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Bimolecular Concerted Elimination as an Elementary Stage in Free-radical Reactions. Reaction of Organocobaloximes with Bromotrichloromethane*

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Abstract—In free-radical reaction of cis-β-phenylvinylcobaloxime with bromotrichloromethane the primary product, phenylacetylene, arises as a result of elimination, and further it adds the bromotrichloromethane. Similarly proceeds the reaction between β-phenylethylcobaloxime with bromotrichloromethane. The values of absolute rate constants and their relation to the nature of the axial ligand completely agree with the assumption that in the reactions in question similarly to the E2 mechanism of nucleophilic elimination the elimination occurs as one-stage bimolecular process with the simultaneous rupture of C–Co and C–H bonds.

It is undoubtedly of interest to investigate the reactivity in free-radical reactions of organocobaloximes $RCo(dmgH)_2L$ where R is hydrocarbon radical, dmgH is a dimethylglyoxime monoanion, L is a neutral organic ligand. These compounds are synthetic analogs of cobalamines, in particular, of vitamin B_{12}, and many reactions of these compounds simulate biochemical processes. The chemical behavior of cobalt complexes to a significant degree depends on the low strength of the σ-bond Co–C (80–100 kJ mol^{-1} [1]). As a result the Co–C bond easily undergoes homolysis yielding a cobalt-centered radical $^{\cdot}Co(dmgH)_2L$. On the one hand this radical shows low activity in the most free-radical reactions (save halogen abstraction). On the other hand the $^{\cdot}Co(dmgH)_2L$ species is a good leaving group in radical reactions. Therefore were successfully carried out relatively rare for organic chemistry reactions, e.g., allyl substitutions [2–4] and cyclization affording cyclopropane structures [5].

The reaction of benzylglyoximate cobalt complexes $PhCN_2Co(dmgH)_2L$ with some free-radical agents affords substitution products at carbon atom (S_H2) [6–9].

$$PhCH_2Co[dmgH)_2L + X^{\cdot} \rightarrow PhCH_2X + {}^{\cdot}Co(dmgH)_2L$$

$$X^{\cdot} = CCl_3,\ ArSO_2.$$

In preceding publications we reported on extensive studies of reaction kinetics of organocobaloximes and bromotrichloromethane at broad spectrum of ligand character and organic fragment structures [10–13]. The reaction of bimolecular homolytic substitution was shown to extend to alkylcobaloximes [13]. We developed a procedure for evaluation of relative [10] and absolute [12] rate constants of S_H2 reaction, and all the kinetic data were consistent with S_H2 mechanism. The comparison of the results obtained with the data on homolysis rate of the substrates studied led to conclusion that the main factors affecting the rate of S_H2 reactions was the dissociation energy of C–Co bond and the steric accessibility of the reaction site [13]. The relations between structure and kinetics were totally like those established for bimolecular nucleophilic substitution.

Taking into account the established similarity of free-radical and nucleophilic substitution reactions we investigated the reaction of bromotrichloromethane and *cis*-β-phenylvinylcobaloxime (**I**) expecting that the reaction would proceed as free-radical vinyl substitution. However the expected reaction product was not obtained neither at thermal nor at photochemical initiation. At the same time we found that the main reaction product of reaction between compound **I** (L = Py) and fivefold excess of bromotrichloromethane in chloroform at 100°C was 1-phenyl-3,3,3-trichloroprop-1-ene (**III**). Besides in the reaction mixture was found a small amount (about 2%) of phenylacetylene. It is presumable that phenylacetylene is a primary reaction product that further adds bromo-

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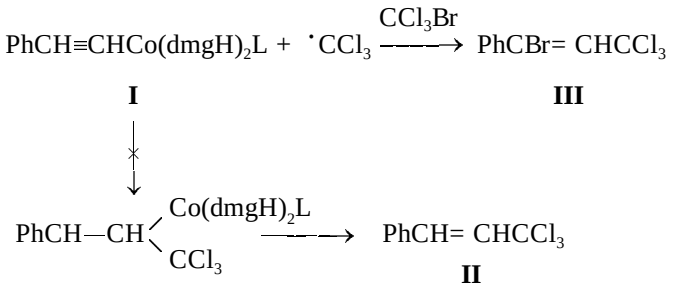


(1)

trichloromethane along free-radical mechanism to afford compound **III**.

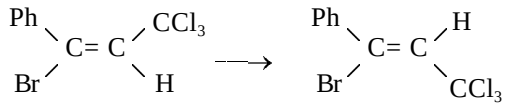
The reaction is initiated by thermolysis of the original cobaloxime **I**.

Further investigation of reaction (1) revealed that the direction of the process is notably affected both by temperature and by the presence in the system of alkylcobaloximes. At 50°C at the lack of free radical initiators compound **I** is stable, and no compound **III** or phenylacetylene form in the system. It is known [13] at the same time that the thermolysis rate of alkylcobaloximes under these conditions is sufficient for initiation of a free-radical process. The stability of compound **I** obviously is due to increase in the C–Co bond strength on going to vinylcobaloximes because of sp^2-hybridization of carbon atom. In this connection further we introduced into the reaction two substrates: phenylvinylcobaloxime (**I**) and benzylglyoximate complex $PhCH_2Co(dmgH)_2Py$ (**IV**). Since under conditions of concurrent reactions the stationary concentration of trichloromethyl radicals arising from reactions $RCo(dmgH)_2L \rightarrow R^{\cdot} + {}^{\cdot}Co(dmgH)_2L$ and $CCl_3Br + {}^{\cdot}Co(dmgH)_2L \rightarrow CCl_3^{\cdot}$ was determined by the rate of decomposition of the more reactive complex, we could expect that applying compound **IV** that decomposed with appreciable rate already at 40°C [10, 13] we would be able to perform reaction (1). Actually we found that at 47.7°C under conditions of concurrent reactions formed both phenylacetylene and product **III**. The study of dependence of reaction products composition on conversion showed that at the early stage of the reaction the phenylacetylene was the only reaction product, and kinetics of its formation fit the equation of the pseudofirst order. Later on formed product **III**, and the variation in time of phenylacetylene concentration is consistent with a kinetic scheme regarding it as an intermediate in the series of consecutive processes (Table 1). Thus all the data obtained evidence that the primary reaction product is phenylacetylene, and its further reaction with bromotrichloromethane affords product **III**.

The GLC analysis of the reaction mixtures revealed that their composition changes both in the course of reaction and at workup. At the early reaction stages the peak of compound **III** is lacking, but accumulates a substance with the retention time very close to that of compound **III**. As the reaction proceeds the relative amount of the unknown compound decreases, and occurs accumulation of product **III**. At further keeping of the reaction mixture the unknown substance completely disappears transformed into product **III**. We reckon that this is due to stereoisomerization of the reaction product in the course of the process. We have shown before [14] that the bromotrichloromethane first adds to methyl propiolate stereospecifically in trans-position, and then the primary product rearranges into a more stable stereoisomer. It is presumable that here the reaction also proceeds as trans-addition and then stereoisomerization of the primary product affords more stable stereoisomer **III**.

Table 1. Composition of products obtained in reaction of *cis*-β-phenylvinylcobaloxime (**I**) with bromotrichloromethane at 47.7°C

Time, h	$[PhC{\equiv}CH] \times 10^3$, mol l^{-1}	$[III] \times 10^4$, mol l^{-1}
0.33	0.08	0
0.58	0.13	0
0.83	0.16	0
1.08	0.16	0
1.5	0.19	0
2.0	0.30	0
3.5	0.44	0
4.5	0.48	0.5
9.5	0.53	2.0



III

β-Phenylethylcobaloxime (**V**) reacts with bromotrichloromethane in a similar way. First styrene is formed that further transforms into addition product **VI**.

$$PhCH{=}CHCo(dmgH)_2Py \xrightarrow{CCl_3Br} PhC{=}CH_2$$

$$\xrightarrow{CCl_3Br} PhCHBrCH_2CCl_3 \qquad (2)$$

Taking into account that free-radical elimination is a relatively rare phenomenon and its mechanism up till now is a subject to discussions we have thoroughly studied the kinetics of reactions (1) and (2) paying special attention to the dependence of the reaction rate on the character of the axial ligand L. Using the method of concurrent reaction we evaluated the k_{rel} at 47.7°C for the pair of compounds **I**/**IV** (Table 2).

$$PhCH{=}CHCo(dmgH)_2Py \xrightarrow{CCl_3Br} PhC{\equiv}CH$$

$$\longrightarrow PhCHBr{=}CHCCl_3$$

$$PhCH{=}CHCo(dmgH)_2Py \xrightarrow{CCl_3Br} PhCH_2CCl_3 \qquad (3)$$

The value of k_{rel} was calculated by the following formula:

$$\frac{k(\mathbf{I})}{k(\mathbf{IV})} = \frac{[PhCCH] + [PhCBr{=}CHCCl_3]}{[PhCH_2CCl_3]} \cdot \frac{[PhCH_2Co(dmgH)_2Py]}{[PhCH{=}CHCoCo(dmgH)_2Py]}$$

We revealed that the value k_{rel} is considerably affected by the concentration of free pyridine in the reaction system (Table 2). We already observed analogous dependence in the kinetic study of reaction between alkylcobaloximes and bromotrichloromethane. It was demonstrated that the effect of the free axial ligand on the reaction rate is due to the possible participation in the reaction of a pentacoordinate alkylglyoximate complex [13]. Therefore further we used only the values of the relative rate constants measured at large excess of pyridine. Since we already determined previously the value of the absolute rate constant for reaction of trichloromethyl radical with compound **IV** (L = Py) [13] we were able to calculate the absolute rate constant of the reaction between this radical and compound **I** (L = Py): $k_{abs} = 3.8 \times 10^3$.

Similarly were measured the relative rate constants of reaction between bromotrichloromethane and β-phenylethylglyoximate complexes **V** [reaction (2)] and complex **IV** [reaction (3)].

$$\frac{k(\mathbf{V})}{k(\mathbf{IV})} = \frac{[PhC{=}CH_2] + [PhCHBrCH_2CCl_3]}{[PhCH_2CCl_3]} \cdot \frac{[PhCH_2Co(dmgH)_2Py]}{[PhCH_2CH_2CoCo(dmgH)_2Py]}$$

The measured values of the relative rate constants for all ligands are listed in Table 3, and the calculated absolute rate constants are given in Table 4.

As seen from Table 3, variation of axial ligand significantly affects the rate of elimination. As we have shown before [13], the main cause of the change in reactivity at variation of the axial ligand is the alteration of the dissociation energy of the C–Co bond. Unlike reaction (1) the rate of reaction (2) is virtually insensitive to the addition of free axial ligand L. This may be connected with unlike stability of the hexacoordinate complexes **I** and **V**. For instance, as measured in [15], the association constant $RCo(dmgH)_2Py \rightleftarrows RCo(dmgH)_2 + Py$ in water at 25°C is for complex **IV** 500 times smaller than that for vinyl complex (R = $CH_3CH{=}CH$).

The kinetic data obtained are sufficient for considering the mechanism of elimination reaction that we had revealed. Analogous to ionic reactions three possible mechanisms should be taken into account.

(1) Unimolecular decomposition with initial homolysis of the C–Co bond followed by disproportionation in the radical pair (analogous to *E*1 mechanism in ionic reactions).

$$PhCH{=}CHCo[dmgH)_2L \rightarrow [PhCH{=}\dot{C}H$$

$$+ \dot{C}o(dmgH)_2L] \rightarrow PhC{\equiv}CH + HCo(dmgH)_2L$$

Table 2. Effect of pyridine addition on the relative rate constants *k*(**I**)/*k*(**IV**) in reaction of organocobaloximes with bromotrichloromethane

Time, h	[Py]/[**I**]	*k*(**I**)/*k*(**IV**)
0.17	0	156
0.33	0	156
0.58	0	156
0.75	0	104
0.22	0.3	121
0.3	0.3	107
0.48	0.3	127
0.12	1.0	18.5
0.3	1.0	26.7
0.48	1.0	21.5
0.75	1.0	20.4
0.33	4.0	9.2
0.67	4.0	9.4
0.67	8.0	7.1
1.0	8.0	7.3
0.5	12	7.1
0.75	12	7.5
1.33	12	7.1
0.17	15	7.3
0.32	15	7.1
0.48	15	6.7
0.72	15	7.3

It is assumed that olefins arise in thermolysis of primary and secondary cobalamines along this mechanism [16, 17]. But for reaction we studied this mechanism should be rejected: Firstly, it does not explain why complex **I** is stable at 47°C in the absence of trichloromethyl radicals but elimination reaction easily starts with it in the presence of benzyl complex **IV**. Secondly, absolute rate constants of homolysis are in the range $10^{-5} \times 10^{-7}$ s^{-1} [13], therefore they are by several orders of magnitude smaller than those of the reactions under study.

(2) Two-stage mechanism with hydrogen abstraction by the trichloromethyl radical with subsequent β-fragmentation of the radical yielding the elimination product (analogous to *E*1*sB* mechanism).

$$\mathrm{PhCH{=}CHCo(dmgH)_2L} + \dot{C}Cl_3$$

$$\rightarrow \mathrm{Ph\dot{C}{-}CHCo(dmgH)_2L} \xrightarrow[-\dot{C}o(dmgH)_2L]{} \mathrm{PhC{\equiv}CH}$$

In this scheme the limiting stage is the first one, since the hydrogen abstraction by trichloromethyl radical is irreversible [18].

Table 3. Relative rate constants *k*(**V**)/*k*(**IV**) in reaction of β-phenylethylcobaloximes with bromotrichloromethane

L	Time, h	[L]/[**V**]	*k*(**V**)/*k*(**IV**)
Py	0.17	0	8.6
Py	0.67	0	9.2
Py	1.33	0	8.6
Py	0.67	8	10.0
Py	1.0	8	9.4
Py	0.5	12	9.0
Py	0.75	12	8.8
Py	1.33	12	8.5
3-MePy	0.5	0	7.72
3-MePy	0.75	0	7.9
3-MePy	1.33	0	8.4
4-MePy	0.5	0	8.15
4-MePy	0.75	0	9.1
4-MePy	1.33	0	9.2
3-BrPy	0.5	0	5.35
3-BrPy	0.75	0	4.64
3-BrPy	1.33	0	5.14
3-BrPy	1.66	0	5.35
Im	0.5	0	11.75
Im	0.75	0	11.5
Im	1.33	0	11.0
PPh_3	0.5	0	6.16
PPh_3	0.75	0	6.66
PPh_3	1.33	0	6.62

Table 4. Absolute rate constants of reaction between β-phenylethylcobaloximes (**V**) and bromotrichloromethane (k_{elim}), of bimolecular homolytic substitution for complexes **IV** (k_{subst}), and constants of homolysis rate of complexes **IV** (k_{hom}) at 47.7°C

L	Py	3-MePy	4-MePy	3-BrPy	Im	PPh_3
$k_{elim} \times 10^{-3}$	4.6	4.6	5.7	7.5	4.6	32.4
$k_{subst} \times 10^{-2}$	5.2	5.7	6.5	14	4.0	50
$k_{hom} \times 10^{6}$	4.0	4.5	6.8	9.0	4.8	47

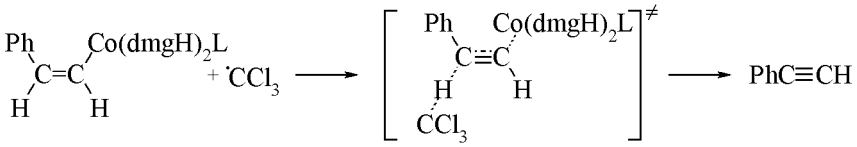
Two-stage mechanism was taken as the main one in the majority of publications on radical elimination reactions.

Therewith as the principal proof of stage-like process were regarded the data on the stereoselectivity of the reaction. It was found that nonstereoselective elimination occurred in reactions of β-bromosulfones [19] and β-bromosulfides [20] with trialkylstannyl radicals. In the cases where the elimination occurred stereoselectively Boothe *et al.*

suggested that the process was two-stage, and the stereoselectivity was due to intermediate formation of bridge-like radicals [21–23]. Unfortunately the lack of kinetic data does not permit considering the multistage mechanism as rigorously proved in the majority of the above publications.

Our data are not consistent with the two-stage mechanism. Firstly, in a reaction proceeding by this mechanism the overall rate of the process should be equal to that of free-radical hydrogen abstraction by trichloromethyl radical. For cyclohexane, toluene, and ethylbenzene these rates are respectively 79 [24], 2.9 [25] and 15 $mol^{-1}s^{-1}$ [26]. These values are considerably smaller than the figures we obtained for elimination reactions (Table 4). Secondly, if the elimination occurs in two stages, and the first one is limiting, then the variation of the leaving group should not affect the reaction rate as is observed in nucleophilic eliminations along *E*1*cB* mechanism. This also is in disagreement with our results (Table 4).

All results we obtained are logically understood in assumption that the reaction is a one-stage process going via transition state **VII** with concerted rupture of C–H and C–Co bonds analogously to the mechanism of bimolecular nucleophilic elimination *E*2.



VII

If the reaction follows this mechanism, a resemblance should be expected to the other processes where the limiting stage consists in the rupture of C–Co bond. This statement is quite consistent with the data of Table 4. An obvious similarity is seen between the rate of the reaction under study and both the rates of bimolecular substitution at carbon atom and organocobaloximes homolysis. The greater reactivity of the C–H bond as compared to reactions of hydrogen transfer is also quite understandable. Same as in *E*2 reactions were the process rate is notably higher than calculated from the kinetic acidity of the compound, the reaction is facilitated due to partial formation of the C=C bond in the transition state. Thus it can be considered as established that the reaction we studied proceeded along one-stage concerted mechanism of free-radical elimination E_R2.

There are published examples suggesting that the concerted mechanism of free-radical elimination is not an exception. For instance, it was shown in [27] that in reaction of dibutylmercury with trimethyl radicals formed in high yield 1-butene evidencing the enhanced reactivity of C–H bond in *2* position. The prevailing *anti*-elimination in the reaction of 3-deutero-3-trimethylstannylethane with trichloromethyl radical [28] and stereoselective course of some other elimination reactions [29–31] also may be interpreted within the framework of the one-stage concerted mechanism.

EXPERIMENTAL

^{1}H NMR spectra were recorded on spectrometer Tesla BS-567A from solutions in deuterochloroform. The GLC analyses were carried out on gas chromatograph Chrom-5 equipped with a flame-ionization detector, carrier gas argon, flow rate 30 ml min^{-1}, glass column 3000 × 2 mm, stationary phase 10% OV on Chromaton-N-Super, oven temperature 165–170°C. The composition of reaction mixtures was analyzed by GLC with the use of authentic reference compounds. The bromotrichloromethane was distilled before use through a Vigreux column (40 cm) collecting the fraction of bp 143–145°C. Phenylacetylene and (2-bromoethyl) benzene were distilled collecting fractions 143–145°C and 93–95°C (15 mm Hg) respectively. Chloroform of "pure for chromatography" grade was used without further purification.

***cis*-(2-Phenylvinyl)cobaloxime (I), 2-phenylethylcobaloximes (V), and benzylcobaloximes (IV).** Complex **I** was prepared along procedure [32] by reaction of phenylacetylene with a highly nucleophilic complex $Na[Co^I(dmgH)_2Py]$. The crystals of the complex were dried in a vacuum-desiccator in the presence of P_2O_5 and purified by column chromatography on silica gel, eluent acetone–ethyl acetate, 1:1. Yield 20%. ^{1}H NMR spectrum ($CDCl_3$, δ, ppm): 1.9 s (12H), 5.5 d (1H, *J* 8.9 Hz), 6.4 d (1H,

J 8.9 Hz), 7.1 m (5H), 7.3 m (2H), 7.7 m (1H). 8.5 m (2H).

Complex V (L = Py) was prepared by procedure [33] proceeding from (2-bromoethyl)benzene. The crystals of the complex were dried in a vacuum-desiccator in the presence of P_2O_5 and purified by column chromatography under the same conditions as above. Yield 60%. ^{1}H NMR spectrum ($CDCl_3$, δ, ppm): 1.7–1.9 m (4H), 2.1 s (12H), 7.1 m (5H), 7.3 m (2H), 7.6 m (1H), 8.6 m (2H).

Complexes **V** with various axial ligands (L = 3-MePy, 4-MePy, 3-BrPy, Im, PPh_3) were prepared and purified in the similar way. The ^{1}H NMR spectra are similar to that of complex **V** (L = Py) save the signals from the axial ligands. The synthesis of benzylglyoximate complexes (**IV**) (L = Py, 3-MePy, 4-MePy, 3-BrPy, Im, PPh_3) we described elsewhere [11]. The purity of all complexes was checked by TLC on Silufol-UV plates, eluent acetone–ethyl acetate, 1 : 1.

1-Bromo-1-phenyl-3,3,3-trichloropropene (III) and 1-bromo-1-phenyl-3,3,3-trichloropropane (VI). Compound **III** was obtained by addition of bromotrichloromethane to phenylacetylene at photochemical initiation (UV lamp of moderate pressure) in a quartz tube at 30–35°C within 20 h. The conversion of phenylacetylene according to GLC data is nearly quantitative. On completing the reaction the excess bromotrichloromethane was removed in a vacuum at room temperature, the residue was distilled in a vacuum (0.2 mm Hg) at 70°C. According to GLC the reaction product contained 92% of compound **III** and 8% of impurity (presumably $C_6H_5CCCl_3$). ^{1}H NMR spectrum (CCl_4, δ, ppm): 6.91 s and 6.95 s (overall 1H), 7.18–7.35 m (5H). Found, %: C 36.60; H 2.03. $C_9H_6BrCl_3$. Calculated, %: C 35.98; H 2.01.

Compound **VI** was prepared under similar conditions by addition of bromotrichloromethane to freshly distilled styrene. The conversion of the initial alkene attained 85%. The excess reagents were distilled off, the residue was distilled in a vacuum (0.3 mm Hg) at 100°C. The obtained adducts mixture contained 85% of compound **VI** and 15% of 1-phenyl1,3,3,3-tetrachloropropane [34]. Yield 60%, mp 49–51°C. ^{1}H NMR spectrum ($CDCl_3$, δ, ppm): 3.66 d (2H, *J* 6.5 Hz), 5.25 t (1H, *J* 6.5 Hz), 7.05–7.35 m (5H).

Kinetic measurements along procedure of concurrent reactions. Into an ampule of 0.5 ml capacity was charged 0.25 ml of 0.1 M chloroform solution containing complexes, internal reference (*o*-dibromobenzene), and fivefold excess of bromotrichloromethane. The solvent was preliminary freed of oxygen traces. The ampule was flushed with argon at 0°C, sealed, and placed into a thermostat at 47.7°C. Intermittently the content of ampules was passed through short (3–4 cm) column packed with silica gel to remove cobalt complexes (eluent dichloromethane). The solution obtained was cautiously evaporated to a volume of 0.2–0.5 ml, and the products were subjected to GLC.

Study of material balance in reaction of complexes I and V with bromotrichloromethane. The reaction mixture of complexes **I** and **IV** with bromotrichloromethane in deuterochloroform after heating to 47.7°C for 20 h was subjected to GLC and ^{1}H NMR. In the ^{1}H NMR spectrum the signals of vinyl protons of the original complex **I** were lacking evidencing virtually total conversion thereof. According to GLC from 0.226 mmol of the original complex formed 0.017 mmol of phenylacetylene and 0.199 mmol of compound **III** corresponding to overall yield of reaction products 95%. Similarly were analyzed the products of reaction between complexes **V** and bromotrichloromethane. Chromatographic yield of the reaction products amounted to 98–100%.

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