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NMR Study of the Composition of Aqueous 2-Aminoethanol Solution Used for Absorption of Carbon Dioxide from Fuel Gases

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Abstract—The compositions of aqueous 2-aminoethanol solutions used in industry for absorption of carbon dioxide resulting from combustion of natural gas have been determined by ^{1}H and ^{13}C NMR spectroscopy. The absorption process does not involve generally accepted paths of thermal decomposition of the absorbent in the reaction with carbon dioxide, but the main path is non-oxidative decomposition of 2-aminoethanol into ammonia and ethylene oxide. Splitting of the NMR signals of carbamate anion formed by reaction of 2-amino-ethanol with carbon dioxide has been rationalized by specific structure of the anion due to intramolecular hydrogen bonding.

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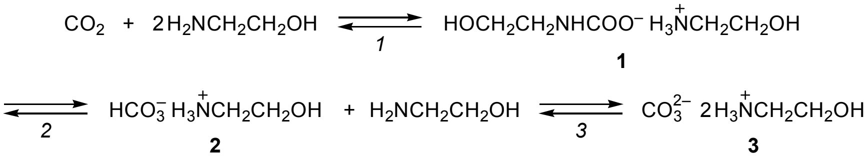
Purification of gases from acid components such as H_2S, CO_2, COS, CS_2, and SO_2 by absorption has been used in industry over many decades. Aqueous 2-aminoethanol solutions are most frequently used as absorbent. Decomposition of 2-aminoethanol in the course of gas purification process is responsible for its consumption, reduction of the capacity, and foaming, as well as for accelerated corrosion of the equipment [1, 2].

Decomposition of 2-aminoethanol during the absorption of carbon dioxide has been studied in detail under both laboratory and industrial conditions. In recent time, the importance of studies in this field is justified by the global greenhouse gases reduction problem and potential use of 2-aminoethanol for binding CO_2 [2, 3].

Saturation of an aqueous solution of 2-amino-ethanol (~15%) with carbon dioxide below 50°C gives mainly carbamate **1** which may be partially hydrolyzed to a mixture of hydrogen carbonate **2** and carbonate **3** [1, 2] (Scheme 1). Equilibrium *3* shifts toward carbonate **3** as the pH increases, i.e., as the amount of absorbed CO_2 decreases [3]. In the absorbent regeneration step (90–120°C) carbamate **1** decomposes into the initial reactants, but this process is accompanied by formation of impurities which reduce the absorption efficiency.

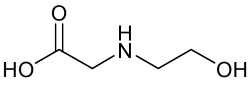
The products of 2-aminoethanol decomposition and their effect on the absorbent performance have been studied in detail. Thermal and oxidative decomposition paths of 2-aminoethanol are commonly considered [2, 4, 5]. The major product of oxidative degradation of 2-aminoethanol is ammonia. Various methods, including NMR spectroscopy, revealed the following acids in 2-aminoethanol solutions used for absorption of carbon dioxide: formic acid (**4**), acetic acid (**5**), glycolic acid (**6**), oxalic acid (**7**), 2-hydroxypropanoic acid (**8**), and 2-aminopropanoic acid (**9**); the corresponding *N*-(2-hydroxyethyl) amides were detected by GC/MS [2, 6–8].

Scheme 1.



$$CO_2 + 2H_2NCH_2CH_2OH \underset{1}{\rightleftarrows} \underset{\mathbf{1}}{HOCH_2CH_2NHCOO^- H_3\overset{+}{N}CH_2CH_2OH}$$

$$\underset{2}{\rightleftarrows} \underset{\mathbf{2}}{HCO_3^- H_3\overset{+}{N}CH_2CH_2OH} + H_2NCH_2CH_2OH \underset{3}{\rightleftarrows} \underset{\mathbf{3}}{CO_3^{2-}\ 2H_3\overset{+}{N}CH_2CH_2OH}$$



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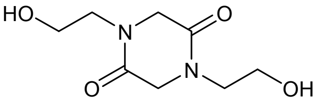

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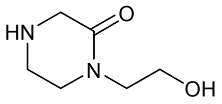

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More specific paths have also been proposed for the transformation of 2-aminoethanol. One of these involves carboxymethylation of 2-aminoethanol with glycolic acid (**6**), which rationalizes formation of compounds **10**–**12** (identified by both NMR and GC/MS in amounts comparable with the amounts of **4**–**9** [6, 8]. The formation of **12** was also explained assuming various redox reactions catalyzed by iron ions which appear in the absorbent as a result of corrosion [6, 8].

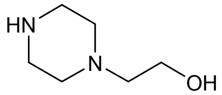
Relatively little attention has been given to 2-aminoethanol decomposition path involving its dissociation into ammonia and ethylene oxide and subsequent reactions of the latter with water and 2-aminoethanol to give ethylene glycol (**13**) and 2,2′-iminodiethanol (**14**) [8]. On the average, the concentration of particular compounds **4**–**14** in the absorbent did not exceed 0.1 wt %.

Thermal degradation paths *4*–*7* [1–7] (Scheme 2) so far assumed to be the main ones were proposed as a rule on the basis of only GC/MS data. As repeatedly noted [8, 9], these paths are inconsistent with the NMR data obtained under both laboratory and industrial conditions. Compounds **15**–**18** were not detected by ^{13}C NMR in a 2-aminoethanol solution used for absorption of CO_2 in the absence of COS and CS_2 [8, 9].

Over years, I analyzed compositions of saturated and regenerated 2-aminoethanol solutions (10–15%) from an industrial absorber in Omsk where they were used to absorb carbon dioxide formed by methane combustion. It was preliminarily concluded that reactions *4*–*7* do not occur under the given conditions [8, 9]. Herein, I report the results of analysis of the NMR spectra of commercial absorbents, which confirm the above conclusions and explain characteristic splitting of NMR signals belonging to carbamate anion of **1**. As far as I know, this fact has never been discussed. The observed signal splitting may be accounted for by cyclic structure of carbamate ion due to formation of intramolecular hydrogen bond. This interesting structural feature of carbamic acid derivatives has been postulated more than 40 years ago; however, since that time it has not been confirmed directly by experimental data.

Figures 1–3 show the ^{13}C and ^{1}H NMR spectra of saturated and regenerated 2-aminoethanol solutions, and ^{13}C signal assignment for compounds **1**–**14** according to [8, 9] is given in table. The spectra given in Figs. 1 and 2 contain no signals assignable to compounds **15**–**18** which were identified by ^{13}C NMR in 2-aminoethanol solutions used for absorption of COS and CS_2 [9]. As found previously [8], compounds **13** and **14** were the major impurities in the absorbent. Thus, the only path of non-oxidative degradation of 2-aminoethanol under the given conditions is its dissociation into ammonia and ethylene oxide.

Two relatively strong signals at δ_C 48.57 and 59.54 ppm (Fig. 2) belong to piperazine **19** provided that the remaining two less intense signals of the 2-hydroxyethyl substituent in **19**, supposedly at δ_C 60 and 62 ppm (calculated values) are overlapped by those of other components.



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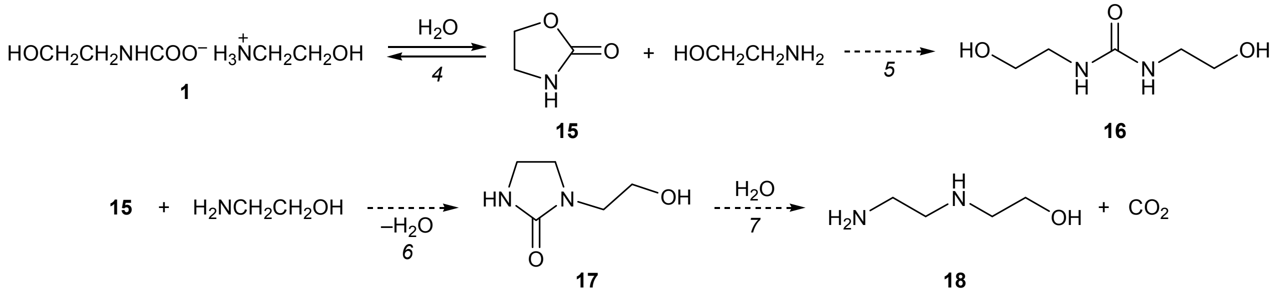
According to the GC/MS data, piperazine **19** (m/z 130 $[M]^+$) is one of the most characteristic components of the absorbent [9]. Presumably, compound **19** was previously erroneously identified as imidazoli-

Scheme 2.



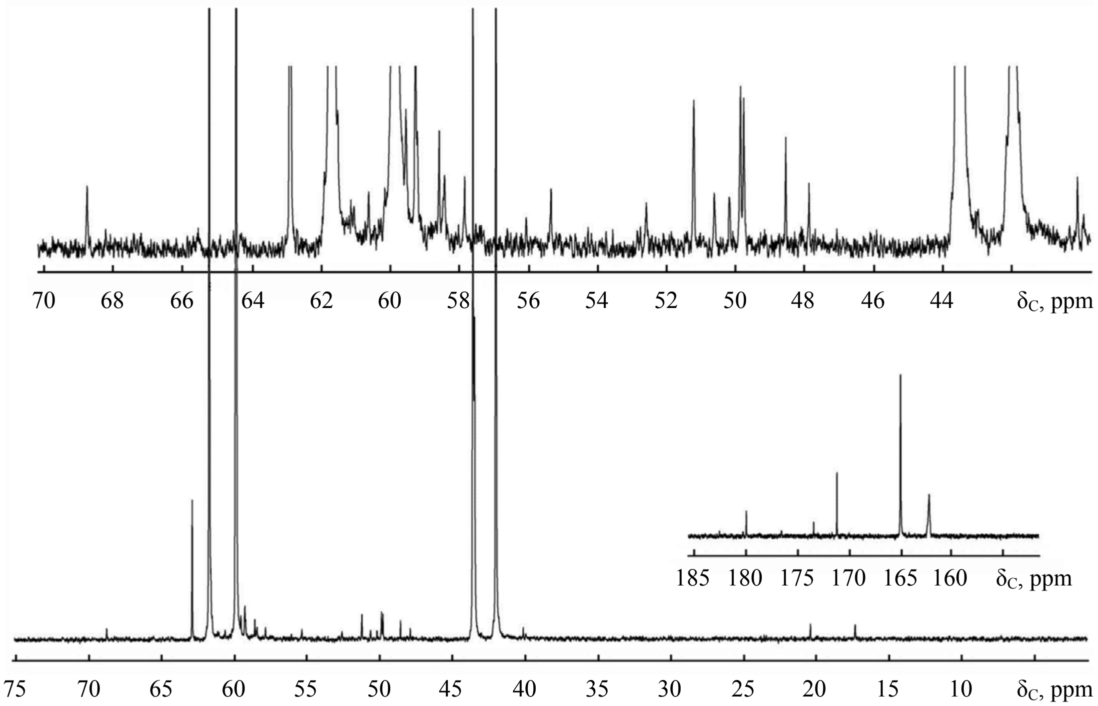


Fig. 1. ^{13}C NMR spectrum of a 12% aqueous solution of 2-aminoethanol saturated with CO_2; UDEFT pulse sequence. For signal assignment, see table.

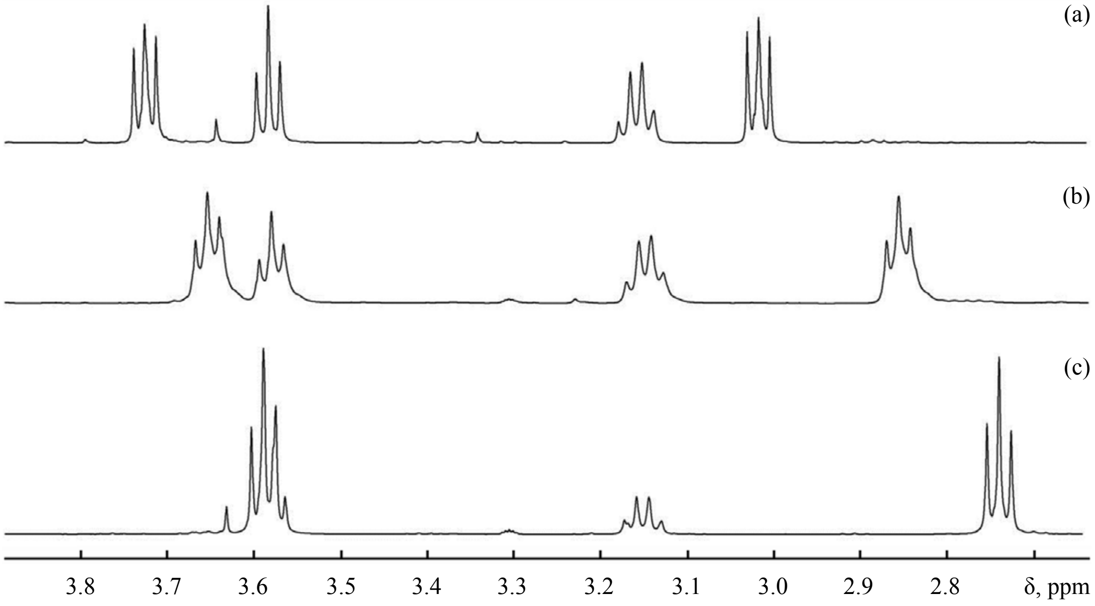


Fig. 2. Fragments of the ^1H NMR spectra of 2-aminoethanol solutions saturated with carbon dioxide by (a) 100, (b) 70, and (c) 40%. Signal assignment in the spectrum of **3a**, δ, ppm: 3.75 t and 2.90 t (**1**, cation); 3.15 and 3.16 d.t and 3.58 t (**1**, anion).

dinone **17** on the basis of the GC/MS data since these compounds are difficult to distinguish by mass spectra. Compound **19** is the reduction product of **12**. Conditions for the reduction of **12** are likely to be created as a result of iron-catalyzed redox reactions during operation of absorbers.

The major signals at δ_C 59.85, 42.01 and 164.7, 61.70, 43.59 ppm in the ^{13}C NMR spectrum (Fig. 1) correspond to *N*-(2-hydroxyethyl)ammonium cation and carbamate anion of **1** [8]. The signal at δ_C ~163 ppm with an intensity comparable with that of the signal of **1** at δ_C 164.7 ppm arises from HCO_3^- and

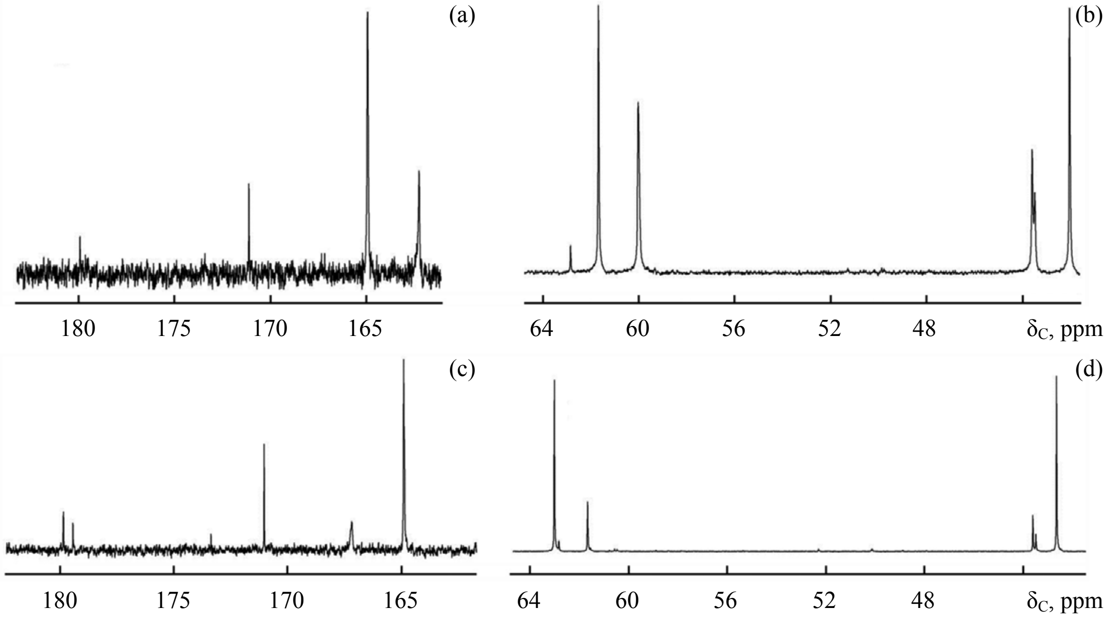


Fig. 3. ^{13}C NMR spectrum of a 12% aqueous solution of 2-aminoethanol (a, b) saturated with CO_2 and (c, d) after regeneration. For signal assignment, see text and table.

Signal assignment in the ^{13}C NMR spectra (Fig. 1) of 2-aminoethanol solutions used for absorption of carbon dioxide under industrial conditions

Compound no.	δ_C, ppm	
	C=O	other carbons
1[a]	165.0	61.74, 59.88, 43.59, 42.01
2, 3[a]	162.2	61.74, 42.01
4	171.1	
5	182.5	23.63
6	179.9	61.61
7	173.4	
8	180.7	68.75, 20.47
9	176.5	58.61, 17.29
10[b]		60.62, 52.60, 50.62
11[b]		59.29, 51.24, 49.91
12[b]		58.42, 57.84, 55.36, 47.90, 40.13
13		62.88
14		59.88, 49.82
15[c]	163.3	66.71, 40.52
16[c]	161.8	62.41, 43.59
17[b, c]		60.02, 47.03, 46.82, 38.34
18[b, c]		60.30, 51.23, 50.75, 39.05

[a] For saturated absorbent.

[b] The intensity of the carbonyl carbon signal was lower than the intensity of the corresponding methylene carbon signals; therefore, it was not detected at a given concentration.

[c] Not detected; δ_C values were taken from [9].

CO_3^{2-} ions of **2** and **3**. Shift of equilibrium *1* upon regeneration of the absorbent is reflected in the ^{1}H and ^{13}C NMR spectra by reduction of the intensity of signals of the carbamate anion of **1** relative to the common signal of the cation and free amine, as well as by considerable shift of the latter to the region typical of the free amine (Figs. 2, 3). Simultaneously, the common signal of the anions of **2** and **3** is displaced downfield, from the position typical of HCO_3^- (δ_C 163 ppm) to the position typical of CO_3^{2-} (δ_C 167 ppm), whereas the signal of **1** does not change its position. Analogous variations in the NMR spectra were observed while studying CO_2 absorption with a solution of NH_3 [3].

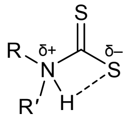
In the ^{1}H NMR spectrum of **1**, the NCH_2 signal of the anion characteristically appears as a quartet formed by two overlapped triplets (Fig. 2); however, this fact was not rationalized in the literature. Furthermore, I previously noted that the ^{13}C NMR spectrum of **1** also contains two NCH_2 signals with equal or comparable intensities (Fig. 1), but the observed splitting was erroneously assigned to the presence of hydrogen carbonate **2** [8]. In fact, it is quite obvious that the NCH_2 signal of **2** should be the same as the signal of 2-hydroxyethylammonium cation rather than of anion of **1**.

The most common reason for splitting of NMR signals in compounds structurally related to carbamate **1** is restricted rotation about the amide C–N bond. However, taking into account published data for carbamates, thiocarbamates, and dithiocarbamtes derived from a number of secondary amines [10], this factor can be completely excluded. Separate signals of rotational isomers were generally observed at low temperature only for thiocarbamates in which the COS^- fragment is unsymmetrical.

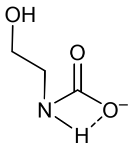
In other cases, splitting of methylene proton signals may be related to their diastereotopicity due to the presence of a neighboring asymmetric center. Even when the tetrahedral nitrogen atom of the anion of **1** were considered to be an asymmetric center, it would be impossible to rationalize splitting of the NCH_2 carbon signal of that anion.

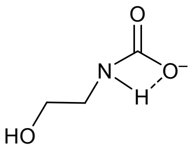
There is one more, also well known, factor responsible for NMR signal splitting, which implies the existence of isomers with axial and equatorial orientation of alkyl substituent on the nitrogen atom in heterocycles like *N*-methylaziridine [11].

Even in earlier studies on the structure of compounds formed by reactions of amines with CO_2, COS, CS_2, and CSe_2 [10] it was proposed that carbamic acids have zwitterionic structure. For instance, dithiocarbamic acid can be represented as cyclic structure with intramolecular hydrogen bond [12]:



Analogous structure of the carbamate anion of **1** simply and appropriately explains the observed splitting of the NMR signals which are likely to belong to isomeric carbamate anions with axial and equatorial orientation of the 2-hydroxyethyl substituent provided that, as in the case of *N*-methylaziridine [11], inversion of the nitrogen atom therein at room temperature is slow on the NMR time scale.





EXPERIMENTAL

Samples of the absorbent (a 12% aqueous solution of 2-aminoethanol) were withdrawn from the absorber and desorber lines of a setup for carbon dioxide production by combustion of natural gas.

The ^{13}C and ^{1}H NMR spectra were recorded on a Bruker Avance 400 spectrometer equipped with a PABBO 400S1 broad-band probe using D_2O for deuterium stabilization and as external standard; Bruker pulse sequences ZG, JMODE, and UDEFT were applied with a relaxation time of 6 s. Accumulation over ~12 h was necessary to detect weak signals in the ^{13}C NMR spectra.

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