

OXIDATION OF ACETALS BY DIMETHYLDIOXIRANE

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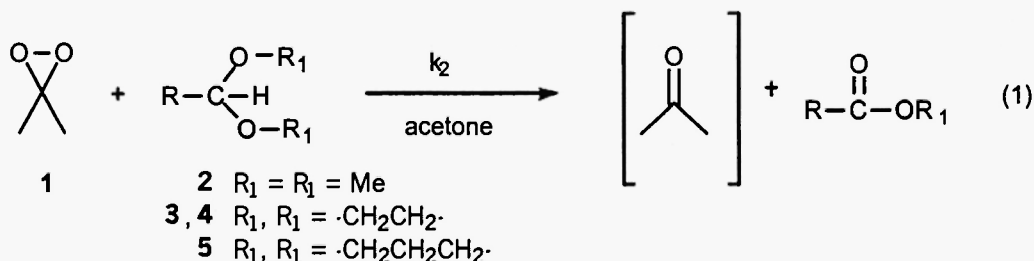
Abstract. Kinetic data (k_2 's, LFER and activation parameters) for the oxidation of a series of acetals by dimethyldioxirane to the corresponding esters in dried acetone are reported; the results are consistent with either a H-atom abstraction or direct insertion mechanism.

Introduction

Dioxiranes are powerful, versatile oxidants for the mild oxidation of a great variety of organic substrates.¹ Dimethyldioxirane is often the reagent of choice rather than the more reactive methyl(trifluoromethyl)dioxirane² because of its inexpensive, facile preparation.³ Dimethyldioxirane has been shown to be useful in epoxidation, heteroatom oxidation and C-H oxidation.¹ Specifically, extensive CH bond oxidation studies have been carried out⁴ on saturated hydrocarbons, phenyl-substituted hydrocarbons, aldehydes, alcohols and ethers. Several reports have appeared⁵ on the reactions of acetals with either dimethyldioxirane or methyl(trifluoromethyl)dioxirane. We report here a kinetic study of the oxidation of a series of acetals by dimethyldioxirane in dried acetone.

Results

The reaction of dimethyldioxirane **1** [isolated; ~0.1 M in dried acetone] with substituted benzaldehyde dimethyl acetals (**2a-c**), 2-aryl-1,3-dioxolanes (**3a-g**), 2-methyl-1,3-dioxolane (**4**) and 2-phenyl-1,3-dioxane (**5**) produced the corresponding esters in good to excellent yields (reaction 1). A threefold excess of **1** was employed to achieve efficient conversion. Product studies in the dark under inert



(N_2) atmosphere, yielded results essentially identical to those obtained when carried out under normal conditions (Table 1). The yields for oxidation of **2a** and **3c** are essentially identical to those previously

reported.^{5a,c} The yield of **4** from reaction with **1** is similar to those found for other 2-alkyl-1,3-dioxolanes.^{5c} The products (methyl benzoates from **2a-c**, 2-hydroxyethyl benzoates⁶ for **3a-g**, 2-hydroxyethyl acetate⁷ from **4**, and 3-hydroxypropyl benzoate⁸ from **5**) were isolated and the structures proven by comparison of physical and spectral properties with literature values.

Kinetic studies were carried out in acetone at 25° employing UV techniques. The reactions were shown to be of the first order in both dioxirane and substrate. The second order rate constants (k_2) were determined under pseudo-first order conditions with **1** in at least 10-fold excess. The results are summarized in Table 1. Interestingly, for reaction with **1** arylaldehyde dimethyl acetals **2a-c** were found to be the least reactive. On the other hand, 2-phenyl-1,3-dioxolane (**3c**) was found to be slightly more reactive than the corresponding 2-phenyl-1,3-dioxane (**5**), both of which were much more reactive than acyclic acetal **2a**. A k_2 value ($4.5 \times 10^{-2} \text{ M}^{-1}\text{s}^{-1}$) at 22 °C has been reported^{5c} for **3c** in (wet?) acetone which is in fair agreement with the results in dried solvent. The larger k_2 value observed for oxidation of **4** relative to that for **3c** is consistent with results^{5c} for other 2-alkyl-1,3-dioxolanes. Phenyl groups with electron-donating substituents increased the k_2 values for the reaction while those with electron withdrawing groups produced

Table 1. Second Order Rate Constants for the Oxidation of Acetals **2-5** by Dimethyldioxirane in Dried Acetone.

Entry	R	R ₁ , R ₂	$k_2 \text{ M}^{-1}\text{s}^{-1}$ a	Ester % yield (lit. value)
2a	Ph	Me, Me	2.7×10^{-4}	92 (95%) ^b
2b	pMeC ₆ H ₄ -	Me, Me	$6.8 \pm 0.3 \times 10^{-4}$	95
2c	pMeOC ₆ H ₄ -	Me, Me	$1.08 \pm 0.02 \times 10^{-3}$	97
3a	pMeOC ₆ H ₄ -	-CH ₂ CH ₂ -	$3.9 \pm 0.1 \times 10^{-2}$	98
3b	pMeC ₆ H ₄ -	-CH ₂ CH ₂ -	$3.14 \pm 0.08 \times 10^{-2}$	95
3c	Ph	-CH ₂ CH ₂ -	$2.08 \pm 0.05 \times 10^{-2}$	96 (95%) ^c
			$1.39 \pm 0.04 \times 10^{-2}$ (15°C)	
			$1.73 \pm 0.03 \times 10^{-2}$ (20°C)	
			$2.35 \pm 0.04 \times 10^{-2}$ (30°C)	
			$3.16 \pm 0.04 \times 10^{-2}$ (35°C)	
			$3.74 \pm 0.04 \times 10^{-2}$ (40°C)	
3d	pFC ₆ H ₄ -	-CH ₂ CH ₂ -	$1.68 \pm 0.03 \times 10^{-2}$	92
3e	pClC ₆ H ₄ -	-CH ₂ CH ₂ -	$1.55 \pm 0.03 \times 10^{-2}$	93
3f	pBrC ₆ H ₄ -	-CH ₂ CH ₂ -	$1.52 \pm 0.03 \times 10^{-2}$	90
3g	pNCC ₆ H ₄ -	-CH ₂ CH ₂ -	$0.91 \pm 0.03 \times 10^{-2}$	82
4	Me	-CH ₂ CH ₂ -	$1.86 \pm 0.04 \times 10^{-2}$	91
5	Ph	-CH ₂ CH ₂ CH ₂ -	$9.1 \pm 0.1 \times 10^{-3}$	90

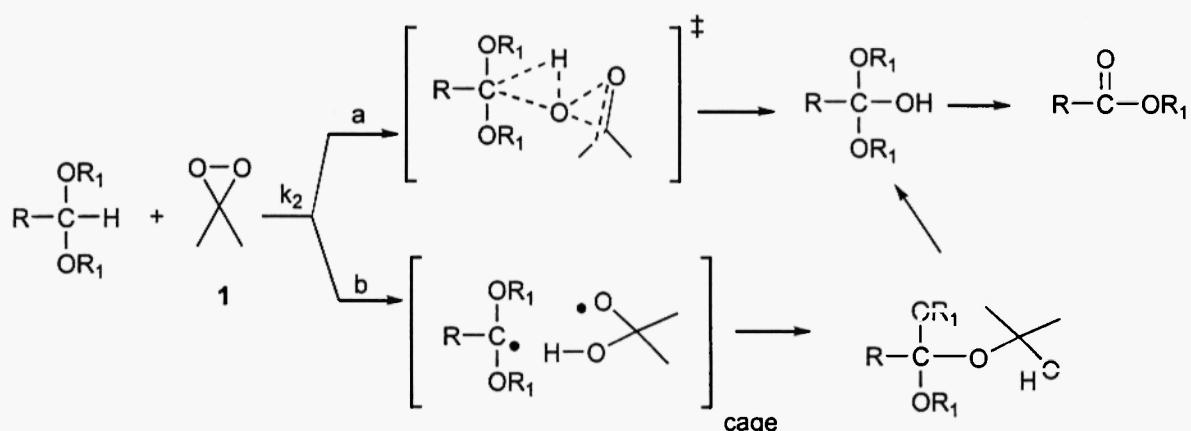
a) at 25°C unless specified; b) Ref. 5a; c) Ref. 5c

the opposite effect. A Hammett plot for the dioxolane series **3a-c** yielded a very good LFER with a rho of -0.72 ± 0.06 ($r = 0.98$). This result is in excellent agreement with our earlier study of the oxidation of ethers by **1** which yielded a rho value of -0.74 .^{4j}

The k_2 values for oxidation of **3c** were determined at 5° intervals from 15° to 40°C. The activation parameters determined by the Arrhenius method, were found to be $\Delta H^\ddagger = 6.4 \pm 0.2$; $\Delta S^\ddagger = -45$ eu.; $\Delta G^\ddagger = 19.8$ ($k_2 = 2.1 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$, 25°C). The results were in agreement with those found^{5c} for the reaction of **1** with 1,3-dioxolane ($\Delta H^\ddagger \approx 9.5$ kcal/mol; $\Delta S^\ddagger > -37$ eu; $k_{22} = 4.83 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$) in (wet?) acetone. The activation parameters for acetal oxidation are considerably different from those^{4j} for ether oxidation by **1**. In particular, the ΔS^\ddagger value is larger, more negative, and similar to those found^{4h} for secondary alcohol oxidation by **1**.

The mechanism for this type of dioxirane oxidation is controversial and subject to debate. Two mechanistic extremes for this reaction—a) concerted (direct) insertion and b) hydrogen-atom abstraction (caged radical pair)—are shown in Scheme 1. Both routes ultimately yield hemiacetal intermediates which would fragment to esters. Recent work⁹ on the related benzyl alcohol oxidation by **1** has been interpreted in favor of the concerted process. Our earlier mechanistic studies have suggested^{4h} a caged radical pair process, but cannot rule out the concerted process. Recent calculations¹⁰ have located genuine TS's,

Scheme 1



diradicaloid in nature, which can lead to final products via radical pair intermediates for alkane CH insertion by dimethyldioxirane. This is in contrast to the results of previous calculations.¹¹ The data for acetal oxidation are consistent with a caged radical pair mechanism but do not distinguish between the two mechanistic possibilities. As pointed out for analogous reactions,^{4j} the trajectory of approach of **1** to the C-H bond remains to be elucidated.

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