RELATIVE ACTIVITIES OF TETRAHYDROFURFURAL ACETALS IN THE DETACHMENT OF A HYDROGEN ATOM BY tert-BUTOXYL RADICALS

O. M. Ramazanov, R. G. Akzamova,
V. V. Zorin, M. R. Skurko,
M. Z. Vagabov, and R. A. Karakhanov

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The reactivities of linear and cyclic acetals of tetrahydrofurfural in the reaction with tert-butoxyl radicals were studied. The k_a/k_d parameters, which are the ratios of the rate constants for the accumulation of tert-butyl alcohol to the rate constants for the formation of acetone, are close to the parameters for 2-alkyl-substituted acetals. Linear acetals are less active than cyclic acetals, the activities of which increase on passing from 2-tetrahydrofuryl-1,3-dioxolane to its sulfur- and nitrogen-containing analogs.

The activities of linear [1] and cyclic [2] acetals and their hetero analogs [3], which are derivatives of aliphatic aldehydes, in the detachment of a hydrogen atom by tert-butoxyl radicals have been studied, and it was found that primarily homolytic cleavage of the C_2—H bond of the acetal occurs in the process [1, 2].

In the present research we studied the activities of linear and cyclic acetals of tetrahydrofurfural, as well as some sulfur- and nitrogen-containing heterocyclic analogs, in the reaction with tert-butoxyl radicals. The reactivity was investigated as a function of the size of the 1,3-dioxa ring, the character of the heteroatoms, and the length of the chain of the dialkoxymethyl substituent in the 2 position of the tetrahydrofuran ring. The k_a/k_d parameter, where k_a (in liters per mole per second) is the rate constant for detachment of hydrogen from the acetal (DH) by a tert-butoxyl radical formed in the decomposition of the tert-butyl peroxide (TBP) initiator,

$$t\text{-BuO}^{\cdot} + \text{DH} \xrightarrow{k_a} \text{D}^{\cdot} + t\text{-BuOH},$$

and k_d (in reciprocal seconds) is the rate constant for decomposition of the tert-butoxyl radical to give acetone and a methyl radical

$$t\text{-BuO}^{\cdot} \xrightarrow{k_d} CH_3COCH_3 + CH_3^{\cdot}.$$

can serve as a measure of the reactivity. The k_a/k_d values were determined from the linear dependences of the ratios of the concentrations of tert-butyl alcohol and acetone ([tert-BuOH]/[CH_3COCH_3]) on the DH concentration. In individual experiments it was shown that under the condition $[TBP]_0 \ll [DH]$ ($[DH] \geqslant 1.0$ mole/liter, and $[TBP]_0 = 0.1$ mole/liter) the conversion of DH can be disregarded, and the following expression is then valid:

$$k_a/k_d = [t\text{-BuOH}] \cdot ([CH_3COCH_3] \cdot [DH])^{-1}.$$

The k_a/k_d parameters for the investigated compounds (Table 1) exceed the value of the analogous ratio of the rate constants for THF (0.5 liter/mole [4]) by an order of magnitude or more. The closeness of the values obtained to the known values for linear and cyclic acetals [1, 2] makes it possible to conclude that radical attack is directed to the acetal fragment.

A slight increase in the activity as the number of methyl groups in the cycloacetal fragment is increased is observed for dioxolanes I-III; this is evidently due to weakening of the C_4—H and C_5—H bonds by the methyl groups; the k_a/k_d parameter is increased by ∿2.0 liters/mole in this case. The minimum value of the parameter that is characteristic for

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N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow 117913. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, pp. 1597-1599, December, 1981. Original article submitted May 20, 1980.

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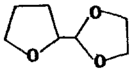
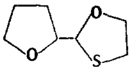
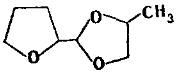
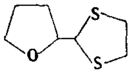
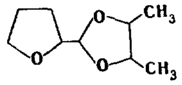
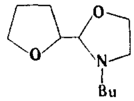
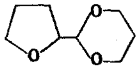
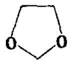
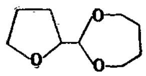
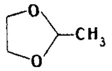
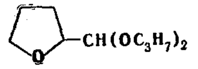
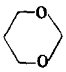
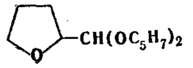
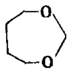
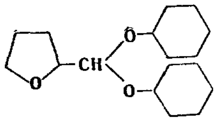
TABLE 1. k_a/k_d Parameters (liters·mole^{-1}) for Tetrahydrofurfural Acetals (DH)

Compound	Formula of DH	k_a/k_d	Compound	Formula of DH	k_a/k_d
I		5,3	IX		7,8
II		7,3	X		12,2
III		9,3	XI		15,5
IV		4,1	XII		5,2*
V		4,8	XIII		6,1†
VI		2,2	XIV		1,3†
VII		2,4	XV		1,9†
VIII		3,6			

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*From [6].
†From [3].

2-(2'-tetrahydrofuryl)-1,3-dioxane (IV) in the I—IV—V series corresponds to its less strained cyclic structure as compared with dioxepane V and dioxolane I.

Linear acetals VI-VIII display lower reactivities than cyclic I-V; this is probably associated with a decrease in the activity of the OCHO bond in the linear fragment and is also common to the aliphatic series [1].

From a comparison of the k_a/k_d values for VI and VII it follows that an increase in the length of the alkoxy substituents has virtually no effect on the relative activities of linear acetals. In the case of cyclohexanol acetal VIII the k_a/k_d parameter is somewhat higher than for VI and VII; this is probably due to the presence of two cyclohexane rings that contain both methylene and methylidyne groups.

Replacement of the oxygen atom in 2-(2'-tetrahydrofuryl)-1,3-dioxolane (I) by sulfur (IX) and particularly nitrogen (XII) atoms leads to an increase in the activity; this is associated with the more favorable combination of polar factors in the transition state of homolytic detachment of a hydrogen atom by the electrophilic tert-butoxyl radical [5] from heterorings that contain less electronegative (than oxygen) heteroatoms.

It should be noted that the activities of the investigated 2-tetrahydrofuran derivatives I-XI with respect to tert-BuO$^\bullet$ are close to the activities for 2-alkyl-substituted 1,3-dioxacyclanes [6], and the effect of the tetrahydrofuran ring can be compared with that of an alkyl substituent.

EXPERIMENTAL

Starting acetals I-XI were obtained and purified by known methods [6, 7]. The purity of all of the substances and solvents was monitored by chromatography. The thermal decomposition of tert-butyl peroxide was carried out in glass ampuls in a nitrogen atmosphere at 130°C for 20 h. Chlorobenzene was used as the solvent. Quantitative analysis was carried out with an LKhM-8MD chromatograph with a thermal-conductivity detector by means of previously constructed calibration dependences. The chromatographic-analysis conditions were as follows: The stationary phase was 10% polyethylene glycol sebacate on Chemosorb AW-HMDS, the column temperature was 80°C, the vaporizer temperature was 100°C, and the carrier-gas flow rate was 20 ml/min.

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LUMINOPHORES OF THE AZLACTONE SERIES WITH A DIFLUOROMETHYLSULFONYL GROUP

B. M. Krasovitskii, I. V. Lysova,
L. Sh. Afanasiadi, and Yu. N. Surov

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Organic luminophores of the azlactone series that contain a strong electron-acceptor substituent, viz., a difluoromethylsulfonyl group, were synthesized. The significant effect of the electronic nature of the substituents on the frequencies of the stretching vibrations of the CO and C=N groups was demonstrated, and the trans configuration of the investigated compounds was confirmed. The introduction of a difluoromethylsulfonyl group in the azlactone molecule promotes the development of intense fluorescence in solutions at room temperature. The character of the substituents and their mutual orientation have a substantial effect on the optical characteristics.

During a study of the spectral-luminescence properties of azlactone derivatives we noted intensification of the fluorescence of these compounds when electron-acceptor substituents are present in the arylidene fragment; this effect increased significantly as the acceptor properties of the substituents became more pronounced [1].

Continuing our search for effective organic luminophores among azlactone derivatives we synthesized I and II, which contain a difluoromethylsulfonyl group, which is a strong electron-acceptor substituent that surpasses the nitro group with respect to the strength of its electron-acceptor effect [2], in various structural fragments of the molecules.

The structures of the compounds obtained were identified by means of their IR spectra. A number of characteristic absorption bands are displayed distinctly in the 1580-1850 cm^{-1} region (Fig. 1). We assigned the high-frequency band at 1790-1800 cm^{-1} to the stretching vibrations of the carbonyl group.

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