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여러 온도 및 용매 하에서 수행된 chromen-2-one 지시약 염료들의 염기성 가수분해 반응에 대한 속도론적 연구

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Kinetics of Base Hydrolysis of Some Chromen-2-one Indicator Dyes in Different Solvents at Different Temperatures

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요 약. 7-hydroxy-2H-chromen-2-one(HC)와 7-hydroxy-2H-chromen-2-one-4-acetic acid(HCA)의 염기성 가수분해반응을 aqueous-methanol과 aqueous-acetone 혼합물에서 283 K에서 313 K의 온도 범위에서 속도론적으로 연구하였다. 반응의 활성화 파라미터를 구하고 토의하였다. 게다가, 물, 물-에탄올, 물-아세톤 혼합물 내에서 화합물들에 대한 활성화 에너지 장벽의 변화를 속도론적 데이터로부터 추정하였다. 활성화 장벽의 변화는 HC and HCA의 가수분해 반응과 거의 같았다. HC와 HCA의 염기성 가수분해는 $k_{obs} = k_2[OH^-]$와 같은 속도법칙을 따른다. 메탄올 또는 아세톤의 비가 증가함에 따라 HC 와 HCA의 속도 상수들이 감소하는 것은 OH^- 이온이 불안정해지기 때문이다. 활성화 엔트로피가 큰 음의 값을 갖는 다는 것은 반응이 중간 착물의 형성을 경유하며 진행된다는 것을 의미하며, 또한 중간 착물이 경직성과 안정도를 갖는다는 것을 의미한다. 그러므로, 중간 착물의 고리 열림이 속도 조절 단계가 될 것이다.

주제어: Chromen-2-ones, 염기성 가수분해, 반응 메카니즘, 용매 효과, 활성화 에너지 장벽, 열역학적 파라미터

ABSTRACT. Base hydrolysis of 7-hydroxy-2H-chromen-2-one (HC) and 7-hydroxy-2H-chromen-2-one-4-acetic acid (HCA) in aqueous-methanol and aqueous-acetone mixtures were studied kinetically at temperature range from 283 to 313 K. The activation parameters of the reactions were evaluated and discussed. Moreover, the change in the activation energy barrier of the investigated compounds from water to water-methanol and water-acetone mixtures was estimated from the kinetic data. It is observed that the change in activation barriers is more or less the same for the hydrolysis of HC and HCA. Base hydrolysis of HC and HCA follows a rate law with $k_{obs} = k_2[OH^-]$. The decrease in the rate constants of HC and HCA as the proportion of methanol or acetone increases is due to the destabilization of OH^- ion. The high negative values of entropy of activation support the proposal mechanism, i.e. the investigated reaction takes place via the formation of an intermediate complex. Moreover, these values refer to the rigidity and stability of the intermediate complex. Thus, the ring opening of the intermediate complex would be the rate controlling step.

Keywords: Hydroxy-chromen-2-ones, base hydrolysis mechanism, solvent effect, activation energy barrier, kinetics

INTRODUCTION

Biological importance of chromen-2-ones

Chromen-2-ones have attracted intense interest in recent years because of their diverse pharmacological properties. Among these properties, their cytotoxic effects were most extensively examined, their broad range of effects on the tumors as shown by various in vitro and *in vivo* experiments and clinical studies discussed.[1] Chromen-2-ones have important effects in plant biochemistry and physiology, acting as antioxidants,[2] enzyme inhibitors and precursors of toxic substances. In addition, these compounds are involved in the actions of plant growth hormones, growth regulators, the control of respiration and photosynthesis. Chromen-2-one derivatives have also found applications as fluorescent dyes,[3,4] anti-inflammatory agents,[5] antineoplastic agents,[6] immunomodulant agents[7] antifungals,[8] anticoagulants,[9] antibacterials,[10] antimicrobial[11,12] insecticides[13] and proliferators of HIV.[14,15] HC is widly used in estimation of enzymatic activity as fluorigenic enzyme substrates[16] and acts as a pH indicator in the range 6.5-8.9.[17,18] HCA is used as laser