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19. ABSTRACT (Continue on reverse if necessary and identify by block number)
Work has primarily been concerned with an in-depth investigation of mustard reactions with hydroxylic solvents and other more powerful nucleophiles and, to a lesser extent, development of polyether-bound "DFPase" and other catalysts for ester hydrolysis. The mustard work has led to a much better understanding of solvent effects on mustard reactivity and mustard reactions with nucleophiles.

In the polyether work it was shown that PEGs dramatically facilitate solution and reaction of mustard and mustard simulants.

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FINAL TECHNICAL REPORT

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A. Summary of Results

Our work has primarily been concerned with an in-depth investigation of mustard reactions with hydroxylic solvents and other more powerful nucleophiles and, to a lesser extent, development of polyether-bound "DFPase" and other catalysts for ester hydrolysis. The mustard work has led to a much better understanding of solvent effects on mustard reactivity and mustard reactions with nucleophiles. In the course of this work we have observed reaction of mustards by E2, S_N2, S_N1 and oxidative mechanisms and we have: (1) shown that some standard probes for nucleophilic involvement fail, and developed new probes; (2) characterized the transition state for mustard hydrolysis; (3) observed the first direct nucleophilic displacement reaction on a mustard derivative, and shown that most nucleophiles do not react with mustard by S_N2 attack; (4) applied phase transfer catalysis to oxidation and elimination reactions of mustards; (5) clearly demonstrated that mustard hydrolysis proceeds exclusively by neighboring sulfur participation to form a sulfonium ion; (6) prepared and characterized a series of mustard analogues including deuterated ones for mechanistic studies; (7) applied the Kamlet-Taft solvatochromic equation to mustard solvolysis and shown that the equation provides chemical insight as well as predictive power; (8) shown that ground-state rather than transition-state solvation can be the dominant factor in controlling mustard solvolysis rates.

In the polyether work we have shown that PEGs dramatically facilitate solution and reaction of mustard and mustard simulants and we have prepared PEG-bound versions of Moss' iodosobenzoate and of Menger's aldehyde hydrate catalysts. The latter compound, CH₃(OCH₂CH₂)_nOCH₂CH₂CHO is 70% hydrated in water, shows promise as a catalyst, and can readily be incorporated into surfactants or attached to solids. Also, we have examined PEG-modification of Tetrahymena thermophila "DFPase" and have found that the resulting enzyme is quite active and soluble in certain organic solvents; however, activity was very low in the organic solvents.

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B. Published Work Acknowledging Support of This Contract

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