Studies on the chemiluminescence mechanism of *Cypridina* luciferin analogues: Dissociation constants of the singlet-excited *Cypridina* oxidluciferin analogues.

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The chemiluminescence reaction of *Cypridina* luciferin analogue (CLA), 2-methyl-6-phenylimidazo[1,2-a]pyrazin-3(7H)-one, with molecular oxygen or superoxide anion in aqueous media gives two light-emitting species, i.e., the singlet-excited state of 2-acetamido-5-phenylpyrazine (1OCLA*) and its conjugate base (1OCLA*⁻), and the ratio of these two species is affected by the medium pH. Also a substituent at the 6-position of the imidazopyrazinone ring is known to have the influence upon the ratio. Although a proton transfer is supposed to be involved among the molecules in the singlet excited states, the detailed mechanism is still unclear. To clarify the molecular mechanism for the formation of these two species, five kinds of 2-acetamido-5-arylpyrazines possessing various substituents at the p-position of the 5-phenyl group were synthesized, and their fluorescent properties, especially the pKa values for the N-H dissociation in the singlet excited states (pKa*) in aqueous media were investigated. The estimated pKa* values were found to be larger than 11, and increased with increasing the electron-donating character of the substituents. A proportional relationship between the Hammett’s substituent constants and the pKa* values was observed. These results indicate the proposed chemiluminescence mechanism of CLA that the anionic 1OCLA*⁻ is produced first and then protonated to give 1OCLA* to be implausible.