

## APPLIED CHEMISTRY

## Optimization of the Synthesis of Methyl Iodide Using Sponge Iron

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The optimization of the conventional synthesis of an important industrial product—methyl iodide—by using iron sponge, iodine, and methanol as precursors is presented. The experiments were carried out under different conditions of molar ratio of the reagents, reaction and distillation temperatures, stirring rate, and rate of addition of methanol. It is shown that the highest yield of the product is reached at the molar ratios of methanol/iron of 1.0 and iodine/iron higher of 1.5. The optimal temperature range for this synthesis is located between 53 and 109 °C for which the highest yields were obtained in coincidence with the temperature range at which the formation of  $\text{FeI}_2$  is also optimal. A relationship between the syntheses of  $\text{FeI}_2$  and the syntheses of  $\text{CH}_3\text{I}$  was elaborated and it was found that the conditions favorable for the syntheses of  $\text{FeI}_2$  are also necessarily favorable for the syntheses of  $\text{CH}_3\text{I}$ .

## Introduction

Methyl iodide is an important industrial product used as an intermediate substance in the manufacture of pharmaceuticals and pesticides,<sup>1</sup> also as a precursor in diverse methylation processes, and as a fumigant to control pests in fruit trees and stored grains.<sup>2</sup> Methyl iodide is rapidly displacing methyl bromide in the market<sup>3,4</sup> despite  $\text{CH}_3\text{I}$ 's higher cost mainly because of its wider scope of applications and its negligible influence on the stratosphere ozone layer.<sup>5</sup>

It is known that methyl iodide remains in the atmosphere for 2 years before its natural destruction.<sup>6</sup> The slower degradation of  $\text{CH}_3\text{I}$  in comparison with methyl bromide determines that, under similar doses of application and for the same soil conditions, the loss by volatilization of  $\text{CH}_3\text{I}$  would likely take longer than that of  $\text{CH}_3\text{Br}$  and the risk for  $\text{CH}_3\text{I}$  to enter the groundwater would likely be higher. Because volatilized  $\text{CH}_3\text{I}$  is quickly decomposed in the air under the action of light, it will not contribute to ozone destruction. The dissipation half-life for  $\text{CH}_3\text{I}$  in water, under exposed outdoor conditions, is on the scale of about 1 day;<sup>7</sup> nevertheless, its massive inhalation can provoke pulmonary oedema, depression of the central nervous system, painful effects on kidney and larynx, and skin irritation, or even burns, depending on how prolonged was the contact with the exposed skin tissue.<sup>8,9</sup> In nature, various species of macroalgae in marine water are known to produce and release methyl halides in considerable amounts.<sup>10</sup>  $\text{CH}_3\text{I}$  vapors have been detected naturally occurring on flooded soils used for rice and oats production, with a higher concentration on those related to rice. It has been suggested that the methyl iodide formation is due to the action of roots, or of microorganisms inhabiting in and around the root system.<sup>11</sup> Some industrial wastes also contain  $\text{CH}_3\text{I}$ .<sup>12</sup>

Selected synthetic methods for  $\text{CH}_3\text{I}$  production start from the following precursors: (1) methanol, phosphorus, and iodine;<sup>13,14</sup> (2) potassium iodide and methyl sulfonate;<sup>15</sup> (3)  $\text{CH}_3\text{I}$ , KOH, and ethanol;<sup>16</sup> (4) iodine, methanol, and iron;<sup>17</sup> (5) iodine, a metal belonging to any one of the groups Ia, IIa–IIIa, Ib, IIb, IIIb, and IVb, and a member of any one of the following families of compounds—alcohols, esters, dialkyl ethers, and diallyl ethers;<sup>18</sup> (6) iodine, hydrogen, and methyl alcohol using as catalyst either rhodium, iridium, or ruthenium; (7) iodine, hydrogen, and methyl acetate or dimethyl ether using either palladium, rhodium, platinum, ruthenium, or nickel as a catalyst, although the high cost of the catalyst and the formation of methane become two very serious disadvantages.

Table 1 shows a summary of the experiments performed by Dangyan for the synthesis of alkyl halides.<sup>17,19–24</sup> Two features of the experiments are worth noting; the ratio of halide to iron was kept nearly constant at 1.5, and the order in which reagents were added depended on the alkyl halide to be obtained.

In 1938, Dangyan obtained methyl chloride from ferric chloride and methanol; ferric hydroxide is a byproduct.<sup>19</sup> Later, in 1940 and as a result of the difficulties for obtaining ferric iodide of high purity, Dangyan synthesized  $\text{CH}_3\text{I}$  directly from iodine, methanol, and iron sponge (obtained by the reduction of iron ores with hydrogen) with a yield of 50.3%.<sup>17</sup> The aim of the present work is to optimize the preparation of methyl iodide from the precursors listed above, namely, the same used by Dangyan in the synthesis of methyl iodide.

## Experimental Section

**Materials and Equipment.** High-purity iron sponge (HPI) produced by the research facilities of Hojalata y Lámina S. A.—Hylsa—at its plant in Monterrey, Mexico, was used directly as supplied after it was ground to 60

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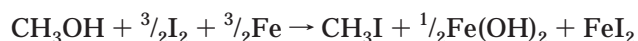
**Table 1. Summary of the Reactions Undertaken by Dangyan for the Synthesis of Alkyl Halides**

reaction synthesis	halide/iron	halide/alcohol	yield %	ref
$\text{FeCl}_3 + 3\text{CH}_3\text{CH}_2\text{OH} \rightarrow 3\text{CH}_3\text{CH}_2\text{Cl} + \text{Fe}(\text{OH})_3$	1.5	0.77	86	21
$\text{FeCl}_3 + 3\text{CH}_3\text{OH} \rightarrow 3\text{CH}_3\text{Cl} + \text{Fe}(\text{OH})_3$			98	22
$\text{CH}_3\text{OH} + \frac{3}{2}\text{I}_2 + \frac{3}{2}\text{Fe} \rightarrow \text{CH}_3\text{I} + \frac{1}{2}\text{Fe}(\text{OH})_2 + \text{FeI}_2$	1.5	1.9	50.3	17
$1.5\text{I}_2 + 2\text{Fe} + 2\text{CH}_3\text{COOC}_2\text{H}_5 \rightarrow 2\text{C}_2\text{H}_5\text{I} + (\text{CH}_3\text{COO})_2\text{Fe} + \text{FeI}_2$	1.5	0.51	96.6	17
$2\text{I}_2 + 2\text{Fe} + 2\text{C}_6\text{H}_5\text{COOC}_2\text{H}_5 \rightarrow 2\text{C}_2\text{H}_5\text{I} + \text{FeI}_2 + (\text{C}_6\text{H}_5\text{COO})_2\text{Fe}$	1.57	0.52	87.2	17
$2\text{Br}_2 + 2\text{Fe} + 2\text{C}_2\text{H}_5\text{OH} \rightarrow 2\text{C}_2\text{H}_5\text{Br} + \text{Fe}(\text{OH})_2 + \text{FeBr}_2$	1.5	0.64	81.7	23
$1.5\text{I}_2 + \text{Al} + 3\text{CH}_3\text{OC}_6\text{H}_5 \rightarrow 3\text{CH}_3\text{I} + (\text{C}_6\text{H}_5\text{O})_3\text{Al}$			70	24
$1.5\text{I}_2 + \text{Al} + 3\text{C}_2\text{H}_5\text{OC}_6\text{H}_5 \rightarrow 3\text{C}_2\text{H}_5\text{I} + (\text{C}_6\text{H}_5\text{O})_3\text{Al}$			62.4	24
$1.5\text{I}_2 + \text{Al} + 3\text{C}_4\text{H}_9\text{OH} \rightarrow 3\text{C}_4\text{H}_9\text{I} + \text{Al}(\text{OH})_3$			70.9	24
$1.5\text{I}_2 + \text{Al} + 3\text{CH}_3\text{COOC}_2\text{H}_5 \rightarrow 3\text{C}_2\text{H}_5\text{I} + (\text{CH}_3\text{COO})_3\text{Al}$			70–90	25
$\text{Br}_2 + \text{Fe} + 2\text{C}_4\text{H}_9\text{OH} \rightarrow 2\text{C}_4\text{H}_9\text{Br} + \text{Fe}(\text{OH})_2$	1.5	0.5	46.4	26

mesh. Resublimed iodine, as provided by Productos Químicos Monterrey with a stated purity of 99.9 mol %, was used directly as supplied. Methyl alcohol, also from Productos Químicos Monterrey, with a stated purity of 99.8 mol % and containing no more than 0.05%  $\text{H}_2\text{O}$ , was distilled in an 80-cm-high packed glass column, the initial and final fractions being discarded. The distilled sample was dehydrated over No. 4 Molecular Sieves (Sigma Chemical Co.) while stored in a Pyrex container. Methyl alcohol purity was determined to be in excess of 99.99 mol % by thermal conductivity detector gas chromatography.

A number of different variables had to be chosen for the study of the syntheses of methyl iodide from iron sponge, iodine, and methanol. Those reaction variables were as follows: the reagents molar ratios and the order in which they were added during the syntheses, reaction and distillation temperatures, stirring rate of the mixture, rate of addition of methanol, and the settling time given to the reaction mixture. It certainly is an important factor how finely ground is the iron sponge for speeding up the reaction; however, a number of preliminary runs were made, searching for a reasonable particle size that combined both a fast reaction and an easy-to-stir mixture. The search produced a 60-mesh powder that was chosen as a fixed variable during the whole set of experiments. Another possible factor affecting the reaction yield was the water contained in the reagents, which although not quantified as such, was altogether eliminated as a variable by dehydration of reagents. A total of 61 experiments were carried out. A gas chromatograph (Varian model 3700) was used for the analytical determination of the reaction products.

A short description of the experimental procedure is given by using the first experimental run as an example: 75 g (0.295 mol) of  $\text{I}_2$  and 20 g (0.305 mol) of iron sponge HPI were ground and placed in a 500-mL three-necked distillation flask. Then, 7 mL (0.173 mol) of methanol was added to this mixture, stirring taking place at a moderate rate. A sharp increase in temperature, rising to 122 °C, was detected, which then decreased to 110 °C and continued decreasing for 5–6 °C every 5 min. As a result of methanol addition, a dark liquid mixture formed with an escaping purple vapor. The mixture was stirred for one more hour in the distillation flask and then stored for 1 day. The overall reaction is given by the following equation:



Distillation of the reaction mixture proceeded from 108 to 135 °C. Temperature at the head of the distilling apparatus was initially at 34.5 °C but a maximum of 44 °C was reached. A red distillate was collected in a 100-mL beaker containing 20 mL of demineralized and

twice-distilled water. The red distillate was introduced below the level of the water in the receiver to diminish the possibility of methyl iodide being lost by evaporation. After distillation, the distillate was mixed with a 10% solution of sodium thiosulfate, becoming uncolored. Two uncolored layers were formed, an upper layer—aqueous—and the lower layer—organic; they were soon separated for quantification purposes, usually 5–10 min after formation, to avoid the reaction of some methyl iodide with thiosulfate. Two methods were tried for the analysis of the distillate, chromatographic and gravimetric, the first one being decided upon for the whole of this work.

Although the experiment described represents in a broad manner the 61 experimental runs, there were several variations to improve the technique used throughout this work; only in experiments 1 and 2 was a bulb-type condenser used during distillation, while for the remaining runs a change to a straight-tube condenser proved better. From experiment 9 two more changes were introduced; methanol was added through a straight-tube condenser to avoid volatilization and stirring became mechanical.

Experimental runs were grouped according to their similarities:

(1) Experiments in which all the variables were kept constant and they were analyzed, searching for any repetition in the results.

(2) Experiments in which all the variables, except one at the time, were kept constant with the aim to weight the effect of every individual variable on the yield of reaction.

(3) This group encompasses the set of experimental runs in which the molar ratios were identical to those used before by Dangyan, although in the majority of these runs a scaling up factor had to be performed because the amounts originally used by Dangyan were very small.

(4) To this group belong all the experimental runs in which an excess, either of iodine or methyl alcohol, was used to evaluate the course of the reaction and its yield.

**Chromatographic Determinations.** The technique of internal standards was followed for the chromatographic determinations. Nine standards were prepared from concentrated  $\text{CH}_3\text{I}$  solutions in  $\text{CH}_3\text{OH}$ . The standards 1–4 were analyzed in a column 10% Carbowax 20-M/chromosorb WHP 80/100 under two different flows of helium. The standards 5 to 9 were analyzed in a column DC-200. Each standard was analyzed at least twice for the same programmed conditions. Operating conditions and related data are presented in Table 2.

Response factors were calculated by taking propyl alcohol as the reference substance through eq 1. The uncertainties in the computed values for the response factors were then calculated by using eq 3. These

**Table 2. Weight Percent of CH<sub>3</sub>I, Methyl Alcohol, and Propyl Alcohol in the Nine Standards Used for the Chromatographic Analysis of the Reaction Products**

standard	wt % of CH <sub>3</sub> I	wt % of methanol	wt % of propanol
1	1.4 ± 0.2	74.8 ± 1.3	23.8 ± 1.3
2	2.1 ± 0.2	74.4 ± 1.3	23.6 ± 1.3
3	2.7 ± 0.2	73.9 ± 1.3	23.4 ± 1.2
4	4.0 ± 0.3	73.0 ± 1.2	23.0 ± 1.2
5	1.5 ± 0.1	2.1 ± 0.2	20.8 ± 1.1
6	3.1 ± 0.2	4.2 ± 0.3	20.6 ± 1.1
7	4.5 ± 0.3	6.3 ± 0.4	20.4 ± 1.1
8	6.0 ± 0.4	8.3 ± 0.5	20.2 ± 1.1
9	7.4 ± 0.5	10.3 ± 0.6	20.0 ± 1.0

equations were obtained as follows: To calculate the uncertainty of any quantity, for instance,  $w = w(A, B, C, D, E)$ , the method of partial derivatives is used; hence,

$$dw = ((\partial w/\partial A)^2 + (\partial w/\partial B)^2 + (\partial w/\partial C)^2 + \dots)^{0.5}$$

The technique of the internal standard was used to calculate the amount of CH<sub>3</sub>I obtained. The method establishes that to a given amount of the sample problem be added a known amount of the standard. The correction factors related to the same standard were previously determined by using a mixture of known composition containing the compounds of interest, to which was added a known amount of the standard. Once the correction factors have been calculated, the chromatograph of the sample problem, and that of the standard, can be performed. The areas under the peaks are measured and, through a simple calculation, the required ratios are computed.

The set of equations used for the computations are summarized as follows:

$$(F_i^* A_i / F_{\text{propanol}}) A_{\text{propanol}} = X_i / X_{\text{propanol}} \quad (1)$$

$$F_i^* \varphi_i / F_{\text{propanol}} = X_i / X_{\text{propanol}} \quad (2)$$

$$dF_1 = ((\partial F_1^* \partial X_1 / \partial X_1)^2 + (\partial F_1^* \partial X_p / \partial X_p)^2 + (\partial F_1^* \partial \varphi / \partial (\varphi))^2)^{0.5} \quad (3)$$

where  $i$  is the compound of interest (in this case it refers to CH<sub>3</sub>I),  $kF_i$  is the response factor measured for the "analyte" component,  $A_i$  is the area under the peak corresponding to the "analyte" component,  $X_i$  is the weight fraction of the "analyte" component,  $\varphi_i$  is the ratio of areas (area of the "analyte" component to the area of propyl alcohol, taken as the reference substance ( $A_i/A_p$ )).

The products were analyzed by applying this method, although for the group of 15 experiments showing a very

**Table 4. Set of Five Experimental Runs with Molar Ratios of Iodine/Methanol and of Iodine/Iron Fixed at 4.42 and 2.992, Respectively**

experiment	stirring rate, rpm	reaction maximum temp, °C	distillation maximum temp, °C	settling time, h	% yield
52	500	41.0	180	24	50.45
53	500	46.5	138	24	44.045
54	1300	46.0	178	4	56.046
55	1300	40.0	60	4	15.62
56	1300	40.0	178	4	48.05

low yield of CH<sub>3</sub>I, lower than 2%, the analysis of the products was carried out by GC only for the three experiments numbered 14, 15, and 16. These three experiments represent the group of reactions for which the products, after due treatment, form the whole of the inorganic phase as a result of the poor yield obtained of CH<sub>3</sub>I. We also selected experiments 45 and 57 as representative examples of the two different groups of experiments showing yields higher than 2%, chiefly because their reaction products, after treatment, form two phases. It is worth noting that experiment 45 corresponds to a high yield of CH<sub>3</sub>I at 57.5%, whereas experiment 57 showed a low yield with only 4.88%. Table 3 reports quantitative data of the methyl iodide obtained after using average response factors.

## Results and Discussion

The discussion is presented below under the headings of two main sections. The first section includes a description of the experiments, by groups, according to the stoichiometric ratios methanol/iron and iodine/iron used for the syntheses. In the second one the experiments are described according to the variables used to define reaction conditions, chiefly the stirring rate, reaction time, maximum reaction temperatures, and rate of methanol addition.

**Stoichiometric Ratios.** The 61 experimental runs can be grouped according to their similarities in the molar ratios used for the synthesis.

As shown in Table 4, a group of five experiments with a molar ratio of iodine/methanol at 4.42, and a molar ratio of iodine/iron at 2.99, showed an average yield of 43%.

A group of 22 experiments with molar ratios of iodine/methanol at 1.71, and iodine/iron at 0.96, showed an average yield of 39.9%.

Three of the experimental runs were performed with molar ratios of iodine/methanol at 1.71, and of iodine/iron at 1.71, to produce the highest average yield of 57.4% combined with the lowest deviation among the 61 runs; deviation amounted to only +0.71% as shown in Table 6. For this group of experiments were used the

**Table 3. Parameters Used throughout the Chromatographic Analysis of the Products in Order to Determine the Amount of Methyl Iodide Obtained in the Reaction**

experiment	45		57		16
methanol response factor	4.0 ± 0.3		3.1 ± 0.2		2.5 ± 0.1
methyl iodide response factor	4.4 ± 0.7		6.5 ± 0.5		8.0 ± 0.3
propanol response factor	1.0		1.0		1.0
phase	organic	inorganic	organic	inorganic	inorganic
peak area for CH <sub>3</sub> I	387625	4069	2420157	27307	5280
peak area for methanol	2090	296161	25071	4070220	1040072
peak area for propanol		552715		2802766	1015614
retention time CH <sub>3</sub> I, min	1.10	1.65	1.27	1.35	2.07
retention time methanol, min	1.73	1.21	2.13	2.22	0.89
retention time propanol, min		3.92		5.27	3.60
methyl iodide obtained, g	14.1	0.82	3.40	0.69	1.10

**Table 5. Methyl Iodide Yield against Temperature and Rate of Addition of Methyl Alcohol, as Obtained for a Set of Six Experiments in Which the Lowest Stirring Rate of Only 50 rpm Was Used**

experimental run	max temp of the reaction (°C)	max temp during distillation (°C)	% yield	time taken for the addition of methyl alcohol (min)
1	122	134	41.8	0.5
2	145	150	24.1	20
3	109	131	44.5	20
4	132	92	33.4	27
5	57	115	45	45
6	53	102	45	40

**Table 6. Experimental Runs Performed with a Molar Ratio of Iodine/Methyl Alcohol Fixed at 1.71 While Changing the Following Factors: Molar Ratio Iodine/Iron, Stirring Rate (rpm), Reaction Maximum Temperature ( $T_{\max}$ /°C), Temperature at the End of the Reaction ( $T_{\text{end}}$ /°C), and Settling Time Given to the Products (STP/h)**

run	iodine/methyl alcohol	iodine/iron	yield	stirring rate, rpm	$T_{\max}$ (°C)	$T_{\text{end}}$ (°C)	STP (h)
1	1.71	0.964	41.76	50	122	40	24
2	1.71	0.964	24.1	50	122	40	24
3	1.71	0.964	44.5	50	109	45	24
4	1.71	0.967	33.4	50	132	70	24
5	1.71	0.964	45	50	57	36	4
6	1.71	0.964	45	50	53	34	24
16	1.71	0.964	3.3				22
17	1.71	0.824	0.0	600			24
18	1.71	0.824	0.0	500			24
19	1.71	0.824	0.0	500			72
20	1.71	0.824	0.0				24
21	1.71	0.824	37.1	500			24
22	1.71	0.824	18.6				24
23	1.71	0.824	0.0				72
24	1.71	0.824	0.0	500			24
25	1.71	0.824	0.0	500			24
26	1.71	0.824	1.86	500			24
27	1.71	0.967	19.9	500			48
28	1.71	0.967	53.8				4
29	1.71	0.964	44.5		64		24
30	1.71	0.964	43.6		60	60	24
31	1.71	0.964	37.1		51		24
32	1.71	0.964	34.3			52	24
33	1.71	0.964	29.7		122	40	24
34	1.71	0.964	43.6	500		72	24
35	1.71	0.964	39.9			72	24
36	1.71	0.964	28.8			61	24
37	1.71	0.964	44.5			60	96
38	1.71	0.964	49.2		54		24
39	1.71	0.964	50.1		67		24
40	1.71	0.967	53.3				24
42	1.71	0.964	39	500	50	82	4
44	1.71	1.705	58	1300	86	86	4
45	1.71	1.705	57.5	1300	69	35	4
48	1.71	0.964	47.5	1300			24
50	1.71	1.705	56.6	500	51	51	24
60	1.71	0.964	51.0	1300	52	57	24
61	1.71	0.964	40.8	500			3

smallest amounts of iron and the results, both high yield and low deviation, have made it quite evident that the molar ratios used for these syntheses are the most appropriate.

**Reaction Conditions. Reaction Temperatures.** Table 5 shows that higher yields are obtained at lower temperatures and, most important, if the temperature is under 110 °C.

**Stirring Rate.** Table 6 shows that experimental runs 42, 48, 60, and 61 were carried out under the same molar ratios, for which different stirrer rates were applied. In all cases the higher yields were obtained at the higher stirring rates.

**Settling Time Given to the Reaction Mixture.** According to the data reported in Table 6, similar experimental

runs for which the only different variable was the settling time given to the mixture, as observed in experimental runs 28 and 29 with settling times of 4 and 24 h, gave yields of 53.81 and 44.53%, respectively. Something similar happened in experimental runs 45 and 48 (again with settling times of 4 and 24 h, respectively) showing a higher yield for the run with a shorter settling time. These observations indicate two interesting aspects of the reaction; a high conversion is reached in a short time while the longer settling times do not favor an increase in yield due perhaps to unaccounted losses by vaporization. Always the highest yields were obtained when  $I_2$  was used in excess.

**Temperature Interval during Distillation.** Experiments 27–40, those in which distillation was carried out in the temperature interval from 95 to 160 °C, showed the highest yields. In contrast, a lower yield was observed in those experimental runs in which the distillation started at 160 °C.

**Order of Addition of Reagents.** Another very important feature in the syntheses is the sequence in which reagents are added to the reaction mixture. It was observed that the reaction has a very slow start if iodine and methyl alcohol are mixed first, followed by the addition of iron to the mixture. The same occurs when mixing first with methyl alcohol and iron, following with the addition of iodine. The fast start was observed only if methyl alcohol was added to a mixture previously prepared with the right amounts of iodine and iron. In the last sequence the reaction occurred with a fast start; it was accompanied by a rapid increase in temperature. A brilliant black solid, viscous and adherent to the glass walls of the flask, was formed immediately. It has been interpreted that iron and iodines must be placed in contact before adding methyl alcohol so that they are able to react and produce  $FeI_2$  and  $FeI_3$ , the latter serving as a catalyst for the main reaction.

**Rate of Addition of Methyl Alcohol.** According to the results of runs 1 and 6 shown in Table 5, a high rate of addition of methyl alcohol seems to favor the formation of methyl iodide. However, for experimental runs 3 and 5 were obtained very similar yields under very different rates of addition of methyl alcohol, an observation that is also verifiable in other experimental runs. It seems that the rate of addition of methyl alcohol is not a key factor affecting the yield of reaction as long as methyl alcohol is added to the mixture of iron and iodine. The variables discussed above (reaction and distillation temperatures, settling time, stirring rate, etc.) are then the most important and they are also those to be closely controlled.

## Conclusions

Several factors have to be taken to optimize the synthesis of methyl iodide starting with methyl alcohol, iodine, and sponge iron. Those factors are summarized as follows.

The highest yields were obtained in the experimental runs with molar ratios of methanol/iron at 1.0 while keeping higher than 1.5 the ratios iodine/methanol and iodine/iron.

The order in the addition of reagents is a key factor; iron and iodine have to be mixed first, reacting both while methyl alcohol is added to form  $FeI_2$  and  $FeI_3$ . One of these iodides,  $FeI_3$ , acts then as a catalyst due to its reactivity with the hydroxyl groups to form stable

compounds, on one side, and actively participates in the double substitution reaction that produces methyl iodide.

The optimal temperature range for this synthesis is located between 53 and 109 °C, for which the highest yields were obtained in coincidence with the temperature range at which the formation of FeI<sub>2</sub> is also optimal. In fact, in the reaction synthesis of FeI<sub>2</sub> of Podorozhnyi and Safonov,<sup>25</sup> the highest yield was obtained at 95 °C under the following conditions: 66.3 mol % of iodine, molar ratio of I<sub>2</sub>/Fe at 2.0, and a reaction time of 40 min. The analysis of the atomic ratio I/F in the product goes up to 2.01, a clear indication of the possibility that also FeI<sub>3</sub> may be produced in the reaction. It is known, however, that iron forms tri-, di-, and mono-iodides and that only FeI<sub>2</sub> is thermodynamically stable in the solid state.

A relationship between the syntheses of FeI<sub>2</sub> and the syntheses of CH<sub>3</sub>I may be elaborated as follows: In the syntheses of CH<sub>3</sub>I the highest yield was obtained at 86 °C under the following conditions: 63 mol % of iodine, molar ratio I<sub>2</sub>/Fe at 1.71, and a reaction time of 60 min. Thus, the conditions favorable for the syntheses of FeI<sub>2</sub> are also favorable for the syntheses of CH<sub>3</sub>I.

The chromatographic analysis of the product was preferred over the gravimetric one and even that showed peculiarities. Reproducibility of response factors was higher in column DC-200 as compared to response factors obtained in the Carbowax column.

The analysis of the results, and the assessment of all the reaction variables involved, allow us to assert at the conditions for the optimization of the synthesis of methyl iodide using sponge iron.

### Literature Cited

- (1) Ohr, H. D.; Grech, N. M.; Sims, J. PCT Int. Appl. WO **1997**, 97(44), 127–136.
- (2) Lindgren, D L. *J. Econ. Entomol.* **1938**, 31, 320–331.
- (3) *Osha Regulated Hazardous Substances. Health, Toxicity, Economic and Technological Data*; Noyes Data Corporation: Park Ridge, NJ, 1990.
- (4) Sitting, M. *Handbook of Toxic and Hazardous Chemical and Carcinogens*, 2nd ed.; Noyes Publications: Park Ridge, NJ, 1985.

- (5) Ramacher. *Bjoern. Ber. Forschungszent. Juelich* (Juel 3424), Hamburg, 1997, 230 pp.
- (6) Ohr, H. D.; Sims, J. J.; Grech, N. M.; Becker, J. O.; McGiffen, M. E. *J. Plant Disease* **1996**, 80, 731–735.
- (7) Jianying, G.; Yates, S. R. *J. Agric. Food Chem.* **1996**, 44, 4001–4008.
- (8) The Merck Index. *An Encyclopaedia of Chemicals, Drugs, and Biologicals*, 11th ed.; Budavari, S., Ed.; Merck and Co. Inc.: Rahway, NJ, 1989.
- (9) *Patty's Industrial Hygiene and Toxicology*; Clayton, G. D., Clayton, F. E., Eds.; John Wiley & Sons: New York, 1981; Vol. II B, third revised.
- (10) Laturus, F.; Adams, F. C. *Geophys. Res. Lett.* **1998**, 25(6), 773–776.
- (11) Yoshida, S.; Muramatsu, Y. *J. Atmos. Environ.* **1995**, 29(1), 21–25.
- (12) Jay, K.; Stieglitz, L. *Chemosphere* **1995**, 30(7), 1249–1260.
- (13) Adams, R.; Voorhees, V. *J. Am. Chem. Soc.* **1919**, 41, 789–798.
- (14) Reynolds, R. B.; Adkins, H. *J. Am. Chem. Soc.* **1929**, 51, 279–287.
- (15) King, H. S. In *Organic Syntheses*; Blatt, A. H., Ed.; John Wiley & Sons, Inc.: New York, 1943; Coll. Vol. II, p 399.
- (16) Huber, F. R.; Schenck, M.; Leslie M. *Method of Manufacturing Alkyl Iodides*. U.S. Patent 3,053,910, Sept 11, 1962.
- (17) Dangyan, M. T. *J. Gen. Chem. (U.S.S.R.)* **1940**, 10, 1668–1669.
- (18) Fujiwa, T.; Koyama, H. *Preparation of Alkyl Iodides or Aryl Iodides*. Patent JP 62,246,527 (US 87,246,527) Oct 27, 1987.
- (19) Dangyan, M. T. *J. Gen. Chem. (U.S.S.R.)* **1938**, 8, 1780–1783.
- (20) Dangyan, M. T. *J. Gen. Chem. (U.S.S.R.)* **1939**, 9, 1907–1910.
- (21) Dangyan, M. T. *J. Gen. Chem. (U.S.S.R.)* **1941**, 11, 108–111.
- (22) Dangyan, M. T. *J. Gen. Chem. (U.S.S.R.)* **1941**, 11, 1215–1217.
- (23) Dangyan, M. T. *J. Gen Chem. (U.S.S.R.)* **1941**, 11, 314–318.
- (24) Dangyan, M. T. *Bull. Armenian Branch Acad. Sci. U.S.S.R.* **1941**, 7(12), 81–84.
- (25) Podorozhnyi, A. M.; Safonov, V. V. *Manufacture of Iron Iodide* U.S.S.R. Patent SU 1,421,701, 1971.

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