

## Synthesis of Novel Acyclonucleosides; Reactions of Diazinone Heterocycles with 4-Bromoacetoacetic acid and Methyl 4-bromoacetoacetate

Sam-Yong Choi, Sung Chul Shin, and Young-Jin Yoon\*

Department of Chemistry, Gyeongsang National University, Chinju 660-701. Received December 26, 1990

Some substituted pyridazin-6-ones(1-4) and two uracils(10, 12) have been converted to the corresponding  $N_1$ -(2-oxopropyl)pyridazin-6-ones(6-9), 1,3-bis(2-oxopropyl)-5-fluorouracil(11) and 2-(2-oxopropylthio)uracil(13) respectively by reaction with 4-bromoacetoacetic acid. Also, 4,5-dichloro-1-(3-carbomethoxy-2-oxopropyl)pyridazin-6-one(15) and 4,5-dichloro-3-nitro-1-(3-carbomethoxy-2-oxopropyl)pyridazin-6-one(16) was synthesized from the corresponding pyridazin-6-ones(1,2) and methyl 4-bromoacetoacetate.

### Introduction

Recently, significant progress has been made in the development of antiviral chemotherapy due to the discovery of nucleoside analogues with potential activities such as acyclovir<sup>1</sup>, DHPG<sup>2</sup> and ribavirin<sup>3</sup>, etc.

Acyclovir has played an important role as a lead compound of acyclonucleoside chemistry since its inception. Thus, major efforts have been directed by the nucleoside researchers toward the synthesis of acyclonucleosides with various side chains and aglycons. In addition, the skeletal modification of the heterocyclic portion of the acyclonucleosides have provided numerous azine nucleosides possessing a wide variety of biological actions.<sup>4</sup>

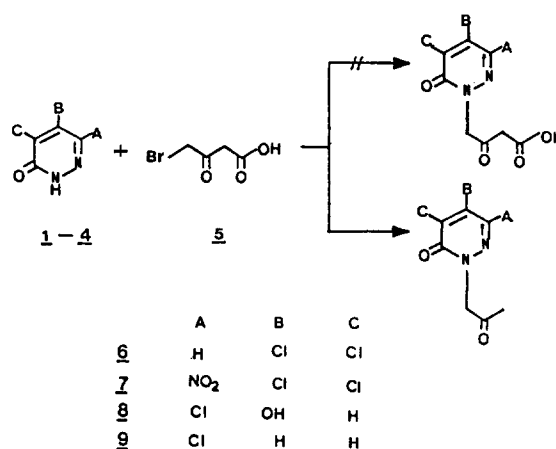
In connection with our research program, we attempted synthesis of some acyclonucleosides with a new alkyl chain. In this paper, we wish to report the reactions of diazinone such as uracils and pyridazin-6-ones with 4-bromoacetoacetic acid and methyl 4-bromoacetoacetate.

### Results and Discussion

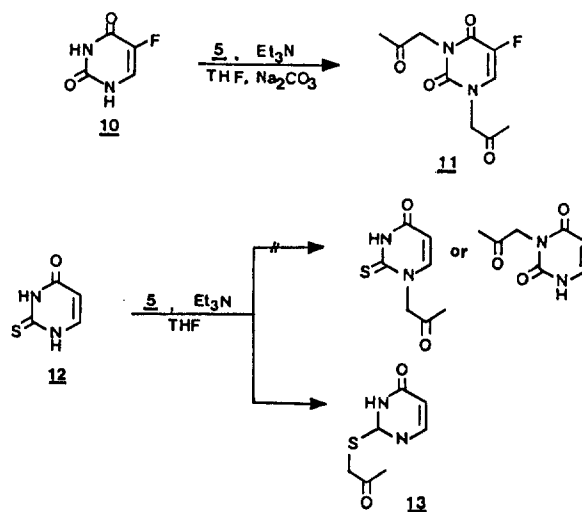
Reaction of pyridazin-6-ones(1-4) with 4-bromoacetoacetic acid in the presence of a base such as potassium carbonate or triethylamine gave the corresponding  $N_1$ -(2-oxopropyl)pyridazin-6-ones(6-9) in 61-91% yield. This 2-oxopropylation, under these condition, was progressed by the decarboxylation of acetoacetic acid. Infrared spectra of compound 6-9 showed in common only two carbonyl absorption peaks at 1684-1685  $\text{cm}^{-1}$ . Proton magnetic resonance spectra of these compounds were observed two proton signals ( $-\text{CH}_2-$  and  $\text{CH}_3$ ), but the proton signal of enolic OH was not detected. Also, the signals of  $\text{C}_1'$ (60.5-72.7),  $\text{C}_2'$ (200.8-204.1) and  $\text{C}_3'$ (26.2-31.4) of these compounds (6-9) was founded on  $^{13}\text{C}$ -nuclear magnetic resonance spectra.

On the other hand, treatment of 5-fluorouracil with 4-bromoacetoacetic acid(5) in the presence of sodium carbonate and triethylamine afforded compound 11 in 24% yield instead of 1-(2-oxopropyl)-5-fluorouracil. Hoshiko, *et al.*<sup>5</sup> synthesized compound 11 by means of phase transfer catalysis. This product was spectroscopically the same as an authentic sample.

We also attempted the synthesis of compound 13 by a similar method. Reaction of compound 12 with 5 in the presence of potassium carbonate gave 2-(2-oxopropylthio)uracil(13) in 43% yield. It was easy to distinguish between N-acetyl compound and S-acetyl compound by the comparison of proton magnetic resonance spectra of compound 11 and 13. A singlet for two protons of  $\text{C}_1'$  of S-acetyl compound (13) appeared at 2.0 ppm, whereas the peak for two protons of  $\text{C}_1'$  of N,N'-diacetyl compound (11) appeared at 4.6 to 4.7 ppm. A band at about 3092  $\text{cm}^{-1}$  in the infrared spectrum for compound 13 is indicative of the uracil N-H bond. Two carbonyl absorption peaks were also found

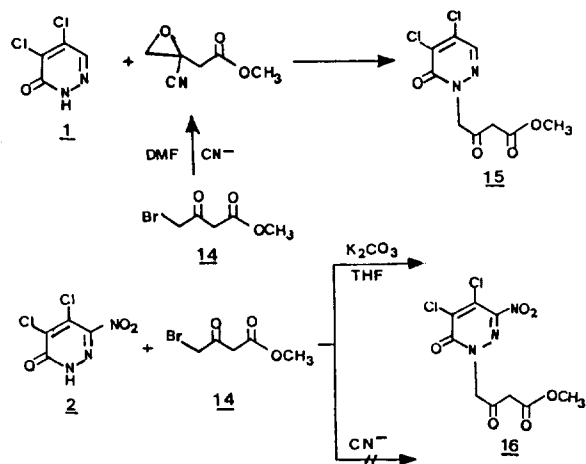


Scheme 1



Scheme 2

uracil(13) in 43% yield. It was easy to distinguish between N-acetyl compound and S-acetyl compound by the comparison of proton magnetic resonance spectra of compound 11 and 13. A singlet for two protons of  $\text{C}_1'$  of S-acetyl compound (13) appeared at 2.0 ppm, whereas the peak for two protons of  $\text{C}_1'$  of N,N'-diacetyl compound (11) appeared at 4.6 to 4.7 ppm. A band at about 3092  $\text{cm}^{-1}$  in the infrared spectrum for compound 13 is indicative of the uracil N-H bond. Two carbonyl absorption peaks were also found



Scheme 3

at 1710 (keto carbonyl) and 1688  $\text{cm}^{-1}$  (amide carbonyl). But the peak of thiocarbonyl function in the infrared spectrum for **13** was not detected.

Reaction of compound **1** with methyl 4-bromoacetoacetate (**14**) in the presence of KCN in DMF gave compound **15** in low yield. But we did not obtain the compound **15** using potassium carbonate or triethylamine instead of KCN. Kato, *et al.*<sup>6</sup> reported the formation of ethyl 3-cyano-3,4-epoxybutanoate as the intermediate from ethyl 4-haloacetoacetate and KCN. Formation of **15** might occur by the way of methyl 3-cyano-3,4-epoxybutanoate that is generated by the reaction of methyl 4-bromoacetoacetate with KCN.

Also, we tried the synthesis of compound **16** from **2** and **14** under similar condition. The treatment of **7** with **14** in the presence of KCN did not give the compound **16**, whereas the reaction of **2** with **14** in the presence of potassium carbonate in THF afforded the corresponding product (**16**) in 27% yield. The structures of the compound **15** and **16** were consistent with data of **15** and **16** obtained from infrared, proton magnetic resonance spectra and elemental analysis.

Further synthetic explorations related to the diazinone acyclonucleoside are in progress, and will be that subject of future reports.

## Experimental Section

Melting points were determined with a Fisher-Johns apparatus and are uncorrected. Proton nuclear magnetic resonance spectra were obtained on a Bruker AW-80 MHz spectrometer with chemical shift values reported in  $\delta$  units (parts per million) relative to an internal standard (tetramethylsilane).  $^{13}\text{C}$ -NMR spectra were obtained from KAIST. Infrared spectral data were obtained on a Hitachi 270-50 spectrophotometer. Elemental analysis were performed with a LECO Micro Carbon Hydrogen Determinator (CHN-800). Open-bed column chromatography was carried out silica gel 60(70-230 mesh, Merck) using gravity flow. The column were packed as slurries with the elution solvent.

**4-Bromoacetoacetic acid 5.** To a solution of diketene (500 mmoles, 42.0g) in 250 ml carbon tetrachloride, a mixture of bromine (5500 mmoles, 26.7 ml) and carbon tetrachloride (100 ml) was slowly added for 1 hour at  $-20^\circ\text{C}$  under nitrogen atmosphere. The reaction mixture was stirred for 5 min under same condition and then cooled to

$-30^\circ\text{C}$ . After 10 ml water was added to the reaction mixture, the resulting mixture was stirred for additional 2 hours at the same temperature. The resulting precipitate was filtered, washed with cold carbon tetrachloride ( $0^\circ\text{C}$ , 25 ml  $\times$  2) and dried in vacuum desiccator to give compound **5** as a white powder in 90% (81.0g) yield; mp  $68-69^\circ\text{C}$  (Lit.<sup>7</sup>  $69-69.5^\circ\text{C}$ ). IR(KBr) 3500-2500, 1772, 1704, 1350  $\text{cm}^{-1}$ .  $^1\text{H}$ -NMR( $\text{CDCl}_3$ )  $\delta$  3.65(m,  $\text{COCH}_2\text{CO}$ ), 3.94(s,  $\text{Br-CH}_2$ -), 5.28(s,  $=\text{CH-}$ ), 9.88(bs, 1H,  $\text{D}_2\text{O}$  exch.), 11.60(bs, enolic OH,  $\text{D}_2\text{O}$  exch.). Anal. Calcd. for  $\text{C}_4\text{H}_6\text{O}_3\text{Br}$ ; C, 26.54; H, 2.78; Found; C, 26.58; H, 2.41.

**Methyl 4-bromoacetoacetate 14.** To a solution of diketene (250 mmoles, 21.0g) in 120 ml dichloromethane, a mixture of bromine (250 mmoles, 40.0g) and dichloromethane (50 ml) was slowly added for 1 hour at  $-20^\circ\text{C}$  under nitrogen atmosphere. The reaction mixture was stirred for 5 min under same condition. Methanol (270 mmoles, 6.9 ml) was added to above solution. The reaction mixture was then stirred for additional 2 hours at room temperature. The fractions boiling at  $106-107^\circ\text{C}$  under reduced pressure (60 mmHg) were collected to give compound **14** as a colorless liquid in 85% (42.0g) yield. bp  $106-107^\circ\text{C}$  (60 mmHg). IR(neat) 3410, 3050, 2970, 1760, 1336  $\text{cm}^{-1}$ .  $^1\text{H}$ -NMR( $\text{CDCl}_3$ )  $\delta$  3.60(s,  $\text{OCH}_3$ ), 3.82(m,  $\text{COCH}_2\text{CO}$ ), 5.20(s,  $\text{C}=\text{CH}$ ), 11.80(bs, enolic OH,  $\text{D}_2\text{O}$  exch.). Anal. Calcd. for  $\text{C}_5\text{H}_7\text{O}_3\text{Br}$ ; C, 30.79; H, 3.62. Found: C, 30.51; H, 3.58.

**4,5-Dichloro-1-(2-oxopropyl)pyridazin-6-one 6.** A mixture of compound **1**<sup>8</sup> (58 mmoles, 9.6g), **5** (77 mmoles, 13.0g) and tetrahydrofuran (50 ml) was stirred for 5 min at room temperature. To a solution triethylamine (100 mmoles, 8.0 ml) was added, and the mixture was then stirred for 2 hours at room temperature. Concentrated hydrochloric acid (36%, 5 ml) was added to the reaction mixture with stirring. The solvent was evaporated under reduced pressure. The resulting residue was then washed with distilled water (100 ml  $\times$  5) and dried over anhydrous magnesium sulfate. After the solvent was evaporated, the residue was applied to the top of open-bed column (20  $\times$  3 cm). The column was eluted with chloroform. 8 ml fraction was collected. The fractions containing the product were combined and evaporated under reduced pressure. The resulting product was recrystallized from carbon tetrachloride-chloroform (4:1 v/v) to give pure compound **6** as a white needle in 91% (11.8g) yield. mp  $136-137^\circ\text{C}$ . IR(KBr) 3000, 2944, 1730, 1674  $\text{cm}^{-1}$ .  $^1\text{H}$ -NMR( $\text{CDCl}_3$ )  $\delta$  2.18(s, 3H), 4.90(s, 2H), 7.88(s, 1H),  $^{13}\text{C}$ -NMR (DMSO- $d_6$ )  $\delta$  31.480 ( $\text{C}_3$ ), 65.814 ( $\text{C}_1$ ), 137.147 ( $\text{C}_4$ ), 140.492 ( $\text{C}_5$ ), 140.822 ( $\text{C}_3$ ), 160.045 ( $\text{C}_6$ ), 205.197 ( $\text{C}_2$ ), 205.197 ( $\text{C}_2$ ). Anal. Calcd. for  $\text{C}_7\text{H}_6\text{N}_2\text{O}_2\text{Cl}_2$ ; C, 38.04; H, 2.74; N, 12.67. Found: C, 38.00; H, 2.62; N, 12.80.

**4,5-dichloro-3-nitro-(2-oxopropyl)pyridazin-6-one 7.** A mixture of compound **2**<sup>8</sup> (300 mmoles, 10.0g), **5** (440 mmoles, 8.0g) potassium carbonate (41 mmoles, 5.6g) and tetrahydrofuran (50 ml), was stirred for 2 hours at room temperature. To above solution, concentrated hydrochloric acid (5 ml, 36%) was added with stirring, and the solvent was then evaporated under reduced pressure. The residue was dissolved in 70 ml chloroform. The chloroform solution was washed with distilled water (100 ml  $\times$  3), dried over anhydrous magnesium sulfate and concentrated to 5 ml. The resulting solution was applied to the top of open-bed column (3  $\times$  20 cm). The column was eluted with chloroform, and 8

ml fraction was collected. The fractions containing the product were combined and evaporated under reduced pressure. The resulting powder was recrystallized from carbon tetrachloride to give compound **7** as a yellow crystal in 85% (8.4g) yield; mp 93–94 °C. IR(KBr) 2992, 2948, 1742, 1684, 1578 cm<sup>-1</sup>. <sup>1</sup>H-NMR(CDCl<sub>3</sub>) δ 2.18(s, 3H), 4.92(s, 2H). <sup>13</sup>C-NMR (DMSO-d<sub>6</sub>) δ 31.307 (C<sub>3</sub>'), 66.042(C<sub>1</sub>'), 134.135(C<sub>4</sub>'), 141.122(C<sub>5</sub>'), 148.722(C<sub>3</sub>'), 159.322(C<sub>6</sub>'). Anal. Calcd. for C<sub>7</sub>H<sub>5</sub>N<sub>3</sub>O<sub>4</sub>Cl<sub>2</sub>: C, 31.60; H, 1.89; N, 15.79. Found: C, 31.36; H, 1.71; N, 15.68.

**3-Chloro-4-hydroxy-(2-oxopropyl) pyridazin-6-one 8.** A mixture of compound **3**<sup>9</sup> (5.0 mmoles, 0.72g), 5(6.6 mmoles, 1.20g), tetrahydrofuran (10 ml) and potassium carbonate (5.0 mmoles, 0.34g) was refluxed for 3 hours. Concentrated hydrochloric acid (2 ml, 36%) was added to above solution. After the solvent was evaporated under reduced pressure, the residue was applied to the top of open-bed column (25 × 2.5 cm). The column was eluted with chloroform-methanol (7:3 v/v). 8 ml fraction was collected. The fractions containing the product were combined, and the solvent was evaporated under reduced pressure to give compound **8** as a white powder in 61% (0.61g) yield. mp 130–131 °C. IR(KBr) 3136, 2944, 1728, 1656, 1590 cm<sup>-1</sup>. <sup>1</sup>H-NMR(DMSO-d<sub>6</sub>) δ 2.21(s, 3H), 4.96(2, 2H), 6.20(d, 1H, J = 4.80 Hz), 12.87(bs, 1H, D<sub>2</sub>O exch.). <sup>13</sup>C-NMR(DMSO-d<sub>6</sub>) δ 26.201(C<sub>3</sub>'), 72.749(C<sub>1</sub>'), 155.321(C<sub>4</sub>'), 156.091(C<sub>3</sub>'), 160.045(C<sub>5</sub>'), 162.138(C<sub>6</sub>'), 201.020(C<sub>2</sub>'). Anal. Calcd. for C<sub>7</sub>H<sub>6</sub>N<sub>2</sub>O<sub>3</sub>Cl<sub>2</sub>: C, 41.71; H, 3.00; N, 13.97. Found: C, 41.30; H, 3.28; N, 13.45.

**3-Chloro-(2-oxopropyl)pyridazin-6-one 9.** A mixture of compound **4**<sup>10</sup> (5.0 mmoles, 0.67g), 5(6.7 mmoles, 1.20g) and potassium carbonate (5.0 mmoles, 0.6g) and tetrahydrofuran (20 ml) was stirred for 3.5 hours at room temperature. After concentrated hydrochloric acid (2 ml, 36%) was added, the solvent was evaporated under reduced pressure. The resulting residue was applied to the top of open-bed column (3 × 10 cm). The column was eluted with chloroform. 8 ml fraction was collected. The fraction containing the product was combined, and the solvent was then evaporated under reduced pressure. The crude product was recrystallized from carbon tetrachloride to give pure compound **9** as a white crystal in 63% (0.66g) yield. mp 100–101 °C. <sup>1</sup>H-NMR(DMSO-d<sub>6</sub>) δ 2.26(s, 3H), 5.02(s, 2H), 7.02(d, 1H, J = 9.74 Hz), 7.63(d, 1H, 9.54 Hz). <sup>13</sup>C-NMR(acetone-d<sub>6</sub>) δ 27.161(C<sub>3</sub>'), 60.531(C<sub>1</sub>'), 132.593(C<sub>5</sub>'), 134.672(C<sub>4</sub>'), 158.263(C<sub>3</sub>'), 160.000(C<sub>6</sub>'), 200.822(C<sub>2</sub>'). Anal. Calcd. for C<sub>7</sub>H<sub>7</sub>N<sub>2</sub>O<sub>2</sub>Cl: C, 45.06; H, 3.78; N, 15.01. Found: C, 45.18; H, 3.81; N, 15.05.

**1,3-Bis(2-oxopropyl)-5-fluorouracil 11.** To a mixture of compound **10** (20 mmoles, 2.61g), solid carbonate (20 mmoles, 5.0g) and triethylamine (54 mmoles, 5.4 ml) was added. After the reaction mixture was stirred for 2 hours at room temperature, concentrated hydrochloric acid (5 ml, 5.4 ml) was added. The solvent was evaporated under reduced pressure, and the residue was then dissolved in chloroform (100 ml). Chloroform solution was washed with distilled water (100 ml × 3), and dried over anhydrous magnesium sulfate. After the solvent was evaporated under reduced pressure, the resulting residue was applied to the top of open-bed column (25 × 3 cm). The column was eluted with chloroform. 8 ml fraction was combined. The solvent was

evaporated under reduced pressure, to give compound **11** as a white powder in 24% (1.2g) yield. mp 133–134 °C (lit.<sup>5</sup> 128–130 °C). IR(KBr) 3096, 2952, 1740, 1718, 1664, 1384 cm<sup>-1</sup>. <sup>1</sup>H-NMR(CDCl<sub>3</sub>) δ 2.26(s, 6H), 4.60(s, 2H), 4.76(s, 2H), 7.18(d, 1H, J = 6.0 Hz). Anal. Calcd. for C<sub>10</sub>H<sub>11</sub>N<sub>2</sub>O<sub>4</sub>F: C, 49.58; H, 4.57; N, 11.56. Found: C, 49.00; H, 4.34; N, 11.83.

**2-(2-Oxopropylthio)uracil 13.** A mixture of **12**<sup>11</sup> (5.0 mmoles, 0.64g), 5(6.6 mmoles, 1.2g), potassium carbonate (10.0 mmoles, 1.2g) and tetrahydrofuran (10 ml) was stirred for 13 hours at 35 °C. After concentrated hydrochloric acid (2 ml, 36%) was added with stirring, the solvent was evaporated under reduced pressure. The resulting residue was applied to the top of open-bed column (20 × 3 cm), and the column was eluted with chloroform-methanol (9:1, v/v.) 8 ml fraction was collected. The fraction containing the product was combined and the solvent was then evaporated under reduced pressure to give compound **13** as a yellow powder in 43% (0.42g) yield. mp 148–149 °C. IR(KBr) 3092, 2932, 1710, 1668, 1564 cm<sup>-1</sup>. <sup>1</sup>H-NMR(DMSO-d<sub>6</sub>) δ 1.76(s, 3H), 2.00(s, 2H), 6.11 (d, 1H, J = 2.83 Hz), 7.82(d, 1H, J = 2.84 Hz). <sup>13</sup>C-NMR(DMSO-d<sub>6</sub>) δ 2.627(C<sub>1</sub>'), 29.927(C<sub>3</sub>'), 112.572(C<sub>5</sub>'), 112.968(C<sub>4</sub>'), 141.613(C<sub>2</sub>'), 157.986(C<sub>6</sub>'), 164.932(C<sub>2</sub>'). Anal. Calcd. for C<sub>8</sub>H<sub>8</sub>N<sub>4</sub>O<sub>2</sub>S: C, 42.10; H, 3.53; N, 12.27. Found: C, 41.48; H, 3.89; N, 12.81.

**4,5-Dichloro-1-(3-carbomethoxy-2-oxopropyl)pyridazin-6-one 15.** A mixture of compound **1**<sup>8</sup> (5.0 mmoles, 0.83g), **14** (5.5 mmoles, 0.6 ml), potassium cyanide (5.5 mmoles, 0.35g) and dimethylsulfoxide (5 ml) was stirred for 3 hours at 50 °C. After the reaction mixture was cooled to room temperature, water (50 ml) was added. The reaction mixture was stirred for additional 1 hour at room temperature. The resulting precipitate was filtered and recrystallized from carbon tetrachloride to give compound **15** as a white powder in 18% (0.47g) yield. mp 112–113 °C. IR(KBr) 3110, 2948, 1740, 1728, 1670 cm<sup>-1</sup>. <sup>1</sup>H-NMR(DMSO-d<sub>6</sub>) δ 3.16(s, 3H), 3.82(s, 2H), 5.16(s, 2H), 8.18(s, 1H). Anal. Calcd. for C<sub>9</sub>H<sub>8</sub>N<sub>2</sub>O<sub>4</sub>Cl<sub>2</sub>: C, 38.73; H, 2.89; N, 10.03. Found: C, 38.59; H, 2.51; N, 10.07.

**4,5-Dichloro-3-nitro-1-(3-carbomethoxy-2-oxopropyl)pyridazin-6-one 16.** A mixture of compound **2**<sup>8</sup> (29 mmoles, 6.0g), **14** (33.84 mmoles, 6.6g), potassium carbonate (13 mmoles, 1.8g) and tetrahydrofuran (50 ml) was refluxed for 6 hours. After the solvent was evaporated under reduced pressure, the residue was applied to the top of open-bed silica gel column (30 × 2.5 cm). The column was eluted with chloroform. 8 ml fractions was combined, and the solvent was evaporated under reduced pressure to give compound **16** as a yellow crystal in 27% (2.5g) yield. mp 89–90 °C. IR(KBr) 3000, 2944, 1754, 1730, 1674, 1440 cm<sup>-1</sup>. <sup>1</sup>H-NMR(CDCl<sub>3</sub>) δ 3.53(s, 2H), 3.62(s, 3H), 5.20(s, 2H). Anal. Calcd. for C<sub>9</sub>H<sub>7</sub>N<sub>6</sub>O<sub>3</sub>Cl<sub>2</sub>: C, 32.62; H, 1.91; N, 12.97. Found: C, 32.62; H, 1.91; N, 12.70.

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## References

1. H. I. Schaffer, L. Bauchamp, D. de Miranda, G. Elion, D.J. Bauer, and P. Collins, *Nature(London)*, **272**, 583

- (1978).
- (a) J. C. Martin, C. A. Dvorak, D. F. Smee, T. R. Matthews, and J. P. H. Verheyden, *J. Med. Chem.*, **26**, 759 (1983). (b) K. K. Ogilvie, U. O. Cheriyan, B. K. Raadatus, K. O. Smith, K. S. Galloway, and W. L. Kennel, *Can. J. Chem.*, **60**, 3005 (1982); (c) A. K. Field, M. E. Davies, C. Dewitt, H. C. Perry, R. Liou, J. I. Germer-shausen, J. D. Karkas, W. T. Ashton, D. B. R. Johnson, and R. L. Tolman, *Proc. Nat. Acad. Sci. (USA)*, **80**, 4139 (1983).
  - "Rivavirin: A broad Spectrum Antiviral Agent", R. A. Smith and W. Kirkpatrick, eds, Academic press, New York, 1980.
  - A. Bloch, *Ann. N. Y., Acad. Sci.*, **255**, 576 (1975).
  - T. Hoshiko, *et al.*, *Heterocycles*, **20**(12), 2429 (1983).
  - Tetsuzo Kato, Masayuki Sato, and Hitoshi Kimura, *J. Chem. Soc. Perkin trans I*, 529 (1979).
  - a. K. J. Boosen, *U.S. Pat.*, 3,950,412 (1976); (b) A. B. Boose, *U.S. Pat.*, 2,209,683 (1936).
  - C. S. Hudson, *J. A. Chem. Soc.*, **31**, 166 (1909).
  - This compound was supplied by Dr. L. B. Townsend, Department of Medicinal Chemistry, The Univ. of Michigan, Ann Arbor.
  - T. Kuraishi, *Pharm. Bull. (Tokyo)*, **4**, 497 (1956).
  - L. Wheeler, *Am. Chem. J.*, **40**, 550 (1908).

## Isotherm for Ni-O<sub>2</sub> Adsorption System

Kyoung-Hee Ham and Woon-Sun Ahn\*

Department of Chemistry, Sung Kyun Kwan University, Suwon 440-746. Received January 18, 1990

The activation energy of dissociative adsorption of oxygen on polycrystalline nickel surface is calculated from adsorption isotherms obtained using X-ray photoelectron spectroscopy. Negative value of this activation energy (-5.9 kJ/mol) indicates that the adsorption takes place through an undissociated precursor state. An adsorption energy for this precursor state is calculated assuming the precursor state as a molecularly physisorbed state ( $E_{ad} = -7.9$  kJ/mol). Finally, an adsorption isotherm equation is derived as a function of the gas exposure, which agrees with the experimental isotherms reasonably good.

### Introduction

The adsorption of oxygen on Ni surface has been extensively studied in connection with oxidation of the metal, heterogeneous catalysis, and adsorption mechanism. According to the results reported so far<sup>1-11</sup>, oxygen is adsorbed dissociatively on Ni surface at the initial stage and forms NiO with the increase of the adsorption amount. There have been recent reports that oxygen is dissociatively adsorbed through a molecularly adsorbed precursor state when oxygen is adsorbed on the surface<sup>12-14</sup>. It is believed that the precursor state species is not experimentally detected at room temperature because of its short life time. It has been, however, confirmed experimentally that oxygen is molecularly adsorbed at low temperature<sup>15,16</sup>.

In studying the interaction of the gas with the metal surface, it is meaningless to give the adsorbed amount of gas as a function of the gas pressure since the rate of desorption is negligibly shown in this adsorption system. At the initial stage of adsorption of oxygen on the Ni surface, the sticking coefficient is known to approach one<sup>17</sup>. Therefore it is much more useful to show the adsorbed amount as a function of the gas exposure. The adsorption of oxygen on metal surface is accompanied by complex reactions such as the diffusion of oxygen into the bulk, therefore it is not easy to interpret theoretically the adsorption isotherm. Benziger *et al.*<sup>18</sup> derived an adsorption isotherm thermodynamically for diatomic molecules such as CO, NO and N<sub>2</sub> on transition metal surfaces. But this was not the adsorption isotherm which showed adsorbed amount as a function of oxygen exposure but an adsorption isobar which showed changes of adsorption

coverage as a function of temperature. The adsorption isobar predicted merely which was dominant adsorption between molecular adsorption and dissociative adsorption in terms of the magnitude of adsorption energy.

In this work, the activation energy of dissociative adsorption is calculated from the adsorption isotherms obtained using X-ray photoelectron spectroscopy and an adsorption isotherm of gaseous oxygen molecule as a function of oxygen exposure is derived theoretically. The adsorption energy of the precursor state, a parameter needed in the derivation, is calculated from pair-wise interaction energy on the assumption that the precursor state is a molecularly physisorbed state.

### Theory

**A. Apparent Activation Energy.** The apparent activation energy of the dissociative adsorption of oxygen on Ni surface is calculated from an empirical adsorption isotherms obtained by Ahn, one of the author, *et al.*<sup>19</sup> (Figure 1). Ahn *et al.* calculated previously the apparent activation energy assuming that the saturation coverage is in  $c(2 \times 2)$  structure. However in this work the apparent activation energy is calculated without assuming any saturation coverage structure. The adsorption rate is obtained as a function of exposure from the slope of the adsorption isotherm, and then Arrhenius plots ( $\ln\langle\text{rate}\rangle$  vs.  $1/T$ ) at various oxygen exposures are made as shown in Figure 2. Finally the activation energy for an oxygen exposure is calculated from slopes of these Arrhenius plots, which is negative values.

The calculated activation energies plotted as a function of