Journal of Inclusion Phenomena and Molecular Recognition in Chemistry **9**: 51–54, 1990.

Inclusion Effects of Cyclodextrins on the Photobleaching of Coumarins

HIROYUKI YAMAGUCHI* and MIWAKO HIGASHI
College of Technology, Ibaraki University, 4-12-1 Nakanarusawa, Hitachi 316, Japan

(Received: 13 March 1989; in final form: 29 November 1989)

Abstract. The effects of cyclodextrins (α-CD, β-CD and γ-CD) on the photobleaching of coumarin 120 (7-amino-4-methylcoumarin) (**1**) and coumarin 151 (7-amino-4-trifluoromethylcoumarin) (**2**) have been investigated by spectrophotometric measurement. It is concluded that β-CD and γ-CD decelerate the rates of photobleaching of **1**, whilst γ-CD accelerates the rate of **2** and β-CD has no effect on the rate of photobleaching of **2**.

Key words. Cyclodextrin, coumarin, photobleaching.

1. Introduction

Cyclodextrins (CDs) are known to influence the rate of various kinds of chemical reactions, showing a feature of enzymatic reaction [1, 2]. The photostability of coumarin dyes during dye laser operation has been of interest for some years [3, 4]. The products of photobleaching of a coumarin dye have been identified in the early report of Winters *et al.* [5].

The aim of the present paper is to examine the effect of CDs (α-CD, β-CD and γ-CD) on the photobleaching of coumarin 120 (7-amino-4-methylcoumarin) (**1**) and coumarin 151 (7-amino-4-trifluoromethylcoumarin) (**2**).

2. Experimental

2.1. MATERIALS

Cyclodextrins (α-CD, β-CD and γ-CD) were obtained from the Sigma Chemical Co. Coumarin 120 (**1**) and coumarin 151 (**2**) were obtained from the Eastman Kodak Co. CDs were recrystallized three times from an aqueous solution. Compounds **1** and **2** were used without further purification.

The inclusion complex of compound **1** or **2** with CDs in 10% ethanol-aqueous solution was used for the irradiation. The concentrations of coumarins and CDs were 6.0×10^{-5} and 1.0×10^{-2} M, respectively.

2.2. INSTRUMENTS

The optical densities at the absorption maximum wavelength (λ_{max}) of the longest wavelength band were recorded at room temperature on a Hitachi U-3200 recording spectrophotometer. The λ_{max} values of **1** and **2** are 344.2 nm and 376.6 nm,

* Author for correspondence.

respectively. The λ_{max} values of the complexes of **1** and **2** with CDs were red-shifted by a few nm. Irradiations were carried out using a 500 W xenon lamp (Ushio UXL-500D-O) with an output of 31 mW/cm^2, equipped with a infrared cut filter (Kenko IRC-65L) and a glass filter (Kenko UV-32). The light below 300 nm and above 750 nm was thus excluded. The light intensity was measured by a surface absorbing disc calorimeter (Scientech, Inc. Model 36-0401).

3. Results and Discussion

The time dependence of the optical densities of **1** and **2** are listed in Table I. The logarithms of the optical densities of **1** and **2** are plotted in Figures 1 and 2, respectively. From these data, the rate constants of photobleaching are determined by the first order reaction. In the absence of CDs, the rate constants of the photobleaching of **1** and **2** are 2.1×10^{-3} and 0.4×10^{-3} min^{-1}, respectively. The rate constant of **1** in the presence of α-CD is 2.1×10^{-3} min^{-1}. The rate constants of **1** in the presence of β-CD and γ-CD are 1.3×10^{-3} and 1.6×10^{-3} min^{-1}, respectively. The rate constant of **2** in the presence of α-CD is 0.4×10^{-3} min^{-1}. The rate constants of **2** in the presence of β-CD and γ-CD are 0.3×10^{-3} and 2.2×10^{-3} min^{-1}, respectively.

The induced circular dichroism (ICD) spectra for **1** or **2** in the presence of CDs were measured on a Jasco J-600 recording spectropolarimeter. The ICD band is in the region of the absorption band for **1** or **2** with β-CD or γ-CD, whereas there is no ICD band for **1** or **2** with α-CD. These ICD spectra show that both **1** and **2** are included in β-CD or γ-CD, while they are not included in α-CD.

The rate constant of **1** and **2** is not affected by the addition α-CD. The photobleaching of **1** is decelerated by making the inclusion complex with β-CD or

Table I. Time dependence of the optical densities of coumarin 120 (**1**) and coumarin 151 (**2**) without or with cyclodextrins (CDs)

Time/min	Coumarin 120 (**1**)				Coumarin 151 (**2**)			
	without CDs	with α-CD	with β-CD	with γ-CD	without CDs	with α-CD	with β-CD	with γ-CD
0	1.02	1.04	0.98	0.99	0.90	0.90	0.87	0.86
10	0.99	1.00	0.96	0.96	0.90	0.89	0.87	0.83
20	0.96	0.98	0.94	0.94	0.90	0.89	0.86	0.81
30	0.94	0.95	0.93	0.93	0.89	0.88	0.86	0.79
40	0.92	0.93	0.92	0.91	0.89	0.88	0.86	0.77
50	0.90	0.91	0.90	0.90	0.88	0.87	0.85	0.74
60	0.88	0.89	0.89	0.88	0.88	0.87	0.85	0.73
70	0.86	0.87	0.88	0.87	0.88	0.86	0.85	0.71
80	0.84	0.85	0.87	0.85	0.87	0.86	0.84	0.69
90	0.82	0.83	0.86	0.84	0.87	0.85	0.84	0.68
120	0.77	0.78	0.83	0.80	0.86	0.84	0.83	0.64
150	0.73	0.74	0.80	0.77	0.85	0.84	0.83	0.60
180	0.69	0.70	0.77	0.73	0.85	0.83	0.82	0.57

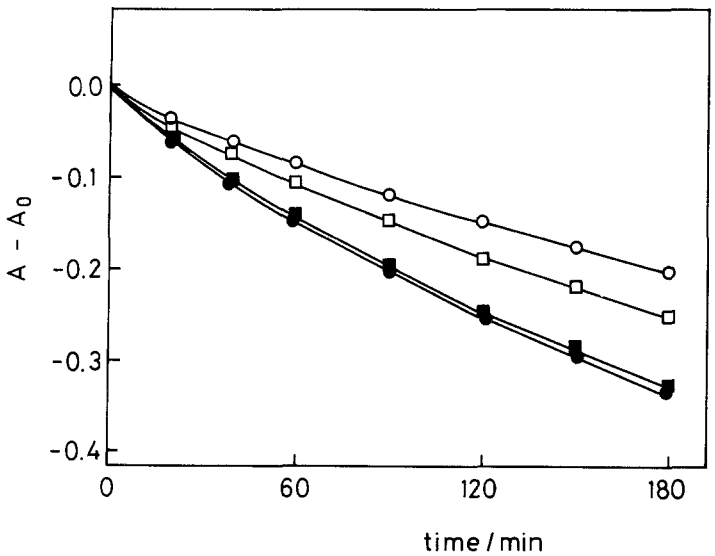

Fig. 1. Time dependence of the optical densities of coumarin 120 (**1**) without CDs (●) and with α-CD (■), β-CD (○) and γ-CD (□). A_0 is the optical density before irradiation.

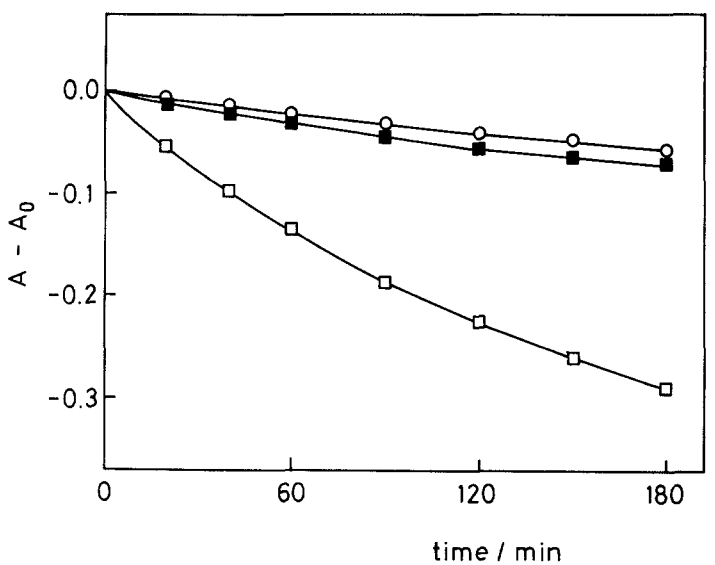

Fig. 2. Time dependence of the optical densities of coumarin 151 (**2**) in the presence of α-CD (■), β-CD (○) and γ-CD (□). Variation of the optical density of **2** without CDs is similar to the curve in the presence of β-CD. A_0 is the optical density before irradiation.

γ-CD. The photobleaching of **2** is accelerated by the presence of γ-CD. The rate constant of **2** with β-CD is similar to that of **2** in the absence of CDs although the ICD spectra suggest that a complex is formed. The fluorine atoms of **2** may affect the rate constant of the photobleaching.

Acknowledgements

We are grateful for financial support of this work by a Grant-in-Aid for Scientific Research (No. 62540315) from the Ministry of Education, Science and Culture, Japan.

References

1. M. L. Bender and M. Komiyama: *Bioorganic Chemistry*, Vol. 1, p. 19 (Ed. E. E. van Temelen), Academic Press, New York (1977).
2. Y. Tanaka, S. Sasaki, and A. Kobayashi: *J. Incl. Phenom.* **2**, 851 (1984).
3. G. A. Reynolds and K. H. Drexhage: *Optics. Commun.* **13**, 222 (1975).
4. F. J. Schimitschek, J. A. Trias, P. R. Hammod, R. A. Henry, and R. L. Atkins: *Optics Commun.* **16**, 313 (1976).
5. B. H. Winters, H. J. Mandelberg, and W. B. Mohr: *Appl. Phys. Lett.* **25**, 723 (1974).