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ABSTRACT: Zwitterionic Lewis base adducts between nitrogen bases and CO₂ play a pivotal role as transient intermediates in many projects aiming at CO₂ capture, storage and utilization. Yet, fundamental questions about the required parameters for the formation of isolable adducts remain and only a single adduct (TBD-CO₂) has been characterized unequivocally. Using a combination of NMR spectroscopy, single-crystal X-ray diffraction, IR spectroscopy and quantum chemistry, we systematically explore the formation and properties of the CO₂ adducts with amidines (DBN), guanidines (MTBD) and Nheterocyclic imines. Spectroscopic and theoretical results show that the stability of the NHI-CO₂ adducts is largely governed by the nature of the N-heterocycle and the substituent at the exocyclic nitrogen atom. The surprising stability of some NHI-CO₂ adducts towards hydrolysis can be ascribed to the hydrophobic CO₂ binding site of the nitrogen bases and offer new opportunities in the field of CO₂ capture and utilization.

Introduction

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Selective and reversible capture of carbon dioxide (CO₂) either from flue gas or directly from air and its transformation into value-added chemicals, materials and fuels is one of the most important challenges to mitigate CO₂ accumulation in our atmosphere.¹⁻³ A key step in many capture-and-release applications as well as in the catalytic conversion of CO₂ is the reversible binding of the CO₂ molecule through low-energy, easily-broken, bonds.⁴ Among the many methods for CO₂ activation the nucleophilic interaction on the electrophilic carbon atom is a main pathway. This mode of CO₂ activation is associated with the bending of the CO₂ molecule and results in the formation of zwitterionic adducts between the Lewis base and CO₂. Apart from some low-valent transition metal complexes containing CO₂ as a η^1 or η^2 ligand, ⁵⁻¹⁰ a variety of organic bases have been reported to form stable adducts of this type.¹¹ Carbon bases involving N-heterocyclic carbenes (NHCs),^{12–14} N-heterocyclic olefins (NHOs)^{15,16} and phosphorus ylides^{17,18} are well known to form Lewis base adducts with CO₂ and have proven to be useful in promoting a variety of catalytic transformations involving CO₂.^{19–23} We recently discovered that electron rich phosphines²⁴ are also capable of forming reversible adducts with CO₂ and can even induce the cleavage of a CO bond of the CO₂ molecule.^{25–27}



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extremely sensitive to hydrolysis and shows fluxional behavior in solution. The stability of TBD–CO₂ in the solid state (up to 40 °C) was attributed to the high basicity of TBD and multiple hydrogen bonding interactions with the carboxylate O atoms, including the intramolecular hydrogen-bonding interaction between the N–H of TBD and O-atom of the carboxylate group (see Scheme 1).

Despite the importance of nitrogen base-CO₂ adducts in the field of CO₂ capture and utilization, water-stable adducts are unknown and the structural parameters governing the stability of such adducts have not yet been identified. Zwitterionic nitrogen base-CO₂ adducts could provide a source of dry CO₂, because water is not involved in their formation. Additionally, there is no energy penalty associated with the desorption of water during the decomplexation of CO₂, which would enhance the efficiency of CO₂ capture systems. Herein, we systematically explore the stereoelectronic requirements of nitrogen bases for the formation of isolable CO₂ adducts and unveil their geometries by X-ray single crystal structure analysis. Based on these results, the first water-stable nitrogen base CO₂ adducts were prepared.

Scheme 1. Three major resonance structures of CO_2 adducts with amidine or guanidine bases.



Results and Discussion

 CO_2 binding with bicyclic amidines and guanidines. We started our investigation on the formation of CO_2 adducts with nitrogen bases by pressurizing acetonitrile solutions of commercially available bicyclic amidines (DBU, DBN) and guanidines (MTBD, TBD) with 2 bar CO_2 pressure under strictly anhydrous conditions. The ¹H and ¹³C NMR spectra of DBU and MTBD were identical to those recorded without CO2 atmosphere whereas Villiers TBD-CO2 adduct was readily Formed 30/66/CO1958 conditions, as evident by its characteristic CO₂ carbon signal at 154.4 ppm in the ¹³C NMR spectrum. For DBN, a broad signal appears at 131.3 ppm in the ¹³C NMR spectrum, shifted to higher frequency compared to free CO_2 (125.9 ppm)⁵¹, which indicates an equilibrium between the free base DBN and its CO2 adduct DBN-CO₂ (1) in solution. Pressurizing a pentane solution of DBN with 2 bar CO₂ led to the immediate precipitation of an off-white crystalline material of 1 in quantitative yield. Single crystals of 1 were obtained from Et₂O solutions. An X-ray diffraction study revealed that the molecule is almost planar with an amidine-CO₂ torsion angle of 9.1° (Figure 1). Similar to TBD-CO₂,^{50,52} the DBN-CO₂ molecules are arranged in columns parallel to the *c* axis with alternating orientation of the dipole moment (Figure S104). The rather long N–CO₂ bond (1.513 Å) and large O–C–O angle (132.2°) compared to Villiers adduct TBD-CO₂ (C-N: 1.480 Å, O-C-O: 128.6°)⁵⁰ indicate that CO₂ is weakly bound to DBN in the solid state.



FIGURE 1. Molecular structure of 1. Thermal ellipsoids are set at 50% probability. Selected bond lengths [Å] and angles [°]: N1–C1 1.513(3), N1–C2 1.330(3), N2–C2 1.322(3), C1–O1 1.233(3), C1–O2 1.228(3), O1–C1–O2 132.2(2), C1–N1–C2 123.6(2), N1–C2–N2 122.2(2), N2–C2–N1–C1 9.1(2).

The adduct **1** can be stored under an atmosphere of dry CO₂, but slowly decarboxylates under argon atmosphere. Rapid loss of CO₂ was observed upon evacuation of **1** or by the attempt to dissolve it in MeCN. Analysis of the thermal stability of **1** by FT-IR spectroscopy reveals that the characteristic v_{as} (CO) stretching band at 1727 cm⁻¹ disappears immediately at temperatures higher than 30 °C. Similar to Villiers TBD–CO₂ adduct, DBN–CO₂ rapidly hydrolyzes in the presence of moisture to forms the dicarbonate salt [DBNH⁺][HCO₃⁻] as evident by the characteristic ¹³C NMR signal of the bicarbonate ion at 161.9 ppm and the asymmetric CO₃ stretch at 1592 cm⁻¹ in the IR spectrum. A single crystal X-ray diffraction study reveals a dimeric assembly that is associated by hydrogen bonding interactions, which is a typical structural motif for amidinium and guanidinium bicarbonates (Figure 2).^{44,50,53}

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FIGURE 2. Molecular structure of $[DBNH^+][HCO_3]$ with ellipsoids set at 50% probability. Selected bond lengths [Å] and angles [°]: N1–C2 1.304(2), N2–C2 1.313(2), C1–O1 1.260(2), C1–O2 1.250(2), C2–N1–O2 113.59(9), N1–C2–N2 124.27(13), N2–C2–N1–O2 1.09(11).

Collectively, these results show that zwitterionic adducts between amidines and CO₂ can be isolated although the basicity of DBN (pK_a (MeCN) = 23.79)⁵⁴ is significantly lower than that of TBD ($pK_a(MeCN) = 26.03$)⁵⁵ and TBD–CO₂ additionally contains a stabilizing intramolecular hydrogen-bonding interaction between the NH of TBD and the oxygen atom of the carboxylate group. Carneiro showed that the strength of the interaction energy of CO₂ with amines correlate with their basicity in a nearly linear relationship.⁵⁶ As a consequence, DBU [pK_a(MeCN) = 24.34] and MTBD $[pK_a(MeCN) = 25.49]$,⁵⁵ being more basic than DBN, should form isolable CO₂ adducts as well. However, similar to Jessops observation for DBU,⁴⁷ no evidence for the zwitterionic CO₂ adducts was observed even upon pressurizing an *n*-hexane solution of MTBD with 14 bar CO₂ pressure, while the salt [MTBDH⁺][HCO₃⁻] rapidly forms in the presence of water (see the Supporting Information for details).

A reasonable explanation for this phenomenon can be derived from the resonance structures of CO₂ adducts with amidine or guanidine bases (Scheme 1). For bicyclic amidines and guanidines, two types of CO₂ adducts can be distinguished: In TBD-CO₂ and DBN-CO₂ (type I) the CO₂ atoms and the amidine/guanidine atoms are nearly coplanar, which enables extended π delocalization according to resonance structures **A**, B and C. Note that resonance structure C contains two formal negative and two formal positive charges and should therefore contribute less to the resonance hybrid. In adducts of type II, steric effects lead to larger C-N-C-O torsion angles up to 90° and therefore to reduced N to CO_2 π donation (resonance structure C), which explains why DBU and MTBD do not form isolable CO₂ adducts, despite their high basicity. In contrast, CO₂ adducts adopting a geometry with an N-C-N-CO₂ torsion angle of 90° (type III) should have an enhanced N=CO₂ double bond character owing to the reduced N_{CO2} to $C_{\text{guanidine}}\,\pi$ bonding.

Given these considerations, we envisaged that N-heterocyclic imines (NHIs) should be excellent candidates for the complexation of CO_2 owing to the following beneficial factors: a) CO_2 adducts with NHIs should adopt type **III** geometry driven by the steric repulsion between the R substituents. Kunetskiy et al. showed that monocyclic imidazolin-2-imines are significantly more basic than bicyclic guanidines owing to the synergistic effect of aromatization of the imidazolium ring and the release of steric strain upon protonation.⁵⁷ The same effect should enhance the stability of CO_2 adducts; b) Bulky R groups at the nitrogen atoms can generate a hydrophobic pocket around the exocyclic N atom, which might give rise to water-stable nitrogen base CO₂ adducts; c) The stability of the CO₂ adducts is an a controlled in a reverse fashion by the controlled in a reverse fashi



 $^a\text{Reagents}$ and conditions: a) Base, $C_2\text{Cl}_6,$ THF b) RNH2, KF, MeCN, RT, 3-7 days, then KOtBu, THF.

Synthesis of N-heterocyclic imines 2-5. Following a synthetic approach by Kunetskiy et al.,⁵⁷ we prepared a series of NHIs (2-5) starting from readily available azolium salts (Scheme 2). Deprotonation and treatment of the free carbenes with hexachloroethane afforded the corresponding 2-chloroazolium salts in very good yields. The KF-mediated coupling of the 2-chloroazolium salts with primary amines in acetonitrile and subsequent deprotonation of the iminium salts gave the NHIs 2-5 in excellent yields. The protic NHIs 2c, 4c, 4d and 4e were synthetized as reported previously via the methanolysis of the corresponding trimethylsilyl compounds.^{58,59}



Synthesis and characterization of NHI-CO₂ adducts. The formation of NHI-CO₂ adducts was explored by pressurizing MeCN-d₃ solutions of the NHIs 2-5 with 2 bar ¹³C-enriched ¹³CO₂ under strictly anhydrous conditions. The room-temperature ¹H and ¹³C NMR spectra of the benzimidazolin-2-imines 2a-c, imidazolin-2-imine 4e and imidazolidin-2-imine 5a were identical to those recorded without CO₂ atmosphere. In contrast, obvious differences in the chemical shift were observed in the ¹H and ¹³C NMR spectra when using 3a-d and 4a-d. In addition to the slightly shifted signals of the NHI, the

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characteristic carboxylate carbon signal of the NHI-CO₂ adduct appears in the range of 155.7 ppm to 157.8 ppm (Table 1). The CO₂ resonances of **7c** (138.9 ppm) and **7d** (140.6 ppm) are broadened and had a similar chemical shift to that of DBN–CO₂ (131.3 ppm), indicating fluxional behavior in solution. Moreover, the signal for the N–H protons [8.93 ppm (**7c**) and 7.75 ppm (**7d**)] are significantly shifted to higher frequency compared to the free bases **4c** (3.76 ppm) and **4d** (3.74 ppm). Notably, low-temperature NMR experiments provided spectroscopic evidence for the formation of CO₂ adducts with **2a** and **2b**. At 240 K, the carboxylate carbon signals appear at 154.9 ppm (for **2a**) and 154.4 ppm (for **2b**), respectively.

Isolation of the CO₂ adducts **6a-d** and **7a-d** was conveniently accomplished by diffusion of CO₂ into a *n*-pentane solution of the NHI. Owing to the poor solubility in aliphatic solvents, the zwitterionic adducts immediately precipitate as a white solid in quantitative yield. The asymmetric CO₂ stretching band of the NHI-CO₂ adducts at 1654–1673 cm⁻¹ (Table 1) are in the range of NHC-CO₂ adducts (1629–1683 cm⁻¹)^{13,14} but appear at significantly lower frequency than that of the bicyclic nitrogen bases DBN–CO₂ (1727 cm⁻¹) and TBD–CO₂ (1712 cm⁻¹).

Table 1. Characteristic spectroscopic data and decarboxylation temperatures (T) of nitrogen-base–CO $_2$ adducts.

| Entry | ¹³ C NMR [ppm] ^a | IR [cm ⁻¹] | т [°С] |
|--|---|---------------------------|-----------------|
| TBD-CO ₂ | 154.4 ^b | 1712 ^b | 40 ^b |
| DBN-CO ₂ (1) | 131.3 | 1727 | 30 |
| (I ^t Bu)NMeCO ₂ (6a) | 157.8 | 1666 | >120 |
| (I ^t Bu)N ^t BuCO ₂ (6b) | 156.9 | 1654 | n.d. |
| (I ^t Bu)N ⁿ PrCO ₂ (6c) | 157.0 | 1665 | 75 |
| (I ^t Bu)N ⁿ OcCO ₂ (6d) | 157.1 | 1666 | 75 |
| (I" ⁱ Pr)NMeCO ₂ (7a) | 156.3 | 1663 | >120 |
| (I" ⁱ Pr)N ^t BuCO ₂ (7b) | 155.7 | 1673 | 100 |
| (I" ⁱ Pr)NHCO ₂ (7c) | 138.9 | 1671 | 30 |
| (I"Me)NHCO ₂ (7d) | 140.6 | 1662 | 35 |
| | | | |

^a recorded in MeCN-d₃, ^b literature values.⁵⁰

The molecular structures of compounds 6a, 6c, 7a, 7b, 7c and 7d were established using single-crystal X-ray crystallography (Figure 4). Selected bond length and angles are collected in Table 2. Short intermolecular O···HC distances around 2.2 Å to the imidazolium ring hydrogen atoms were found for 6a and 6c. Such hydrogen-bonding interactions have been postulated to be vital for efficient catalysis in the context of imidazoliumpromoted CO₂ transformations.⁶⁰ The CO₂ adducts of the protic NHIs 7c and 7d are stabilized by O…HN hydrogen-bonding interactions forming dimeric (7c) and polymeric (7d) arrangements. For the NHI-CO₂ adducts with alkyl substituents at the exocyclic nitrogen atom, the plane defined by the CO₂ moiety is essentially perpendicular to the plane spaned by the imidazolin atoms ranging from 85° (6c) to 89° (6a). Larger deviation from this orientation of type III was observed for the protic NHIs (7c: 76°, 7d: 69°). The exocyclic nitrogen atom of the CO₂ adducts are located in the plane spaned by the imidazoline

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atoms (deviation < 0.1 Å). In contrast, the exocyclic Antrogen atom of **6b** is dislocated by 0.3 Å, seemingly resulting from the bulkyness of the *tert*-butyl substituents. Very similar C1–N1 bond lengths (1.432–1.464 Å) were found that are significantly shorter than those in **1** (1.513 Å) or TBD–CO₂ (1.480 Å) which agrees with the expected enhanced double bond character of the C1–N1 bond. The O–C–O angles of the NHI-CO₂ adducts (129.1–131.4°) are slightly larger (by ca. 2°) than in NHO-CO₂ adducts¹⁵ and are in the range of NHC-CO₂^{13,14} or phosphine- $CO_2^{25,27}$ adducts. Hydrogen bonding intaractions between the carboxylate O atoms and acidic NH protons, as present in **7c**, **7d** and TBD–CO₂, seem to induce smaller O–C–O angles.

Thermal stability. The thermal stability of the NHI-CO₂ adducts 6a-d and 7a-d were examined by FT-IR monitoring of the asymmetric CO₂ stretching band of the solids kept under an argon atmosphere, while increasing the temperature in steps of 5 °C (Table 1). This analysis revealed that the substituent at the exocyclic nitrogen atom has a profound influence on the decarboxylation temperature of the NHI-CO₂ adduct, showing the trend that an increased size of the alkyl substituent leads to a decrease in decarboxylation temperature. The CO₂ adducts of the methyl substituted NHIs (6a and 7a: >120 °C) decompose at higher temperature than those carrying *n*-alkyl (6c and 6d: 75 °C) or tert-butyl (7b: 100 °C) substitutents at the exocyclic nitrogen atoms. In this respect, complete decarboxylation and recovery of the free nitrogen bases was observed after heating solid samples of 6c and 6d for 5 minutes at 75 °C or upon evacuating the solids for 15 minutes at room temperature. The thermally more stable adducts 6a, 7a and 7b can be shortly dried under vacuum without noticeable loss of CO₂. The lowest decarboxylation temperatures were found for the protic NHI-CO₂ adducts 7c (30 °C) and 7d (35 °C) which can be rationalized by the significantly lower basicity of the protic NHIs compared to the NHIs with alkyl substituents (vide infra).

Thermal fragmentation of 6b. Examination of the thermal stability of NHI-CO₂ adduct **6b** revealed the unexpected fragmentation of **6b** into 1,3-di-tert-butyl-2-imidazolinone and tert-butyl-isocyanate. NMR monitoring showed that the fragmentation of **6b** in MeCN-d₃ solution is slow at room temperature (29% conversion within 4 h). Complete conversion was observed after heating the solution to 50 °C for 3 hours (Figure S94-S99). The unusual reactivity of the sterically encumbered CO₂ adduct **6b** is likely to be driven by the release of steric strain as indicated in the solid-state structure of 6b. The decomposition process was further probed by DFT calculations including implicit solvation. The results from the study of NHI-CO₂ adducts **6a** and **6b** are summarized in Figure 3. The CO₂ binding energy for **6a** is by -2.8 kcal mol⁻¹ more exergonic than that of **6b**. Moreover, the reaction energy for the fragmentation of 6b (-24.2 kcal mol⁻¹) is significantly more exergonic than that of **6a** (-10.0 kcal mol⁻¹). According to the IRC scan the fragmentation into the corresponding urea and isocyanate derivates is a one-step reaction. In the transition-state structure one oxygen atom of the CO₂ fragment is connected to the imidazoline C2 atom forming an OCNC four-membered ring, which contains an elongated C2-N1 bond of 1.74 Å. The reaction barrier associated with this step is significantly higher

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for **6a** ($\Delta G_{298} = 35.3$ kcal mol⁻¹) compared to that of **6b** ($\Delta G_{298} = 26.0$ kcal mol⁻¹) and explains the slow fragmentation of **6b** at room temperature. Phosphazene superbases have been found to react with CO₂ in a similar manner to give the respective phosphine oxides and isocyanates.^{61,62}



FIGURE 3. Computed Gibbs free energy profile for the thermal fragmentation of **6a** (black) and **6b** (red) along with optimized transition state structure (bond lengths in Å). Energies were obtained as ΔG_{298} in solution (MeCN) with density functional theory at the PW6B95-D3// TPSS-D3/def2-TZVP + COSMO-RS(MeCN) level.

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|--|--|--------------|
| | | |
| FIGURE 4. Solid-state structures of NHI-CO ₂ adducts 6a-c and 7a-d. CH-hydroger | n atoms are omitted for clarity. Thermal ellipsoids are set at 50% | probability. |
| | | P |

| Table 2 . Selected bond lengths [Å] and angles [deg] of nitrogen base CO_2 adducts. | | | | | | | | | | | |
|--|-----------------------|-------------------------|-----------------------|-----------------------|-----------------------|---------------------------------|--|--|--|--|--|
| Entry | C1N1 | C2-N1 | C2-N2 | C1-01 | 01–C1–O2 | imidazole-CO ₂ angle | | | | | |
| | | | C2-N3 | C102 | | | | | | | |
| TBD-CO ₂ | 1.480(3) ^a | 1.369(3)ª | 1.332(2) ^a | 1.257(3) ^a | 128.6(2) ^a | 4.4(2) ^{a,c} | | | | | |
| | | | 1.338(3) ^a | 1.229(2) ^a | | | | | | | |
| DBN-CO ₂ | 1.513(3) | 1.330(3) | 1.322(3) | 1.233(3) | 132.2(2) | 9.1(2) ^c | | | | | |
| | | | | 1.228(3) | | | | | | | |
| 6a | 1.439(2) | 1.3729(14) | 1.3552(14) | 1.2487(14) | 130.56(11) | 88.9(2) | | | | | |
| | | | 1.349(2) | 1.2432(14) | | | | | | | |
| 6b | 1.456(4) ^b | 1.381(4) ^b | 1.361(4) ^b | 1.249(4) ^b | 130.0(3) ^b | 86.1(4) ^b | | | | | |
| | | | 1.363(4) ^b | 1.237(4) ^b | | | | | | | |
| 6c | 1.441(2) ^b | 1.3701(19) ^b | 1.356(2) ^b | 1.242(2) ^b | 130.5 ^b | 84.8(3) ^b | | | | | |
| | | | 1.377(2) ^b | 1.246(2) ^b | | | | | | | |
| 7a | 1.443(3) | 1.376(2) | 1.340(3) 1.343(3) | 1.244(3) | 131.4 | 87.8(3) | | | | | |
| | | | | 1.239(3) | | | | | | | |
| 7b | 1.4637(10) | 1.3779(10) | 1.3475(10) | 1.2476(11) | 130.39(8) | 87.3(9) | | | | | |
| | | | 1.3450(10) | 1.2385(11) | | | | | | | |
| 7c | 1.4386(13) | 1.3668(14) | 1.3441(14) | 1.2437(13) | 129.78(10) | 76.2(1) | | | | | |
| | | | 1.3506(13) | 1.2536(13) | | | | | | | |
| 7d | 1.4317(11) | 1.3679(11) | 1.3384(11) | 1.2506(11) | 129.09(9) | 68.9(1) | | | | | |
| | | | 1.3925(11) | 1.2430(11) | | | | | | | |
| ^a literature values. ^{50 b} average values. ^c torsion angle C1-N1-C2-N2 | | | | | | | | | | | |

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Computational Studies. To better understand the influence of the substitution pattern at the Nheterocycle on the stability of the NHI-CO₂ adducts, the gas-phase basicities (GB) and free energies for binding of CO_2 (ΔG_{298}) were determined for a series of nitrogen superbases with PW6B95-D3//TPSS-D3/def2-TZVP (Figure 5). The COSMO-RS solvation model for acetonitrile was used for the determination of the ΔG_{298} values. The weak CO₂ binding energies of the bicyclic nitrogen bases, showing the trend DBU < MTBD < DBN < TBD, agree with the experimental observation that DBN-CO2 and TBD-CO2 are fluxional in solution, while no interaction with CO₂ was detected for DBU and MTBD. The fact that DBN-CO₂ is isolable despite its endergonic binding energy can be attributed to stabilizing intermolecular interactions in the solid state (see Figure S104). The CO₂ binding energies of the NHIs agree very well with the experiment and illustrate that the stability of the CO₂ adducts is largely governed by the nature of the N-heterocycle showing the general trend: benzimidazoline (2) < imidazolidine (5) < imidazoline (3) < 4,5-dimethylimidazoline (4), while it is also sensitive to the steric profile of the NHIs. Both, the GB [kcal mol-1]

gas-phase basicity and the magnitude of the CO₂ binding energy increase with the +I effect of the alkyl substituents at the nitrogen atoms, showing the highest values for **3a-d** and **4b**. This trend is particularly prominent for the substituents at the exocyclic N atoms, as evident by the series **2c**, **2a**, **2b** and the series **4c**, **4a**, **4b**. However, it should be mentioned that the calculated values do not take account of the additional stabilization *via* hydrogen bonding interactions as observed in the solid-state structures of **7c** and **7d**, respectively. Steric strain around the exocyclic N atom in **5a** and **4y** might be responsible for their deviation from the general trend.

The geometric parameters of the calculated NHI-CO₂ adducts show linear correlations with the CO₂ binding energies (Figure S117–S120). With increasing CO₂ binding energy the O–C–O angles get smaller, the C1–N1 bond distances get shorter and the C2–N1 as well as the average C1–O distances get longer. Noticeable deviations from this trend are observed for **5a**, which show unusually long C2–N1 bond and short C1–N1 bond lengths, indicating steric strain around the exocyclic N atom.



FIGURE 5. Plot of calculated gas-phase basicities (GB) versus free energies for CO₂ binding (ΔG_{298}) of selected nitrogen superbases determined with PW6B95-D3//TPSS-D3/def2-TZVP. The COSMO-RS solvation model for acetonitrile was used for the ΔG_{298} values. Color code of ΔG_{298} values according to experimental observations: CO₂ adduct isolable (green), not isolable (red), not determined (black).

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FIGURE 6. Hydrolysis study of DBU-CO2, TBD-CO2 and NHI-CO2 adducts (6a-d, 7a-d) in MeCN-d₂ at room temperature.

Stability towards Water. Based on the structural parameters of the NHI-CO₂ adducts we were curious how the substitution pattern would influence the stability of the NHI-CO₂ adducts towards hydrolysis. The stability of the isolable nitrogen base-CO₂ adducts towards water was evaluated by adding portions of water to MeCN-d₃ solutions of TBD–CO₂, DBN-CO₂, **6a**, **6c**, **6d**, and 7a-d at room temperature. Thirty minutes after the addition and short mixing, the ratio between the CO₂ adduct and the bicarbonate salt [baseH⁺][HCO₃⁻] was determined by ¹H NMR analysis of the reaction mixture (Figure 6). As expected, the addition of 2.7 equivalents of water to TBD-CO₂ and DBN- CO_2 led to the quantitative formation of the bicarbonate salts. Similar behaviour was observed for the protic NHIs 7c and 7d. In contrast, the addition of 2.7 equivalents of water to the aprotic NHI-CO₂ adducts resulted in the incomplete hydrolysis of 6b (86%), 6c (19%), 6d (27%) and 7b (78%). Subsequent changes among those ratios were not observed according to prolonged ¹H NMR-monitoring of the solutions (up two three weeks). However, the addition of further equivalents of water to the mixture resulted in increased hydrolysis. Surprisingly, 6a and **7a** did not react with water even in the presence of a large excess and upon heating the solutions at 70 °C for 24 h (see Figure S101 and Figure S102). Collectively, these results show that among the NHI-CO₂ adducts with alkyl groups at the exocyclic nitrogen atom the stability towards hydrolysis largly depends on the size of the alkyl substituent, indicating the trend of decreasing stability with larger alkyl groups.

Conclusion

In conclusion, a systematic study on the formation and properties of zwitterionic Lewis base adducts between nitrogen bases and CO₂ is reported. In this context, weak adducts (2a, 2b,

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7c, 7d), showing fluxional behaviour, have been identified in solution and the first CO₂ adducts with amidines (1) and Nheterocyclic imines (6a-d, 7a-d) have been isolated and characterized, including by X-ray crystallography. The NHIs are easily acessible from cheap and commercially available starting materials and allow for the facile variation of the steric and electronic properties. DFT calculations reveal that the CO₂ binding energy of the NHIs linearly correlates with the gasphase basicity, and that it is strongly governed by the nature of the N-heterocycle and the substitution pattern. FT-IR analysis of the NHI-CO₂'s thermal stability shows that the decarboxylating ability largely depends on the substituent at the exocyclic nitrogen atom. For the sterically overloaded NHI 3b, the thermal decomposition of the NHI-CO₂ adduct **6b** into 1,3-ditert-butyl-2-imidazolinone and tert-butyl isocyanate was observed. Computational studies confirm that the fragmentation reaction is driven by the release of steric strain leading to a rather low energy barrier of 26.0 kcal mol⁻¹. Examination of the reactivity with water shows that the NHI-CO₂ adducts are surprisingly stable towards hydrolysis, while the stability largely depends on the size of the alkyl substituent at the exocyclic nitrogen atom. This unprecedented property for nitrogen bases can be attributed to the hydrophobic nature of the CO₂ binding site and offer new prospects for the field of CO₂ capture and utilization. Follow-up studies on the utilization of NHIs as organocatalysts and their application in direct air CO₂ capture systems are under current investigation in our laboratories.

Conflicts of interest

There are no conflicts to declare.

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