KINETICS OF THE REACTIONS OF RADICALS FORMED ON PULSED ELECTRON RADIATION OF CYCLIC ALCOHOLS IN THE LIQUID PHASE

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Pulsed radiolysis of cyclic alcohols to obtain the kinetic and spectral characteristics of the radicals formed was studied in [1-4]. The optical absorption in the UV region (290-340 nm) at λ_{max} = 314 nm at a temperature of ~25°C, which occurs in irradiation of evacuated cyclohexanol (I) [1], was assigned to absorption of α-hydroxycyclohexyl radicals (II). The spectrum of $C_6H_{10}OH$ radicals (II) was subsequently [2] recorded in the 220-350-nm region with an absorption band maximum at 240 nm, and the radiochemical yield of these radicals $G_{(II)}$ · 7.8 radicals per 100 eV of absorbed energy was determined based on the yield of the products of radiolysis of (I).

There is no information in the literature on the effect of temperature on the kinetics of quenching of hydroxycycloalkyl radicals (HCR), and the kinetic and spectral parameters of the radicals of higher alcohols are also not described.

The present study concerns the pulsed radiolysis of cyclohexanol and cyclododecanol (III) in order to obtain more precise data on radicals (II) and to perform a comparative analysis of the kinetic and spectral characteristics of the HCR obtained. A pulsed radiolysis setup which combined an ÉLU-10 electron accelerator with a spectral apparatus was used. The accelerator operated in the mode of single pulses lasting for 1.5 μsec (dose per pulse of ~0.5 kJ/liter). A DKSSh-1000 xenon lamp was the light source. After passing through the sample and a ZMR-3 monochromator, the light beam fell on a FÉU-97 photomultiplier. The optical absorption signal was recorded with a S8-12 memory oscillograph. It was found that distortion-free luminescence signals could be obtained 10-15 μsec after the electron pulse ended. The error of measurement of the optical absorption was ±7%.

Alcohols (I) and (III) were irradiated in the liquid state in the 26-150°C temperature range in cylindrical quartz cells 3.5 cm long with optical windows and a thermostatically controlled jacket. The measurements of the topography of the electron beam from the accelerator in the center of an empty cell using Nitto Radcolor Film No. 381 dosimetric films showed that the zone of the radiation effect was equal to 1.8 cm. The precision of the thermostatic control was ±1°C.

(I) with a mp of 24.6°C and a concentration of cyclohexanone (the basic impurity) of $<10^{-4}$ M was used . For attaining such a high degree of purity, the rectified cyclohexanol was washed with a 10% aqueous solution of KOH and water, the water was evaporated, and it was vacuum distilled in the presence of 2,4-dinitrophenylhydrazine; it was then vacuum rectified in an atmosphere of inert gas using a packed glass column at 76°C and pressure of 31 HPa and sampling the narrow middle fraction. Compound (III) from Huls (FRG) was repeatedly recrystallized from reference n-hexane and n-pentane, and the residues of the latter were eliminated by vacuum evaporation at 50°C. The concentration of cyclododecanone in (III), intended for irradiation (mp 79.5°C), was $<10^{-3}$ M.

With a change in the phase state, (III) crushed the quartz cells filled with it, and the oxygen from the air dissolved in (III) was displaced by blowing through hp He for 40 min (concentration of O_2 <0.001%) immediately after filling the cells with the melted alcohol, and passage of He was continued during irradiation of the samples. The inert gas current did not interfere in the passage of the light probe. He was blown through (I) and then evacuated. During tuning of the optical system, the alcohols were protected from photolysis by a ZhS-12 light filter.

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TABLE 1. Maxima of the Optical Absorption Spectra λ_{max}, Extinction Coefficients ε_{max}, Rate Constants $2k_t$, and Observed Activation Energies E_{abl} of Quenching of HCR in Reactions with Each Other

Alcohol	Electron energy, MeV	Pulse duration, μsec	Dose per pulse, kJ/liter	T., °C	Radical	λ_{max}, nm	ε_{max}, liter • mole/cm	$2k_t \cdot 10^{-8}$, liter/mole • sec	Reference
(I)	6	5	1,5	25	(II)	314	–	3,4±1,5	[1]
(I)	2,3	0,03	0,14	22	(II)	240	1700	0,65	[2]
(I)	10	1,5	0,52	26–150	(II)	280	800	$1{,}5 \cdot 10^3 \cdot \exp(-19{,}2/RT)$	
(III)	10	1,5	0,52	80–135	(IV)	300	800	$64 \cdot \exp(-13{,}7/RT)$	

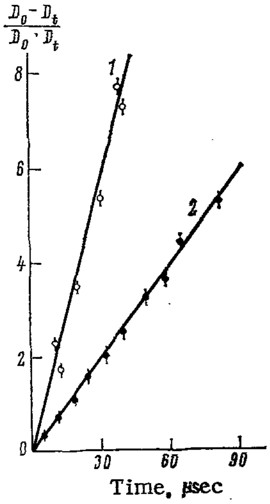

Fig. 1

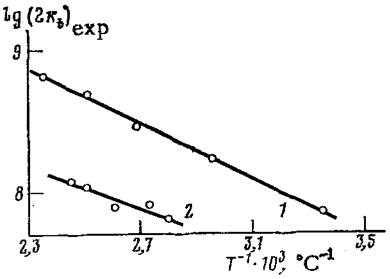

Fig. 2

Fig. 1. Determination of the order of the reaction of quenching of the radicals formed by accelerated electrons in liquid cyclohexanol (1) and cyclododecanol (2) in the absence of oxygen at 100 (1) and 94°C (2), at λ_{max}, nm: 1) 280; 2) 300.

Fig. 2. Dependence of the logarithms of the rate constants on the temperature in Arrhenius coordinates for cyclohexanol (1) and cyclododecanol (2) in the absence of oxygen.

DISCUSSION OF RESULTS

The HCR formed in pulsed irradiation of (I) and (III) in the absence of oxygen exhibited optical absorption bands at λ_{max} at 280 and 300 nm, respectively. The position of the maximum of radicals (II) differed from the previous data (Table 1). The extinction coefficients at λ_{max} were determined with the radiochemical yield of free radicals for (I), equal to 6.8 per 100 eV of absorbed energy, according to the data in [4]. This value was obtained for (I) of the same degree of purity and was 20% higher than the value of 5.65 per 100 eV cited in [3] in the discussion of the results of pulsed radiolysis of a cyclohexanol solution (10^{-3} M) of nitromethane. In the case of the more exact definition of the radiochemical yield of free radicals, the kinetic and spectral information obtained in the present study can be easily revised.

The maximum optical density of (I) immediately after termination of the microsecond pulse at 26°C was 0.53 ± 0.03, and the extinction coefficient of the radicals (II) formed was consequently ε_{max} = 800 ± 100 liter/mole•cm. Since the radiochemical yield of free radicals is not known for (III), the value of ε_{max} found for radicals (II) was used in the calculations of the rate constants of the reactions of the hydroxycyclododecyl radicals (IV) with each other. The causes of the differences in the values of λ_{max} and ε_{max} obtained in the present study from the published data (see Table 1) are unclear. They are apparently related to the different degree of purity and deaeration of the samples of (I) used for irradiation.

Examples of the processing of the experimental data for establishing the order of the reaction of the disappearance of the radicals in the microsecond range are shown in Fig. 1. The data obtained confirm that the radicals are quenched in reactions of recombination and disproportionation. The possibility of the formation of radicals other than α-hydroxycycloalkyl radicals is not excluded. However, either the rate constants of quenching of these radicals do not differ from the rate constant of quenching of HCR or they are formed in insignificant quantities and are thus not detected in kinetic studies [1]. The values of the experimentally determined rate constants of the recombination and diproportionation of HCR at different temperatures, $(2k_t)_{exp}$, are reported in Table 2.

The values of $(2k_t)_{exp}$ for (I) at ~20°C obtained in the present study and in [2] do not differ and are less than the value of $(2k_t)_{exp}$ determined in [1]. The differences could be related both to the purity of the irradiated (I) and to a difference in the extinction coefficients used for the calculations. The comparison of the results obtained with the data in [1] should be considered random, since different extinction coefficients corresponding to different wavelengths were used for the calculation.

The dependence of the logarithms of the rate constants on the temperature in Arrhenius coordinates is linear (Fig. 2) and can be analytically expressed by the equation

$$(2k_t)_{exp}\ (\mathrm{II}) = 1.5\cdot 10^{11}\cdot \exp\,(-19.2\ \mathrm{kJ/mole}\quad RT),\ \mathrm{liter/mole\cdot sec}$$
$$(2k_t)_{exp}\ (\mathrm{IV}) = 6.4\cdot 10^{9}\cdot \exp\,(-13.7\ \mathrm{kJ/mole}\quad /RT),\ \mathrm{liter/mole\cdot sec}$$

At the same temperature, the values of the rate constants of quenching of (II) are always higher than the corresponding values for radicals (IV).

A comparison of the experimental rate constants with the values of the diffusion-controlled rate constants of quenching of these radicals in second-order reactions at different temperatures, $(2k_t)_{dif}$, calculated with the Smolukhovskii equation [5], is reported below

$$(2k_t)_{dif} = 1.11\cdot 10^{5}\cdot \frac{T}{A}\cdot \exp\,(-B/RT),\ \mathrm{liter/mole\cdot sec}$$

where T is the absolute temperature, °K; A and B are constant values in the equation for the viscosity of the corresponding alcohol

$$\eta = A\cdot \exp\,(B/RT),\ \mathrm{g/cm\cdot sec}$$

The data on the viscosity of (I) is contained in [6]; the values of the viscosity of (III) at different temperatures are reported in Table 3. Coefficients A and B for (I) and (III) are, respectively, equal to $1.38\cdot 10^{-8}$ and $1.15\cdot 10^{-6}$ g/cm•sec and 43.1 and 34.0 kJ/mole.

The calculated values of the constants $(2k_t)_{dif}$ for the HCR of (II) and (IV) are reported in Table 2. Note that the rate of quenching of the radicals is not limited by diffusion, but by the rate of their chemical reaction in the temperature range investigated, even with insignificant viscosity of the alcohols. The contact model of chemical reactions [7] establishes the ratio between the rate constants of a diffusion-controlled reaction, $(k_t)_{dif}$, the chemical reaction in the cage, $(k_t)_{chem}$, and the experimentally determined rate constants, $(k_t)_{exp}$ as

$$\frac{1}{(k_t)_{exp}} = \frac{1}{(k_t)_{dif}} + \frac{1}{(k_t)_{chem}}$$

TABLE 2. Values of the Rate Constants of Quenching of HCR (liter/mole•sec•10^{-8}) in the Corresponding Alcohols at Different Temperatures in the Absence of Oxygen

T., °C	Radical	$(2k_t)_{exp}$	$(2k_t)_{dif}$	$(2k_t)_{chem}$	T., °C	Radical	$(2k_t)_{exp}$	$(2k_t)_{dif}$	$(2k_t)_{chem}$
26	(II)	0,70±0,06	0,77	–	85	(IV)	0,60±0,06	3,9	0,71
65	(II)	1,7±0,2	6,1	2,4	94	(IV)	0,81±0,08	5,1	0,96
100	(II)	2,8±0,3	30	3,2	110	(IV)	0,80±0,08	8,8	1,10
125	(II)	5,0±0,5	72	5,4	125	(IV)	1,10±0,10	13,2	1,20
150	(II)	6,7±0,5	220	6,9	135	(IV)	1,20±0,10	17,5	1,40

TABLE 3. Dynamic Viscosity η of Cyclododecanol at Different Temperatures*

T., °C	η, g/cm · sec · 10^2	T., °C	η, g/cm · sec · 10^2
90	9,67	160	1,41
100	6,72	180	1,02
120	3,65	200	0,706
140	2,10		

*The data were obtained in the Laboratory of Physicotechnical Studies at the State Scientific-Research and Planning Institute of the Nitrogen Industry and Organic Synthesis Products and were kindly supplied by I. F. Golubev.

For the determination of $(k_t)_{chem}$ at different temperatures, we used the experimental values of $(k_t)_{exp}$ and the calculated values of $(k_t)_{dif}$ (see Table 2).

In contrast to the chemical reaction of hydrocarbon radicals in a medium of the corresponding hydrocarbons [5], the event of the chemical reaction of HCR is characterized by a marked activation energy (see Table 2), 13-16 kJ/mole, and is not dependent on the number of C atoms in the ring of the cyclic alcohol molecules. The expressions for $(2k_t)_{chem}$ of these radicals are

$$(2k_t)_{\text{chem}}(\text{II}) = 4.0 \cdot 10^{10} \cdot \exp\ (-15\ \text{kJ/mole}/RT),\ \text{liter/mole} \cdot \text{sec}$$
$$(2k_t)_{\text{chem}}(\text{IV}) = 8.0 \cdot 10^{9} \cdot \exp\ (-14\ \text{kJ/mole}/RT),\ \text{liter/mole} \cdot \text{sec}$$

CONCLUSIONS

1. The kinetics of quenching of the radicals formed under the effect of electron irradiation on liquid cyclohexanol and cyclododecanol in the absence of oxygen were investigated by pulsed radiolysis, and the absolute rate constants of α-hydroxycyclohexyl and α-hydroxycyclododecyl radicals in the 26-150°C and 85-135°C range were determined.

2. The rates of quenching of these α-hydroxycycloalkyl radicals are limited by the rates of their chemical reaction.

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