On the mechanism of the Kharash reaction catalyzed by $Fe(CO)_5$
3.* Thermal decomposition of $Fe(CO)_5$ in the presence of CCl_3X ($X = Br, Cl$) and the effect of DMF

*V. I. Tararov, A. P. Pisarevskii, and Yu. N. Belokon**

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: +7 (095) 135 5085

$Fe(CO)_5$ is sufficiently stable at 80 °C in benzene solution and its thermal decomposition is not accelerated in the presence of phenyl cinnamate or/and DMF. The decomposition is accelerated by CCl_3Br (drastically) and by CCl_4 (to a lesser extent). DMF accelerates the reaction of $Fe(CO)_5$ with CCl_4. The $[FeCl(DMF)_5]^{2+}[Cl_3FeOFeCl_3]^{2-}$ complex has been isolated as a product; its composition and structure have been determined by X-ray analysis. The obtained data indicate the absence of coordination of DMF or/and an olefin with Fe^0 species at the stage preceding oxidation. The mechanisms of the generation of $^{\cdot}CCl_3$ radicals in thermal and photochemical Kharash reactions in the presence of $Fe(CO)_5$ are basically different. The probable pathways of the effect of DMF on the rate of the oxidative decomposition of $Fe(CO)_5$ are discussed.

Key words: Kharash reaction, catalysis, iron pentacarbonyl, kinetics, thermal stability, thermal reaction with CCl_3X ($X = Br, Cl$), effect of olefin and DMF.

The insertion of olefins into a carbon—halogen bond in polyhaloalkanes, usually called the Kharash reaction, is catalyzed by $Fe(CO)_5$ on heating.[2,3] The so-called nucleophilic cocatalysts (L), *e.g.*, HMPA, DMF, and PPh_3, increase the catalytic activity of the latter.[2,3]

Study of the stereochemistry of the $Fe(CO)_5$-catalyzed Kharash reaction using chiral substrates has shown that the reaction is of radical character and the addition of DMF or PPh_3 does not change the mechanism principally.[1,4]

The main problem of any catalytic reaction is the stability of the catalyst during the reaction. It is known that $Fe(CO)_5$ is not inert with respect to polyhalomethanes.[5—7] Depending on the conditions, halides of the oxidized forms of iron partially[7] or completely[5,6] devoid of the carbonyl ligands are formed. In accordance with our observations and literature data,[7] gaseous products are evolved and red, insoluble, iron-containing compounds are formed under conditions of the Kharash reaction in the presence of $Fe(CO)_5$.

In this connection, the stability of $Fe(CO)_5$ in the presence of all of the components of the Kharash reaction, namely, CCl_4, CCl_3Br, DMF, and phenyl cinnamate (**1**), is studied in the present work.

Results and Discussion

The thermal stability of $Fe(CO)_5$ was estimated by the amount of CO evolved on heating under the conditions given in Table 1.

As can be seen from Table 1, the benzene solution of $Fe(CO)_5$ is quite stable at 80 °C (entry *1*); the addition of DMF (entry *2*), **1** (entry *3*), and DMF + **1** (entry *4*) does not affect significantly the rate of decomposition. The mean value of the rate constant of decomposition of $Fe(CO)_5$ calculated from the initial rates (entries *1—4*) is $1.3 \cdot 10^{-5}$ s^{-1}, which is comparable to the value $5.1 \cdot 10^{-5}$ s^{-1} (110 °C, hexadecane),[8] thus indicating the correctness of the procedure used in the present work.

Fast and almost stoichiometric evolution of CO was observed in the reaction of $Fe(CO)_5$ with CCl_3Br (entry *5*). Under actual conditions of the Kharash reaction, in the presence of of DMF as an additive, fast evolution of CO also occurs (entry *6*) and the adduct, phenyl β-bromo-α-trichloromethyldihydrocinnamate (**2**), is formed in 10—15 % yield. The adduct was identified by TLC on SiO_2 (hexane—benzene, 2:1) using authentic **2** prepared from **1** and CCl_3Br using initiation with benzoyl peroxide (BP).

The reaction of $Fe(CO)_5$ with CCl_4 (entry *7*) proceeds more slowly than that with CCl_3Br; however, this process is faster than the thermal decomposition of

---

* For Part 2, see Ref. 1.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 4, pp. 916—919, April, 1996.

Table 1. Effects of DMF, phenyl cinnamate (**1**), and CCl_3X on the decomposition of $Fe(CO)_5$ (C = 0.035 mol L^{-1}) at 80 °C in benzene

Entry	X in CCl_3X	DMF	Olefin (**1**)	Fe:CCl_3X:DMF:**1**	Time/min	Yield of CO (%)[a]
1	—	—	—	1:0:0:0	60	5.9
2	—	+	—	1:0:2.9:0	60	4.6
3	—	—	+	1:0:0:6.5	60	3.6
4	—	+	+	1:0:3:6.5	60	4.8
5	Br	—	—	1:11.3:0:0	20	99
6	Br	+	+	1:11.1:3:6.5	30	100[b]
7	Cl	—	—	1:10:0:0	60	20
8	Cl	+	—	1:10.9:2.9:0	60	72

[a] The yield was calculated according to the following equation: $Fe(CO)_5 = Fe + 5\ CO$.

[b] In benzene solution, the formation of 10—15 % of adduct **2** was observed by TLC.

$Fe(CO)_5$ (entry *1*) and is accelerated significantly in the presence of DMF (entry *8*).

Under conditions of entry *8*, the complex $[FeCl(DMF)_5]^{2+}[Cl_3FeOFeCl_3]^{2-}$ (**3**) was isolated; its structure was determined by X-ray analysis (Fig. 1). As can be seen from Fig. 1, one Fe atom is located in the cationic part and two Fe atoms connected by the oxygen bridge are located in the anionic part. The cationic part contains five DMF molecules coordinated to the metal atom. The appearance of the oxygen atom in the molecule is apparently not related to the main reaction and may be explained as the result of hydrolysis (secondary process). Initially, the reaction mixture represented two immiscible liquid phases. On storage in air an in open vessel for two weeks, the lower, red phase transformed to a crystalline substance, from which a single crystal was taken for X-ray analysis.

It should be noted that in all cases of the interaction of CCl_3X with $Fe(CO)_5$, the reaction mixtures became heterogeneous after several minutes. In the presence of DMF, the benzene phase is colored more intensely than in the absence of DMF.

The isolation of compounds of oxidized iron from the reaction of $Fe(CO)_5$ and polyhalomethanes in previous studies (Refs. 5—7) and in this study confirms unequivocally the assumption of the redox character of these processes, and the identification of hexachloroethane[5,7] proves the generation of the $^{\cdot}CCl_3$ radicals.

The data presented in Table 1 demonstrates altogether that fast decomposition of $Fe(CO)_5$ was observed only in the presence of an oxidant. In other words, the electron transfer from Fe^0 causes a significant decrease in the Fe—CO bond energy.

The electron transfer (apparently, reversible), as well as the cleavage of the Fe—CO bond in the oxidized iron carbonyl, may determine the overall rate of the process. In the first case, the accelerating effect of DMF is possibly related to its participation in the stage of the electron transfer. In the second case, the participation of DMF is possibly related to the substitution of CO of the oxidized iron carbonyl, taking into account that the oxidation gives the species with a larger Lewis acidity. A more complex variant implying the accumulation of a relatively stable intermediates, *viz.*, iron carbonyl halides cannot be excluded, and the observed effect of DMF is due to their decomposition also occurring by the substitution mechanism.

One can assume that the observed increase in the yield of the adducts in the presence of DMF correlates in some way with the acceleration of decomposition of $Fe(CO)_5$. However, at the present stage of the investigation it is not possible to reveal this correlation, and a more detailed study should be performed to this end.

Nevertheless, some important conclusions related to the mechanism of the thermal Kharash reaction in the presence of $Fe(CO)_5$ can be made.

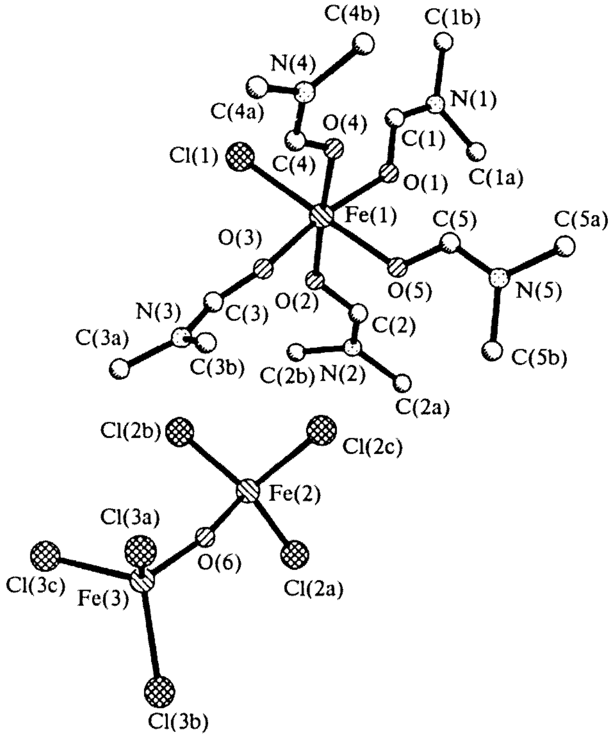

Fig. 1. Structure of complex **3**.

The data obtained by us indicate that in the generation of $^{\cdot}CCl_3$ radicals from CCl_3X under the action of $Fe(CO)_5$ on heating, the prior formation of $(Alkene)Fe(CO)_4$ and $(DMF)Fe(CO)_4$ complexes does not occur (see Table 1), as might be expected according to the schemes of redox-catalysis postulated previously.[2,9,10]

On the other hand, generation of the $^{\cdot}CCl_3$ radicals under thermal conditions also cannot be described by the mechanism accepted[11,12] for the photochemical reaction involving the formation of $Fe(CO)_4$. If this mechanism exists under thermal conditions, the rate of the reaction of $Fe(CO)_5$ with CCl_3X should be determined by the rate of the thermal decomposition of $Fe(CO)_5$, which is in contradiction with the data in Table 1 (entries *1* and *5—8*).

The photochemical mechanism for thermal conditions can also be excluded on the basis of another consideration. It was established by IR spectroscopy[8] that the thermal decarbonylation of $Fe(CO)_5$ proceeds synchronously with the elimination of all five CO groups. More precise methods demonstrate that the energy of the Fe—CO bond decreases in the series: $Fe(CO)_5 > Fe(CO)_4 > Fe(CO)_3 > Fe(CO)_2 > Fe(CO)$.[13] Therefore, $Fe(CO)_4$ and other coordinatively unsaturated carbonyls cannot be kinetically independent particles in the thermal reactions.

Thus, the pathways of photochemical and thermal generations of the $^{\cdot}CCl_3$ radical under the action of $Fe(CO)_5$ are different. In the photochemical Kharash reaction, preliminary coordination of an olefin and/or L with Fe^0 is quite possible.

Taking into account that under preparative conditions the reaction time is significantly longer than in this study (for example, see Refs. 1, 4), it is less probable that $Fe(CO)_5$ is a real catalyst involved in several cycles. The addition of DMF decreases this possibility significantly. The observed catalysis may be explained by the participation in the reaction of different iron compounds formed upon oxidation of $Fe(CO)_5$. This is confirmed by the activity of Fe^{II} carbonyl halides,[7] $FeCl_2$ complexes,[14] and the complexes of polynuclear, mixed $Fe^{II,III}$ chlorides of Fe [15] in the Kharash reaction.

Experimental

All of the reagents used were no less than chemically pure grade. Benzene was distilled over P_2O_5 under Ar. DMF was preliminarily kept over NaOH and distilled *in vacuo* under Ar. $Fe(CO)_5$ was used without additional purification. Freshly distilled CCl_3Br and CCl_4 were used in the reactions. TLC was carried out on SiO_2 plates (Merck 60 F_{254}). The ^1H NMR spectra were recorded with a Bruker WP-200 instrument with HMDS as the internal standard.

The decomposition of $Fe(CO)_5$ was studied with an apparatus consisting of a round-bottom flask (20 mL) connected through a reflux condenser and a washer filled with conc. H_2SO_4 with a gasometric burette (100 mL) filled with water. The lower part of the burette was connected with a funnel used for equilibration of the internal pressure with the atmospheric pressure. A batch of $Fe(CO)_5$ (*ca.* 0.065 g) (the mass of the batch was accurate within three significant figures), the corresponding ingredients, and benzene (10 mL) were placed in the flask. The burette was purged several times with pure N_2. Pure N_2 was passed through the system for 10 min at a moderate rate. The system was isolated, connected with the burette, and the residual gas volume was measured (V_r). The reaction mixture was heated rapidly to boiling and refluxed for a definite period. After that, the system was cooled to the ambient temperature and equilibrated with the atmospheric pressure. The total gas volume (V_s) was measured after 1 and 1.5 h. The difference in the measurements did not exceed a systematic error (0.5 mL). The increase in the gas volume $\Delta V = V_s - V_r$ was adjusted to the normal conditions, and the value obtained was used to calculate the yield of CO. Experimental conditions and experimental data are given in Table 1.

Phenyl β-bromo-α-trichloromethyldihydrocinnamate (2). A solution of compound **1** (3 g, 13.4 mmol), CCl_3Br (2.7 mL, 27.4 mmol), and BP (0.1 g, 0.41 mmol) in benzene (3 mL) was refluxed for 7 h. Three more portions of BP (0.1 g) after each 7 h were added and refluxing was continued. The hot

Table 2. Atomic coordinates (×10^4) and equivalent isotropic thermal factors (U_{iso}) in structure **3**

Atom	*x*	*y*	*z*	$U_{iso} \cdot 10^3/Å^2$
Fe(1)	4705(1)	2137(1)	1035(1)	24(1)
Cl(1)	4112(2)	1865(2)	−197(1)	40(1)
O(1)	3634(4)	3106(4)	1129(3)	27(2)
O(2)	5458(4)	3387(4)	853(3)	31(2)
O(3)	5853(4)	1218(4)	1108(3)	35(2)
O(4)	3974(4)	886(4)	1284(3)	30(2)
O(5)	5198(4)	2368(4)	2120(3)	27(2)
N(1)	2210(5)	3946(5)	875(3)	29(2)
N(2)	6091(5)	5004(5)	1100(3)	34(2)
N(3)	7207(5)	536(5)	920(4)	35(3)
N(4)	3711(5)	−833(5)	1390(4)	37(3)
N(5)	5061(4)	2299(5)	3287(3)	24(2)
C(1)	2767(7)	3134(6)	829(4)	28(3)
C(1a)	2601(7)	4869(7)	1304(5)	47(3)
C(1b)	1176(6)	3978(7)	538(5)	47(4)
C(2)	5679(6)	4157(7)	1268(4)	31(3)
C(2a)	6352(8)	5871(7)	1615(5)	60(4)
C(2b)	6365(7)	5102(7)	408(5)	50(4)
C(3)	6501(7)	1184(6)	760(4)	33(3)
C(3a)	7885(7)	428(8)	466(6)	58(4)
C(3b)	7299(7)	−172(7)	1539(5)	52(4)
C(4)	4193(6)	−42(6)	1221(4)	32(3)
C(4a)	4050(8)	−1905(6)	1362(6)	54(4)
C(4b)	2853(8)	−661(7)	1658(6)	66(5)
C(5)	4709(6)	2259(5)	2581(4)	26(3)
C(5a)	4456(6)	2192(7)	3812(4)	40(3)
C(5b)	6081(7)	2454(7)	3587(4)	43(3)
Fe(2)	8878(1)	3232(1)	1507(1)	31(1)
Fe(3)	10650(1)	1350(1)	1627(1)	24(1)
Cl(2a)	9523(3)	4764(2)	1867(2)	84(1)
Cl(2b)	8272(2)	3261(2)	298(1)	64(1)
Cl(2c)	7739(2)	2892(2)	2091(1)	46(1)
Cl(3a)	10310(2)	−165(2)	2075(1)	48(1)
Cl(3b)	12077(2)	1907(2)	2273(1)	37(1)
Cl(3c)	10737(2)	1132(2)	478(1)	43(1)
O(6)	9768(4)	2262(4)	1692(3)	45(2)

reaction mixture was filtered, cooled, and left for 12 h at 10 °C. The precipitate was filtered off, washed with a 1:1 hexane—benzene mixture, and recrystallized from a 2:1 hexane—benzene mixture giving compound **2** (2.4 g, 42.4 %), m.p. 134—134.5 °C. Found (%): C, 45.21; H, 2.77. $C_{16}H_{12}BrCl_3O_2$. Calculated (%): C, 45.99; H, 2.84. ^1H NMR ($CDCl_3$), δ: 4.63 (d, 1 H, $CHCCl_3$, J = 10 Hz); 5.70 (d, 1 H, CHBr, J = 10 Hz); 7.1—7.7 (m, ArH, 10 H).

X-ray analysis of 3 was carried out with a Siemens P3/PC diffractometer (Mo-Kα radiation, θ-2θ scanning, 293 K). Crystallographic parameters: molecular formula $C_{15}H_{35}Cl_7Fe_3N_5O_6$, molecular weight 797.2, space group $P_{2(1)n}$, monoclinic syngony, a = 14.272(20), b = 12.838(20), c = 18.834(30) Å, α = 90, β = 103.50(2), γ = 90°, V = 3355.5 Å^3, Z = 4, d = 1.578 g cm^{-3}. The number of reflections with $I > 3\sigma(I)$ was 2345, R = 0.0441, R_w = 0.0454. All structures were solved by the direct method and refined in the full-matrix anisotropic approximation for nonhydrogen atoms. Hydrogen atoms were revealed by differential Fourier synthesis and refined in the anisotropic approximation. The atomic coordinates are presented in Table 2. All calculations were performed using the SHELXTL program package.

The present work was financially supported by the International Science Foundation (Grants Nos. M2Q000 and M2Q300) and the Russian Foundation for Basic Research (Project No. 93-03-4497).

References

1. V. I. Tararov, T. F. Savel'eva, and Yu. N. Belokon', *Izv. Akad. Nauk, Ser. Khim.*, 1996, 649 [*Russ. Chem. Bull.*, 1996, **45**, 610 (Engl. Transl.)].
2. E. Ts. Chukovskaya, R. G. Gasanov, I. I. Kandror, and R. Kh. Frei'dlina, *Zh. Vsesoyuz. Khim. obshch. im. D. I. Mendeleeva*, 1979, **24**, 161 [*Mendeleev Chem. J.*, 1979, **24** (Engl. Transl.)].
3. R. Kh. Frei'dlina, F. K. Velichko, S. S. Zlotskii, D. L. Rakhmankulov, and A. B. Terent'ev, *Radikal'naya telomerizatsiya* [*Radical Telomerization*], Khimiya, Moscow, 1988, 288 pp. (in Russian).
4. V. I. Tararov, T. F. Savel'eva, Yu. T. Struchkov, A. P. Pisarevskii, N. I. Raevskii, and Yu. N. Belokon', *Izv. Akad. Nauk, Ser. Khim.*, 1996, 640 [*Russ. Chem. Bull.*, 1996, **45**, 600 (Engl. Transl.)].
5. A. Mittasch, *Z. angew. Chem.*, 1928, **41**, 827.
6. P. P. Singh and R. Rivest, *Can. J. Chem.*, 1968, **46**, 1773.
7. F. K. Velichko, *D. Sc. (Chem.) Thesis*, Institute of Organoelement Compounds, Acad. Sci. USSR, Moscow, 1980, 370 pp.
8. I. V. Spirina, A. V. Kholodalova, S. A. Sergeev, and V. P. Maslennikov, *Metalloorg. Khim.*, 1992, **5**, 1028 [*Organomet. Chem. USSR*, 1992, **5**, 499 (Engl. Transl.)].
9. A. B. Terent'ev, S. I. Gapusenko, and T. T. Vasil'eva, *Izv. Akad. Nauk, Ser. Khim.*, 1993, 1418 [*Russ. Chem. Bull.*, 1993, **42**, 1352 (Engl. Transl.)].
10. C. H. Bamford, *Reactivity, Mechanism and Structure in Polymer Chemistry*, John Wiley and Sons, London, New York, 1974.
11. R. G. Gasanov, L. V. Ivanova, and R. Kh. Frei'dlina, *Izv. Akad. Nauk USSR, Ser. Khim.*, 1983, 1045 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1983, **32**, 946 (Engl. Transl.)].
12. R. G. Gasanov, *Izv. Akad. Nauk USSR, Ser. Khim.*, 1986, 322 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1986, **35**, 295 (Engl. Transl.)].
13. V. N. Smirnov, *Kinet. Katal*, 1993, **34**, 591 [*Kinet. Catal.*, 1993, **34** (Engl. Transl.)].
14. J. Igbal, B. Bhatia, and N. Nayyar, *Chem. Rev.*, 1994, **94**, 519.
15. E. A. Lavrent'eva, V. I. Ponomarev, and I. P. Lavrent'ev, *Izv. Akad. Nauk USSR, Ser. Khim.*, 1990, 2794 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1990, **39**, 2534 (Engl. Transl.)].

Received October 30, 1995;
in revised form November 20, 1995