# LABORATORY INSTALLATION FOR THE ISOLATION OF 2,2,6,6-TETRACHLOROCYCLOHEXANONE

## Yu. I. Laz'yan, A. I. Bokanov, V. A. Kuzovkin, N. M. Dorofeeva, T. Yu. Talantova, and V. G. Granik

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The 2,2,6,6-tetrachlorocyclohexanone (TCC) (I) is utilized for the synthesis of 2,6-dichlorobenzonitrile, which is a herbicide [1], dichlorophenol, which can be used as the basis for the synthesis of more than 10 practically important chemical substances [2], as well as for the synthesis of 2,6-dichloroaniline and 2,6-dichlorodiphenylamine [3] – key intermediates in the production of the medicinal preparations klofelin and ortofen. The TCC is obtained by the chlorination of cyclohexanone in the solution of carbon tetrachloride or in the melt of TCC itself, with the mp 80-84°C [1, 2].



The reaction proceeds with the release of heat, and the temperature of the reaction mass is maintained in the range of  $85 \pm 5^{\circ}$ C, regulating the removal of heat. It is known [1] that cyclohexanone has a tendency to undergo oxidative polymerization. In order to inhibit the polymerization in the synthesis of TCC, the process is carried out by maintaining the minimal concentration of cyclohexanone in the reaction mass, which is guaranteed on account of the gradual simultaneous dispensing of the cyclohexanone and chlorine into the melt of TCC with the strict maintenance of the molar ratio of cyclohexanone:chlorine from 1:4.5 to 1:5.

The object of the present work was to develop the technology for the isolation of TCC, having not less than 95% of the content of the basic substance, suitable for utilization in different syntheses without its preliminary recrystallization. For the solution of this problem, a laboratory installation with the serviceable volume of 220 ml and units for the dispensing of cyclohexanone and chlorine and for the neutralization of waste gases was developed and assembled. The determination of the maximal rate of dispensing of the components and research into the means of increasing the removal of TCC from the unit volume of the reactor were undertaking for the investigators at the installation.

### EXPERIMENTAL

The Chlorination of Cyclohexanone Was Carried Out in the Melt of TCC. It was shown by preliminary investigations that lutidine or dimethylacetamide can be utilized as the catalyst for the chlorination [2]. Dimethylacetamide was chosen by us as the more available and inexpensive catalyst in the development of the technology for the synthesis.

The synthesis of TCC utilized distilled cyclohexanone and dimethylacetamide.

The TCC ( $\sim$  75 g) from preceding operations, with the 95-96% content of the basic substance, was fed into the reactor as the medium before the experiment.

The scheme of the experimental installation for the chlorination of cyclohexanone is presented in Fig. 1.

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Fig. 1. Scheme of the experimental installation (explanations in the text).

**Description of the Laboratory Installation.** The chlorination of cyclohexanone was performed in a glass reactor 1, equipped with a stirrer, a jacket for heating (cooling), a lower outlet, a thermometer 14, a pocket for two thermocouples 12 and 13, a bubbler 7 for the introduction of chlorine, and a connecting pipe for the introduction of cyclohexanone. The hydroseal 2 was filled with carbon tetrachloride; the lower part of the hydroseal served as an air condenser and had an outlet for gases.

The required temperature regime was guaranteed by the introduction of hot water into the jacket of the reactor from the thermostat 3. The rate of circulation of the heat carrier comprised ~38 liters/h. The regulation of the warming of the heat carriers was accomplished using the coil 4, additionally included in the circulation circuit, which was made of steel tubing and heated ohmically, and the regulator of the MK ZOZK type. The coil 4 was heated by the current from the reducing transformer 21, switched into the circuit system via the laboratory autotransformer (LATR) 22, which allowed the accuracy of the positional regulation of the temperature of the reaction mass to be guaranteed in the range of  $\pm 1^{\circ}$ C. The current in the primary coil of the transformer 21 was thereby monitored by the ammeter 23.

Cyclohexanone entered the reactor from the graduated burette 8, having a tube for pressure transfer. The line for the introduction of cyclohexanone into the reactor had a T-valve 17, also utilized for the discharge of the liquid from the burette. The air space of the burette 8 was connected with the burette 9, which was filled with water, via the T-valve 20. Water was supplied to the burette with a peristaltic pump 10 from the tank 11. The pressure transfer of the cyclohexanone from the burette 8 to the reactor proceeded by the operation of the pump with the valves 18 and 19 closed. The pump allowed the graded regulation of the rate of introduction of the cyclohexanone to be accomplished in the range of 0.1-0.9 ml/min using a hose with the internal diameter of 1 mm. The utilization of the described scheme of introduction avoided the direct contact of the cyclohexanone with the hose of the pump.

Chlorine was supplied to the reactor 1 from the cylinder 5, equipped with a pressure regulator. Monitoring of the flow rate of the chlorine was conducted from the rheometer 6, filled with concentrated sulfuric acid. The calibration of the rheometer was performed with air using the further recalculation with the calibration curve by the method presented in [4]. Waste gases – hydrogen chloride and excess chlorine – from the reactor proceeded via the bubble trap 24 to the absorbing column 26, mounted on the receiver 25 having the capacity of 2 liters. Irrigation of the absorbing column with the aqueous solution of alkali was accomplished using the circulating pump 28. The packing utilized in the column was polyethylene netting twisted into a roll. The internal diameter of the column comprised 18 mm; the height comprised 250 mm. The column had a jacket for water cooling, and was connected with the water-jet pump 27. In order to exclude a vacuum in the system and to exclude the introduction of the absorbing solution into the reactor, the line between the air condenser 2 and the trap 24 was connected with the atmosphere. The monitoring of the usage of the alkaline solution was accomplished with indicator paper.

	Value of parameter		
Parameter	in chlorination	at the stage of exposure	
Rate of supply of cyclohexanone, ml/min (g/min)	0,35 (0,336)	-	
Rate of supply of chlorine, liters/ min (g/min)	0,38 (1,21)	-	
Temperature of the reaction mass, °C Temperature of the heat carrier at	81-83	85-87	
the intake to the jacket of the	74 76	86.99	
Rate of circulation of the heat	/4-/0	80-88	
carrier, liters/h	38		
Yield of TCC, %	95		
Content of the basic substance in TCC, %	96-	97	

TABLE 1.	Method	Parameter	s and I	Main	Indicators	of
the Process	of Chlo	rination of	Cyclo	hexan	one	

TABLE 2.	Comparison	of the	Indicators	of Product	ivi-
v for the l	Processes of (	Chlorin	nation of (	velohexaoi	ne

96-97

Indicator	Chlorination with limited priming with cyclohexanone	Chlorination by the remov- able filling method
Outlay of time for the operation, ht preparation of the installation for		
operation and the melting of TCC	1	1
chlorination	3,17	6.33
exposure	1	2
discharge of the product	0.1	0.2
Production of TCC with deduction of the priming, g	129	260
Outlay of time calculated for 100 g of the product produced, h	4,02	3.67

Method for Performing the Experiment. The chlorination was performed on the installation described by two methods - with the limited removal of the product, and by the removable filling method.

In the first case, the calculated amount of the catalyst, comprising 7 mass % based on the primed cyclohexanone content, was primed into the reactor before the beginning of the chlorination together with the TCC. The dispensing of the reagents was completed after the filling of the reactor.

In the chlorination by the second method, the catalyst was introduced together with the cyclohexanone in the form of a solution. After the filling of the reactor and the completion of the exposure, part of the product was occurred off, and the dispensing of the initial products into the melt of TCC remaining in the reactor was resumed.

The temperature of the chlorination was maintained at 80-85°C. Before the discharge of the product, the reaction mass was maintained at 85-87°C for 1 h while the chlorine was blown off with nitrogen. At the end of the operation, the lower outlet of the reactor was heated with a specially prepared electric heater for the free discharge of TCC, controlling the temperature of heating using a thermocouple placed in the heater.

The working of the process of chlorination commenced with the low rate of supply of cyclohexanone, which was then increased in turn. It was established that the rate of dispensing of cyclohexanone to obtain TCC of the required quality should not exceed 0.4 ml/min for the given installation. When the rate of supply of cyclohexanone was 0.55 ml/min and higher, the violet color of the crystals of TCC was observed with products of the oxidative polymerization of cyclohexanone, the formation of which was associated with the deterioration in the conditions of mass transfer and the increase of the cyclohexanone concentration in the reaction mass. Recrystallization from hexane was required for the purification of the TCC obtained in such experiments.

The analytical monitoring of the process of chlorination and the analysis of the isolated product were accomplished by the method of GLC under the following conditions: the column of length 1 m, with internal diameter 3 mm and filled with sorbent 5% OV-17 on Chromaton N-super of the granulation 0.125-0.160 mm. The temperature of the unit of the sample input was 250°C. The regime for the programming of the column temperature was as follows: the  $T_{init}$  125°C (0 min), the rate of heating 10°C/min, and the  $T_{final}$  235°C (15 min). The gas carrier was nitrogen (30 ml/min). The detector was of the flame-ionization type.

Not only the objective product, but also possible impurities [trichlorocyclohexanone (II), as well as trace amounts of 2,6-dichlorophenol and 2,6-dichlorocyclohexanone] were determined quantitatively under the conditions indicated.

#### DISCUSSION

When the rate of dispensing of cyclohexanone was 0.34 ml/min, the TCC was obtained steadily with the content of the basic substance 96-97%; the yield of the product comprised approximately 95%. According to the data of chromato-mass spectrometry,<sup>\*</sup> the main impurities in the product are the catalyst dimethylacetamide (up to 3%), trichlorocyclohexanone (up to 1.3%), and (II) (up to 1.4%).



The path of formation of (II) is unclear; other impurities containing four atoms of chlorine or more are absent. Moreover, 2,6-dichlorophenol and 2,6-dichlorocyclohexanone are present in trace amounts in the product.

Table 1 presents the regime parameters of the chlorination. Table 2 compares the indicators characterizing the removal of the product and the productivity of the reactor in accomplishing the chlorination under conditions indicated in Table 1 with the limited priming of cyclohexanone and using the removable filling method. It can be seen that, after only two cycles of chlorination, the productivity of the reactor with the removable filling method increases by 9% due to the economy of time for the operation of priming and melting of TCC.

With the utilization of the removable filling method of chlorination on the installation described, the batch of TCC comprising 2.5 kg was made. Evidently, when the number of cycles of chlorination and the scale of the installation increase, the comparative effectiveness of the proposed removable filling method increases. Therefore, the removable filling method of chlorination with the number of cycles guaranteeing the production of the required amount of TCC should be recommended for industrial production.

We calculated the heat of chlorination of cyclohexanone to TCC to be  $\Delta H = -4.135 \cdot 10^3 \text{ kJ/kg} (-406 \text{ kJ/mole})$  for the estimation of the technical chlorination reactor. The standard heats of formation of the substances required for the calculation of the heat of the process were taken from published data [5, 6] or were estimated utilizing the approximation method of the introduction of corrections for the substitution of hydrogen in the six-membered ring by different functional groups [6, 7]. It should be noted that the heats of formation calculated by the method indicated and also, consequently, the value of  $\Delta H$  calculated from them pertain to substances in the ideal gas state.

Therefore, the highly productive technology for the isolation of TCC, excluding the application of ecologically harmful solvents or solvents with fire hazard such as carbon tetrachloride and hexane, was worked out at the stage of laboratory tests, and sufficient data necessary for the scaling of the process were obtained.

#### REFERENCES

- 1. U. S. Pat. 3,927,106, (1975); Chem. Abstr., 84, No. 105096 (1976).
- 2. E. C. Gilbert, R. E. Jones, D. C. McLean, and E. Sherman, Industr. Eng. Chem. Prod. Res. Develop., 14, No. 1, 1-11 (1975).
- 3. Eur. Pat. Appl. 313,740, (1989); Chem. Abstr., 111, No. 173731 (1989).
- 4. Ya. Pinkava, Laboratory Technique of Continuous Chemical Processes [in Russian], Moscow (1961).

<sup>\*</sup>The mass spectrometric investigation was performed by E. F. Kuleshova.

- 5. Yu. M. Zhorov, Thermodynamics of Chemical Processes [in Russian], Moscow (1985).
- 6. A. S. Kazanskaya and V. A. Skoblo, Calculations of Chemical Equilibrium [in Russian], Moscow (1985).
- 7. O. A. Hougen, K. M. Watson, and R. A. Ragatz, Chemical Process Principles. Pt. 2: Thermodynamics, New York (1959).