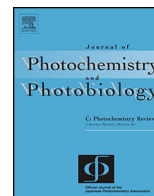




Contents lists available at ScienceDirect

# Journal of Photochemistry and Photobiology C: Photochemistry Reviews

journal homepage: [www.elsevier.com/locate/jphotochemrev](http://www.elsevier.com/locate/jphotochemrev)

## Review

## Thermodynamic vs. kinetic control of excited-state proton transfer reactions

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## ARTICLE INFO

## Article history:

Received 19 April 2014

Received in revised form

26 September 2014

Accepted 30 September 2014

Available online 2 October 2014

## Keywords:

Excited-State Intramolecular Proton Transfer

Excited-State Intramolecular Charge Transfer

Excited-state reaction

Reversibility

3-Hydroxychromones

## ABSTRACT

The “Excited-State Intramolecular Proton Transfer” (ESIPT) reactions in a number of organic fluorophores are among the fastest basic chemical reactions known so far and their rates can be observed even on femtosecond time scale. Accordingly, the reactant concentration, as monitored by its emission, should be negligibly small. In sharp contrast to this conventional wisdom, however, the coexistence of the reactant and the product of this reaction is so frequently observed in condensed media. We then discuss two possible origins of these effects: when the ESIPT reaction is perturbed and hence is slow on the time scale of emission (kinetic control) or when the reverse reaction repopulating the reactant state is fast and leads to the excited-state equilibrium (thermodynamic control). Upon reviewing a great number of ESIPT prototypical systems, we summarize and discuss different criteria for distinguishing these cases based on the steady-state and time-resolved spectroscopic studies and derive correlations between reversibility of these reactions and the solvent-dependent effects observed in fluorescence spectra.

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<http://dx.doi.org/10.1016/j.jphotochemrev.2014.09.005>

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## 1. Introduction

Reversibility is one of the basic characteristics of any chemical event that provides the strategy for elucidating its mechanism. The proton transfers, belonging to the most fundamental processes in chemistry and biochemistry, offer unique possibilities for these studies [1–4]. Of particular interest are the "Excited-State Intramolecular Proton Transfer" (ESIPT) reactions that have been studied by both steady-state and time-resolved techniques [5–9] in different media and conditions [9–11]. In the most interesting case, what if both reactant and product species are brightly emissive, the characteristic opens many possibilities for molecular and supramolecular modeling that allow the data analysis in terms of interatomic distances, interaction energies and reaction rates [6,12]. The progress in the analysis of these data has led to the belief that ESIPT can serve as an important model for understanding also the basic steps in "dark" proton-transfer reactions that are in the heart of many chemical and biochemical phenomena [13–16]. Still, reversibility of these reactions is often obscure. The researchers imply different arguments and criteria addressing this issue, and the general concept is presently lacking.

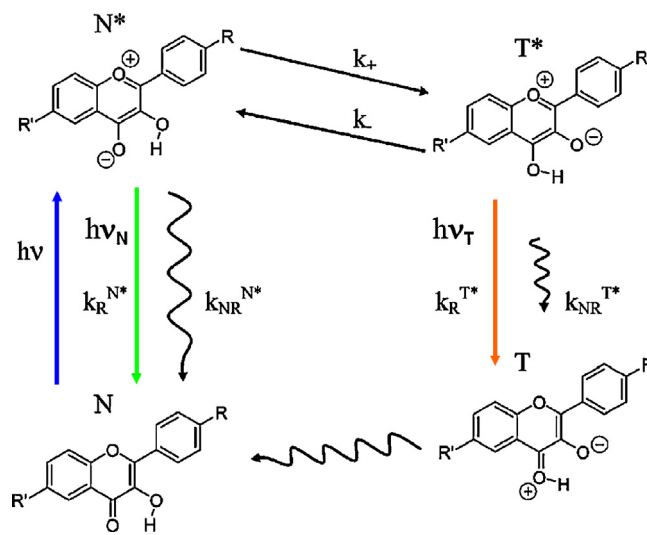
The interest to the ESIPT reactions is not only academic. The broad-scale applications of ESIPT compounds were heated up by the development of novel materials for optoelectronics [7], probing of materials [17], chemical sensing [18,19], biosensing [20–22] and cell imaging [23,24] and white light LED [25]. The heart of these novel technologies is an easily detected and finely modulated switching between two emissive forms [9,26].

Basically, the ESIPT reaction starting from the ground  $N$  state and returning to the same state after four-level reaction cycle is fully reversible [27] (Fig. 1). The absorption of light quantum

leads to normal excited-state form ( $N^*$ ). In the course of ESIPT this form converts into the excited photoproduct, the so-called phototautomer,  $T^*$ , by the translocation of proton and hence the alteration of the electronic configuration.  $T^*$  is recognized by fluorescence spectrum strongly shifted to longer wavelengths. The  $T^*$  relaxation (i.e., the fluorescence emission plus the decay via radiationless channels) leads to the ground-state tautomer ( $T$ ) that undergoes a fast back proton transfer with the recovery of  $N$  species, closing the reaction cycle.

When observed, the fluorescence band of initially excited  $N^*$  form exhibits a significant Stokes shift (defined as the difference between absorption and emission peak frequencies). It should be accepted therefore that the fluorescent  $N^*$  state is not the initially excited Franck–Condon ( $F-C^*$ ) state but rather a state being accessed after some steps of relaxation to a local energy minimum. Meantime the most significant Stokes shift is observed for the  $T^*$  form; this shift can be as large as  $6000\text{--}12000\text{ cm}^{-1}$ . Such anomalously large separation between the absorbed and emitted energies signifies the fact that the absorption and emission bands originate from two different proton-transfer isomers. Formally, we have to consider the presence of at least two minima on the excited-state reaction coordinate and this explains the simultaneous appearance of two bands in steady-state emission spectra.

An optical electronic excitation changes drastically the distribution of electronic density on a scale that is much faster than any nuclear motion. After this instantaneous change, the whole system relaxes to its equilibrium state(s) including electrons, protons and heavier nuclei forming at least two excited states connected by ESIPT reaction. The structural prerequisite for this connection is the close location of proton donor and acceptor groups bridged with a hydrogen bond (H-bond) [3,27–29]. Hydroxyl or amino groups generally serve as the proton donors, and carbonyl oxygen or azo nitrogen as the proton acceptors. Upon electronic excitation, the redistribution of electronic charge makes the proton donor more acidic and the acceptor more basic. Because of coupling of charge transfer and proton transfer the four electronic states,  $N$ ,  $T$ ,  $N^*$  and  $T^*$ , possess different distribution of charges and hence interact differently with the surrounding environment. The consequence of the enhancement in the excited-state basicity/acidity factor, which is several



**Fig. 1.** The four-level diagram for a typical Excited-State Intramolecular Proton Transfer (ESIPT) shown with correspondent rate constants. This reaction occurs between the proximate proton donor and acceptor groups connected by a hydrogen bond in the same photoexcited molecule. A number of radiative and non-radiative processes accompany this reaction. The 3-hydroxyflavone derivatives were chosen as examples. R and R' are the hydrogen atoms or their electron-donor or electron-acceptor substituents.

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