

Status of organochlorine (DDT) pollutants and steps toward electrocatalytic reductions*

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Abstract: The accumulation of DDT in the environment over the years is a major concern in the world today. The extent to which DDT may be absorbed and translocated from ¹⁴C-*p,p'*-DDT contaminated soils into cowpea plant tissues, and the variation of uptake of *p,p'*-DDT by the plants in relation to the dissipation of *p,p'*-DDT in the soils was studied using a radioisotope technique. Significant absorption and accumulation of residues was observed for the cowpeas grown in two different sites, coastal and highland regions. The degree of uptake varied with soil type and growing conditions. Further results indicated that the higher the water retention by the soil the higher the rate of evaporation of *p,p'*-DDT. Coastal region *p,p'*-DDT soil samples showed DDE to be the major metabolite. DDT residue in the plants ranged from 0.94 to 7.73 mg/kg, while that in the soils ranged from 88.9 to 32.0 mg/kg. Preliminary electrode reactions indicated lowering of overpotential for reduction of *p*-chlorophenol by about 1 V, using copper phthalocyanine tetrasodium tetrasulfonate as the catalyst in microemulsion. Microemulsions and appropriate catalysts are a promising system for the decomposition of DDT.

INTRODUCTION

DDT [1,1-bis(*p*-chlorophenyl)-2,2,2-trichloroethane] is one of the pesticides known to build up in the environment, waters, aquatic life, and animal tissues because it is not broken down (metabolized) rapidly. Due to its persistence in the environment, DDT is one of the most severely limited pesticides in use. However, accumulation of DDT in nontarget species and the decline of some are some of the main reasons for placing severe limitations on its use (banned in the United States in 1973). For instance, following the introduction of DDT there was a general decline in arthropod variety in forested ecosystems [6,7].

Our original aim was to explore the possibility of detoxifying organohalide pollutants, found in nontarget areas. However, we decided first to establish that DDT is actually absorbed by plants and related ecosystems. This article is a review of this work, where various parameters were determined to provide evidence of DDT pollutant in nontarget areas. Extensive use of pesticides has made many countries self-sufficient in food production [1]. However, this has led to accumulation of pesticides in the environment and destruction of nontarget organisms such as birds [2–4]. One of the commonly used pesticides includes formulation of chlorinated hydrocarbons. 1,1-bis(4-Chlorophenyl)-2,2,2-trichloroethane (DDT) is a classic organohalide pesticide. It has been banned in many countries owing to its persistence in the environment and side effects on living organisms. However, DDT is still being used in countries within the tropics owing to health implications, particularly malaria infections. Bacterial decomposition and chemical hydrodechlorination of DDT take place very slowly [5]. Thus, there is urgent need to devise methods of decomposing DDT in the environment.

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Apart from persistence of DDT in the environment, other factors have been found to effect dissipation of organohalides. These include growing conditions of the plant [8], temperature, and soil and pesticide type [9].

In the present work, our goal was to establish the extent of absorption of DDT by cowpea plants, and determination of DDT metabolites under field conditions. No detailed information exists on the effect of DDT uptake on the growing rate of plants, particularly on plants grown within the tropics. Thus, it was also the aim to investigate in detail how temperature influences DDT dissipation in soils, used to grow cowpeas. The soil temperature tested ranged from -20 to 120 °C and an average room temperature of 21 ± 3 °C.

In this work, the metabolites of DDT, over a period of 292 days, were determined. Besides, studies were performed to show the effect of other factors such as soil type and climatic conditions on dissipation of *p,p'*-DDT in the two areas considered [10].

Following this work, it was clear that there is need to clean up the environment, thereby removing toxic residues like DDT. Electrolytic methods, using appropriate catalyst and solution media, can stepwise remove functional groups like halogen, thereby replacing it with hydrogen and ultimately rendering the pollutant to be much less toxic [11,12]. Previously, such electrode processes were carried out using organic solvents, which are often toxic and expensive, in addition to disposal problems. Our lab has embarked on using aqueous surfactant media, which are nontoxic and environmentally friendly, for electrochemical detoxification of organohalide pollutants. The aqueous surfactant media that we have been using range from simple micellar solutions [12,13] to microemulsions [14–16].

After this general introduction, we first discuss the absorption of DDT by growing cowpea plants and then discuss briefly preliminary results on the stepwise removal of chlorine from related organohalides in a bicontinuous microemulsion. The idea here is that if chlorine can be stepwise removed from organohalides, then the possibility of detoxifying DDT residue in a given environment may exist. The use of appropriate catalyst and media for detoxifying DDT was tried. Overall, this paper reviews DDT uptake by plants and attempts toward dechlorination of DDT in microemulsions.

ABSORPTION AND TRANSLOCATION OF DDT

The results obtained from the cowpeas growing in DDT-contaminated soils demonstrated that DDT was absorbed and translocated into plants grown in soils containing DDT residues (Tables 1 and 2). This, perhaps, is not only as a result of absorption and translocation processes, but also due to adsorption of the pesticide that might occur on the plants internally and externally. Moreover, the results demonstrated strong evidence that the amount of DDT taken up by the plants with time increases with plant age and weight, regardless of the soil type, climatic, and other growing conditions (Tables 1 and 2). Furthermore, the analyses of the bound and extractable residues indicated that the percentage of bound residue increases with increase in age of the plant, implying that older plants tend to retain a higher per-

Table 1 Amounts of DDT residue recovered from dried Mombasa plants.

Sampling time (days)	Total ($\mu\text{g/g}$)	Extractable ($\mu\text{g/g}$)	Bound ($\mu\text{g/g}$)	Ratio of extractable to bound
15	0.945 ± 0.04	0.80 ± 0.066	0.084 ± 0.008	9.5
30	1.53 ± 0.01	1.28 ± 0.019	0.18 ± 0.002	7.1
45	3.44 ± 0.11	2.86 ± 0.35	0.48 ± 0.011	5.9
60	3.79 ± 0.017	3.07 ± 0.14	0.59 ± 0.010	5.2
75	7.88 ± 0.240	6.24 ± 0.035	1.36 ± 0.014	4.6
90	7.77 ± 0.211	6.11 ± 0.038	1.39 ± 0.003	4.4

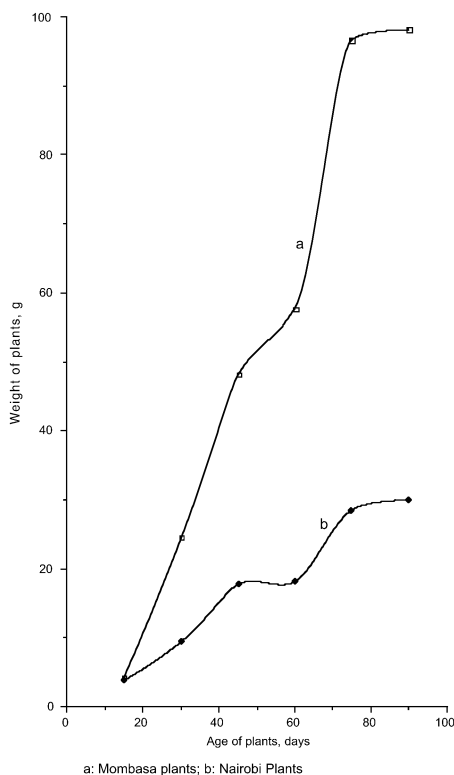
Table 2 Amounts of DDT residue recovered from dried Nairobi plants.

Sampling time (days)	Total ($\mu\text{g/g}$)	Extractable ($\mu\text{g/g}$)	Bound ($\mu\text{g/g}$)	Ratio of extractable to bound
15	1.14 ± 0.030	1.03 ± 0.011	0.080 ± 0.002	12.9
30	1.92 ± 0.017	1.73 ± 0.016	0.160 ± 0.002	10.8
45	2.30 ± 0.007	2.04 ± 0.010	0.214 ± 0.003	9.50
60	2.25 ± 0.011	1.96 ± 0.018	0.252 ± 0.003	7.80
75	3.10 ± 0.010	2.63 ± 0.012	0.366 ± 0.004	7.20
90	3.24 ± 0.007	2.74 ± 0.014	0.411 ± 0.007	6.70

centage of the residues as nonextractable (bound). Mombasa plants exhibited high growth rate compared to Nairobi plants (Fig. 1).

From the comparison of the data obtained from the two sites (Tables 1 and 2), the degree of uptake was found to depend on the growth rate and soil composition, but not on soil residue concentration. The results demonstrated that height, weight, and age make the tendency of the plants to take up *p,p'*-DDT greater. Even among the plants of the same site, there was always a high degree of DDT uptake for tall and heavy plants. The best example is the trend of residue accumulation observed for the plants aged more than 75 days. In both sites, the residue level tended to level off after 75 days where there was no much difference in the size of the plants (Tables 1 and 2).

In these experiments, the plant uptake of DDT residue increased with time despite the decrease in the concentration of the DDT residue in the soil (Fig. 2). This suggests that the concentration of DDT remaining in the soil is sufficiently high during the life span of the plant, which is 15 to 90 days.

**Fig. 1** Variation of weights of plant samples with time.

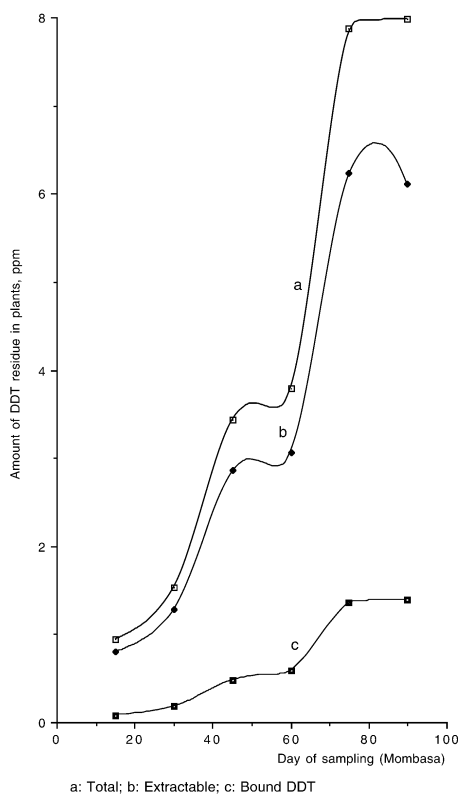


Fig. 2 Variation of DDT residue levels (Mombasa plants) with age of plant.

On the other hand, according to the experiment carried out for one sample, which has been analyzed for the determination of DDT residue in different parts of the plant, leaves, stems, and roots demonstrated significant differences for the three forms of residues (Table 3). This was done in order to obtain a true picture regarding the distribution of DDT in various parts of the plant. From the comparison of the data, the amount of DDT in the parts of the plant was found to be in the order of stems < leaves < roots. According to this limited data, the majority of the residue seems to be found in the roots, which actually accumulated five-fold concentration of either of the other two parts. This is attributed mainly to the variation in the degree of exposure of either part to the DDT residue. This agrees with previous work reported by Shahamet [9] in the case of oats. Although the roots were washed thoroughly with distilled warm water and even rinsed with methanol before analysis. It is likely that apart from the residue that enters the roots through similar biological processes that applies to the leaves and stems, some residue could still have remained adsorbed on the roots. Overall, terminal zones seem to

Table 3 Amount of DDT residue recovered from different parts of a plant sample.

Part of the plant	Total ($\mu\text{g/g}$)	Extractable ($\mu\text{g/g}$)	Bound ($\mu\text{g/g}$)
Leaves	3.42 ± 0.012	3.12 ± 0.074	0.17 ± 0.008
Stems	3.27 ± 0.009	2.88 ± 0.12	0.262 ± 0.007
Roots	19.56 ± 0.007	16.82 ± 0.098	2.197 ± 0.009

accumulate a significant amount of DDT relative to the middle parts. However, the percentage of extractable residue for the parts of the plant has been found to decrease in the same order. This is consistent with what is expected due to nutrient transport to leaves and stems from the roots. Further investigation on the effect of soil composition revealed that Nairobi soil, which has been found to have higher organic content than Mombasa soil, gave lower uptake of DDT by the plants. This observation compares favorably with what was reported previously [17], regarding the phytotoxicity of lindane, where organic rich soils were found to cause the least effect and it was directly related to the organic matter content in the soil. Moreover, this result suggests that the presence of high organic carbon content in Nairobi soil may have decreased the availability of *p,p'*-DDT ready uptake by the plants. This fact has also been manifested in the differences observed in terms of the amount of extractable residue, which were higher relative to the bound in Nairobi soil (Tables 1 and 2, column 4).

Effect of temperature on soil-DDT residues

Overall, the three forms of DDT residues (total, extractable, and nonextractable or bound) were affected significantly by temperature variation. The total and extractable residues decreased with temperature, whereas the bound residues increased with temperature (Figs. 3 and 4). This experimental result suggested that dissipation increased with temperature regardless of the soil type, until the total residue attains a limiting value close to that of the bound residue at a temperature beyond 120 °C. This demonstrated a boundary condition where a limited amount of extractable DDT residue exists. For Nairobi (highland) soil, which has a texture of clay soil, a temperature of 0 °C seems suitable for retention of DDT. However, Mombasa (coastal) soil, which consist of sandy soil, had maximum extractable DDT residue at -20 °C.

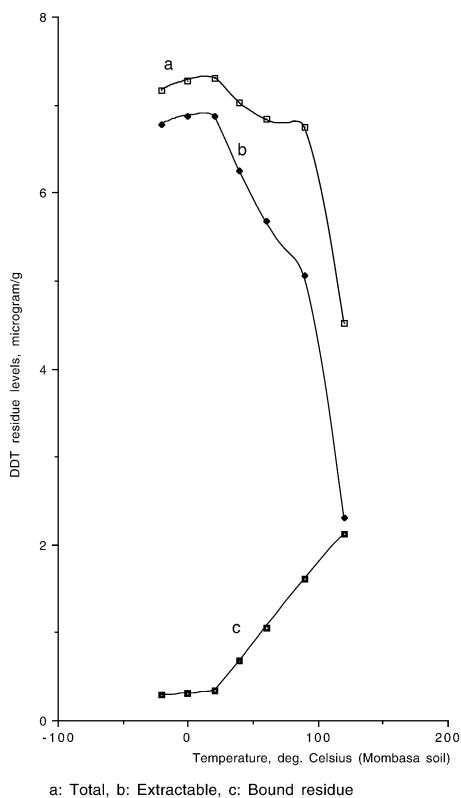


Fig. 3 Dependence of DDT dissipation on temperature, Mombasa soil.

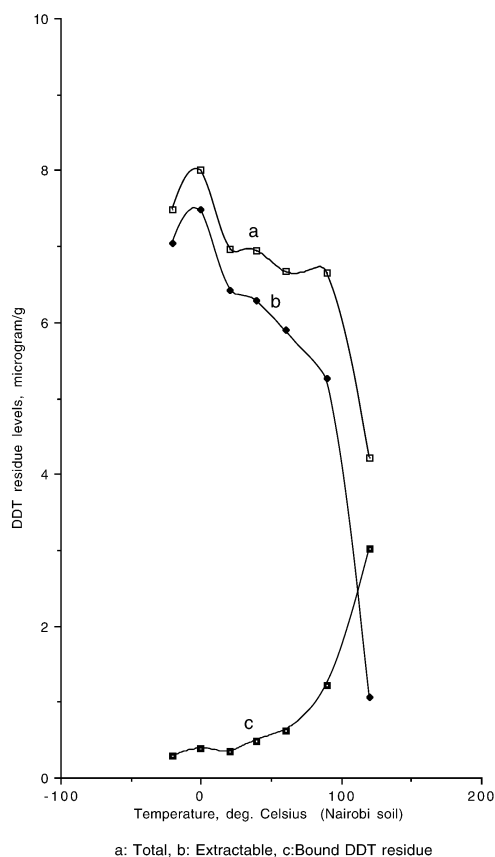


Fig. 4 Dependence of DDT dissipation on temperature, Nairobi soil.

Coastal soil-DDT samples

Identification of metabolites by GC (electron capture detector), GC-MS, and thin-layer chromatography (linear analyzer) of radioactive DDT embedded in soils (coast), over a period of 292 days, revealed the presence of *p,p'*-DDE as the major metabolite. The components of interest eluted in less than 10 min. The peak at retention time 6.4 min was due to 2,4-dimethyldecane other than that of DDD. Moreover, thin-layer chromatography indicated presence of only one metabolite. The absence of a significant amount of DDD is supported by the fact that DDT is degraded to DDD by microorganisms under anaerobic condition [18]. The present work was performed under aerobic conditions (open field). Over a period of 292 days, DDT decreased with time, whereas the amount of *p,p'*-DDE increased with time (Fig. 5). Figure 6 shows the decomposition pathways of DDT.

Having established the fact that DDT residue is found at the point of application (soil) and in the other parts of the growing and mature plant, we explored methods of detoxifying it.

REDUCTION OF ORGANOHALIDES AT THE ELECTRODE

We first investigated the electrode process for dehalogenation of organohalide, using microemulsion and copper phthalocyanine tetrasodium tetrasulfonate, CuPcTS^4 . The substrate used was *p*-chlorophenol.

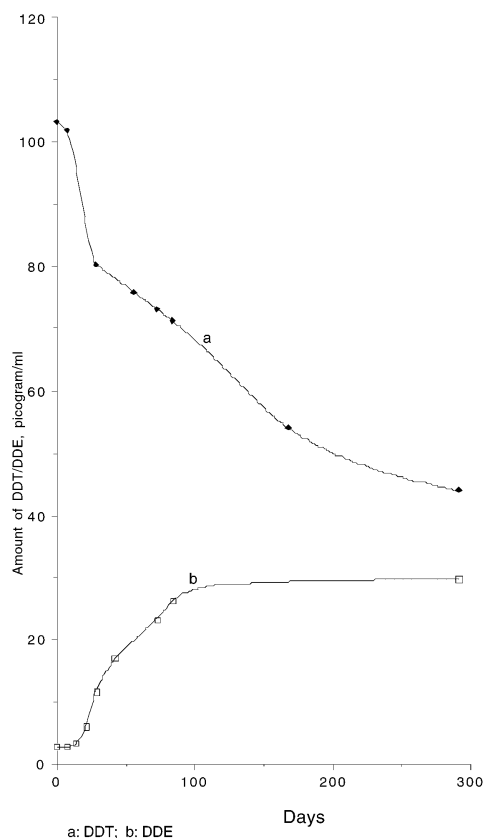


Fig. 5 Fate of DDT in coastal soil samples over a period of 292 days.

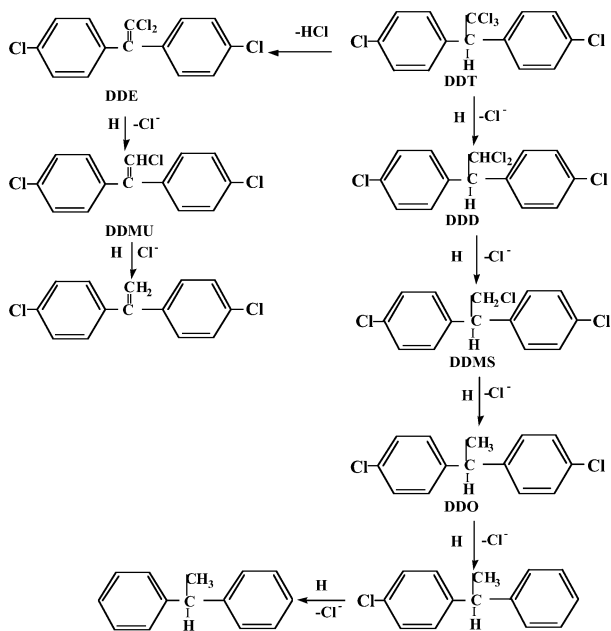


Fig. 6 Reduction pathways of DDT.

Cyclic voltammetry experiments for Cu(II)PcTS^{4-} revealed two reduction peaks involving diffusion and adsorption on the glassy carbon electrode. At low scan rates, two diffusion-controlled peaks were observed in acetonitrile–water solution at -0.65 and -1.4 V vs. SCE. As the scan rate was increased, at least one additional peak appeared at potentials more positive than the second diffusion peak (Fig. 7). On addition of *p*-chlorophenol (substrate) to the CuPcTS^{4-} solution, the second wave at -1.10 V vs. Ag/AgBr showed a marked increase in peak current (Fig. 8; a = catalyst, b = catalyst + substrate). This is due to regeneration of the CuPcTS^{5-} or CuPcTS^{4-} at the surface of the electrode in the presence of added *p*-chlorophenol. The catalytic efficiency $[i_{(c+s)}/i_c]$ was greater than 1.3 in the range of scan rates employed. In pure acetonitrile solution, *p*-chlorophenol alone gave two irreversible reduction waves centered around -0.7 and -2.1 V vs. Ag/AgBr, respectively. During the electrocatalytic

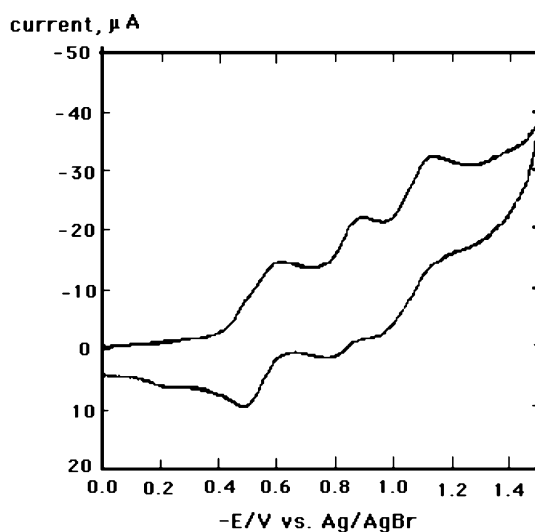


Fig. 7 Cyclic voltammogram of $0.2 \text{ mM CuPcTS}^{4-}$ in acetonitrile/water (1:1) at 100 mVs^{-1} .

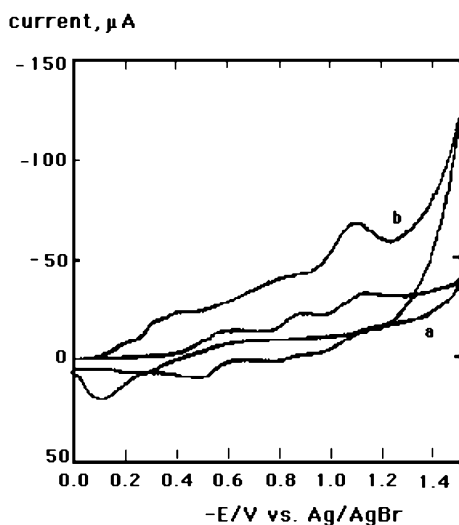


Fig. 8 Electrocatalytic reduction of *p*-chlorophenol by $0.2 \text{ mM CuPcTS}^{4-}$ in acetonitrile water (1:1) at 50 mVs^{-1} . Curves “a” and “b” correspond to reduction of CuPcTS^{4-} in absence and presence of $2 \text{ mM } p\text{-chlorophenol}$, respectively.

reduction experiment. It is the second wave of the catalyst that increases, suggesting that in the presence of catalyst, *p*-chlorophenol is reduced at around -1.10 V vs. Ag/AgBr. Thus, a lowering of overpotential of about 1.0 V is obtained for the decomposition of *p*-chlorophenol. Similar experiments for catalytic reduction of *p*-chlorophenol by CuPcTS⁴⁻ in microemulsion gave low catalytic efficiencies, compared to acetonitrile–water solutions. The next phase of our research work is to use appropriate catalysts and microemulsion media for dehalogenation of DDT substrate.

Moreover, attempts to optimize the reaction conditions aimed at lowering the energy for reduction and enhancing signals for detection of the organohalides in the environment.

CONCLUSION

Results of uptake of DDT by cowpeas suggest that a significant amount of DDT is absorbed by plants. Dehalogenation of organohalides by bicontinuous microemulsion is a promising media for electrode decomposition. The study indicated that 0.94–7.73% *p,p'*-DDT was taken up by cowpeas, over a period of 90 days. Moreover, the uptake was found to vary with the soil type, plant height, weight, and age; and temperature. Variation of temperature largely affects DDT dissipation, with bound DDT residue increasing with temperature relative to extractable DDT residues. Nairobi soil samples exhibited high water content, which influenced fast dissipation relative to Mombasa soil samples. DDE was found to be the major metabolite during degradation of DDT. While highlighting the danger of possible hazards owing to the plant uptake of DDT, this study could point to new pest-control measures.

Microemulsions provide a relatively environment-friendly aqueous media, which is not only less expensive but is also capable of solubilizing both polar and nonpolar solutes. The other attractive aspect of microemulsions is the ability to engineer the environment to enhance reaction rates or optimize specific conditions, such solubilization sites for a particular reaction and substrate. This manipulation of media is not possible with isotropic solvents. The bicontinuous microemulsion so prepared shows promise for enhanced rates for detoxification of organohalides and the possibility of electrosynthesis of the starting material, urgently needed by industry. From an economical point of view, it would be reasonable to have microemulsions with the minimum surfactant necessary for the task at hand. Attempts to achieve these goals promise profound research possibilities for the future.

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