Soviet-era science, translated into English

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1965

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Abstract

Full Text

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THE REACTION OF CHLOROFORM WITH HEPTENE-1, INITIATED BY IRON PENTACARBONYL IN COMBINATION WITH AMINES

Homolytic addition of chloroform to the double bond of olefins may proceed according to scheme (1) with cleavage of a C—H or C—Cl bond:

$$CHCl_3 + CH_2{=}CHC_5H_{11} \begin{cases} \longrightarrow CCl_3CH_2CH_2C_5H_{11} & A \\ \longrightarrow CCl_2HCH_2CHClC_5H_{11} & B \end{cases} \qquad (1)$$

Reaction 1A is initiated by peroxides, aliphatic azo compounds, and other usual initiators of radical processes (^{1}).

The reaction with cleavage of the C—Cl bond was first described by Asher and Vofsi (^{2}) using as an example the interaction of octene-1 with chloroform in an alcohol solution in the presence of copper or iron halides. The authors attributed this phenomenon to a specific transfer of chlorine through iron halide according to the scheme:

$$\begin{aligned} &\text{a)}\quad Fe^{2+} + CHCl_3 \rightarrow Fe^{2+}Cl + \dot{C}HCl_2 \\ &\text{b)}\quad \dot{C}HCl_2 + CH_2{=}CHR \rightarrow CHCl_2CH_2\dot{C}HR \qquad (2) \\ &\text{c)}\quad CHCl_2CH_2\dot{C}HR + Fe^{2+}Cl \rightarrow CHCl_2CH_2CHClR + Fe^{2+} \end{aligned}$$

As was noted by two of the authors of the present article jointly with B. A. Englin (^{3}), step c) of scheme (2), involving attack of an electrophilic radical on an electrophilic iron salt, is unlikely.

It was shown that the reaction via the C—Cl bond of chloroform takes place mainly in the simultaneous presence of an iron compound and an alcohol or acetonitrile, whereas in the absence of alcohol, iron compounds, as well as peroxides, initiate the reaction with cleavage of the C—H bond (^{3}). The authors proposed a scheme including chain transfer between an electrophilic radical and an electrophilic iron compound with the aid of a nucleophilic "mediator" (alcohol). Thus, the reaction involving isopropyl alcohol may be represented as follows:

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$$\begin{array}{ll}
\text{a)} & \mathrm{CHCl_3 + Fe^{2+} \rightarrow \dot{C}HCl_2 + Fe^{2+}Cl} \quad \text{initiation} \\
\end{array}$$

$$\left.\begin{array}{ll}
\text{b)} & \mathrm{\dot{C}HCl_2 + CH_2{=}CHR \rightarrow CHCl_2CH_2\dot{C}HR} \\
\text{c)} & \mathrm{CHCl_2CH_2\dot{C}HR + \underset{(C)}{(CH_3)_2CClOH} \rightarrow CHCl_2CH_2CHClR + (CH_3)_2\dot{C}OH} \\
\text{d)} & \mathrm{(CH_3)_2\dot{C}OH + Fe^{2+}Cl \rightarrow (CH_3)_2CClOH + Fe^{2+}} \\
\text{e)} & \text{radicals} \rightarrow \text{chain termination products}
\end{array}\right\} \begin{array}{l}\text{chain}\\ \text{transfer}\end{array}$$

$$\begin{array}{ll}
\text{f)} & \mathrm{(CH_3)_2CClOH \rightarrow HCl + (CH_3)_2CO}
\end{array} \qquad (3)$$

It may be expected that not only alcohols but also other compounds capable of reacting with halomethanes with formation of intermediate products containing labile chlorine (analogous to C) may serve as mediators in the reaction under consideration, directing the process according to equation (1B).

In the present work, as such substances we studied tertiary amines, presented in Table 1: aliphatic, aliphatic-aromatic, and heterocyclic, with a wide range of basicity (from $pK_b = 3.3$ for $(C_2H_5)_3N$ to 9.2 for C_9H_7N). As is evident from the data of Table 1, all the amines studied (or their hydrochlorides), over a wide concentration range,

amine and, with a sufficiently long reaction time, caused the formation of 1,1,3-trichlorooctane as the main product (scheme (1B)).

It is interesting to note that there is a certain initial period of the reaction during which predominantly 1,1,1-trichlorooctane is formed.

Table 1a

Reaction of heptene-1b (37 mmoles) with chloroform (112.5 mmoles) in the presence of Fe(CO)5 (0.4 mmole) at 130°

Experiment No.	Amine, pK_b^{v}	Amount of amine, mmol	Reaction time, h	Ratio, %, 1,1,1-trichlorooctane	Ratio, %, 1,1,3-trichlorooctane	Yield of trichlorooctanes, % (of theory)
1	N(C2H5)3(pK_b = 3.3)	112.5	18	26.7	73.3	4.8
2	Same	56.3	18	30.7	69.3	5.7
3e	» »	56.3	18	1.3	98.7	27.5
4	» »	1.3	18	5.5	94.5	23.0
5	» »	0.63	18	2.7	97.3	21.5
6e	» »	0.62	18	2.4	97.6	22.6
7	» »	0.35	18	3.1	96.9	43.8

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Experiment No.	Amine, pK_b^v	Amount of amine, mmol	Reaction time, h	Ratio, %, 1,1,1-trichlorooctane	Ratio, %, 1,1,3-trichlorooctane	Yield of trichlorooctanes, % (of theory)
8zh	» »	0.38	18	3.3	96.7	32.1
9	» »	0.11	18	8.0	92.0	19.5
10	» »	0.42	0.5	58.1	41.9	1.8
11zh	» »	0.41	0.5	86.0	14.0	1.7
12	» »	0.48	1.0	69.2	30.8	6.2
13e	» »	0.44	1.0	35.5	64.5	6.2
14	$N(CH_2CH_2OH)_3$ (pK_b = 4.2)	56.3	18	91.1	8.9	12.4
15	Same	0.55	18	39.1	60.9	13.4
16	$N(CH_2CH_2OCOCH_3)_3$g (pK_b = 3.8)	56.3	18	3.1	96.9	24.4
17	*n*-$[(CH_3)_2N]_2C_6H_4$d (pK_b = 7.65)	112.5	18	18.5	81.4	2.6
18	Same	56.3	18	20.9	79.1	5.1
19	» »	0.74	18	8.9	91.1	22.4
20	$C_6H_5N(CH_3)_2$ (pK_b = 8.9)	56.3	18	7.0	93.0	21.8
21	Same	28.1	18	11.2	88.8	21.1
22	» »	0.42	18	3.5	96.4	28.5
23	Pyridine (pK_b = 8.8)	56.3	18	26.6	73.4	11.0
24	Same	0.59	18	21.9	78.1	11.6
25e	» »	0.61	18	10.1	89.9	12.8
26zh	» »	0.84	18	26.1	73.9	10.3
27	» »	56.3	9.0	34.8	65.2	5.7
28	» »	56.3	4.5	65.1	34.9	4.0
29zh	» »	56.3	4.5	83.1	16.9	5.1
30	» »	56.3	0.5	89.4	10.6	1.4
31	» »	0.62	1	76.3	23.7	6.2
32e	» »	0.61	1	76.9	23.1	6.4
33	Quinoline (pK_b = 9.2)	56.3	18	11.3	88.7	18.0
34	Same	0.42	18	8.4	91.6	18.7
35	» »	56.3	4.5	12.8	87.2	4.0
36	» »	56.3	0.5	47.6	52.4	<1

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Fig. 1

Figure 1: Fig. 1

Experiment No.	Amine, pK_b^v	Amount of amine, mmol	Reaction time, h	Ratio, %, 1,1,1-trichlorooctane	Ratio, %, 1,1,3-trichlorooctane	Yield of trichlorooctanes, % (of theory)
37	Acridine ($pK_b = 8.4$)	56.3	18	2.5	97.5	23.3
38	Without amine	–	18	93.1	6.9	9.3

a) Chloroform was washed free of stabilizing additives, dried, and distilled on a column. The amines were dried over KOH and distilled over acetic anhydride on a column. The reaction was carried out with stirring in sealed ampoules in an inert-gas atmosphere. The reaction mixture was washed with dilute HCl, extracted with ether, and dried over Na2SO4. The isomeric trichlorooctanes were analyzed by GLC. For more detail see the preceding communication (3). The experiments presented in Table 1 were reproduced 2–4 times. b) According to the Manual (4), α-olefins isomerize in the presence of Fe(CO)5 when the reaction is carried out in open vessels. Addition of pyridine lowers the isomerization temperature. In special experiments we established that under our conditions this isomerization does not exceed 3–5%. v) For pK_b values of the amines, see (5). g) pK_b was calculated by the method of Clark and Perrin (6). Triacetate of triethanolamine was synthesized by the method of Jones et al. (7). d) Obtained by the method of (8). e) Its hydrochloride was used instead of the amine. zh) The experiment was carried out with the addition of 2 mmoles of water.

The duration of this period differs for amines of different structures. This phenomenon is shown both for triethylamine (experiments Nos. 7, 10) and for pyridine (experiments Nos. 23, 27, 28, 30) or quinoline (experiments Nos. 35, 36).

This period is longest for pyridine (Fig. 1, A and A'); for quinoline (Fig. 1, B and B'). The formation of 1,1,3-trichlorooctane gradually begins (Fig. 1, A and B), the concentration of which subsequently increases continuously.

These facts indicate that in the initial period of the reaction some intermediate compound accumulates up to the minimum concentration necessary for changing the direction of the reaction, proceeding according to equation (1), from A to B.

Fig. 1

In the literature there are data on reactions of tertiary amines with anhydrous ferric chloride. It has been established that in these reactions complex amine cation-radicals are formed ([9,10]) according to equation (4):

$$R_3N : + 2FeCl_3 \to [R_3N]^+Cl^-FeCl_3 + FeCl_2. \tag{4}$$

Amine cation-radicals are characterized by an intense blue-green color and are the more stable the higher the pK_b of the amine ([11]). The most stable are amine cation-radicals of aromatic ([9]) and heterocyclic ([12]) amines. However, amine salts have also been described for aliphatic amines ([10]).

On the other hand, for highly basic aliphatic amines a radical reaction with polychloromethanes initiated by iron salts is known ([13]):

$$
\begin{aligned}
& CCl_4 \xrightarrow{Fe^{2+}} CCl_3^\bullet + Fe^{2+}Cl \\
& CCl_3^\bullet + R_2NCH_2R' \to CCl_3H + R_2\dot{N}CHR' \\
& \qquad\qquad\quad Cl \\
& \qquad\qquad\quad | \qquad (E) \\
& R_2\dot{N}CHR' + CCl_4 \to R_2NCHR' + CCl_3^\bullet \\
& \qquad\qquad\quad F
\end{aligned} \tag{5}
$$

According to this scheme, CCl_4 reacts most readily. Chloroform, although more slowly, also reacts with amines ([14]).

It seems to us that the peculiarities of the influence of various amines on the mechanism of reaction (1) can be explained from the standpoint of chain transfer with the participation of an intermediate according to the scheme:

$$
\begin{aligned}
&\text{a)}\quad CHCl_3 + Fe^{2+} \to \dot{C}HCl_2 + Fe^{2+}Cl \\
&\text{b)}\quad \dot{C}HCl_2 + CH_2{=}CHC_5H_{11} \to CHCl_2CH_2\dot{C}HC_5H_{11} \\
&\text{c)}\quad Fe^{2+}Cl + :N \to [N^\bullet]^+Cl^- + Fe^{2+} \\
&\text{d)}\quad CHCl_2CH_2\dot{C}HC_5H_{11} + [N^\bullet]^+Cl^- \to CHCl_2CH_2CHClC_5H_{11} + :N \\
&\text{e)}\quad \text{radicals} \to \text{products; chain termination}
\end{aligned} \tag{6}
$$

$$[N^\bullet]^+Cl^-$$

is analogous to D of scheme (4) or F of scheme (5).

At the first stage of the reaction, while the concentration of K is very small, chain transfer is effected through chloroform, i.e., it proceeds according to equation (1A). As K accumulates in the reaction mixture, transfer begins to proceed

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according to equations c) and d) of scheme (6). In some cases, for low-basicity amines, we also observed the characteristic intense blue-green color of the amine cation-radical at the early stages of the reaction. For aliphatic

is very unstable; an α-chloroamine may serve as the mediator at stages c) and d) of scheme (6).

However, the fact that the direction of reaction (1) is changed from A to B by additions of both aliphatic and aliphatic-aromatic, as well as heterocyclic, amines that do not have a mobile α-hydrogen capable of being substituted by chlorine according to scheme (5), confirms our assumption about the role of the aminium salt as a mediator in chain transfer.

According to Döbenek and Lenerer (10), water decomposes aminium salts. We found that the addition of small amounts of water (5 moles per 1 mole of $Fe(CO)_5$) slows, at the initial stage of the process, the course of the reaction according to equation (1)B (experiments Nos. 10, 11, 28, 29). In connection with this, in studying the mechanism of the reaction under consideration it is better to use iron compounds that do not contain water of crystallization. When the reaction is carried out for a longer time, these small additions of water do not affect the final ratio of isomeric trichlorooctanes as measured (experiments Nos. 7, 8, 24, 26). It should be noted that, when the reaction is carried out for a long time, amine hydrochlorides exert the same influence on the direction of reaction (1) as do free amines (experiments Nos. 5, 6, 24, 25). Comparison of the duration of the initial period for experiments carried out in the presence of the free amine or its hydrochloride shows that, for weakly basic amines, the free amine and its hydrochloride give identical results (experiments Nos. 31, 32). In the case of strongly basic amines, the use of the amine hydrochloride decreases the initial period of the reaction (experiments Nos. 12, 13).

Varying the amine:$Fe(CO)_5$ ratio from 1 to 280 showed that, in the case of weakly basic amines (experiments Nos. 17-19, 20-22, 23-24, 33-34), a change in the amine concentration does not affect the ratio of the isomeric trichlorooctanes formed. For strongly basic amines such as $(C_2H_5)_3N$ or $N(CH_2CH_2OH)_3$, with increasing amine concentration the relative content of 1,1,3-trichlorooctane in the mixture of isomers decreases (experiments Nos. 2, 4, 14, 15). As noted above, for aliphatic amines the mediator may be an α-chloroamine, and in the case of triethanolamine, which is an amino alcohol, the mediator may also be a compound of type C (scheme 3).

The observed different influence of an excess of amine can be explained by the fact that strongly basic amines readily form insoluble hydrochlorides (15); therefore, excess amine can rapidly react with the mediator, removing it from the reaction sphere. An analogous influence of ethylene oxide or strongly basic amines on the mechanism of the reaction of ethylene with CCl_4 in the presence of alcohol was noted earlier (16). If, instead of an excess of free strongly basic amine, its hydrochloride is used (experiments Nos. 3, 6), which is no longer capable of trapping chlorine from the mediator, then a decrease in the relative

SovietRxiv

content of 1,1,3-trichlorooctane in the mixture of isomers is not observed.

Thus, all the observed facts concerning the influence of the structure, basicity, and concentration of the amine, as well as the duration of the reaction, on the ratio of the yields of isomeric trichlorooctanes find the most comprehensive explanation from the standpoint of chain transfer with participation of a mediator.

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Received
5 II 1965

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