

METALLOCOMPLEX CATALYST OF THE ADDITION REACTION OF  $\text{CCl}_4$   
TO ETHYLENE

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The catalyst  $\text{Fe}^{\text{II}}\text{Fe}_2^{\text{III}}\text{Cl}_8(\text{DMA})_6$ -iron(2+)diiron(3+)octachlorohexakis(dimethylacetamide), was isolated from the media of the catalytic synthesis of 1,1,1,3-tetrachloropropane ( $\text{C}_3$ ), and characterized by physicochemical methods. A counter synthesis of the catalyst was carried out. The telomerization of ethylene with  $\text{CCl}_4$  proceeds with a 98% selectivity with respect to  $\text{C}_3$  in its presence, while the conversion of  $\text{CCl}_4$  reaches 55-60% after 4 h. A coordination-ionic mechanism of the reaction of  $\text{CCl}_4$  with  $\text{C}_2\text{H}_4$  was proposed, which followed the concept of the donor-acceptor electron-transporting systems (the DAET systems), thus accounting for its high selectivity.

The catalytic synthesis of 1,1,1,3-tetrachloropropane ( $\text{C}_3$ ) from ethylene and  $\text{CCl}_4$  proceeds in the presence of several iron compounds and systems based on it [1, 2]. The selectivity of the process increases in the presence of aprotic dipolar compounds having high electronic polarizability, such as amides (hexamethylphosphorotriamide, dimethylacetamide, etc.). It was noted that an effective catalyst of this process is the system comprising the mixed valence complex  $\text{Fe}^{\text{II}}\text{Fe}_2^{\text{III}}\text{Cl}_8(\text{CH}_3\text{CN})_6$  (I)-dimethylacetamide (DMA) [3].

The aim of the present work was to determine the optimal ratio of the components of the complex (I)-DMA catalytic system and to elucidate the composition and structure of the catalytically active complex - the conversion product of (I) in the course of the synthesis of  $\text{C}_3$ .

#### EXPERIMENTAL

In a standard experiment the telomerization of  $\text{C}_2\text{H}_4$  with  $\text{CCl}_4$  was carried out in a thermostated glass reactor or a Teflon-lined autoclave. The solvents were dried and distilled before use. In the synthesis of the complexes, a "specially pure 13-2" grade iron carbonyl powder was used.

The electronic spectra were recorded on a "Specord UV-VIS" spectrophotometer, and the IR spectra on a UR-20 spectrophotometer in KBr tablets and in mineral oil.

The products of the catalytic reaction of ethylene with  $\text{CCl}_4$  were analyzed by the GLC method using a heat conductivity detector and 3 m × 3 cm columns filled with a Celite-545 carrier with 15% Apieson L, at a column thermostat temperature of 190°C. The chromatograms were calculated by the method of internal standardization.

Iron(2+)-diiron(3+)octachlorohexakis(dimethylacetamide) $\text{Fe}^{\text{II}}\text{Fe}_2^{\text{III}}\text{Cl}_8(\text{DMA})_6$  (II). A mixture of 0.5 g (0.01 mole) of iron carbonyl pressed into a tablet, 16 ml (0.16 mole) of  $\text{CCl}_4$ , and 1.7 ml (0.2 mole) of DMA was held at a temperature of 20-40°C for several days with periodic shaking. Iron gradually dissolved, forming two layers, on the phase boundary of which yellow-green crystals grew, which were separated and washed several times with  $\text{CCl}_4$ , pentane and ether, mp 95-97°C. Found: C 29.6; H 5.8; Cl 31.1; N 8.00; Fe 17.2;  $\text{Fe}^{2+}$  5.5%.  $\text{C}_{24}\text{H}_{54}\text{Cl}_8\text{Fe}_3\text{N}_6\text{O}_6$ . Calculated: C 29.6; H 5.5; Cl 29.2; N 8.6; Fe 17.2 ( $\text{Fe}^{2+}$  5.7;  $\text{Fe}^{3+}$  11.5) %.

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TABLE 1. Influence of the Ratio of Components of the  $\text{Fe}^{\text{II}}\text{Fe}_2^{\text{III}}\text{Cl}_8(\text{CH}_3\text{CN})_6$  (I)-DMA Catalytic System on Conversion of  $\text{CCl}_4$  and Yield of 1,1,1,3-tetrachloropropane in the Reaction of Ethylene with  $\text{CCl}_4$ \*

DMA, ml; moles	$\text{CH}_3\text{CN}$ , ml	DMA/(I) moles	Conversion of $\text{CCl}_4$ , %	Yield of reaction products, mole %	
				$\text{C}_3$	$\text{C}_5$
0,1; $1 \cdot 10^{-3}$	4,9	1	38,9	98,3	1,7
0,2; $2 \cdot 10^{-3}$	4,8	2	75,3	97,3	2,7
0,4; $4 \cdot 10^{-3}$	4,6	4	90,0	98,4	1,6
1,0; $1 \cdot 10^{-2}$	4,0	10	90,3	98,1	1,9
2,0; $2 \cdot 10^{-2}$	3,0	20	82,8	98,0	2,0

\*Reaction conditions. (I) -  $1 \cdot 10^{-3}$  mole;  $\text{CCl}_4$  - 10 ml,  $1 \cdot 10^{-1}$  mole;  $V_{\text{CH}_3\text{CN}} + V_{\text{DMA}} = 5$  ml = const,  $P_{\text{C}_2\text{H}_4} = 20$  atm,  $130^\circ\text{C}$ , 4 h.

The IR spectrum parameters ( $\nu$ ,  $\text{cm}^{-1}$ ): 405 m, 443 w, 600-610 s (doublet), 445, 980 m, 1030-1080 s (doublet), 1120 w, 1200 m, 1260 m, 1360 sh, 1395-1415 m (doublet), 1490 w, 1580-1600 v.s, 1740 sh, 2815 w, 2870 sh, 2935 m, 3020 w.

The parameters of the absorption spectra in the UV and visible regions of solutions of the complex in  $\text{CH}_3\text{CN}$  ( $C \sim 0.6 \cdot 10^{-4}$  mole/liter) for  $\text{FeCl}_4^-$  were ( $\lambda$ , nm): 240.5 s, 268 sh, 312.5 m, 363.5 s, 530 s.

Addition of  $\text{CCl}_4$  to Ethylene in the Presence of  $\text{Fe}_3(\text{DMA})_6\text{Cl}_8$  (II) in Acetonitrile. A 10 ml portion ( $1 \cdot 10^{-1}$  mole) of  $\text{CCl}_4$ , 5 ml ( $1 \cdot 10^{-1}$  mole) of  $\text{CH}_3\text{CN}$ , and 0.97 g ( $1 \cdot 10^{-3}$  mole) of  $\text{Fe}_3(\text{DMA})_6\text{Cl}_8$  were placed in a thermostated reactor, and the mixture was heated with vigorous shaking for 4 h at  $130^\circ\text{C}$  under a constant ethylene pressure of 20 atm.

After cooling, the reaction mixture was washed with water, dried over  $\text{MgSO}_4$  and the composition and content of the reaction products was determined by GLC. The conversion of  $\text{CCl}_4$  was 58%, the ratio of tetrachloroalkanes, the reaction products 1,1,1,3-tetrachloropropane ( $\text{C}_3$ ) and 1,1,1,5-tetrachloropentane ( $\text{C}_5$ ), was  $\text{C}_3:\text{C}_5 = 98:2$  (molar %).

Addition of  $\text{CCl}_4$  to Ethylene in the Presence of  $\text{Fe}^{\text{II}}\text{Fe}_2^{\text{III}}\text{Cl}_8(\text{CH}_3\text{CN})_6$  in a Mixture of Acetonitrile and DMA. A 10 ml portion ( $1 \cdot 10^{-1}$  mole) of  $\text{CCl}_4$ , 2 ml ( $2 \cdot 10^{-2}$  mole) of DMA, 3 ml of  $\text{CH}_3\text{CN}$  and 0.7 g ( $1 \cdot 10^{-3}$  mole) of  $\text{Fe}^{\text{II}}\text{Fe}_2^{\text{III}}\text{Cl}_8(\text{CH}_3\text{CN})_6$  (I) were heated at  $130^\circ\text{C}$  for 4 h in a thermostated reactor with vigorous stirring and at an ethylene pressure of 20 atm.

The conversion of  $\text{CCl}_4$  was 80%, and the molar ratio of tetrachloroalkanes, 1,1,1,3-tetrachloropropane ( $\text{C}_3$ ) and 1,1,1,5-tetrachloropentane ( $\text{C}_5$ ), was 97:3. To isolate the catalytically active complex, 15 ml of  $\text{CCl}_4$  was added to the reaction mixture after cooling, whereby the latter separated into two layers: an upper yellow-brown colored layer - a solution of iron compounds, and a lower layer - a mixture of  $\text{CCl}_4$  and tetrachloroalkanes.

From the upper layer a complex was isolated, the elemental analysis and spectral characteristics of which correspond to  $\text{Fe}_3\text{Cl}_8(\text{DMA})_6$  (II). Found: C 29.0; H 4.8; N 7.2; Fe 17.3%.  $\text{C}_{24}\text{H}_{54}\text{Cl}_8\text{Fe}_3\text{N}_6\text{O}_6$ . Calculated: C 29.6; H 5.5; N 8.6; Fe 17.2; Cl 29.2%.

## RESULTS AND DISCUSSION

The influence of the ratio of the components of the  $\text{Fe}^{\text{II}}\text{Fe}_2^{\text{III}}\text{Cl}_8(\text{CH}_3\text{CN})_6$  (I)-DMA catalytic system on the conversion of  $\text{CCl}_4$  and the yield of 1,1,1,3-tetrachloropropane in the reaction of ethylene with  $\text{CCl}_4$  is shown in Table 1. It is seen that even at a 1:1 ratio, the conversion of  $\text{CCl}_4$  reaches 38.9%, while the yield of  $\text{C}_3$  is 98.3% (in the absence of DMA the reaction practically does not occur). The optimal ratio of the DMA-(I) components is equal to 4 (the conversion of  $\text{CCl}_4$  is 90.9%, and the selectivity with respect to  $\text{C}_3$  98.4%), while further increase in the amount of DMA leads to decrease in the conversion to 82.8% with the retention of the selectivity value with respect to  $\text{C}_3$ . This indicates the decisive role of

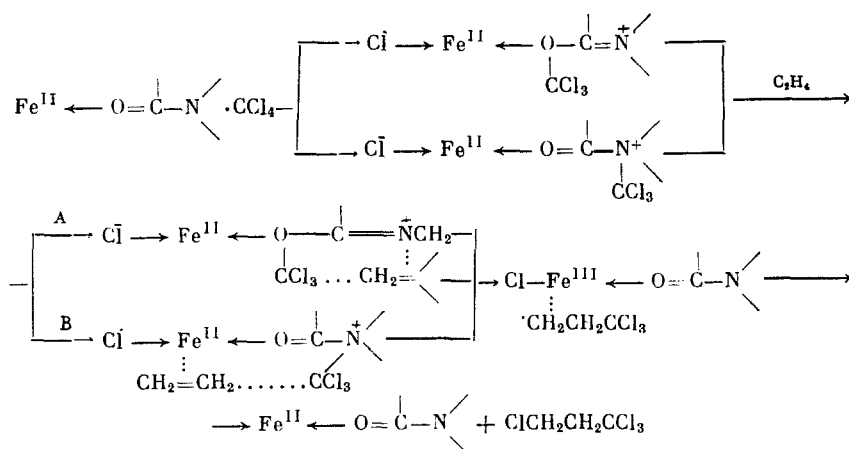
DMA in the catalytic reaction . It is possible that the specific influence of DMA on the course of the addition of  $\text{CCl}_4$  to ethylene is not explained solely by its influence on the redox potential of the system due to complexation with an iron ion. For example, in the presence of amines, which are strong donors, the selectivity with respect to  $\text{C}_3$  does not exceed 59% [4], while hexamethylphosphorotriamide, triethyl phosphite, as well as amides of organic acids cause the telomerization reaction to become essentially an addition reaction.

This may indicate that DMA participates in the formation of the catalytically active complex. After the catalytic synthesis of  $\text{C}_3$ , a complex with the composition  $\text{Fe}^{\text{II}}\text{Fe}_2^{\text{III}}\text{Cl}_8 \cdot (\text{DMA})_6$  (II) was isolated from the reaction medium and characterized.

The results of the x-ray diffraction studies showed that the iron atoms in the  $\text{Fe}^{\text{II}}\text{Fe}_2^{\text{III}}\text{Cl}_8 \cdot (\text{DMA})_6$  (II) crystal are present in a typically octahedral and tetrahedral environment in a 1:2 ratio. The coordination of DMA ligands occurs through the oxygen atoms, but because of large oscillation amplitude of the atoms at room temperature, the coordinates of other DMA atoms (C, N, the  $\text{CH}_3$  group) are established with a high degree of indefiniteness, which indicates the high mobility of DMA ligands in the crystal. The x-ray diffraction experiment (diffractometer, No, Cu radiation) is strongly limited by large thermal oscillations of the atoms.

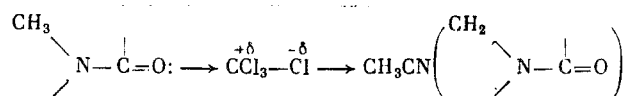
The electronic absorption spectrum of compound (II) in acetonitrile shows all the bands characteristic for  $\text{FeCl}_4^-$  [5], and in the IR spectrum, the  $\text{C}=\text{O}$  ( $1600 \text{ cm}^{-1}$ ), most characteristic for DMA, is shifted to the long-wave region by  $55 \text{ cm}^{-1}$  compared with  $\text{C}=\text{O}$  of a free (liquid) DMA ( $1655 \text{ cm}^{-1}$ ) [6], indicating a coordination of DMA with  $\text{Fe}^{2+}$  through the O atom.

It was found that this complex is also active as a catalyst in the addition of  $\text{CCl}_4$  to ethylene. In acetonitrile, the selectivity of the process with respect to  $\text{C}_3$  is 98% at a 58% conversion of  $\text{CCl}_4$  (under comparable conditions), which is somewhat lower than in the  $\text{Fe}^{\text{II}} \cdot \text{Fe}_2^{\text{III}}\text{Cl}_8(\text{CH}_3\text{CN})_6$  (I)-DMA system. It is possible that in the reaction medium several complexes of the type  $\text{Fe}^{\text{II}}\text{Fe}_2^{\text{III}}\text{Cl}_8(\text{CH}_3\text{CN})_n(\text{DMA})_m$  are formed (where  $n + m = 6$ ), having a varied catalytic activity (including also a complex (II) ( $n = 0$ ) - the product of conversion of complex (I) ( $m = 0$ ) - a precursor of the reaction catalyst). The experimental data obtained indicate that the amide - a bifunctional dipolar compound  $\left[ \text{N}-\text{C}=\text{O} \leftrightarrow \overset{+}{\text{N}}=\text{C}-\text{O}^- \right]$ , plays a specific role in the reaction of  $\text{CCl}_4$  with ethylene, thus causing the telomerization reaction to become solely an addition reaction. No clearcut explanation of this phenomenon can be given within the concepts on the donor-acceptor electron transporting systems (the DEAT systems) [7]. It was noted in [8, 9] that both ethylene and  $\text{CCl}_4$  interact with paramagnetic iron ions ( $\text{Fe}^{\text{II}}$ ,  $\text{Fe}^{\text{III}}$ ), but no unequivocal conclusion can be made on the character of their coordination - extra- or intraspheric. It is not to be excluded that the reason for the high selectivity of the process with respect to  $\text{C}_3$  in the presence of (II)- $\text{CH}_3\text{CN}$  or (I)-DMA systems is due to the ability of the  $\text{CCl}_4$ -amide donor-acceptor system to form a molecular complex [10], the further conversion of which, stimulated by the action of the metal ion, leads to the alkylation of the amide



It is seen from the scheme that the chain of chemical bonds produced in this case, contains an acceptor center ( $=\overset{+}{\text{N}}\langle$  or  $-\overset{+}{\text{N}}\langle$ ) and conjugated with it a donor ( $=\text{O}$ : or  $\rangle\text{O}$ ):

center coordinatively bound with the metal. This promotes an electron transfer from Fe<sup>II</sup> to the acceptor, while the complex-bound amide thus plays the role of an electron carrier. Since the alkylation of the amide is possible at both the oxygen atom (A), and the nitrogen atom (B), two types of coordination of ethylene can be assumed in a catalytically active complex. According to steric concepts, an "insertion" of ethylene into the system in the outer sphere is most probable during the alkylation at the oxygen, and this leads to the formation of an intermediate weakly bound six-membered heterocycle. During alkylation at the nitrogen atom, ethylene may coordinate directly with the metal atom, also drawn into an intermediate heterocyclic ring. The catalytic unit, playing the role of a matrix for ethylene, hinders the movement of the radicals (<sup>1</sup>Cl<sub>3</sub>C and <sup>1</sup>CH<sub>2</sub>CH<sub>2</sub>CCl<sub>3</sub>) into the bulk, and the development of a telomerization reaction with the formation of telomer homologs. Thus, the oxidation of Fe<sup>II</sup> into Fe<sup>III</sup> by an alkylated amide eventually leads to a radical addition reaction of <sup>1</sup>CCl<sub>3</sub> to ethylene, but in this case, in the coordination sphere of the metal. Bifunctionality is not a characteristic feature of acetonitrile (in contrast to dimethylacetamide) and it does not become alkylated. This is may be the reason for complex (I) without an amide to be catalytically inactive. However, in contrast to amines,\* which are only electron donors, both donor and acceptor properties are characteristic for amides and nitriles, which favors the heterolytic cleavage of the  $\text{>C}^{\delta+}-\text{Cl}^{\delta-}$  bond in CCl<sub>4</sub>,



The formation of onium salts is characteristic for amines, such as for example  $\left[ \begin{array}{c} \diagdown \\ \text{N}^+-\text{CCl}_3 \\ \diagup \end{array} \right] \text{Cl}^-$ . However, the oniumcation thus formed does not contain a donor center capable of coordination with a metal, i.e., a "matrix" for ethylene is not formed. This may be the reason for the low selectivity of the process with respect to C<sub>3</sub> in the presence of amines.

Thus, the activity of the catalytic telomerization of ethylene with CCl<sub>4</sub> and its selectivity, leading to practically a single reaction product 1,1,1,3-tetrachloropropane, is due, in our opinion, to specific properties of the ligand, the readily polarizable bifunctional bipolar compound - the amide.

#### LITERATURE CITED

1. L. G. Korableva, I. P. Lavrent'ev, and M. L. Khidekel', Inventor's Certificate No. 421,354 (USSR); Byull. Izobret., No. 12, 11 (1974).
2. T. Asahara, M. Seno, and T. Sato, Kagaku Kagaku Zasshi, 74, No. 11, 2288 (1971).
3. E. A. Lavrent'eva, A. N. Kitaigorodskii, I. P. Lavrent'ev, and M. L. Khidekel', Summaries of Lectures at the 7th All-Union Conference on Catalytic Reactions in Liquid Phase [in Russian] Vol. 3, Alma-Ata (1988), p. 7.
4. T. Asahara, M. Seno, and Ch-Ch. Wu, Kagaku Kagaku Zasshi, 72, No. 8, 1822 (1969).
5. B. J. Hathaway and D. J. Holah, J. Chem. Soc., 2408 (1964).
6. N. A. Parpiev, G. V. Tsintsadze, Yu. P. Kharitonov, et al., Coordination Compounds of Metals with Formamide [in Russian], Fan, Tashkent (1980), p. 99.
7. I. P. Lavrent'ev, Summaries of Lectures of the 14th All-Union Chernyaevskii Conference on the Chemistry and Technology of Platinum Metals [in Russian], Vol. 1, Novosibirsk (1989), p.26.
8. A. N. Kitaigorodskii, E. A. Lavrent'eva, L. G. Korableva, et al., Zh. Fiz. Khim., 56, No. 4, 969 (1982).
9. A. N. Kitaigorodskii, E. A. Lavrent'eva, and I. P. Lavrent'ev, Izv. Akad. Nauk SSSR, Ser. Khim., No. 12, 2828 (1985).
10. G. A. Nifontova, I. P. Lavrent'ev, A. F. Makarov, and M. L. Khidekel', Summaries of 11th All-Union Conference on Chemistry, Analysis and Technology of Platinum Metals [in Russian], Leningrad (1979), p. 60.
11. V. Gutman, The Donor-Acceptor Approach to Molecular Interaction, Plenum Press, New York (1978), p. 20.

\*t-BuNH<sub>2</sub>: donor number DN = 57 (according to Gutman [11]); MeCN: DN = 14.1; acceptor number (AN) = 19.3; Me<sub>2</sub>NC(Me)O: DN = 27.8; AN = 13.6.