

Action of Ultrasound on Aqueous Solutions of Hydrocarbons

I. Studies by Ultraviolet Absorption Spectroscopy

By

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The present investigation was undertaken to determine quantitatively the effects of ultrasound on each of twenty eight hydrocarbons in aqueous media by the absorption spectroscopy with the base line method.

Aqueous solutions of alkylbenzenes listed in the order of decreasing sonochemical conversion %, were as follows, ethylbenzene > benzene, toluene; m-xylene, mesitylene > o-xylene > p-xylene; cumene > p-cymene; etc..

Aqueous solutions of polycyclic hydrocarbons, arranged in the order of decreasing sonochemical conversion %, were as follows,

diphenyl > naphthalene > α -, β -methylnaphthalene;
anthracene, phenanthrene > naphthalene > pyrene > fluorene > benzene;
naphthalene > tetralin > decalin; etc..

Carcinogenic hydrocarbons, i. e., 3,4-benzopyrene and 20-methylcholanthrene in aqueous media were cracked by ultrasound.

I. INTRODUCTION

Since pioneer work in chemical ultrasound was done in 1927 by Richards and Loomis¹⁾, many chemical reactions have been observed to occur in an ultrasonic field.

For the sonochemical reactions of hydrocarbons, oxidation²⁾ and cracking³⁾ of paraffins with a catalyst, polymerization⁴⁾ of olefins (e. g. ethylene, propylene, styrene) with an initiator, and depolymerization⁵⁾ of hydrocarbon polymers (e. g. polyethylene, polyisobutylene, polystyrene) are reported to be accelerated by ultrasound.

Aqueous solution of aromatic hydrocarbons (benzene, toluene) subjected to ultrasound have been investigated by several groups of workers—Prudhomme and Graber⁶⁾, Khenokh and Lapinskaya⁷⁾, Parks and Taylor⁸⁾, Currell and Zechmeister⁹⁾, Kandzas and Mokina¹⁰⁾.

The experiments done by these investigators have clarified the next facts. Hydroxylation and oxidative destruction occur in an ultrasonic field and are accompanied by changes in the ultraviolet absorption spectra with disappearance of the typical bands. The solutions of benzene yield acetylene⁹⁾, formaldehyde, nitrobenzene⁶⁾, phenol, pyrocatechin, pyrogallol and hydroquinone¹⁰⁾.

The solutions of toluene yield formaldehyde, phenol and cresol⁷⁾⁸⁾ etc..

In relation with these experiments, the present investigation has been undertaken to determine quantitatively the effects of ultrasound on each of twenty eight hydrocarbons in aqueous media by ultraviolet absorption spectroscopy.

In this report, data will be presented which show the degree of sonochemical conversion of hydrocarbons in water.

II. EXPERIMENTAL

Ultrasonic generator (with a Hartley circuit, using Toshiba Tube T 311) was used in this work.

This apparatus operates as a frequency of 304 kc/sec with an electrical output of 36.1 watts.

The corresponding acoustical power inside the reaction vessel was 4.4 watts.

The transducer element was cylinder shaped, (38 mm in outside diameter, 20 mm in inside diameter, 30 mm in height) and was of barium titanate with a ceramic glaze.

The reaction vessel, for example, a test tube which contains 5 ml sample solution is clamped in the center of cylindrical transducer in the oil covering the transducer element.

The excessive temperature rise during the ultrasonic treatment was prevented with circulation of cooled oil.

The irradiation with ultrasound was always kept for 5 mins throughout this experiment.

Hitachi 139 type visible and ultraviolet spectrophotometer was used through this investigation to determine the ultraviolet absorption spectra of aqueous solutions of hydrocarbons.

Special grade of hydrocarbons was obtained from the Tokyo Kasei Co. etc..

III. RESULTS AND DISCUSSION

1. Water irradiated with ultrasound

Although there was an extensive literature¹¹⁾ which reported the formation of HNO_2 , H_2O_2 , and HNO_3 in water subjected to ultrasound, air saturated water in an ultrasonic field has been investigated as a preliminary experiment.

The spectrum of the water subjected to ultrasound, together with that of NaNO_2 , H_2O_2 , and HNO_3 in water is indicated in Fig. 1.

Assume that the spectrum of HNO_2 is identical with that of NaNO_2 , that only HNO_2 , H_2O_2 , and HNO_3 are formed in the water subjected of ultrasound, and that Beer's law, respectively, operates.

Then, three equations of absorbance at three wave lengths - 210, 220, 230 $\text{m}\mu$ can be solved for the concentration of HNO_2 , H_2O_2 , and HNO_3 .

The concentration of HNO_2 , H_2O_2 , and HNO_3 was found to be 4.95×10^{-5} mol/l, 2.72×10^{-5} mol/l, 1.35×10^{-5} mol/l respectively, listed in the order of decreasing yield, $\text{HNO}_2 > \text{H}_2\text{O}_2 > \text{HNO}_3$.

This is in agreement with the results of experiments reported in literature¹¹⁾.

And it seems to be necessary to note that the absorbance elevation of aqueous solutions of hydrocarbons by ultrasonic treatments as described below is probably attribute in part to that caused by the formation of HNO_2 , H_2O_2 , and HNO_3 in water.

2. Determination of hydrocarbons by the base line method.

The spectrophotometric determination of hydrocarbons in water was conducted with the background absorption correction.

The simplest type of the correction is, what is often termed, the base line method¹²⁾ as illustrated in Fig. 2.

A straight line is drawn between two points on the absorbance curve at two fixed wave lengths which are conveniently taken as the positions of minima for the pure compound on each side of the band to be used.

It is known that the height A_x from this base line to the band maximum is directly proportional to the concentration of the hydrocarbon present.

At first, the validity of the base line method to determination of hydrocarbons in water was tested.

Firstly, a benzene solution I (in 5 ml water) and a benzene solution II (in 2.5 ml water plus 2.5ml water subjected to ultrasound) were prepared in the same concentration - 2.7×10^{-4} mol/l.

The absorbance curves of two benzene solutions I, II are indicated in Fig. 3.

Plots of A_x obtained by the base line method at 255 $\text{m}\mu$ in the 230 to 270 $\text{m}\mu$ range in I and II were found to be identical.

Secondly, the effect of NaNO_3 addition upon the absorbance curves of aqueous solutions of benzene has been examined. Plots of A_x of benzene solutions in aqueous NaNO_3 (0.9×10^{-3} mol/l) are found to be placed upon the linear line between the concentration of benzene and A_x

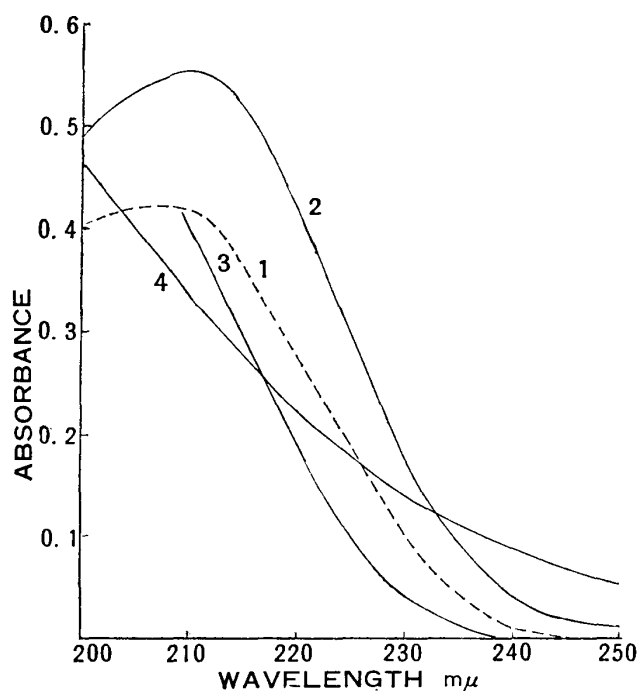


Fig. 1 Absorption spectra of

- 1 H₂O After Ultrasonic Treatment
- 2 Aqueous NaNO₂ 1.0×10^{-4} mol/l
- 3 // HNO₃ 4.0×10^{-5} //
- 4 // H₂O₂ 2.28×10^{-3} //

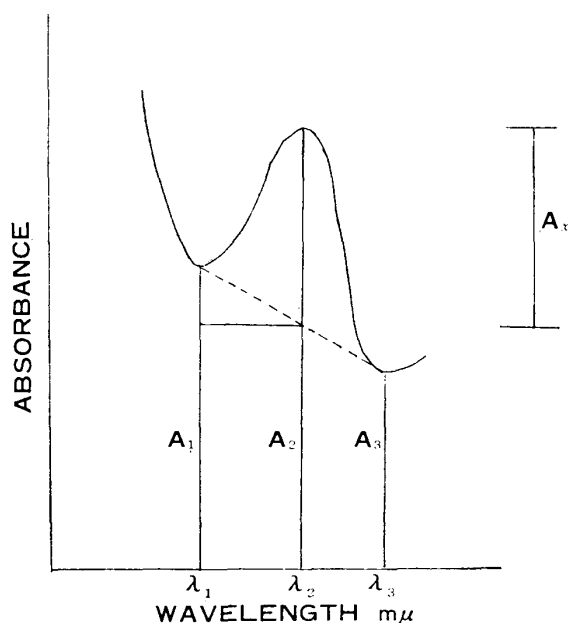


Fig. 2 Base Line Method of Background Correction.

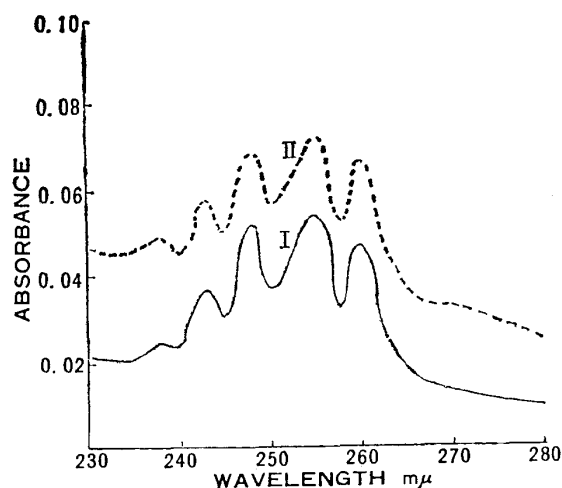


Fig. 3 Absorption spectra of I C₆H₆ in 5ml H₂O, II C₆H₆ in 2.5 ml H₂O and 2.5 ml H₂O subjected to Ultrasound C₆H₆ conc. in both I and II 2.7×10^{-4} mol/l

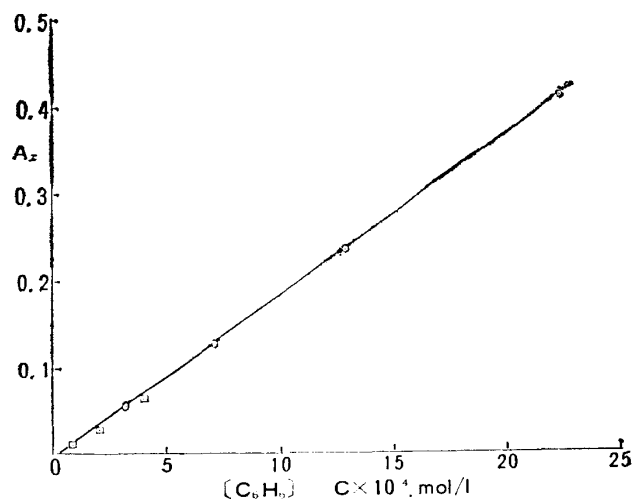


Fig. 4 Plots of A_x vs. C₆H₆ concs.

- in H₂O
 □ in Aqueous NaNO₃ 0.90×10^{-3} mol/l

in aqueous solutions of benzene in the 230 to 270 $m\mu$ range as shown in Fig. 4.

In view of the above facts, it seemed reasonable to assume that the determination of other hydrocarbons in water could also be made with the base line method.

Although this method was known¹³⁾ to give good results for very sharp absorption peaks where the wave length position on opposite sides of the peak were close together, the sharp absorption peaks in aqueous solutions of hydrocarbons except benzene and naphthalene could not be obtained.

Therefore, it was found necessary to apply the method to aqueous solutions of various hydro-

carbons in two far apart positions of wave length, in spite of the low accuracy, in order to compare with each other.

3. Aqueous solutions of the various hydrocarbons irradiated with ultrasound.

The concentration of hydrocarbons in water was obtained from the observed values of absorbance and the literature values¹⁴⁾ of molar absorptivity at maximum absorption wave length, in agreement with the aqueous solubility data in the Landolt - Börnstein's table¹⁵⁾.

There was a definite concentration range in which absorbance measurements could be accurately made for each hydrocarbon.

Moreover, a concentration range of hydrocarbon which could dissolve in water was limited.

Therefore, it was difficult to investigate the aqueous solutions of hydrocarbons in the same concentration in order to compare with each other.

The ultraviolet absorbance curves of aqueous solutions of hydrocarbons in the presence and absence of ultrasonic treatments are indicated in Fig. 5. ~ Fig. 28.

In these figures, a broken line shows absorbance curve after ultrasonic irradiation for 5 mins and full line gives that before ultrasonic irradiation.

The absorbance curves of n-hexane, cyclohexane, 1-hexene and cyclohexene in water, respectively, are shown in Fig. 5, 6. Since there was no maximum absorption peak in 200~250m μ region, the determination of the hydrocarbons could not be made by the base line method.

In the case of benzene, toluene, o-xylene, m-xylene, cumene, diphenyl, naphthalene, α - or β -methylnaphthalene in water, their absorbance curves could be obtained with a concentration variation.

A sonochemical conversion % of hydrocarbons in water was obtained as the ratio of the concentration of the hydrocarbons lost by ultrasonic treatment against the initial concentration of the hydrocarbons.

Since plots of A_x in the base line method are proportional to the concentration of the hydrocarbons, the ratio of A_x in the presence of ultrasonic treatment, i. e., A_u to A_x in the absence of ultrasonic treatment, i. e., A_i is identical with the ratio of the concentration of the hydrocarbon remained after ultrasonic irradiation to the initial concentration of the hydrocarbon.

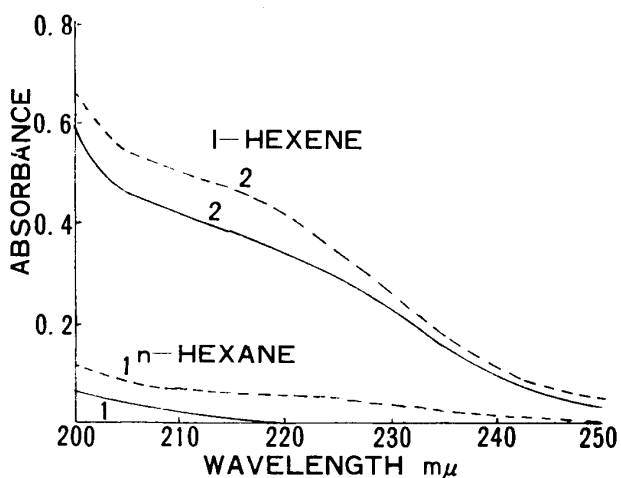


Fig. 5 Absorption Spectra of n-Hexane and 1-Hexene Before and After (a broken line) Ultrasonic Treatment.

1 n-Hexane 1.3×10^{-3} mol/l } Solvent H₂O
 2 1-Hexene 0.77×10^{-4} // }

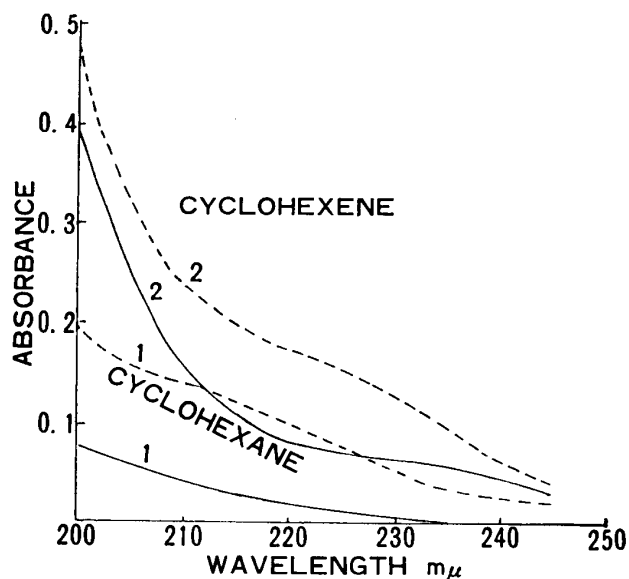


Fig. 6 Absorption Spectra of Cyclohexane and Cyclohexene Before and After (a broken line) Ultrasonic Treatment.

1 Cyclohexane 2.38×10^{-3} mol/l } solvent H₂O
 2 Cyclohexene 1.0×10^{-4} // }

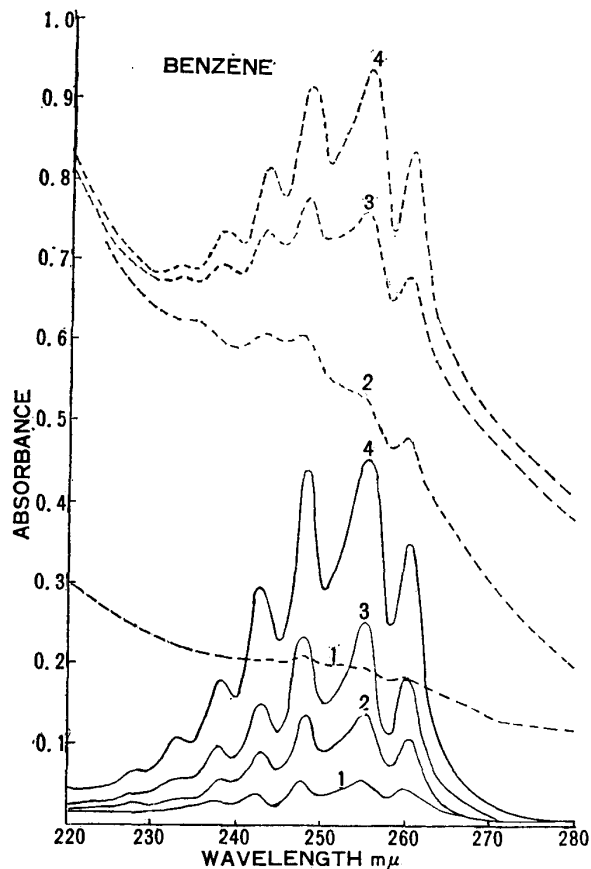


Fig. 7 Absorption Spectra of Benzene Before and After (a broken line) Ultrasonic Treatment.

Benzene Concs.	1	3.3×10^{-4} mol/l
Solvent H ₂ O	2	7.1 " "
	3	12.9×10^{-4} mol/l
	4	22.5 " "

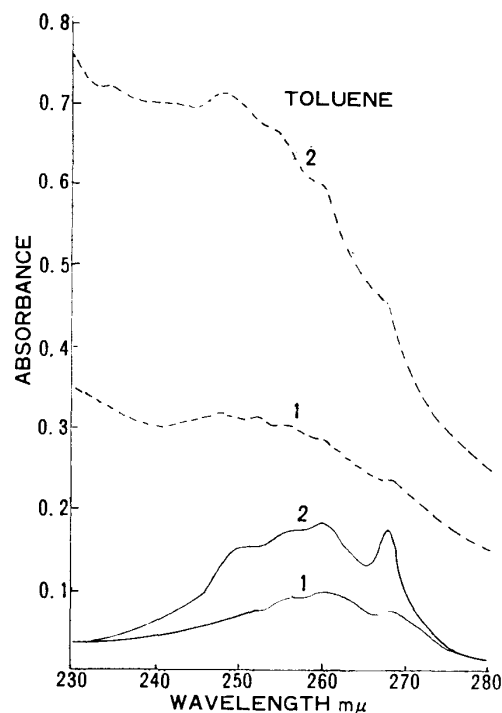


Fig. 8 Absorption Spectra of Toluene Before and After (a broken line) Ultrasonic Treatment.

Toluene Concs.	1	4.26×10^{-4} mol/l
Solvent H ₂ O	2	7.83 " "

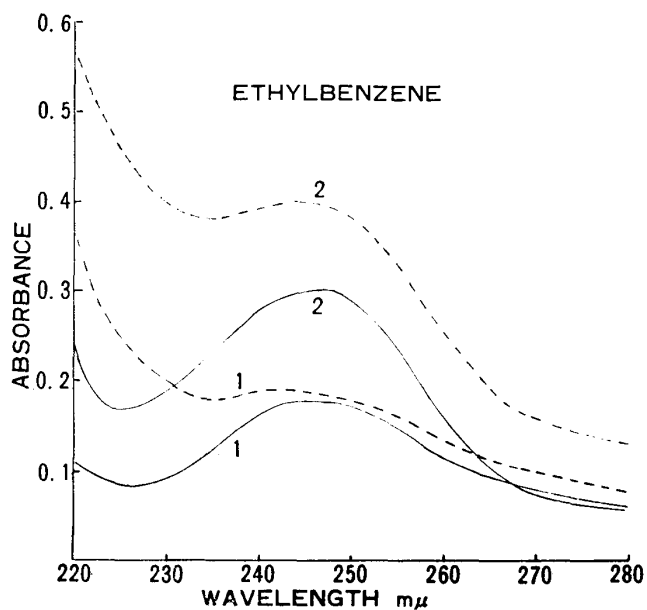


Fig. 9 Absorption Spectra of Ethylbenzene Before and After (a broken line) Ultrasonic Treatment.

Ethylbenzene Concs.	1	10.9×10^{-4} mol/l
Solvent H ₂ O	2	18.7 " "

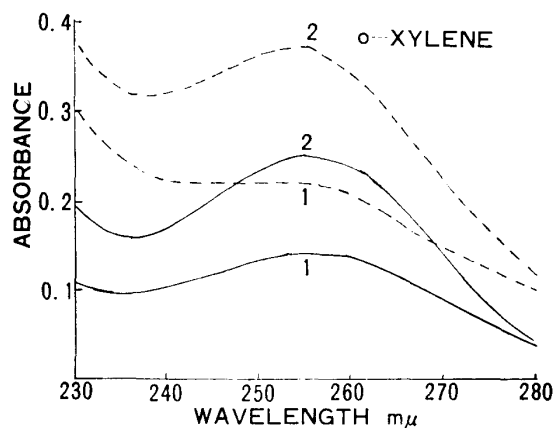


Fig. 10 Absorption Spectra of o-Xylene Before and After (a broken line) Ultrasonic Treatment.

o-Xylene Concs.	1	6.18×10^{-4} mol/l
Solvent H ₂ O	2	10.6 " "

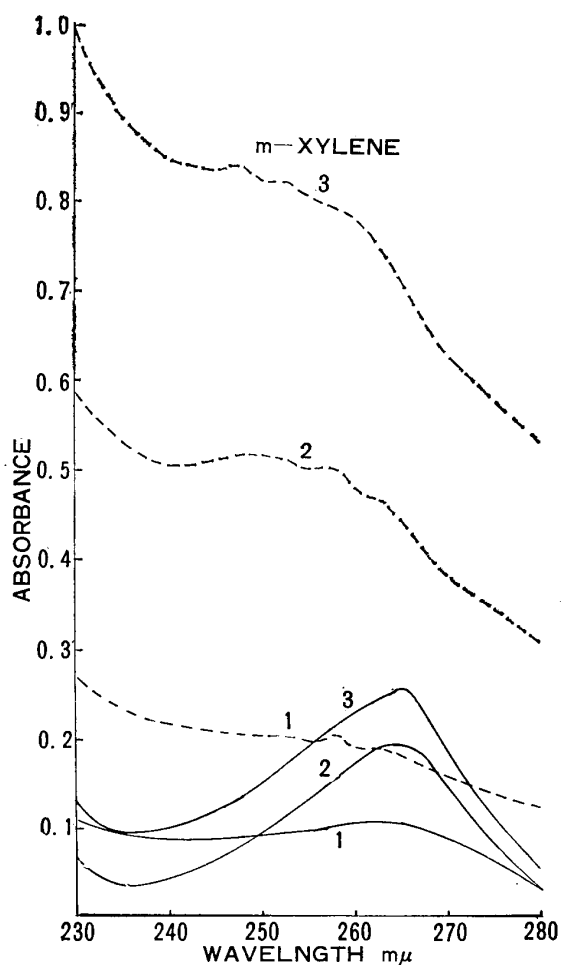


Fig. 11 Absorption Spectra of m-Xylene Before and After (a broken line) Ultrasonic Treatment.
 m-Xylene Concs. 1 3.47×10^{-4} mol/l
 Solvent H₂O 2 6.74 // //
 3 8.45 // //

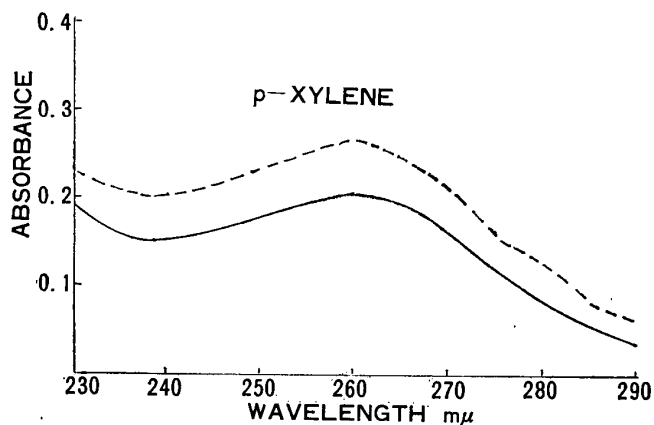


Fig. 12 Absorption Spectra of p-Xylene Before and After (a broken line) Ultrasonic Treatment.
 p-Xylene Conc. 3.6×10^{-4} mol/l
 Solvent H₂O

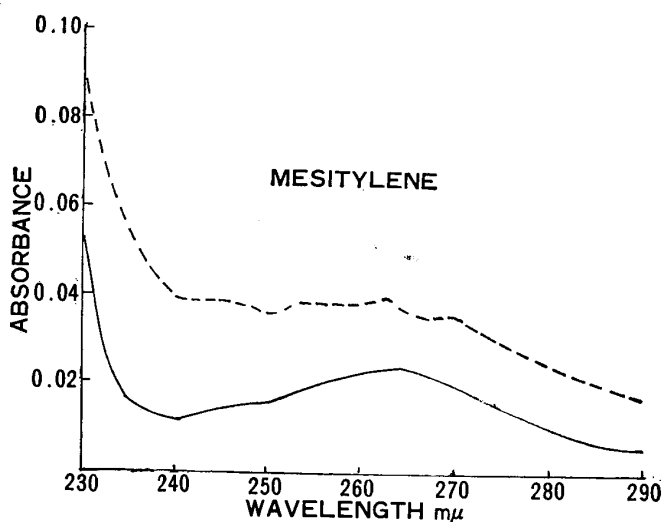


Fig. 13 Absorption Spectra of Mesitylene Before and After (a broken line) Ultrasonic Treatment.
 Mesitylene Conc. 1.67×10^{-4} mol/l
 Solvent H₂O

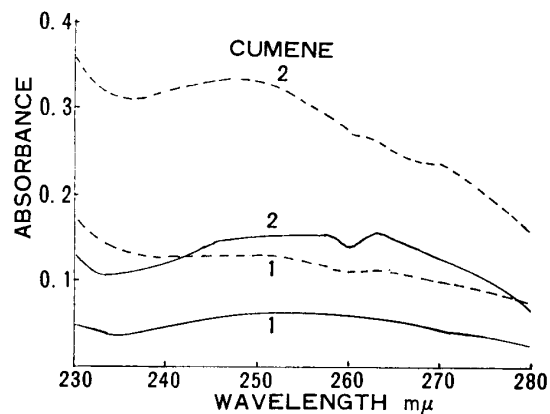


Fig. 14 Absorption Spectra of Cumene Before and After (a broken line) Ultrasonic Treatment.
 Cumene Concs. 1 2.36×10^{-4} mol/l
 Solvent H₂O 2 6.12 // //

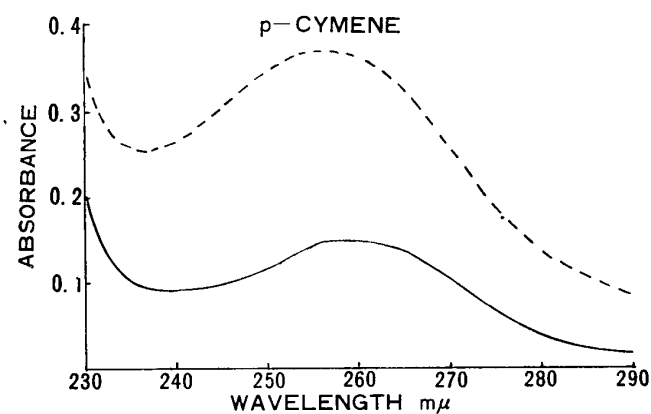


Fig. 15 Absorption Spectra of p-Cymene Before and After (a broken line) Ultrasonic Treatment.
 p-Cymene Conc. 5×10^{-4} mol/l
 Solvent H₂O

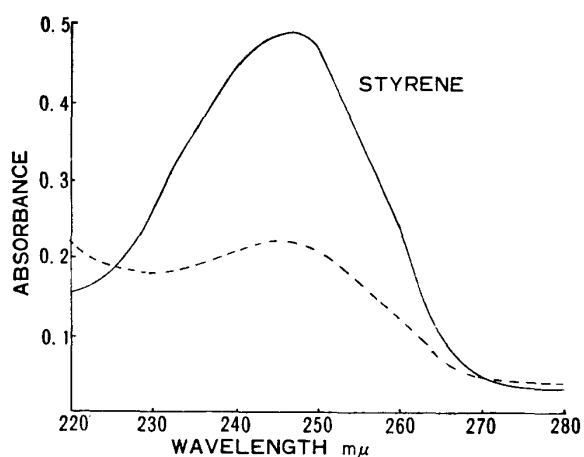


Fig. 16 Absorption Spectra of Styrene Before and After (a broken line) Ultrasonic Treatment.
Styrene Conc. 0.616×10^{-4} mol/l
Solvent H_2O

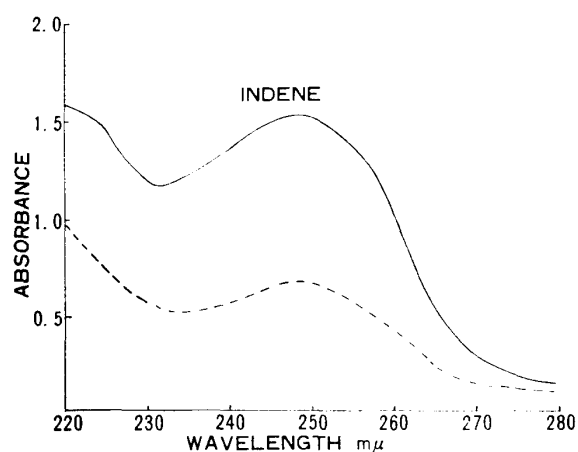


Fig. 17 Absorption Spectra of Indene Before and After (a broken line) Ultrasonic Treatment.
Indene Conc. 1.63×10^{-4} mol/l
Solvent H_2O

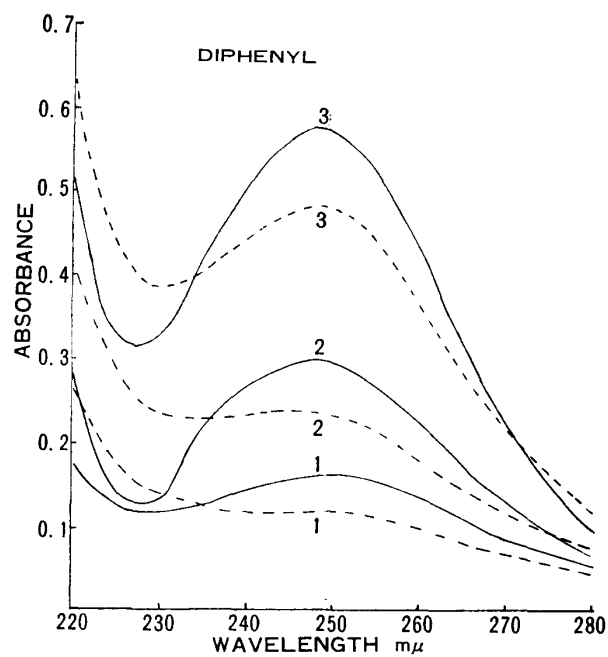


Fig. 18 Absorption Spectra of Diphenyl Before and After (a broken line) Ultrasonic Treatment.
Diphenyl Concs. 1 1.00×10^{-5} mol/l
Solvent H_2O 2 1.77 " "
3 3.45 " "

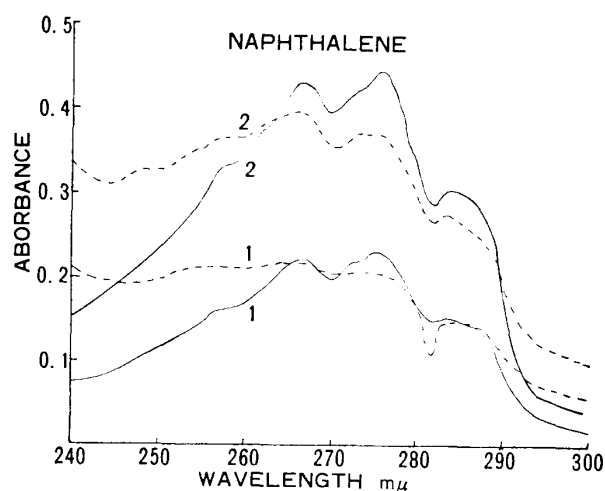


Fig. 19 Absorption Spectra of Naphthalene Before and After (a broken line) Ultrasonic Treatment.
Naphthalene Concs. 1 0.523×10^{-4} mol/l
Solvent H_2O 2 1.02 "

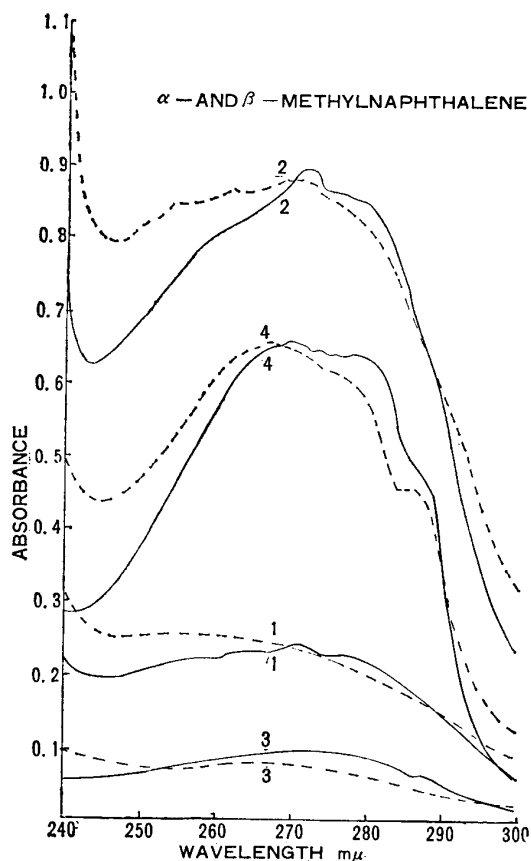


Fig. 20 Absorption Spectra of α - and β -Methylnaphthalene Before and After (a broken line) Ultrasonic Treatment. Solvent H_2O

1	α -Methylnaphthalene	0.50×10^{-4}	mol/l
2	"	1.84	"
3	β -Methylnaphthalene	0.21	"
4	"	1.38	"

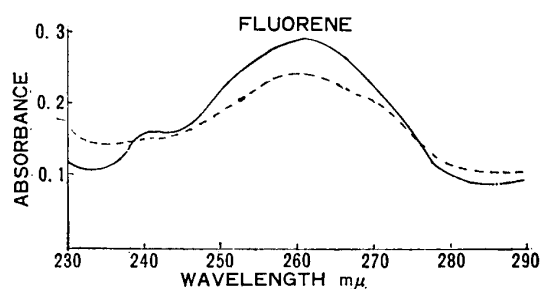


Fig. 21 Absorption Spectra of Fluorene Before and After (a broken line) Ultrasonic Treatment. Fluorene Conc. 1.59×10^{-5} mol/l Solvent H_2O

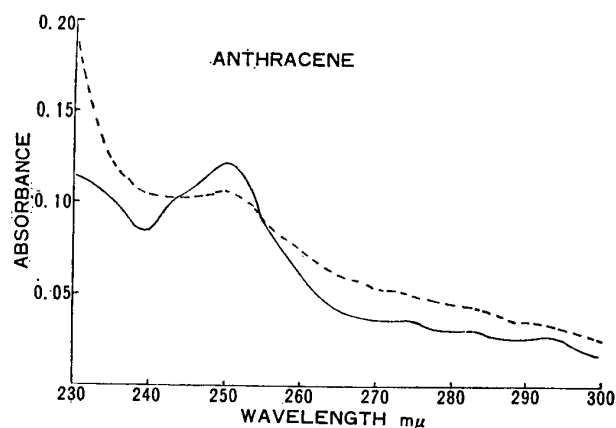


Fig. 22 Absorption Spectra of Anthracene Before and After (a broken line) Ultrasonic Treatment. Anthracene Conc. 4×10^{-7} mol/l Solvent H_2O

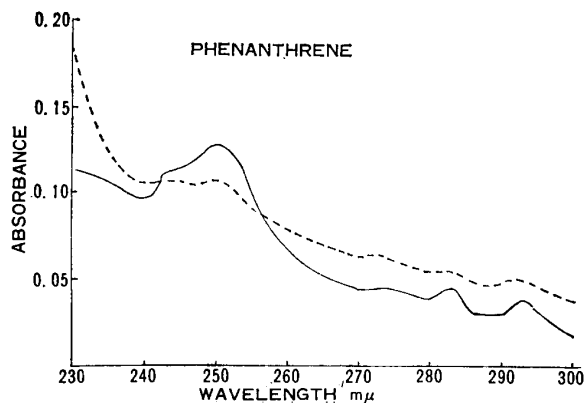


Fig. 23 Absorption Spectra of Phenanthrene Before and After (a broken line) Ultrasonic Treatment. Phenanthrene Conc. 2.6×10^{-6} mol/l Solvent H_2O

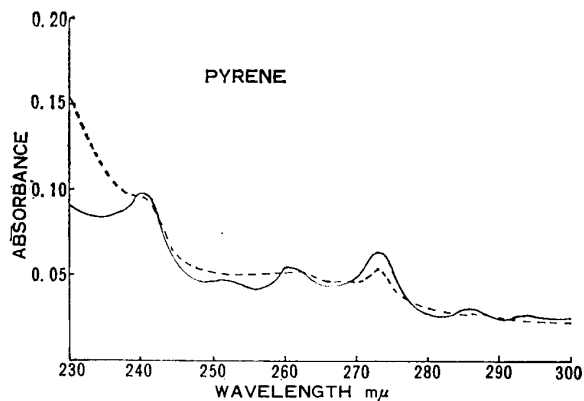


Fig. 24 Absorption Spectra of Pyrene Before and After (a broken line) Ultrasonic Treatment. Pyrene Conc. 8×10^{-7} mol/l Solvent H_2O

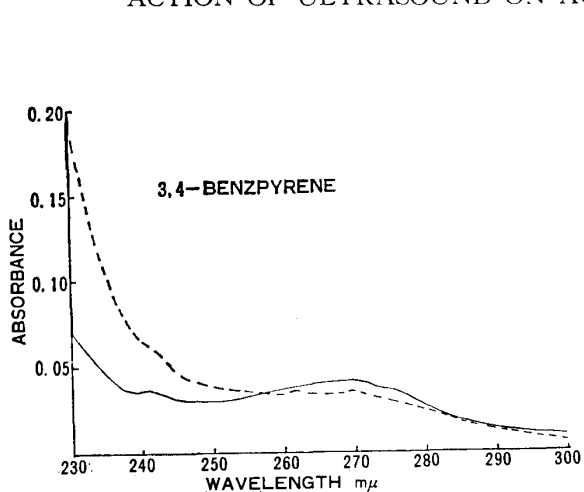


Fig. 25 Absorption Spectra of 3, 4-Benzpyrene Before and After (a broken line) Ultrasonic Treatment.

3,4-Benzpyrene Conc. 1.6×10^{-8} mol/l
Solvent H_2O

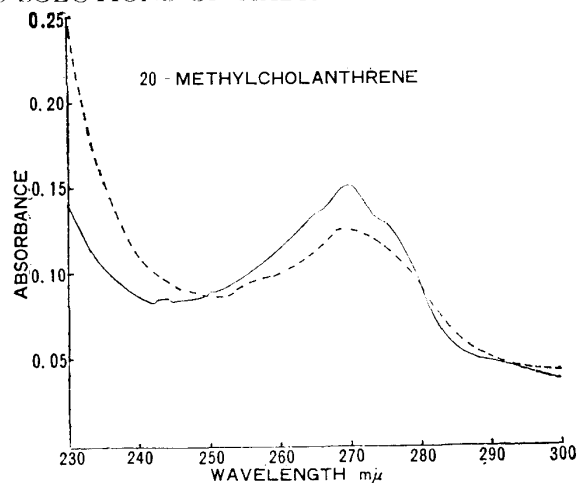


Fig. 26 Absorption Spectra of 20-Methylcholanthrene Before and After (a broken line) Ultrasonic Treatment.

20-Methylcholanthrene Conc. 5.6×10^{-9} mol/l
Solvent H_2O

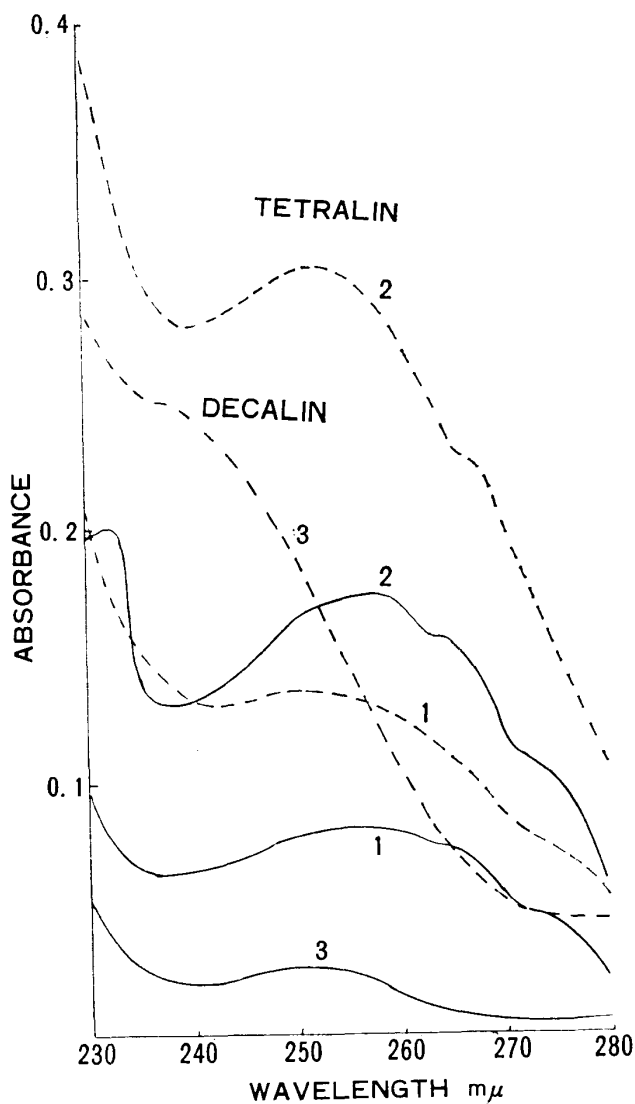


Fig. 27 Absorption Spectra of Tetralin and Decalin Before and After (a broken line) Ultrasonic Treatment.

1 Tetralin 1.55×10^{-4} mol/l
Solvent H_2O 2 " 3.22 " "
3 Decalin Saturated Solution

Table Sonochemical Conversion % of Hydrocarbons in Aqueous Media

Hydrocarbons	Initial Conc. C × 10 ⁴ mol/l	Selected wave length m μ λ_2	Range m μ		Absorbance Ratio Au/Ai*	Conversion % (1 - Au/Ai) × 100	Fig. No.	Remarks λ_{\max} Shift m μ
			λ_1	λ_3				
Benzene	3.3	255	230	270	0.60	40	7.1	
	7.1				0.79	21	2	
	12.9				0.87	13	3	
	22.5				0.89	11	4	
Toluene	4.26	260	240	280	0.77	23	8.1	260→248
	7.83				0.83	17	2	
Ethylbenzene	10.9	245	230	270	0.35	65	9.1	248→244
	18.7				0.58	42	2	
o-Xylene	6.18	255	235	280	0.84	16	10.1	
	10.6				1.0	0	2	
m-Xylene	3.47	265	235	280	0.41	59	11.1	265→248
	6.47				0.49	51	2	
	8.45				0.52	48	3	
p-Xylene	3.6	262	238	290	1.0	0	12	
Mesitylene	1.67	263	240	290	0.60	40	13	
Cumene	2.36	263	235	280	0.65	35	14	263→250
	6.12				0.69	31		
p-Cymene	5	255	240	280	(2.0)	0	15	
Styrene	0.616	248	220	270	0.23	77	16	
Indene	1.63	250	230	270	0.36	64	17	
Diphenyl	0.100	248	228	280	0.26	74	18.1	
	0.177				0.33	67	2	
	0.345				0.57	43	3	
Naphthalene	0.523	275	240	300	0.42	58	19.1	
	1.02				0.49	51	2	
α -Methyl naphthalene	0.50	270	245	300	0.50	50	20.1	
	1.84				0.67	33	2	
β -Methyl naphthalene	0.21	270	245	300	0.51	49	3	
	1.38				0.76	24	4	
Fluorene	0.159	260	235	285	0.60	40	21	
Anthracene	0.004	250	240	270	0.38	62	22	
Phenanthrene	0.026	250	240	270	0.37	63	23	
Pyrene	0.008	273	265	280	0.50	50	24	
3, 4-Benzpyrene	0.00016	270	250	290	0.50	50	25	
20-Methyl cholanthrene	0.000056	270	250	290	0.68	32	26	
Tetralin	1.55	258	238	280	0.78	22	27.1	258→253
	3.22				1.0	0	2	
Decalin	Sat. Solution	230	215	245	(2.6)	0	3	
α -Pinene	//	250	235	270	1.0	0	28	

* Au.....A α after ultrasonic treatment
 Ai.....A α before //

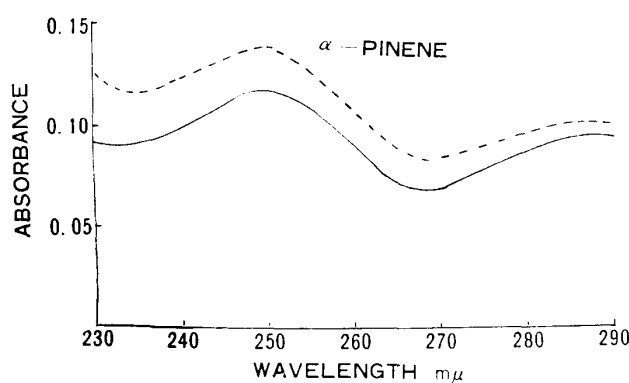


Fig. 28 Absorption Spectra of α -Pinene Before and After (a broken line) Ultrasonic Treatment. Saturated Aqueous Solution.

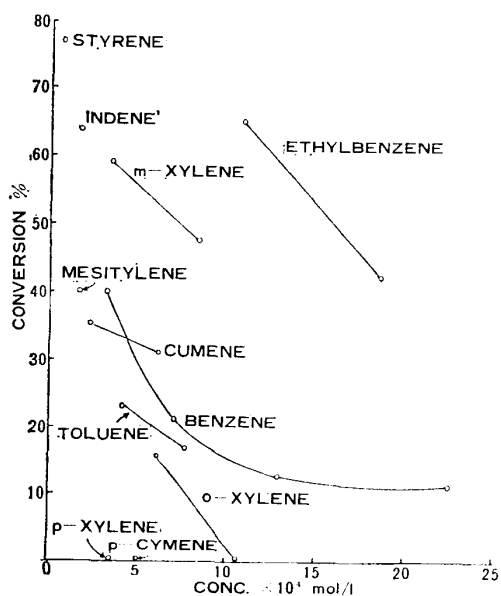


Fig. 29 Sonochemical Conversion % of Alkylbenzenes in Aqueous Media

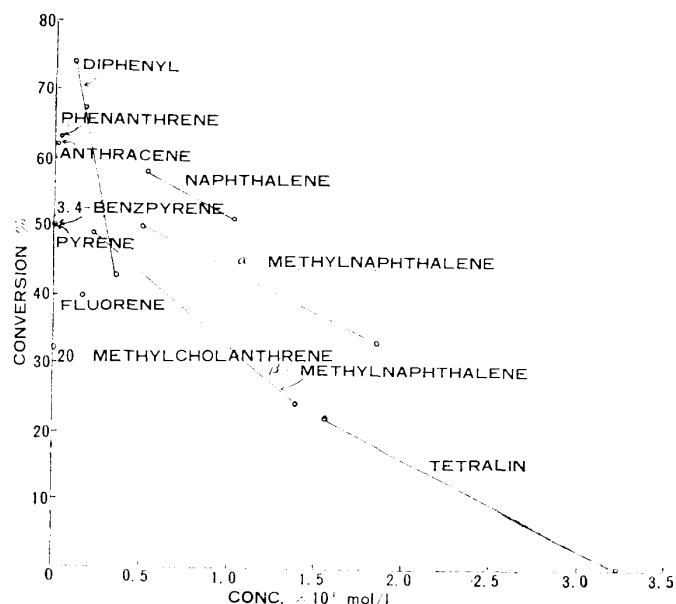


Fig. 30 Sonochemical Conversion % of Polycyclic Hydrocarbons in Aqueous Media

All results of a sonochemical conversion % of hydrocarbons in water are summarized in the accompanying table and Fig. 29, 30.

According to the table and the figures, it is apparently deduced that a sonochemical conversion % of hydrocarbons in water, in general, becomes lower with increasing concentration.

And, alkyl substituted aromatic hydrocarbons, listed in the order of decreasing conversion %, were known to be

ethylbenzene > benzene, toluene,
m-xylene, mesitylene > o-xylene > p-xylene,
cumene > p-cymene, etc..

By other several investigators, the ultraviolet absorption spectra of iodine - methylbenzene complex¹⁶⁾, vapor pressure of HF- BF₃- methylbenzene complex¹⁷⁾ and chlorination rate of methylbenzenes¹⁸⁾ were measured. And it was consistently concluded that m-xylene was most basic or reactive of the xylenes i. e. m > o > p and mesitylene was more basic or reactive than the xylenes.

It is also described in the Fieser's textbook¹⁹⁾ that the order of reactivity of three xylenes as indicated by the sulfonation and desulfonation reactions is m > o > p and mesitylene undergoes ready substitution.

This is in agreement with the results obtained in this work and the previous work²⁰⁾ about the action of ultrasound in aqueous silver nitrate.

The value of a conversion % of styrene or indene was high, compared with alkylbenzenes as shown above.

It will probably be related to the easiness of oxidation or polymerization of the hydrocarbon.

In the case of the polycyclic aromatic hydrocarbons, a particularly high conversion % was obtained.

It seems to be probably attributed to the high reactivity caused by a extremely low concentration, namely the presence of large amounts of water around the hydrocarbon, the great reactivity to substitution such as hydroxylation and the easiness of the ring cleavage.

The order of decreasing conversion % of the polycyclic aromatic hydrocarbons was as follows,

diphenyl > naphthalene > α -, β -methyl-naphthalene;

anthracene, phenanthrene > naphthalene > pyrene > fluorene (>benzene).

With regard to the reactivity to oxidation¹⁸⁾, the polycyclic aromatic hydrocarbons arranged in decreasing reactivity are reported to be

pyrene, anthracene > phenanthrene > naphthalene > benzene.

It is probably suggested that the order of the reactivity to substitution such as hydroxylation is listed in a similar manner.

In addition, Kinney and Bel²¹⁾ investigated the pyrolytic behavior of polycyclic unsubstituted aromatic hydrocarbons in the region of 800 to 1000°C in contact with coke, and found that the conversion of anthracene or pyrene to carbon proceeds with far greater ease than with either benzene or naphthalene as next, anthracene > pyrene > naphthalene > benzene.

This is fairly consistent with the results obtained in this work.

Accordingly, in view of the above results, it is concluded that the ring cleavage and the substitution predominate in the sonochemical conversion of these hydrocarbons in aqueous media.

Concerning with carcinogenic hydrocarbons, i. e., 3,4-benzopyrene and 20-methylcholanthrene, it was shown that both these hydrocarbons were cracked by ultrasound as will be seen in Fig. 25, 26.

In the table, it is convinced that a sonochemical conversion % becomes lower as the saturation degree of the hydrocarbon increases in general.

For example, the order of decreasing conversion % was listed as follows, naphthalene > tetralin > decalin.

It appears that the non reactivity of α -pinene in an ultrasonic field is due to the saturation of the hydrocarbon, as shown in tetralin.

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