Acetals and Ethers: XV. Reactivity of Mono- and Disubstituted Cyclic Acetals Toward Ozone in Aqueous Solution[1]

A. Piasecki[a], A. Sokolowski[a], B. Burczyk*[a] and K. Piasecka[b]
[a]Institute of Organic and Polymer Technology, Technical University of Wroclaw, Poland, and [b]Research Development Centre of Water Ozonization Technology, Municipal Enterprise for Water and Sewarage, Wroclaw, Poland

Mono- and disubstituted derivatives of 1,3-dioxolane and 1,3-dioxane were oxidized by ozone in aqueous solutions containing monosodium carbonate. In both alkyl-substituted 1,3-dioxacyclane series the rates of oxidation increase with increasing length of alkyl substituents at the C-2 dioxacyclane carbon atom. However, the alkyl derivatives of 1,3-dioxane (III, IV, V) are more resistant toward ozone than the respective 1,3-dioxolane derivatives (I, II). The pseudo-first order rate constants for the oxidation of glycerol acetals (VIIa–VIId) decrease in the order: *cis*-dioxolane > *trans*-dioxolane > *cis*-dioxane > *trans*-dioxane.

The derivatives of cyclic acetals constitute a major group among recently developed, chemically degradable surfactants (2–7). In aqueous solutions they undergo hydrolysis or oxidation leading to products which are expected to be much more biodegradable than the surfactants themselves. While the reactions of hydrolysis of various acetals, including cyclic ones, have been widely investigated (8), much less is known about their oxidation in aqueous media. This concerns particularly the oxidation of cyclic acetals by ozone in aqueous solutions. As is well known, ozone is a very effective oxidizing agent, more and more widely used in municipal water treatment (9,10). In this work we report on the oxidation by ozone of 2-alkyl-1,3-dioxolanes (I, II), 2-alkyl-1,3-dioxanes (III, IV, V), *cis*- and *trans*-2-ethyl-4-methyl-1,3-dioxolanes (VIa, VIb), *cis*- and *trans*-2-n-propyl-4-hydroxymethyl-1,3-dioxolanes (VIIa, VIIb), and *cis*- and *trans*-2-n-propyl-5-hydroxy-1,3-dioxanes (VIIc, VIId) in aqueous solutions containing monosodium carbonate. The structures and alkyl chain lengths of these compounds are given in Scheme 1. Pseudo-first order rate constants (k_{obs}) and relative rate constants (k_{rel}), determined by using the competition method as described by Hammett (11), are presented.

EXPERIMENTAL

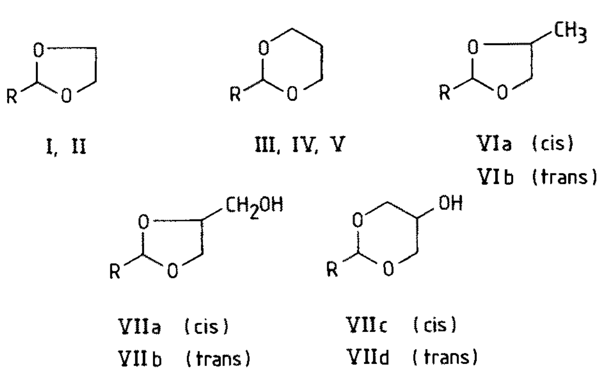
The cyclic acetals (I–VI) were obtained in an acid-catalyzed condensation of appropriate aliphatic aldehydes with ethylene glycol (I, II), trimethylene glycol (III, IV, V) or 1,2-propylene glycol (VIa + VIb) (12). The mixture of *cis*- and *trans*-2-n-propyl-4-hydroxymethyl-1,3-dioxolane and *cis*- and *trans*-2-n-propyl-5-hydroxy-1,3-dioxane, the so-called glycerol acetals (VIIa–VIId), was obtained by condensation of n-butyric aldehyde with glycerol (13). The purity of compounds was checked chromatographically (GLC) and their structure confirmed by ^{1}H NMR.

Chromatography. Chromatographic analyses were made on Perkin-Elmer F-11 apparatus equipped with a flame ionization detector (FID). A glass column 0.004 × 1 m packed with 3% Carbowax 20 M on Chromosorb G/AW DMCS (80/100 mesh) alkalyzed with 0.3% KOH was used. Nitrogen was a carrier gas. For quantitative analysis, the internal standard method was used with known amounts of the appropriate individual butyl monoethers of ethylene glycol or triethylene glycol.

Kinetic measurements. The ozonization was carried out in a 0.25 dm^3 glass reactor equipped with a tube terminated with a fine porous glass filter through which an air-ozone mixture was introduced, a valve enabling sample withdrawal and a set of three scrubbers filled with KJ solution in which unreacted ozone in the gas leaving the reactor was absorbed. The air-ozone mixture was generated in a laboratory ozonizer Labo 70 (Trailigaz, France). Prior to each run, the ozonizer was brought to stable working conditions and the concentration of ozone in the generated gas was determined iodometrically. The air-ozone mixture was then introduced, at a constant rate, to the reactor containing 0.1 dm^3 of aqueous solution of acetals mixture in which 0.5 g of $NaHCO_3$ was dissolved. At predetermined time intervals, samples of solution were withdrawn from the reactor and introduced to $NaHCO_3$ solutions containing known amounts of GLC internal standards. The rate of oxidation was followed by measuring the amount of unreacted acetals.

RESULTS AND DISCUSSION

Deslongchamps and Moreau (14) have shown that the oxidation of acetals by ozone gives esters with high yields



I, II

III, IV, V

VIa (cis)
VIb (trans)

VIIa (cis)
VIIb (trans)

VIIc (cis)
VIId (trans)

	I	II	III	IV	V	VI	VII
R	C_2H_5	n-C_4H_9	C_2H_5	n-C_3H_7	n-C_4H_9	C_2H_5	n-C_3H_7

SCHEME 1

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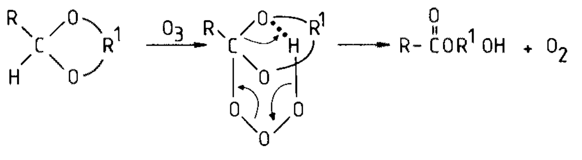
[1]Part XIV is reference 1.

*To whom correspondence should be addressed at Institute of Organic and Polymer Technology, Technical University of Wroclaw, 50-370 Wroclaw, Poland.

and, as later found out (15,16), the reaction proceeds via unstable acetal hydrotrioxide. In the case of cyclic acetals, the reaction with ozone yields a monoester of glycol as shown in Scheme 2. Detailed kinetic studies have shown that reactions of cyclic acetals carried out in organic solvents proceed stoichiometrically and are first-order reactions with respect to each reagent (17,18). In aqueous media, it becomes difficult to distinguish the reactions of direct oxidation of acetals by ozone from side reactions in which oxidants formed by reactions of ozone with water take part. Among the so-called secondary oxidants, the most reactive are hydroxyl radicals (OH˙) (10). To avoid their interference, we carried out the oxidation of acetals (I–VII) in the presence of $NaHCO_3$ which acted as a scavenger of hydroxyl radicals and also prevented hydrolysis and/or transacetalization of the acetals.



SCHEME 2

The following mixtures of acetals: (I + II), (III + IV + V), (VIa + VIb) and (VIIa–VIId), were oxidized. The rate of oxidation was followed by measuring the changes of acetal concentration with the time of oxidation. For the mixture (I + II), the relationship $\log(H_i/H_s)$ vs time is shown in Figure 1.

H_i and H_s are the heights of peaks in chromatograms for the appropriate acetal and standard substance, respectively. These kinds of plots gave straight lines up to high conversions of acetals, thus providing the relative rate constants, k_{rel}, for the first-order kinetic relationship. The conditions of measurements, conversion degrees of acetals, values of k_{rel} as well as the pseudo-first order rate constants of oxidation for individual acetals, k_{obs}, are given in Table 1. The latter values were calculated on the basis of the observation (17) that for oxidation of cyclic acetals by ozone in organic solvent, k_{rel} values determined by the competition method and those calculated from the ratio k_1/k_2 determined in measurements performed for individual compounds are almost the same.

It can be seen by examining the values of k_{obs} that the derivatives of 1,3-dioxane are more resistant against oxidation than the derivatives of 1,3-dioxolane. For a given homologous series of derivatives, the rate of oxidation gradually increases with increasing length of hydrocarbon substituents. This result is similar to that obtained in the reaction of ozone with alkyl substituted

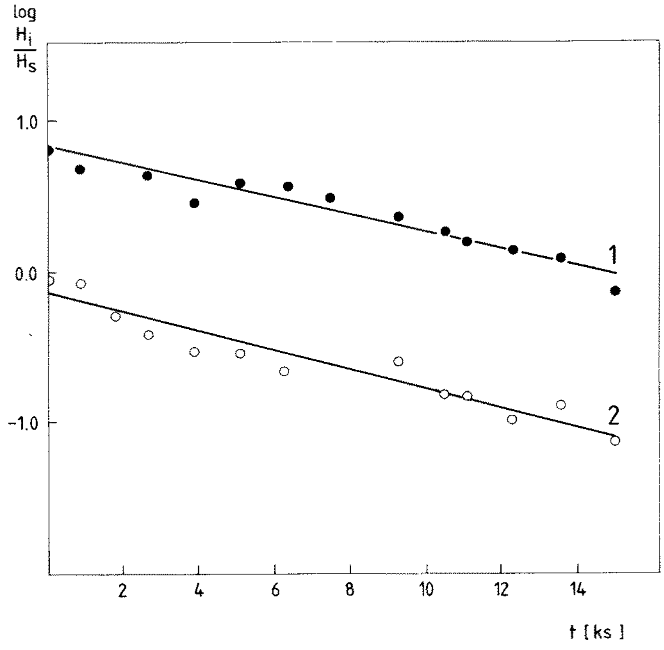


FIG. 1. Pseudo-first order plot for the oxidation by ozone of: (1) 2-ethyl-1,3-dioxolane (I), and (2) 2-n-butyl-1,3-dioxolane (II). H_i, peak height of the acetal studied; H_S, peak height of the reference substance.

TABLE 1

Reaction Parameters and Rate Constants for the Oxidation of Cyclic Acetals (I–VII) by Ozone in Water

Oxidized mixture (mmole)	Compounds	Temperature (°C)	Ozone input (mmole)	Ozone reacted (mmole)	Acetal conversion (%)	Rate constants	
						k_{rel}	$k_{obs}\cdot10^4$ [s^{-1}]
I + II (6.260)	I	25	17.96	5.39	86.1	1	1.16
	II					1.26	1.47
III + IV + V (6.412)	III	15	33.64	3.25	50.6	1	0.41
	IV					1.24	0.51
	V					1.63	0.67
VIa + VIb (4.037)	VIa	15	13.32	3.61	89.5	1.38	2.26
	VIb					1	1.64
VIIa–VIId (12.300)	VIIa	22	13.92	3.27	26.6	6.4	1.05
	VIIb					3.0	0.49
	VIIc					1.6	0.26
	VIId					1	0.16

1,3-dioxacyclanes in organic solvents (18). Among the dialkyl substituted derivatives of 1,3-dioxolane, (VIa) and (VIb), the *cis*-isomer is oxidized at a higher rate than the *trans*-isomer. This result is consistent with the higher susceptibility of *cis*-isomers to hydrolysis (19). Among the four isomeric glycerol derivatives (VIIa–VIId), the *cis*-dioxolane is oxidized at the highest rate and the *trans*-dioxane at the lowest. We did not find any results on the ozonation reaction of glycerol acetals in the literature. It seems specific and worth noticing, however, that the rates of acidic hydrolysis of isomeric acetals (VIIa–VIId) decrease in the order: *cis*-dioxolane > *trans*-dioxolane > *trans*-dioxane > *cis*-dioxane with the relative rate constants 9.8:5.6:1.4:1 (20).

The investigations shed some light on the oxidative degradation of cyclic acetal-type surfactants in an aqueous environment. The results can provide an additional choice criterion of appropriate derivatives of 1,3-dioxacyclanes as hydrophobic intermediates for surfactant manufacturing.

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Surfactants for Hard-Surface Cleaning: Mechanisms of Solid Soil Removal[1]

Michael F. Cox
Vista Chemical Co., P.O. Box 500, Ponca City, OK 74602

Soil-submersion tests were performed with several solid, organic soils to examine the effects of surfactant structure on soil removal. Results show that hydrophobe size and Hydrophile-Lipophile Balance (HLB) affect soil removal processes. Data also indicate that soil removal first requires penetration of the surfactant (and associated water molecules) into the soil. After this liquefaction process begins, other processes (e.g., emulsification, mechanical action, reduction in soil adhesion) can commence which actually remove soil.

There are three principal mechanisms for removing soil from hard surfaces (Fig. 1). Detergency, or surface-chemical processes, employ surfactants to achieve soil removal. In contrast, mechanical processes use some sort of physical means (abrasion, etc.), and chemical processes involve the use of solvents. In most applications, soil removal is achieved through detergency because it offers a more cost-effective and versatile approach. Most detergency processes, however, rely on some degree of mechanical action to achieve soil removal. Some also rely on chemical solvation of the soil to aid in soil removal (e.g., addition of caustic to saponify and solubilize natural oils and fats).

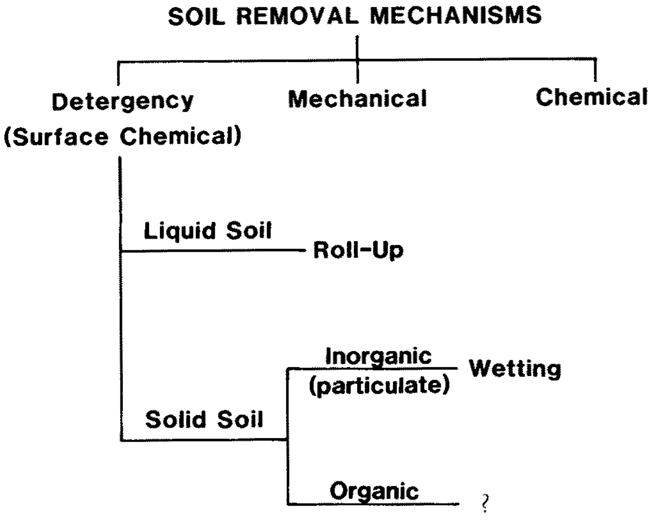

FIG. 1. Major mechanisms involved in the removal of soils from hard surfaces.

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