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Solvent-dependent effect by carbon dioxide on the photoreactions of (9-anthryl)alkylamines

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Abstract—The effect of CO_2 on a photoreaction was first studied systematically by using (9-anthryl)alkylamines (APA, AEA, and AMA) as the starting compound. From close scrutiny of the results, the CO_2 effect was clearly observed and was well rationalized by the previously reported novel solvent dependence of the amine–CO_2 reversible reactions. For instance, the yield of the dimer (**h**–**t** from APA or AEA, **h**–**t**+**h**–**h** from AMA) obtained in MeOH or DMSO was higher under CO_2 than under argon and this was ascribed to formation of either ammonium bicarbonate/carbonate in MeOH or carbamic acid in DMSO, which will prevent the nitrogen lone pair from being involved in electron-transfer reactions. In fact, the electron-transfer side reactions producing **1**–**3** in DMSO were strongly inhibited under CO_2. Also, due to formation of noncovalent linkage between the ammonium cation and the carbamate anion in 2-PrOH, the proportion of **h**–**h** relative to **h**–**t** produced from AMA in 2-PrOH was increased by carrying out the reaction under CO_2.

1. Introduction

Many amines react with carbon dioxide to form carbamic acids (Eq. 1).[1] The acids are unstable and easily dissociate back to amines and CO_2, or react with another amine molecule to form ammonium carbamates (Eqs. 1 and 2). In aqueous solution, ammonium bicarbonates/carbonates are also formed (Eq. 3). These reactions are reversible and have recently been utilized for preparation of a variety of reversible supramolecular materials such as switchable solvent systems,[2] switchable surfactants,[3] switchable polymeric hosts,[4] reversible organogels,[5] and reversible organosilicas.[6] They have also been used for controlling the underlying thermal reactions, e.g., enhancement of the reaction rate and the product selectivity.[7]

$$RNH_2 + CO_2 \rightleftarrows RNHCO_2H \tag{1}$$

$$RNHCO_2H + RNH_2 \rightleftarrows RNHCO_2^- RNH_3^+ \tag{2}$$

$$RNH_2 + CO_2 + H_2O \rightleftarrows RNH_3^+ HCO_3^- \tag{3}$$

For the past few years we have studied the solvent dependence of the formation of carbamic acid species (i.e., carbamic acid and ammonium carbamate) from particular amines and CO_2: for our previous papers on the amine–CO_2 reaction system, see Ref. 8. In protophilic, dipolar, aprotic solvent such as DMSO, DMF, pyridine, or dioxane (unlike in water), the equilibrium of Eq. 2 lay so far to the left for the amines studied.[8a,b,e] Concurrently, we attempted to apply this solvent dependence to manage photochemical reactions. Now, we wish to report the effect of CO_2 on the photoreactions of ω-(9-anthryl)alkylamines. The original aim was to control their photodimerization regioselectivity by using the ammonium carbamate ionic linkage as a noncovalent linker (see the structure A, which is proposed in Scheme 5). Although we could achieve only a limited success for this purpose, the overall CO_2 effects observed here were consistent with the previously reported[8a,b] novel solvent dependence in the amine–CO_2 reversible reactions (Eqs. 1–3). To our knowledge,

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Keywords: Carbon dioxide; Anthryl amine; Carbamic acid; Ammonium carbamate; Solvent dependence; Photoreaction; Reaction control.

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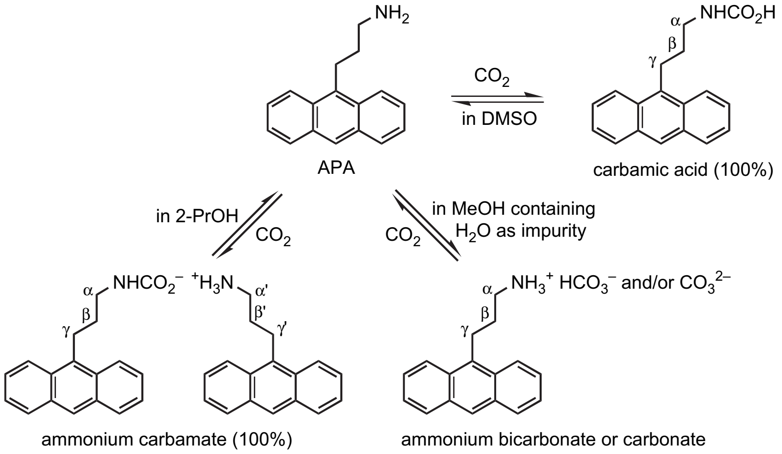


Scheme 1. Solvent dependence of the 3-(9-anthryl)propylamine (APA)–CO_2 reaction.

the photochemistry of the carbamic acid species has not been systematically studied so far.[†]

2. Results and discussion

2.1. Reaction of APA with CO_2

We have already performed detailed investigations about the solvent dependence of the formation of carbamic acid species from ω-(1-naphthyl)alkylamines.[8a,b] The results were obtained mainly on the basis of NMR and IR analyses before and after bubbling of CO_2 through the amine solution. In a DMSO solution, 3-(1-naphthyl)propylamine (NPA) was exclusively converted to the corresponding carbamic acid, whereas in 2-PrOH or in MeOH it was converted to the ammonium carbamate or to the ammonium bicarbonate/carbonate, respectively.[8a]

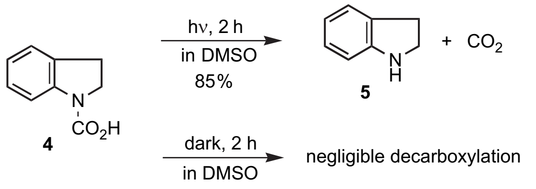
Here the same experiment was repeated for 3-(9-anthryl)propylamine (APA) and exactly the parallel solvent dependence was observed, i.e., formation of carbamic acid in DMSO, ammonium carbamate in 2-PrOH, and ammonium bicarbonate/carbonate in MeOH (Scheme 1). In diethyl ether, the ammonium carbamate precipitated as a pale yellow solid. The main features of the NMR and IR spectra that were obtained after the CO_2 bubbling, are given below ((a)–(c)). These are exactly analogous with those found for NPA.[8a]

(a) *In DMSO*. The presence of only three signals corresponding to the three methylene groups could be seen from the ^1H and ^{13}C NMR spectra (i.e., the carbamic acid yield is 100%). The α-methylene proton was considerably shifted to a lower field upon bubbling of CO_2 ($\Delta\delta$ 0.43 ppm) and resonanced as a quasi-quartet at δ 3.18. The NH proton appeared as a broad triplet at δ 6.97. The carboxy carbon of the carbamic acid appeared at δ 157.0 ppm. An HMBC cross peak was observed between the α-methylene proton and the carboxy carbon. The stretching frequency $\nu_{C=O}$ of NCOOH was 1700 cm^{-1}.

(b) *In 2-PrOH*. There were six methylene-proton signals and six methylene-carbon signals in the ^1H and ^{13}C NMR spectra. This corresponds to the formation of the carbamate anion and the ammonium cation. The α-methylene proton appeared at δ 3.33 and the α′-methylene proton appeared at δ 3.00. ^1H NMR can neither distinguish between the carbamate anion and the coexistent carbamic acid, nor between the ammonium cation and the coexistent free amine.[8a] However, the observed six methylene-proton signals were almost equal in intensity. Hence, the yield of the ammonium carbamate may be nearly 100%. A broad signal of the carboxy carbon of the carbamate anion resonanced at δ 160.5 ppm. There was an HMBC cross peak between the α-methylene proton and the carboxy carbon.

(c) *In MeOH*. Like in DMSO, three methylene signals were observed by the ^1H and ^{13}C NMR measurements. The downfield shift of the α-methylene proton was relatively small ($\Delta\delta$ 0.29 ppm) and it resonanced at δ 3.12. The formation of bicarbonate or carbonate was indicated by the ^{13}C NMR peak at δ 161.3 ppm and by the strong IR bands at 1636 and 1310 cm^{-1}. However, the amount of the residual free amine cannot be estimated, because it is indistinguishable from the ammonium species by ^1H NMR.[8a]

[†] The decarboxylation of several *N*-aralkyl- and *N*-arylcarbamic acids, which are formed in situ from the corresponding amines in CO_2-saturated DMSO-d_6,[8a,b] was investigated by us.[8e] It was promoted by irradiation (through Pyrex at room temperature) and an especially large acceleration was observed for certain *N*-arylcarbamic acids. For example, the indoline-derived carbamic acid **4** was decarboxylated in 85% yield into indoline (**5**) after 2 h of irradiation (Eq. 4). In the dark, the decarboxylation was negligible (Eq. 5). The slow decarboxylation in the dark is plausible, because it is an endergonic reaction (ΔG=9 kcal/mol) as mentioned below. Unlike *N*-aralkylamines such as APA (Scheme 1) and 3-(1-naphthyl)propylamine (NPA), *N*-arylamines can be converted only partly to the carbamic acid in CO_2-saturated DMSO-d_6, e.g., **4** vs **5**=22:78.[8a,b] The content of **4**, however, increased at lower temperatures and reached nearly 100% at −52 °C in CO_2-saturated DMF-d_7 (see ^1H and ^{13}C NMR in Figs. 1 and 2). The temperature dependence of [**5**]/[**4**] (Fig. 1) was thermodynamically analyzed (Fig. 3) and the free energy change ΔG for the reaction $\mathbf{4} \rightleftarrows \mathbf{5}+CO_2$ was estimated as +9 kcal/mol. The theoretical evaluation of ΔG for $NH_2COOH \rightleftarrows NH_3+CO_2$ afforded +10.5 kcal/mol.[9,1]



(4)

(5)