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Probing intermediate process and active intermediate by positronium

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ABSTRACT

A synthesis reaction of catalyst, olefin complex of rhodium, was chosen to explore the feasibility of probing active intermediate and intermediate process by positronium:

Three different initial concentrations of Rh(III), 7.6×10^{-3} , 3.8×10^{-2} and $4.5 \times 10^{-2} \text{M}$ were sampled. The relations between positronium lifetime τ_3 , intensity I_3 and the concentration of Rh(III), ethylene, as well as of the products were determined. The k_{obs} of the reaction between positronium and Rh(III) was obtained to be $4.51 \times 10^9 \text{M}^{-1} \text{s}^{-1}$.

On the basis of the yield of product $[(\text{C}_2\text{H}_4)_2\text{RhCl}]_2$ given in reference [1], the reaction rate constant was calculated to be 0.152h^{-1} for first-order reaction and 1.776h^{-1} for second-order. Using these two constants and the measured relation between τ_3 and Rh(III) concentration, according to the equations $\ln C = \ln C_0 - k_1 t$ and $1/C = 1/C_0 + k_2 t$, the theoretical relation between τ_3 and reaction time t for first-order and second-order reaction respectively were calculated. However, both the measured values of lifetime τ_3 and intensity I_3 obviously departed from the calculated values, no matter it's first or second-order. The extra reduces of τ_3 and I_3 were discussed and attributed to the presence of an active intermediate Rh(II). In the light of the change tendency of τ_3 with t , this synthesis process approximated to a second-order reaction. It showed that a dipolymer $[(\text{C}_2\text{H}_4)(\text{CH}_2\text{-CH}_2\text{-})\text{RhCl}_2]_2$ might be formed in the first step of the synthesis.

INTRODUCTION

We have investigated the Redox reaction of unusual valence Ni(IV) and RSH by positronium [2]. In the light of the extra reduce of positronium lifetime τ_3 and intensity I_3 , we have suggested the presence of an active intermediate Ni(III) and discussed the way of investigating intermediate process and active intermediate by positronium. In order to

make further investigation, in this paper a very useful preparative reaction of catalyst, rhodium compound $[(C_2H_4)_2RhCl]_2$, was chosen to probe active intermediate and to explore intermediate process by positronium. $Rh_2(CO)_4Cl_2$ is a superior catalyst in many organic syntheses which involve reactions of olefins. The synthesis of dichlorotetracarbonyldirrhodium, $[(C_2H_4)_2RhCl]_2$, from rhodium trichloride is a basic reaction for preparing $Rh_2(CO)_2Cl_2$.

$Rh(III)$ is reduced to $Rh(I)$ by bubbling ethylene in methanolic solution at room temperature. This reaction is important, but its mechanism is not yet explained clearly. There are two possible ways reducing $Rh(III)$ to $Rh(I)$ by ethylene, either directly reducing to $Rh(I)$ by two electrons transfer or successively reducing to $Rh(II)$ and $Rh(I)$ by one electron transfer. Detecting intermediate is one of the best way to understand a multistep reaction mechanism, however, the proposed intermediates are usually extremely reactive, short-lived, and difficult to study independently. Considering the positronium has high chemical reactivity and very short quenching lifetime, it should easily perturbed by reactive intermediates. It will result in the abnormal changes of τ_3 and I_3 . The changes are related to characters of intermediate. One can generally state that all interactions of positronium with matter lead to shortening its lifetime. The extent of change will depend on strength of the interaction. The changes of I_3 mainly relate on the intermediate to be the electron-acceptor or electron-donor, the former inhibits positronium formation and leads to decrease of I_3 .

As a probe, positronium usually does not destroy and disturb the investigated systems. Measurements can be made in reaction vessel, so that sampling with its attendant errors can be eliminated. It is also possible to record the change in lifetime and intensity of positronium automatically and continuously. The relation between positronium lifetime and concentrations of reactants and of products can be separately determined. The departure of these relations during reaction can suggest the presence of active intermediate and intermediate process, which give us some information of the reaction mechanism.

EXPERIMENTS AND RESULTS

For each experiment 5ml measured solution was put into a nickel-plating stainless steel vessel. In order to keep a shorter distance between two detectors, the vessel was made in a flat shape, its width is 7mm only and wall thickness 0.3mm. The ^{22}Na source of about $7\mu Ci$ was sealed in two pieces of 5μ Kapton foil with a special glue. It was propped up with a frame and put in center of vessel. The source effect was estimated about 10%. No any activity leak was found standing the test of long time. For decreasing contact with air, the vessel was sealed in a small bag of plastic foil. The resolution of lifetime spectrometer is 410 ps, the efficiency is high.

Removing oxygen from solution by high pure nitrogen

The investigated reaction took place in the methanolic solution with 6% H_2O , so

all the contrast measurements were aimed at such component solution.

We have checked the effects of oxygen on τ_3 and I_3 in such solution. In this work the solvents, methanol and 6% H_2O were treated with bubbling high pure (>99.99%) nitrogen for one or half an hour to remove oxygen. The values of τ_3 respectively are 3.000ns and 3.286ns in methanol with 6% H_2O before and after degassing. They are consistent with the values given in reference[3,4], and also with the value extrapolated the relation between τ_3 and concentration C to zero. It shows that the influence of remained oxygen is negligible after treatment with nitrogen.

Determination of relation between τ_3 and concentration of $RhCl_3$

$RhCl_3$ is the major reactant in the investigated reaction. Its concentration, C, gradually decreases with reaction time t. For probing this reaction by positronium, we have to understand the effects of $RhCl_3$ on positronium, namely, the relation between τ_3 , I_3 and concentration of $RhCl_3$. The measured solutions with different concentration of $RhCl_3$ were prepared by dissolving rhodium trichloride trihydrate in a few water, then diluted to the necessary concentration by degassed methanol. The results showed that it seemed a linear relation between τ_3 and C as the concentration lower than $5 \times 10^{-2} M$ and between I_3 and C as the concentration lower than $3 \times 10^{-2} M$.

$$\tau_3(ns) = (3.237 \pm 0.008) - (31.89 \pm 0.44) C$$

$$I_3(\%) = (18.59 \pm 0.08) - (130.1 \pm 7.4) C$$

A satisfactory linear relation between τ_3 and C was obtained by least square fit (Fig.1).

$$\lambda_3(ns^{-1}) = (0.304 \pm 0.001) + (4.51 \pm 0.09)C$$

According to $k_{obs} = (\lambda_3 - \lambda_p)/C$, where λ_p is the reciprocal of positronium lifetime in solvent, the rate constant of reaction between positronium and $Rh(III)$ was obtained to be $4.51 \times 10^9 M^{-1}s^{-1}$.

Influences of other components in the reaction system on positronium

Besides $RhCl_3$ the other reactant in this synthesis reaction is ethylene. Because of the continuous bubbling ethylene, its concentration can be considered constant in the system. The measured value of τ_3 is 3.318, I_3 is 17.389% in methanol saturated with ethylene, thus suggesting that the ethylene is irrelevant to positronium. Besides the insoluble product $[(C_2H_4)_2RhCl]_2$, the products also include CH_3CHO and HCl . The concentration of HCl is very limited, it could not affect positronium. The τ_3 and I_3 were measured in methanolic solution of $8 \times 10^{-2} M$ CH_3CHO to be 3.291ns and close on 18.0% respectively. No effect was found too. These results indicated that the other components did not affect positronium lifetime and intensity in this system except $RhCl_3$.

Observation of relation between τ_3 and reaction time t

The positronium lifetimes τ_3 and intensities I_3 were measured along with the time t of bubbling ethylene in three solutions with different $RhCl_3$ initial concentrations $7.6 \times 10^{-3} M$, $3.8 \times 10^{-2} M$ and $4.5 \times 10^{-2} M$ respectively. For each sampling 5ml initial solution was transferred to the vessel, then stirred by continuous bubbling ethylene with an inserted syringe needle. The lifetime spectrum was measured every one hour, and accumulated to 7×10^5 counts for each measurement. The experimental results are show in Fig2 - Fig4.

DISCUSSION

On the basis of $[(C_2H_4)_2RhCl]_2$ yield given in reference[1], bubbling ethylene for 7 hours produced 65.4% $[(C_2H_4)_2RhCl]_2$, we respectively estimated the rate constant to be $0.152h^{-1}$ and $1.776h^{-1}M^{-1}$ for first-order and second-order reaction. Using these two rate constants and the equation of concentration C and reaction time t for first-order and second-order reaction

$$\ln C = \ln C_0 - k_1 t \quad (\text{first-order reaction})$$

$$1/C = 1/C_0 + k_2 t \quad (\text{second-order reaction})$$

we calculated the theoretical values of $Rh(III)$ concentration as a function of reaction time t . Fig2a,3a showed respectively the relations between C and t in two solutions with initial $Rh(III)$ concentration $4.5 \times 10^{-2}M$ and $3.8 \times 10^{-2}M$. According to equations $\tau_3 = 3.237 - 31.89 C$ and $I_3 = 18.59 - 130.1C$, these relations can be alternated to τ_3 against t (Fig2b,3b) and I_3 against t (Fig4).

Fig.2-4 show that as the reaction going on, the measured relations between τ_3 and t , C and t , as well as I_3 and t departed dramatically from the theoretic relations. Both the τ_3 and I_3 were obviously lower than expected, whereas it looked as if the concentrations of $Rh(III)$ to be higher than the proper. The similar result was obtained in the solution of $7.6 \times 10^{-3}M$.

The departure gradually decreased in the later stage of reaction, and τ_3 approached to the values of the second-order reaction. It suggested that some active intermediates are present in the reaction process. They led to positronium lifetime shortening and the formation to be inhibited. The proposed intermediate should be a complex of two-valent rhodium, in other words the synthesis from $RhCl_3$ to $[(C_2H_4)_2RhCl]_2$ included two steps of one-electron transfer:

In view of the tendency of τ_3 variation, the reaction seemed to be second-order. Judging from the electron structure of $Rh(II)$, the $Rh(II)$ complex with five coordinations using the dsp^3 mixed orbit may be more reasonable. In the first step of reaction two molecules of $Rh(III)$ joined and were reduced to form a bridge dipolymer $[(C_2H_4)(CH_2-CH_2-)RhCl_2]_2$.

Such unstable intermediate should be a strong oxidizing agent for positronium and resulted in a further shortening of τ_3 and in the departure of relation between τ_3 and t .

As the second-order reaction requires the collision of two $Rh(III)$ molecules, the reaction probability is low. To a certain extent it reflected this synthesis reaction taking such a long time. The fact that the measured values of τ_3 and I_3 during reaction were much shorter and lower than the calculated values also showed the rate constant k_2 to be not very high. $Rh(II)$ is an unstable state and more reactive, but reducing to $Rh(I)$ to form $[(C_2H_4)_2RhCl]_2$ is not very fast. So that the intermediate $Rh(II)$ could be accumulated a considerable amount to cause the extra drop of τ_3 and I_3 . According to the maximum departure of τ_3 from the theoretical relation between τ_3 and t in the system with initial $RhCl_3$ concentration $3.8 \times 10^{-2}M$, we made a rough estimate of k_2 using the equation of

second-order reaction.

Consider the concentration of ethylene, $[C_2H_4]$ to be constant in our experiment

$$d[Rh(II)]/dt = k_1 [Rh(III)]^2 - k_2 [Rh(II)]$$

$$[Rh(II)]_{\max} = (k_1 / k_2) [Rh(III)]^2$$

$$\text{with } \Delta\lambda_{\max} = k_{\text{obs}} [Rh(II)]_{\max}$$

$$[Rh(II)]_{\max} = \Delta\lambda_{\max} / k_{\text{obs}}$$

$$k_2 = k_1 k_{\text{obs}} [Rh(III)]^2 / \Delta\lambda_{\max}$$

k_1 took $1.776h^{-1}M^{-1}$, suppose the rate constant of Rh(II) and positronium, k_{obs} , reaching $10^{11}M^{-1}s^{-1}$. The measured $\Delta\lambda_{\max}$ took the value of $3.4 \times 10^7 s^{-1}$ at t to be 11th hour. The concentration of Rh(III) should be 2.18×10^{-2} at this time. Thus, k_2 was obtained to be $2.5h^{-1}$.

The value of I_3 raised with reaction time t , but it obviously departed from the theoretic values even in the later stage of reaction. It indicated that the intermediate strongly inhibited positronium formation. Even if its concentration is very low, its effect is still observable. Using an empirical equation describing "total inhibition of positronium formation" $I_3(c)/I_3(0) = 1/(1 + KC)$ [5], in principle the inhibition constant of the intermediate Rh(II) can be suggested by taking an estimated value of Rh(II) concentration.

On the basis of the experimental results we think that probing fast intermediate processes and active intermediates in slower reaction by positronium is valid and feasible.

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Fig.1 λ_3 vs RhCl_3 Concentration

Fig.2a Concentration vs Reaction time

Fig.2b τ_3 vs Reaction time

Fig.3a Concentration vs Reaction time

Fig.3b τ_3 vs Reaction time Fig.4 I_3 vs Reaction time

Figure Caption

Fig.2a,2b and Fig.4 — The initial concentration of RhCl_3 $C_0 = 4.5 \times 10^{-2} \text{ M}$

Fig.3a,3b — The initial concentration of RhCl_3 $C_0 = 3.8 \times 10^{-2}$

A — theoretic curve (first-order reaction)

B — theoretic curve (second-order reaction)

C — experiment curve