KINETICS OF EPOXIDATION OF α,β -UNSATURATED CARBONYL COMPOUNDS AND ENOL ESTERS BY DIMETHYLDIOXIRANE

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Abstract. Kinetic data for epoxidation of several series of α,β -unsaturated carbonyl compounds and enol esters by dimethyldioxirane in dried acetone are reported.

Introduction

Dioxiranes are efficient oxygen-atom transfer reagents for a wide variety of organic substrates.¹ Numerous synthetic transformations have been performed either *in situ*² or in isolated³ solution with these powerful oxidants. In particular, dimethyldioxirane has been found to be a versatile epoxidizing agent.¹ The reaction of dimethyldioxirane with a wide variety of alkenes including α,β -unsaturated compounds has been shown to be electrophilic and stereospecific.¹ For simple epoxidation, a concerted "spiro" transition state process⁴ has been generally accepted. Structural influences on alkene epoxidation have been extensively investigated.⁵ Limited kinetic data on epoxidation of α,β -unsaturated compounds with dimethyldioxirane are available.⁶ We report here the results of a kinetics study of the epoxidation of several series of α,β -unsaturated carbonyl compounds and enol esters by dimethyldioxirane in dried acetone.

Results and Discussion

The reaction of dimethyldioxirane (1) with a series of α,β -unsaturated ketones **2-14**, α,β -unsaturated esters **15-20** and enol esters **21-25** produced the corresponding epoxides in essentially quantitative yields (reaction 1). The epoxides were isolated and characterized by comparison of spectral data with

literature values. Kinetics studies were carried out in dried acetone at 23 °C employing UV techniques. The reactions were found to be of the first order with respect to both 1 and the substrates. The k_2 values determined under pseudo first order conditions with 10:1 or 1:10 ratios of dioxirane to substrate were identical. The kinetics results are listed in Table 1.

Table 1. Second Order Rate Constants for Epoxidation of α,β -Unsaturated Carbonyl Compounds **2-20** and Enol Esters **21-25** by Dimethyldioxirane **1** in Dried Acetone at 23°C.

Entry	α,β -Unsaturated Ketone	Structure	$k_2 \text{ M}^{-1}\text{s}^{-1}$
2	2-cyclopentenone		$2.1 \pm 0.1 \times 10^{-4}$
3	2-methyl-2-cyclopenten-1-one		$9.3 \pm 0.2 \times 10^{-4}$
4	3-methyl-2-cyclopenten-1-one		$3.0 \pm 0.1 \times 10^{-4}$
5	2-n-pentyl-2-cyclopenten-1-one		$7.2 \pm 0.1 \times 10^{-4}$
6	2-cyclohexen-1-one		$8.7 \pm 0.2 \times 10^{-4}$
7	2-methyl-2-cyclohexen-1-one		$2.4 \pm 0.4 \times 10^{-3}$
8	3-methyl-2-cyclohexen-1-one		$2.0 \pm 0.3 \times 10^{-3}$
9	4,4-dimethyl-2-cyclohexen-1-one		$8.9 \pm 0.3 \times 10^{-4}$
10	2,4,4-trimethyl-2-cyclohexen-1-one		$1.8 \pm 0.1 \times 10^{-3}$
11	(R)-(+)-pulegone		$1.2 \pm 0.1 \times 10^{-2} \text{ }^a$

12	phorone		$1.6 \pm 0.1 \times 10^{-2} \text{ b}$
13	2-cyclopentylidene-cyclopentanone		$3.9 \pm 0.4 \times 10^{-2}$
14	2-benzylidene-1-tetralone		$7.3 \pm 0.1 \times 10^{-3}$
15	5,6-dihydro-2H-pyran-2-one		$1.8 \pm 0.1 \times 10^{-4}$
16	2(5H)-furanone		$2.3 \pm 0.2 \times 10^{-3}$
17	α -methylene- γ -butyrolactone		$1.9 \pm 0.1 \times 10^{-3}$
18	ethyl sorbate		$2.4 \pm 0.1 \times 10^{-2}$ b,c
19	methyl methacrylate		$3.9 \pm 0.3 \times 10^{-4}$
20	methyl crotonate		$2.3 \pm 0.2 \times 10^{-3}$
21	vinyl acetate		$8.6 \pm 0.1 \times 10^{-3}$
22	vinyl benzoate		$1.1 \pm 0.1 \times 10^{-2}$
23	isopropenyl acetate		$1.7 \pm 0.1 \times 10^{-2}$
24	α -angelicalactone		$4.1 \pm 0.2 \times 10^{-1}$
25	γ -methylene- γ -butyrolactone		$3.7 \pm 0.2 \times 10^{-1}$

a) 2:1 Ratio of diastereomeric epoxides. b) k_2 value for monoepoxidation. c) γ,δ -double bond epoxidation

For the α,β -unsaturated ketone series, **2-14**, the 5-ring compounds have lower k_2 values than the structurally analogous 6-ring compounds. For cyclic α,β -unsaturated compounds, formal increased methyl

substitution has a slightly greater effect at the α -position than that at β . However, the magnitude of the increase in k_2 's is generally smaller than that observed for simple alkenes.⁵ Entries **11-13** are the most reactive compounds in the α,β -unsaturated ketone series. As expected, α,β -unsaturated esters⁷ **15-20** are less reactive than the corresponding ketones while the enol esters are more reactive.

Our kinetic study of the epoxidation of chalcones by **1** indicated⁶ that the reaction proceeded via an electrophilic process. The observed sensitivity to structural variation for the present series of α,β -unsaturated compounds and enol esters is consistent with the electrophilic mechanism. As noted for alkenes, the process is sensitive to steric influences.

In conclusion, the k_2 values for epoxidation of α,β -unsaturated compounds and enol esters by dimethyldioxirane show considerable variation with structure. The relative reactivity of the substrates is high enough to be of synthetic utility.

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References and Notes

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