

INVESTIGATION OF THE REACTION CONDITIONS OF PHOSGENE PRODUCTION

By

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Phosgene is an acylizing agent applied in a number of chemical processes [1]. It is widely used in the pharmaceutical, dyestuff, plastic, textile and cosmetics industry as well as in the preparation of insecticides and plant protectives. During the past years we have dealt with some reaction and application problems of phosgene, both from theoretical and from industrial points of view [2, 3, 4]. As the industrial importance of phosgene is increasing all over the world, it is imperative to study the optimum reaction conditions of industrial phosgene production.

In industrial processes phosgene is produced by reacting carbon monoxide and chlorine. The reaction can be promoted by ultraviolet light. The effect of the UV light as well as the mechanism of the reaction catalyzed by UV radiation was first investigated by BODENSTEIN [5, 6, 7].

The results of the above investigations have been developed by other workers [8, 9, 10]. The effect of UV radiation, however, has not been utilized in economical processes. Industrial methods for phosgene preparation apply the catalytic effect of different active carbons. Although phosgene production by contact catalysis on charcoal was described as early as in the past century [11], and this process was already used for industrial phosgene production during World War I, the detailed investigation of the process has only been developed in the past few years. The contact catalytic reaction was studied by POTTER and BARON [12], in a temperature range lower than the industrial conditions (below 100 °C); and some correlations have been found concerning the reaction mechanism.

In our work phosgene production was studied using an equipment constructed in accordance with the industrial conditions. In the experiments optimal temperature, molar ratio and space velocity values were determined.

As reaction vessel a flow reactor was used, surrounded by thermostating jacket and filled with charcoal catalyst (Fig. 1). Temperature was measured by thermocouples at different locations of the reactor. Chlorine and carbon monoxide were mixed in a chamber and the gas mixture was fed into the reactor. The pure carbon monoxide required was prepared by dropping formic

acid into sulfuric acid. The gas was passed through a washer containing sulfuric acid, and through a drop catcher into a buffer vessel. The pressure in this vessel had to be kept constant in order to ensure constant feeding rate for a given carbon monoxide quantity. For this purpose also a pressure regulator was inserted into the flow. The flow rate of the gas was measured by a previously calibrated differential manometer. Chlorine was taken from a gas bottle, under similar conditions.

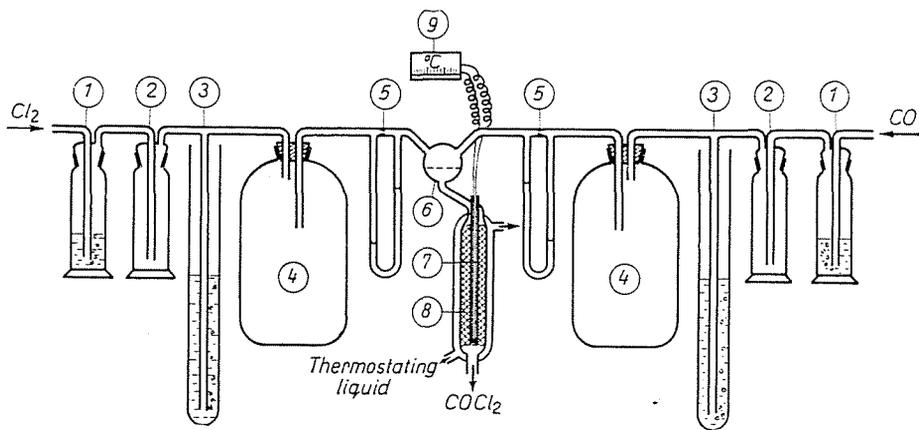


Fig. 1. 1. Washer with sulfuric acid. 2. Drop catcher. 3. Pressure regulator. 4. Buffer vessel. 5. Differential manometer. 6. Mixing chamber 7. Thermometer. 8. Catalyst bed. 9. Temperature reading

The gas mixture leaving the reactor was sampled and assayed to determine the conversion in the reactor.

Classical chemical methods for assaying the gas sample are inefficient for this purpose owing to the low volume and the small chlorine and carbon monoxide content of the sample, therefore gas chromatography was used as analytical method.

For the simultaneous determination of phosgene, chlorine and carbon monoxide, a special gaschromatograph was constructed. To avoid corrosion, the apparatus was made of glass. As detector, heat conductance cell containing tungsten wire and sealed with teflon has been used. Owing to the glass casing, great care had to be taken on the thermostation of the cell.

Using silica oil on termolite carrier as partitioning liquid and nitrogen as carrier gas, the following retention time values have been found (column charge length: 2m, column temperature: 25 °C):

Carbon monoxide:	80 sec,
Chlorine:	217 sec,
Phosgene:	370 sec

The flow rate of carrier gas was 50 ml/min, the theoretical plate number of the column was 350 for phosgene. The sampler valve battery of the gas chromatograph was attached to the phosgene reactor, and at intervals a sample was passed into the gas chromatograph by the appropriate adjustment of valves. The equipment was previously calibrated by pure gases, and then the composition percentage by volume of the mixture leaving the reactor was determined. In knowledge of the feed rate of chlorine and carbon monoxide, and of the composition of the product gas, the conversion data of the reactor were calculated.

In accordance with the theory of catalytic reactors, the space velocity is defined as the mass rate per unit mass of catalyst.

$$\text{Space velocity} = \frac{\text{mass rate in the reactor, g/sec}}{\text{mass of the catalyst, g}}$$

In isotherm flow reactors reaction time is equal to the residence time calculated from the space velocity, therefore the composition of the product gas, i.e. the conversion in the reactor can be applied for reaction kinetic calculations. At the elevated temperature of industrial phosgene syntheses (above 100 °C) the reaction cannot be made isotherm along the total length of the reactor, because the reaction heat, due to the relatively poor heat transfer conditions, cannot be perfectly led away.

The synthesis was investigated at temperatures of 40, 60, 80, 100, 120, 150 and 170 °C, of the thermostating liquid. In the first third part of the reactor a temperature maximum could be observed. The temperature in the middle of the reactor approached that of the thermostating liquid, and in the lowest part the previously set temperature could be observed. The value of the maximum depended on the space velocity and on the carbon monoxide to chlorine molar ratio. A part of the experimental results is listed in Table 1. In the first column the temperature values measured on the top of the catalyst bed are listed, in columns 3 and 4 those measured in the middle and at the bottom of the bed, respectively. In column 2 the maximum temperature values are given.

The chlorine content of the product gas was studied at different temperature values, as the function of the carbon monoxide to chlorine ratio for different space velocities. It has been found that the chlorine impurity decreased with increasing carbon monoxide excess, and increased with increasing space velocity. The results of one test series are plotted in Fig. 2.

Investigating the least carbon monoxide excess required for obtaining chlorine-free phosgene, optimum thermostating temperature was found to be 150 °C. For the space velocity values listed in Table 2, at 150 °C, chlorine-free phosgene could be produced with carbon monoxide to chlorine ratios of 1.08 and 1.22, respectively (Table 2).

Table 1
 Temperature gradient in the reactor for different
 molar ratios and space velocities

Thermo- station temp. (degrees C)	Space velocity ($10^{-3} \frac{g/sec}{g}$)	CO : Cl ₂ molar ratio	Temperature in the reactor				Cl % in phosgene
			1.	2.	3.	4.	
170	4.54	1.00	230	330	172	170	6.5
170	4.54	1.25	220	280	170	170	0.0
170	2.70	1.00	210	290	171	170	5.0
170	2.70	1.11	196	240	170	170	0.0
150	2.74	1.00	186	280	152	150	4.0
150	2.66	1.16	170	269	150	150	0.0
120	2.70	1.00	140	218	122	120	8.0
120	2.73	1.28	132	205	120	120	0.0
120	4.58	1.00	150	266	123	120	9.4
120	4.54	1.60	138	235	120	120	0.0
100	2.72	1.00	135	195	100	100	12.0
100	2.71	1.45	120	180	100	100	0.0
100	5.08	1.00	150	235	103	100	14.3
100	4.98	2.10	110	130	100	100	0.0
80	2.88	1.05	125	190	81	80	15.7
80	2.93	2.40	105	120	80	80	0.0
80	3.69	1.20	125	196	82	80	14.1
80	3.68	3.40	100	118	80	80	0.0

Furthermore, the chlorine content of the product gas was investigated as the function of the thermostating temperature. Linking together the values belonging to similar molar ratios, the optimum temperature value is seen to be 150 °C for every molar ratio (Figs. 3, 4).

Thus, the reaction temperature has its optimum at 150 °C. In the upper part of the reactor the temperature rises to about 300 °C, depending on the space velocity, in the middle the temperature is 150 to 160 °C, and the temperature of the product gas is 150 °C.

Investigating the percentage yield separately for chlorine and carbon monoxide, again 150 °C has been found as optimal temperature.

In the experiments charcoal of Nuxit BO type was used. In some cases charcoal of Nuxit BD type was also used as catalyst, and it has been found that the results obtained with the latter are in good agreement with those obtained with Nuxit BO. This can be explained by the fact that the micro-structure of both charcoals is similar and their pore distribution is the same.

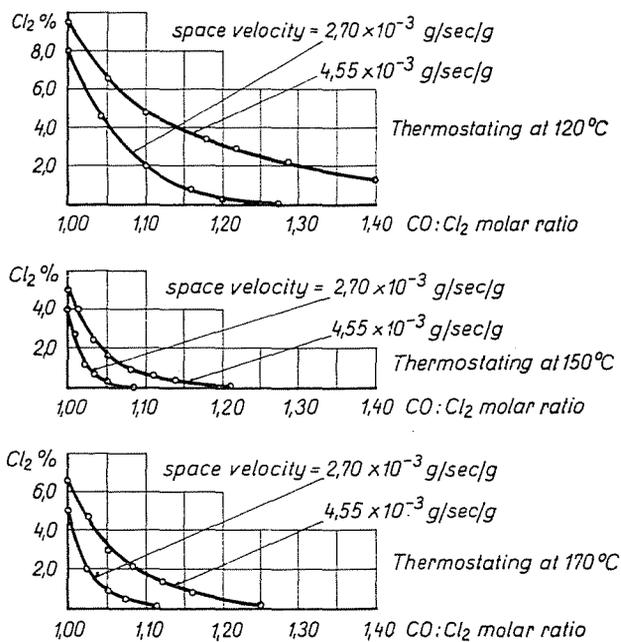


Fig. 2. The dependence of the chlorine content of phosgene on the molar ratio of reactants

Table 2

Minimum carbon monoxide to chlorine ratio required for the production of chlorine-free phosgene

Thermo- station temp. (degrees C)	Space velocity in $10^{-3} \frac{\text{g/sec}}{\text{g}}$	CO to Cl ₂ molar ratio
40	1.70	5.00
60	2.40	3.40
60	4.54	5.00
80	2.94	2.40
80	3.70	3.40
100	2.70	1.45
100	5.60	2.10
120	2.70	1.28
120	4.55	1.60
150	2.70	1.08
150	4.55	1.22
170	2.70	1.11
170	4.55	1.25

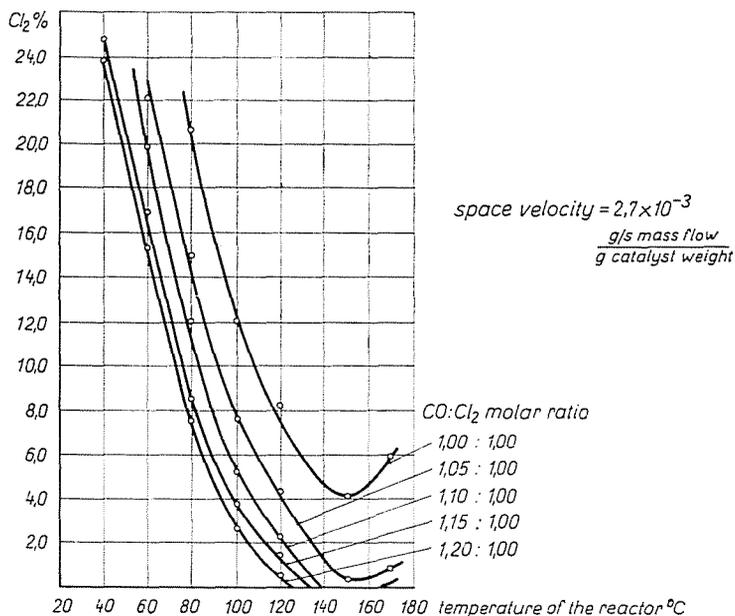


Fig. 3. The chlorine content of phosgene prepared at different temperatures

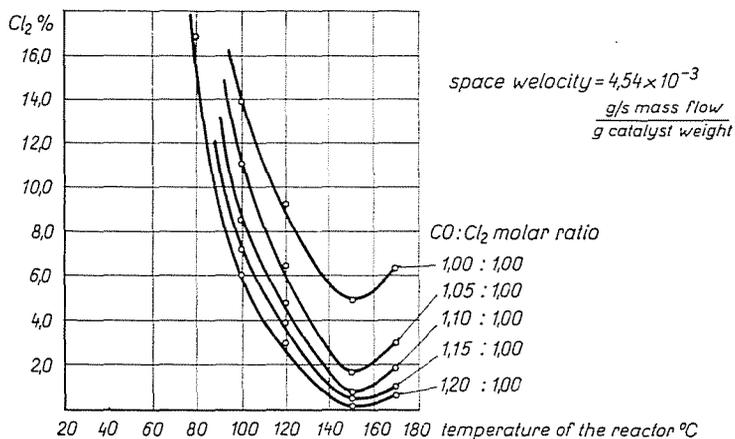


Fig. 4

Furthermore, the effect of an inert gas (nitrogen) and of oxygen on the production of phosgene was investigated. Adding nitrogen to the carbon monoxidechlorine mixture, a reduction in phosgene yield as compared to pure mixture was observed. Using the same molar ratio and space velocity, the chlorine content of the product gas was higher, and increased with increasing

percentage of nitrogen. For the same percentage of conversion, or for producing chlorine-free phosgene, greater carbon monoxide excess is required in the presence of nitrogen (Table 3).

Table 3
The effect of nitrogen on phosgene formation
(Thermostating at 150 °C)

CO to Cl ₂ ratio	N ₂ %	Space velocity in 10 ⁻³ $\frac{\text{g/s}}{\text{g}}$	Cl ₂ content of product gas %
1.00	0.0	2.74	4.0
1.00	4.1	2.73	5.0
1.00	8.0	2.76	7.4
1.00	10.1	2.79	9.7
1.02	0.0	2.72	1.2
1.02	4.1	2.74	2.6
1.02	8.2	2.73	4.2
1.02	10.1	2.64	5.9
1.08	0.0	2.66	0.0
1.08	3.9	2.68	0.7
1.08	8.1	2.68	1.2
1.08	9.9	2.69	1.8

When adding nitrogen to the mixture, the temperature of the reaction space is lower. When thermostating the system at the same temperature as in the case without nitrogen, a similar temperature gradient develops in the reactor, the temperature maximum, however, decreases, depending on the amount of nitrogen.

The differences between the steady states of systems containing nitrogen and those containing no foreign gas can be explained as follows.

As nitrogen is present in a non-negligible amount, the reactants (i.e. carbon monoxide and chlorine) are diluted, resulting in lower equilibrium conversion. As the composition of the product gas is almost at the equilibrium, the above effect reduces the measured conversions.

Also, the catalyst bed is of a lower temperature, as a result of the lower reaction rate caused by the reduced partial pressures, the decrease of the heat capacity referred to the end product.

Under our test conditions, the operation of the reactor was also impeded by the lower temperature maximum.

Consequently, the catalyst is neither contaminated nor inhibited by nitrogen, its role being a mere diluting effect. This is in good agreement with

the literature data. Investigating the mechanism of phosgene formation, POTTER and BARON [12] have found similar role for nitrogen. Their experimental method, however, differed from the our one; and the reaction was investigated in a substantially lower temperature range (40 to 90 °C). Despite this fact, the reaction mechanism outlined by them can also be applied to reactions taking place at higher temperatures.

The effect of oxygen on phosgene formation was also investigated in the model-reactor previously described. Instead of pure oxygen, however, air was added to the reaction mixture, because most industrial processes for carbon monoxide preparation apply air as oxidizing agent, and so industrial carbon monoxide contains both nitrogen and oxygen impurities. Consequently, their effect on phosgene formation should be investigated jointly.

Adding air to the mixture of carbon monoxide and chlorine, phosgene formed is less than without air addition, and the yield is nearly the same as in the experiments carried out with nitrogen (Table 4).

Table 4
The effect of oxygen on phosgene formation

CO to Cl ₂ ratio	N ₂ %	O ₂ %	Space velocity in 10 ⁻² $\frac{\text{g/s}}{\text{g}}$	Cl ₂ cont. of prod. gas %
1.00	0.0	0.0	2.74	4.0
1.00	2.1	0.5	2.72	4.5
1.00	4.9	1.0	2.75	5.5
1.00	7.8	1.9	2.88	9.7
1.08	0.0	0.0	2.66	0.0
1.08	2.0	0.5	2.63	0.5
1.08	4.0	1.0	2.68	0.8
1.08	8.1	2.2	2.76	1.8

For the same molar ratio and space velocity the chlorine content of the product gas mixture is higher in the presence of air, and increases with increasing percentage of air. Under such conditions greater carbon monoxide excess is required for the preparation of chlorine-free phosgene.

In the literature there are no numerical data on the effect of the presence of oxygen or air on phosgene formation. From our experiments it can be concluded that 0 to 2% oxygen (i.e. 0 to 10% air) fed into the reactor, causes no difference in phosgene yield from the experiments with pure nitrogen. Dilution or better reduction of partial pressures, slows down the reaction and the yield is less than it would be without dilution. The lower reaction rate influences the

temperature of the reactor, as well. In such cases the temperature in the reactor is lower, with a similar temperature gradient.

When air is added, the temperature is higher than in the case of nitrogen addition. This is an indication of oxidation processes; on the one hand carbon catalyst is oxidized, on the other hand, — to a minor extent — carbon dioxide is formed from carbon monoxide. The burning process causes certain catalyst loss, therefore it is disadvantageous. The effect of a limited air amount, however, is not notable. This is supported by the fact that in our experiments no loss in catalyst activity was observed. In such cases the temperature elevation in the reactor due to combustion is small as well, so that no remarkable oxidation is likely to take place. More than 1 to 2% of oxygen added may induce considerable catalyst loss especially at an industrial scale.

Summary

An experimental model reactor has been constructed for studying phosgene synthesis. The equipment has been built with the intention that the reaction phenomena observed could be applied to the design and operation of industrial phosgene reactors.

A special gas chromatograph has been constructed for the direct assay of gas mixtures containing phosgene, chlorine and carbon monoxide. Attaching this apparatus to the reactor the reaction has been properly traced.

The optimum temperature, as well as the temperature gradient of the reactor has been established for charcoal catalysts Nuxit BO and BD. For given space velocity values the minimum carbon monoxide excess required for preparing practically chlorine-free phosgene has been determined.

The reaction has also been investigated using nitrogen or air as diluting agent and conclusions have been drawn about the effect of dilution on the reaction.

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