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10. ^{1}H NMR (80 MHz, $CDCl_3$)δ1.60 (m, 9H), 2.08(m, 8H), 4.90-5.40(m, 6H), 5.95(*q*.*J*=8Hz, 1H).
11. The biological activity test of the synthetic alarm pheromone for aphids Lipaphis erysimi K. and Myzus persicae S. has been conducted by Department of Entomology, Institute of Agricultural Science, O.R.D., Suwon 170, Korea with good results. The results will be reported later.

Kinetic Studies on Dimerization of Pentachlorooxomolybdate(V) in Hydrochloric Acid

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It is known that basic structures of molybdenum(V) such as $Mo_2O_2(OH)_{2(aq)}^{4+}$, $Mo_2O_{3(aq)}^{4+}$, and $Mo_2O_{4(aq)}^{2+}$, in solution are obtained as hydrogen ion concentration of pentachlorooxomolybdate(V) solution decreases. However, the nature of the dimers in solution is not secure and may be $Mo_2O_2(OH)_2(OH)_2Cl_8^{4-}$.[1,2] Paramagnetic dimer, $Mo_2O_2(OH)_{2(aq)}^{4+}$, is predominate species in the region of [HCl] = 4-6M, and diamagnetic $Mo_2O_{3(aq)}^{4+}$ and $Mo_2O_{4(aq)}^{2+}$ are predominate species at lower acidity (<4M HCl)·[2] Monomeric $MoOCl_5^{2-}$ in concentrated hydrochloric acid changes to brown species and its magnetic moments decrease by addition of water.[3] This fact indicates that two $MoO_{(aq)}^{3+}$ ions dimerize to diamagnetic $Mo_2O_{3(aq)}^{4+}$ or $Mo_2O_{4(aq)}^{2+}$ by way of paramagnetic $Mo_2O_2(OH)_{2(aq)}^{4+}$ at low acidity. We describe here the results of our investigation of the dimerization (1) of $MoOCl_5^{2-}$ when concentration of hydrochloric acid is lowered to 5-6M.

$$MoOCl_5^{2-}+H_2O \rightleftharpoons Mo_2O_2(OH)_2Cl_8^{4-}+2H^++2Cl^- \qquad (1)$$

The dihydroxo-bridged oxomolybdenum(V) produced[4,5] when concentration of hydrochloric acid is lowered to 2M undergoes further condensation with a water molecule,[6] yielding a single oxygen-bridged oxomolybdenum(V) dimer. With solutions of pH 2-5 and low [Cl$^-$], $Mo_2O_{4(aq)}^{2+}$ is the predominate species and in more basic media further poymerization occurs, resuting in a gelatinous hydroxide.[1]

Excess chloride, in the form of lithium chloride, was added to this solution to convert $Mo_2O_2(OH)_2Cl_8^{4-}$ to $MoOCl_5^{2-}$. It is obtained that electronic spectrum of oxomolybdenum(V) in solution containing 4M LiCl and 6M HCl is identical to that obtained in 12M HCl. This result indicates that a predominant oxomolybdenum(V) species in 10 M HCl or Cl$^-$ is $MoOCl_5^{2-}$ and $Mo_2O_2(OH)_2Cl_8^{4-}$ is highly stable in 5-6 M hydrochloric acid. We attempted to isolate a paramagnetic oxomolybdenum (V) dimer in 5M HCl, but could not obtain a crystal from solutions because of its remarkable solubility.

Second-order rate constants for dimerization of $MoOCl_5^{2-}$ in 5-6M HCl were observed with the equation: $-[MoOCl_5^{2-}]/dt = k_2[MoOCl_5^{2-}]^2$. Graph of $(A_0-A_t)/(A_t-A_\infty)$ vs. time[7] was linear for at least three half-lives as shown in Figure 1. From this slope (slope = k_2 $[MoOCl_5^{2-}]_0$, R = 0.998) we can obtain a second-order rate constant (k_2). Figure 2 shows that the second-order rate constants depend on concentrations of hydrochloric acid and chloride ion according to rate equation (1).

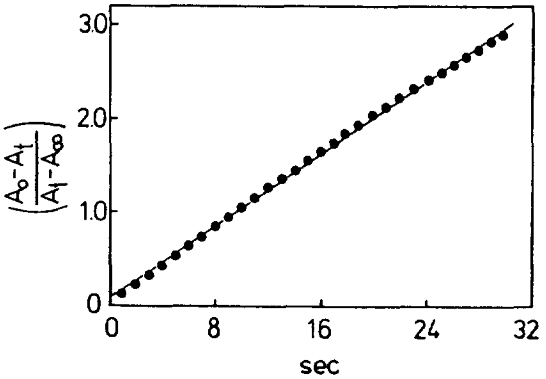

Figure 1. Plot of $(A_0-A_t)/(A_t-A_\infty)$ vs. time for dimerization of $[MoOCl_5^{2-}]$ at 5°C. $[MoOCl_5^{2-}]$ = 3.10 × 10^{-3}M, [HCl] = 3.0M, [LiCl] = 3.0M.

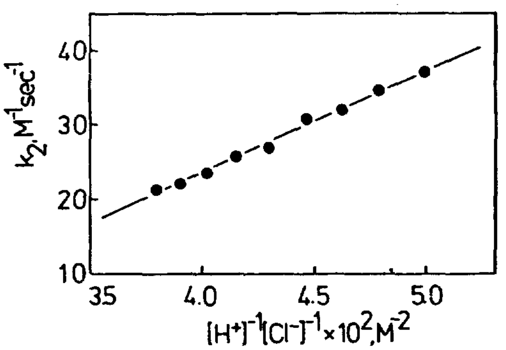

Figure 2. [HCl] and [Cl⁻] dependence of second-order rate constants for dimerization of $MoOCl_5^{2-}$ at 5°C. $[MoOCl_5^{2-}] = 3.10 \times 10^{-3}$ M, $[Cl^-] = 6.0$M.

$$-d[MoOCl_5^{2-}]/dt = k_2[MoOCl_5^{2-}]^2 = k[HCl]^{-1}[Cl^-]^{-1}[MoOCl_5^{2-}]^2 \quad (1)$$

From equation (1) $k_2 = k[HCl]^{-1}[Cl^-]^{-1}$. A straight line of Figure 2 gives k to be negative first-order.function of $[HCl]^{-1}$ and $[Cl^-]^{-1}$, respectively.

The form of the rate equation (1) is consistent with the following mechanism.

$$MoOCl_5^{2-} + H_2O \overset{K_1}{\rightleftharpoons} MoOCl_4(H_2O)^- + Cl^-$$

$$MoOCl_4(H_2O)^- + MoOCl_5^{2-} \overset{K_2}{\rightleftharpoons} \underset{(I)}{Cl_4Mo(O)-OH-Mo(O)Cl_5^{4-}} + H^+$$

$$I + H_2O \xrightarrow{k} \underset{(II)}{Cl_4Mo(O)-OH-Mo(O)Cl_4(H_2O)^{3-}} + Cl^-$$

$$II + H_2O \xrightarrow{fast} Cl_4Mo(O)-(OH)_2-Mo(O)Cl_4^{4-} + H^+$$

Rate determining step is process of the formation of the aqua complex by displacement of second water coordinated to molybdenum of I. If K_1 and K_2 were small, then rate $= k[I] = kK_1K_2[MoOCl_5^{2-}]^2[HCl]^{-1}[Cl^-]^{-1}$ and $k_2 = kK_1K_2$.

Although the final product is not isolated as crystals from solutions we are considered that predominant compound in 6M hydrochloric acid is bis-(μ-hydroxooxomolybdenum(V)), $Mo(O)-(OH)_2-Mo(O)$ known as paramagnetic dimer. There is ample evidence for di-μ-hydroxo dimeric $M-(OH)_2-M$ with certain transition metals.[8]

Mechanisms of these reactions deserve further attention and should be the subject of future investigations.

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A Synthesis of 1,2-O-Isopropylidene-(S)-Glyceraldehyde

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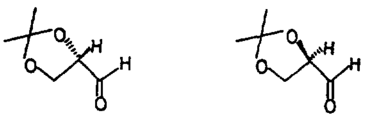
1,2-0-Isopropylidene-(S)-glyceraldehyde(**1**) and 1,2-0-isopropylidene-(R)-glyceraldehyde(**2**) (Figure 1) have been extensively used as chiral starting materials for the synthesis of optically active natural products.[1] The (R)-enantiomer, 1,2-O-isopropylidene-(R)-glyceraldehyde(**2**) is readily available from inexpensive natural D-mannitol.[2] However, the (S)-enantiomer(**1**) was prepared from unnatural L-mannitol or L-arabinose in several steps.[3] Recently, the synthesis of (S)-enantiomer (**1**) from L-galactono-1,4-lactone[4] and L-tartaric acid[5] has been reported. Now we wish to report an asymmetric synthesis of (S)-enantiomer(**1**) from readily available allylic alcohol (Scheme 1).

Sharpless' (+)-tartrate-mediated asymmetric epoxidation[6] of allyl alcohol afforded (S)-epoxyalcohol(**3**),[7] which was directly used for the next step without further purification. The crude epoxide(**3**) was treated with thiophenol and NaOH (reflux, 3h) to give (S)-1-(phenylthio)-2,3-propanediol(**4**). Recrystallization from petroleum ether gave the diol(**4**)[8] as a white solid(71%). Isopropylidination of the diol(**4**) was effected with 2,2-dimethoxypropane and D-camphorsulfonic acid to give phenylthio acetonide(**5**)[8] in 95% yield, which was separated by flash chromatography using 20% ether-hexane as eluents(Rf 0.62). The phenylthio compound(**5**) was oxidized with m-chloroperoxybenzoic acid to give the sulfoxide(**6**)[8] in 89% yield, which was separated by flash chromatography



(S)-1 (R)-2

Figure 1.