Evidence of Conversion from Carbon Dioxide to Unstable Carbon Oxides

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Synopsis. A reaction of reduction products of carbon dioxide by benzoin carbanion with sodium dithionite gave a substance showing only one ^{13}C NMR absorption signal at 75.4 ppm, which was tentatively attributed to a signal of an oligomer having a $-C(SO_3Na(H))_2-$ structure as a repeating unit.

Interest has been stimulated in the reaction of carbon dioxide (CO_2) in view of the use of resources. It has been well-known that CO_2 reacts with various organic compounds to give carboxylic acids,[1] carbonate,[2] substituted 3-oxazolin-5-ones,[3] substituted 2-oxazolidinones,[4] and lactones.[5] In these reactions CO_2 incorporates into organic compounds keeping CO_2 unit. There seems to be no example that CO_2 is converted to compounds having C=C bond and only carbon atom of CO_2 is given to oragnic or inorganic compounds. However, it has been reported that unstable carbon oxide such as C_2O, which has structure :C=C=O, gives a carbon atom to ethylene derivatives or tetrahydrofuran to give allen derivatives[6] or cyclobutanone,[7] respectively. If CO_2 is converted to unstable carbon oxides, there is a possibility that compounds having C=C bond(s) are formed and that the only carbon atom of CO_2 is given to organic or inorganic compounds.

In the present report it will be shown that carbon atom of the unstable carbon oxides, which are formed by the reduction of CO_2 with benzoin carbanion (**1**) (structure is shown in Eq. 1), is given to inorganic compound by the reaction of carbon oxides with sodium dithionite. In the preliminary report it was reported that saturated hydrocarbons were formed[8] by the reaction of sydnones with the carbon oxides formed by the reduction of CO_2 with **1**.[9]

Results and Discussion

Reaction of the reduction products of CO_2 by **1** with sodium dithionite was carried out as described in Experimental. Products were separated as partially exchanged sulfonic acid salt ($-SO_3Na(H)$) by treatment with ion exchange resin (see Experimental). Although the instabilities of the products and insolubilities of the products in organic solvents prevent perfect purification and characterization of the products, observations obtained seem to be worthy to be reported.

Two sorts of the products (products A and B) were obtained by the reaction of sodium dithionite with the reduction products (unstable carbon oxides) formed by the reduction of CO_2 with **1**. The product A was obtained by the reaction of sodium dithionite with the reduction products which were formed when CO_2 was introduced into the solution of **1** in rapid speed at -78 °C for 20 min. The product B was obtained by the reaction of sodium dithionite with the reduction products which were formed when CO_2 was introduced in slow speed at -78 °C for 1 h.

The product A was isolated in a yield of 29%.[10] The product A showed only one ^{13}C NMR signal at 75.4 ppm as is shonw in Fig. 1-a. IR spectrum of the product A is shown in Fig. 2-a. Elemental analyses of the product A were C, 4.99; H, 0.98; S, 26.80; Na, 13.23%, which indicated that S/C was nearly 2. The product A did not show signals in ^1H NMR spectrum other than that of H_2O. This fact indicates that the product A does not have C–H bonds. Since IR spectrum shown in Fig. 2-a resembles closely to that of hydrated sulfonic acids or sulfonic acid salts, the product A is considered to be sulfonic acid or sulfonic acid salt. Reaction of product A with *S*-benzylthiuronium chloride[11] gave a white precipitate.

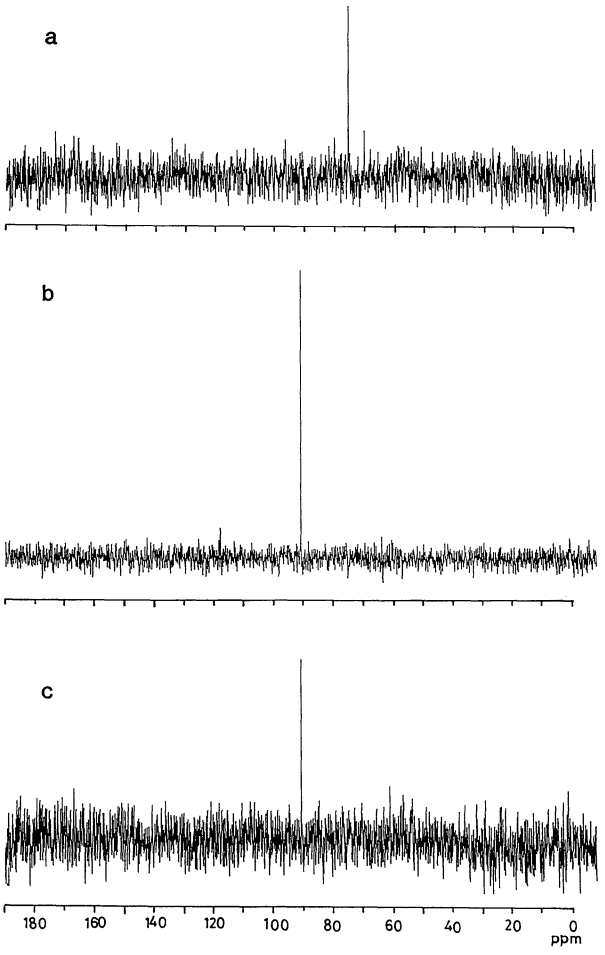

Fig. 1. ^{13}C NMR spectra (in D_2O) of the reaction products. a: product A; b: the spectrum of the product A measured after standing of D_2O solution of it for several days at room temperture; c: product B.

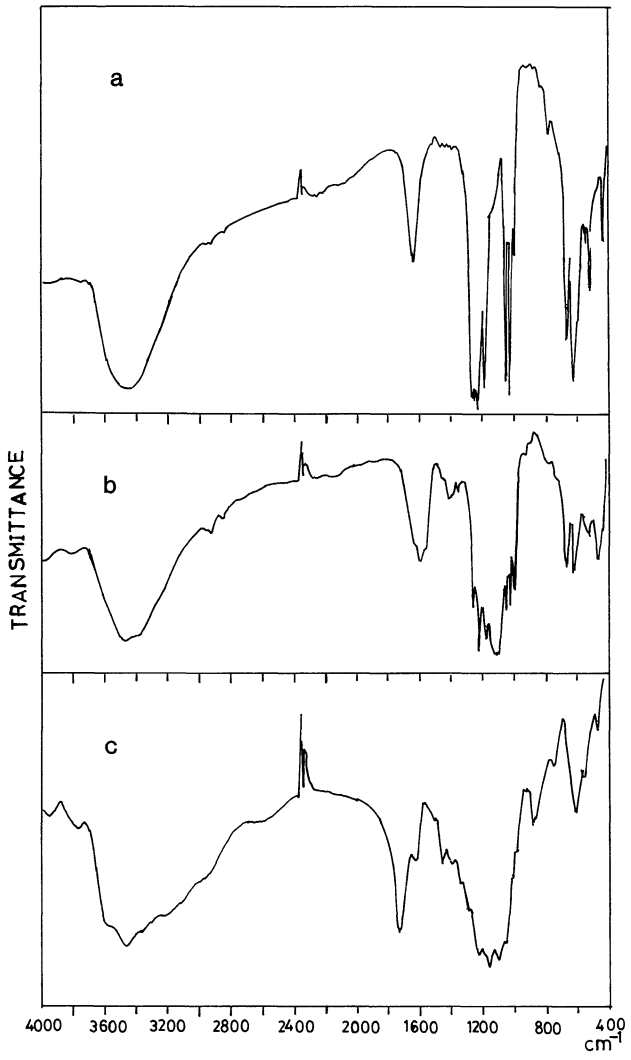

Fig. 2. FT-IR spectra of the reaction products. a: product A; b: the spectrum of the compound containing carbon, which was separated from the solution described in Fig. 1-b; c: product B.

Elemental analyses of the precipitate were almost coincident with the calculated value for $-(C_6H_5CH_2SC(NH_2)_2O_3S)_2C-$ (see Experimental). These all facts indicate that the product A has $-C(SO_3Na(H))_2-$ structure as a repeating unit. Determination of molecular weight of A by means of gel permeation chromatography was impossible because of insolubility of the product A in organic solvents. Since the product A is a mixture of sodium salt of sulfonic acid and free sulfonic acid and contains water and small amount of silica gel,[12] determination of the molecular weight by means of vapor phase osmometry was not undertaken. Although molecular weight of the product A was not determined, the fact that the product A has only one signal in ^{13}C NMR indicates that the product A is an oligomer having $-C(SO_3Na(H))_2-$ structure as a repeating unit. The formation of the product A is summarized in Eq. 1.

$$CO_2 \xrightarrow[-78\,^\circ C\ (THF)]{C_6H_5-\overset{\overset{O}{\|}}{C}-\underset{\underset{OLi}{|}}{C}-C_6H_5\ (\mathbf{1})} \left[\begin{array}{l} C_xO_y \text{ or} \\ C_xO_yLiz \end{array}\right] \xrightarrow[\text{reflux (THF-}H_2O)]{Na_2S_2O_4} -C(SO_3Na)_2- \xrightarrow[\text{product A}]{\text{ion exchange resin}} -C(SO_3Na(H))_2- \quad (1)$$

When a D_2O solution of the product A was allowed to stand for several days at room temperature, ^{13}C NMR spectrum of the solution changed in the chemical shift from 75.4 to 91.0 ppm as is shown in Fig. 1-b. Filtration of the D_2O solution and evaporation of filtrate gave a residue. This residue was separated by means of TLC using methanol as an eluent to give a compound containing carbon. IR of this compound is shown in Fig. 2-b. Elemental analyses of it were C, 7.59; H, 1.23; S, 20.11; Na, 13.70%, which indicated that S/C was nearly 1. This compound does not show signals in ^1H NMR spectrum other than that of H_2O. Appearance of IR absorption at around 1100 cm^{-1} in Fig. 2-b (compare with Fig. 2-a) and the change of the ratio of S/C from 2 (product A) to 1 indicate that the product A is converted to a oligomer having $-C(OH)(SO_3Na(H))-$ as a repeating unit.[13]

The product B was isolated in a yield of 84%.[10] ^{13}C NMR and IR spectra of the product B are shown in Fig. 1-c and Fig. 2-c, respectively. Elemental analyses of the product B were C, 11.50; H, 2.60; S, 16.35; Na, 1.99%, which indicated that S/C was 0.53.

^{13}C NMR and IR spectra of the product B are almost same with those (Figs. 1-b and 2-b) of the compound which was obtained by standing of D_2O solution of the product A for several days. This fact indicates that the product B is also a oligomer having $-C(OH)(SO_3Na(H))-$ as a repeating unit. However, S/C of the product B is lower than 1. This low value of S/C and high yield of the product B (84%) calculated from the carbon content[10] suggest that the product B is contaminated by other several impurities each of which exists in small amount. One of impurities can be seen in IR spectrum (at 1730 cm^{-1}, Fig. 2-c) and ^{13}C NMR spectrum (at 167 ppm, Fig. 1-c).

Formation of the product A suggests that the carbon oxides formed have polymerizable C=C bond in their structures. Various sorts of unstable carbon oxides such as C_2O,[6,14] C_3O,[14] C_4O,[14] and C_6O[14] have been reported. These carbon oxides have been considered to have a structure $:C=(C)_n=C=O$. C_2O has a ability to eject :C: but does not have ability to eject :C=C:. Therefore, a possible candidate for the carbon oxides formed by the reduction of CO_2 with **1** would be $:C=(C)_n=C=O$ ($n>0$). Reaction of the carbon oxides formed with sodium dithionite presumably gives an olefin having a structure, $(NaO_3S)_2C=C(SO_3Na)_2$. Heating under

reflux of the solution of this olefin presumably gives the oligomer A.

Slow introduction of CO_2 would keep the basicity of the solution higher. As a result, impurities, which catalyses conversion of the product A to the product B, would be formed in this case.[17]

Experimental

General Procedure. Instruments and reaction vessel used and thin-layer chromatography procedure were described in the previous paper.[9] Preparation of **1** was described in the previous paper.[9]

Reaction of Sodium Dithionite with Carbon Oxides Formed by the Reduction of CO_2 with 1. After finishing of introduction of CO_2 to the solution of **1** (4.5 mmol), a serum cap was put off from one neck of two-necked 100 ml flask and a 30 cm long Liebig cooler was put on the neck of the flask. Water solution (10 ml) containing 1.57 g (9 mmol) of sodium dithionite was added dropwise from a top of the cooler. During the addition the reaction solution was kept at −78 °C, taking care so that the solution did not blow up. After addition of $Na_2S_2O_4$ solution the mixture was allowed to warm up to room temperature taking care so that CO_2, which was contained in the solution, did not blow up abruptly. The solution was heated under reflux with stirring under nitrogen atmosphere. At the biginning of reflux additional 10 ml of $Na_2S_2O_4$ (1.57 g) solution was added, followed by reflux for 1 h. At the end of the reflux for 1 h additional 5 ml of $Na_2S_2O_4$ (0.78 g) was added to the mixture, followed by heating under reflux for additional 0.5 h.

Separation Procedure of the Reaction Products of Sodium Dithionite with Carbon Oxides Formed by the Reduction of CO_2 with 1. The above stated reaction mixture of $Na_2S_2O_4$ with the reduction products of CO_2 was totally evaporated using a rotary evaporator and a pump at room temperature. The residue obtained was extracted with water to give 50 ml of water solution, which gave about 7 g of the residue by evaporation using a pump. This residue was extracted with small portion of water repeatedly and all of the water solutions were passed successively through 80 g of DOWEX 50W-X4 (50-100 Mesh, H Form) ion exchange resin.[16] The aqueous solution initially flowing out from the resin (60—80 ml) was evaporated to give pale yellow residue. This pale yellow residue was extracted with methanol and the extracts were separated by means of TLC using methanol as an eluent.

Salt of the Product A with *S*-Benzylthiuronium Chloride. A reaction of the Product A with *S*-benzylthiuronium chloride by the procedure shown in the literature[11] gave a white precipitate. Since this precipitate is not soluble in water or organic solvents, NMR spectrum was not taken. IR spectrum of the salt shows following absorptions; 3300—2800 (broad), 1657, 710 cm^{-1} (these absorptions are seen in that of *S*-benzylthiuronium chloride), and 1454, 1232, 1153, 1074, 997 cm^{-1}. Elemental analyses of the salt were: Found: C, 39.81; H, 4.69; S, 26.47; N, 11.51%. Calcd for $-(C_6H_5CH_2SC(NH_2)_2O_3S)_2C-$: C, 40.30; H, 4.38; S, 25.31; N, 11.06%. Since the reaction procedure for making this salt[11] presumably brings about a little decomposition of the product A, a little discrepancy between these values is unavoidable.

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10) Yield of the product A or B was calculated as (amount (g) of A or B)×(C% of A or B)/(12.011×(mol of CO_2 reduced)). Since data in Table 1 of the previous paper[9] indicate that 0.6 mol of CO_2 was reduced with 1 mol of **1** at −78 °C, mol of CO_2 reduced in the present experiment is 0.0045×0.6.

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12) Since the product A and B were not soluble in organic solvent, methanol was used as a eluent for the separation of A or B in TLC procedure. Silica gel is a little soluble in methanol. Amount of SiO_2 contained in A or B were determined to be 3 wt% using ammonium molydbdate by the method of Govett (G. J. S. Govett, *Anal. Chim. Acta.*, **25**, 69 (1961)).

13) Free sulfonic aicd group in the product A presumably facilitates substitution of neighboring $-SO_3Na(H)$ group to OH group to give an oligomer having $-C(OH)(SO_3N_a(H))-$ as a repeating unit.

14) The references are cited in the previous paper.[9]

15) It was sometimes difficult to obtain good reproducible results. Sometimes the product B was formed even in the case of rapid introduction of CO_2.

16) Ion exchange resin was used to remove salts of diisopropylamine with CO_2 and to decompose unreacted $Na_2S_2O_4$. Na ion of sulfonic acid salts was partially exchanged during the treatment of 7 g of the product residue by 80 g of the resin. Use of larger amount of the resin brought about totally decomposition of the oligomers.