



Synthesis of *sec*-Butyl Disulfide by Phase Transfer Catalysis

XINQI LIU¹, JIA WANG², SONGFANG ZHAO³ and GUOQIN HU^{2,*}

¹Henan Vocational College of Chemical Technology, Zhengzhou 450042, Henan Province, P.R. China

²College of Chemical Engineering and Energy, Zhengzhou University, Zhengzhou 450001, Henan Province, P.R. China

³Henan Province Engineering Technology Research Center of sulphydryl compounds, Sanmenxia 472100, Henan Province, P.R. China

*Corresponding author: Tel/Fax: +86 371 67781712; E-mail: huguoqin@zzu.edu.cn

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sec-Butyl disulfide was synthesized from sulfur, sodium hydroxide and *sec*-butyl chloride using tetrabutyl ammonium bromide as the phase transfer catalyst. The optimal experiment condition obtained by orthogonal design and the average product yield was 84.95 %. The samples synthesized under optimal conditions were characterized by infrared spectrometry, gas chromatography-mass spectrometer.

Keywords: Phase transfer catalysis, Alkyl halide, *sec*-Butyl disulfide, Orthogonal experiment.

INTRODUCTION

sec-Butyl disulfide is an important fine chemical intermediates used in thiosulfates sulfur and oxygen compounds synthesized simultaneously with pesticides, biology, materials, petrochemicals, dyes and food science wide range of uses. In recent years, with the expansion of downstream products, di-*sec*-disulfide market demand is increasing year by year, attracted wide attention at home and abroad.

Combination of all the literature¹⁻⁷, di-*sec*-disulfide synthesis of different materials are divided into: thiol method, 1,3-butadiene method, Grignard reagent and halogenated hydrocarbons law. Currently, the largest reported in the literature is the mercaptan as raw materials, but especially in low-carbon chain thiol mercaptan fetid, volatile, pollution, corrosive, so the industry is generally not used for this synthesis.

The authors focus on research halogenated hydrocarbons as raw material, phase transfer catalysis synthesis of butyl disulfide. Pre-emphasis to the *sec*-bromine as raw materials to carry out research work^{8,9}. Butyl bromide activity is high, but the price is expensive and difficult byproduct sodium bromide recovery. Therefore, the authors focused on readily available and inexpensive raw material of butyl chloride as raw materials, tetrabutylammonium bromide as a phase transfer catalyst synthesis of butyl disulfide.

EXPERIMENTAL

AB204-N-type electronic analytical balance (Mettler-Toledo Instruments Co., Ltd.); JJ-1 electric blender (Jiangsu-jintan Shuangjie Instrument); HH-type water bath (Jintan City,

Jiangsu Zhongda Instrument Factory) ; RE-52AA rotary evaporator (Haiya Wing instrument); SHB-III type multi-purpose water circulating pump (Zhengzhou Great Wall Industry and Trade Co., Ltd.); WQF-510 infrared spectrometer (Beijing Rayleigh Analytical instrument Corporation); GPC-GCMS type GC-MS (Shimadzu Corporation); 202 electric oven (Shanghai electro-optical instrument Factory).

Chlorinated secondary butane (99 %), nine water sulfide, sulfur sublimation, chloroform, anhydrous sodium sulfate, tetrabutylammonium bromide were of analytical grade.

Synthesis: In 100 mL three-necked flask equipped with a thermometer and a stirring motor, the measurement was added sodium sulfide, sulfur powder and distilled water, 50 °C water bath with stirring 40 min, the mixture became a red-brown solution is sodium bisulfite solution (easily oxidized should now with the current).

In the above measurement was added a freshly prepared solution of sodium sulfide and chlorinated butane secondary phase transfer catalyst, the reaction was refluxed under constant stirring, the reaction is followed by gas chromatography.

The reaction was allowed to stand stratification, the upper organic phase was yellow, orange lower aqueous phase. The aqueous phase was extracted three times with a small amount of chloroform and the combined organic phase was washed three times with distilled water and removal of inorganic salts, plus a certain amount of anhydrous sodium sulfate and left for 5 h, filtered to give a pale yellow or colourless two-butyl disulfide The crude product. After distillation under reduced pressure, followed by a two-butyl sulfide, disulfide and trisulfide.

RESULTS AND DISCUSSION

Orthogonal test results: Impact of $n(\text{Na}_2\text{S})$, reaction temperature, reaction time on the yield of di-*sec*-disulfide: The experimental study focused on the amount of catalyst, water usage, $n(\text{S}):n(\text{C}_4\text{H}_9\text{Cl})$, $n(\text{S})$. Therefore, the present study L_{25} (5^6) orthogonal arrangement to the yield of di-*sec*-disulfide measure. The results are shown in Table-1.

As can be seen from the size range R, R larger the value the greater the impact on the experiment, so the impact of factors affecting the order of the experiment: the amount of catalyst > time > $n(\text{S}):n(\text{C}_4\text{H}_9\text{Cl}) > n(\text{S}):n(\text{Na}_2\text{S}) > \text{amount of water} > \text{reaction temperature}$, the best combination of the experiment is $\text{A}_5\text{B}_2\text{C}_4\text{D}_2\text{E}_3\text{F}_4$.

Experimental results under optimized conditions:

Obtained by orthogonal experiment optimum synthesis conditions, in accordance with 1 optimization in the experimental program was repeated twice, yields were 84.9 and 85 %. The results showed that under the optimal combination of process scheme for the synthesis target product, the average yield of the product reached 84.95 %. Orthogonal table above yields a set of experiments yield either to verify the correctness and accuracy of the experimental results.

Infrared spectroscopy: Fig. 1 shows bands at 2964, 2874, 1458 and 1377 cm^{-1} , respectively for methyl CH bond asymmetric stretching vibration peak, symmetric stretching vibration, bending vibration of antisymmetric and symmetric

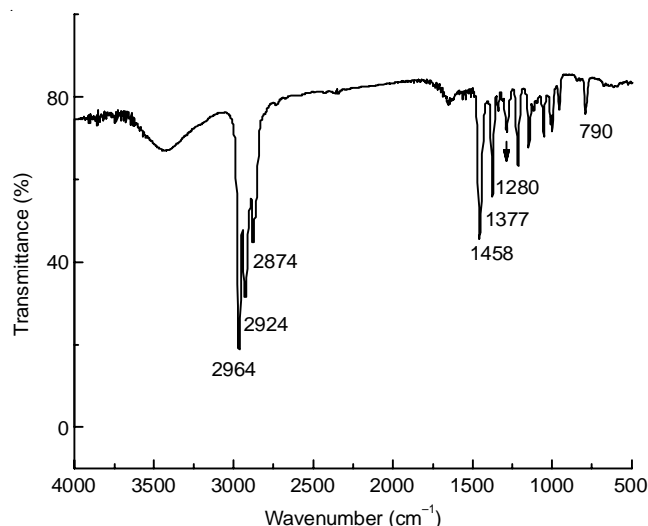


Fig. 1. FT-IR spectrum of *sec*-butyl disulfide

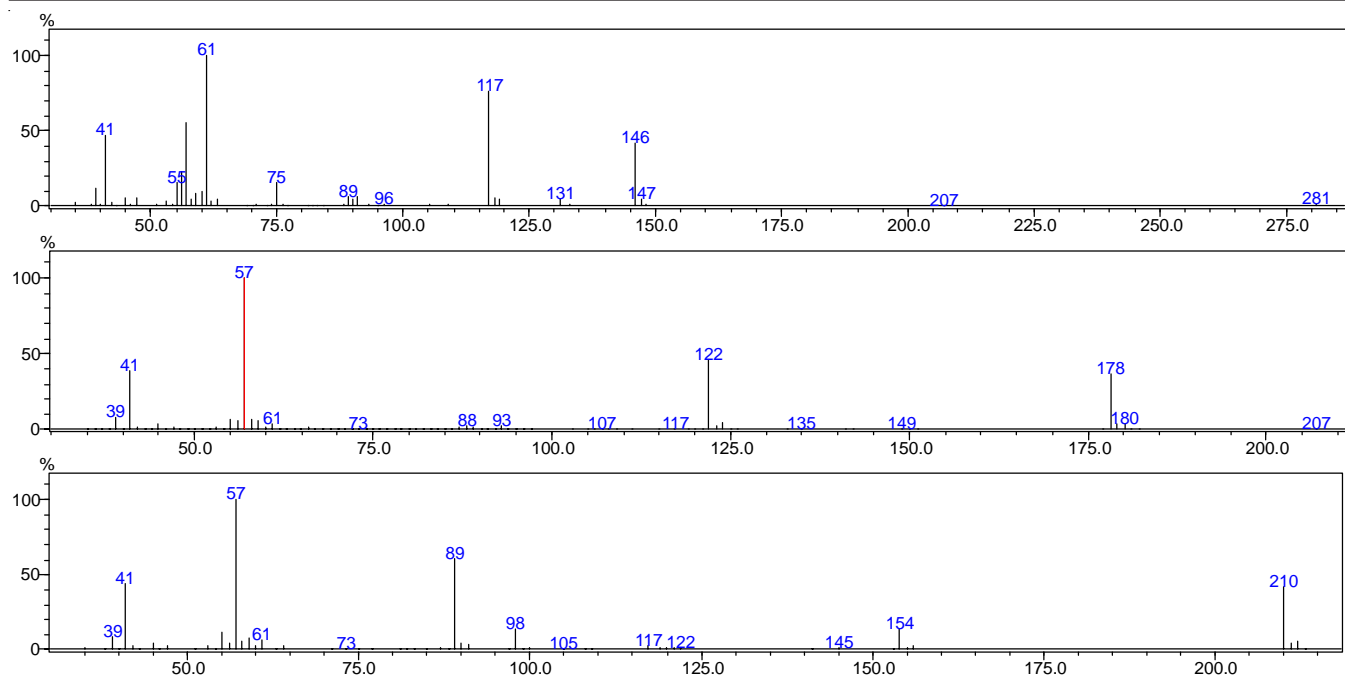
stretching vibration; 2924 and 790 cm^{-1} , respectively for methylene base in CH bond asymmetric stretching vibration peak and peak plane rocking; 1280 as bending vibration of methylene CH bond. This is consistent with the standard second-butyl disulfide pattern¹⁰.

Gas chromatography-mass spectrometry: The reaction product obtained was diluted with methanol in a volume ratio of 50 times, for the GC-MS analysis. Gas chromatographic

TABLE-1
RESULTS OF ORTHOGONAL DESIGN ($\text{L}_{25} 5^6$)

Entry	A	B	C	D	E	F	Yield (%)
1	2.5	4	0.725:1	0.51:1	43	7.5	66.7
2	2.5	5	0.75:1	0.53:1	46	8.5	68.7
3	2.5	6	0.775:1	0.55:1	49	9.5	73.8
4	2.5	7	0.8:1	0.57:1	52	10.5	77.6
5	2.5	8	0.825:1	0.59:1	55	11.5	59.71
6	3	4	0.75:1	0.55:1	52	11.5	68.7
7	3	5	0.775:1	0.57:1	55	7.5	77.7
8	3	6	0.8:1	0.59:1	43	8.5	68.0
9	3	7	0.825:1	0.51:1	46	9.5	78.1
10	3	8	0.725:1	0.53:1	49	10.5	84.8
11	3.5	4	0.775:1	0.59:1	46	10.5	75.8
12	3.5	5	0.8:1	0.51:1	49	11.5	84.7
13	3.5	6	0.825:1	0.53:1	52	7.5	74.4
14	3.5	7	0.725:1	0.55:1	55	8.5	76.0
15	3.5	8	0.75:1	0.57:1	43	9.5	77.4
16	4	4	0.8:1	0.53:1	55	9.5	82.4
17	4	5	0.825:1	0.55:1	43	10.5	80.8
18	4	6	0.725:1	0.57:1	46	11.5	78.3
19	4	7	0.75:1	0.59:1	49	7.5	69.2
20	4	8	0.775:1	0.51:1	52	8.5	77.7
21	4.5	4	0.825:1	0.57:1	49	8.5	75.2
22	4.5	5	0.725:1	0.59:1	52	9.5	81.7
23	4.5	6	0.75:1	0.51:1	55	10.5	84.8
24	4.5	7	0.775:1	0.53:1	43	11.5	84.4
25	4.5	8	0.8:1	0.55:1	46	7.5	81.4
Mean value 1	69.3	73.76	77.5	78.4	75.44	73.86	-
Mean value 2	75.46	78.72	73.74	78.92	76.46	71.98	-
Mean value 3	77.62	75.84	77.88	76.14	77.54	78.5	-
Mean value 4	77.68	77.06	78.82	77.22	76	80.76	-
Mean value 5	81.5	76.18	73.62	70.88	76.12	75.16	-
Range R	12.2	4.96	5.2	8.04	2.1	8.78	-

^AAmount of catalyst used (%); ^BAmount of water (g); ^C $n(\text{S}):n(\text{Na}_2\text{S})$; ^D $n(\text{S}):n(\text{C}_4\text{H}_9\text{Cl})$; ^EReaction temperature ($^{\circ}\text{C}$); ^FReaction time/h

Fig. 2. GC-MS spectrum of *sec*-butyl disulfide

conditions described above, the MS conditions: Ion source EI, the ionization voltage of 70 eV, ion source temperature was 200 °C, scan range of 30-300 *m/z*.

Fig. 2 followed by retention time in the gas phase spectra from short to long sequence of spectra of each peak, the system searches through the mass of data, were recognized as two *sec*-sulfide, di-*sec*-butyl disulfide and two three sulfide.

Conclusion

By orthogonal test under optimum conditions, *i.e.*, the amount of tetrabutylammonium bromide 3.5 %, the amount of water is 7 g, n(S): n(Na₂S) = 0.775:1, n(S) : n(C₄H₉Cl) = 0.53:1, temperature 49 °C, reaction time of 10.5 h. The experiment was repeated twice in this condition and the average yield was 84.95 %. The product of infrared spectroscopy, gas-mass spectrometry to characterize the experimental results agree with the standard.

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