

Effect of addition of calix[*n*]arenes on photooxygenation of 4,5-diphenylimidazolones

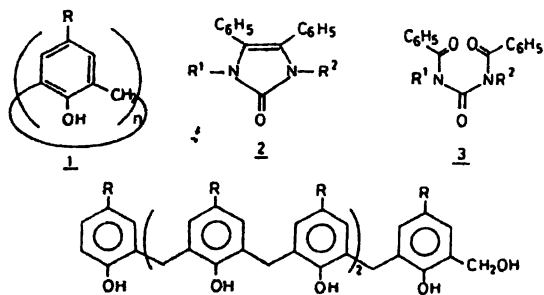
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Manuscript received 23 October 1998, revised 12 July 1999, accepted 13 September 1999

Rates of dye sensitized photo-oxygenation of 4,5-diphenylimidazolones increase markedly on addition of calix[*n*]arenes. The effect of addition of calix[6]arenes is more pronounced than that of calix[4]- and calix[8]arenes and it varies with the size of the alkyl group (octyl > hexyl > *t*-butyl > methyl > H) in the same calixarene series.

Calixarenes (1) are phenolic metacyclophanes having immense potential for developing molecular receptors suitable for recognition of ions and small organic molecules^{1,2}. An important feature of calix[*n*]arenes is that they have a high degree of pre-organization of groups in their structural array and they can assume suitable conformations due to strong flip-flop hydrogen bonding¹. Their cyclodextrin-like molecular architecture¹ can be further modified by manipulating their upper or the lower rim functionality³. We report herein that in contrast to the inhibition of hydrolysis of phenylbenzoates⁴, methylene blue sensitized photooxygenation of 4,5-diphenylimidazolones are speeded up markedly on addition of calix[*n*]arenes. The effect of added calix[*n*]arene is dependent upon the chain-length of appended alkyl groups and it is more pronounced in calix[6]arenes than in calix[4]arenes and calix[8]arenes for the same R. The earlier case of reaction rate enhancement in the presence of calix[6]arenes was reported by Shinkai *et al*⁵.



4,5-Diphenylimidazolones (2) were synthesized and their solution in chloroform-methanol (1 : 1, v/v; $\approx 10^{-3}$ – 10^{-4} M) was subjected to methylene blue sensitized photooxygenation as described earlier^{6,7}. The light source employed was tungsten filament lamp while potassium chromate screen was used to filter off UV radiation. Corresponding diphenylureas (3) were isolated and identified as the only products of photooxygenation as reported earlier⁶. That sin-

glet oxygen was involved in the reaction was inferred from repeated experiments in the absence of a sensitizer or of light and by using well known singlet oxygen quenchers (DABCO) when no reaction was found to take place⁸. However, when the reaction was performed in the presence of dilute solutions ($\approx 10^{-4}$ M) of calix[*n*]arenes (synthesized and characterized by the reported procedures⁹), the same products (as those formed in the absence of calixarenes) were obtained but the rates of photooxygenation for the first 20% of the reaction were found to increase markedly as compared to a situation when no calixarene was added. Similar photooxygenation experiments without 4,5-diphenylimidazolones revealed no reaction even after 20 h and calixarenes were recovered unchanged. Repeated experiments proved that rates of photooxygenation of imidazolones varied with the structure of calixarenes, the size of the pendant alkyl group (Fig. 1) and the structure of the substrate (2). For example, addition of a small amount of *p*-

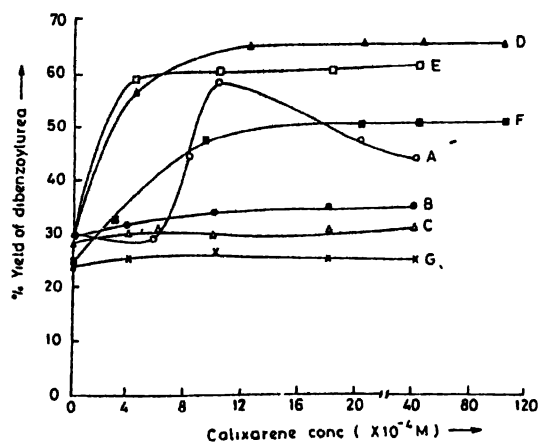


Fig. 1. Effect of different concentrations of calix[*n*]arenes on the yield of dibenzoylurea (A) *p*-*tert*-butylcalix[4]arene, (B) *p*-methylcalix[5]arene, (C) tetrahydroxycalix[4]arene, (D) *p*-octylcalix[6]arene, (E) *p*-*tert*-butylcalix[6]arene, (F) *p*-*tert*-butylcalix[8]arene, (G) octaacetate of *p*-*tert*-butylcalix[8]arene

octylcalix[6]arene did not affect the rate of photooxygenation of 1,4,5-triphenyl- and 1,3,4,5-tetraphenylimidazolin-2-ones while some of the imidazolin-2-ones reacted so fast that the effect of added calix[*n*]arenes on their photo-oxygenation could not be studied conveniently with the facilities available. Therefore, for a detailed study, a moderately reactive 4,5-diphenylimidazolone-2-one was chosen as the substrate for photooxygenation.

To semiquantify the effect of calix[*n*]arenes⁷ on photooxygenation of 4,5-diphenylimidazolone, the reaction was carried out for a fixed interval (20 min) and the product was isolated and its yield determined from comparison with a concentration-optical density (at λ_{\max} 245 nm) calibration curve of the product (diphenylbenzoylurea) (Perkin-Elmer-Lamba 3B spectrophotometer). The yield of the product obtained in other reactions performed by adding varying concentrations of calix[*n*]arenes to a solution of 4,5-diphenylimidazolone was calculated by using this calibration curve while keeping identical conditions of photoflux, solvent, reaction time and volume of solution to be photooxygenated in all the experiments. Computation of reaction rates (assuming first order reaction with respect to both the reactants) indicated that they follow the same pattern as that of the variation in yield of the product.

The results (Fig. 1) reveal that addition of calix[*n*]arene enhances the rates of photooxygenation of 4,5-diphenylimidazolones. It was observed that the effect of calix[*n*]arene addition is dependent upon the chain-length of the alkyl group in the same series of calixarenes. For instance, in the calix[4]arene series, the rate enhancement was maximum when the alkyl group was octyl as compared to the case when it was hexyl, *t*-butyl, methyl or hydrogen. The cavity dimensions of calix[*n*]arenes were also observed to have differential effects. For example, with a fixed R (*p*-*tert*-butyl), calix[6]arenes were found to be better than calix[4]arenes and calix[8]arenes for rate enhancement though all the used calix[*n*]arenes influenced the photooxygenation under identical conditions. That only the cyclic macrocycles represented by calix[*n*]arenes were effective for rate enhancement, was inferred from the effect of addition of open-chain analog (4) which neither altered the rate nor the major product in the photooxygenation studied⁷. It is interesting to note that the nature of % yield vs calixarene concentration plot is different in the case of *p*-*tert*-butylcalix[4]arene from those of other calixarenes. The mechanism of action of

calix[4]arenes seems to be different from the one involved in the case of other calixarenes. The nature of this apparent anomaly is being investigated further but unpublished results reveal that there may be self-aggregation in calix[4]arenes. Though the reaction is being investigated further, it is important to report that rate enhancements were not observed when completely acylated calixarenes (e.g. *p*-*tert*-butylcalix[8]arene octaacetate) were introduced during photo-oxygenation which suggests the involvement of calixarene hydroxyls in some manner.

Acknowledgement

The authors thank the Departments of Science and Technology and Biotechnology, New Delhi, for financial assistance.

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