57. Optical Absorption Spectra for the Solvated Electron Observed in the Pulse Radiolysis of *cis*- and *trans*-Isomers of 3- and 4-Methylcyclohexanols

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The absorption band maximum of solvated electrons, $\lambda_{max}(e_s^-)$, in 3- or 4-methylcyclohexanols is observed at longer wavelengths (818–837 nm), if the OH group is axial, and at shorter wavelengths (721–723 nm), if it is equatorial. It is surmised that the size of cavity for the solvated electron is larger in the former case and smaller in the latter.

Introduction. – The solvated electron is one of the characteristic reactive species in the radiolysis of polar and some nonpolar liquids. The optical absorption spectra for the solvated electrons in polar liquids such as alcohols have been already measured [1–5]. Especially, *Hentz* and *Kenney-Wallace* [5] have made a systematic study on the characteristics of the absorption band for the solvated electron in 25 different alcohols by using pulse-radiolysis technique. They have shown that the alcohols can be roughly classified into the three categories, *i.e.* the *primary, secondary,* and *tertiary* alcohols, according to the magnitudes of $\lambda_{max}(e_s^-)$.

In the present study, we have observed the stereochemical effect on $\lambda_{max}(e_s^-)$ by pulse radiolysis of the *cis*- and *trans*-isomers of 3- and 4-methylcyclohexanols (hereafter abbreviated as MCH).

Results and Discussion. – To calibrate our optical detection system, we have measured the absorption spectrum of the solvated electron in EtOH immediately after a pulse of 0.50 µs with the result shown in the *Figure, a.* The absorption spectrum of the solvated electron is characterized by the structureless, broad absorption band ranging from UV to near IR.

Since $\lambda_{max}(e_s^-)$ has been measured in EtOH [1–5], it may serve as a standard. However, the values at room temperature reported range from 681 [4] to 729 [5] nm, indicating the difficulty of accurate determination of $\lambda_{max}(e_s^-)$. Our $\lambda_{max}(e_s^-)$ value of 684 nm agrees well with that recently determined by *Freeman* and coworkers [4].

Included in the *Figure, a,* are the transient absorption spectra observed in *cis*- and *trans*-4-MCH. $\lambda_{max}(e_s^-)$ for the *cis*-isomer is found at distinctly longer wavelength than for the *trans*-isomer.

The *Figure, b,* shows the transient absorption spectra in *cis*- and *trans*-3-MCH. Again, $\lambda_{max}(e_s^-)$ value for the *cis*-isomer is well separated from the value for the *trans*-isomer. It is worthwhile to note that $\lambda_{max}(e_s^-)$ for *cis*-3-MCH and *trans*-4-MCH are essentially the same and are found at shorter wavelength than for *trans*-3-MCH and *cis*-4-MCH.

The *Table* summarizes some characteristics of the absorption bands of the solvated electron in the alcohols studied.

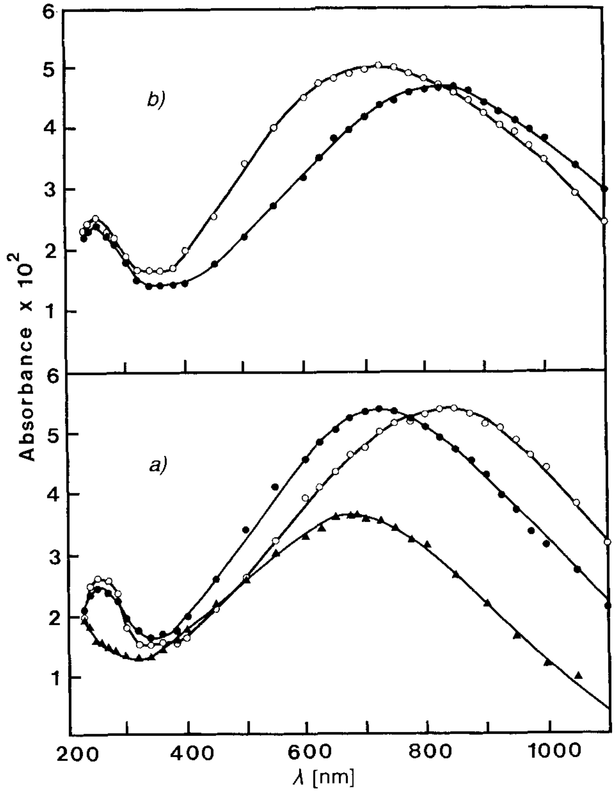

Fig. a) *Absorption spectra of the transient species produced on pulse radiolysis of EtOH* (▲), cis-*4-methylcyclohexanol* (○), *and* trans-*4-methylcyclohexanol* (●); b) *absorption spectra of the transients in* cis-*3-methylcyclohexanol* (○) *and* trans-*3-methylcyclohexanol* (●). Pulse duration, 0.50 µs; dose per pulse, 3.4 krad; irradiation temp., 25 ± 2°.

Table. *Some Characteristics of the Absorption Bands for the Solvated Electron in the Alcohols Observed in Pulse Radiolysis*[a])

Alcohol	$\lambda_{max}(e_s^-)$[b])		$w_{1/2}$[c])	$G \cdot \varepsilon(e_s^-)_{max}$[d])	Reference
	[nm]	[eV]	[eV]	10^{-4} [100 eV · M · cm]$^{-1}$	
EtOH	681	1.82	1.59	1.56	[4]
EtOH	684	1.81	1.70	1.26	This work
cis-3-Methylcyclohexanol	723	1.72	1.69	1.53	This work
trans-3-Methylcyclohexanol	818	1.52	1.38	1.42	This work
cis-4-Methylcyclohexanol	837	1.48	1.37	1.62	This work
trans-4-Methylcyclohexanol	721	1.72	1.57	1.64	This work

[a]) Pulse length = 0.50 µs. Dose per pulse = 3.4 krad. Irradiation temp. = 25 ± 2°.

[b]) Mean deviation = ± 1%.

[c]) Width of the absorption band at half-height.

[d]) This quantity depends on the dose per pulse and pulse length.

With EtOH, we could observe in the UV region an absorption band extending to VUV which has already been measured by *Arai* and *Sauer* [2] and assigned to 1-hydroxyethyl radical $CH_3\dot{C}HOH$. In the case of 3- and 4-MCH, the narrow UV absorption bands are also observed which may correspond to 1-hydroxy-3- and 1-hydroxy-4-methylcyclohexyl radicals, respectively. The UV absorption bands for the radical species are characterized by their slow decay compared with rapid decay of the absorption bands for the solvated electron. The UV absorption bands are, however, not the primary concern in the present study.

An interesting point in the present study is that the conformation of Me group remote from the OH group has a striking effect on $\lambda_{max}(e_s^-)$. Interpretation of the absorption spectrum of the solvated electron has, so far, been made on the basis of semiempirical [6] [7] to *ab initio* [8] methods. However, such methods may not be suitable to explain the observed effect in view of the complexity of MCH.

An attempt is made to qualitatively rationalize our finding. The stable conformations of MCH isomers are known from the analysis of ^{13}C-NMR spectra [9] as follows: *cis*-3-MCH (eq-OH, eq-CH_3), *trans*-3-MCH (ax-OH, eq-CH_3), *cis*-4-MCH (ax-OH, eq-CH_3), and *trans*-4-MCH (eq-OH, eq-CH_3).

Thus, the solvated electrons are considered to mainly be surrounded by the equatorial OH groups in the case of *cis*-3-MCH and *trans*-4-MCH. On the other hand, the solvated electrons should be surrounded by the axial OH groups in the case of *trans*-3-MCH and *cis*-4-MCH. Now, when the absorption maximum of the solvated electron is interpreted in terms of 'the particle-in-a-box model', a bathochromic shift is known to occur with widening the box size. Then, the size of the cavity surrounded by the axial OH groups is inferred to be larger than that surrounded by the equatorial OH groups. A more detailed discussion of the structure of the solvated electron will be reported elsewhere.

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Experimental Part

Materials. cis- and *trans*-3-MCH *(ICN Biomedicals)*, and *cis*- and *trans*-4-MCH *(Aldrich)* were used after purification by *Pye* prep. GLC (model *104*). The MCHs were first purified through a 5-m *Igepal CO 880* column and subsequently through a 5-m *Apiezon L* column. The *cis*-isomer of MCH was not well separated from the *trans*-isomer of MCH by our prep. GLC. The purified *cis*-3-MCH and *trans*-3-MCH thus contained 1.0 mol-% *trans*-3-MCH and 0.4 mol-% *cis*-3-MCH, respectively. Similarly, 0.1 mol-% *trans*-4-MCH and 0.2 mol-% *cis*-4-MCH were found in the purified *cis*-4-MCH and *trans*-4-MCH, respectively. The MCHs purified by prep. GLC were refluxed with $NaBH_4$ *(Fluka, purum)* at 70° for 24 h under Ar to eliminate reducing impurities. The refluxed MCHs were dried over freshly activated granular CaO for one week under vacuum. Abs. EtOH *(Fluka, puriss. p.a.)* was refluxed with $NaBH_4$ and subsequently dried over freshly activated molecular sieve (3 Å) for one week. H_2O contents in the purified EtOH and MCHs were determined to be < 0.03 wt-% both by anal. GLC equipped with a 50-cm *Poropak Q* column and the *Karl Fischer* titration method. H_2O used for dosimetry was purified by a *Millipore Milli-Q* system. KSCN *(Merck, pro analysi)*, Ar (*l'air liquide*, 99.9997%), and O_2 *(Carbagas)* were used as received.

Procedures. The alcohol (3 ml) was put in a quartz cell (1 cm deep, 1 cm optical path, 5 cm high) fitted with two *Teflon* stopcocks. The samples were deaerated by bubbling with Ar for 2 h before irradiation with 0.5-µs pulses of 3-MeV electrons from a *Van de Graaff* accelerator (*High Voltage*, Model *KS 3000*). The current intensity was 250 mA. The irradiation temp. was 25 ± 2°.

A pulsed Xe arc lamp (*Hanovia, L-5237000*, 450 W) was used as a continuum light source for optical-absorption measurements. Light transmitted by the sample was focused on the slits of a *Bausch & Lomb 33-86-25* monochromator connected with either a *33-86-77* IR or *33-86-76* VIS, or *33-86-79* UV/VIS grating. An appropriate *Schott* glass filter was placed between light source and irradiation cell to eliminate second-order contributions. Measurements between 230 and 450 nm were made using an *RCA 4840* photomultiplier. Above 450 nm, an *RCA C 30808* silicon photodiode was used. The output signal from the photodetector was recorded on a *Tektronix 2430* digital oscilloscope coupled with a *Tektronix 7834* storage oscilloscope.

The dose absorbed per pulse was measured using O_2-saturated 5 mM KSCN aq. solns. as dosimetry. The dose per pulse was determined as 3.4 krad taking $G \cdot \varepsilon\ ((SCN)_2^-) = 2.1 \times 10^4\ (\text{M} \cdot \text{cm} \cdot 100\ \text{eV})^{-1}$ at 478 nm [10].

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