Guest–host interactions in the alkaline bleaching of triphenylmethane dyes catalysed by *β*-cyclodextrin

V RAJ, A SARATHI, T CHANDRAKALA, S DHANALAKSHMI, R SUDHA and
K RAJASEKARAN*

Post Graduate and Research Department of Chemistry (DST–FIST Sponsored),
Virudhunagar Hindu Nadars' Senthikumara Nadar College, Virudhunagar 626 001
e-mail: krsekaran@yahoo.com

Abstract.   The rates of alkaline bleaching of triphenylmethane dyes crystal violet (CV), malachite green (MG) and rosaniline (RA) have been measured spectrophotometrically in an aqueous medium at 30°C in the presence of *β*-cyclodextrin (CD). At lower concentrations of CD, CV forms productive 1 : 1 (G : H) complex. At higher concentrations of CD, it forms unproductive 1 : 2 (G : H) complex. For the bleaching of MG, CD accelerates or decelerates the rate depending on pH of the medium by forming 1 : 1 (G : H) inclusion complex. Analysis of rate data shows that MG undergoes fading by mixed order process. CD decelerates the water reaction and accelerates hydroxide ion reaction. In the case of RA, both water reaction as well as hydroxide ion reaction are retarded by CD by the formation of inclusion complex.

Keywords.   Crystal violet; malachite green; rosaniline; *β*-cyclodextrin; guest–host interactions.

1. Introduction

β-Cyclodextrin (CD) consists of seven $\alpha - (1,4)$-linked D-glycopyranose units forming a conical cylinder. The seven primary hydroxy groups are situated at the narrower end of the cylinder and fourteen secondary hydroxy groups form the wider rim.[1,2] CD forms inclusion complexes through non-covalent interactions with molecules of specific size and shape. The main factors affecting the stability of the inclusion complexes are:[3] van der Walls interaction; hydrophobic interactions; hydrogen bonding; field effects. The stability of cyclodextrin complexes in solution, covalent–catalysis and field effects on organic reactions are reviewed.[4,5] The well-defined cavity of CD has been frequently used as micro reactor which can catalyse or inhibit organic reactions by including the substrate in the cavity.[6,7] The effects of CD on chemical reaction can arise in a number of ways:

(i)   CD can hide certain parts of guest molecule and expose other parts

(ii) they can change the conformation of the guest

(iii) their lipophilic cavity provides a non-polar medium for the guest within polar solvents

(iv) the OH groups of CD can participate in the reaction either directly as bases or nucleophiles.

Bleaching of triphenylmethane dyes is useful for studying chemical reactivity in organized media. In the present study, effect of *β*-cyclodextrin on the bleaching rates of triphenylmethane dyes crystal violet (CV), malachite green (MG) and rosaniline (RA) have been investigated in alkaline medium with a view to understand the guest–host interaction in these system.

2. Experimental

The dyes are all commercial samples. *β*-cyclodextrin from Fluka was dried at 95°C and used. Doubly distilled water was used for all the kinetic measurements. Carbonate free NaOH solutions were prepared by washing sodium hydroxide pellets (AR) repeatedly with water and standardised by potassium hydrogen phthalate standard. In the reaction medium pH was maintained by borax–borate buffers. All the pH measurements were made in Philips pH meter. All the kinetic measurements were made in an aque-

*For correspondence

ous system at 30°C. The rates of bleaching of the dyes were measured by monitoring the OD of the solution at the λ_{max} of the dye (CV = 602 nm; MG = 634 nm; RA = 543 nm) using Perkin–Elmer Hitachi 200–20 UV–Visible spectrophotometer provided with thermostatic cell holder. Concentration of the dyes *ca* 2×10^{-5} M. The pseudo first-order rate constants, k_{obs}, were evaluated from the plot of log A_t versus time by the method of least squares (A_t is the absorbance of the solution at time '*t*'). The bleaching of the dye is almost complete under the reaction conditions employed.

3. Results and discussion

3.1 *Bleaching of crystal violet (CV)*

The bleaching of triphenylmethane dyes is due to the formation of colourless carbinol by the nucleophilic attack of H_2O and OH^- on the dye cation.

$$Ar_3C^+ \xrightarrow[\text{OH}^-]{\text{H}_2\text{O}} Ar_3COH. \tag{1}$$
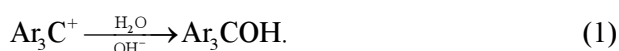
The rate law for the above reaction is

$$k_{obs} = k_{H_2O} + k_{OH}[OH^-], \tag{2}$$

where k_{H_2O} is the pseudo first-order rate constant for water reaction and k_{OH} is the second order rate constant for hydroxide ion reaction.

The rates of bleaching of CV was measured spectrophotometrically in the absence of CD in varying
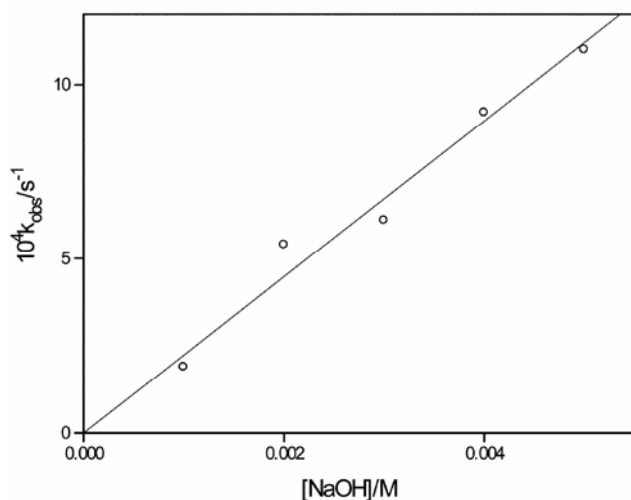
Figure 1. Variation of k_{obs} with [OH$^-$] for bleaching of crystal violet at 30°C.

amount of NaOH. Figure 1 is the plot of k_{obs} versus [OH$^-$], which is linear with negligible intercept and a slope value of 0·22. Under the reaction conditions employed $k_{H_2O} \approx 0$ and $k_{OH} = 0.22$ mol dm^{-3} s^{-1}. Ritchie *et al*[8] reported ($k_2 = 0.22$ mol dm^{-3} s^{-1}) for fading of CV.

The rate of bleaching was also measured in the presence of varying amount of CD in 0·001, 0·003 and 0·005 M NaOH. Figure 2 is the plot of k_{obs} versus [CD] for the bleaching of CV in 0·001 M NaOH at 30°C. Initially k_{obs} value increases with an increase of [CD], reaches a maximum and then decreases. Similar results were obtained in 0·003 and 0·005 M NaOH. Such rate maxima were reported in the cleavage of esters by CD[9,10] and in peroxide bleaching of Green S[11] in the presence of CD. This type of rate behaviour is due to the formation of productive 1 : 1 (G : H) complex at lower concentrations of CD and formation of unproductive 1 : 2 (G : H) complex at higher concentrations of CD.

The reaction proceeding through 1 : 1 complex can be represented as shown in scheme 1.

The rate law for the scheme 1 is

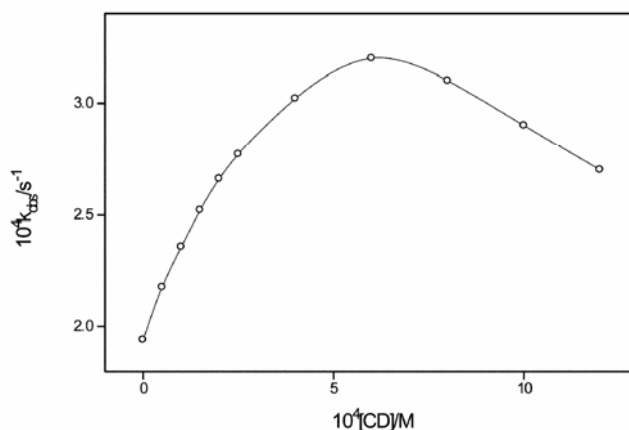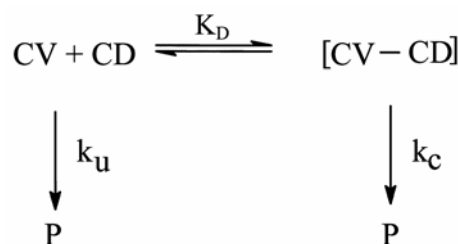$$k_{obs} = \frac{k_u K_D + k_c[CD]}{K_D + [CD]}, \tag{3}$$

Figure 2. Effect of [CD] on bleaching rate of crystal violet in 0·001 M NaOH at 30°C.
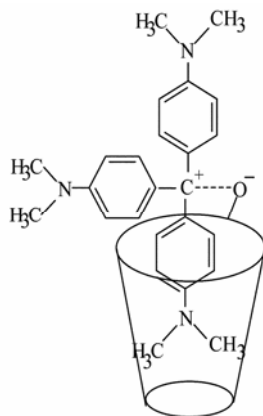
Scheme 1.

Table 1. Rate-constant and complex-dissociation constant for [CV–CD] complex at 30°C.

[NaOH]/M	$k_u \times 10^4$ (s^{-1})	$k_c \times 10^4$ (s^{-1})	k_c/k_u	$K_D \times 10^4$ (mol dm^{-3})
0·001	1·9	4·0	2·1	4·1
0·002	5·4	10·0	1·9	4·6
0·003	6·1	13·8	2·3	3·3
0·100*	162·0	240·0	1·5	3·6

*Data from ref. 12

Figure 3. [CV–CD] 1 : 1 inclusion complex.

where k_u and k_c are the rate constants for uncatalysed and catalysed path ways respectively and K_D is the dissociation constant of [CV–CD] complex.

Equation (3) can be re-arranged to (4)

$$(k_{obs} - k_u) = -K_D \frac{(k_{obs} - k_u)}{[CD]} + (k_c - k_u). \qquad (4)$$

By fitting the rate data in raising portion of the curve, employing (4), k_c and K_D value for [CV–CD] complexes were evaluated and summarized in table 1.

For the purpose of comparison, the literature data reported by Rio *et al*[12] is also included in the table 1. The K_D value evaluated by us is close to that of the literature value. For [CV–CD] 1 : 1 complex, Liu *et al*[13] have reported K_D as $5·3 \times 10^{-4}$ mol dm^{-3} (25°C pH = 7·2) by spectrophotometric method. The rate acceleration in CD catalysed reaction is usually measured by the ratio k_c/k_u. The data in table 1 show that CD accelerates the bleaching rate of CV marginally by formation of 1 : 1 (G : H) complex. The structure of the inclusion complex of CV with CD has been proposed by Rio *et al*[12] based on NMR spectral measurements. In the [CV–CD] complex, the dye enters into the hydrophobic cavity through the wider rim. One phenyl group is accommodated within the CD cavity (figure 3). The secondary hydroxy group of CD is weakly acidic[14] (pK$_a$ = 12·2). Under alkaline condition, this hydroxy group is ionized. The nucleophilic attack of the ionized secondary hydroxy group of CD on the dye cation may be the reason for the rate acceleration. This is similar to the rate acceleration caused by CDs on the cleavage of phenyl esters.[15]

At higher concentrations of CD, another aryl ring of CV may occupy the cavity of second CD molecule leading to 1 : 2 (G : H) complex. Steric crowding around the reaction centre may retard the rate of the reaction.

3.2 *Bleaching of malachite green and rosaniline*

The rates of bleaching of malachite green (MG) and rosaniline (RA) were measured in 0·001 M NaOH and borax–borate buffers of several pH in the presence of varying amount of CD. For malachite green, in 0·001 M NaOH, k_{obs} values increase with an increase of [CD]. In borax–borate buffers, the variation of k_{obs} with [CD] is interesting. At pH 10, 9·7 and 9·4, k_{obs} increases with increase of [CD]. At pH 9·1, k_{obs} is insensitive to [CD]. At pH 8·8, k_{obs} decreases with increase of [CD] (figure 4).

For RA, the rate of bleaching decreases with an increase of [CD] in 0·001 M NaOH (figure 5).

Similar rate retardation was observed in all the borax–borate buffers. By analysing the rate data in terms of (4), the apparent rate constants k_u^a and k_c^a and K_D values for [MG–CD] complex and [RA–CD] complex were evaluated (tables 2 and 3).
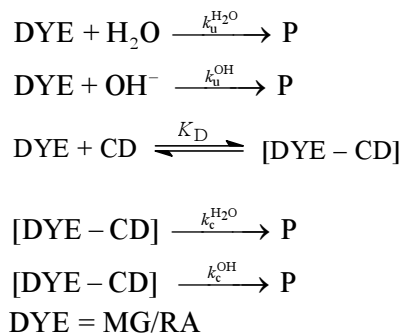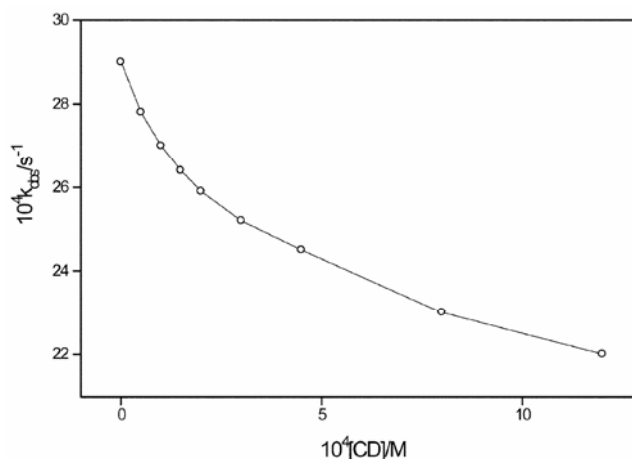
It is well-known that unlike CV, bleaching of MG and RA is a mixed order process (i.e.) both water reaction and hydroxide ion reaction are significant.[16] Therefore for bleaching of MG and RA, the following scheme 2 can be envisaged.

Both the complexed and uncomplexed dye undergo bleaching by reaction with H$_2$O and hydroxide

Table 2. Rate constants and equilibrium constants for the bleaching of MG in presence of CD at 30°C.

pH*	$k_u^a \times 10^4$ (s^{-1})	$k_c^a \times 10^4$ (s^{-1})	k_u^a / k_c^a	$K_D \times 10^4$ (dm^{-3} mol)
8·8	3·9	3·2	0·8	2·7
9·1	4·7	4·7	1·0	.....
9·4	4·9	5·5	1·1	.....
9·7	5·8	6·9	1·2	.....
10·0	7·8	13·5	1·7	.....
0·001M NaOH	18·5	38·3	2·0	5·4

*Borax–borate buffer
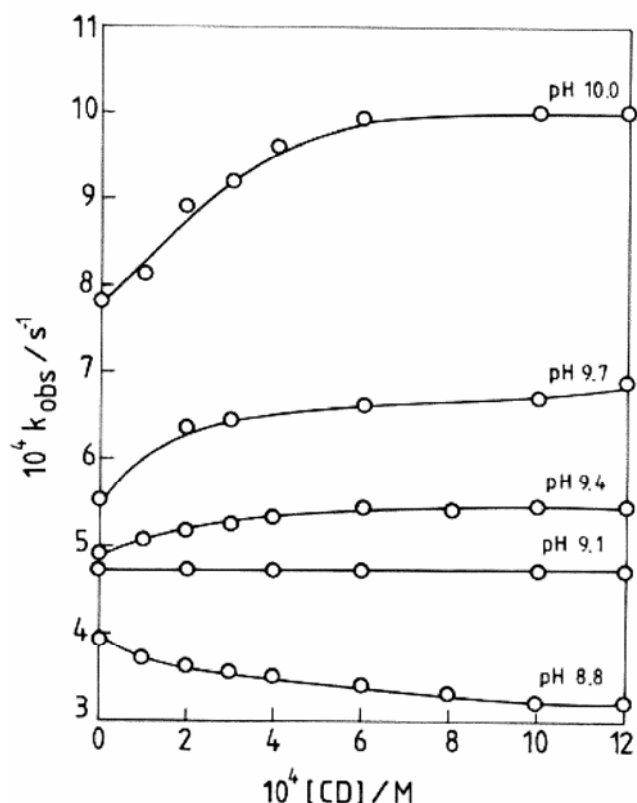
Figure 4. Variation of k_{obs} with [CD] for bleaching of malachite green in borax–borate buffers at 30°C.

DYE + H$_2$O $\xrightarrow{k_u^{H_2O}}$ P

DYE + OH$^-$ $\xrightarrow{k_u^{OH}}$ P

DYE + CD $\xrightleftharpoons{K_D}$ [DYE – CD]

[DYE – CD] $\xrightarrow{k_c^{H_2O}}$ P

[DYE – CD] $\xrightarrow{k_c^{OH}}$ P

DYE = MG/RA

Scheme 2.

Figure 5. Effect of [CD] on the rate of bleaching of rosaniline in 0·001 M NaOH at 30°C.

ion. The k_a^u and k_a^c values reported in tables 2 and 3 are all composite rate constants and can be expressed in terms of (5) and (6).

$$k_u^a = k_u^{H_2O} + k_u^{OH} \, [OH^-] \tag{5}$$

$$k_c^a = k_c^{H_2O} + k_c^{OH} \, [OH^-]. \tag{6}$$

The values of k_u^a and k_c^a are dependent of pH. They are fitted in terms of equations 5 and 6, by the method of least squares and pH independent rate constants $k_u^{H_2O}$, k_u^{OH}, $k_c^{H_2O}$ and k_c^{OH} for the uncomplexed and complexed dye cations for water and hydroxide reactions of MG and RA are evaluated and presented in table 4.

Examination of data in table 4 shows that CD accelerates hydroxide ion reaction with MG but it decelerates the water reaction. The rate acceleration in hydroxide ion reaction may be explained as in the case of CV. One of the aryl rings containing –N(CH$_3$)$_2$ substituent (which is more hydrophobic

Table 3. Rate constants and equilibrium constants for the bleaching of RA in presence of CD at 30°C.

pH*	$k_u^a \times 10^4$ (s^{-1})	$k_c^a \times 10^4$ (s^{-1})	k_u^a / k_c^a	$K_D \times 10^4$ dm^{-3} mol
8·8	7·1	3·8	0·54	.....
9·1	8·3	5·6	0·67	.....
9·4	8·6	5·9	0·68	.....
9·7	9·2	6·3	0·68	.....
10·0	12·6	9·0	0·71	.....
0·001M NaOH	29·0	22·0	0·76	2·4

*Borax–borate buffer

Table 4. pH independent rate constants for the bleaching of complexed and uncomplexed dyes (MG and RA) at 30°C.

Malachite green	Water reaction	$k_u^{H_2O}$ $3·9 \times 10^{-4}$ s^{-1}	$k_c^{H_2O}$ $2·7 \times 10^{-4}$ s^{-1}	$k_c^{H_2O} / k_u^{H_2O}$ $0·7$
	OH$^-$ reaction	k_u^{OH} $10·4$ dm^3 mol^{-1} s^{-1}	k_c^{OH} $3·9$ dm^3 mol^{-1} s^{-1}	k_c^{OH} / k_u^{OH} $2·7$
Rosanaline	Water reaction	$k_u^{H_2O}$ $8·3 \times 10^{-4}$ s^{-1}	$k_c^{H_2O}$ $5·4 \times 10^{-4}$ s^{-1}	$k_c^{H_2O} / k_u^{H_2O}$ $0·65$
	OH$^-$ reaction	k_u^{OH} $2·1$ dm^3 mol^{-1} s^{-1}	k_c^{OH} $1·7$ dm^3 mol^{-1} s^{-1}	k_c^{OH} / k_u^{OH} $0·80$
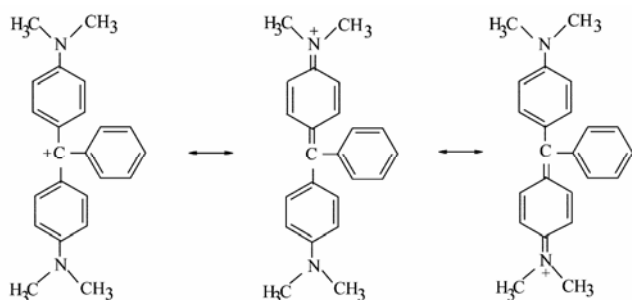
Figure 6. Delocalisation of positive charge on central carbon of MG into the aromatic rings.

than the unsubstituted phenyl ring) is incorporated into the hydrophobic cavity of CD. The ionized secondary hydroxy group of CD catalyses the bleaching rate.

The rate retardation in water reaction may be explained as follows: due to direct conjugation between the alkylamino substituents and the positive charge on the central carbon atom contiguous to aromatic rings, the positive charge is delocalized over the aromatic rings (figure 6).

The approach of the nucleophile, water, brings about a change in the hybridisation of the central atom and the activation process brings about signifi-

cant attenuation of direct conjugation of carbonium ion with ring substitutents (i.e.) the approach of nucleophile results in enhancement of positive charge density on central carbon. The negative volume of activation[17,18] observed for MG–water reaction is in accordance with the formation of new bond between the substrate and nucleophile by the localization of the initially dispersed charge on reactant.

For such reactions, the rate of the reaction will decrease as the polarity of the solvent decreases. The rate retardation by inclusion in the CD cavity can be explained by a micro solvent effect. The hydrophobic cavity of CD is similar to a solvent of low dielectric constant. In the inclusion complex, the dye is inserted into the non-polar region within the ring of sugar residues and is expected to decelerate the fading process just as it would be if the medium were less polar by the addition of an organic solvent of low dielectric constant.

The interior of micelles are hydrophobic, similar to cavity of CD. Dynstee *et al*[19] showed that for MG, the water reaction is retarded by both cationic micelle and anionic micelle. This is attributed to the fact that for water reaction the transition state resembles that of the reactant Ar$_3$C$^+$ and may be represented as [Ar$_3$C....OH$_2$]$^+$. Koth Wada *et al*[20] re-

ported that in fading of triphenylmethane dye addition of alcohol retards the rate. There is similarity between CD catalysed and micellar catalysed reaction of bleaching of the triphenylmethane dyes for water reaction.

For RA, CD decelerates the rate of both water and hydroxide ion reaction (table 4). This is contrary to the results obtained for CD–MG reaction.

The aryl rings of CV and MG contain the hydrophobic $-N(CH_3)_2$ group. But in RA, the aryl ring contains the hydrophilic $-NH_2$ group. The amino group of the aryl ring can form H–bond with hydroxy group of CD.[21] Usually the host–guest hydrogen bondings come from the primary hydroxy groups (C–6) of CD which are flexible and can rotate about C (5)–C (6) bond. In contrast the secondary hydroxy groups on C(2) and C(6) are rigid. Further, attractive $-N-H...O$ interactions can occur between the included guest and the array of lone pairs on oxygen[22] atom of CD. These H-bonding plays significant role in the mode of insertion of guest molecule inside the CD cavity.[23]

Connors *et al*[24] suggested that benzoic acid bind α-CD with the COOH at the narrow end of the cavity. But in benzoate ion, the carboxylate moiety is positioned at the wider secondary hydroxy end of CD.

The wide rim of the CD is distinctly hydrophilic while the narrow rim bearing the primary hydroxy group is intensely hydrophobic.[25] The dye cation may form an inclusion complex in which NH_2 group may be positioned either nearer to narrow rim or wider rim of CD. From the kinetic data alone it will not be possible to predict the mode of insertion of dye.

The stabilization of the ground state by H-bonding may be the reason for the reduced reactivity of the complexed dye in the case of RA.

4. Conclusion

Fading of crystal violet is second order process. At low concentrations, CD accelerates the rate of bleaching of CV by forming productive $1:1$ (G:H) complex. At higher concentrations of CD, unproductive $1:2$ (G:H) complex is formed. Bleaching of malachite green and rosanaline is a mixed order process. For MG, CD accelerates the hydroxide ion reaction and decelerates the water reaction by the formation of $1:1$ (G:H) complex. In the case of RA, CD decelerates both water and hydroxide ion reaction due to the stabilization of ground state by H-bonding with the host.

References

1. Bender M and Komiyana M 1978 *Cyclodextrin chemistry* (New York: Springer-Verlag)
2. Wenz G and Angew 1994 *Chem. Int. Ed. Egl.* **33** 803
3. Inoue Y 1993 *Ann. Rep. NMR Spectrosc.* **27** 59
4. Connors K A 1997 *Chem. Rev.* **97** 1325
5. Takahashi K 1998 *Chem. Rev.* **98** 2013
6. Viola L and de Rossi R H 1999 *Can. J. Chem.* **77** 860
7. Granados A M and de Rossi R H 2001 *J. Org. Chem.* **66** 1548
8. Ritchie C D, Wright D J, Huang D S and Kamego 1975 *J. Am. Chem. Soc.* **97** 1163
9. Davies M D and Deary M E 1999 *J. Chem. Soc. Perkin Trans II* 1027
10. Tee O S and Xian-Xian Du 1988 *J. Org. Chem.* **53** 1839
11. Henri d'Hausen P, Tait C N and Davies D M 2002 *J. Chem. Soc. Perkin Trans II* 398
12. Rio L G, Leis J R, Mefulo J C, Navarro-Vazquez A, Pe'rez-Jusle J and Rodriguez-Da-fonte P 2004 *Langmuir* **20** 606
13. Yu Liu, Bin Li, Chans-Chans You, Takehikowada and Yoshihisa Inove 2001 *J. Org. Chem.* **66** 225
14. Tee O S, Mazza C and Xian-Xian Du 1990 *J. Org. Chem.* **55** 3603
15. Van Etten R L, Sebastian J F, Clowes G A and Bender M L 1967 *J. Am. Chem. Soc.* **89** 3242
16. Ritchie C D, Skinnan G A and Badding V G 1967 *J. Am. Chem. Soc.* **89** 2063
17. Obaid Hassan Abed and Neil Isaacs S 1983 *J. Chem. Soc. Perkin Trans II* 841
18. Le-Noble W J, Gebicka E and Sri Vastava S 1982 *J. Am. Chem. Soc.* **104** 3153
19. Duynslee E F J and Grunwald E 1959 *J. Am. Chem. Soc.* **81** 4542
20. Patel M S, Kothwada D M and Nagar T N 2003 *Asian J. Chem.* **15** 202
21. Hamilton J A and Chen L Y 1988 *J. Am. Chem. Soc.* **110** 5833
22. Steiner T and Saenger W 1992 *J. Am. Chem. Soc.* **114** 10146
23. Yi Z P, Chen H L, Huary Z Z, Huang G and Yu J S 2000 *J. Chem. Soc. Perkin Trans II* 121
24. Connors K A, Lin S F and Wong A B 1982 *J. Pharm. Sci.* **71** 217
25. Lipkowitz K B 1998 *Chem. Rev.* **98** 1829