

TEST OF CHEMISTRY

Department of Chemistry	化 学 専 攻
-------------------------	---------

December 6, 2007 (平成 19 年 12 月 6 日) 9 : 00 ~ 11 : 00

General Directions (注 意 事 項)

1. Answer all problems in English or in Japanese. (すべての問題に英語または日本語で解答せよ。)
2. Check the number of sheets. (以下の用紙の枚数を確認せよ。)

Problem Sheets (問題用紙)	3 枚
Answer Sheets (解答用紙)	3 枚

[I] Answer the following problems (a) and (b). (次の問 (a) と (b) に答えよ。)

(a) The spectral and magnetic properties of the complex salt Cs_3CoCl_5 are different from those of the complex salt $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, while both are the high spin complexes of cobalt(II). (錯塩 Cs_3CoCl_5 の分光的及び磁氣的性質は錯塩 $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ とは異なるが、両方とも高スピンのコバルト(II)錯体である。)

(i) Write the three-dimensional structure of each of these complexes. (これらの各錯体の立体構造を記せ。)

(ii) Draw energy-level diagrams for both complexes showing the d-electron configuration on the basis of crystal-field splittings of the d-orbitals. (両錯体について、d 軌道の結晶場分裂に基づいて d 電子配置を示すエネルギー準位図を描け。)

(b) Dichlorodiammineplatinum(II) exists in two forms. The α form is obtained by the reaction of $[\text{PtCl}_4]^{2-}$ with ammonia, and the β form results from substitution upon heating $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$. (ジクロロジアンミン白金(II)には2つの形が存在する。 α 形は $[\text{PtCl}_4]^{2-}$ とアンモニアの反応から得られ、 β 形は $[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$ を加熱した際の置換反応で生じる。)

(i) Write each of the isomeric structures of the α and β forms. (α と β 形の異性体の構造をそれぞれ記せ。)

(ii) Explain the reason why the synthesis of the different geometrical isomers is accomplished by such treatments. (そのような処理によって、なぜ異なった幾何異性体の合成が達せられるか、その理由を説明せよ。)

[II] Answer the problems (a) and (b). (次の問(a)と(b)に答えよ。)

(a) Answer the following problems. (次の問に答えよ。)

Figure 1 shows energy level diagram and photo-physical processes of molecules in the condensed phase. The straight lines indicate the radiative processes and the wavy lines indicate the non-radiative processes. (図1に、凝集相での分子のエネルギー準位と光物理過程を示す。直線は輻射過程、波線は無輻射過程を表す。)

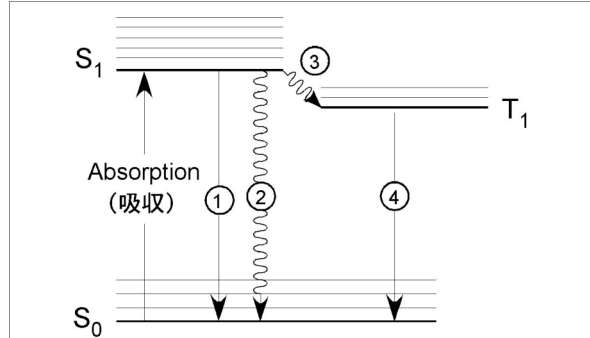


Fig.1 Energy level diagram of molecules. S_0 , S_1 and T_1 denote ground electronic, first singlet excited and first triplet states, respectively. (図1, 分子のエネルギー準位図。 S_0 , S_1 および T_1 は、それぞれ基底電子状態、一重項電子励起状態、三重項励起状態である。)

(i) Give most appropriate words for ①—④, respectively. (①~④にそれぞれ最も適当な言葉を入れよ。)

(ii) Show the rate equations for the concentrations of the S_1 and T_1 states, respectively, after the photo-excitation to the S_1 state. The rate constants of the processes ①, ②, ③ and ④ are denoted by k_1 , k_2 , k_3 and k_4 , respectively. (S_1 状態への光励起後の S_1 および T_1 状態の濃度の時間変化を微分方程式で記述せよ。ここで ①, ②, ③, および ④の過程の速度定数をそれぞれ k_1 , k_2 , k_3 , k_4 とする。)

(b) Answer the following problems. (次の問に答えよ。)

The bond strengths and lengths of molecules can be compared by calculating the bond order defined by the following equation. (分子の結合強度や距離は、次式で定義される結合次数を用いて比較することができる。)

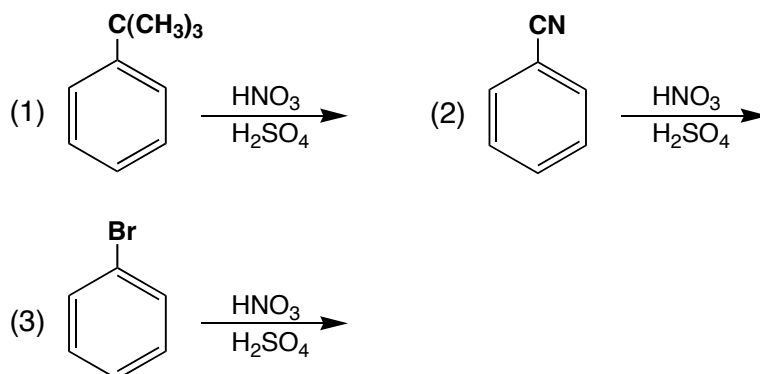
$\text{bond order} = \frac{(\text{number of occupied electrons in the bonding orbitals}) - (\text{number of occupied electrons in the anti-bonding orbitals})}{2}$
$\text{結合次数} = \frac{(\text{結合性軌道にある電子数}) - (\text{反結合性軌道にある電子数})}{2}$

(i) Show the molecular orbital energy level diagram of O_2 and the electron configuration in its ground electronic state. (O_2 の分子軌道エネルギー準位図と電子基底状態の電子配置を記述せよ。)

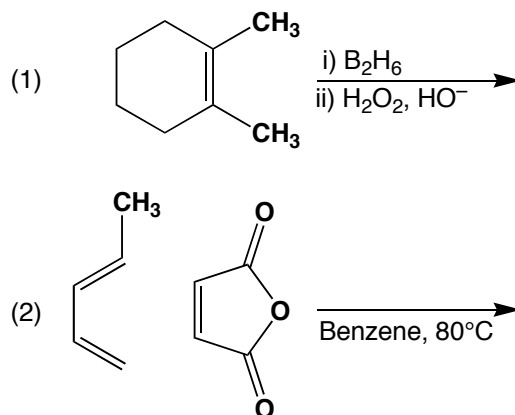
(ii) Obtain the bond orders for O_2 , O_2^+ , and O_2^- , respectively, and compare their bond lengths. (O_2 , O_2^+ , O_2^- の結合次数をそれぞれ求め、3つの分子の結合距離を比較せよ。)

[III] Answer the following problems (a) – (c). (次の問(a)～(c)に答えよ)。

- (a) Write structural formulas of the major products for the reactions (1) – (3). Explain the reason why the major products form selectively. (次の反応(1)～(3)の主生成物の構造を記せ。また、主生成物が選択的にできる理由も説明せよ。)



- (b) Write structural formulas of the principal products for the reactions (1) and (2), including all aspects of their stereochemistry. (次の反応(1)と(2)の生成物の構造を立体化学がわかるように示せ。)



- (c) Indicate which of the following two conformations **A** and **B** is more stable. Explain your reasoning. (配座 **A** と **B** どちらが安定か、理由と共に記せ。)

