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Isotope and temperature effects on photochemical reactions of uranyl ion in H_2O–D_2O mixtures

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Abstract

Luminescence decay of uranyl ion (UO_2^{2+}) in H_2O–D_2O mixtures was observed. Rate constants for quenching of the excited UO_2^{2+} ($*UO_2^{2+}$) were determined by varying the mole fraction χ_{H_2O} of H_2O and temperature to estimate Gibbs free energies, $\Delta G^{\ddagger}$, enthalpies, $\Delta H^{\ddagger}$, and entropies, $\Delta S^{\ddagger}$, of activation. The rate constant and the isotope effect for the quenching by water molecules increased with increasing χ_{H_2O} and temperature, respectively. The $\Delta H^{\ddagger}$ was the determining factor for variation of χ_{H_2O} and the $\Delta S^{\ddagger}$ for variation of the proton concentration. The rate constants and $\Delta G^{\ddagger}$ for the quenching by ethanol (EtOH), in which the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ compensated each other, were almost constant in the present region of χ_{H_2O}, suggesting that EtOH could be regarded as reacting with $*UO_2^{2+}$ directly; i.e., not via the solvating water. © 1998 Elsevier Science S.A.

Keywords: UO_2^{2+}; Quenching; H_2O–D_2O mixtures; Temperature; Eu^{3+}

1. Introduction

Photochemistry of uranyl ion (UO_2^{2+}), which would involve H-abstraction, electron and energy transfer, has been extensively investigated in aqueous solutions with inorganic and organic materials as quenchers or reducing agents [1–6], and various mechanisms have been proposed. The effect of water molecules in the solvation shell was applied to some proposals in which the quenching or reduction of excited UO_2^{2+} ($*UO_2^{2+}$) was supposed to take place via OH radicals originating from the H_2O [4,6]. However, the OH radical has never been observed spectrophotometrically in this system. Therefore, it is not clear whether $*UO_2^{2+}$ reacts with the quenchers directly or indirectly via its solvating water molecules.

On the other hand, H_2O is well-known to function as an effective quencher for excited trivalent metal ions in H_2O–D_2O mixtures, where a main pathway of the quenching has been shown to be the vibrational energy transfer of the metal to O–H oscillators of the solvating water but not to O–D oscillators. Thus, the fluorescence decay constants have been used to calculate the number of the metal-coordinated water molecules for some lanthanide and actinide ions such as Eu^{3+}, Tb^{3+} [7–9] and Cm^{3+} [10]. Such an experiment in H_2O–D_2O mixtures could provide more useful information about the participation of the solvating water in the photochemical reaction.

In this work, luminescence decays of $*UO_2^{2+}$ in H_2O–D_2O mixtures were observed for varying mole fractions, χ_{H_2O}, of H_2O and temperatures to study the quenching by H_2O/D_2O and ethanol (EtOH). The rate constants were determined and the Gibbs free energies, $\Delta G^{\ddagger}$; enthalpies, $\Delta H^{\ddagger}$ and entropies, $\Delta S^{\ddagger}$, of activation were calculated from the Arrhenius plots to evaluate the kinetic behavior of water around $*UO_2^{2+}$ and its participation in the reactions thermodynamically. For the purpose of comparison, the same experiments were performed for Eu^{3+}.

2. Experimental

2.1. Reagents

UO_2^{2+} stock solution was prepared from trioxouranium (JAERI-U2) and sulfuric acid and Eu^{3+} stock solution from Eu_2O_3 (Wako Pure Chem. Ind., Ltd.) and perchloric acid. A sample with a specific mole fraction of H_2O was prepared by diluting the stock solution with double-distilled water and 99.5 at. % D_2O (Aldrich Chemical Company, Inc.). The concentration of UO_2^{2+} and Eu^{3+} for sample solutions was adjusted to 1.0 mmol l^{-1}. The proton concentration for both the samples was 5.0 mmol l^{-1}

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unless otherwise specified. All chemicals in this work were of reagent grade and used without further purification.

2.2. Apparatus

The apparatus for the observation of luminescence decays has been described elsewhere. [8–10] Briefly, a XeCl excimer ($\lambda = 308$ nm)-PBBO dye pulsed laser system (Lambda Physik) was employed to obtain monochromatic light around 400 nm, the intensity, pulse-width and repetition of which were ca. 2.5 mJ per pulse, 15 ns, 10 Hz, respectively. The excitation (λ_{ex}) and emission (λ_{em}) wavelength for UO_2^{2+} solutions were 415 and 510 nm, respectively, which correspond to an absorption and emission maxima of UO_2^{2+}, while $\lambda_{ex} = 394$ nm ($^7F_0 \rightarrow {}^5L_6$) and $\lambda_{em} = 592$ nm ($^5D_0 \rightarrow {}^7F_1$) were employed for Eu^{3+} solutions. The samples were contained in 1-cm fluorimetry quartz cells which, for the solution samples, were covered with a water jacket combined with a thermostat to maintain a specific temperature ($T = 278.15$–323.15 K). Since there were no differences in observed luminescences in the presence and absence of dissolved O_2, each sample was irradiated without degassing. Several measurements were made for the same sample, leading to the experimental error of less than 3%.

3. Results and discussion

3.1. Quenching by H_2O and D_2O molecules

In order to understand the quenching of $*UO_2^{2+}$ by water molecules, the luminescence decays in H_2O–D_2O mixtures were determined while varying mole fraction χ_{H_2O} of H_2O. In Fig. 1 the observed rate constants k_{obs} in the mixtures as a function of χ_{H_2O} are shown. It was found that the k_{obs} increased linearly with increasing χ_{H_2O} as those for trivalent lanthanide ions [7–11]. However, the value remained of the same order even at $\chi_{H_2O} = 0.0$, which is different from those for the trivalent ions, suggesting that D_2O would participate in the quenching as well as H_2O and that the energy transfer for UO_2^{2+} would take place more efficiently than that for the trivalent ions. The k_{obs} could be expressed with the rate constant k_w for the quenching by water in the following equation:

$$k_{obs} = k_0 + k_w \cdot \chi_{H_2O} \tag{1}$$

,where k_0 indicates the rate constant for the luminescence (k_f) and nonradiative decay by all other pathways. The k_f for UO_2^{2+} and Eu^{3+} have been reported to be 8.8×10^2 [1] and 1.9×10^2 s^{-1} [12], respectively, both of which could be negligible in the following discussion. The isotope effect can be estimated from intercepts of the plot at $\chi_{H_2O} = 0.0$ and 1.0 and increased from 2.0 at $T = 278.15$ K to 3.2 at 323.15 K.

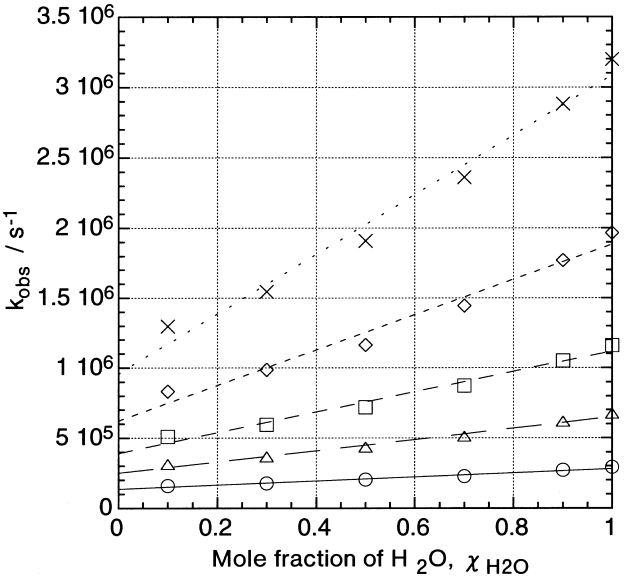

Fig. 1. The isotope effect of the quenching of excited UO_2^{2+} by water molecules in H_2O–D_2O mixtures: $T = 278.15$ K (○); 293.15 K (△); 303.15 K (□); 313.15 K (◇); 323.15 K (×).

In order to discuss this effect thermodynamically, the k_{obs} was plotted with the Arrhenius plots as shown in Fig. 2(a). The equation can be described as follows:

$$k_{obs} = A \cdot \exp(-E_a/RT) \tag{2}$$

,where A is the pre-exponential factor, E_a the activation energy and R the gas constant ($= 8.3143$ J K^{-1} mol^{-1}). In Fig. 3 the plots for $Eu^{3+}$are also shown. The k_{obs} for Eu^{3+} at the same χ_{H_2O} was nearly independent of temperature. Similar behavior for Eu^{3+} has been observed down to 77 K [11]. It indicates that for $*Eu^{3+}$, water in the solvation shell but not bulk water, especially the H_2O, could only be responsible for the quenching. On the other hand, the temperature dependence of k_{obs} for UO_2^{2+} suggests not only H_2O and D_2O in the inner solvation shell, but also bulk water responsible for the quenching. This could be explained by proposing that the vibrational energy of the O–H or O–D oscillators would propagate from the solvating water to the bulk water as previously discussed in acid solutions [3]. The Arrhenius plots can further give Gibbs free energies $\Delta G^{\ddagger}$, enthalpies $\Delta H^{\ddagger}$ and entropies $\Delta S^{\ddagger}$ of activation in the following equations:

$$E_a = RT + \Delta H^{\ddagger} \tag{3}$$

$$\begin{aligned} k &= \kappa(k_b T/h) \cdot \exp(-\Delta G^{\ddagger}/RT) \\ &= e \cdot \kappa(k_b T/h) \cdot \exp(\Delta S^{\ddagger}/R) \cdot \exp(-\Delta H^{\ddagger}/RT) \end{aligned} \tag{4}$$

,where k_b and h indicate the Boltzmann (1.3805×10^{-23} J K^{-1}) and Planck (6.626×10^{-31} J s) constants, respectively. Assuming adiabatic change for the reaction, the transmission coefficient κ could be unity. In Table 1, the thermodynamic parameters for the quenching of $*UO_2^{2+}$ (a)

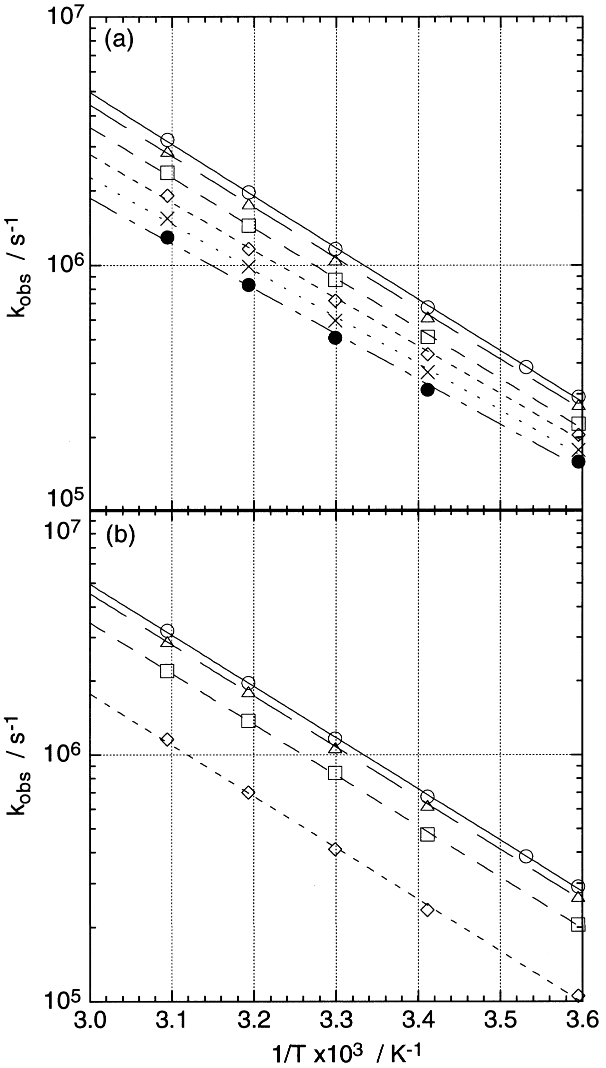

Fig. 2. The Arrhenius plots for the quenching of excited UO_2^{2+} by water molecules. (a) In H_2O–D_2O mixtures: $\chi_{H_2O}=1.0$ (○); 0.9 (△); 0.7 (□); 0.5 (◇); 0.3 (×); 0.1 (●). (b) In H_2O: $[H^+]=5$ mmol l^{-1} (○); 25 mmol l^{-1} (△); 0.1 mol l^{-1} (□); 0.5 mol l^{-1} (◇).

and *Eu^{3+} (b) are shown. The $\Delta G^{\ddagger}$, indicating the isotope effect of k_{obs}, decreased with increasing χ_{H_2O} for both the ions. The $\Delta S^{\ddagger}$ increased while the $\Delta H^{\ddagger}$ increased for UO_2^{2+} and decreased for Eu^{3+}. It should be noted that the $\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$ (or E_a) and $\Delta S^{\ddagger}$ (or log A) for UO_2^{2+} have a linear relationship with χ_{H_2O}. When the $\Delta H^{\ddagger}$ was compared with $T\Delta S^{\ddagger}$, $|\Delta H^{\ddagger}|>|T\Delta S^{\ddagger}|$ was found for UO_2^{2+} while $|\Delta H^{\ddagger}|\ll|T\Delta S^{\ddagger}|$ was found for Eu^{3+}. This indicates that, in spite of the similar reactions, the $\Delta H^{\ddagger}$ would be the determining factor for the quenching of *UO_2^{2+} and the $\Delta S^{\ddagger}$ for that of *Eu^{3+}. Consequently, these facts could be ascribed to differences between the binding abilities of H_2O and D_2O to *UO_2^{2+} and between the reaction modes of O–H and O–D oscillator for the energy transfer from *Eu^{3+}.

Protons have been reported to enhance the lifetime of *UO_2^{2+} [2,3,6]; i.e., to reduce the k_{obs} for the quenching by water. In order to clarify this effect thermodynamically, the k_{obs} at $\chi_{H_2O}=1.0$ was measured by varying the proton concentration $[H^+]$ from 5.0×10^{-3} to 0.5 mol l^{-1}. The Arrhenius plots were obtained as shown in Fig. 2(b). The plots were nearly parallel to each other in the present region of $[H^+]$, indicating that the $\Delta H^{\ddagger}$ was almost constant. On the other hand, the $\Delta S^{\ddagger}$ decreased with increasing $[H^+]$. Although $|\Delta H^{\ddagger}|>|T\Delta S^{\ddagger}|$, the $\Delta S^{\ddagger}$ was sequentially found to be the determining factor for the variation of $[H^+]$. Assuming that the quenching by water can be related to the propagation of the vibrational energy of the O–H or O–D oscillators from the solvating water to the bulk water as mentioned above, the decrease in the $\Delta S^{\ddagger}$ would be ascribed to be the inhibition of propagation by protons.

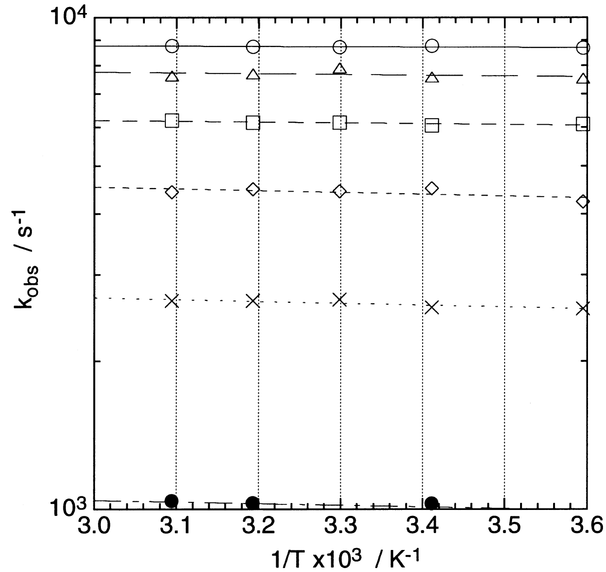

Fig. 3. The Arrhenius plots for the quenching of excited Eu^{3+} by water molecules in H_2O–D_2O mixtures: $\chi_{H_2O}=1.0$ (○); 0.9 (△); 0.7 (□); 0.5 (◇); 0.3 (×); 0.1 (●).

3.2. Quenching by EtOH

Photoreduction of UO_2^{2+} with EtOH has been extensively studied [1–5] because EtOH is well known to be a reducing agent for *UO_2^{2+}. The rate-determining step of the quenching would be followed by α-H abstraction of *UO_2^{2+} from EtOH and the thermalization into UO_2^{2+} and EtOH [2,3]. In preliminary experiments, the quenching of *Eu^{3+} by EtOH is not observed and is not considered in the following discussion. The observed rate constant k_{obs} in the presence of a quencher Q in H_2O–D_2O mixtures can be expressed as follows:

$$k_{obs}=k_o+k_w\cdot\chi_{H_2O}+k_q\cdot[Q] \tag{5}$$

,where k_q indicates the rate constant for the quenching by Q and can be obtained from the k_{obs} in the absence and

Table 1
Thermodynamic parameters for the quenching of excited UO_2^{2+} (top) and Eu^{3+} (bottom) by water

χ_{H_2O}	A (s^{-1})	E_a (kJ mol^{-1})	$\Delta H^\ddagger$	$\Delta S^\ddagger$	$\Delta G^\ddagger$
(a) UO_2^{2+} solutions					
0.1	5.82×10^{11}	35.1	32.6 ± 1.1	-28.0 ± 3.6	40.9 ± 2.1
0.3	1.02×10^{12}	36.1	33.6 ± 0.8	-23.4 ± 2.8	40.6 ± 1.7
0.5	1.76×10^{12}	37.0	34.5 ± 0.8	-18.9 ± 2.7	40.1 ± 1.6
0.7	4.43×10^{12}	38.9	36.4 ± 0.5	-11.2 ± 1.7	39.7 ± 1.0
0.9	6.32×10^{12}	39.3	36.8 ± 0.5	-8.2 ± 1.8	39.2 ± 1.1
1.0	8.81×10^{12}	39.9	37.4 ± 0.4	-5.4 ± 1.2	39.0 ± 0.7
(b) Eu^{3+} solutions					
0.1	1.30×10^{3}	622	-1.86 ± 0.34	-194 ± 1	55.9 ± 0.7
0.3	3.49×10^{3}	713	-1.77 ± 0.28	-185 ± 1	53.5 ± 0.6
0.5	5.81×10^{3}	688	-1.80 ± 0.50	-181 ± 2	52.2 ± 1.0
0.7	6.91×10^{3}	309	-2.18 ± 0.12	-180	51.4 ± 0.2
0.9	8.62×10^{3}	297	-2.19 ± 0.46	-178 ± 2	50.9 ± 0.9
1.0	9.14×10^{3}	116	-2.37 ± 0.08	-177	50.5 ± 0.2

Units of parameters: kJ mol^{-1} for $\Delta G^\ddagger$ and $\Delta H^\ddagger$; J K^{-1} mol^{-1} for $\Delta S^\ddagger$; $[UO_2^{2+}]=[Eu^{3+}]=1.0$ mmol l^{-1}; $[H^+]=5.0$ mmol l^{-1}; $\mu=$ca. 0.01; $T=298.15$ K.

presence of Q. The Arrhenius plots of k_q for the quenching by EtOH are shown in Fig. 4. The k_q was found to be plotted with the same line regardless of different χ_{H_2O}. It has also been reported that the k_q at ambient temperature is almost constant, independent of solvent, such as H_2O, D_2O [4] and acid solutions ($HClO_4$, H_2SO_4 and H_3PO_4) [2,3] and their concentration. In these respects, EtOH seems to react directly with $*UO_2^{2+}$. In order to discuss the quenching in further detail, the $\Delta G^\ddagger$, $\Delta H^\ddagger$ and $\Delta S^\ddagger$ were estimated. The $\Delta H^\ddagger$ and $\Delta S^\ddagger$ varied with χ_{H_2O}, suggesting the participation of water in the interaction between $*UO_2^{2+}$ and EtOH. However, the $\Delta H^\ddagger$ and $T\Delta S^\ddagger$ compensated each other as shown in Fig. 5 with the slope of $T\Delta S^\ddagger/\Delta H^\ddagger=1.0$, so that EtOH could be regarded as reacting with $*UO_2^{2+}$ directly; i.e., not via the solvating water. Furthermore, the compensation shows that the $\Delta G^\ddagger$ became almost constant in the mixtures, leading to the linear free energy relationship where the Taft equation [13] can be applied strictly to the quenching of $*UO_2^{2+}$ by aliphatic alcohols followed by the α-H abstraction from the alcohols as follows:

$$\log(k/k_0)=\rho^*\cdot\Sigma\sigma^* \tag{6}$$

,where ρ^* and σ^* are the reaction and polar substituent constants, respectively. The k_q for methanol, ethanol and iso-propanol have been previously obtained at 298.15 K as 4.0×10^6 ($\Sigma\sigma^*=+0.98$), 2.5×10^7 ($\Sigma\sigma^*=+0.49$) and 5.0×10^7 l mol^{-1} s^{-1} ($\Sigma\sigma^*=0.00$), respectively. [3,5] Based on k_q and $\Sigma\sigma^*$, $\rho^*=-1.1$ was obtained for the quenching by the alcohols as reported by Matsushima and co-worker [5]. Instead of the k_q, the quantum yield ϕ of the photoreduction of UO_2^{2+} with the alcohols is likely to be used at lower [Q] to obtain the ρ^* [5] but not at much

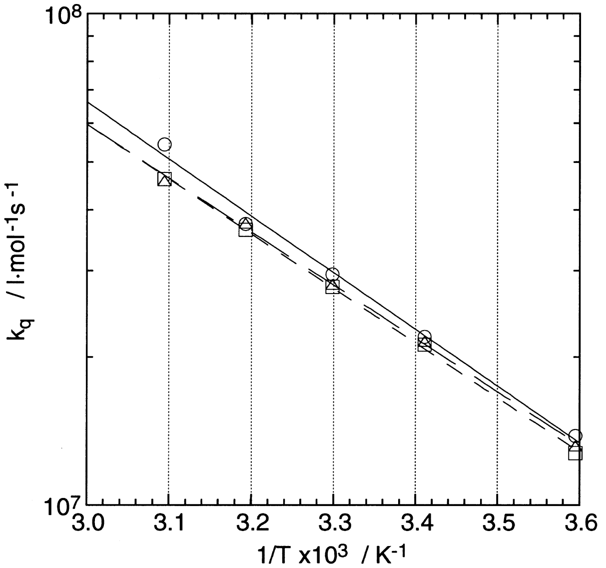

Fig. 4. The Arrhenius plots for the quenching of excited UO_2^{2+} by ethanol in H_2O–D_2O mixtures: $\chi_{H_2O}=1.0$ (○); 0.5 (△); 0.1 (□). [ethanol]$=0.1$ mol l^{-1}.

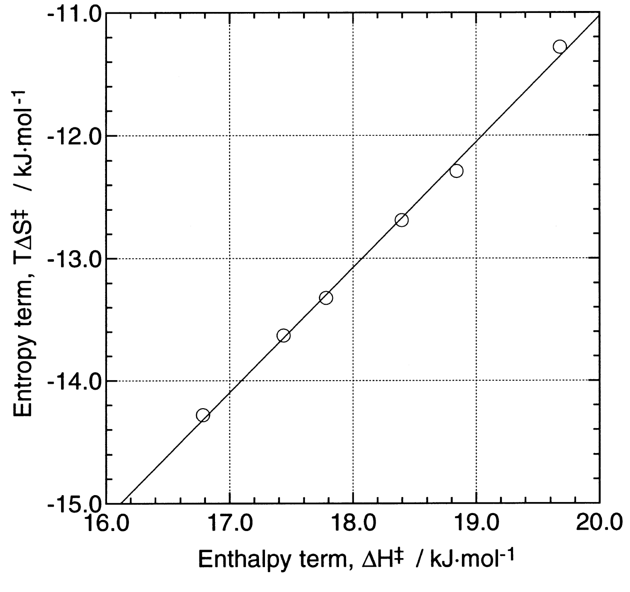

Fig. 5. The correlation between $\Delta H^\ddagger$ and $T\Delta S^\ddagger$ for the quenching of excited UO_2^{2+} by ethanol in H_2O–D_2O mixtures ($T=298.15$ K).

higher [Q] where the ϕ would reach the same maximum less than unity regardless of the alcohols [3].

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