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RADICALS IN THE γ-IRRADIATED HYDRATES OF THE THREE-MEMBERED CYCLES.

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We have discovered the striking increase in stability of the radicals formed by γ-irradiation of clathrate hydrates of cyclopropane, ethylene oxide and propylene oxide [1,2].

The ESR-spectrum of irradiated cyclopropane hydrate (fig.1, table) displays five well-resolved doublets and might be assigned to the radicals R_1 (see table), which has $a_\alpha = 6.51$ g and $a_\beta = 23.42$ g in liquid phase [4]. At $-196\,^\circ C$ the relative intensities ratio is somewhat different from (but at $-120\,^\circ C$ close to) a binominal one. No other changes in the spectrum were observed during increase in temperature up to that of recombination ($-15\,^\circ C$). Furthermore there is a doublet spectrum ($a \sim 503$ g) from stabilized hydrogens, which recombine at $-110\,^\circ C$.

The spectrum of pure cyclopropane irradiated at $-196\,^\circ C$ (fig.1, table) can be explained by formation of a mixture of the radicals. At $-160\,^\circ C$ the lines of radicals R_1 disappear and the line intensities of R_2 enhance , i.e. the radicals R_1 may undergo along with recombination also a conversion to R_2 (for which $a \sim 25$ g is an average of a_α and a_β [5]), probably via an intermediate isomerization to allyl radicals, revealed in the irradiated liquid cyclopropane[4]. At further increase in temperature the radicals R_2 disappear and at $-135\,^\circ C$ there are only the lines of radicals, for which structure R_3 is most probable. Thus in this system cyclopropyl radicals R_1 are most unstable, which being isolated in a cavity of

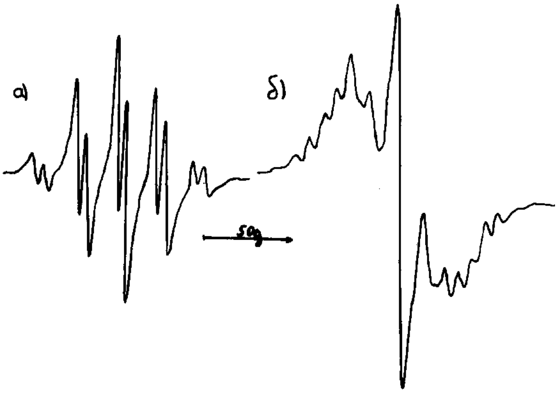

Fig.1.ESR-spectra of γ-irradiated:a)clathrate hydrate of cyclopropane at -120°C b)pure cyclopropane at -196°C.

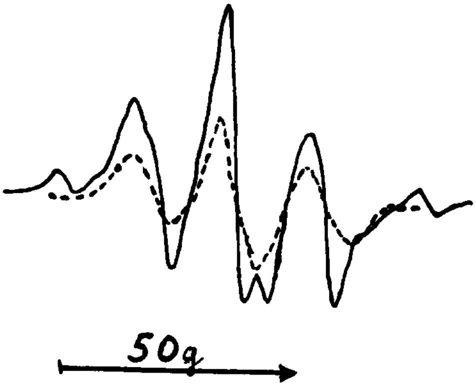

Fig.2.ESR-spectra of γ-irradiated clathrate hydrate of ethylene oxide at -150°C (solid line) and at-50°C (dashed line).

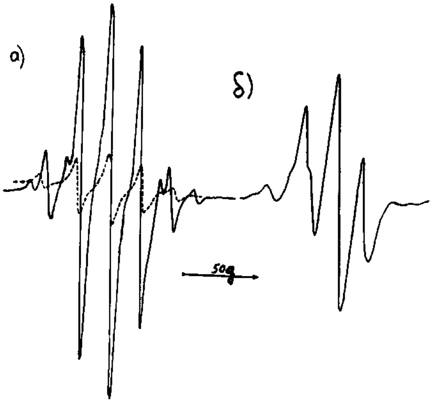

Fig.3ESR-spectra of γ-irradiated:a)clathrate hydrate of propylene oxide at -196°C (solid line)and at -40°C (dashed line); b)pure propylene oxide at -196°C.

Table

Compound	Matrix	Suggested radicals[a]	hf-splitting, g[b]	$T^{\circ}_{rec.}$ C
$\underbracket{CH_2CH_2CH_2}$	Hydrate[c]	$\underbracket{CH_2\dot{C}HCH_2}$(R_1)	a_α =6.6 a_β =24	-15
	Pure	R_1 $-CH_2\dot{C}HCH_2-$ (R_2) $-CH_2CH\doteq CH\doteq CH_2-$($R_3$)	a_α=6.5 a_β=24 $(a_\alpha + 4a_\beta)/5=25$ a_β =21	-160 -135 -130
$\underbracket{CH_2OCH_2}$	Hydrate[d]	$ROCH_2\dot{C}H_2$ (R_1') $RO\dot{C}H_2$ (R_2')	$(a_\alpha + a_\beta)/2 = 20.5$ a_α =19	-50 -15
	Pure	R_2' $H\dot{C}O$ (R_3')	a_α =19 a_α =135	-130 -130
$\underbracket{CH_2OCH}CH_3$	Hydrate	$\underbracket{CH_2O\dot{C}}CH_3$ (R_1'') $RO\dot{C}HCH_3$ (R_2'')	a_β =21 $(a_\alpha +3a_\beta)/4=20.5$	-40 -15
	Pure[e]	R_1'' R_2'' $RO\dot{C}H_2$ (R_3'')	a_β =22 $(a_\alpha +3a_\beta)/4$ =22 a_α =19	-70 -35 -105

a) Samples were irradiated at -196°C in a sealed ampoules with Co-60 source at the total irradiation dose 3 Mrad.

b) The ESR-spectra were taken on an ЭПР-2 ИХФ Model instrument.

c) A mixture of liquid cyclopropane and H_2O was frozen at stirring first at -70°C, then at -196°C.

d) Prepared by the method as [2].

e) Sample was evacuated to $p=10^{-2}$ Hg before irradiation.

clathrate hydrate stabilize and give well-resolved ESR-spectrum.

In the γ-irradiated three-membered heterocyclic compounds the radicals form mostly (or only) throgh the opening of cycles (see table).At -150°C (fig.2)the spectrum of irradiated ethylene oxide hydrate corresponds to the mixture of radicals R_1' and R_2';the broader pattern refering to R_1',similar to the radicals producing at irradiated 1,3-dioxolane hydrate[3].At -50°C there appears only a triplet with intensities relating as 1:2:1 resulting from the radicals R_2' recombined only at -15°C.In the pure compound the radicals R_2' and R_3' recombine at the essentially lower temperature.

In the clathrate hydrate of propylene oxide (fig.3) the radicals R_2'' stability increases analogously (table).

Increased stability of the radicals caved by clathrate hydrates facilitates identification of the generated radicals and enables to trace their transformations in the larger temperature interval in respect to the pure compunds.On the other hand it gives opportunity to study the conformations of radicals[7] as it has been shown recently[3].

Detailed analysis of date obtained will be published.

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