ACTA CHEMICA SCANDINAVICA 27 (1973) 3180–3194

Studies of the Sulfoxidation of Alkanes

I. The Dependence of the Sulfoxidation Rate on the Conversion and the SO_2/O_2 Ratio

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It is shown that in purified dry cyclohexane or n-alkane the sulfoxidation reaction starts spontaneously after an induction period. The reaction rates as a function of time have been determined for different mol ratios SO_2/O_2. Initially the reaction rate seems to be growing exponentially. The reaction constant characterizing this behaviour increases with the SO_2/O_2 ratio. This result is ascribed to a competition between the reactions

$$R\cdot + SO_2 \rightarrow RSO_2\cdot \qquad (1)$$

and

$$R\cdot + O_2 \rightarrow RO_2\cdot \qquad (2)$$

where the formation of alkylperoxy radicals leads to termination according to

$$RO_2\cdot + \text{radical} \rightarrow \text{stable product}$$

With high gas flows and good mixing the reaction rate reaches a maximum value and then decreases in a manner which indicates inhibition by the products formed. It is shown that addition of sulfuric acid inhibits the reaction. The sulfonic to sulfuric acid molar product ratio is for low conversions 1.3 – 1.9. This value increases with reaction time. As a part of this investigation the solubilities of oxygen and sulfur dioxide in cyclohexane, $C_{10}-C_{13}$ and $C_{13}-C_{17}$ n-alkanes were also determined.

The possibility to sulfoxidate cyclohexane and n-alkanes is known since 1940.[1] The reaction is a free-radical chain process and a variety of chain-initiating catalysts, *e.g.* γ-rays, UV-light, ozone and peroxides[2] have been used. From a study on cyclohexane Graf[3] suggested the following mechanism

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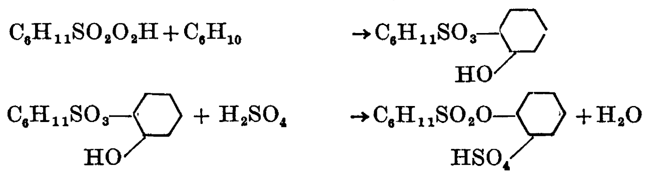
$$\text{Propagation}\quad\left\{\begin{array}{lll} C_6H_{11}\cdot + SO_2 & \rightarrow C_6H_{11}SO_2\cdot & (1)\\ C_6H_{11}SO_2\cdot + O_2 & \rightarrow C_6H_{11}SO_2O_2\cdot & (2)\\ C_6H_{11}SO_2O_2\cdot + C_6H_{12} & \rightarrow C_6H_{11}SO_2O_2H + C_6H_{11}\cdot & (3)\end{array}\right.$$

$$\begin{array}{l}\text{Branching and}\\ \text{product formation}\end{array}\quad\left\{\begin{array}{lll} C_6H_{11}SO_2O_2H & \rightarrow C_6H_{11}SO_3\cdot + OH\cdot & (4)\\ C_6H_{11}SO_3\cdot + C_6H_{12} & \rightarrow C_6H_{11}SO_3H + C_6H_{11}\cdot & (5)\\ OH\cdot + C_6H_{12} & \rightarrow H_2O + C_6H_{11}\cdot & (6)\\ H_2O + C_6H_{11}SO_2O_2H + SO_2 & \rightarrow C_6H_{11}SO_3H + H_2SO_4 & (7)\end{array}\right.$$

$$C_6H_{11}SO_2O_2H + C_6H_{12} \rightarrow C_6H_{11}SO_3H + C_6H_{10} + H_2O \qquad (8)$$



(9)

(10)

$$C_6H_{11}SO_2O_2\cdot + C_6H_{11}SO_2\cdot \rightarrow 2\ C_6H_{11}SO_3\cdot \qquad (11)$$

The steps (1) to (7) have commonly been accepted as correct. If all water produced in reaction (6) were to participate in reaction (7) a 2:1 ratio of RSO_3H to H_2SO_4 should result. The reported ratio using anhydrous reactants is appreciably higher and the steps (8) to (11) were proposed to explain this effect as well as the diolester formation. This explanation has been questioned by Black and Baxter[4] who instead suggested two alternative explanations. All the water might not be available for the reduction reaction due to hydrate formation. The rate of reduction is very slow and hence an appreciable concentration of water built up before the rate of reduction of persulfonic acid can approach that of its decomposition. It is also earlier known that, once started, the reaction continues even after the removal of the radical producing agent. Keller[5] has shown that using high pressures and temperatures of 50 – 60°C the sulfoxidation reaction of n-alkanes starts spontaneously if the molar ratio SO_2 to hydrocarbon in the liquid phase is bigger than one. In this work it is shown that after an induction period the sulfoxidation of purified, dry cyclohexane as well as higher n-alkanes also starts at room temperature and atmospheric pressure without addition of any catalysts.

Contradictory statements are found in the literature concerning the reaction rate dependence on the SO_2/O_2 ratio. Graf[3] studied the UV-initiated sulfoxidation of cyclohexane. SO_2 and O_2 in different ratios were bubbled through the hydrocarbon and the product was allowed to separate from the reaction mixture and collected at the bottom of the reaction vessel. The highest reaction rates were reported for the molar ratio $SO_2/O_2 = 2$. Graf states that with a higher SO_2-content in the gas-phase than 70 % the reaction rate is proportional to the partial pressure of O_2. Results similar to Graf's are reported by Black[4] and Dzjagatspanyan.[6] Bertram[7,8] γ-irradiated closed ampoules containing hexane in which SO_2 and O_2 were dissolved. In this investigation he found that the chain length was proportional to the square of the SO_2 concentration and independent of the oxygen concentration. In several patents [9,10] it is claimed that in the technical sulfoxidation of higher n-alkanes the preferred SO_2/O_2 ratio is between 6:1 and 15:1.

In the present investigation the reaction rates as function of time have been followed by measuring the gas consumption in the uncatalysed sulfoxidation of cyclohexane and n-alkanes for different SO_2/O_2 mol ratios. The effects of adding small amounts of water and sulfuric acid have also been investigated.

EXPERIMENTAL

Materials. The cyclohexane (Merck *p.a.*) and n-alkanes, respectively, (BP CD 331 and CD 364) were shaken with oleum 25 % in SO_3 (1 part oleum per 10 parts alkane) until the UV absorption caused by aromatics and olefines completely vanished. The acid breakdown products as well as SO_2 and SO_3 were extracted with 1 M NaOH. The hydrocarbons were then dried with alkali pellets. The pellets were changed at least twice due to the formation of a white precipitate on the pellets. Finally the hydrocarbons were allowed to stand with the pellets. Immediately before use the alkali pellets were filtered of and the purity once again controlled by UV-spectrometry.[1] [1]The gas chromatographically determined composition of the alkane mixtures are given in Table 1.

Table 1. Gaschromatographic analysis of the n-paraffin composition.

Number of C atoms	Per cent of the mixture $C_{10}-C_{13}$ paraffin	$C_{13}-C_{17}$ paraffin
9	0.3	–
10	6.7	–
11	31.3	3.6
12	32.7	3.5
13	24.4	5.4
14	3.1	22.8
15	0.1	26.7
16	–	22.4
17	–	12.8
18	–	1.2
19	–	–

The gases were dried first with concentrated sulfuric acid and then with P_2O_5.

Measurement of the sulfoxidation reaction rate. The reaction rates were followed by means of gas consumption measurements. The gas flow before and after the reaction vessel was measured with soap-bubble flow meters. Before and after the flow meters the gases were dried.

With gas flow velocities of 500 ml/min the precision of the measurements is better than ± 2 ml/min. The difference in gas flow was calculated assuming that the gases can be treated as ideal. When cyclohexane was used it was necessary to compensate for the vapour pressure. This was done assuming equilibrium between the liquid and the leaving gas stream. Losses of cyclohexane were eliminated by bubbling the gas stream through cyclohexane at 25°C. The pressure in front of the reaction vessel never increased more than 3 – 4 torr during an experiment. The influence of this effect on the measured gas consumption can be neglected. Due to the finite measuring time, approximately 3 minutes, slightly distorted curves are obtained for experiments in which the increase or decrease in gas consumption is very sharp. Approximately 80 % of the consumed gases are recovered as products. This figure is independent of the hydrocarbon conversion in the interval studied. The fact that less than 100 % of the gases are recovered can probably be seen as result of the high solubility of SO_2 in the product.

Experimental conditions. The reaction vessel, all glass, was filled with 100 ml of a hydrocarbon which first was freed from dissolved O_2 by N_2-bubbling and then equilibrated with a gas mixture of SO_2 and N_2 by bubbling. The time necessary for equilibrating the system was 4 h after which the gas stream leaving the system reached a steady-state value. The reaction was started by substituting the N_2-stream fully or only partly, with an O_2-stream. In some experiments with a long induction period during which the system could reach equilibrium, the hydrocarbon was saturated with SO_2 and the reaction started by mixing O_2 into the gas stream. The reaction mixture was vigorously stirred and thus the products did not separate. The temperature was 25 ± 0.2°C and the gas flow approximately 500 ml/min.

The reaction was stopped by adding water and due to the heat then evolved it was found necessary to cool the reaction mixture in order to get an uncoloured product.

The water used in the study of the effect of water addition was presaturated with gas of the same composition as used for the reaction. Sulfuric acid added during the reaction was made water-free by mixing with oleum. The liquids were added with a syringe through a septum above the hydrocarbon surface.

Determination of solubilities. The hydrocarbons were saturated with oxygen of atmospheric pressure at 25 ± 0.2°C and a sample of 1.00 ± 0.05 ml solution was transferred into an evacuated system. The hydrocarbon was frozen out with liquid N_2, and O_2 was transferred by a Toepler pump to a gas buret. After a number $(8-10)$ of freeze-pump-thaw cycles the oxygen was collected and measured.

To determine the SO_2-solubility the alkane was first freed from oxygen by N_2-bubbling in order to avoid the formation of sulfonic acids. The N_2-stream was then mixed with SO_2 and from rotameter values the mixing ratio and hence the partial pressure of SO_2 was known within 1 %. Four hours SO_2-N_2-bubbling was used to ensure that equilibrium was reached. The dissolved SO_2 was determined iodometrically.[12] The results of the solubility determination are given in Table 2 and Fig. 1. In those cases where these values could be compared with those given in the literature, the agreement is good. The SO_2- and O_2-concentrations given for the sulfoxidation experiments are based on these determinations and it has been assumed that the O_2-solubility is proportional to the pressure and independent of the SO_2-concentration. The gas consumption in the reaction causes changes in the composition of the gas stream leaving the reaction vessel. In calculations of concentrations, equilibrium has been assumed to exist between leaving gas stream and the reaction mixture.

Table 2. Determined solubilities of SO_2 and O_2 in the hydrocarbons used, $t = 25$°C, $p = 1$ atm.

Hydrocarbon	Solubility of SO_2 mol/l	Solubility of O_2 mol/l	References
Cyclohexane	0.340 ± 0.015	0.0112 ± 0.0010	this work
Cyclohexane		0.0115	[a]
$C_{10} - C_{13}$ n-Alkanes	0.284 ± 0.015	0.0104 ± 0.0007	this work
Dodecane		0.0083	[a]
$C_{13} - C_{17}$ n-Alkanes	0.261 ± 0.015	0.0087 ± 0.0007	this work
$C_{13} - C_{17}$ n-Alkanes	0.254 (20°C)	0.0084 (20°C)	21
Hexadecane		0.0077	[a]

[a] from Landolt-Börnstein.

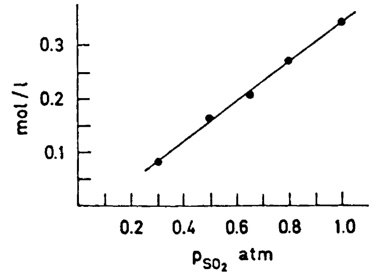


Fig. 1. SO_2-concentration in cyclohexane as a function of p_{SO_2} at $t = 25°C$.

Product analysis. The product mixture was freed from dissolved SO_2 in a rotating vacuum-evaporator and the analysis of the product phase was made by pH-titration in an acetone – water (9:1) mixture.[13]

RESULTS AND DISCUSSION

Initial period characterized by increasing reaction rates. The gas consumption as a function of time for the cyclohexane experiments are shown in Figs. 2 – 4. From the mechanism suggested by Graf, which describes the sulfoxidation as a linearly branched chain reaction, an exponentially increasing reaction rate is expected. As can be seen from Fig. 5 the results for the initial period of the sulfoxidation seems to be in agreement with this assumption. The first part of all curves has thus been fitted to the function Ae^{kt} and the resulting constants, k, are given in Table 3.

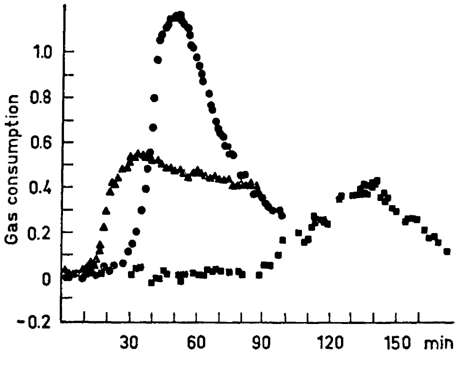


Fig. 2. The gas consumption (l gas (NTP)/l cyclohexane min) as a function of time for different SO_2/O_2-ratios at $t = 25°C$. a, ▲ $p_{SO_2} = 0.91$; $p_{O_2} = 0.09$; b, ● $p_{SO_2} = 0.84$; $p_{O_2} = 0.16$; c, ■ $p_{SO_2} = 0.67$; $p_{O_2} = 0.33$.

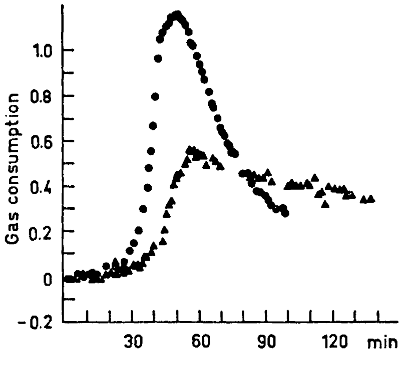


Fig. 3. The gas consumption (*cf.* text to Fig. 2) as a function of time for the sulfoxidation of cyclohexane at $t = 25°C$. a, ● $p_{SO_2} = 0.84$; $p_{O_2} = 0.16$; b, ▲ $p_{SO_2} = 0.68$; $p_{O_2} = 0.16$.

From Fig. 2 can be seen that the reaction constant k increases with increasing SO_2/O_2 ratio. In Figs. 3 and 4, respectively, this effect has been

Table 3. Results on the sulfoxidation of cyclohexane.

Curve	p_{SO_2}	p_{O_2}	p_{N_2}	c_{SO_2}	c_{O_2}	$\frac{c_{SO_2}}{c_{O_2}}$	Max. reaction rate	Integrated gas consumption to the maximum	Time constant k	Induction period
No.	atm	atm	atm	M	M		$\frac{\text{l gas NTP}}{\text{l min}}$	l NTP/l	min^{-1}	min
2a	0.91	0.09	–	0.31	0.0010	300±60	0.55	7	0.258±0.062	16
2b (3a)	0.84	0.16	–	0.28	0.0018	159±33	1.16	14	0.167±0.009	29
2c (4d)	0.67	0.33	–	0.22	0.0037	59± 2	0.40	12	0.039±0.023	97
3b (4b)	0.68	0.16	0.17	0.22	0.0017	128± 8	0.71	8	0.133±0.025	38
4a	0.68	0.08	0.25	0.22	0.0084	264±25	0.40	6	0.201±0.043	25
4c	0.68	0.18	0.14	0.22	0.0020	111±15	0.70	13	0.086±0.006	69
	0.89	0.11	–	0.30	0.0013	239±27	0.63	8	0.33 ±0.13	17
	0.71	0.29	–	0.23	0.0033	71± 3	0.72	12	0.101±0.028	73
	0.51	0.11	0.39	0.16	0.0012	134±18	0.67	13	0.117±0.006	67
	0.30	0.13	0.48	0.08	0.0014	≈60				> 300
	0.50	0.50	–	0.16	0.0056	≈30				> 300

Pressures and concentration relates to gas streams leaving the reaction vessel at half the maximum reaction rate. SO_2/O_2-consumption-ratio used in calculations = 2 corresponding to the assumption that gas not refound as products represents SO_2. Concentration ratio limits corresponding to zero reaction rate and maximum reaction rate.

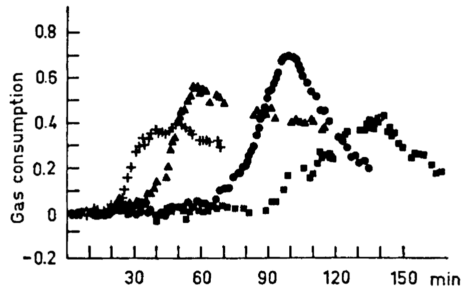


Fig. 4. The gas consumption (*cf.* text to Fig. 2) as a function of time for cyclohexane at $t=25°C$. a, + $p_{\mathrm{SO}_2}=0.68$; $p_{\mathrm{O}_2}=0.075$; b, ▲ $p_{\mathrm{SO}_2}=0.68$; $p_{\mathrm{O}_2}=0.16$; c, ● $p_{\mathrm{SO}_2}=0.68$; $p_{\mathrm{O}_2}=0.18$; d, ■ $p_{\mathrm{SO}_2}=0.67$; $p_{\mathrm{O}_2}=0.33$.

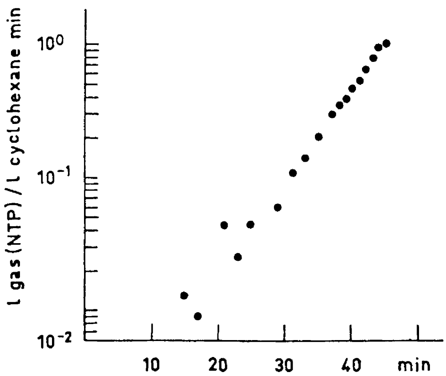


Fig. 5. Reaction rate as a function of time for the sulfoxidation of cyclohexane. $p_{\mathrm{SO}_2}=0.84$ atm; $p_{\mathrm{O}_2}=0.16$ atm.

separated into a positive SO_2-dependence and a negative O_2-dependence, respectively. The most reasonable explanation to the negative O_2-dependence is a competition between the reactions

$$R\cdot + SO_2 \rightarrow RSO_2\cdot \qquad (1)$$

$$R\cdot + O_2 \rightarrow RO_2\cdot \qquad (12)$$

where reaction (12) leads to termination. The rate constant for the reaction between cyclohexylperoxy radical and cyclohexane is very low. *G*-values of resulting products from γ-irradiation of cyclohexane containing O_2 make clear that liquid phase oxidation of alkanes is not a chain reaction at 25°C.[14] As the sulfonylperoxy radical does not seem to react with SO_2, this possibility could probably also be disregarded for the cyclohexylperoxy radical.

Applying the mechanism suggested by Graf and assuming reaction (12) to be the dominating radical consuming reaction k is expected to be proportional to the O_2-concentration. As can be seen from Fig. 6 a reasonable fit to a linear

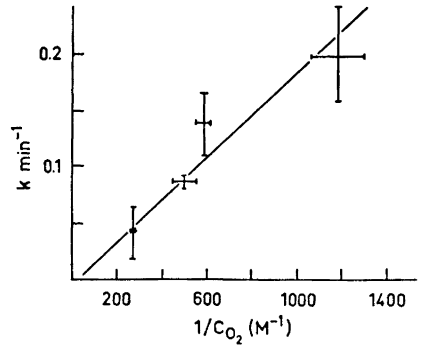


Fig. 6. The reaction constant k for the sulfoxidation as a function of 1/oxygen concentration. $p_{\mathrm{SO}_2}=0.68$ atm.

relation results when k is plotted as a function of $1/[O_2]$ for constant SO_2-concentration. Competition between reaction (1) and (12) gives a first order dependence of k on the SO_2-concentration. Due to the low precision no conclusion can be drawn concerning the SO_2-dependence. The conditions for which no reaction is observed (Table 3) indicate that at least for low SO_2-concentrations the initial period of the sulfoxidation is not determined solely by the concentration ratio SO_2/O_2. This is in agreement with Bertram's[7] finding that the reaction shows a second order dependence on the SO_2-concentration. Graf has shown that in SO_2-saturated cyclohexane the persulfonic acid forms a complex with SO_2. If the branching rather takes place according to

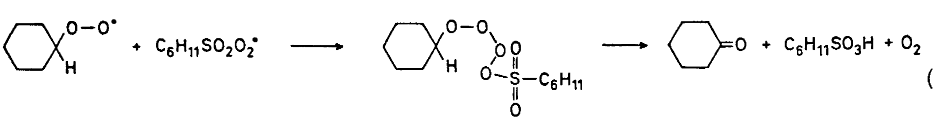
$$RSO_2O_2H{\cdot}SO_2 \rightarrow RSO_3{\cdot} + HSO_3{\cdot} \qquad (4a)$$

the SO_2 dependence might be influenced by the equilibrium

$$RSO_2O_2H + SO_2 \rightleftharpoons RSO_2O_2H{\cdot}SO_2 \qquad (13)$$

Bertram's results that the chain length is independent of the O_2-concentration might be due to trace amounts of impurities consuming radicals. The present experiments are less sensitive towards impurities as these should be consumed in such an early state of the reaction that their influence on k-values are negligible. The conditions in works[3-5] leading to the conclusion that the optimal SO_2/O_2 ratio is approximately two, differ from those in the present work as the product was allowed to separate continuously from the reaction mixture. The optimum SO_2/O_2 ratio of two relates to the steady-state, which as a result of the slow product separation might correspond to a point on the falling part of the rate *versus* time curves presented in Figs. 2 – 4.

Concerning the fate of the cyclohexylperoxy radical the propagation reactions (1) and (2) are addition reactions and probably very fast. Reaction (3) on the other hand is an abstraction reaction where the abstracting entity is a peroxy radical. Normally this type of reaction is very slow at room temperature[15] and thus the sulfonylperoxy radical is assumed to be the dominating radical in the reaction mixture. The probable fate of a cyclohexylperoxy radical will then be to take part in a recombination reaction with a sulfonylperoxy radical. In analogy with the Russel mechanism for recombination of primary and secondary alkylperoxy radicals[16] this reaction might probably involve the decomposition of a cyclic transition state in which one of the α-hydrogen atoms is transferred to give the products ketone and sulfonic acid.

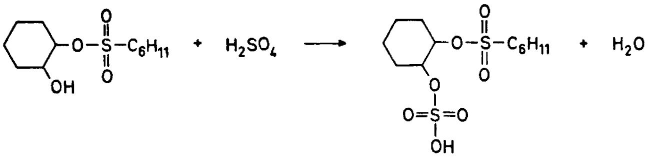


(14)

In the presence of sulfuric and sulfonic acids, respectively, the following steps could appear [reactions (15) and (16)].

Assuming inhibition according to reactions (12) and (14) thus gives an alternative possibility to explain the formation of cyclohexandiol-(1,2)-cyclohexylmonosulfonate found in the product as a sulfuric acid ester.[3]

(15)



(16)

Compared with the mechanism for the diolester production suggested by Graf, the above given mechanism has the advantage of correctly interpreting the variation of diol formation with the SO_2/O_2 ratio. For the SO_2/O_2 ratio corresponding to the limit of a self-sustained reaction Graf gives the product ratio sulfonic acid/sulfuric acid/acidic diolester as 3:1:1. The limit of a self-sustained reaction corresponds to the point where radical consumption equals radical production, *i.e.* with the above given mechanism, the gas composition for which the rates of reactions (4) and (13) are equal. As the water formed in the reaction (16) should be consumed in reaction (7) this condition gives exactly the product ratios found by Graf. Secondly, for those conditions for which Graf reports a decreased reaction rate with increased oxygen pressure, this decrease of the reaction rate is also connected with an increased ester formation.

The molar ratio sulfonic acid to sulfuric acid in the product for a number of experiments broken off at low conversion falls between 1.3 and 1.9.

The following reaction sequence seems to give a reasonable description of the present knowledge of the initial period of the sulfoxidation in cyclohexane.

$(R\cdot = C_6H_{11}\cdot)$

Propagation	$R\cdot + SO_2$	$\rightarrow RSO_2\cdot$	(1)
	$RSO_2\cdot + O_2$	$\rightarrow RSO_2O_2\cdot$	(2)
	$RSO_2O_2\cdot + RH$	$\rightarrow RSO_2O_2H + R\cdot$	(3)
Branching and product formation	$RSO_2O_2H + SO_2 \rightleftharpoons RSO_2O_2H\cdot SO_2$		(13)
	$RSO_2O_2H\cdot SO_2$	$\rightarrow RSO_3\cdot + HSO_3\cdot$	(4a)
	$RSO_3\cdot + RH$	$\rightarrow RSO_3H + R\cdot$	(5)
	$HSO_3\cdot + RSO_2O_2H$	$\rightarrow RSO_3\cdot + H_2SO_4$	(6a)
Termination	$R\cdot + O_2$	$\rightarrow RO_2\cdot$	(12)
	$RO_2\cdot + RSO_2O_2\cdot$	$\rightarrow$ stable product	(14)

The exponential increase in reaction rate might either be due to an increase of the persulfonic acid concentration or alternatively due to product catalysis of reaction (4a).

Initiation. The present investigation gives very little information concerning the nature of the spontaneous initiation. Untreated *p.a.* and *purum* cyclohexane also give a spontaneous reaction but with an increased induction period. Distillation of the purified cyclohexane under argon atmosphere immediately before use did not influence the results. Extrapolating the exponentially increasing gas consumption to $t=0$ and assuming the resulting gas consumption to be equal to $(2k_1[SO_2]/2k_{12}[O_2]) \times$ (radical production) gives values for the radical production of the order of $10^{-9}-10^{-10}$ M s^{-1} $(k_1 \approx k_{12})$. For the liquid phase oxidation of n-decane the corresponding value at 150°C has been determined to be 2.6×10^{-9} M s^{-1}.[14] In this case the radical production is ascribed to the reaction

$$RH + O_2 + RH \rightarrow 2R\cdot + H_2O_2 \tag{17}$$

For the sulfoxidation the least endothermic radical producing reactions seems to be

$$RH + SO_2 \rightarrow HSO_2\cdot + R\cdot \tag{18}$$

The strength of the $H-SO_2$ bond has been given as approximately $50-60$ kcal/mol.[17] From this value the reaction should be endothermic with an energy of $30-40$ kcal/mol. The uncertainties in the initial gas consumptions are very great due to the extrapolations made and from the present investigation no certain conclusion can be drawn concerning the SO_2- and O_2-dependence, respectively.

Product inhibition. In experiments with relatively high oxygen concentrations in the gas phase a maximum in reaction rate appears after a gas consumption of approximately 0.6 mol in cyclohexane and then the reaction rate starts to fall. When the oxygen content in the gas mixture is low, no marked maximum appears and an approximately constant reaction rate is reached at relatively low conversions. The reaction rate reached in these experiments are found to depend on the gas flow velocity and it seems clear that the reaction rate is limited by the diffusion of oxygen. For a mol ratio SO_2/O_2 of 9 it has been found that the production of sulfonic acid is approximately 6 times the sulfuric acid production at high conversions (Fig. 7). The high molar product ratio resulting when oxygen diffusion limits the reaction rate could be due to competition between reaction (2) and one of the reactions

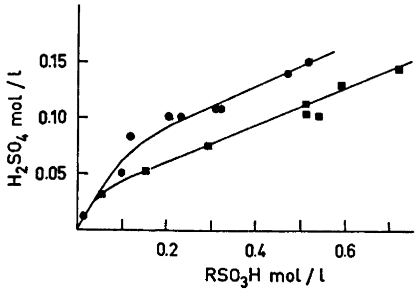


Fig. 7. Sulfuric acid yield as a function of the sulfonic acid yield in cyclohexane, at $t=25$°C. ● $p_{SO_2}=0.67$ and $p_{O_2}=0.33$; ■ $p_{SO_2}=0.90$ and $p_{O_2}=0.10$.

$$RSO_2\cdot + RSO_2O_2H \rightarrow RSO_3H + RSO_3\cdot \quad (19)$$

$$RSO_2\cdot + RSO_2O_2\cdot \rightarrow RSO_3\cdot + RSO_3\cdot \quad (20)$$

suggested by Bertram and Graf, respectively.

Experiments with higher oxygen content in the gas phase show a similar behaviour. As the maximum reaction rate is approached the sulfonic acid to sulfuric acid ratio starts to increase. The main difference compared with experiments with lower oxygen content in the gas phase is that this increase starts at higher conversion. As pointed out above Graf has found proportionality between oxygen pressure and sulfoxidation rate at conditions which might correspond to high conversions. In the present experiments the decay of the reaction rate is faster the lower the oxygen pressure is. Together these facts indicate that the decay of the reaction rate may be connected with one of the reactions (19) or (20) becoming important.

The experiments with water addition (Figs. 8a – 8c) show that reaction (7) must be fast. Free water in concentrations high enough to explain the deviation in product ratio from 2 should not be possible. The momentary increase in gas consumption, following the water addition, is attributed to the fact that the solubility of SO_2 is higher in sulfuric acid than in water.

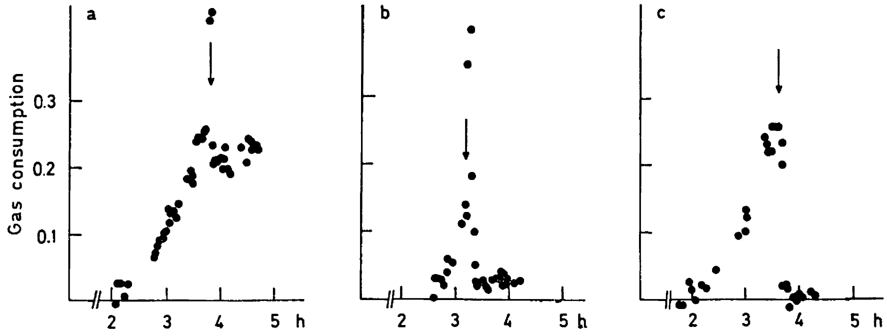


Fig. 8. The effect of water addition on the sulfoxidation of $C_{10}-C_{13}$ n-alkanes. The water was presaturated with SO_2 and O_2. Time for the addition indicated by the arrow. SO_2/O_2-ratio = 9:1; $t = 25°C$. *a*, 20 μl water added; *b*, 0.2 ml water added; *c*, 1.0 ml water added. Ordinate: l gas (NTP)/l n-paraffin ($C_{10}-C_{13}$) min.

Fig. 9 shows that addition of sulfuric acid inhibits the reaction and thus the decrease in reaction rate is most probably caused by build up of the main products. The position of the maximum seems to be determined solely by the degree of conversion. A visible phase separation could normally be detected 5 – 10 min before the maximum reaction rate was reached indicating that the size of the product drops is increasing.

Asinger and Saus[18] have studied the sulfoxidation of $C_{13}-C_{17}$ n-paraffins and found a very high content of disulfonic acid in the product. This was explained by the assumption that the reaction to an appreciable extent was taking place in the polar product phase. This should be true also for the sulfoxidation of cyclohexane, but in this case the disulfonic acid production is suppressed as all the hydrogen atoms in the monosulfonic acid are protected against abstraction by the presence of the sulfonic group in the molecule.[18] In this connection it is interesting to note that Asinger and Saus's data show that the increase in the disulfonic acid to monosulfonic acid ratio is very fast up to ≈5 % conversion and then levels out.[19] The maximum in the reaction rate in our experiments also appears at approximately 5 % conversion.

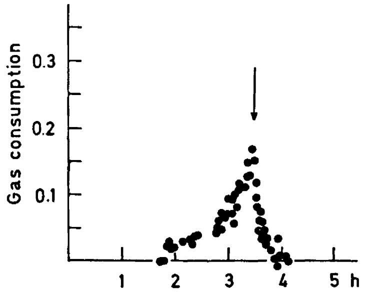


Fig. 9. The effect of sulfuric acid addition on the sulfoxidation of $C_{10}-C_{13}$ n-alkanes. 0.6 ml H_2SO_4 added; SO_2/O_2-ratio = 9:1.

Fig. 10. The gas consumption as a function of time for the sulfoxidation of $C_{10}-C_{13}$ n-alkanes; $t = 25°C$. ▲ $p_{SO_2} = 0.95$ and $p_{O_2} = 0.05$; ● $p_{SO_2} = 0.90$ and $p_{O_2} = 0.10$; ■ $p_{SO_2} = 0.81$ and $p_{O} = 0._{2}19$.

The solubility of O_2 in the product could be expected to be low, analogous with what is known for concentrated sulfuric acid. A marked increase in the size of the product drops connected with the fact that the reaction to an appreciable extent takes place in the product phase could explain that oxygen

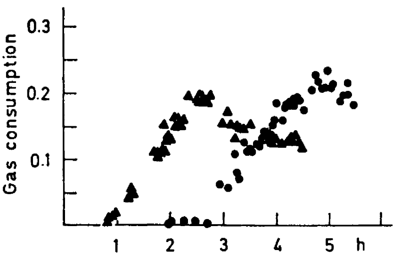


Fig. 11. The gas consumption as a function of time for the sulfoxidation of $C_{13}-C_{17}$ n-alkanes at $t = 25°C$. ▲ $p_{SO_2} = 0.95$ and $p_{O_2} = 0.05$; ● $p_{SO_2} = 0.90$ and $p_{O_2} = 0.10$.

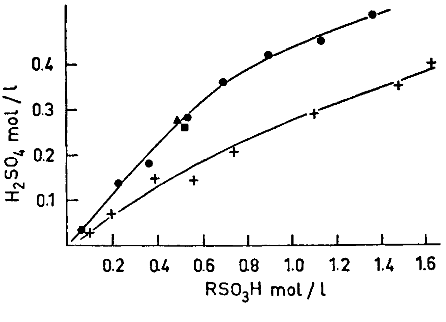


Fig. 12. Sulfuric acid yield as a function of the sulfonic acid yield in n-alkanes at $t = 25°C$. ● $p_{SO_2} = 0.90$ and $p_{O_2} = 0.10$ (with stirring); ▲ $p_{SO_2} = 0.80$ and $p_{O_2} = 0.20$ (with stirring); ■ $p_{SO_2} = 0.95$ and $p_{O_2} = 0.05$ (with stirring); + $p_{SO_2} = 0.90$ and $p_{O_2} = 0.10$ (without stirring).

Table 4. Results on the sulfoxidation of n-alkane mixtures.

Hydrocarbon	p_{SO_2} atm	p_{O_2} atm	Max. reaction rate $\frac{\text{l gas NTP}}{\text{l min}}$	Integrated gas consumption to the maximum l NTP/l	Induction period h	Time-constant k min^{-1}	Relative value of k.[a]	Relative length of reaction sequence according to Ref. 19 (cyclohexane = 1.00)
C_{10}-C_{13} n-Alkanes	0.95	0.05	0.23	12	1.7	0.035 ± 0.023		
»	0.90	0.10	0.30	17	3.3	0.023 ± 0.004	0.089	
»	0.81	0.19	0.22	20	4	0.014 ± 0.006	0.083	
»	0.67	0.33			> 6			
C_{13}-C_{17} n-Alkanes	0.95	0.05	0.19	10	1.7			
»	0.90	0.10	0.22	17	3.3			
»	0.80	0.20			> 6			
n-Decane								0.21
n-Dodecane								0.093
n-Hexadecane								0.059

[a] In cyclohexane $k = 1$, for the pressure used.

diffusion becomes limiting and that thus one of the reactions (19) or (20) starts to compete with reaction (2). This might then explain the product inhibition as well as a proportionality between O_2-concentration and reaction rate at high conversions. If the sulfuric acid production is connected with the radical production as suggested by Graf (reactions (4) – (7)), the picture is incomplete and some radical consuming reaction also must contribute to the product yield.

Sulfoxidation of higher n-alkanes. As can be seen from Figs. 10 and 11 the $C_{10}-C_{13}$ and $C_{13}-C_{17}$ n-alkanes, respectively, show the same principal behaviour as cyclohexane but increased SO_2/O_2 ratios are necessary to achieve a spontaneous reaction. With increased hydrocarbon chain length the induction period increases and at the same time the maximum reaction rate decreases. For $C_{13}-C_{17}$ n-alkanes the time dependence of the reaction rate cannot be described by a simple exponential function. The results are summarized in Table 4. At low conversions the product ratio sulfonic to sulfuric acid for $C_{10}-C_{13}$ n-alkanes is slightly lower than 2 (Fig. 12). A marked increase of this value is not noted before conversions occur appreciably higher than what corresponds to maximum reaction rate. The product ratio in this case seems to be relatively insensitive to changes of the SO_2/O_2 ratio from 9/1 to 19/1 resp. 4/1. Performing the experiment without any stirring except what is achieved with the gas bubbling results in a marked increase in the sulfonic acid/sulfuric acid product ratio. The observed behaviour is probably connected with the low reaction rate which makes oxygen diffusion a limiting factor only when the reaction is performed without stirring.

For comparison the kinetic chain length reported by Cerny [20] is given in Table 4. The change in k-value going from cyclohexane to $C_{10}-C_{13}$ n-alkanes is in reasonable agreement with the results of Cerny. The very marked decrease in k when going to the n-alkanes cannot be ascribed to different solubilities of SO_2 and O_2, respectively, in the hydrocarbons as can be seen from Table 2. A condition which could be expected to change appreciably is the distribution of the intermediate radicals and the persulfonic acid between hydrocarbon and product phase. With increased hydrocarbon chain length the intermediates to a greater extent will be found in the hydrocarbon phase. Comparing the concentration ratio $[SO_2]/[O_2]$ in hydrocarbon and product phase, respectively, makes clear that radical recombination according to the reactions (12) and (14) will mainly take place in the hydrocarbon phase and thus an increase in the hydrocarbon chain length will give increased radical recombination rates. Another effect might contribute to the decrease in k if the rate of reaction (4a) is faster in the product phase than in the hydrocarbon phase. The fact that the product inhibition appears at somewhat higher integrated gas consumptions in the sulfoxidation of the n-alkanes might also be due to an increased solubility of the intermediates in the hydrocarbon phase.

Acknowledgements. The author wants to thank Professor Torbjörn Westermark and Professor Martin Nilsson for their interest and support. Thanks are also given to Mr. A. Axelsson and Mr. G. Wennergren who assisted with the experimental work as well as to the *Swedish Board for Technical Development* whose financial support made this work possible.

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Received April 12, 1973.