Convenient Method of Deactivating Reactive Esters under Micellar and Microemulsion Media

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Deactivation of reactive esters or phosphates used for pesticides or chemical warfare (CW) agents was widely studied from the viewpoint of the environmental protection and the disposal of stockpiled chemical weapons.[1,2] Various nucleophilic catalysts for the cleavage of reactive substrates were tested in organized assemblies such as micelle, vesicle, or microemulsion due to the inherent low solubilities of organic toxic chemicals together with the rate enhancements by concentration effect.[3-12] In particular, *o*-iodosobenzoate and a few metal complexes showed excellent reactivities for the cleavage of reactive ester simulants along with high turnover capabilities. Polymer-supported catalysts were also introduced for the practical purposes of recovery, recycle, and long term storage.[13,14]

Although the catalysts developed so far are effective for treatment of small spill, disposal of bulk agents should be handled in different ways, considering such factors as safety of the process, remaining reagents after the process, by-products, fume, cost of maintenance, and so forth. To overcome the difficulties in practical applications, we propose an electrolytic hydrolysis method which utilizes hydroxide ions generated at the cathode from the electrolysis of water. As shown in the equation below, hydroxide ions are mainly produced around the cathode and disappear by recombining with proton ions coming from the anode.[15] Actually, we found that aqueous solution with phenolphthalein indicator became pink only around the cathode and pH near the cathode went as high as 12 during the electrolysis of water. Thus reactive substrates on surfactant aggregates can be hydrolyzed near the cathode where plenty of hydroxide ions are continuously produced while electric current flows. From practical points it is advantageous that pH and ionic strength of the solution need not to be adjusted unlike catalytic hydrolysis, and maintenance of electrolytic hydrolysis system costs much less than that of catalytic system. Utilization of electricity is not new in the area of organized assemblies. For example, Menger has applied AC field in electroformation method for preparing giant unilamellar vesicles (GUV).[16] Although we designed and tested a few types of electrolytic hydrolysis system, correct cleavage rate constants could be measured with the system shown in Figure 1. In this paper, we would like to report the results for the deactivation of reactive esters under micellar and microemulsion media by the electrolytic hydrolysis system.

Cathode Reaction: $4\,H_2O + 4\,e^- \rightarrow 2\,H_2 + 4\,OH^-$

Anode Reaction: $2\,H_2O \rightarrow O_2 + 4\,H^+ + 4\,e^-$

Total Reaction: $6\,H_2O \rightarrow 2\,H_2 + O_2 + \underline{4\,H^+ + 4\,OH^-}$

$4\,H_2O$

Net Reaction: $2\,H_2O \rightarrow 2\,H_2 + O_2$

As shown in the schematic of electrolytic hydrolysis system (Figure 1), hydrolysis was directly observed in the cuvette spectrophotometically. In the beginning hydrolysis was monitored by circulating reaction mixture between the reaction vessel and a flow cell, but slow flow rate made it difficult to correctly measure the faster cleavage rate. In this system true cleavage rate could be measured by carrying out the hydrolysis in a cuvette. Two 0.3 mm-diametered pt wires were used as electrodes and were immersed in a 1 cm quartz cell in a way that did not interfere the light path of the UV-VIS spectrophotometer (HP 8453 A). Two electrodes were separated by 1 mm and connected to a rectifier (Jeong Woo Elecletric Model JR-1110) which converted 110 V AC to DC. DC voltage and current were variously controlled and recorded by installed meters. Deionized water instead of buffer solution was used for the hydrolysis because pH should be freely varied depending on the applied voltage during electrolysis.

Although some hydrogen and oxygen gas evolved during the electrolyses at the cathode and the anode respectively, the monitored reaction profile showed good correlation without interrupting the progress of reaction. With the reactor system ready, cleavage of the reactive ester simulants such as *p*-nitrophenyldiphenylphosphate (PNPDPP), and *p*-nitrophenylacetate (PNPA) were tested, while varying the concentration of surfactant, voltage, the concentration of substrate, and the kinds of electrolytes. As a surfactant, non-ionic Brij-58, anionic SDS, and cationic CTAB were used. Test results are summarized in Table 1. As the applied voltage was raised from 1 V to 10 V, the rate constants also

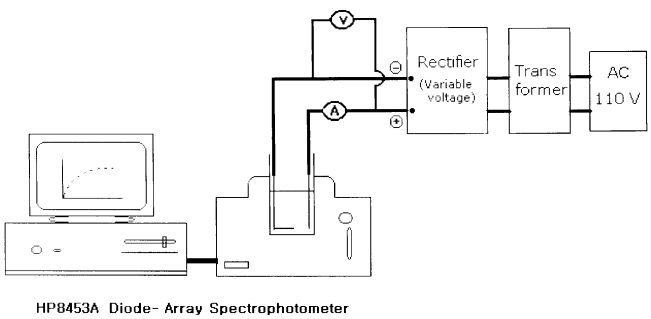

Figure 1. Schematic presentation of the electrolytic hydrolysis system.

Table 1. Observed Rate Constants for the Cleavage of Reactive Esters in Micellar Condition[a]

[surf.], mM[b]	substrate	10^5 [substrate], M	voltage, V[c]	k_{ψ}, s^{-1}	$t_{1/2}$, min
1	PNPDPP	2.5	8	0.0022	5.3
3	PNPDPP	2.5	8	0.0037	3.2
5	PNPDPP	2.5	8	0.0053	2.2
10	PNPDPP	2.5	8	0.0090	1.3
3	PNPDPP	5.0	8	0.0064	1.8
3	PNPDPP	10	8	0.0055	2.1
3	PNPDPP	2.5	3	0.0012	9.6
3	PNPDPP	2.5	5	0.0030	3.8
3	PNPA	2.5	8	0.010	1.2
3	PNPA	5.0	8	0.014	0.83
3[d]	PNPDPP	2.5	8	0.0012	9.6

[a]Pseudo-first-order rate constants were the average of two independent experiments. 10 mM KNO_3 was added as an electrolyte. Correlation was better than 0.99. Hydrolysis was not observed for Brij-58 surfactant. [b]CTAB was used as the surfactant. [c]The currents corresponding to the voltages are 1 ± 0.2 mA for 3 V, 3 ± 0.2 mA for 5 V, and 10 ± 0.2 mA for 8 V. [d]SDS was used as the surfactant.

increased. The DC voltage was kept under 10 V because the cell was too heated to control at above 10 V. With more substrates, any significant decreases in rate constants were not observed. KNO_3 was used as an electrolyte and selection of other electrolytes such as $NaNO_3$, NaCl, and Na_2SO_4 did not improve the cleavage rates. Figure 2 shows that pseudo-first-order rate constants increase linearly with the concentration of CTAB. Cleavages of PNPDPP and PNPA were not observed at [CTAB] < 0.7 mM which was below the critical micelle concentration (CMC) of CTAB (0.9 mM),[17] and foam formation prohibited further measurement at [CTAB] > 10 mM. As for SDS, rate constants should also be measured at less than 10 mM. In order to check the effectiveness of the system against various toxic chemicals we set the standard reaction condition as 3 mM CTAB, 10 mM KNO_3, and 8 V. In control experiments where one of the essential factors such as applied voltage, surfactant, and electrolyte was absent, hydrolysis was not observed.

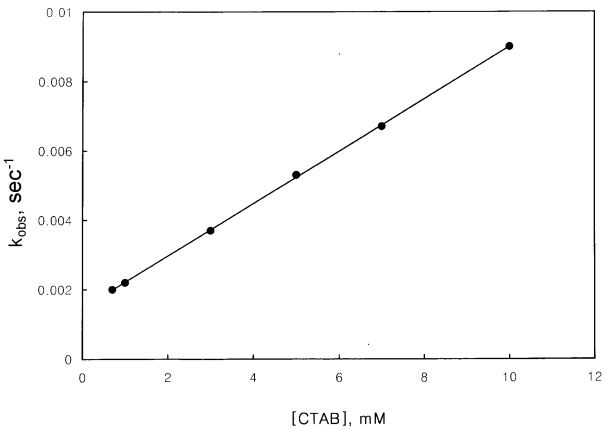

Figure 2. Pseudo-first-order rate constants *vs*. CTAB concentration for the cleavage of PNPDPP under micellar conditions.

Because hydroxide ions were more tightly attracted to the Stern layers of cationic micelles where most of the substrates reside, CTAB micelles brought higher chances of collisions between hydroxide ions and the substrates. The cleavage rate was slowed by *ca*. 3 times with anionic SDS micellar solution and no cleavage was observed in nonionic Brij-58 micellar solution under comparable conditions. Therefore, most of the experiments were carried out in CTAB micellar solution. In Table 1, cleavage rate was shown to be controlled by both voltage and concentration of CTAB, but the kind of electrolyte and it's concentration did not affect the rate. We interpret the results as follows. By Ohm's and Faraday's law higher voltage produced higher current and more hydroxide ions around the cathode, which leaded to a faster cleavage. In the electrolytic hydrolysis system hydroxide ions appeared near the cathode and micelles carrying the substrates should move closer to the cathode for the cleavage reaction to occur. Thus more micellar carriers were formed with the increase of CTAB concentration and made the reaction between hydroxide ions and the substrates more probable. But we were not able to measure the highest rate constant which could be at [CTAB] > 10 mM due to foam formation.

As hydroxide ions were continuously produced, addition of more substrates did not slow the cleavage reaction, and reduced activity of reactants was not observed in this system. More substrates could be dissolved in microemulsion (ME) system, which was very important in practical application for the disposal of large quantity of toxic chemicals.[18,19,20] Therefore, we tried the electrolytic hydrolysis system with oil in water (o/w) ME that was generally composed of a surfactant, a cosurfactant, an organic solvent and water. We selected a combination of CTAB, *n*-butanol, and cyclohexane as a surfactant, a cosurfactant, and an oil, respectively, because it was one of the proven ME systems in decontamination area.[21] Deionized water was used as aqueous component instead of buffer which was used in other catalytic ME systems. Titration of surfactant/cosurfactant/oil mixture with water at various compositions provided ternary phase diagram and the clear and stable ME was used as the reaction media (see the composition in Table 2). Gen-

Table 2. Observed Rate Constants For the Cleavage of Reactive Esters in Microemulsion[a]

Entry	Substrate[b]	Voltage, V[c]	k_{ψ}, sec^{-1}	$t_{1/2}$, min
1	PNPDPP	5	0.0022	5.3
2	PNPDPP	8	0.0038	3.0
3	PNPDPP	10	0.0068	1.7
4	PNPA	5	0.0057	2.0
5	PNPA	8	0.0069	1.7
6	PNPA	10	0.0078	1.5

[a]Oil in water microemulsion was composed of 88% water, 10% CTAB/*n*-BuOH (1/1), 2% of cyclohexane by weight. [b]Substrate concentration was 2.5×10^{-5} M. Pseudo-first-order rate constants were the average of two independent experiments. 10 mM KNO_3 was added as an electrolyte. Correlation was better than 0.99. [c]The currents corresponding to the volatages are 2 ± 0.3 mA for 5 V, 5 ± 0.3 mA for 8 V, and 8 mA ± 0.3 for 10 V.

erally, cleavage rates in ME were slower than those in micellar solution, but in large scale detoxification lower reactivities could be acceptable, considering the higher solubilities of substrates in ME. Actually, the rate constants in our ME system had almost same order of magnitudes as those in micellar solution as shown in Table 2. In the best case, the pseudo-first-order rate constant went as high as 0.0068 sec^{-1} which was equal to an half life of 1.7 min and comparable to that in micellar solution. The cleavage rates in ME could be also increased by voltage adjustment and we found that ME was more applicable to decontamination area, considering the high solubilizing capacity and comparable reactivity to micellar solution.

In conclusion, we designed and assembled an electrolytic hydrolysis system which can directly observe and perform the cleavage reaction, and successfully tested the new method in the cleavage of reactive ester simulants. In cationic CTAB micellar solution, the half life is less than 5 min, which meets the requirement of the half-life within a "cigarette break" for the decontamination of toxic agents.[22] In ME the half lifes range from 1 to 5 minutes, which is also a encouraging result, thinking of the large dissolving capacity. Electrolytic hydrolysis system has some advantages over catalytic hydrolysis system. (1) pH of the reaction mixture does not have to be adjusted to basic condition with buffer as in some catalytic systems. (2) Slow turnover of the catalysts does not matter in our system, because the hydroxide ions are continuously produced. (3) Excess hydroxide ions disappear after the reaction by combining with proton ions generated simultaneously at the anode. (4) Evolved hydrogen and oxygen gas can be used as energy source if the electrolytic hydrolysis system runs in industrial scale. (5) This system is very competitive in the cost of assembly and maintenance, comparing with synthetic catalytic systems which are not applicable to the large scale detoxification due to cost, stability of catalyst, and disposal of remaining reactants, etc. (6) Electricity, a convenient, cheap, and safe energy source, is used in the system that can be flexibly designed in size and capacity depending on the demands. Developing safe and efficient methods for detoxification is very important and urgent under the circumstance of potential threat from chemical warfare agents and toxic wastes pollution. Now we are testing the system for the decontamination of other reactive chemicals.

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