

## RADIATION INDUCED SULFOCHLORINATION

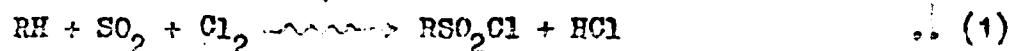
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### Sulfochlorination and Sulfoxidation

The sulfochlorination and sulfoxidation reactions accomplish the introduction respectively of the  $-SO_2Cl$  and  $-SO_3H$  group in a molecule - generally a hydrocarbon. The resulting products, viz., the sulfonyl chlorides or sulfonic acids as the case may be, have commercially important and useful properties. Thus, the sodium alkane sulfonates with chain lengths from  $C_{12}$  to  $C_{16}$  have good detergent properties and are at the same time biodegradable. This latter property is of great importance in connection with problems associated with sewage and prevention of water pollution. The cation exchange resins, widely used in the chemical industry both for water purification as well as for separation and purification of metal compounds is nothing but sulfonated polystyrene. Another commercial product is sulfochlorinated polyethylene, known by the trade name of 'Hypalon'. This is an elastomeric (i.e. rubbery) material with several outstanding properties such as weather, heat and chemical resistance, and hence used for chemical resistant lining for storage tanks, acid hoses, hot conveyor belts, flexible steam pipes etc. In addition, the sulfonyl chlorides and sulfonic acids are useful intermediates in the synthesis of other industrially important compounds such as dyes and the sulfa drugs.

The conventional method of preparing the sulfonic acids and sulfonyl chlorides is to treat the hydrocarbon with either fuming sulfuric acid, or with sulfuric chloride in the presence of light and catalyst (e.g. pyridine). A novel way of accomplishing these syntheses has now become feasible by employing  $\gamma$ -radiation to 'catalyse' the direct sulfochlorination of hydrocarbons with a mixture of sulfur dioxide and chlorine. For example, it has been found<sup>(1,2)</sup> that on  $\gamma$ -irra-

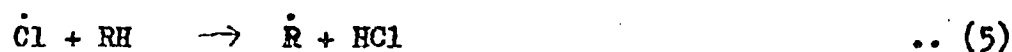
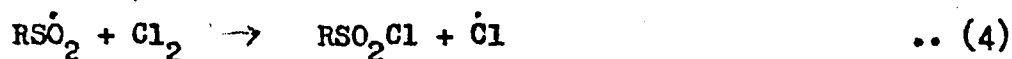
diation of heptane or cyclohexane through which a stream of sulfur dioxide and chlorine is continuously passed, the corresponding sulfonyl chloride is formed in high yield. The overall reaction which can be written as:



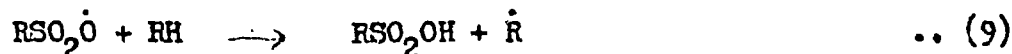
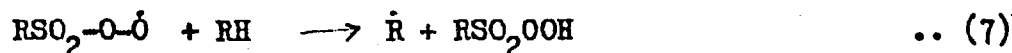
proceeds by a free radical chain mechanism, initiated by the free radicals formed by the action of radiation on the hydrocarbon:



The suggested mechanism is:



with Cl atom as the chain carrier. Similarly  $\gamma$ -radiation induced sulfoxidation of hydrocarbons with a mixture of sulfur dioxide and oxygen is also possible<sup>(3)</sup>, the mechanism of which is represented by the following equations:



with OH radical as the chain carrier. The advantage of these direct, radiation induced methods over the conventional methods is that the former require the relatively cheaper chemicals  $SO_2$ ,  $Cl_2$  ( or  $O_2$ ) as compared to the synthetic chemicals sulfuryl chloride (or fuming  $H_2SO_4$ ) required by the latter method. Also, as these radiation induced reactions are chain reactions and therefore have high ( $10^2$  to  $10^4$ ) G-values, the use of radiation becomes economical. Of the two processes, viz., radiation induced sulfoxidation and sulfochlorination, the former is less attractive for the following reasons. First, the G-values for sulfoxidation are lower, being  $\sim 250$ , as compared to  $\sim 10^4$  for sulfochlorination at the same dose

rate of  $\sim 3 \times 10^5$  rads/hr. (Being chain reactions, the G-values for these processes are dose rate dependent). Secondly at a given level of conversion of the hydrocarbon, the extent of di (and multi) sulfonation is much more in the sulfoxidation process, than in the sulfochlorination process. Thus, for example, in the case of sulfoxidation at a total conversion of  $\sim 34\%$  on the hydrocarbon, the product contains only  $\sim 50\%$  of the monosulfonic acid, the rest being di- and poly sulfonic acids. On the other hand, in the case of sulfochlorination, the product contains about  $80\%$  of the monosubstituted product at  $34\%$  conversion. Technically it is wasteful getting a product containing the di- and multisubstituted compounds, since they are not surface active, and moreover they reduce the surface active property of the monosulfonic acid. Hence we have chosen the sulfochlorination process for our study.

#### Applicability of this kind of study in India

As already mentioned, one of the important uses of sulfonic acids is in the detergent field. In India, the total production of soap was  $2 \times 10^5$  tonnes in 1968 of which  $1.7 \times 10^4$  tonnes were synthetic detergents. The use of synthetic detergents is increasing as would be obvious from the fact that in 1967 only  $1.1 \times 10^4$  tonnes were manufactured whereas in 1970 this is expected to go up to  $4.5 \times 10^4$  tonnes. Chlorine is readily available in the country as there is not enough demand for it at present. For example in 1967,  $2.3 \times 10^5$  tonnes of caustic soda were manufactured from electrolysis of sodium chloride, which would have yielded  $2.1 \times 10^5$  tonnes of chlorine. The actual production of chlorine was only about  $8 \times 10^4$  tonnes since the industry could not utilise more than this amount. Hence any process like the present one which utilises chlorine should be welcome. The cost of chlorine is Rs.340/- per tonne in Bombay.

As for sulfur dioxide, sulfur is to be imported as there are no sulfur deposits in the country. The cost of sulfur dioxide is about Rs.4000/- per ton.

Large radiation sources are now available although the cost is still high

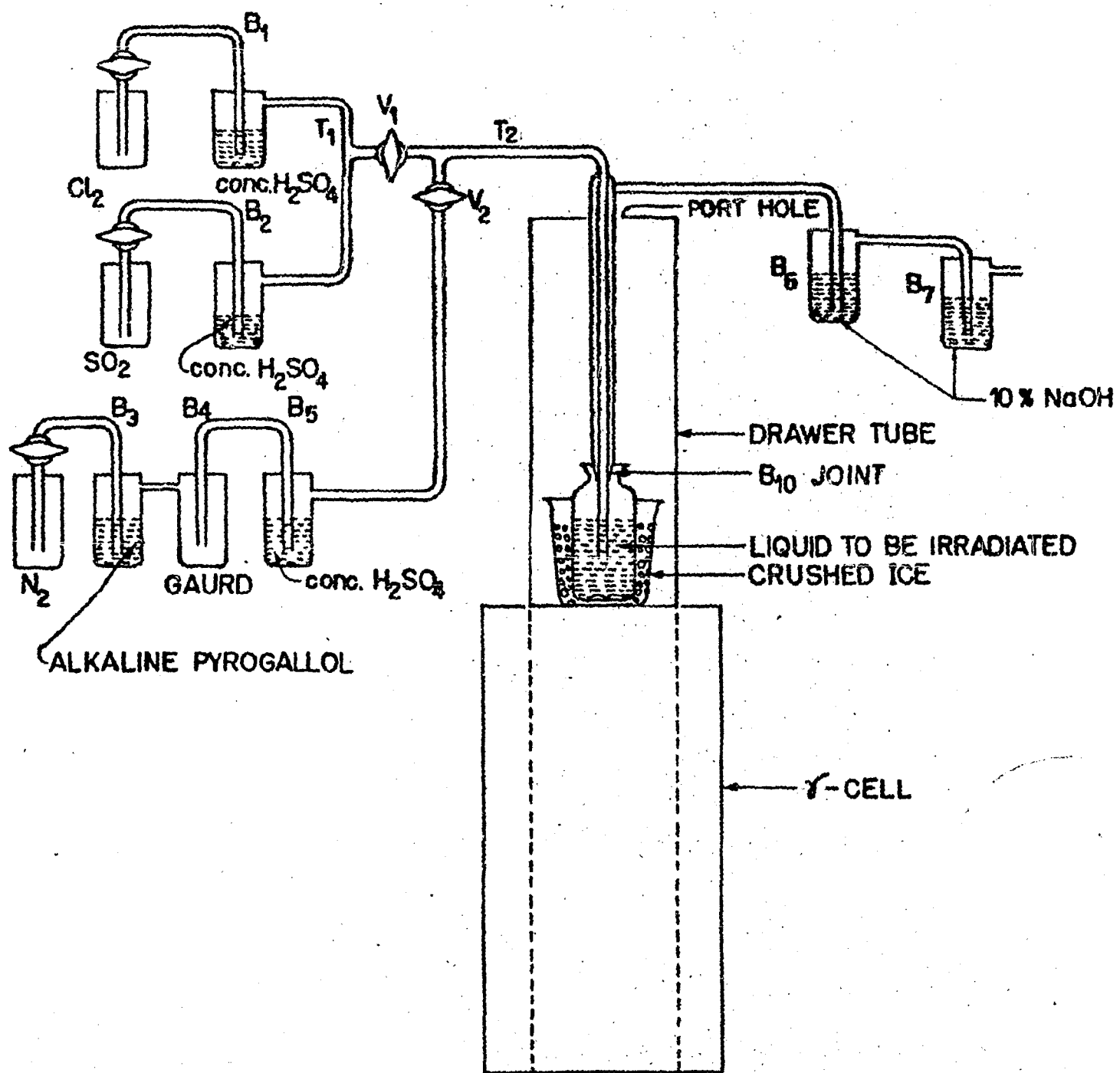


Fig .1. SCHEMATIC DIAGRAM OF THE SET UP FOR  $\gamma$ -RADIATION INDUCED SULFOCHLORINATION.

in India. The price is expected to go down in future as the production of radio-cobalt increases. The current price in India is about Rs.10/- per curie.

The hydrocarbons such as kerosene, liquid paraffin, solid paraffin etc. are all available from petroleum refineries. Suitable cuts can be selected for production purposes.

#### Experimental Set-up for $\gamma$ -irradiation

All  $\gamma$ -irradiations were performed in a B.A.R.C. made  $\text{Co}^{60}$   $\gamma$ -source, similar in design to the 'AECL -cell 220'. The experimental set-up is shown schematically in Fig.1. This set up allows initial flushing with pure nitrogen gas, followed by saturation of the hydrocarbon with a mixture of  $\text{SO}_2$  and  $\text{Cl}_2$  and irradiation in a stream of these gases. The unreacted gases are finally swept out by a stream of nitrogen gas.

#### Results

In all the reaction products, the IR spectra revealed the presence of  $-\text{SO}_2\text{Cl}$  groups characterised by the peaks<sup>(1)</sup> in the  $1161-1165 \text{ cm}^{-1}$  and  $1370-1376 \text{ cm}^{-1}$  regions. The G-values and percent conversion figures for sulfochlorination of the different hydrocarbons investigated are given in Table I. These results have been discussed in detail in an earlier publication<sup>(7)</sup>. It is seen that the G-values for the sulfochlorination are quite high ( $10^3-10^4$ ) with all the liquids investigated, comparable to the value ( $4.36 \times 10^3$ ) reported<sup>(1)</sup> for cyclohexane at about the same dose rate. At lower dose rates they will be still higher as there are fewer radicals for chain termination. In any case, the G-values are high enough to be worthy of consideration for commercial exploitation.

Based on the experimental data obtained in the case of kerosene, we have carried out calculations for the pilot-plant scale sulfochlorination of this material. The results are given in Table II.

We are currently working on the sulfochlorination of polymeric materials such as polythene, polystyrene, textile fibers etc.

Table I.

$\gamma$ -Radiation induced sulfochlorination of hydrocarbons: Results (Dose rate =  $4.28 \times 10^{17}$  ev/ml/min; Fricke Dosimeter)

Run No.	Hydrocarbon	Total Dose absorbed in 30 ml (ev $10^{-20}$ )	(Approx) Total $Cl_2$ passed through system (mole)	(Approx) Total $SO_2$ passed through system (mole)	$\theta$ ( $\pm SO_2Cl$ ) $\times 10^{-3}$	(Approx) Percent conversion based on Hydrocarbon	$Cl_2$	$SO_2$
1	Kerosene	1.029	0.1	0.2	6.4	10.3	10.8	5.4
2	"	2.058	0.2	0.4	7.5	24.0	12.6	6.3
3	"	4.630	0.45	0.9	9.7	70.0	16.4	8.2
4	"	1.029	0.15	0.3	8.9	14.3	10	5
5	"	"	0.2	0.4	9.5	15.3	18	4
6	"	"	0.05	0.1	0.27	0.43	0.9	0.5
7	Stalliol	0.975	0.1	0.2	15.3	24.5	24.5	12.3
8	Dekalin	1.149	"	"	17.4	16.9	32.7	16.4
9	L. Paraffin CCl (50/50 w/w)	1.128	"	"	1.1	1.74	2	1

Table II.

Results of calculations for pilot plant scale sulfochlorination of kerosene by  $\gamma$ -radiation (based on data of run No.2, Ref. Table I.)

Vessel 5 cm i.d., 15 cm ht.,  $\frac{3}{4}$  filled ( $\sim 222$  ml)

Dose rate  $\sim 4.28 \times 10^{17}$  ev/ml/min.

Batch operation

Irradiation times: 20 min/batch

Average duration of batch: 24 min, i.e. 60 batches per day.

	Per batch (g)	Per day (kg)
Kerosene employed	176	10.6
" consumed	42	2.52
$Cl_2$ passed	105	6.3
" consumed	13.2	0.79
$SO_2$ passed	190	11.4
" consumed	12.0	0.72
NaOH consumed for hydrolysis	15.0	0.9
R- $SO_2Na$ produced	61.0	3.55
NaCl produced (by product)	10.9	0.65
HCl produced (by product)	6.8	0.41

Acknowledgements

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DISCUSSION

- R.S. Mani : Have you evaluated the products for detergent properties?
- Answer : Yes, only on qualitative basis so far.
- P. Sudarsan : Are you aware of any pilot scale developmental facilities for this process?
- Answer : No, not in India.