Am. Chem. Soc., **86**, 1089 (1964); (q) H. C. Brown and B. C. Subba Rao, *ibid.*, **80**, 5377 (1958); (r) H. C. Brown, C. J. Shoaf, and C. P. Garg, *Tetrahedron Lett.*, 9 (1959); (s) H. C. Brown and C. P. Garg, *J. Am. Chem. Soc.*, **86**, 1085 (1964); (t) T. Izawa and T. Mukaiyama, *Bull. Chem. Soc. Jpn.*, **52**, 555 (1979); (u) I. D. Entwistle, P. Boehm, R. A. W. Johnstone, and R. P. Telford, *J. Chem. Soc., Perkin Trans*, **1**, 27 (1980); (v) M. Mukai and Mukaiyama, *Chem. Lett.*, 215 (1975); (w) R. O. Hutchins and M. Markowitz, *Tetrahedron Lett.*, 813 (1980); (x) J. H. Babler and B. J. Invergo, *ibid.*, 11 (1981); (y) L. I. Zakharkin, V. V. Gavrilenko, D. N. Maslin, and I. M. Khorlina, *ibid.*, 2087 (1963); (z) T. E. Cole and R. Petit, *ibid.*, 781 (1977).

3. (a) H. C. Brown, J. S. Cha, B. Nazer, and N. M. Yoon, *J. Am. Chem. Soc.*, **106**, 8001 (1984); (b) H. C. Brown, J. S. Cha, N. M. Yoon, and B. Nazer, *J. Org. Chem.*, **52**, 54 (1987); (c) J. S. Cha, J. E. Kim, S. Y. Oh, J. C. Lee and K. W. Lee, *Tetrahedron Lett.*, **28**, 2389 (1987); (d) J. S. Cha, J. E. Kim and K. W. Lee, *J. Org. Chem.*, **52**, 5030 (1987).

4. For other efforts, see:
(a) A. O. Bedenbaugh, J. H. Bedenbaugh, W. A. Bergin, and J. D. Adkins, *J. Am. Chem. Soc.*, **92** 5774 (1970); (b) H. C. Brown, P. Heim, and N. M. Yoon, *J. Org. Chem.*, **37**, 2942 (1972); (c) M. Muraki and T. Mukaiyama, *Chem. Lett.*, 1447 (1974); (d) F. Sato, T. Jinbo, and M. Sato, *Synthesis*, 871 (1981); (e) T. Fujisawa, T. Mori, S. Tsuge, and T. Sato, *Tetrahedron Lett.*, 1543 (1983); (f) L. I. Zakharkin and I. M. Khorlina, *Zh.*

Obsch. Khim., **34**, 1029 (1964); (g) T. D. Hubert, D. P. Eyman, and D. F. Wiemer, *J. Org. Chem.*, **49**, 2279 (1984).

5. (a) J. S. Cha, J. E. Kim, S. Y. Oh, and J. D. Kim, *Tetrahedron Lett.*, **28**, 4575 (1987); (b) J. S. Cha, J. E. Kim, M. S. Yoon, and Y. S. Kim, *Tetrahedron Lett.* (1987), in press.

6. (a) H. C. Brown, P. Heim, and N. M. Yoon, *J. Am. Chem. Soc.*, **92**, 1637 (1970); (b) N. M. Yoon, C. S. Park, H. C. Brown, S. Krishnamurthy, and T. P. Stocky, *J. Org. Chem.*, **38**, 2786 (1973).

7. C. F. Lane, *Aldrichimica Acta*, **8**, 20 (1975), and references cited therein.

8. (a) H. C. Brown and A. W. Moerikofer, *J. Am. Chem. Soc.*, **84**, 1478 (1962); (b) H. C. Brown and G. J. Klender, *Inorg. Chem.*, **1**, 204 (1962); (c) H. C. Brown, S. Krishnamurthy, and N. M. Yoon, *J. Org. Chem.*, **41**, 1778 (1976).

9. E. J. Corey, S. M. Albonico, V. Koelliker, T. K. Schaaf, and R. K. Varma, *J. Am. Chem. Soc.*, **93**, 1491 (1971).

10. H. C. Brown, C. P. Mathew, C. Pyun, J. C. Son, and N. M. Yoon, *J. Org. Chem.*, **49**, 3091 (1984).

11. Li 9-BBNH is readily prepared by hydridating 9-BBN with lithium hydride or *tert*-butyllithium: See.
(a) ref. 9; (b) ref. 10; (c) S. Krishnamurthy and H. C. Brown, *J. Org. Chem.*, **41**, 3065 (1976); (d) S. Krishnamurthy, *Aldrichimia Acta*, **7**, 55 (1974).

12. H. C. Brown, G. W. Kramer, A. B. Levy, and M. M. Midland, "Organic Syntheses via Boranes", Wiley-Interscience, New York, 1975, Chapter 9.

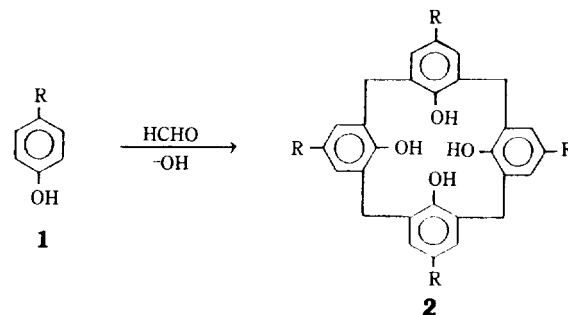# The Syntheses of *p*-Acylcalix[4]arenes

Kwanghyun No* and Younhee Kim

Department of Chemistry, Sookmyung Women's University, Seoul 140. Received November 18, 1987

Starting with readily available *p-tert*-butylcalix[4]arene **3** *tert*-butyl groups are removed by AlCl₃-catalyzed de-alkylation reaction, and the calix[4]arene **4** formed is converted into the tetraacyl esters. These compounds undergo Fries rearrangement to yield *p*-acylcalix[4]arenes. *p*-Acetyl, *p*-propionyl, *p*-butyryl, and *p*-benzoylcalix[4]arene **10, 11, 12** and **14** are synthesized in 70-80% yields by treatment of the corresponding esters **5, 6, 7** and **9** with AlCl₃ in nitrobenzene. When the tetraisobutyryl ester **8** was treated with the same condition, only two isobutyryl groups were rearranged to the para-positions of calix[4] arene, and remaining two groups were simply cleaved.

Introduction

Since the interesting prospects for enzyme model building were proposed by Gutsche[1], various calixarenes have been tried to synthesize by the base-induced condensation reaction between *p*-alkylphenols and formaldehyde as shown on scheme 1[2]. As the results of the research work, the synthetic procedures and the cyclic structure of *p-tert*- butylcalixarenes and some other calixarenes are well established.

If calixarenes are to serve as enzyme mimics it is necessary that they carry various functional groups that can act as active catalystic sites or binding sites[3]. Because the carbonyl

Scheme 1

The Syntheses of p-Acylcalix[4]arenes

Bull. Korean Chem. Soc., Vol. 9, No. 1, 1988 53

group can be converted to various functional groups by many ways, such as oxidation, reduction, Grignard reaction and Wittig reaction, *p*-acylcalix[4]arene can serve as admirable precursor for the functional group introduction. Therefore we repetitiously attempted to introduce carbonyl functions to the para positions of calix[4]arene via Friedel Crafts reaction and Reimer-Tieman type reactions, without success.

The Fries rearrangement[4], in which phenol esters rearrange to ortho- and para-acylphenol in the presence of Lewis acid, has been used in the preparation of para-acylphenols. Since all the ortho positions in calix[4]arene are occupied by the methylene bridges, *p*-acylcalix[4]arene would be the expected product of rearrangement of calix[4]arene acyl ester. Recently we reported the successful preparation of *p*-acetylcalix[4]arene using Fries rearrangement of calix[4]arene acetate[5]. Here we report the syntheses of *p*-acylcalix[4]arenes prepared by Fries rearrangement of the corresponding calix[4]arene acyl esters as shown on scheme 2.

	R	
5	CH₃-	**10**
6	CH₃CH₂-	**11**
7	CH₃CH₂CH₂-	**12**
8	CH₃ CH₃ CH-	**13**
9	⟨O⟩-	**14**
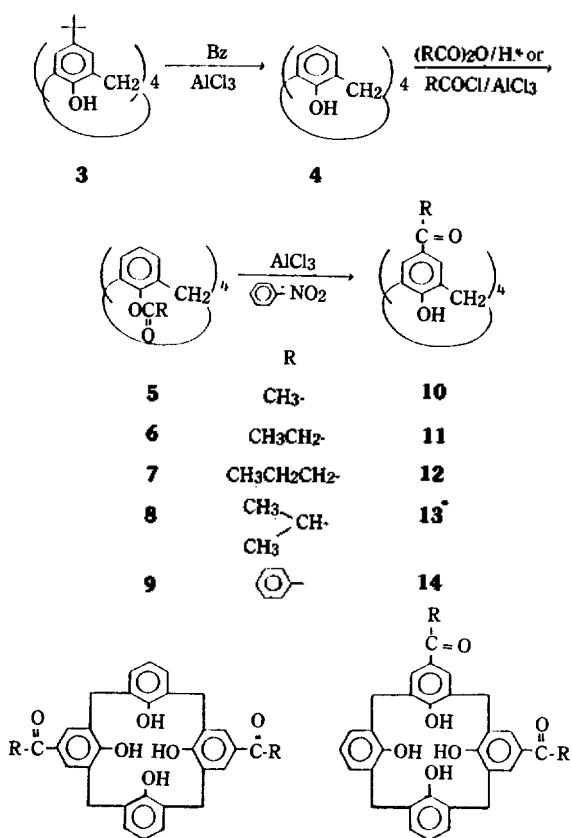
Scheme 2

Calix[4]arene **4**, obtained in 74% yield[5] by AlCl₃-catalyzed removal of the *tert*-butyl groups from *p-tert*-butylcalix[4]arene **3** which was prepared readily[6] from the base-induced condensation of *p-tert*-butylphenol and formaldehyde, was used as starting material for the preparation of various calix[4]arene acyl esters **5-9**. Calix[4]arene alkyl esters **5-8** were prepared by treatment of **4** with the corresponding acid anhydride and conc H₂SO₄ as catalyst using the general procedures for the esterification of calix[4]arene[2a]. Compound **9** was prepared by published procedure[7] in which CH₂Cl₂ solution of **4** was treated with benzoyl chloride and AlCl₃ catalyst. In this reaction there was no indication of *p*-benzoylcalix[4]arene by

Friedel Crafts benzoylation reaction.

Two conformers were isolated from the preparation of butyrate, isobutyrate and benzoate. The elemental analysis and spectral comparison confirmed that these compounds are tetra acyl esters of calix[4]arene in each case. The interconversion between calix[4]arene conformers is almost free at room temperature[3]. However, as the hydroxyl groups of calixarene are replaced with larger groups, such as acyl groups, the interconversion becomes impossible, therefore conformers can be isolated. Gutsche and coworkers[7,8] isolated two conformers from the preparation of calix[4]arene acetate and benzoate. When calix[4]arene **4** is treated with isobutyric anhydride, two products were isolated; one decomposes at 315-317°C **8a**, the other melts at 286-288°C **8b**. The ¹H-nmr spectrum of the higher melting compound **8a** has three singlets in the ratio of 2:1:1 arising from the methylene hydrogens of the calixarene and three sets of doublet in the ratio of 1:2:1 arising from the methyl hydrogens of isopropyl groups. This pattern is commensurate with a partial cone conformation. That of the lower melting compound **8b** has a singlet arising from the methylene hydrogens of calixarene, and one set of doublet from the methyl hydrogens of isopropyl groups, which is commensurate with a 1,3-alternate conformation. ¹H-nmr spectrum of the low melting isomer **7b** (mp 224-225°C) obtained from the preparation of calix[4]arene butyrate indicates that it is the 1,3-alternate conformation; that of the high melting isomer **7a** (mp 309-310°C) indicates that it is partial cone or 1,2-alternate conformation. As reported by Gutsche[7], in the preparation of benzoate also, two isomers are isolated; one melts at 301-302°C (partial cone), and the other does not melt until 400°C (1,3-alternate).

At an early stage of present work, the Fries rearrangement reaction was attempted without solvent. When a mixture of calixarene acetate **5** and AlCl₃ was heated, the product was found to be a mixture of starting material and the desired product **10**, from which the *p*-acetylcalix[4]arene was isolated in 64% yield. However, other calixarene acyl esters **6-9** were treated with similar condition, not only the yields varied from 0% to as high as 30% but also the duplication of the results was difficult. Sometimes the pure porduct could not be isolated from the complex product mixture.

When a solution of calixarene ester and AlCl₃ in nitrobenzene was stirred overnight at room temperature, the product was found to be a mixture of the *p*-acylcalix[4]arene and small amount of starting material. The rearrangement was confirmed by spectral comparison between starting material and product. In infrared spectrum, the OH stretching band appeared and the position of carbonyl stretching band was shifted from 1735 cm⁻¹ of ester to 1670 cm⁻¹ of aromatic ketone. ¹H-nmr spectrum also showed the resonance peak from the OH protons. The peak from phenyl protons was slightly down field shifted due to the introduction of carbonyl function into the phenyl ring

When compound **8** was treated with AlCl₃, only two isobutyryl groups were rearranged to the para positions of calix[4]arene, and remaining two groups were simply cleaved. This was confirmed by ¹H-nmr spectrum and elemental analysis. ¹H-nmr spectrum has two envelopes of resonance peak in the ratio of 2:3 arising from the phenyl hydrogens. One comes from the four protons of two *p*-isobutyryl substituted benzene rings, the other from the six protons of two benzene

rings without isobutyryl substituent. Trabell and Fanta[9] reported that the increasing substituent of methyl group on the -carbon of the ester could be expected to hinder the Fries rearrangement.

The compound 13 can exist in two isomers depending on the positions of isobutyryl substituents as shown on scheme 2. For the unambiguous assignment of the structure of compound **13**, X-ray crystallographic determination is under investigation.

Experimental

IR spectra were obtained by using a Shimadzu IR-435 or Perkin-Elmer 170B spectrophotometer, and [1]H-nmr spectra were recorded on Varian EM-360A instrument with TMS as internal standard. Melting points were measured in sealed capillary tube using Sybron thermolyne apparatus with polarizing microscope and were not corrected. The analytical samples were dried for at least 24 h at 110°C and 1-2 mmHg of pressure.

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrahydroxycalix[4]arene 3 was prepared in 52% yield from *p-tert*-butylphenol and formaldehyde as described elsewhere[6]; mp 344-346°C (lit[7] 344-346°C).

25,26,27,28-Tetrahydroxycalix[4]arene 4 was prepared in 74% yield by $AlCl_3$-catalyzed removal of the *tert*-butyl groups from the compound **3** following the published procedure[6]; mp 315-317°C (lit[8] 314-318°C).

25,26,27,28-Tetraacyloxycalix[4]arene 5,6,7,8. Compound **4** was treated with the corresponding acid anhydride and 1-2 drops of conc sulfuric acid. The mixture was heated under reflux (140-180°C) for 2-4h and poured into water. The resulting precipitate was collected by filtration, washed with dil $NaHCO_3$ solution, with water, and then dried to yield crude product which was purified as follows.

Compound 5 (acetate) was obtained in 75% yield as colorless crystalline solid from twice recrystallizations from benzene; mp 395-397°C (dec) (lit[10] 399-402°C dec).

Compound 6 (propionate) was obtained in 76% yield as colorless crystalline solid from a recrystallization from ether/hexane; mp 310-312°C (dec); IR(KBr) 1735 cm⁻¹(C = O stretching); [1]H-nmr (CDCl₃) δ 7.06 (s, 12H, ArH), 3.72 (s, 8H, CH₂), 1.63 (q, 8H, CH₂), 1.00 ppm (t, 12H, CH₃); Anal. C, 81.92; H, 6.75 (calcd. for $C_{40}H_{40}O_8$; C, 82.15; H, 6.90).

Compound 7a (butyrate). Crude product was triturated with small amount of acetone. Acetone insoluble material was collected by filtration and washed with cold acetone to give colorless crystalline solid in 13% yield; mp 309-310°C; IR(KBr) 1735 cm⁻¹ (C = O stretching); [1]H-nmr (CDCl₃) δ7.30-7.06 (m, 12H, ArH), 3.80 (s, 4H, CH₂), 3.60 (s, 2H, CH₂), 3.40 (s, 2H, CH₂), 1.75-1.20 (m, 16H, CH₂), 0.90 ppm (b, 12H, CH₃). Anal. C, 74.57; H, 6.80 (calcd for $C_{44}H_{48}O_8$; C, 74.96; H, 6.88).

Compound 7b (butyrate). The acetone filtrate and washing from above were combined and evaporated. The resulting slightly waxy solid was purified by flash chromatography (eluent was 2:7 mixture of acetone to hexane). The residue obtained by evaporation of eluent was triturated with hexane to give colorless crystalline solid in 64% yield; mp 224-225°C; IR(KBr) 1740 cm⁻¹ (C = O stretching); [1]H-nmr (CDCl₃) δ7.01 (s, 12H, ArH), 3.75 (s, 8H, CH₂), 1.63 (br.s, 8H, CH₂), 1.60 (br.s, 8H, CH₂), 0.93 ppm (br, 12H, CH₃). Anal. C, 74.60; H, 6.82 (calcd for $C_{44}H_{48}O_8$; C, 74.96; H,

6.88).

Compound 8 (isobutyrate). The crude product was treated with the same way as compound **7**. Acetone insoluble product **8a** was obtained in 13% yield as colorless crystalline solid; mp 315-317°C (dec); IR(KBr) 1735 cm⁻¹ (C = O stretching); [1]H-nmr (CDCl₃) δ 7.00 (s, 12H, ArH), 3.64 (s, 8H, CH₂), 2.20 (m, 4H, CH), 1.01 ppm (d, 24H, CH₃); Anal. C, 74.62; H, 6.80 (calcd for $C_{44}H_{48}O_8$. C, 74.96; H, 6.88). Acetone soluble product **8b** was obtained in 55% yield as colorless crystalline solid; mp 286-288°C; IR(KBr) 1735 cm⁻¹ (C = O stretching); [1]H-nmr (CDCl₃) δ7.30-6.90 (m, 12H, ArH), 3.80 (s, 4H, CH₂), 3.53 (s, 2H, CH₂), 3.47 (s, 2H, CH₂), 2.54 (m, 4H, CH), 1.35 (d, 6H, CH₃), 1.30 (d, 12H, CH₃), 0.38 ppm (d, 6H, CH₃). Anal. C, 74.59; H, 6.78 (calcd for $C_{44}H_{48}O_8$. C, 74.96; H, 6.88).

25,26,27,28-Tetrabenzoxycalix[4]arenes 9a, 9b were prepared by the literature procedure[8]. **9a** was obtained in 13% yield as colorless plates; not melt or decompose until 400°C (lit[8] mp>450°C). **9b** was obtained in 42% yield as colorless needle; mp 301-302°C (lit[8] 301-302°C).

5,11,17,23-Tetraacyl-25,26,27,28-tetrahydroxycalix[4]arenes 10,11,12,13,14. A solution of tetraacyloxycalix[4]arene **5-9** in nitrobenzene was treated with $AlCl_3$ (**2** mole equivalent per a carbonyl function of calixarene ester), and the mixture was stirred for overnight at room temperature. The resulting mixture was treated with water, nitrobenzene was removed by steam distillation. The residue was collected by filtration, crushed into powder, washed with water several times and then dried. The desired products **10-14** were obtained by following method. *p*-Acetylcalix [4] arene 10 was obtained in 70% yield as colorlesss crystalline solid by the published procedure[4]; mp 318-320°C (dec); IR(KBr) 3200cm⁻¹ (OH stretching), 1665 (C = O stretching); [1]H-nmr (CDCl₃) δ 10.3 (s, 4H, OH), 7.82 (s, 8H, ArH), 4.00 (br, 8H, CH₂), 2.50(s, 12H, CH₃). *p*-Propionylcalix [4] arene 11. The crude product was treated with ice-cold ether to remove unreacted starting material. The cold ether insoluble material was collected and recrystallized from ether to give colorless crystalline solid in 80% yield; mp 335-337°C (dec); IR(KBr) 3200cm⁻¹ (OH stretching), 1670 (C = O stretching); [1]H-nmr(CDCl₃) δ 10.27 (s, 4H, OH), 7.83 (s, 8H, ArH), 4.00 (s, 8H, CH₂), 2.90 (q, 8H, CH₂), 1.16 ppm (t, 12H, CH₃). Anal. C, 82.30; H, 6.71 (calcd for $C_{40}H_{40}O_8$. C, 82.15; H, 6.90). *p*-**Butyrylcalix [4] arene 12**. The crude product was dissolved in CH_2Cl_2, treated with charcoal and then evaporated to dryness. The residue was triturated with ether to give colorless crystalline solid in 74% yield; mp 230-232°C; IR(KBr) 3200cm⁻¹ (OH stretching), 1675 (C = O stretching); [1]H-nmr (CDCl₃) δ 10.3 (s, 4H, OH), 7.83 (s, 8H, ArH), 4.00 (b, 8H, CH₂), 2.83 (t, 8H, CH₂), 1.66(m, 8H, CH₂), 0.97ppm (t, 12H, CH₃). Anal. C, 74.78; H, 6.79 (calcd for $C_{44}H_{48}O_8$. C, 74.96; H, 6.88). *p*-**Isobutyrylcalix [4] arene 13**. After the crude product was dissolved in acetone, the acetone solution was standed for 3h at room temperature an then cooled in an ice bath. The precipitate was collected to give the colorless crystalline solid in 66% yield. An additional 14% of product was isolated from flash chromatographic separation (eluent was 5:6 mixture of acetone to hexane) of the residue obtained from the evaporation of acetone filtrate. Total yield was 80%; mp 335-336°C; IR(KBr) 3170cm⁻¹ (OH stretching), 1670 (C = O stretching); [1]H-nmr (CDCl₃) δ 10.3 (s,4H OH), 7.83 (s, 4H, ArH),

Gamma-Radiolysis of Carbon Dioxide (IV)

Bull. Korean Chem. Soc., Vol. 9, No. 1, 1988 55

7.37-6.95 (m, 6H, ArH), 4.00 (br, 8H, CH$_2$), 3.80-3.18 (m, 2H, CH) 1.18ppm (d, 12H, CH$_3$). Anal. C, 76.15; 6.52 (calcd for C$_{36}$H$_{36}$O$_6$. C, 76,56; H, 6.44). *p*-**Benzoylcalix [4] arene 14.** The crude product was purified by flash chromatography (eluent was 7:4 mixture of acetone to hexane). The residue obtained by evaporation of eluent was triturated with hexane to give the desired product in 76% yield as colorless crystalline solid; mp not melt or decompose until 400°C; IR(KBr) 3400cm^{-1} (OH stretching), 1640 (C=O stretching); ^{1}H=nmr (CDCl$_3$) δ 10.3 (s, 4H, OH), 7.75-6.93 (m, 28H, ArH), 3.90 ppm (b, 8H, CH$_2$). Anal. C, 79.69; H, 4.78 (calcd for C$_{56}$H$_{40}$ O$_8$. C, 79.98; H, 4.84).

References

1. C. D. Gutsche, T. C. Kung, M. L. Hsu, Abstracts of the 11th Midwest Regional Meeting of the ACS, Carbondale

Ill. 1975, no 517.

2. (a) C. D. Gutsche, B. Dhawan, K. H. No, R. Muthukrishnan, *J. Am. Chem. Soc.*, **103**, 3782 (1981); (b) A. Ninagawa, H. Matsuda, *Makromol, Chem. Rapid Commun.*, **3**, 65 (1982); (c) Y. Nakamoto, S. Ishida, *ibid.*, **3**, 705 (1982); (d) R. Buriks, A. R. Fauke, J. H. Munch, US Patent 4,259,464 (1981).
3. C. D. Gutsche, *Acc. Chem. Res.*, **16**, 161 (1983).
4. (a) K. Fries, G. Finck, *Ber.*, **41**, 4241 (1908); (b) A. H. Blatt, *Org. React.*, **1**, 342 (1942).
5. K. H. No, Y. J. Noh, Y. H. Kim, *Bull. Korean Chem. Soc.*, **7**, 442 (1986).
6. K. H. No. Y. J. Noh, *ibid.*, **7**, 314 (1986).
7. C. D. Gutsche, L. G. Lin, *Tetrahedron*, **42**, 1633 (1986).
8. C. D. Gutsche, J. A. Levine, *J. Am. Chem. Soc.*, **104**, 2652 (1982).
9. D. S. Tarbell, P. E. Fanta, *J. Am. Chem. Soc.*, **65**, 2169 (1943).
10. C. D. Gutsche, B. Dhawan, J. A. Levine, K. H. No, L. J. Bauer, *Tetrahedron*, **39**, 409 (1983).

Gamma-Radiolysis of Carbon Dioxide (IV). Effect of the Addition of Alcohols on the Gamma-Radiolysis of Gaseous Carbon Dioxide[*]

Joon Ha Jin, Jae Ho Choi[‡], Hyung Chick Pyun[§], and Sang Up Choi[*]

Department of Chemistry, Sogang University, Seoul 121. Received November 16, 1987

The gaseous carbon dioxide has been irradiated with Co-60 gamma-radiation in the presence and absence of various alcohols, and the radiolysis products analyzed by gas chromatography. Experimental results indicate that no detectable amount of carbon monoxide is formed when pure carbon dioxide is irradiated. By adding small quantities of alcohols to carbon dioxide, however, considerable amount of carbon monoxide, ketones, alcohols and other organic products have been detected. By adding 0.1% of methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-methyl-1-propanol, 2-butanol, and 2-methyl-2-propanol, G(CO) values obtained are 4.4, 4.5, 5.2, 4.4, 5.2, 5.0, 4.7 and 4.1, respectively. These high yields of carbon monoxide suggest that the oxidation reactions of carbon monoxide may be suppressed by scavenging oxygen atom with the alcohols. The main radiolytic decomposition reactions of the alcohols present in small quantity in carbon dioxide may be supposed to be the reactions with the oxygen atom produced by the radiolysis of carbon dioxide. The decomposition reactions seems to follow pseudo-first order kinetics with respect to the alcohols. The decomposition rate measured with 2-propanol is the fastest and that with 2-methyl-2-propanol the slowest. The mechanisms of the radiolytic decomposition reactions of the alcohols present in carbon dioxide are discussed on the basis of the experimental results of the present study.

Introduction

It was reported in the literature that the G(CO) value observed in the gammaradiolysis of pure carbon dioxide was practically negligible because of the rapid reoxidation of carbon monoxide.[1,2] By the radiolysis of carbon dioxide with various additives, however, considerable amount of carbon monoxide was found to be formed. A number of workers reported the effects of various additives on the yields of carbon

monoxide. Thus, some of inorganic gases,[3,4] such as nitrogen dioxide and sulfur dioxide, some organic gases,[5,6] such as methane and propane, and some solid materials,[7,8] such as graphite and glass beads, were proved to be effective additives to suppress the possible reoxidation reactions of carbon monoxide.

In a paper of this series, we reported the results of the studies on the effect of methanol, ethanol, formaldehyde, and acetaldehyde on the gamma-radiolysis of gaseous carbon dioxide.[9] It was found that the organic compounds mentioned above were effective additives to suppress the possible back reactions, or the reoxidation of carbon monoxide. Since the systematic investigations, however, were not yet carried out regarding the organic additives, more detailed studies were desirable.

In the present study, a series of alcohols such as