. *ChemSusChem* **2009**, *2*, 951.
- (295) (a) Gavrilov, K. N.; Zheglov, S. V.; Vologzhanin, P. A.; Maksimova, M. G.; Safronov, A. S.; Lyubimov, S. E.; Davankov, V. A.; Schäffner, B.; Börner, A. *Tetrahedron Lett.* **2008**, *49*, 3120. (b) Grishina, T. B.; Maksimova, M. G.; Zheglov, S. V.; Davankov, V. A.; Schäffner, B.; Börner, A.; Rosset, S.; Bailat, G.; Alexakis, A. *Eur. J. Org. Chem.* **2009**, *23*, 3923. (c) Gavrilov, K. N.; Zheglov, S. V.; Vologzhanin, P. A.; Rastorguev, E. A.; Shiryaev, A. A.; Maksimova, M. G.; Lyubimov, S. E.; Benetsky, E. B.; Safronov, A. S.; Petrovskii, P. V.; Davankov, V. A.; Schäffner, B.; Börner, A. *Izv. Akad. Nauk. Ser. Khim.* **2008**, *11*, 2264. (d) Gavrilov, K. N.; Zheglov, S. V.; Vologzhanin, P. A.; Rastorguev, E. A.; Shiryaev, A. A.; Masimova, M. G.; Lyubimov, S. E.; Benetsky, E. B.; Safronov, A. S.; Petrovskii, P. V.; Davankov, V. A.; Schäffner, B.; Börner, A. *Russ. Chem. Bull. Int. Ed.* **2008**, *57*, 2311.
- (296) (a) Chen, D.; Schmitkamp, M.; Franció, G.; Klankermayer, J.; Leitner, W. *Angew. Chem., Int. Ed.* **2008**, *47*, 7339. (b) Schäffner, B.; Holz, J.; Börner, A. Unpublished results.
- (297) Behr, A.; Handwerk, H.-P. *Fat. Sci. Technol.* **1992**, *94*, 443.
- (298) Behr, A.; Naendrup, F.; Obst, D. *Adv. Synth. Catal.* **2002**, *344*, 1142.
- (299) Behr, A.; Bahke, P.; Klinger, B.; Becker, M. *J. Mol. Catal. A: Chem.* **2007**, *267*, 149.
- (300) (a) Behr, A.; Brehme, V. *Adv. Synth. Catal.* **2002**, *344*, 525. (b) Behr, A.; Brehme, V. *J. Mol. Catal. A: Chem.* **2002**, *187*, 69.
- (301) Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 259.
- (302) Behr, A. *Carbon Dioxide Activation by Metal Complexes*; VCH: Weinheim, 1988.

- (303) (a) Behr, A.; Obst, D.; Schulte, C.; Schosser, T. *J. Mol. Catal. A: Chem.* **2003**, *206*, 179. (b) Behr, A.; Fängewisch, C. *J. Mol. Catal. A: Chem.* **2003**, *197*, 115.
- (304) Behr, A.; Roll, R. *J. Mol. Catal. A: Chem.* **2005**, *239*, 180.
- (305) With *p*-xylene as mediator: (a) Behr, A.; Obst, D.; Turkowski, B. *J. Mol. Catal. A: Chem.* **2005**, *226*, 215. (b) With NOP and NMP as mediator: Behr, A.; Henze, G.; Obst, D.; Turkowski, B. *Green Chem.* **2005**, *7*, 645.
- (306) Massie, S. N. *Chem. Abstr.* **1976**, *84*, 121119. U.S. Patent 3,992,453, 1976.
- (307) (a) Selent, D.; Wiese, K.-D.; Börner, A. O-Acylphosphites: New and promising ligands for isomerizing hydroformylation. In *Catalysis of Organic Reactions*; Sowa, J. R., Ed.; Taylor & Francis Group: Boca Raton, 2005; Vol. 20, p 459. (b) Möller, O.; Fridag, D.; Borgmann, C.; Hess, D.; Wiese, K.-D. *Chem. Abstr.* **2004**, *140*, 217293. U.S. Patent 7,317,130, 2008.
- (308) Deshpande, R. M.; Bhanage, B. M.; Divekar, S. S.; Chaudhari, R. V. *J. Mol. Catal.* **1993**, *78*, L37.
- (309) (a) Birkholz, M.-N.; Dubrovina, N. V.; Jiao, H.; Michalik, D.; Holz, J.; Paciello, R.; Breit, B.; Börner, A. *Chem.—Eur. J.* **2007**, *13*, 5896. (b) Shuklov, I. A.; Dubrovina, N. V.; Barsch, E.; Ludwig, R.; Michalik, D.; Börner, A. *Chem. Commun.* **2009**, 1535.
- (310) Schäffner, B.; Holz, J.; Verevkin, S. P.; Börner, A. *Tetrahedron Lett.* **2008**, *49*, 768.
- (311) In *Phosphorus Ligands in Asymmetric Catalysis*; Börner, A., Ed.; Wiley-VCH: Weinheim, 2008; Vols. I–III.
- (312) Bisphospholanes: (a) Holz, J.; Monsees, A.; Jiao, H.; You, J.; Komarov, I. V.; Fischer, C.; Drauz, K.; Börner, A. *J. Org. Chem.* **2003**, *68*, 1701. (b) Holz, J.; Zayas, O.; Jiao, H.; Baumann, W.; Spannenberg, A.; Monsees, A.; Riermeier, T. H.; Almena, J.; Kadyrov, R.; Börner, A. *Chem.—Eur. J.* **2006**, *12*, 5001. (c) DuPHOS: Burk, M. J. *J. Am. Chem. Soc.* **1991**, *113*, 8518. (d) Burk, M. J.; Feaster, J. E.; Nugent, W. A.; Harlow, R. L. *J. Am. Chem. Soc.* **1993**, *115*, 10125. (e) Burk, M. J. *Acc. Chem. Res.* **2000**, *33*, 363. (f) BINAP: Noyori, R. *Adv. Synth. Catal.* **2003**, *345*, 15. (g) Akutagawa, S. In *Organic Synthesis in Japan: Past, Present, and Future*; Noyori, R.; Hiraoka, T.; Mori, K.; Murahashi, S.; Onoda, T.; Suzuki, K.; Yonemitsu, O., Eds.; Tokyo Kagaku Dozin: Tokyo, 1992. (h) JosiPHOS: Togni, A.; Breutel, C.; Schnyder, A.; Spindler, F.; Landert, H.; Tijani, A. *J. Am. Chem. Soc.* **1994**, *116*, 4062. (i) Salen-type ligands: Larrow, J. F.; Jacobsen, E. N.; Gao, Y.; Hong, Y.; Nie, X.; Zepp, C. M. *J. Org. Chem.* **1994**, *59*, 1939. (j) PHOX: Wüstenberg, B. Dissertation, University of Basel, 2003. (k) Schrems, M. G.; Neumann, E.; Pfaltz, A. *Angew. Chem., Int. Ed.* **2007**, *46*, 8274. (l) Markert, C.; Neuburger, M.; Kulicke, K.; Meuwly, M.; Pfaltz, A. *Angew. Chem., Int. Ed.* **2007**, *46*, 5892.
- (313) Schäffner, B.; Andrushko, V.; Bayardon, J.; Holz, J.; Börner, A. *Chirality* **2009**, *21*, 857.
- (314) Preetz, A.; Drexler, H.-J.; Fischer, C.; Dai, Z.; Börner, A.; Baumann, W.; Spannenberg, A.; Thede, R.; Heller, D. *Chem.—Eur. J.* **2008**, *14*, 1445.
- (315) Mazuela, J.; Verendel, J. J.; Coll, M.; Schäffner, B.; Börner, A.; Anderson, P. G.; Pàmies, O.; Diéguez, M. *J. Am. Chem. Soc.* **2009**, *131*, 12344.
- (316) Blackburn, T. F.; Schwartz, J. J. *Chem. Soc., Chem. Commun.* **1977**, 157.
- (317) North, M.; Omedes-Pujol, M. *Tetrahedron Lett.* **2009**, *50*, 4452.
- (318) North, M.; Pizzato, F.; Villuendas, P. *ChemSusChem* **2009**, *2*, 862.
- (319) Reetz, M. T.; Lohmer, G. *Chem. Commun.* **1996**, 1921.
- (320) Behr, A.; Schmidke, H. *Chem. Ing. Tech.* **1993**, *65*, 568.
- (321) Behr, A.; Döring, N.; Durowicz-Heil, S.; Ellenburg, B.; Kozik, C.; Lohr, C.; Schmidke, H. *Fat. Sci. Technol.* **1993**, *95*, 2.
- (322) Okamoto, M.; Sugiyama, J.-I.; Takeuchi, K. *J. App. Polym. Sci.* **2007**, *106*, 2840.
- (323) Okamoto, M.; Sugiyama, J.-i.; Yamamoto, T. *J. Polym. Sci.* **2008**, *110*, 3902.
- (324) Gamez, A.; Köhler, J.; Bradley, J. *Catal. Lett.* **1998**, *55*, 73.
- (325) Wu, X.-M.; Sun, W.; Xin, J.-Y.; Xia, C.-G. *World J. Microbiol. Biotechnol.* **2008**, *24*, 2421.
- (326) Poizot, P.; Laffont-Dantras, L.; Simonet, J. *Electrochem. Commun.* **2008**, *10*, 864.
- (327) (a) Mortreux, A.; Petit, F.; Mutez, S.; Paumard, E. *Chem. Abstr.* **1990**, *112*, 181863. EP 335765, 1989. (b) Mortreux, A.; Petit, F.; Mutez, S. *Chem. Abstr.* **1987**, *106*, 35091. Paumard WO 8605415, 1986. (c) Paumard, E.; Mortreux, A.; Petit, F. *Chem. Commun.* **1989**, 1380. (d) Mutez, S.; Paumard, E.; Mortreux, A.; Petit, F. *Tetrahedron Lett.* **1989**, *30*, 5759.
- (328) Ross, S. D.; Finkelstein, M.; Petersen, R. C. *J. Am. Chem. Soc.* **1958**, *80*, 4327.
- (329) Kronick, P. L.; Fuoss, R. M. *J. Am. Chem. Soc.* **1955**, *77*, 6114.
- (330) Jones, M. A.; Gilkerson, W. R. *J. Solution Chem.* **1979**, *8*, 871.
- (331) Friedman, H. L. *J. Phys. Chem.* **1967**, *71*, 1723.
- (332) Röder, J.; Dawidowski, D. *Chem. Abstr.* **2009**, *150*, 329958. WO 2009030447, 2009.
- (333) Richter, A. M.; Ster, D.; Schönewerk, J. *Chem. Abstr.* **2009**, *151*, 92688. DE 102007063416, 2009.
- (334) Albert, B.; Jansen, M. Z. *Anorg. Chem.* **1995**, *621*, 1735.
- (335) Mori, S.; Ida, K.; Ue, M. *Chem. Abstr.* **1988**, *110*, 212114. U.S. Patent 4,892,944, 1990.
- (336) Ue, M.; Tekeda, M.; Takahashi, T.; Takehara, M. *Electrochem. Solid-State Lett.* **2002**, *5*, 119A.
- (337) (a) Holbrey, J. D.; Reichert, W. M.; Tkatchenko, I.; Bouajila, E.; Walter, O.; Tommasi, I.; Rogers, R. D. *Chem Commun.* **2003**, 28. (b) Fischer, J.; Siegel, W.; Bomm, V.; Fischer, M.; Mundinger, K. *Chem. Abstr.* **2000**, *132*, 137391. U.S. Patent 6,175,019, 2001.
- (338) Kuczynski, J. P.; Mulholland, L. M. *Chem. Abstr.* **1998**, *128*, 231116. U.S. Patent 6,008,266, 1999.
- (339) Ansmann, A.; Boutty, B.; Dierker, M. *Chem. Abstr.* **2008**, *149*, 17219. EP 1930331, 2008.
- (340) Cosmetic Ingredient Review (CIR) *J. Am. Coll. Toxicol.* **1987**, *6*, 23.
- (341) Baiersdorf, A. G. *Chem. Abstr.* **2008**, *149*, 314913. DE 20 2008 007 029, 2008.
- (342) Doscher, P. A. *Chem. Abstr.* **1990**, *112*, 121161. U.S. Patent 5,007,969, 1991.
- (343) Chretien, O. D.; Delaite, A. M.; Papavoine, B. G. *Chem. Abstr.* **2007**, *147*, 191220. U.S. Patent Application 2009/0005284, 2009.
- (344) Machac, J. R., Jr.; Woodrum, S. A.; Klein, H. P.; Marquis, E. T. *Chem. Abstr.* **2002**, *136*, 281213. U.S. Patent 6,596,677, 2003.
- (345) Elepaño, N. P.; Schnur, W. H.; Jorgensen, J. L. *Chem. Abstr.* **1985**, *103*, 24112. U.S. Patent 4,508,634, 1985.
- (346) (a) Burckhalter, A.; Hooper, A. M.; Nazario, C.; Springer, J., Jr.; Stone, K. R. *Chem. Abstr.* **1996**, *126*, 61596. Proceedings, Annual Meeting - Air & Waste Management Association 1995, 88, 95-RP138.04, 6. (b) EPA/600/SR-94/176, 1984.
- (347) Marquis, E. T. *Chem. Abstr.* **2000**, *132*, 68415. U.S. Patent 6,015,550, 2000.
- (348) Weuthen, M.; Hees, U. *Chem. Abstr.* **1995**, *123*, 202971. DE 4335947, 1995.
- (349) Kohl, A. L.; Buckingham, P. A. *Oil Gas J.* **1960**, *58*, 146.
- (350) (a) Gupta, M.; Coyle, I.; Thambimuthu, K. CO2 Capture Technologies and Opportunities in Canada, 1st Canadian CC&S Technology Roadmap Workshop, Calgary, Canada, 2003. (b) Mak, J.; Nielsen, D.; Schulte, D.; Graham, C. *Hydrocarbon Process. Int. Ed.* **2003**, *82*, 87. (c) Schendel, R. L. *Chem. Abstr.* **1983**, *99*, 125134. Proceedings of the gas conditioning conference 1983, 33, M1-M18. (d) White, C. M.; Strazisar, B. R.; Granite, E. J.; Hoffmann, J. S. *J. Air Waste Manage. Assoc.* **2003**, *53*, 645.
- (351) Lewis, D. C.; Salazar, L. C.; Machac, J. R. *Chem. Abstr.* **2009**, *151*, 201801. WO 2009094285, 2009.
- (352) Xia, J.; Ragsdale, M. E.; Stephens, E. B. *Chem. Abstr.* **2001**, *136*, 38897. U.S. Patent 6,607,591, 2003.
- (353) *Integrierter Umweltschutz bei bestimmten industriellen Tätigkeiten, Teilband 1*; Environmental Agency: Berlin, Germany, 2002.
- (354) (a) Schmidt, S. *Chem. Abstr.* **2004**, *142*, 375279. Proceedings-Electrical Insulation Conference and Electrical Manufacturing & Coil Winding Technology Conference, Indianapolis, IN, 2003, p 93. (b) Schmidt, S.; Nickel, H. *Chem. Abstr.* **2004**, *140*, 255015. *Farbe Lack* **2004**, *110*, 60.
- (355) Ishida, K. S. *Chem. Abstr.* **2009**, *150*, 308435. U.S. Patent 20090068343, 2009.
- (356) Hanley, T. R., Jr.; Schumann, A. M.; Langvardt, P. W.; Rusek, T. F.; Watanabe, P. G. *Toxicol. Appl. Pharmacol.* **1989**, *100*, 24.
- (357) Ono, Y. *Appl. Catal. A: Gen.* **1997**, *155*, 133.
- (358) (a) Tundo, P.; Selva, M. *Acc. Chem. Res.* **2002**, *35*, 706. (b) Tundo, P.; Rossi, L.; Loris, A. *J. Org. Chem.* **2005**, *70*, 2219.
- (359) Nederberg, F.; Lohmeijer, B. G. G.; Leibfarth, F.; Pratt, R. C.; Choi, J.; Dove, A. P.; Waymouth, R. M.; Hedrick, J. L. *Biomacromolecules* **2007**, *8*, 153.
- (360) (a) Kendall, J. L.; Canelas, D. A.; Young, J. L.; DeSimone, J. M. *Chem. Rev.* **1999**, *99*, 543. (b) Darensbourg, D. J. *Chem. Rev.* **2007**, *107*, 2388.