

LIPOPHILIC SULFONIC ACIDS AS THE PHASE TRANSFER CATALYSTS  
IN THE HYDROLYSIS OF p-NITROPHENYL ACETATE

Waichiro Tagaki, Noriko Iwamoto, Kenji Suzuki, and Seizo Tamagaki  
Department of Applied Chemistry, Faculty of Engineering, Osaka  
City University, 3-138 Sugimoto 3-chome, Sumiyoshi-ku, Osaka 558  
Japan

Lipophilic dialkoxybenzenesulfonic acids effectively catalyze the acid-hydrolysis of p-nitrophenyl acetate in a benzene-H<sub>2</sub>O two-phase system. Examination of the effects of varying the alkyl-chain length and catalyst concentration on the rate suggests the reaction involving some micellar aggregates of these catalysts in the organic phase.

Since the pioneering works of Makosza<sup>1)</sup> and Starks,<sup>2)</sup> interest and activity in phase transfer catalysis (PTC) which mediates two-phase reactions have grown dramatically over the past decade. As part of our interest in the developments and uses of lipophilic biphasic catalysts, we have recently reported the application of lipophilic catalysts for the hydroxylation of benzene in an aqueous benzene system.<sup>3)</sup>

This report describes the successful use of highly lipophilic sulfonic acids for the hydrolysis of p-nitrophenyl acetate (PNPA). In spite of considerable activity in ester hydrolyses, there thus far have been known virtually no report of an effective PTC catalyst for acid-hydrolysis.<sup>4),5)</sup>

The reaction was conducted in a benzene-water (10:1 v/v %) two-phase system at 70°C in the presence of a series of sulfonic acid derivatives (I's and II's). Their catalytic activity was tested by using PNPA as a standard

substrate and was compared to each other under the identical conditions. The results are shown in Table I. In every case examined, the reaction is first-order in ester and proceeds without the influence of stirring rates on reaction kinetics, demonstrating that the reaction takes place in the organic phase but not at the interphase.

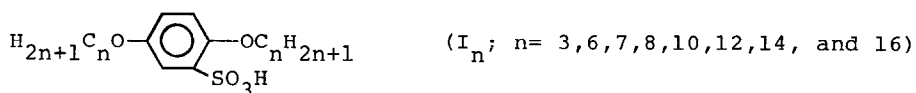


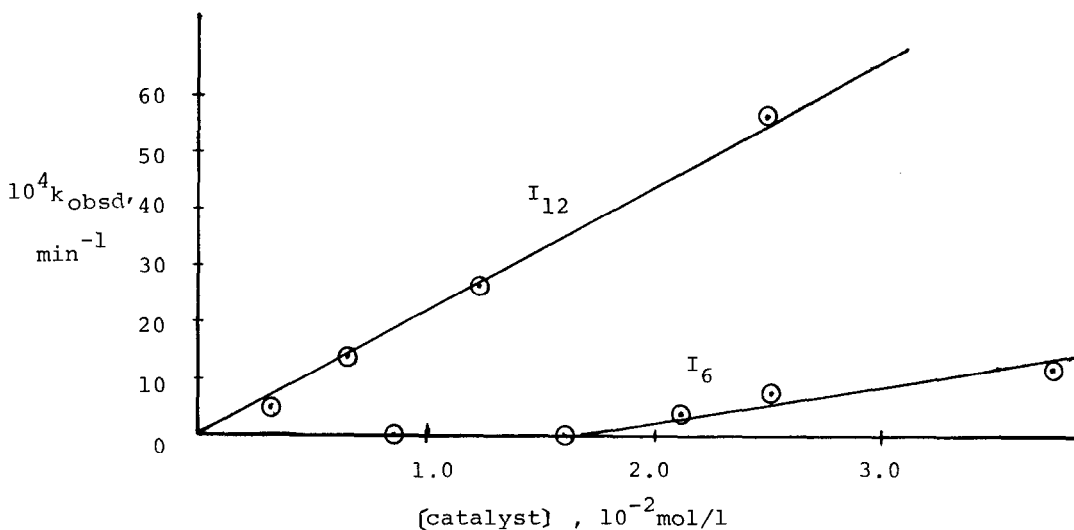
Table I. Rate constants for the hydrolysis of p-nitrophenyl acetate at 70°C in benzene-H<sub>2</sub>O [PNPA]=0.125 mol/l; [catalyst]=0.025 mol/l in benzene

catalyst	$10^4 k_{\text{obsd}}, \text{ min}^{-1}$
H <sub>2</sub> SO <sub>4</sub>	0
II <sub>1</sub>	0
II <sub>12</sub>	8.1
I <sub>3</sub>	0
I <sub>6</sub>	7.1
I <sub>7</sub>	19.4
I <sub>8</sub>	29.5
I <sub>10</sub>	35.2
I <sub>12</sub>	55.6
I <sub>14</sub>	52.1
I <sub>16</sub>	55.9

In general, as is readily apparent from Table I, hydrophilic catalysts such as  $\text{H}_2\text{SO}_4$ ,  $\text{II}_1$ , and  $\text{I}_3$  exhibit no catalytic activity. However, the reaction with the catalysts (I's) except  $\text{I}_3$  is enhanced and increased with increasing alkyl-chain length of these catalysts and the maximum activity is attained with catalysts bearing alkyl-chains more than 12 carbon atoms.<sup>6)</sup>  $\text{I}_6$  is as effective as is a typical surfactant with only one long chain, dodecylbenzenesulfonic acid ( $\text{II}_{12}$ ).

Given in Fig. I are the data illustrating the effect of altering the quantity of added catalysts. It is apparent that, unlike  $\text{I}_{12}$ ,  $\text{I}_6$  does not catalyze the reaction until the catalyst concentration reaches 0.02 mol/l. This finding together with the result of the alkyl group effect on the rate obviously suggest the micellar aggregates of inverted type being involved in the benzene phase. It is a well known fact that, with decreasing bulk of alkyl group in surfactant, the critical micellar concentration (CMC) increases.<sup>7),8)</sup>

Fig I. The dependence of the rate on catalyst concentration<sup>9)</sup>



Thus, more lipophilic acids ( $\text{I}_{12}$ ,  $\text{I}_{14}$ , and  $\text{I}_{16}$ ) are not only far more effective than hydrophilic ones for ester hydrolysis, but also are synthetically more applicable as phase transfer catalysts than commercially available dodecylbenzenesulfonic acid because they exhibit little or no ability of emul-

sifying the reaction mixture which makes the work-up difficult. It may also be advantageous that those catalysts can be readily prepared by the alkylation of inexpensive hydroquinone. Further studies on the amphiphilic properties of these unique acids ( $I_{12}$ - $I_{16}$ ) are in progress together with the synthetic application to other substrates or related electrophilic reactions.

#### References

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- 6) The majority of catalysts ( $I$ 's except  $I_3$ ) is solubilized in the organic phase.
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- 9) Unless noted otherwise, the reaction conditions were the same as those described in Table I.

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