Study of the mechanism of the addition of benzyl bromide to trimethylvinylsilane in the presence of the $Fe(CO)_5$ —DMF system

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The general kinetics of the addition of benzyl bromide to trimethylvinylsilane in the presence of the $Fe(CO)_5$ —DMF system has been studied. The reaction orders with respect to each reagent found in the study correspond to a radical chain mechanism of the process. The metal-complex system takes part only in the initiation stage and only at a strictly defined ratio of the components.

Key words: benzyl bromide, trimethylvinylsilane, addition; radicals; metal-complex initiation; kinetics; mechanism.

The use of metal-complex systems to initiate radical addition and telomerization reactions involving substrates that react due to cleavage of the C-Hal bond has opened new prospects for the synthesis of polyfunctional organohalogen compounds.¹ The initiators based on $Fe(CO)_5$ with the addition of a nucleophilic cocatalyst (DMF, HMPA, PrⁱOH) are particularly interesting. It has been shown for a number of examples that iron salts and $Fe(CO)_5$ participate only in the initiation stage. However, certain data imply that, at least for reactions involving polyhalomethanes, a metal-complex system, e.g., $Fe(CO)_5$ -DMF, not only initiates the reactions but also takes part in the chain transfer step, thus significantly facilitating the transfer of halogen to the growing radical.² The synthetic use of these systems has proven to be useful, since reactions with organohalogen compounds whose C-Hal bonds cannot be cleaved under the conditions of peroxide initiation become possible. Moreover, telomerization with the use of the above systems is accompanied by an abrupt shift in the telomer distribution toward the lower members of the series.² The investigation of the mechanism of these reactions by the methods of general kinetics has shown that its nature (a radical chain mechanism or redox catalysis) depends substantially on the nature of the metal, the complex composition, and the type of bond to be cleaved. Most of the studies have been carried out with complexes containing different ligands: $[Mo_{2}(CO)_{6}(\eta^{5}-C_{5}H_{5})_{2}],^{3} [Cr(CO)_{3}(\eta^{6}-C_{10}H_{8})],^{4} [RuCl_{2}(PPh_{3})_{3}],^{5} [Cr(CO)_{\underline{6}}],^{6}$

and $[Fe_2(CO)_4(\eta-C_5H_5)_2]^7$

However, there are no data on the mechanisms of action of systems such as $Fe(CO)_5$ coupled with a nucleophilic cocatalyst, which are the most easily available and the most efficient in radical-complex processes. The present kinetic study deals with the addition of

benzyl bromide (BB) to trimethylvinylsilane (TMVS) in the presence of the $Fe(CO)_5$ -DMF system. We have previously studied this reaction in relation to synthesis.⁸ It was shown that the reaction proceeds with sufficient selectivity and with a satisfactory yield. Telomerization does not occur in this case either, and the reaction results in the $C_6H_5CH_2CH_2CH_2CHBrSiMe_3$ adduct, a minor amount of $C_6H_5CH_2CH_2CH_2SiMe_3$, and dibenzyl. Under the conditions chosen in the present kinetic study, unidentified products are formed in minor amounts.

The relative kinetics data⁹ allowed us to obtain evidence that the addition step in the process studied proceeds by a free radical mechanism. The formation of benzyl radicals is corroborated by the identification of dibenzyl in the reaction mixture⁸ and by the detection of C_6H_5 CH₂ radicals by means of ESR in the analogous reaction involving benzyl chloride.¹⁰

It is most likely that the reaction under study occurs according to one of two mechanisms, *viz.*, a radical chain mechanism [Scheme 1, steps (1)-(6)] or a catalytic mechanism [redox catalysis, *cf.* Scheme 1, steps (1)-(3), (5), and (7)].

Treatment of this scheme with the method of quasistationary states and starting with condition that T_1^{Br} is the principal reaction product while T_1^{H} is formed in a much lower amount than T_1^{Br} , *i.e.*, $d[T_1^{Br}]/dt \gg$ $d[T_1^{H}]/dt$, led to the expressions [(8a) and (8b)] for the rate of adduct formation in the case of the radical chain mechanism.

Two cases were considered: a) when the [FeL] intermediate does not accumulate during the reaction but rather reacts with BB as it forms [Eq. (8a)]; b) when the formation of [FeL] occurs very quickly and is completed within the initial period of the reaction [Eq. (8b)].

Scheme 1

$$Fe(CO)_{5} + x DMF \xrightarrow{k_{1}} [Fe(CO)_{5-x}(DMF)_{x}] + x CO,$$
(1)
[FeL]

$$[FeL] + C_6H_5CH_2Br \xrightarrow{k_2} [Fe(CO)_{4-x}(DMF)_xBr] + C_6H_5\dot{C}H_2 + CO, \qquad (2)$$

S [FeLBr]

$$C_{6}H_{5}\dot{C}H_{2} + CH_{2}=CHSiMe_{3} \xrightarrow{k_{3}} C_{6}H_{5}CH_{2}CH_{2}\dot{C}HSiMe_{3}, \qquad (3)$$

$$M \qquad \dot{R}$$

$$\dot{\mathbf{R}} + \mathbf{C}_{6}\mathbf{H}_{5}\mathbf{C}\mathbf{H}_{2}\mathbf{B}\mathbf{r} \xrightarrow{k_{4}} \mathbf{C}_{6}\mathbf{H}_{5}\mathbf{C}\mathbf{H}_{2}\mathbf{C}\mathbf{H}_{2}\mathbf{C}\mathbf{H}\mathbf{B}\mathbf{r}\mathbf{S}\mathbf{i}\mathbf{M}\mathbf{e}_{3} + \mathbf{C}_{6}\mathbf{H}_{5}\dot{\mathbf{C}}\mathbf{H}_{2}, \qquad (4)$$

$$\dot{R}$$
 + DH $\xrightarrow{k_5}$ C₆H₅CH₂CH₂CH₂SiMe₃ + \dot{D} , (5)
T₄^H

$$2 C_6 H_5 \dot{C} H_2 \xrightarrow{k_6} (C_6 H_5 C H_2)_2, \tag{6}$$

$$\dot{\mathbf{R}}$$
 + [FeLBr] $\xrightarrow{k_7}$ C₆H₅CH₂CH₂CHBrSiMe₃ + [Fe(CO)_{4-x}(DMF)_x], (7)

where DH is a hydrogen donor.

$$v(T_1^{Br}) = \frac{d[T_1^{Br}]}{dt} = \frac{k_3 k_1^{1/2}}{k_5^{1/2}} [Fe(CO)_5]_0^{1/2} [DMF]_0^{x/2} [M]_0 \quad (8a)$$

$$v(T_1^{Br}) = \frac{k_3 k_2^{1/2}}{k_6^{1/2}} [FeL]_0^{1/2} [S]_0^{1/2} [M]_0$$
(8b)

The following expressions for the rate of adduct formation under the redox catalysis conditions were derived using the same assumptions [Eq. (9a) and (9b), respectively]:

$$v(T_1^{Br}) = k_1[Fe(CO)_5]_0[DMF]_0^x$$
 (9a)
 $v(T_1^{Br}) = k_2[FeL]_0[S]_0$ (9b)

One can see from the above expressions that it is possible to distinguish between the two mechanisms by studying the concentration dependencies of the reaction rate with respect to each of the reagents and determining the orders of the respective reactions.

Results and Discussion

The kinetic study was performed using the method of initial rates. The experimental data on the determination of reaction orders for each reagent, treated according to the procedure reported in ref. 11, are presented in Figures 1-5.

As is seen from Fig. 1 (curve *I*), the dependence of the rate of formation of the T_1^{Br} adduct on TMVS concentration corresponds satisfactorily to a first order reaction ($n_c = 0.82 \pm 0.04$). The study of the dependence of $v(T_1^{Br})$ on the initial concentration of $C_6H_5CH_2Br$ (Fig. 2, *I*) afforded an order of about one half ($n_c = 0.59 \pm 0.04$). Thus, the experimental data are in agreement with Eq. (8b), which suggests that the reaction proceeds according to a radical chain mechanism. It was most interesting to study the dependence of



Fig. 1. Dependence of the logarithm of reaction rates on $\log[CH_2=CHSiMe_3]_0$: *I*, $\log v(T_1^{Br})$; *2*, $\log v(T_1^{H})$. $[CH_2=CHSiMe_3]_0 = 0.05 \div 0.5 M$; $[C_6H_5CH_2Br]_0 = 0.1 M$; $[Fe(CO)_5]_0 = 0.01 M$; $[DMF]_0 = 0.03 M$.



Fig. 2. Dependence of the logarithm of reaction rates on $\log[C_6H_5CH_2Br]_0$: *1*, $\log v(T_1^{Br})$; *2*, $\log v(T_1^{H})$. $[C_6H_5CH_2Br]_0$ = 0.05÷0.75 *M*; $[CH_2=CHSiMe_3]_0$ = 0.322 *M*; $[Fe(CO)_5]_0$ = 0.01 *M*; $[DMF]_0$ = 0.03 *M*.

logv

the reaction rate, $v(T_1^{Br})$, on the concentrations of the components of the Fe(CO)₅-DMF initiating system, as well as on its total concentration, when the ratio $[DMF]_0$: $[Fe(CO)_5]_0 = 3$ was constant. In the former two cases, when variation of the concentration of one of the components severely violated the usual ratio employed for this system, the dependence was rather complicated (Figs. 3 and 4). The points obtained in the $\log v(T_1^{Br}) - \log [Fe(CO)_5]_0$ coordinates (Fig. 3) do not lie on a straight line. One of the possible explanations for this fact may be inhibition of the reaction when there is a high excess of DMF with respect to $Fe(CO)_5$. In fact, the study of the dependence of the reaction rate on DMF concentration revealed that $v(T_1^{Br})$ decreased with increasing [DMF] (Fig. 4). Moreover, one can see from the plot that $v(T_1^{Br})$ is almost constant at $[DMF]_0$: $[Fe(CO)_5]_0$ ratios of 1-3 [the maximum value of $v(T_1^{Br})$] or 10-30 [the minimum value of $v(T_1^{Br})$]. The shape of the curve makes it possible to assume that a different number of DMF molecules are coordinated to the iron atom at different $[DMF]_0$: $[Fe(CO)_5]_0$ ratios, which changes the properties of the initiating complex. We consider that while the $[DMF]_0$: $[Fe(CO)_5]_0$ ratio remains constant, the composition of the [FeL] intermediate formed in the first reaction step [cf. Scheme 1, Eq. (1)] also remains unchanged. The dependence of



Fig. 3. Dependence of $\log v(T_1^{Br})$ on $\log[Fe(CO)_5]_0$. $[Fe(CO)_5]_0$ = 0.0025÷0.03 *M*; $[DMF]_0$ = 0.09 *M*; $[C_6H_5CH_2Br]_0$ = 0.1 *M*; $[CH_2=CHSiMe_3]_0$ = 0.3 *M*.

the reaction rate, $v(T_1^{Br})$, on the total concentration of the initiating system, when the concentration is changed but the ratio $[DMF]_0$: $[Fe(CO)_5]_0 = 3$ is constant, is linear in logarithmic coordinates (Fig. 5). Thus, the kinetic data confirm the observation made previously in synthetic studies that the successful course of the principal reaction, accompanied by a minor amount of byproducts, requires that the ratio of components in the initiating system should be kept within rather a narrow



Fig. 4. Dependence of $v(T_1^{Br})$ on $[DMF]_0$. $[DMF]_0 = 0.015 \div 0.45 \ M$; $[Fe(CO)_5]_0 = 0.015 \ M$; $[C_6H_5CH_2Br]_0 = 0.1 \ M$; $[CH_2=CHSiMe_3]_0 = 0.3 \ M$.



Fig. 5. Dependence of $\log v(T_1^{Br})$ on $\log[Fe(CO)_5 - DMF]_0$ at Fe(CO)₅:DMF = 1:3. $[Fe(CO)_5 - DMF]_0 = 0.025 \div 0.02 M$; $[C_6H_5CH_2Br]_0 = 0.1 M$; $[CH_2 = CHSiMe_3]_0 = 0.3 M$.

range, 1–3. This requirement probably arises from the composition of the intermediate complex. As follows from Scheme 1, presuming that [FeL] reacts with one BB molecule to give one benzyl radical, the reaction order with respect to [FeL] should be 1/2. However, the experimentally determined reaction order with respect to the initiating system was about 1/4 ($n_c = 0.26\pm0.03$).

This suggests that the formation of the [FeL] active complex, whose concentration under the conditions studied is directly proportional to $[Fe(CO)_5]^{1/2}$, has a rather complicated mechanism and, probably, consists of multiple steps.

It was also of interest to study how the rate of formation of T_1^{H} , $v(T_1^{H})$, depends on the concentrations of the reagents. The appearance of T_1^{H} in the reaction products is due to the presence of a hydrogen donor. BB and TMVS, for example, can serve as hydrogen donors. Taking into account the above conditions used to derive Eq. (8b), the rate $v(T_1^{H})$ of the radical chain reaction may be represented by the Eq. (10).

$$v(\mathbf{T}_{1}^{\mathbf{H}}) = \frac{k_{5}k_{3}k_{2}^{1/2}}{k_{4}k_{6}^{1/2}} \cdot \frac{[\text{FeL}]_{0}^{1/4}[\mathbf{M}]_{0}[\mathbf{DH}]_{0}}{[\mathbf{S}]_{0}^{1/2}}$$
(10)

As follows from the experimental data (see Fig. 1,2), the reaction under consideration is second order with respect to the monomer ($n_c = 1.97$). Thus, one may suppose that TMVS is the hydrogen donor ([DH] = [M]). A study of the dependence of $v(T_1^{\text{H}})$ on the initial concentration of $C_6H_5CH_2Br$ (Fig. 2,2) revealed the reaction order to be close to -0.5 ($n_c = 0.41$). Thus, the kinetic data for the formation of T_1^{H} also imply the free radical mechanism.

Proceeding from the dependencies of $v(T_1^{Br})$ on $[M]_0$, $[S]_0$, and $[FeL]_0$, we found the following apparent reaction rate constants: $3.57 \cdot 10^{-6} \text{ s}^{-1}$, 5.19 \cdot 10⁻⁶ L^{-1/2} mol^{1/2} s⁻¹, and 5.77 \cdot 10⁻⁶ L^{-3/4} mol^{3/4} s⁻¹, respectively. The overall reaction rate constant was determined taking into account the experimental values of n_C with respect to the concentrations of all of the reagents: $k_{ov} = (5.0\pm0.7) \cdot 10^{-5} \text{ L}^{3/4} \text{ mol}^{-3/4} \text{ s}^{-1}$ ($k_{ov} = k_3 k_2^{1/2} / k_6^{1/2}$).

The results obtained in the kinetic study allowed us to establish the rate constants for the individual steps of the reaction as well as the reaction mechanism. Thus, Scheme 1 implies the relation

$$\frac{v(T_1^{Br})}{(v(DB))^{1/2}} = k_3 \frac{[M]_0}{k_6^{1/2}} , \qquad (11)$$

from which k_3 can be calculated. The rate of dibenzyl formation determined in a series of experiments at different values of $[M]_0$ was found to be $(4.3\pm 0.2) \cdot 10^{-7}$ L mol⁻¹ s⁻¹. As would be expected, this rate is virtually independent of $[M]_0$. The value of $k_6 = 4 \cdot 10^{10}$ L mol⁻¹ s⁻¹ was derived from the known rate constant for the recombination of benzyl radicals in cyclohexane¹² with consideration of the viscosity of *n*-hexane and the reaction temperature, using the Debye equation for the rate constants of diffusion-controlled reactions: $k = 8RT/(3000\eta)$ (cf. ref. 13). Treatment of relation (11) by the least-squares method afforded the rate constant for the addition of benzyl radicals to TMVS, $k_3 = (1.2\pm 0.1) \cdot 10^3$ L mol⁻¹ s⁻¹.

The constant for the initiation rate, $k_2 = 6.9 \cdot 10^{-5} \text{ L}^{1/2} \text{ mol}^{-1/2} \text{ s}^{-1}$, was determined from the expression for k_{ov} , using the calculated values of k_6 and k_3 .

As a whole, we have obtained evidence that the reaction of interest proceeds by a free-radical chain mechanism rather than by a redox catalysis mechanism. The ratio of the components of the $[Fe(CO)_5-DMF]$ system, which is involved only in the initiation step, should be maintained in the range 1 : $(1\div3)$.

Experimental

GLC analyses were carried out on a LKhM-80 chromatograph (1500×3 mm steel column filled with 15 % SKTFT-50Kh on Chromaton N-AW (0.16–0.20 mm)) with helium (60 mL min⁻¹) as the carrier gas and a catharometer as the detector. The temperature program was 150 \rightarrow 200 °C (6 degrees min⁻¹).

The starting reaction mixtures were prepared using *n*-hexane as the solvent. The solvent was dried with a NaA zeolite and distilled over metallic Na in a stream of Ar. TMVS was washed with water, dried with $CaCl_2$ and then with melted KOH, and distilled in a stream of Ar in the vacuum of a water-jet pump. BB was obtained by bromination of toluene with elementary bromine in the presence of benzoyl peroxide, isolated by double vacuum fractionation with the use of a 20 cm deflegmator in a stream of Ar, and passed through a column with silica gel. Technical grade $Fe(CO)_5$ was used without special treatment. The starting reaction mixture was prepared in a volumetric flask (V = 100 mL) and then diluted with *n*-hexane to 100 mL.

The solution was poured in 2 mL portions into glass ampules, which were degassed by several freezing—evacuation—thawing cycles under an argon atmosphere and sealed. The reaction was carried out in a thermostatted oil bath at 140 °C. In order to determine the concentrations of the original compounds and the reaction products by means of GLC analysis, the ampules with the reaction mixtures were withdrawn from the oil bath at equal time intervals and quickly cooled.

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