KINETICS AND MECHANISM OF THE INITIATED OXIDATION OF A NUMBER OF 1,3-DIOXACYCLANES

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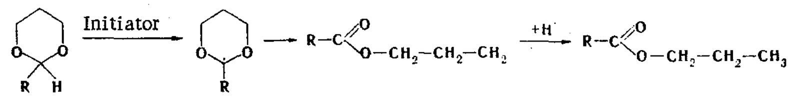
The initiated oxidation of a number of cyclic acetals at 50-95°C was studied by kinetic methods. It was found that the examined 1,3-dioxacyclanes are oxidized via a free-radical mechanism with quadratic termination of the chains in the peroxide radicals. The strengths of the carbon-hydrogen bonds undergoing attack by the peroxide radicals range from 80 to 90 kcal/mole.

The free-radical isomerization of cyclic acetals leads to extremely valuable esters [1]. The process is a radical-chain unbranched reaction:



In the presence of oxygen the reaction may be accompanied by oxidation of 1,3-dioxacyclanes [2, 3]. Considerable accumulation of 2-hydroperoxides in the initial step of the oxidation has been noted [4]. Only the products of oxidation of 2-alkyl- and 2-alkenyl-1,3-dioxolanes have been studied [5]. Quantitative data on the reactivities of cyclic acetals in the oxidation reaction are not available.

In the present research we have studied the initiated oxidation of substituted 1,3-cyclanes (Table 1) by kinetic methods in order to determine the effect of their structure on their reactivities.

The compounds under consideration are oxidized at a rate the square of which depends linearly on the initiator concentration (Fig. 1). In all of these experiments the rate of oxidation considerably exceeds the rate of initiation calculated from the literature data [6]. It follows from this that all of the investigated cyclanes are oxidized via a chain pathway with quadratic termination of the chain.

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*Deceased.

TABLE 1. Physicochemical Characteristics of 1,3-Dioxacylanes

Compound	Name	bp, °C	d_4^{20}	n_D^{20}	Found, %			Calc., %		
					C	H	O	C	H	O
I	1,3-Dioxane	103 (745)	1,0342	1,4165	54,50	9,05	36,40	54,57	9,09	36,34
II	1,3-Dioxepane	117	1,0157	1,4319	58,80	9,76	31,45	58,78	9,79	31,43
III	4-Methyl-1,3-dioxane	115	0,9758	1,4170	58,75	9,70	31,46	58,78	9,79	31,43
IV	2,2-Pentamethylene-4-methyl-1,3-dioxane	120—122 (7)	1,028	1,4550	62,27	10,26	20,56	69,21	10,27	20,54
V	2-Phenyl-1,3-dioxane	95—97 (1)	—	1,5260	73,04	7,31	19,53	73,09	7,31	19,51
VI	2-Methyl-1,3-dioxane	107—108	0,9890	1,4140	58,80	9,74	31,40	58,78	9,79	31,43
VII	2,4-Dimethyl-1,3-dioxane	118—118,5	0,9970	1,4130	62,00	9,50	27,52	62,10	9,47	27,58

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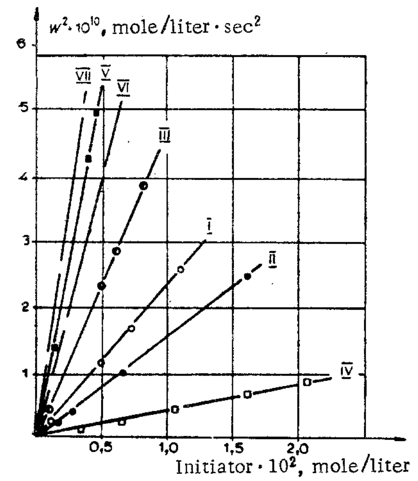


Fig. 1. Relationship between the rate of oxidation and the initiator concentration in pure 1,3-dioxacyclanes at 70°C with 2,2'-azobisisobutyronitrile as the indicator.

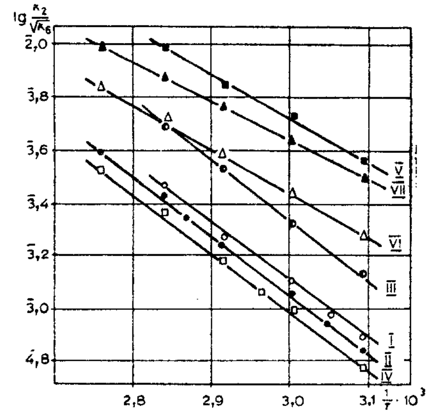


Fig. 2. Dependence of the rate constant for oxidation of 1,3-dioxacyclanes on the temperature in Arrhenius coordinates.

The rate of oxidation of 1,3-dioxane is independent of the oxygen concentration for gas mixtures containing from 100 to 5% oxygen. For the remaining dioxanes this independence was established by experiments with gas mixtures containing 100 and 50% oxygen. Inasmuch as all of these experiments were carried out in a pure oxygen atmosphere, the oxidation chains were consequently terminated only in the peroxide radicals under the investigated conditions.

The rate of oxidation depends linearly on the concentration of the acetals in chlorobenzene, and this constitutes evidence for a reaction that is first-order in substrate.

The experimental results obtained show that the oxidation of the investigated dioxanes occurs via the well-known radical-chain mechanism and that its rate is determined by the following expression for degrees of conversion that are not very high:

$$W=\frac{k_2}{\sqrt{k_6}}[DH]\sqrt{W_i},$$

where [DH] is the molar concentration of the dioxacyclanes, W_i is the rate of initiation in moles per liter per second, k_2 is the rate constant for detachment of a hydrogen atom in the cyclane by the peroxide radical in liters per mole per second, and k_6 is the rate constant for recombination of two peroxide radicals leading to termination of the chain in liters per mole per second.

A study of the dependence of the rate on the temperature (it is presented in Arrhenius coordinates in Fig. 2) enabled us to determine the effective energy of activation of the reaction and to calculate the preexponential factor (Table 2).

As seen from a comparison of the $k_2/\sqrt{k_6}$ at a single temperature (70°), the reactivities of 1,3-dioxane (I) and 1,3-dioxepane (II) are identical, i.e., an increase in the size of the ring by one methylene group does not affect the reactivity; 4-methyl-1,3-dioxane (III) is oxidized more easily than dioxane I. This is evidently associated with the weakening of the C_4-H bond of the methyl group. The reactivity of this bond can be evaluated from the $k_2/\sqrt{k_6}$ value for dioxane IV, in which the reactivities of the five methylene groups of the carbocyclic ring should be identical to the reactivities of the methylene groups of cyclohexanes. If it is assumed that the k_6 values for dioxanes VII and IV differ only slightly, one can use the known $k_2/\sqrt{k_6}$ value for cyclohexane [7] to evaluate the reactivities of the methylene groups in dioxane IV:

$$\left(\frac{k_2}{\sqrt{k_6}}\right)_{\mathrm{IV}}-\frac{5}{6}\left(\frac{k_2}{\sqrt{k_6}}\right)_{\mathrm{VIII}}=1.54\cdot10^{-3}-0{,}1\cdot10^{-3}=1{,}44\cdot10^{-3}\;[\text{liter}/(\text{mole}\cdot\text{sec})]^{1/2}$$

The value obtained characterizes the reactivity of the C_4-H bond activated by a methyl group and of the $C-H$ bonds in the 5 and 6 positions of the dioxane ring. By substracting this value from the $k_2/\sqrt{k_6}$ value for dioxane III, one can, within the same approximation, evaluate the reactivities of the C_2-H bonds of the 1,3-dioxane ring:

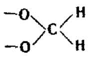
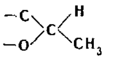
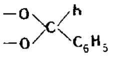
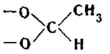
$$\left(\frac{k_2}{\sqrt{k_6}}\right)_{\mathrm{III}}-1.44\cdot10^{-3}=1.93\cdot10^{-3}[\text{liter}/\text{mole}\cdot\text{sec}]^{1/2}\ (70°)$$

This value turns out to be equal to $k_2/\sqrt{k_6}$ for dioxanes I and II. Consequently, their reactivities are practically completely associated with attack by the peroxide radical on the methylene group in the 2 position, and the $C-H$ bonds in the remaining positions practically do not increase the reactivities.

TABLE 2. Kinetic Parameters for the Oxidation of Cyclic Acetals

Compound	Name	E, kcal/mole	A, [liter/mole sec]$^{1/2}$	$k_2/\sqrt{k_6}\cdot 10^3$ (70°), [liter/mole·sec]$^{1/2}$
I	1,3-Dioxane	9,7±0,5	$3{,}1\cdot 10^3$	1,93±0,15
II	1,3-Dioxepane	10,1±0,5	$4{,}8\cdot 10^3$	1,82±0,15
III	4-Methyl-1,3-dioxane	10,3±0,5	$1{,}3\cdot 10^4$	3,37±0,30
IV	2,2-Pentamethylene-4-methyl-1,3-dioxane	10,2±0,8	$5{,}1\cdot 10^3$	1,54±0,18
V	2-Phenyl-1,3-dioxane	7,2±0,7	$3{,}0\cdot 10^2$	7,2±0,6
VI	2-Methyl-1,3-dioxane	7,5±0,5	$2{,}5\cdot 10^2$	4,3±0,4
VII	2,4-Dimethyl-1,3-dioxane	6,8±0,5	$1{,}23\cdot 10^2$	5,6±0,4

TABLE 3. Partial Values of the Relative Oxidation Rate Constants for the Corresponding C−H Bonds of 1,3-Dioxacyclans

Bond type	$k_2/\sqrt{k_6}\cdot 10^3$ [liter/mole·sec]$^{1/2}$ 70°
	1,93±0,15
	1,54±0,18
	7,2±0,6
	3,9±0,4

The $k_2/\sqrt{k_6}$ value calculated at 70° for one C_2-H bond increases by a factor of 7.5 on passing from dioxane I to its phenyl derivative (V). This sharp increase in the reactivity of the C−H bond when a phenyl group is introduced in the 2 position is evidently associated with a considerable increase in the stability of the radical formed when the hydrogen atom in the 2 position is detached due to conjugation of the unpaired electron with the π electrons of the aromatic ring. Similarly, the $k_2/\sqrt{k_6}$ value (at 70°) referred to one C_2-H bond increases on passing from dioxane I to dioxane VI by a factor of four. In this case partial stabilization of the resulting radical is ensured by the electron−donor properties of the methyl group.

However, one should bear in mind that the increase in $k_2/\sqrt{k_6}$ on passing from dioxane I to its dimethyl derivative (V) and phenyl derivative (VI) is apparently associated not only with weakening of the C_2-H bonds but also with the decrease in the k_6 value, for these compounds form tertiary peroxide radicals that recombine more slowly than secondary and primary radicals. For this same reason, the comparative evaluation of the reactive positions within the approximation of equal k_6 values for different cyclanes is extremely approximate when secondary and tertiary C−H bonds are compared.

$$\left(\frac{k_2}{\sqrt{k_6}}\right)_{C_2-H} = 9{,}7\cdot 10^{-4}\ [\text{liter/mole}\cdot\text{sec}^{1/2}] < 1{,}4\cdot 10^{-3}\ [\text{liter/mole}\cdot\text{sec}^{1/2}]\ (70°)$$

Thus, according to the estimates, the reactivity of the C−H bond in the 4 position, which has a methyl group, is higher by a factor of 1.5 than the reactivity of the C−H bond in dioxane I. However, inasmuch as recombination of tertiary peroxide radicals occurs, as a rule, more slowly than recombination of secondary peroxide radicals [6], one might expect that $k_2\ (C_2-H) > k_2\ (C_4-H)$, i.e., the C−H bond in the 2 position undergoes homolytic cleavage more readily than the tertiary C−H bond in the 4 position.

In fact, if one compares the $k_2/\sqrt{k_6}$ values for dioxanes IV and VI, the reactive C−H bonds of which are tertiary bonds and are adjacent to identical methyl substituents, one can see that the C_2-H bond in dioxane VI is twice as reactive as the C_4-H bond in dioxane IV.

It is interesting to note that the $k_2/\sqrt{k_6}$ value (at 70°) for dioxane VII is equal, with good accuracy, to the sum of the $k_2/\sqrt{k_6}$ values (at 70°) for dioxanes IV and VI. It follows from this that oxidation proceeds independently with respect to the two weakest C_2-H and C_4-H bonds, and the peroxide radicals formed in the 2 and 4 positions apparently actually do not differ in their reactivities in either the propagation reaction or in chain termination.

On the basis of the estimates presented above, which are given in Table 3, it can be stated that the primary site of attack by the peroxide radical is the C_2-H bond, particularly when an alkyl or phenyl substituent is present, and also the C_4-H bond activated by alkyl substituents, whereas the reactivities of all the remaining methylene C−H bonds are lower by a minimum of one order of magnitude. The principal products of the initial step of the oxidation are therefore 2-hydroperoxides for cyclanes I, II, V, and VI and 4-hydroperoxides for cyclanes IV. In the case of III and VII, one might expect the formation of dihydroperoxides in addition to 2- and 4-monohydroperoxides (with predominance of the 2-hydroperoxide).

The experimentally determined energies of activation represent the difference between the energies of activation of chain propagation (E_2) and half the energy of activation of recombination of the peroxide radicals (E_6): $E_{exp} = E_2 - 1/2E_6$. Although the E_6 values above 4 kcal/mole are known for secondary peroxide radicals in hydrocarbon media ($E_6 = 4.3$ kcal/mole for tetralylperoxy radicals), E_6 does not exceed 2.0 kcal/mole for most secondary peroxide radicals, whereas E_6 is, on the average, relatively high for tertiary peroxide radicals (5-8 kcal/mole [6]).

According to empirical principles that relate the strength of the C—H bond to the energy of activation (E_2) of detachment of a hydrogen atom by a peroxide radical, $E_2 = -27 + 0.45\ D_{C-H}$ [8], where D_{C-H} is the strength of the bond undergoing cleavage in kilocalories per mole. The E_2 value calculated with allowance for the assumptions made above is 10-13 kcal/mole, and the corresponding D_{C-H} values range from 80 to kcal/mole.

EXPERIMENTAL

The kinetics of the oxidation of the cyclanes were studied from the absorption of oxygen with a volumetric apparatus with mercury drops moving in a horizontal buret. A gas mixture with a known percentage of oxygen was prepared in a gasometer, and the reactor and the buret were then purged with it and subsequently thermostatted. Stirring with a magnetic stirrer insured rapid dissolving of the oxygen in the liquid phase. The starting 1,3-dioxacyclanes (Table 1) were obtained by the method in [9]. Their purity was checked by gas chromatography; the absence of hydroperoxides was monitored iodometrically, and the absence of oxo compounds was monitored from the IR spectra in the region of the characteristic absorption band of the carbonyl group.

The chlorobenzene used as the solvent was purified by the method in [10]. Benzoyl peroxide and 2,2'-azobisisobutyronitrile were purified by crystallization from ethanol.

The oxidation rates (W) in the experiments were determined from the change in the volume of oxygen:

$$W = Z\frac{P \cdot V}{T \cdot \tau \cdot a},$$

where Z is the apparatus constant, V is the volume of absorbed oxygen in cubic centimeters, P is the atmospheric pressure in millimeters (mercury column), T is the temperature in degrees Kelvin, τ is the time in seconds, and a is the volume of the reaction mass in cubic centimeters.

The $k_2/\sqrt{k_6}$ values were determined from the W and $W_i = k_i$[initiator] values obtained. The initiation constant (k_i) was taken from a handbook [6]. The working initiator concentrations were $(0.1\text{-}2) \cdot 10^{-2}$ mole/liter, and the working substrate concentrations were 0.5-11 mole/liter. The W/W_i values in all of the experiments ranged from 20 to 150.

The accuracy in the parameters presented was determined with a mean-square error.

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