

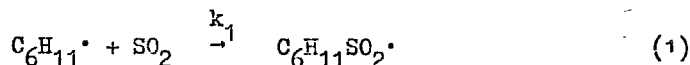
Studies of the sulfoxidation of alkanes II

A pulseradiolysis study on the reactions of cyclohexyl radical with SO₂ and O₂ respectively

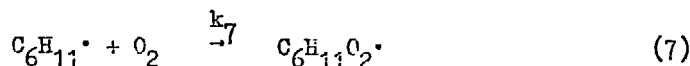
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Summary: The transient absorptions produced by pulses of high-energy electrons into pure cyclohexane resp. into cyclohexane containing SO₂ or O₂ have been studied. The UV-absorption spectra observed are ascribed to cyclohexyl-, cyclohexylsulfinyl- resp. cyclohexylperoxyradicals. The cyclohexylradical spectrum has a maximum at $\lambda \leq 240$ nm and $\epsilon_{240} = (2,3 \pm 0,7) \cdot 10^3 \text{ M}^{-1} \text{ cm}^{-1}$. The cyclohexylsulfinylradical probably has a maximum at $\lambda = 355$ nm $\epsilon_{355} = (1,0 \pm 0,3) \cdot 10^3 \text{ M}^{-1} \text{ cm}^{-1}$. Contrary to what is earlier reported for the cyclohexylperoxyradical we have found only one absorption maximum with $\lambda_{\text{max}} = 255$ nm and $\epsilon_{255} = (4 \pm 1) \cdot 10^3 \text{ M}^{-1} \text{ cm}^{-1}$.

The rate-constants for the reactions



and



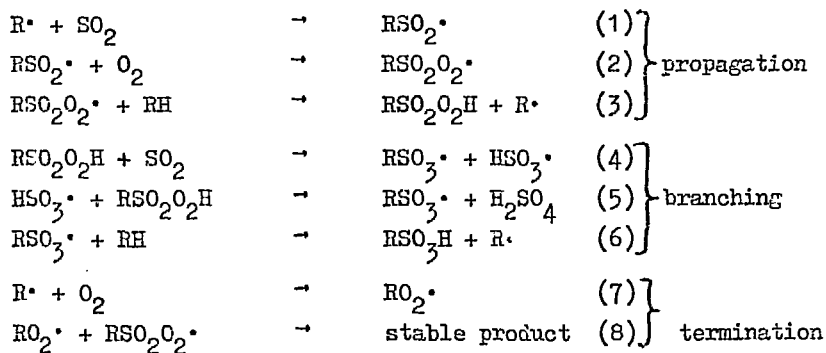
have been determined to $k_1 = (2,0 \pm 1) \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$
and $k_7 = (3,4 \pm 0,6) \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$.

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It is concluded that the competition between reactions (1) and (7) determines the kinetic chain-length in the initial stage of the sulfoxidation of pure hydrocarbons. Reported G-values for the sulfoxidation in the presence of water are higher than expected from this competition and this is attributed to the fact that reaction (1) to an appreciable extent takes place in the polar phase.

Introduction:

In an earlier work /1/ it was shown that initially the reaction-rate of the spontaneous sulfoxidation grows exponentially. The time constant was found to increase with the SO_2/O_2 - ratio. The following reaction sequence was suggested:



The competition between reactions (1) and (7) was assumed to be responsible for the observed dependence on SO_2 -resp. O_2 -concentration. The reactions (1) and (7) have earlier been studied in the gas-phase for $\text{R}^\bullet = \text{C}_2\text{H}_5^\bullet$ /2/ and the ratio k_1/k_7 was found to be $\approx 10^{-2}$ x). It is commonly accepted that radiolysis of liquid cyclohexane produces

x) If this very low value had any relevance for the liquid phase sulfoxidation the above given reaction mechanism seems impossible.

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cyclohexylradicals as the dominating radical /3, 4, 5/. Pulserradiolysis studies on cyclohexane containing small amounts of SO_2 and O_2 thus should make it possible to determine k_1 and k_7 in the liquid phase. The constant k_7 has earlier been measured by ESR-technique and was found to be $4.3 \cdot 10^7$ /6/. The aim of this work was to determine k_1 and k_7 in the liquid phase in order to clarify the importance of reaction (7) for the sulfoxidation of alkanes.

Experimental

Materials: The cyclohexane (Merck p a) used in the pulse radiolysis experiments was treated with oleum (25 % in SO_3 1 part oleum per 10 parts-cyclohexane) until the UV-absorption ($\lambda \approx 200$ nm) caused by aromatics and olefins completely vanished. The acid breakdown products as well as SO_2 and SO_3 were extracted with 1 M NaOH. The hydrocarbon was then dried with alkali pellets and distilled. The cyclohexane purity was once more controlled by UV-spectrophotometry /7/.

O_2 was generally used directly from the tube, while SO_2 was dried either with concentrated sulfuric acid or calcium sulphate.

Preparation of samples: The optical cells used in the experiments were of Suprasil quartz, cylindrical in shape, 20 mm long and with a diameter of 20 mm. The cyclohexane was degassed on a vacuumline by conventional freeze-pump-thaw cycles until the residual pressure was $< 5 \cdot 10^{-5}$ torr at -196 °C. The SO_2 was measured with a gas buret Toepler-pump combination and freed out together with the degassed cyclohexane in the cell. In order to determine the rate constant of the reaction (7) small amounts (0.3-0.9 ml) air saturated cyclohexane were added to the degassed liquid.

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To measure the rate-constants k_1 and k_7 , SO_2 - and O_2 - concentrations in the range $5 \cdot 10^{-4}$ - $5 \cdot 10^{-5}$ were used. The determination of the transient absorption spectrum in SO_2 -containing cyclohexane was made in 10^{-3} M solutions. For the recording of the peroxyradical spectrum air saturated cyclohexane was used.

Irradiation and measurements: The kinetic spectrophotometer for pulse radiolysis is described in details elsewhere /8/. The microtron-accelerator produces single pulses of 7 MeV electrons at peak currents 100 ± 20 mA. Second order decays were produced from 4-4.5 μs pulses and the sweep-rate on the oscilloscop was adjusted to 5 or 20 $\mu\text{s}/\text{cm}$. In order to measure the pseudo-first order rate-constants 1-2 μs electron pulses were used and the sweep-rate was 1-5 $\mu\text{s}/\text{cm}$. The influence of stray light was reduced by a number of filters available at the exit slit of the monochromator. The dose was measured with a secondary emission chamber earlier calibrated by a $\text{K}_4\text{Fe}(\text{CN})_6$ dosimeter /9/.

Results: Changes in the optical transmission of pure and SO_2 - containing cyclohexane have been determined. Graphs of $1/\text{O.D.}$ (O.D. = optical density) as function of time as well as of (O.D.) \cdot time as function of O.D. were produced. For pure cyclohexane and cyclohexane 10^{-3} M in SO_2 the initial part of all decay curves show good agreement with second order kinetics (fig. 1). As the optical density has decreased to 0.003 - 0.004 slight deviations from linearity appear. This effect, mainly due to a statistical uncertainty in the position of the base line, may be due to disturbance from the mains.

From the $\frac{1}{kc_0}$ - resp. $\frac{k}{\epsilon}$ - values the rate-constants and extinction coefficients have been calculated assuming the G-value of cyclohexylradical formation to be 4 ± 0.5 /5/. The absorption spectra are given in fig. 2 resp. 3 and

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numerical values of k and ϵ in tables 1 and 2.

With the oscilloscope sweep-rate used (20 $\mu\text{s}/\text{cm}$) the optical density of air saturated cyclohexane reaches a constant value after the pulse. The resulting absorption spectrum is shown in fig. 4.

The reaction $\text{R}^{\cdot} + \text{O}_2$ has been followed at 280 nm as an increase of optical density after the pulse. Similarly the reaction $\text{R}^{\cdot} + \text{SO}_2$ was followed at 360 nm. In both cases the observed pseudo-first order rate constants were found to be proportional to the concentration of dissolved gases.

Discussion:

Transient spectra: The absorption-spectrum for the cyclohexylradical obtained in this work is given in fig. 2 together with the spectrum given by Sauer and Mani /4/. The ordinate has been chosen as $\frac{\epsilon}{k}$ to make the comparison independent of faults in dosimetry as well as differences in assumed G-values. A very good agreement is observed for $\lambda \geq 260$ nm, but for $\lambda < 260$ nm the $\frac{\epsilon}{k}$ -values found in this work are significantly higher. Due to the fact that accurate measurements at shorter wavelengths than 235 nm could not be made the position of the maximum can not be determined. As the spectrum of Sauer and Mani seems to be influenced by stray-light it can be concluded that the maximum may be found at a wavelength shorter than 240 nm. The rate-constant for the reaction $\text{C}_6\text{H}_{11}^{\cdot} + \text{C}_6\text{H}_{11}^{\cdot}$ is found to be $k = (1.8 \pm 0.5) \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$. As can be seen from table 1 the agreement with earlier reported results is fairly good. The extinction coefficient at $\lambda = 240$ nm thus should be $(2.3 \pm 0.7) \cdot 10^3 \text{ M}^{-1} \text{ cm}^{-1}$. The true value may eventually be higher as the interference by scattered light can not be fully excluded.

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The cyclohexylperoxyradical spectrum (fig. 4) shows no resemblance with what has earlier been reported /10, 11/. The spectra have, however, been recorded with somewhat different experimental conditions. In our work N_2 has been present and the oxygen concentration has been $\approx 2 \cdot 10^{-3}$ M as compared to $\approx 1 \cdot 10^{-2}$ M in the earlier work.

It seems somewhat unreasonable that the discrepancy should be due to these differences. Assuming a G-value for the peroxyradical formation of 4 ± 0.5 the extinction coefficient can be estimated to be $\epsilon_{255} = (4 \pm 1) \cdot 10^3 \text{ M}^{-1} \text{ cm}^{-1}$. The rate-constant for the formation of the peroxyradical was found to be $(3.4 \pm 0.6) \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$.

The absorption observed in cyclohexane containing SO_2 is ascribed to be $C_6H_{11}SO_2$ - radical formed in a reaction between the cyclohexylradical and SO_2 . In a 10^{-4} M SO_2 -solution we assume that no other species than the cyclohexylradicals will react with SO_2 (i.e. no electron or hydrogenradical scavenging occurs). The rate-constants for the reaction (1) was then determined to be $2 \pm 1 \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$. The decay of the absorption obeys second order kinetics in a 10^{-3} M solution. We suggest that the reaction observed is the combination of two $C_6H_{11}SO_2$ -radicals possibly forming the mixed anhydrid of sulfonic and sulfinic acid. Oae and Ikura /12/ believe that they have prepared a sulfinyl sulfonate and Kice and Favstritsky /13/ have suggested that this compound is formed by the recombination of two $ArSO_2$ ·-radicals. The value found for $\frac{\epsilon_{355}}{2k}$ is $(7.2 \pm 0.5) \cdot 10^{-6}$. Assuming $G(C_6H_{11}SO_2 \cdot)$ to be 4 ± 0.5 we get $k = (7.1 \pm 1.5) \cdot 10^8 \text{ M}^{-1} \text{ s}^{-1}$ and $\epsilon_{355} = (1.0 \pm 0.5) \cdot 10^3 \text{ M}^{-1} \text{ cm}^{-1}$.

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Sulfoxidation of cyclohexane: If the kinetic chain-length K_L of the sulfoxidation reaction in cyclohexane is assumed to be determined by the competition between reactions (1) and (7), where $RO_2\cdot$ combines with a chain propagating radical in reaction (8), the results of this work give

$$0.12 \cdot \frac{C_{SO_2}}{C_{O_2}} < K_L < 0.54 \cdot \frac{C_{SO_2}}{C_{O_2}}$$

In the presence of water the sulfoxidation is an unbranched chain-reaction due to the fast reaction between persulfonic acid and water. In this case the G-value for the γ -initiated reaction should be determined by the product of the radiation-yield of radicals, which can initiate the reaction, G_i and the chain-length

$$G (\text{sulfonic acid}) = G_i \cdot K_L \quad (\text{I})$$

It seems reasonable to believe that the reaction is initiated not only by the sulfinylradicals formed but also by the $HSO_2\cdot$ -radicals. The bond strength of $HSO_2\cdot$ has been estimated to be 50-60 kcal mole⁻¹ /14/ and gas phase studies show that the reaction $H\cdot + SO_2 + M$ is fast /14, 15/. In cyclohexane containing high concentrations of SO_2 we assume that the sum of $G(RSO_2\cdot) + G(HSO_2\cdot)$ is approximately 6. From this value the rate-constants and solubilities we calculate the G-value for sulfonic acid production in the presence of water at 25 °C and $P_{SO_2} / P_{O_2} = 2$ to be $40 < G (\text{sulfonic acid}) < 180$. Compared with earlier reported G-values for the sulfoxidation in alkanes (table 4) this value seems somewhat smaller. As both reaction (1) and (7) probably are diffusion controlled, the ratio $\frac{k_1}{k_7}$ should be rather insensitive to temperature and approximately constant for different hydrocarbons. The SO_2 - and O_2 -concentrations in cyclohexane were determined for the experimental conditions used by Hummel et al. /16/

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($t = 15^\circ\text{C}$ and $P_{\text{SO}_2}/P_{\text{O}_2} = 2$).

Using these values ($0.30 \text{ M}^- \text{SO}_2$ and $0.004 \text{ M}^- \text{O}_2$) and the $\frac{k_1}{k_7}$ - ratio found in this work the G-value for sulfonic acid production is 150 ± 90 . This value is approximately a factor 2 smaller than the experimental G-value. The difference is probably due to the fact that reaction (1) to an appreciable extent takes place in the polar phase, where the concentration ratio SO_2/O_2 from the solubilities of respectively SO_2 and O_2 in concentrated H_2SO_4 can be expected to be much higher than in the hydrocarbon /17/. This assumption is also in agreement with the high disulfonic acid production reported for the sulfoxidation of $\text{C}_{13} - \text{C}_{17}$ n-paraffins /18, 19/.

According to Gubelt /20/ the sulfonic group gives an efficient protection of C-H-bonds in the α -, β - and γ -positions. The low disulfonic acid production reported for the sulfoxidation of cyclohexane /16, 21/ is most probably due to this protecting effect.

The relatively short kinetic chain-length found in the hydrocarbon phase, of the order 10-30, clearly indicates that the reactions (7) and (8) are the dominating radical consuming reactions during the initial stage of the water-free sulfoxidation in pure hydrocarbons. The kinetic behaviour is complicated by the fact that as the conversion increases not only the persulfonic acid concentration but also the kinetic chain-length increase. This means that an exponential increase of the reaction rate according to Ae^{kt} only could give an approximate description of the experimental results /1/.

In the propagation sequence of the sulfoxidation the reactions (1) and (2) are expected to be very fast compared to reaction (3). To which extent the reaction (1) proceeds

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in the polar phase will thus be determined by the solubilities of the $\text{RSO}_2\text{O}_2^\cdot$ - radical in hydrocarbon respectively product-phase. This might, at least partly, explain the decrease observed in the sulfoxidation rate with increasing chain-length of the hydrocarbons/1, 22/, as the reaction to an increased extent will take place in the hydrocarbon phase.

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Studies of the
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- 1 Bjellqvist B
to be published
- 2 Good A and Thynne J C J
Trans Faraday Soc 63 (1967) 2708
- 3 Fessenden R W and Schuler R H
J Chem Phys 39 (1963) 2147
- 4 Sauer M C and Mani I
J Phys Chem 72 (1968) 3856
- 5 Perner D and Schuler R H
J Phys Chem 70 (1966) 2224
- 6 Smaller B, Remko J R and Avery E C
J Chem Phys 48 (1968) 5174
- 7 Nilsson O
Acta Chem Scand 21 (1967) 1501
- 8 Reitberger T
to be published
- 9 Rabani J and Matheson M S
J Phys 70 (1966) 761
- 10 McCarthy R I and MacLachlan A
J Chem Phys 35 (1961) 1625
- 11 McCarthy R I and MacLachlan
Trans Faraday Soc 56 (1960) 1187
- 12 Oae S and Ikura K
Bull Chem Soc Jap 40 (1967) 1420
- 13 Kice J L and Favtritsky N A
J Org Chem 35 (1970) 114
- 14 Kallend A S
Trans Faraday Soc 63 (1967) 2442
- 15 Fennimore C P and Jones C W
J Phys Chem 69 (1965) 3593
- 16 Hummel D O, Menzel W and Schneider C
Liebig's Ann Chem 673 (1964) 13
- 17 Landolt-Börnstein Vol II:2b
(6th edition) p 1-36 resp. 1-41

Studies of the
sulfoxidation ... II

- 18 Asinger F and Saus A
Symposium on the utilization of large radiation
sources and accelerators in industrial processing,
München 18-22 Aug. 1969. Proceedings p 77
- 19 Rösinger S
Ibid p 91
- 20 Gubelt B
Dissertation, TH, Aachen (1967)
- 21 Graf R
Liebigs Ann Chem 578 (1952) 50
- 22 Černý O
Coll Czech Chem Commun 33 (1968) 257
- 23 Ebert M, Keene J P and Swallow A J
Proc Roy Soc Ser A (1965) 1
- 24 Burkhardt R D
J Phys Chem 73 (1969) 2703
- 25 Carlsson D J and Ingold K U
J Am Chem Soc 90 (1968) 7047
- 26 Dingley D P and Calvert J G
J Am Chem Soc 85 (1963) 856
- 27 Jolley J E
J Am Chem Soc 79 (1957) 1537
- 28 Fricke H and Thomas J K
Radiation Res suppl 4 (1964) 35
- 29 Black J F and Baxter E F
2nd United Nations International Conference
on the peaceful uses of atomic energy,
Geneva 1958. Proceedings vol 20 162

TABLE 1 RATE CONSTANTS

Reaction	k $M^{-1} s^{-1} \cdot 10^{-9}$	t $^{\circ}C$	Measuring technique	References
$C_6H_{11}^{\cdot} + C_6H_{11}^{\cdot}$	$1,8 \pm 0,5$	$25^{\circ}C$	pulse radiolysis	this work
	$2,0 \pm 0,6$		pulse radiolysis	/4/
	1,25		pulse radiolysis	/23/
	1,25	$10^{\circ}C$	pulse radiolysis	/6/
	0,6		rotating sector	/24/
	1,35		rotating sector	/25/
$C_6H_{11}^{\cdot} + O_2$	$3,4 \pm 0,6$	$25^{\circ}C$	pulse radiolysis	this work
	0,043	$25^{\circ}C$	pulse radiolysis	/6/
$C_2H_5^{\cdot} + O_2$	4,2	$25^{\circ}C$	gas flash photolysis	/26/
	0,06	$35^{\circ}C$	gas photolysis	/27/
$H^{\cdot} + O_2$	26		pulse radiolysis	/28/
$C_6H_{11}^{\cdot} + SO_2$	2 ± 1		pulse radiolysis	this work
$C_2H_5^{\cdot} + SO_2$	0,0004		gas photolysis	/2/
$C_6H_{11}SO_2^{\cdot} + C_6H_{11}SO_2^{\cdot}$	$0,71 \pm 0,15$		pulse radiolysis	this work

TABLE 2 WAVE LENGHT FOR ABSORPTION MAXIMA AND EXTINCTION COEFFICIENTS

Radical	Solvent	λ_{\max} nm	ϵ_{\max} $M^{-1} \text{cm}^{-1} \cdot 10^{-3}$	References
$C_6H_{11}\cdot$	cyclohexane	≤ 240	$\geq 2,3 \pm 0,7$	this work
	cyclohexane	240	$2,1 \pm 0,4$	/4/
	cyclohexane, A-saturated	250	$0,34^*$	/23/
$C_6H_{11}O_2\cdot$	cyclohexane, air saturated	255	4 ± 1	this work
	cyclohexane, O_2 -saturated	275, 297	$\epsilon_{275} \approx 2$ $\epsilon_{297} \approx 1$	/10/
$C_6H_{11}SO_2\cdot$	cyclohexane, $10^{-3}M$ in SO_2	355	$1,0 \pm 0,3$	this work
$C_6H_{11}(OH)SO_2\cdot$	cyclohexanol, SO_2 -saturated	390	--	/11/

* According to the authors, the value is probably too low due to the interference of scattered light.

TABLE 3 G-VALUES FOR SULFOXIDATION IN THE PRESENCE OF WATER

hydrocarbon	temperature °C	$\frac{P_{SO_2}}{P_{SO_2}}$	G-value molecules/100 eV	References
cyclohexane	15°C	2	350	/16/
cetane	30°C	2,4	211	/29/
cetane	55°C	2,4	59,2	/29/
C ₁₃ -C ₁₈ -n-paraffins	40°C	2	120	/18/

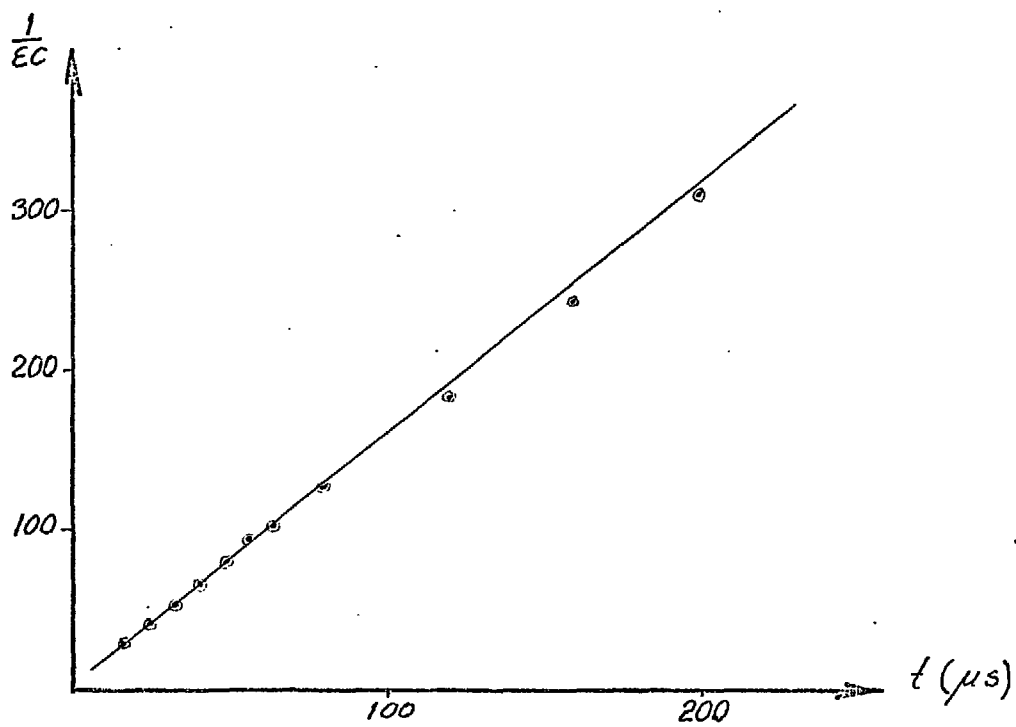


Fig. 1 a $1/\epsilon c$ as a function of t for cyclohexane at 240 nm

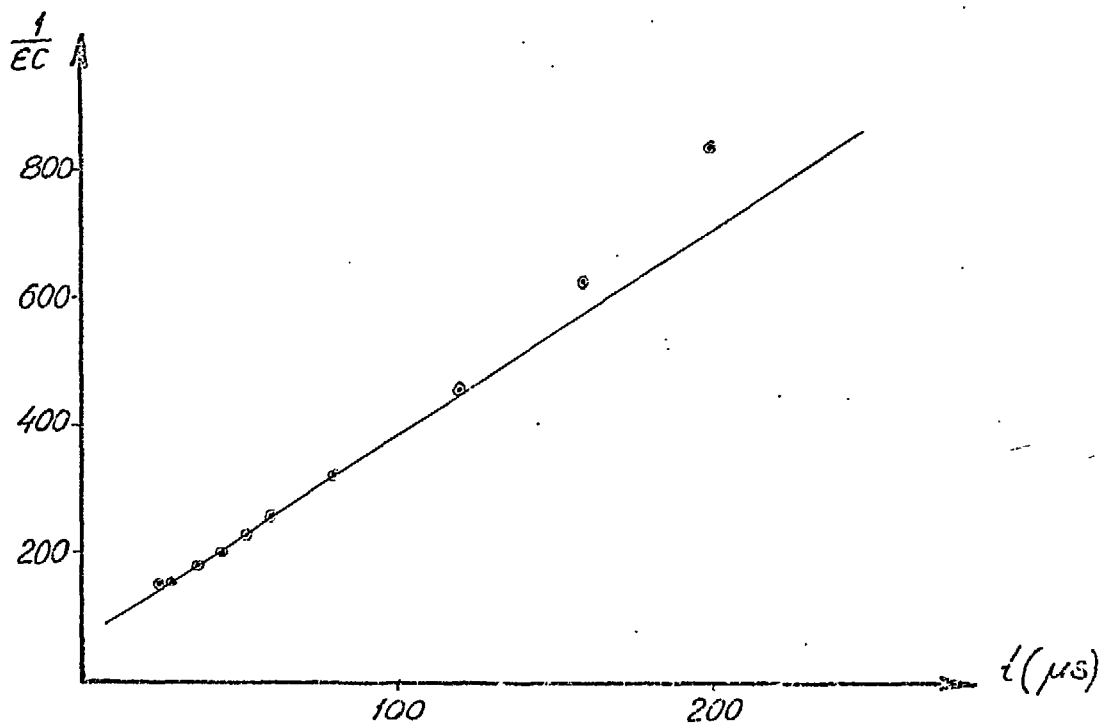


Fig. 1 b $1/\epsilon c$ as a function of t for cyclohexane 10^{-3} M in SO_2 at $\lambda = 355$ nm

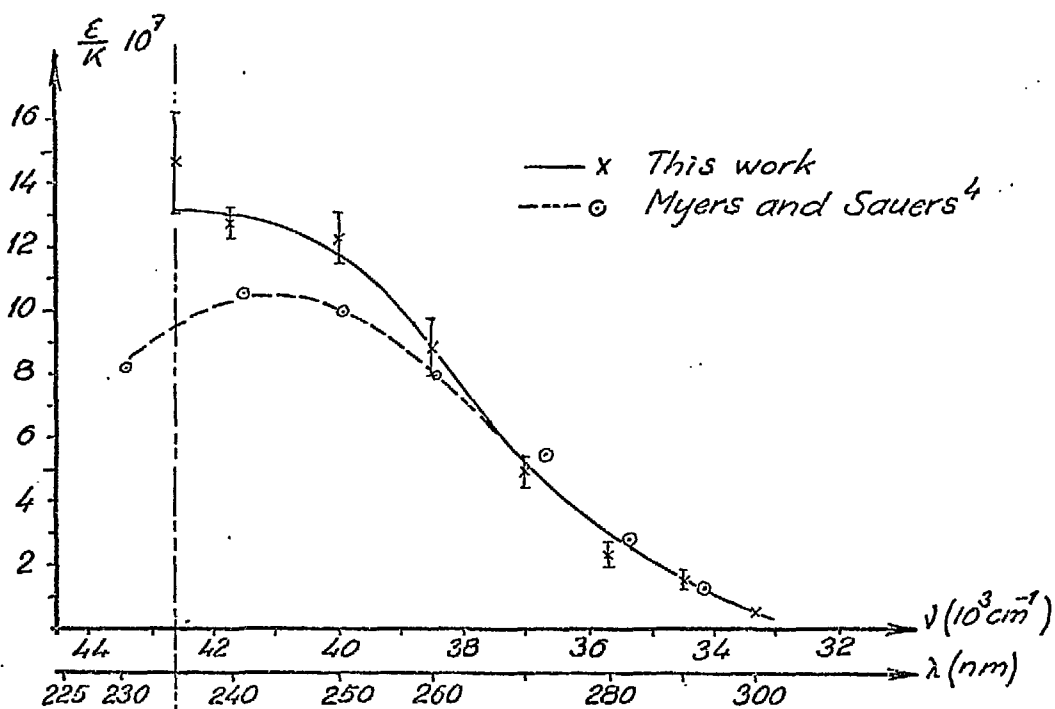


Fig. 2 Transient absorption spectrum in pure cyclohexane

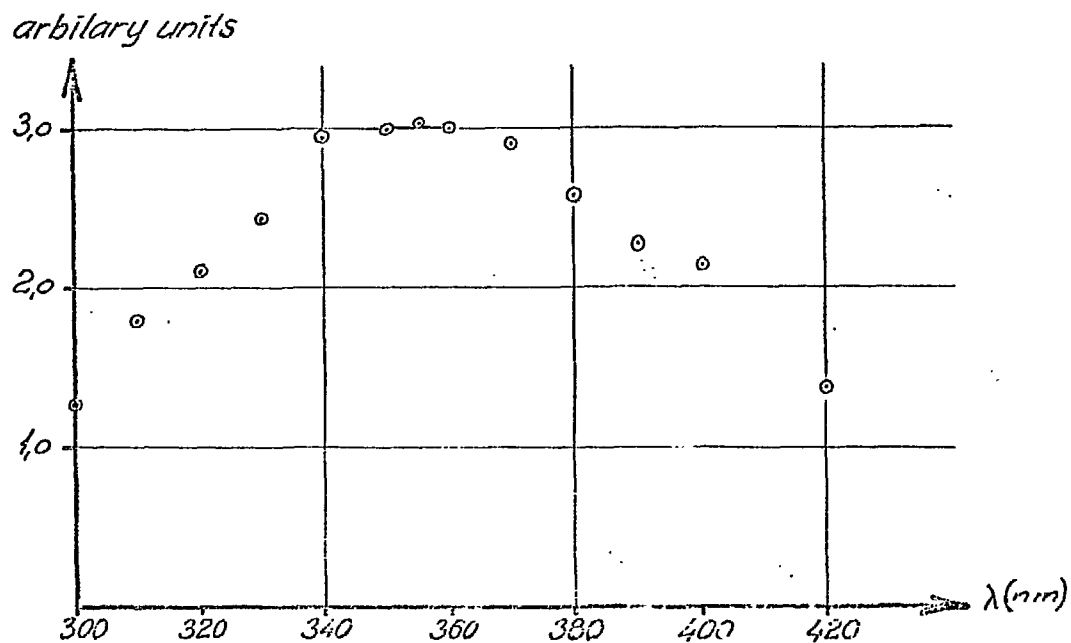


Fig. 3 Transient absorption spectrum in cyclohexane 10^{-3} M in SO_2

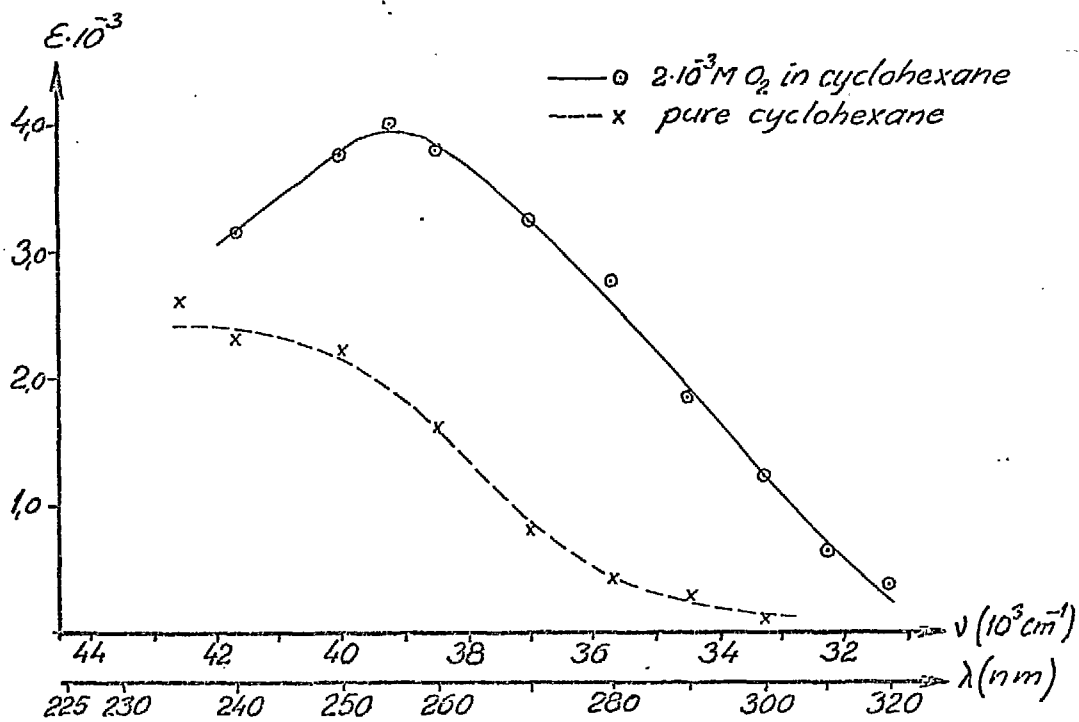


Fig. 4 Transient absorption spectra in pure cyclohexane and in cyclohexane containing O_2

