STM JOURNALS

International Journal of
Photochemistry and
Photochemical Research

ISSN: 3107-6785
Volume 4, Issue 1, 2026
January–June
DOI Journal: 10.37591/IJPPR

https://journals.stmjournals.com/ijppr

Research IJPPR

Activation Energy in Photochemical and Thermally Driven Reactions: Mechanistic Insights, Kinetic Modelling and Photocatalytic Applications

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Abstract

Chemical reactions constitute fundamental processes in which reactants are transformed into products through the breaking and formation of chemical bonds. In photochemical systems, these transformations are initiated or influenced by the absorption of light, making energy transfer mechanisms particularly significant. A key parameter governing reaction kinetics is activation energy, defined as the minimum energy required for reactant molecules to undergo a successful transformation. This article focuses on the role of activation energy within the context of photochemical and photophysical processes. It discusses various types of chemical reactions with particular emphasis on light-induced reactions, where photons act as the primary energy source to overcome activation barriers. The influence of external factors such as light intensity, wavelength, temperature, and reactant concentration on activation energy and reaction rates is critically examined. Furthermore, the role of photocatalysts is highlighted, as they facilitate reactions by providing alternative pathways with reduced activation energy under light irradiation, without being consumed in the process. Such mechanisms are central to advancements in areas including solar energy conversion, environmental remediation, and photo-driven synthesis. Understanding activation energy in photochemical systems enables reaction conditions, thereby enhancing efficiency and sustainability in diverse applications ranging from green chemistry to biological photo processes.

Keywords: Photochemical processes, photoactivation energy, photoreaction kinetics, photocatalysis, excited-state energy barriers, molecular collision dynamics, temperature effects on photoreactions, photochemical reaction mechanisms, light-induced kinetics, photoenzymatic catalysis

INTRODUCTION

Chemical reactions and activation energy are fundamental concepts in photochemistry, significantly influencing reaction kinetics and mechanistic pathways under light irradiation. In photochemical systems, activation energy is not solely governed by thermal inputs but is often modulated by photon absorption, leading to electronically excited states that alter reaction pathways. This overview highlights the thermodynamic and photophysical interpretation of activation energy, its experimental determination, and its role in governing light-driven chemical reactivity. Such insights are essential in advancing applications in photocatalysis, solar energy conversion, environmental remediation, and photo-assisted synthesis [1–3].

A chemical reaction involves the transformation of reactant molecules into products through bond breaking and formation.

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Received Date: April 20, 2026
Accepted Date: April 23, 2026
Published Date: May 10, 2026

Citation: Pushpa Mehdoo, Meena Bandhan and S. Ravichandran. Activation Energy in Photochemical and Thermally Driven Reactions: Mechanistic Insights, Kinetic Modelling and Photocatalytic Applications. International Journal of Photochemistry and Photochemical Research. 2026; 4(1): 21–26p.

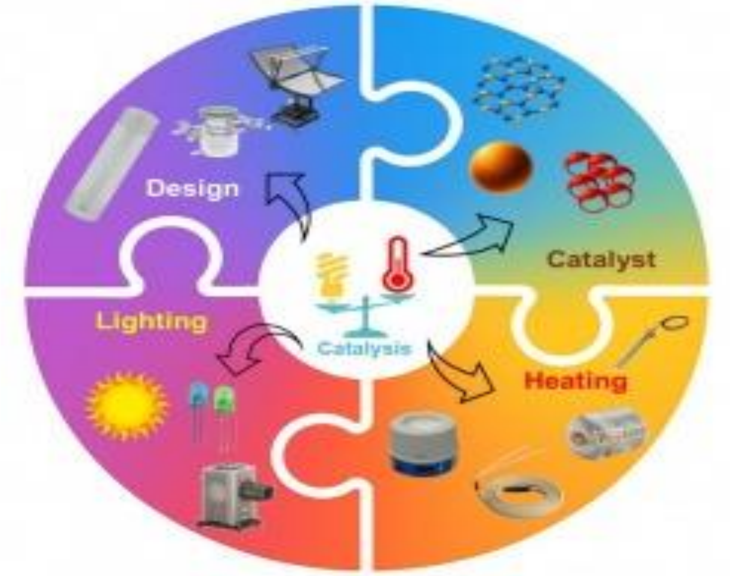

Figure 1. Overview of light-driven catalytic and thermal interactions involved in photochemical reaction activation and process design.

In photochemical reactions, this transformation is initiated or accelerated by the absorption of light, typically in the ultraviolet or visible region, resulting in excited singlet or triplet states as shown in fig. 1. These excited states possess distinct energy profiles compared to ground-state species, thereby reducing or bypassing the conventional thermal activation energy barrier. Consequently, photochemical reactivity is governed by parameters such as light intensity, wavelength, quantum yield, and excited-state lifetime, in addition to traditional kinetic factors [4].

Activation energy (Ea) in photochemical systems represents the minimum energy required to promote reactants to a reactive excited state or to overcome barriers in subsequent steps of the reaction mechanism. Unlike purely thermal reactions, where Ea is supplied by heat, photochemical processes utilize photon energy (hv) to facilitate transitions to higher energy states. This often leads to alternative reaction pathways with lower effective activation energies and enhanced selectivity. In complex photochemical reactions, factors such as solvent environment, presence of photosensitizers, and light penetration depth play critical roles. Systems involving poorly soluble reactants, unstable intermediates, or multi-step mechanisms often require optimization of irradiation conditions, including wavelength selection, light source intensity, and reactor design. Advanced techniques such as laser irradiation, microwave-assisted photochemistry, and flow photoreactors further enhance reaction efficiency and control. Overall, understanding activation energy in the context of photochemical processes provides a deeper mechanistic insight and enables the rational design of efficient, sustainable, and light-driven chemical systems [5–7].

BASICIDEAS

Chemical reactions, particularly in photochemical systems, involve the transformation of one or more substances into new chemical entities under the influence of light. In such processes, activation energy (Ea) represents the minimum energy required to initiate a reaction; however, in photochemistry, this energy is typically supplied through photon absorption rather than thermal input. The absorption of light promotes molecules from the ground state to electronically excited states, thereby effectively overcoming the energy barrier and enabling reaction pathways that may not be accessible under conventional thermal conditions. Thus, activation energy remains a crucial parameter for understanding reaction kinetics and mechanisms, especially in light-induced transformations such as photooxidation, photoreduction, and photocatalysis. Insight into Ea allows for the rational design of efficient photochemical systems for applications including solar energy conversion, environmental remediation, and photochemical synthesis [8–10].

Potential energy surfaces (PES) play a central role in describing the behavior of molecules during photochemical reactions. These surfaces represent the variation in potential energy as a function of nuclear configurations and are particularly important in mapping both ground and excited electronic states. In photochemical processes, transitions between different PES, such as those involving excited singlet and triplet states, are fundamental to understanding reaction pathways. One-dimensional representations of PES along a reaction coordinate illustrate the progression from reactants to products via transition states, while minima correspond to stable species and intermediates. Saddle points represent transition states, which, in photochemistry, may involve excited-state configurations with distinct geometries and energies compared to ground-state analogues. The transition state remains the highest energy point along the reaction pathway and governs the reaction rate, although in photochemical systems, non-radiative processes such as internal conversion and intersystem crossing can significantly influence the reaction dynamics [11].

Reaction Coordinates and Potential Energy Surfaces

Chemical reactions, particularly in photochemical systems, involve the transformation of reactants into products through a sequence of elementary steps initiated or influenced by the absorption of light. In such processes, molecules absorb photons and are promoted to electronically excited states, which significantly alters their reactivity compared to the ground state. The progression from reactants to products occurs via a high-energy transition state, and the energy difference between this state and the ground-state reactants is defined as the activation energy (Ea). In photochemical reactions, however, the effective activation barrier is often reduced due to the involvement of excited states, enabling reactions to proceed under milder conditions [12].

The potential energy of a molecular system depends on nuclear coordinates, representing interatomic distances and molecular geometry. In photochemistry, these energy variations are described using reactive potential energy surfaces (PES), which incorporate both ground and excited electronic states. These surfaces are typically visualized along a reaction coordinate (RC), a conceptual parameter that tracks the progress of a reaction from reactants to products. In photochemical pathways, multiple PES may intersect, leading to phenomena such as internal conversion and intersystem crossing, which play critical roles in determining reaction mechanisms and product distribution [13–16]. The reaction coordinate in complex photochemical systems is often associated with bond dissociation or formation, particularly in processes involving hydrogen abstraction or light heteroatoms. Due to relatively weak bonding and high sensitivity to electronic excitation, such systems are suitable for computational modeling using molecular mechanics and quantum chemical approaches to explore reaction dynamics and energy transfer processes. The temperature dependence of reaction rates is commonly described by the Arrhenius equation:

$$k=Ae−Ea/RT$$

In photochemical reactions, the rate constant (k) may depend not only on temperature but also on light intensity and wavelength. A plot of ln(k) versus 1/T yields a straight line with slope –Ea/R and intercept lnA for thermally activated processes. The apparent activation energy derived from such plots provides valuable insight into the energy barriers governing the reaction. In photochemical systems, this parameter reflects both thermal and photonic contributions, offering a deeper understanding of reaction pathways, excited-state kinetics, and catalytic efficiency under irradiation conditions [17].

Determination of activation energy remains essential in photochemical research, as it helps elucidate reaction mechanisms, optimize light-driven processes, and design efficient photocatalysts for applications in energy conversion, environmental remediation, and synthetic chemistry [18].

Activation Energy in the Real World

Chemical reactions constitute fundamental processes across diverse domains including photochemistry, environmental chemistry, materials science, and biochemical systems. In photochemical systems, these reactions are initiated or influenced by the absorption of light, making the understanding of activation energy and reaction kinetics particularly crucial. Activation energy governs the efficiency of photon-induced transformations, where electronic excitation alters the energy landscape and facilitates otherwise inaccessible reaction pathways. Therefore, both thermal and photonic contributions to reaction mechanisms must be considered for a comprehensive kinetic interpretation [19].

The concept of the potential energy surface (PES) plays a central role in describing reaction pathways in photochemical processes. Upon absorption of light, molecules are promoted to excited electronic states, resulting in modified PES profiles compared to ground-state reactions. The reaction coordinate framework is often employed to simplify this multidimensional surface into a one-dimensional representation, enabling the identification of energy minima corresponding to stable intermediates and saddle points representing transition states. In photochemical reactions, these transition states may involve excited-state configurations or intersystem crossing points, which are critical in determining reaction efficiency and product distribution [20].

Activation energy in photochemical reactions differs significantly from purely thermal processes. Instead of relying solely on thermal energy to overcome energy barriers, photons provide discrete energy packets that promote molecules to higher energy states. Consequently, the effective activation energy may be reduced or bypassed entirely. Factors such as light intensity, wavelength, solvent interactions, and photocatalysts strongly influence this process. The temperature dependence of reaction rates in such systems is often described using the Arrhenius equation, although deviations are common due to non-thermal excitation pathways. A more rigorous treatment of reaction kinetics is provided by the Eyring equation, developed within the framework of transition-state theory. This approach relates reaction rates to thermodynamic parameters such as Gibbs free energy, enthalpy, and entropy of activation. In photochemical systems, the Eyring model is particularly useful for analyzing excited-state dynamics and understanding the influence of molecular structure and environment on reaction rates. Overall, integrating photophysical and kinetic perspectives enables a deeper understanding of light-driven chemical transformations, which is essential for advancements in photocatalysis, solar energy conversion, and environmental remediation [21].

Theory of Transition States and Arrhenius Behaviour

Chemical processes in photochemistry involve the reorganization of atoms or molecular groups initiated by the absorption of light energy. In such systems, reactant molecules are promoted to electronically excited states upon irradiation, which significantly alters their reactivity compared to ground-state species. The reaction pathway typically proceeds through excited-state intermediates or transition states before forming final products. Unlike purely thermal reactions, photochemical transformations are governed not only by temperature and pressure but also by parameters such as wavelength, light intensity, quantum yield, and the nature of the absorbing species.

In photochemical reactions, energy input is primarily provided by photons, enabling molecules to overcome the energy barrier required for bond cleavage or formation. This process may involve singlet or triplet excited states, intersystem crossing, and energy or electron transfer mechanisms. Consequently, the rate of a photochemical reaction depends on both the efficiency of light absorption and the subsequent kinetic steps that lead to product formation. The reaction rate in such systems is often described in terms of photochemical kinetics, where the velocity of reaction is influenced by photon flux and the probability of productive molecular collisions in the excited state. A key concept in this context is the activation energy (E_a), which represents the minimum energy required for a reaction to proceed. In photochemical systems, the effective activation energy may be significantly reduced due to excitation by light, thereby enhancing reaction rates under mild conditions.

k = Ae-fracERT

where

k is the rate constant, which connects the speed of the reaction to the concentration of the reactants - EA is the activation energy (kJ/mol) needed to turn reactants into products - A is the pre-exponential factor, which shows how many times the reactants have tried to cross the energy barrier and is very dependent on the type of reaction - T is the absolute temperature - R is the universal gas constant (8.314 J/(Kmol))

CONCLUSION

For chemical synthesis, engineering, and catalysis, it is important to know how activation energy affects kinetic characteristics and the distribution of products. Nonetheless, the correlation between activation energy and these occurrences is frequently established without a comprehensive analysis. This discussion summarises the basic ideas behind transitions and activation energy. It also talks about significant experimental and computational ways to measure these things. Based on the ideas and evidence discussed, the following conclusions can be drawn.

1. Energy of Activation and Rate Dependence. The Arrhenius equation is a common way to write out the rate constant for an elementary process that has to do with beginning and transition states. The activation energy derived from experimental data may fluctuate under different conditions; nonetheless, calculated values generally remain within a prolonged range specific to the system under investigation (U. E. Gonçalves et al., 2020).
2. The function of potential energy surfaces in kinetics. Potential energy surfaces, which are based on the arrangement of nuclei in a molecular system, are used to describe chemical reactions. Potential energy profiles along reaction coordinates explain elementary reactions. These profiles start at a minimum in the beginning state, go to a saddle point in the transition state, and end at a minimum in the final state. This method 1 captures the essence of chemical reactivity and the connections between concentration, rate, and mechanism.
3. Activation Energies' Dependence on Temperature. The apparent activation energy derived from kinetic data analysis is acknowledged to represent characteristics of underlying mechanisms and possible paths, rather than mere approximations of barriers or associated variations in Gibbs free energy.

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