Table I.[a,b] Rate Constants for the Reaction $X^- + CH_3Y \rightarrow CH_3X + Y^-$

X	Y	Rel rate	k_{rxn} (exptl)	k_{coll} (exptl)	k_{gs} (calcd)[c]	k_d (calcd)[d]	ΔH_{rxn}
F	Cl	10	$8.0 \pm 0.9 \times 10^{-10}$	$19 \pm 3 \times 10^{-10}$	14.8×10^{-10}	23.6×10^{-10}	−28.8
F	Br	8	6.0 ± 0.6	19 ± 3	14.8	22.5	−37.0
Cl	Cl	~0.1	$\sim 0.06 \pm 0.02$	18 ± 3	12.1	19.3	0
Cl	Br	1	0.80 ± 0.10	18 ± 3	11.6	17.7	− 8.2
CH_3S	Cl	1	0.78 ± 0.12	17 ± 3	11.1	17.8	−32.7
CH_3S	Br	2	1.4 ± 0.2	18 ± 3	10.5	16.0	−40.9

[a] Absolute rate constants expressed in cm^3 $molecule^{-1}$ sec^{-1}. [b] Heats of formation of ions from ref 9 and K. J. Reed, Stanford University (personal communication). [c] Reference 8b. [d] Reference 8c.

rapidly; the Cl^- then reacts somewhat more slowly to produce Br^-. Although the nucleophilic order, $F^- > CH_3S^- > Cl^-$, is maintained for both methyl chloride and methyl bromide, the relative nucleophilicity F^-:CH_3S^-:Cl^- changes from 10:1:0.1 toward methyl chloride, to 8:2:1 toward methyl bromide. Even more striking is the reversal in leaving group ability (LGA) dependence on the nucleophile. Thus the relative LGA of Cl^-:Br^- is 10:8 when F^- is the nucleophile, 1:2 when CH_3S^- is the nucleophile, and 1:10 when Cl^- is the nucleophile. Such reversals are not unique to the gas phase but have been observed in solution both for nucleophilicity[11] and LGA.[12] Steric effects in ion–molecule nucleophilic displacements have been previously suggested for both nucleophile[4b] and neutral reactant.[13] The variation of nucleophile size may be involved in the difference in absolute rate between F^- and CH_3S^-, but similar arguments seem unprofitable for comparison of Cl^- and CH_3S^-. In summary, it is impossible to establish any general scale or order of either nucleophilicity or leaving group ability without direct reference to the specific reaction.[14]

The data appear to be best correlated with a model in which the rate is relatively fast when the nucleophile and leaving group have similar properties. The phenomenon which we observe here is strongly reminiscent of that observed in solution and discussed by Bunnett.[15] Such synergistic or "symbiotic" behavior in which polarizable nucleophiles are relatively more effective in displacing polarizable leaving groups has also been discussed extensively by Pearson and Songstad.[16] The zeroth order explanation of the effect, in which resonance contributions to the transition state of the form $X\text{–}R\ Y^- \leftrightarrow X^-\ R\text{–}Y$ are maximized when X and Y are similar, breaks down for the identity reaction $Cl^- + CH_3Cl \rightarrow ClCH_3 + Cl^-$, which is quite slow. Thus, as suggested previously,[15] other effects such as exothermicity must be considered. The fact that this reaction is the slowest of those studied also suggests that energy barriers rather than orientations or steric effects are the key factors which affect the reaction rates. It is unreasonable to expect either of the latter effects to slow this reaction selectively. However, its lack of exothermicity would be expected to raise the activation energy relative to the exothermic reactions. Most other ion–molecule reactions have no apparent activation barriers.[17] Our experimental findings of a barrier are in agreement with theoretical calculations of SN2 reactions.[18]

The changes observed here are modest, but they are quite significant in terms of ion–molecule reaction rates which usually tend to be relatively insensitive to structural change.[19] Consequently, we feel that, because of the absence of solvent, these experiments provide strong evidence for the existence of interactive effects in nucleophilic displacement reactions.

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Stereoselective Epoxidation of Octadiene Catalyzed by an Enzyme System of *Pseudomonas oleovorans*

Sir:

Recent work from this laboratory has established that the "ω-hydroxylation" system of *Pseudomonas oleovorans* catalyzes the epoxidation of olefins[1–5] in addition to the previously known methyl group hydroxylation of alkanes and fatty acids.[6–12] Accordingly, the substrate 1,7-octadiene, which does not con-

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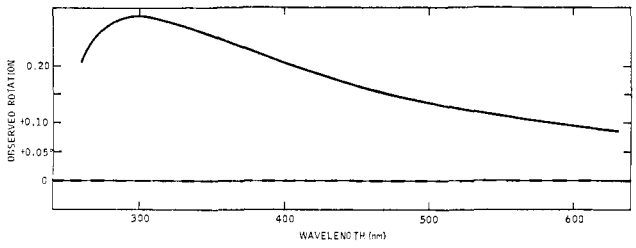

Figure 1. ORD curves for enzymatically produced (solid line) and chemically synthesized (dashed line) 7,8-epoxy-1-octene. The spectra were obtained using neat samples in a 1-mm path length cell.

tain a terminal methyl group, is converted exclusively to 7,8-epoxy-1-octene, and this product is in turn further oxidized to 1,2;7,8-diepoxyoctane. We wish to report that the epoxidation of octadiene catalyzed by this enzyme system proceeds with a high degree of stereoselectivity, and thus this reaction provides a clear example of enzymatic asymmetric synthesis.

The enzymatic epoxidation of octadiene on a preparative scale was carried out as follows. Three 3-l. Fernbach flasks, each containing 1000 ml of P_1 medium,[13] 10 ml of octane, 10 ml of fractionally distilled octadiene (bp 115°), and a 10 ml inoculum of a resting cell suspension of *P. oleovorans* strain TF4-1L[13,14] (approximately 10^9 cells/ml), were incubated for 20 hr at 30° on a gyrotory shaker at 200 rpm. The broths were then combined, extracted four times with 400-ml portions of hexane, and concentrated to 14 ml on a rotary evaporator. Gas chromatographic assay[2] showed that the recovered hexane contained a total of 2.5 g of 7,8-epoxy-1-octene. The product was purified by preparative gc using a 20 ft × 0.25 in. column of 10% Carbowax 20M on 80/100 Chromosorb W, maintained isothermally at 180°. Chemically synthesized 7,8-epoxy-1-octene was prepared from octadiene and *m*-chloroperbenzoic acid as described previously[2] and was purified using the same preparative gc procedure.

Mass spectral analysis gave parent peaks at *m/e* 126 and similar fragmentation patterns for both the enzymatic and chemical products, and both products gave identical peak area ratios when assayed by quantitative gc with 2-octanol as an internal standard.[2] The nmr spectra of the two products were identical and showed the typical terminal epoxide pattern: (δ, CCl_4) 2.70 (m, 1), 2.53 (d of d, 1), 2.26 (d of d, 1). *Anal.* Calcd for $C_6H_{14}O$: C, 76.14; H, 11.18. Found for enzymatic product: C, 76.01; H, 10.80. Found for chemical product: C, 75.61; H, 10.86.

Figure 1 shows the ORD curves obtained with neat samples of the enzymatic and chemical products. It is apparent that chemically synthesized 7,8-epoxy-1-octene is racemic, whereas the enzymatic product has a positive rotation, with $[\alpha]^{25}D$ +12.2°. By comparison, Coke and Shue[15] have recently reported an $[\alpha]^{16}D$ value of +12.4° for chemically synthesized (*R*)-(+)-1,2-epoxybutane. Thus, the enzymatic epoxidation of octadiene proceeds with a high degree of stereoselectivity to give preferentially (*R*)-(+)-7,8-epoxy-1-octene. The optical purity of the enzymatic product was determined by nmr using the chiral shift reagent tris[3-(trifluoromethylhydroxymethylene)-*d*-camphorato]europium(III) and was found to be greater than 80%.[16]

If the enzyme-catalyzed epoxidation reaction involves the concerted addition of molecular oxygen to the π-electron system of the double bond, then formation of (*R*)-(+)-7,8-epoxy-1-octene must involve attack at the *si–si* face of the prochiral octadiene molecule. By comparison, it has been pointed out that the formation of (−)-(2*R*,3*R*)-*trans*-epoxysuccinate from fumarate by some strains of *Aspergillus fumigatus* must involve attack at the *re–re* face of fumarate.[17] The factors which are important in determining the mode of substrate binding to the epoxidation system of *P. oleovorans*, and an understanding of the role such factors play in imparting an unusual substrate specificity[4] and stereoselectivity to the epoxidation reaction, remain to be delineated.[18]

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Synthesis and Molecular Structure of a Six-Coordinate Iron(IV) Complex with a New 1,1-Dithiolate Ligand

Sir:

Outstanding among the characteristics of the dithioacid and 1,1-dithiolate complexes[1] is the diversity of their redox properties. Numerous N,N′-substituted dithiocarbamate complexes which contain metal ions in unusually high formal oxidation states, such as Fe(IV),[2] Cu(III),[3] Ni(IV),[4] Mn(IV), Cr(IV),[5] Co(IV), Rh(IV), and Ru(IV),[6] have been described. Various reasons have been advanced for the apparently anomalous coexistence of a metal in a high oxidation state with the readily oxidizable sulfur ligands. Predominant among these are (a) delocalization of positive charge onto the ligand,[5,7] and (b) oxidative interligand interactions.[4] The importance of Fe–S bonding in numerous metalloproteins, such as the nonheme iron pro-

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