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Mechanism and Rate of the Intramolecular Energy Transfer in Rare Earth Chelates

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The intramolecular energy transfer in rare earth (RE) chelates under excitation by near-ultraviolet light has been the subject of several recent investigations. Three mechanisms by which the excitation energy is transferred from the ligand to the RE ion in RE chelates have been proposed.

As no luminescence is observed from the RE levels higher than T_1,[*1] Crosby *et al.* proposed the mechanism I: the energy transfer from S_1 to the *RE* ion *via* T_1 ($S_1 \rightsquigarrow T_1 \rightsquigarrow RE$ level→emission),[1] while Kleinerman proposed the mechanism II: the direct transfer of energy from S_1 to the *RE* ion ($S_1 \rightsquigarrow RE$ level→emission).[2] Later, Bhaumik *et al.* proposed the mechanism III: the energy is transferred from S_1 to an upper intermediate *RE* level and then is transferred back to T_1 and returns to a lower *RE* level ($S_1 \rightsquigarrow RE$ level higher than $T_1 \rightsquigarrow T_1 \rightsquigarrow RE$ level lower than T_1→emission).[3] Though many other investigators supported the mechanism I on the basis of studies such as that of the intermolecular triplet-triplet energy transfer phenomenon,[4] the possibility of the mechanism II or III has not yet been fully denied. This is mainly due to the fact that the energy-transfer process from the lowest ligand triplet state to the RE ion was too fast to be observed. Bhaumik and El-sayed estimated this time to be $\sim 10^{-10}$ sec.

In this note, we will show some experimental confirmation that the time for this $T_1 \rightsquigarrow RE$ level transfer is about $\sim 10^{-8}$ sec and that the intramolecular energy transfer occurs by means of the mechanism I.

Experimental

Synthesis of β-Diketones. Naphthoyltrifluoroacetone (NFA) and benzylidenetrifluoroacetylacetone (BZDTF) were prepared by the condensation of ethyltrifluoroacetate with naphthoyltrifluoroacetone and benzylideneacetone respectively in a manner similar to that described by Reid and Calvin.[5] Some other β-diketones, benzoyltrifluoroacetone (BFA), and thenoyltrifluoroacetone (TTA) were obtained from Tokyo Kasei and were used without further purification.

Synthesis of RE Chelates. The RE chelates used in this study were prepared by the methods described in the literatures.[6-8] Tris and tetrakis chelates of europium, gadolinium, and terbium were prepared.

Luminescence Studies. All the chelates were studied at 300 and 77°K at a concentration of 10^{-3} mol/*l* in the following solvents; (1) EPA: mixed solvent of ether, isopentane, and ethanol (8 : 3 : 5 by volume ratio), (2) ethanol, and (3) acetonitrile. The details of the stroboscopic studies and the numerical calculations undertaken in order to obtain the luminescence rise times are given in Ref. 9.

Results and Discussion

The ligand triplet-state energies were obtained from the phosphorescence spectra of the Gd chelates. These data are presented in Fig. 1, along with several electronic states of Eu^{3+} and Tb^{3+}.

The triplet states of all the Eu chelates except $Eu(BZDTF)_4 \cdot HP$ lie above the $^5D_1$ state of Eu^{3+}. In these cases the time-resolved emission spectra can be accounted for as follows: the population of the $^5D_1$ state occurs in a time of the order of $\sim 10^{-8}$ sec; then the depopulation of the $^5D_1$ sate occurs in about 2 μsec through radiative and nonradiative transitions to the ^7F manifold as well as through simultaneous nonradiative transition to the $^5D_0$ state; On the other hand, the population of $^5D_0$ occurs in about 2 μsec, which is nearly the same as the decay time of $^5D_1$; finally, radiative and nonradiative transitions from $^5D_0$ to the ^7F manifold occur in about 500 μsec. However, in the

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[*1] Here we used the following abreviations:
S_1: the lowest excited singlet state of the organic ligand.
T_1: the lowest triplet state of the ligand.

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TABLE 1. RISE AND DECAY TIMES OF RE-ION LUMINESCENCE IN SOME RE CHELATES

Chelate	Solvent	$^5D_1$ rise (μsec)		$^5D_1$ decay (μsec)		$^5D_0$ rise (μsec)		$^5D_0$ decay (μsec)		$^5D_4$ rise (μsec)		$^5D_4$ decay (μsec)	
		77°K	300°K	77°K	300°K	77°K	300°K	77°K	300°K	77°K	300°K	77°K	300°K
Eu(BFA)$_4$·HP	EPA	$\sim 10^{-2}$		2.45	1.46	2.18	1.28	460	398				
	EtOH		$\sim 10^{-2}$	2.45	1.51	2.02	0.98	462	432				
	CH$_3$CN		$\sim 10^{-2}$		1.34		1.23		678				
Eu(BZDTF)$_4$·HP	EPA	(a)		(a)		$\sim 10^{-2}$	(a)	408	(a)				
Tb(BFA)$_4$·HP	EPA									$\sim 10^{-2}$	(b)	485	(b)

a) The luminescence is not sensitized.
b) Data were not obtained because the luminescence is weak.

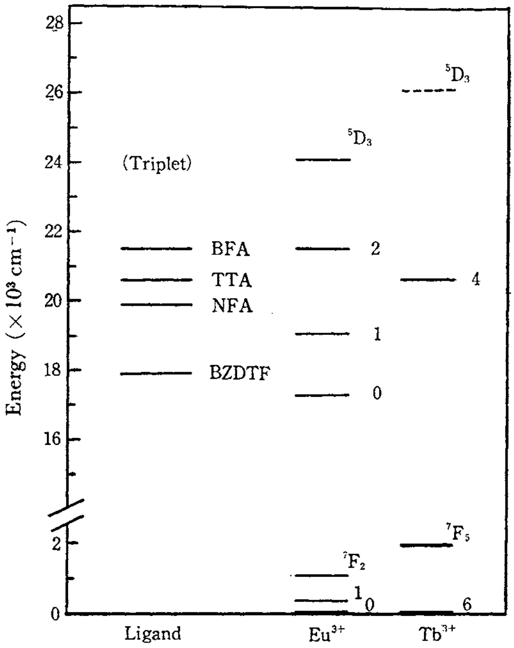

Fig. 1. The triplet states of organic ligands and the f-electronic states Eu^{3+} and Tb^{3+} ion.

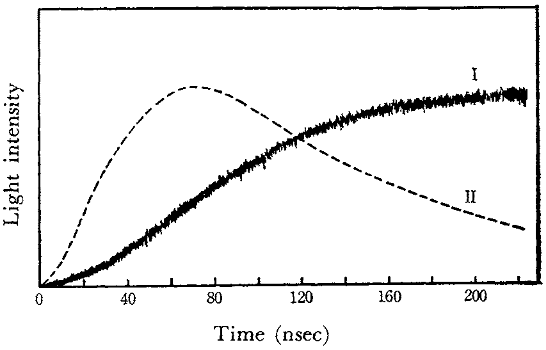

Fig. 2. (I) The typical rise curve of the ion luminescence of Eu, Tb chelates. (II) The rise curve of the excitation flash light.

case of Eu(BZDTF)$_4$·HP, where the lowest ligand triplet is situated between $^5D_1$ and $^5D_0$, no emission from the $^5D_1$ level is observed. The population of $^5D_0$ occurs in a time of the order of $\sim 10^{-8}$ sec, and this is followed by radiative and nonradiative transitions to the ^7F manifold in about 500 μsec. In the cases of the Tb chelates, Tb(BFA)$_4$·HP, Tb(BFA)$_3$·2H$_2$O, and Tb(TTA)$_3$·2H$_2$O, the population of $^5D_4$ occurs in a time of the order of $\sim 10^{-8}$ sec and decays in about 500 μsec.

The luminescence-rise curve of the $^5D_0 \rightarrow {}^7F_2$ transition (613 mμ) of Eu(BZDTF)$_4$HP is shown in Fig. 2. The rise curves of the $^5D_1 \rightarrow {}^7F_1$ transition (538 mμ) in other Eu chelates and of the $^5D_4 \rightarrow {}^7F_5$ transition (545 mμ) in Tb chelates have almost the same behavior as is shown in Fig. 2. These rise times can be estimated to be about 10^{-8} sec. The time-resolved spectroscopic data on several RE chelates are given in Table 1.

From the results stated above, the following conclusions can be reached: First, since the luminescence from RE levels which are higher than T_1 is not observed, as Crosby[1)] reported, and since the time for energy transfer is too long to account for the direct transfer from S_1, there is no possibility of the mechanism II. Second, the mechanism III can also be rejected, because the rise times of the RE-ion luminescence in several RE chelates investigated are nearly the same, *i.e.* 10^{-8} sec, in spite of the fact that the energy differences between the intermediate RE level and T_1 are not similar. Therefore, we can conclude that the energy transfer occurs by means of the mechanism I.