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Abstract

Full Text

Chemistry

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Study of the Kinetics of the Reaction of Direct Substitution of the Nitro Group by Chlorine in Nitrobenzene and *m*-Chloronitrobenzene under the Action of Carbon Tetrachloride

(Presented by Academician A. V. Topchiev, July 2, 1960)

Nitro compounds, especially aromatic ones, have been well studied ([1]) and, owing to their availability, are widely used as starting materials for the synthesis of various organic compounds. We are investigating the preparation of aromatic halogen derivatives from nitro compounds by means of the direct substitution reaction of the nitro group by a halogen. For the reaction of direct substitution of the nitro group by chlorine, we have proposed a series of new agents, including CCl_4 ([2–5]). Carbon tetrachloride contains a high–

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–percentage of chlorine (92.2%) and has a number of other advantages over the most frequently used agent, PCl_5.

In view of the fact that direct substitution of the nitro group by chlorine with the aid of CCl_4 may find broad application both in laboratories and in technology, we carried out a study of the kinetics of the reaction of certain nitro compounds with CCl_4. Nitrobenzene and *m*-chloronitrobenzene were taken as the nitro compounds.

The study of the kinetics of the reaction of CCl_4 with the indicated nitro compounds was carried out on a thermophotometer of the A. A. Ponomarenko system, which we previously called a thermophotocolorimeter ([6]). The instrument makes it possible to measure the intensity of absorption of light by a sealed glass

Fig. 2. Dependence of the duration of the reaction of CCl_4 with nitrobenzene on the percentage filling of the tube capacity with reagents. The reaction was carried out at 290°

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tube containing the reagents, in the visible region of the spectrum during the course of the reaction.

We established that, in the reaction of CCl_4 with aromatic nitro compounds, NO_2, NO, NOCl, $COCl_2$, CO, CO_2, H_2O, aromatic chlorine-containing compounds, and certain other substances are obtained as intermediate or final products. In the reaction of CCl_4 with nitrobenzene, chlorobenzene was obtained in a yield of 82% of the theoretical amount and a small

dichlorobenzene. *m*-Dichlorobenzene was obtained from *m*-chloronitrobenzene in a yield of 92% of theory.

Of all the substances mentioned, NO_2 and NOCl are colored. The first compound is formed at the very beginning of the process, the latter at its end. The reaction of substitution of the nitro group by chlorine proceeds with the appearance, accumulation, and decrease of the NO_2 content in the tube during the course of the reaction.

Reaction of CCl_4 with $C_6H_5NO_2$. The compounds were taken into the reaction on the basis of 0.0337 g of $C_6H_5NO_2$ and 0.0840 g of CCl_4 (1 : 2) per 1 ml of tube capacity ($v \sim 6.2$ ml). The sealed tubes were placed in a thermophotometer adjusted to the required temperature. In Fig. 1 a plot is given of the dependence of the reaction rate on temperature, showing that at 250° (curve 1) the reaction with formation of nitrogen dioxide begins at the 17th min. The absorption of light (I, %) increases rather rapidly, reaching its maximum value at the 35th min. Then, for 15 min, I remains practically constant, after which over the course of 38 min a slow decrease in its value occurs. At the 87th min, I reaches its minimum. At this point, as specially designed experiments showed, the reaction of conversion of the nitro compound into the chloro compound is practically completed. From the moment of NO_2 evolution to the end of the reaction, 70 min elapsed. At temperatures of 260, 270, 280, 290, and 300° the reaction begins earlier—respectively after 12, 10, 8, 6, and 5 min—and ends more rapidly—after 40, 27, 17, 11, and 7 min. The values found for the temperature coefficient of the reaction (250–300°) fluctuated within the limits 1.48–1.75. When the temperature was raised from 250 to 300°, the reaction rate increased 10-fold.

Fig. 2. Dependence of the duration of the reaction of CCl_4 with nitrobenzene on the percentage filling of the tube capacity with reagents. The reaction was carried out at 290°.

For the reaction of nitrobenzene with CCl_4, the activation energy was calculated from the Arrhenius equation (8, 9):

$$\ln \frac{k_1}{k_2} = \frac{Q}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right).$$

Substituting in this equation k_1/k_2 by t_2/t_1, where t_1 and t_2 are the times necessary to reach 40% absorption of light by the tubes (the time was counted from the moment of increase in the value of I until the required percentage of light absorption by the tube was reached at the end of the substitution process) at temperatures of 270 and 280°, we obtain the gross activation energy of the complex reaction occurring between nitrobenzene and CCl_4, equal to 34.5 kcal/mole.

The dependence of the rate of the reaction of nitrobenzene with CCl_4 on the percentage filling of the tube capacity with reacting substances is evident from Fig. 2. When the tubes are filled with nitrobenzene and CCl_4 (1 : 2) to 2, 4, 6, 8, and 10% of their capacity, the duration of the reaction is respectively 157, 33, 14, 10, and 7 min. Increasing the percentage filling of the tube capacity from 2 to 10 causes an acceleration of the reaction by 22.4 times. These data show the strong dependence of the reaction rate of the compounds studied on pressure.

On the basis of the amount of components taken into the reaction, the approximate pressure in the tubes at the moment when NO_2 evolution by the system began was calculated. It was found that when the tube was filled with reacting substances to 2% of its capacity, the pressure was about 12 atm. When filled to 4 and 6%, the pressure would be about 18 and 23 atm.

Reaction of CCl_4 with *m*-$C_6H_4ClNO_2$. The compounds were taken into the reaction on the basis of 0.0430 g of *m*-chloronitrobenzene and 0.0840 g of CCl_4 (1 : 2) per 1 ml of tube capacity. The reaction was carried out at temperatures of 260, 270, and 280°. The duration of the reaction at the indicated temperatures proved to be respectively 52, 30, and 22 min. The temperature coefficient of the reaction for the interva-

for the temperatures 260–270° and 270–280° is 1.73 and 1.36. The gross activation energy is 23.5 kcal/mole.

The reaction of nitrobenzene, *m*- and *p*-chloronitrobenzene with CCl_4 proceeds analogously. To decipher the mechanism of the reaction of the first two compounds with CCl_4, we shall present data obtained in the study of the reaction of NOCl and $COCl_2$ with *p*-chloronitrobenzene, as well as that of NO_2 with CCl_4.

Reaction of CCl_4 with NO_2. Into a tube of 6.8 ml capacity were placed 0.0592 g of NO_2 and 0.2652 g of CCl_4. When the tube was heated on a thermophotometer for 276 min at a temperature from 14 to 290°, the following change in light absorption was observed:

τ, min.	0	15	30	40	60	70	90	110	130	150	180	200	276
t, °C	14	51	138	186	246	269	290	290	290	290	290	290	290
I, %	0	33	84	85	85	83	81	75	64	43	21	20	25

Phosgene, nitrosyl chloride, and chlorine were found in the tube. The reaction taking place can be written by the following equation:

$$2CCl_4 + 2NO_2 \rightarrow 2COCl_2 + 2NOCl + Cl_2.$$

NO_2, being a radical ([10]), at a temperature above 250° will evidently react with CCl_4 by a radical mechanism:

$$NO_2 + CCl_4 \rightarrow CCl_3 - NO_2 + Cl,$$
$$Cl + Cl \rightarrow Cl_2,$$
$$CCl_3 - NO_2 \rightarrow COCl_2 + NOCl\ (7)$$

or

$$NO_2 + CCl_4 \rightarrow CCl_3 + NO_2Cl,$$
$$CCl_3 + NO_2 \rightarrow CCl_3 - NO_2,$$
$$CCl_3 - NO_2 \rightarrow COCl_2 + NOCl\ (7),$$
$$NO_2Cl \rightarrow NO_2 + Cl,$$
$$Cl + Cl \rightarrow Cl_2.$$

Reaction of $COCl_2$ with *p*-$C_6H_4ClNO_2$. Into a tube of 9.1 ml capacity were placed 0.110 g of *p*-$C_6H_4ClNO_2$ and 0.160 g of $COCl_2$.

τ, min.	0	41	42	45	48	50	53	55	64	68	80
τ, °C	16	215	218	225	234	238	245	250	266	273	290
I, %	0	0	1	3	12	24	40	46	28	18	25

From the reaction product, *p*-dichlorobenzene was isolated in 87% yield of theoretical. $COCl_2$, CO_2, and NOCl were found in the gases.

Phosgene is a source of molecular and, under certain conditions, possibly atomic chlorine ([11]). Taking into account this reaction, which proceeds at temperatures above 220°, one may write:

$$COCl_2 \rightleftarrows CCO + Cl_2 \text{ and } CO + Cl_2 \rightleftarrows CO + 2Cl,$$
$$Cl_2 + M \rightarrow Cl + Cl + M,$$
$$Cl + p\text{-}C_6H_4ClNO_2 \rightarrow p\text{-}C_6H_4Cl_2 + NO_2,$$
$$NO_2 + Cl_2 \rightarrow NO_2Cl + Cl,$$
$$2NO_2Cl \rightarrow 2NO_2 + Cl_2 \text{ or } NO_2Cl \rightarrow NO_2 + Cl,$$
$$CO + NO_2 \rightarrow CO_2 + NO,$$
$$NO + Cl \rightarrow NOCl.$$

Reaction of NOCl with p-$C_6H_4ClNO_2$. When *p*-chloronitrobenzene was heated with NOCl, taken in excess, at 205°, the light absorption by the tube during its heating for 0; 2; 5; 7; 10; 15; 20; 25; 30 and 35 min was 0; 13; 25; 35; 42; 48; 51; 55; 54; 55%. After cooling, a dark liquid with a bluish tint condensed in the tube. In the reaction product were found *p*-dichlorobenzene, NO, NO_2, and NOCl.

As N. N. Semenov indicates ([10]), nitrosyl chloride can decompose with formation of NO and atomic chlorine, capable of initiating a chain process. In that case the reaction between NOCl and *p*-chloronitrobenzene

occurring above 200°, can be represented as a chain reaction:

$$2NOCl \rightarrow 2NO + Cl_2 \text{ and } NOCl \rightarrow NO + Cl,$$
$$Cl + n\text{-}C_6H_4ClNO_2 \rightarrow n\text{-}C_6H_4Cl_2 + NO_2,$$
$$NO_2 + Cl_2 \rightarrow NO_2Cl + Cl,$$
$$2NO_2Cl \rightarrow 2NO_2 + Cl_2,$$
$$NO_2Cl \rightarrow NO_2 + Cl.$$

Mechanism of the reaction of CCl_4 **with** $C_6H_5NO_2$**.** Polychloroalkanes, for example CCl_4, react with aliphatic hydrocarbons by a radical mechanism already at 130-140° ([11]). Taking into account the high temperature at which the reaction between CCl_4 and aromatic nitro compounds proceeds, as well as the nature of the substances formed as intermediate products, it should be assumed that the reaction between the indicated compounds proceeds by a chain mechanism:

chain initiation:

$$CCl_4 \rightarrow CCl_3 + Cl \quad (^{12});$$

chain propagation:

General scheme of the reaction process for nitrobenzene with carbon tetrachloride

Figure 3: General scheme of the reaction process for nitrobenzene with carbon tetrachloride

$$C_6H_5 - NO_2 + Cl \to C_6H_5Cl + NO_2,$$
$$NO_2 + CCl_4 \to CCl_3 - NO_2 + Cl,$$
$$CCl_3 - NO_2 \to COCl_2 + NOCl \quad (^7),$$
$$NOCl \to NO + Cl \quad (^{10}),$$
$$COCl_2 \to CO + Cl_2 \text{ and } COCl_2 \to CO + 2Cl \quad (^{11}),$$
$$Cl_2 + M \to Cl + Cl + M.$$

Chain termination may occur through recombination of radicals and atoms, and also by other routes.

The study of the kinetics of the reaction of aromatic nitro compounds with CCl_4 showed that this reaction is complex, with a number of consecutive and parallel reactions proceeding simultaneously. In the case of nitrobenzene the process may be represented by the following general scheme:

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Note: Figure translations are in progress. See original paper for figures.