RELATIVE KINETICS OF THE RADICAL ADDITION OF BENZYL BROMIDE TO UNSATURATED COMPOUNDS

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The relative rate constants of the addition of the $C_6H_5CH_2$ *radical to unsaturated compounds* $CH_2{=}CHX$ *(X =* C_4H_9*,* $SiMe_3$*,* CF_3*,* CO_2Me*, CN) were determined under the conditions of initiation by the* $Fe(CO)_5$ *+ DMF system or by benzoyl peroxide. Depending on the values of the relative addition rate constants, the monomers can be arranged into the following series (X):* $CF_3 \approx C_4H_9 < SiMe_3 < CO_2Me < CN$*. The relatively nucleophilic character of the benzyl radical has been shown. It was found that under the initiation conditions by the* $Fe(CO)_5$ *+ DMF system, the addition stage proceeds by a free radical mechanism.*

Keywords: *radical addition, relative kinetics, benzyl bromide, benzyl radical, unsaturated compounds, iron pentacarbonyl, dimethylformamide.*

The study of the kinetics of the radical addition makes it possible to obtain a quantitative evaluation of the reactivity of the radicals at the stage of addition to monomers and also on using α-olefins $CH_2{=}CHX$ containing substituents X of variegated polarities, and to qualitatively evaluate the polar characteristics of the radicals. This approach is of particular interest in the investigation of reactions which can be obtained under the conditions of a peroxide (or UV), or a metallocomplex (MCI) initiation, where a comparison of the data on the relative kinetics of the addition stage under various initiation conditions gives additional means for the study of the mechanism of the occurrence of the separate reaction stages under the MCI conditions.

We have previously carried out the reactions of benzyl bromide with $CH_2{=}CHX$ monomers (X = C_4H_9, $SiMe_3$, CF_3, CO_2Me, CN) with initiation by the $Fe(CO)_5$ + DMF (HMPA) system [1]. The initiating systems based on $Fe(CO)_5$ are widely used for reactions proceeding with the splitting of the C−Hal bond [2], which attracts continued interest in the investigation of the mechanism of their action.

We have studied the relative kinetics of the addition of the benzyl radical to the above-named monomers under the conditions of competitive reactions, in which the addition of $C_6H_5CH_2$ to vinyltrimethylsilane (VTMS) was chosen as the standard process. The relative rate constants of the addition were obtained under the conditions of initiation by the $Fe(CO)_5$ + DMF system (140 and 100°C) and, moreover, for one pair of monomers (1-hexene−VTMS) the kinetic investigations were also carried out with the initiation by benzoyl peroxide (BP) (100°C). The main series of experiments was carried out at 140°C. For comparison of the kinetic data obtained under the conditions of peroxide and MC-initiation, parallel series of experiments [with BP and $Fe(CO)_5$ + DMF] were carried out at 100°C. The experiments were carried out under strictly controlled conditions at relatively low conversions of the initial reagents (up to 20%), at minimal concentrations of the MCI components. The variation of the ratio of the concentrations of the monomers and the monomer/substrate ratio was carried out in intervals ensuring the maximal formation of the adducts and telomers and the minimal formation of by-products of the reaction (in particular, dibenzyl — a recombination product of the benzyl radicals).

The general scheme of competitive reactions, proceeding with the simultaneous use of two monomers is given below:

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$$C_6H_5CH_2Br \xrightarrow{Fe(CO)_5 + DMF} C_6H_5\dot{C}H_2,$$

$$C_2H_5\dot{C}H_2 + CH_2{=}CHSiMe_3(M^{SiMe_3}) \xrightarrow{k_{add}^{SiMe_3}} C_6H_5CH_2CH_2\dot{C}HSiMe_3\,(R_1^{SiMe_3}),$$

$$R_1^{SiMe_3} \xrightarrow[DBr]{k_{tr\ 1}^{SiMe_3}} C_6H_5CH_2CH_2CHBrSiMe_3(T_1^{SiMe_3}),$$

$$R_1^{SiMe_3} + nM^{SiMe_3} \xrightarrow{k_{prop,\,n}^{SiMe_3}} C_6H_5CH_2(CH_2CHSiMe_3)_nCH_2\dot{C}HSiMe_3(R_{n+1}^{SiMe_3}),$$

$$R_{n+1}^{SiMe_3} \xrightarrow[DBr]{k_{tr,\,n+1}^{SiMe_3}} C_6H_5CH_2(CH_2CHSiMe_3)_{n+1}Br\,(T_{n+1}^{SiMe_3}),$$

$$C_6H_5\dot{C}H_2 + CH_2{=}CHX(M^X) \xrightarrow{k_{add}^X} C_6H_5CH_2CH_2\dot{C}HX(R_1{}^X),$$

$$R_1{}^X \xrightarrow[DBr]{k_{tr\ 1}^X} C_6H_5CH_2CH_2CHBrX\,(T_1{}^X),$$

$$R_1{}^X + nM^X \xrightarrow{k_{prop,\,n}^X} C_6H_5CH_2(CH_2CHX)_nCH_2\dot{C}HX\,(R_{n+1}^X),$$

$$R_{n+1}^X \xrightarrow[DBr]{k_{tr,\,n+1}^X} C_6H_5CH_2(CH_2CHX)_{n+1}Br\,(T_{n+1}^X),$$

where X = C_4H_9, CO_2Me, CF_3, CN; k_{tr} is the transfer rate constant, DBr is the donor bromine at the chain transfer stage.

To calculate the relative addition rate constants (k_{add}), we used expression (1), which was deduced on the basis of the above scheme of reactions using a method of quasistationary concentrations:

$$\frac{k_{add}^X}{k_{add}^{SiMe_3}} = \frac{\sum[T^X]}{\sum[T^{SiMe_3}]} \cdot \frac{[M^{SiMe_3}]_0}{[M^X]_0}, \tag{1}$$

where $\Sigma[T^X]$ and $\Sigma[T^{SiMe_3}]$ are the overall molar concentration of adducts and telomers obtained as a result of the addition of the benzyl radical to the monomer M^X and VTMS, respectively; $[M^X]_0$ and $[M^{SiMe_3}]_0$ are molar concentrations of the monomer M^X and VTMS in the initial reaction mixture, respectively.

To calculate the addition rate constants of the benzyl radical to the monomers, we evaluated the content of adducts and telomers in the reaction medium, i.e., the end products of the reaction. We assumed that the majority of the adduct-radicals are eventually converted into adducts and telomers, which were identified and accounted for in the calculation.

In the study of the reaction mixtures of the competitive reactions by means of chromato-mass spectrometry it was found that in the case of the VTMS–acrylonitrile and VTMS–methyl acrylate pairs, cotelomers are formed in substantial amounts. The only cotelomer formed in the benzyl bromide + VTMS + acrylonitrile system was isolated in a pure state, and it was shown using ^{13}C NMR that it has the structure of $C_6H_5CH_2CH_2CH(CN)CH_2CHBrSiMe_3$ ($T_2{}^{CN,SiMe_3}$) can be represented by the scheme:

$$C_6H_5\dot{C}H_2 + CH_2{=}CHCN \xrightarrow{k_{add}^{CN}} C_6H_5CH_2CH_2\dot{C}HCN\ (R_1^{CN}),$$

$$R_1^{CN} + CH_2{=}CHSiMe_3 \rightarrow C_6H_5CH_2CH_2CH(CN)CH_2\dot{C}HSiMe_3(R_2^{CN,\,SiMe_3}),$$

$$R_2^{CN,\,SiMe_3} \xrightarrow{DBr} C_6H_5CH_2CH_2CH(CN)CH_2CHBrSiMe_3\,(T_2^{CN,\,SiMe_3}).$$

In this case, in accordance with the polar characteristics of the monomers, a complete alternation is observed — the electrophilic adduct radical $R_1{}^{CN}$ adds only to the nucleophilic VTMS, giving the only cotelomer $T_2{}^{CN,SiMe_3}$, while the homotelomers T_2 are absent. In the case of the benzyl bromide + VTMS + methyl acrylate system, among the telomers with two monomeric units, also cotelomer $T_2{}^{CO_2Me,SiMe_3}$ is formed and in addition one homotelomer $T_2{}^{CO_2Me,CO_2Me}$, but their proportion in the sum of the reaction products is considerably smaller. Considering the similarity of the polar characteristics of acrylonitrile and methyl acrylate, in this case the structure of the telomer $T_2{}^{CO_2Me,SiMe_3}$ was accepted by analogy: $C_6H_5CH_2CH_2CH(CO_2Me)CH_2CHBrSiMe_3$. The establishment of the structure of the cotelomers made it possible to take into account the corresponding amount of the adduct-radicals $C_6H_5CH_2CH_2CHCN$ and $C_6H_5CH_2CH_2CHCO_2Me$ formed in the reaction, by calculating the relative rate constants of the addition reaction.

TABLE 1. Relative Addition Rate Constants of the $C_6H_5CH_2$ Radical to 1-Alkenes and Conditions of Carrying Out the Kinetic Experiments

M^X	$\frac{(M^X + M^{SiMe_3})}{S^*}$, mole/mole	Initiator, mole % wrt S*	T, °C	Conversion of S,*%	Telomers in the reaction products, %	$\frac{[M^{SiMe_3}]_0}{[M^X]_0}$, mole/mole	$\frac{\sum[T^X]}{\sum[T^{SiMe_3}]}$, mole/mole	$\frac{k_{add}^X}{k_{add}^{SiMe_3}}$
$CH_2=CHC_4H_9$	5.9–6.4	$Fe(CO)_5$ 2% + + DMF 6%	140	8–11	70–80	0.20–3.22	1.57–0.08	0.29±0.04
»	6.0–6.4	»	100	0.3–0.6	85–90	0.21–1.64	1.57–0.19	0.29±0.04
»	5.9–6.3	BP 2%	100	2–4	70–80	0.09–2.22	2.74–0.12	0.26±0.01
$CH_2=CHCF_3$	5.8–6.2	$Fe(CO)_5$ 2% + + DMF 6%	140	7–15	60–80	0.11–2.18	2.93–0.06	0.22±0.08
» »	5.9–6.4	»	100	3–6	35–65	0.11–1.88	2.64–0.10	0.23±0.04
$CH_2=CHCO_2Me$	6.0–6.4	»	140	10–18	90–95	0.51–5.03	25.11–2.29	11.9±1.7
$CH_2=CHCN$	6.1–6.5	»	140	6–12	90–95	0.54–5.13	31.20–5.36	24.0±5.1

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*Benzyl bromide.

The kinetic data obtained are listed in Table 1, where the values of $k_{add}^X/k_{add}^{SiMe_3}$ and the conditions of carrying out the kinetic experiments are given. Carrying out of the experiments in a wide range of the monomer ratios showed a fairly good reproducibility of the kinetic values, obtained by using Eq. (1). The data in Table 1 also show a good coincidence of the values of constants obtained at various temperatures. According to the influence of substituent X in the monomers on the value of the addition rate constants, these constants can be arranged into the following series:

$$k_{add}^{CF_3} \approx k_{add}^{C_4H_9} < k_{add}^{SiMe_3} (\equiv 1) < k_{add}^{CO_2Me} < k_{add}^{CN}$$

It is seen from this series that the benzyl radical adds considerably more effectively to the electrophilic methyl acrylate and acrylonitrile than to the nucleophilic 1-hexene ($k_{add}^{CO_2Me}/k_{add}^{C_4H_9} = 41$, while $k_{add}^{CN}/k_{add}^{C_4H_9} = 83$). This demonstrates a relatively nucleophilic character of the benzyl radical. Judging from the value of the $k_{add}^{CN}/k_{add}^{C_4H_9}$ ratio, the polar factor plays a substantial role in changing the addition rate constant depending on the nature of the monomer. Thus, in the study of the addition kinetics of the authentically nucleophilic cyclohexyl radical to the $CH_2=CXC_6H_5$ monomers, where the decisive role of the polar factor has been established, the ratio $k_{add}^{CO_2Et}/k_{add}^{Me} = 46$ [3], i.e., it is of the same order of magnitude as the ratio obtained in our experiments.

The series of experiments with the VTMS – 1-hexane pair of monomers shows the similarity of the values of $k_{add}^{C_4H_9}/k_{add}^{SiMe_3}$, obtained on carrying out the reaction under the conditions of initiation with the $Fe(CO)_5$ + DMF and BP systems. This gives strong support for the conclusion that the addition stage under the MCI conditions proceeds by the free radical mechanism as in the case of the initiation by the peroxide.

In the analysis of the data of Table 1, a fairly unexpected result is observed — the ratio $k_{add}^{CF_3}/k_{add}^{SiMe_3}$ is close to that for 1-hexene and not methyl acrylate, which like 3,3,3-trifluoro-1-propene (TFP), contains an electron-acceptor group at the double bond. One of the possible explanations for this result was found in the EPR study of the behavior of the authentically generated adduct-radicals $C_6H_5CH_2CH_2CHX$ [4]. It was shown that in the case of X = CF_3, the adduct-radical undergoes a β-fragmentation with cleavage of the C–C bond at a constant rate $k_{fr} = 6.5 \cdot 10^3$ sec^{-1}, which probably eventually leads to decrease in the content of the adduct in the reaction mixture and a too-low value of the relative rate constant of the addition for TFP:

$$C_6H_5CH_2CH_2CHCF_3 \xrightarrow{k_{fr}} C_6H_5CH_2 + CH_2=CHCF_3.$$

Thus our kinetic data made possible not only the evaluation of the reactivity of benzyl radicals at the stage of addition to various monomers, but also the discovery of the characteristic features of the behavior of adduct-radicals formed in the reaction with TFP.

EXPERIMENTAL

The GLC analysis of the reaction mixtures was carried out on a steel column (1300 × 3 mm) with 15% of SKTFT-50Kh on Chromaton N-AW (0.16-0.20 mm), carrier gas helium (60 ml/min), katharometer 70-270°C (6 deg/min).

The ^{13}C NMR spectra of the separated compounds were run in a $CHCl_3$ solution in a Jmodecho regime on a Bruker WP-200 spectrometer.

The chromatomass spectral investigation was carried out on an NR 5971A mass-selective detector, using an ionic source, 180°C, 70 eV, quartz capillary column OV-1 (50 m × 0.25 mm), thickness of the stationary phase 0.3 μ, 50°C (5′), 4 deg/min — 200°C, 8 deg/min — 285°C (20′).

KINETIC INVESTIGATIONS

All the kinetic investigations were carried out for pairs of various monomers. In each pair one of the monomers was VTMS, which was taken as standard. The ratio VTMS/monomer being compared was varied over a wide range (0.1-5), whereby the ratio of the sum of the monomers to benzyl bromide remained constant for all the experiments and equal to 6. For each pair, 4-6 experiments were carried out at various ratios of the monomers, such that repeated experiments were carried out for each ratio.

a. Reactions Initiated by the $Fe(CO)_5$ + DMF System. Compounds $Fe(CO)_5$, DMF, benzyl bromide, VTMS, and the monomer to be compared were charged into a 5-ml glass ampul so as to give a molar ratio of $Fe(CO)_5)$:DMF:benzyl bromide:(VTMS + the monomer to be compared) equal to 0.02:0.06:1:6. The reaction mixture was degassed by the "freezing−evacuation−thawing" method in an argon atmosphere. The sealed ampul was held in an oil bath at the required temperature (140 or 100°C).

After the ampul was opened, the reaction mixture was treated with diluted (1:1) hydrochloric acid, washed with water, and dried over $CaCl_2$.

b. Reactions Initiated by BP. Benzoyl peroxide, benzyl bromide, VTMS, and the monomer to be compared were charged into a glass ampul in such a way that the mole ratio of BP:benzyl bromide:(VTMS + the monomer to be compared) was equal to 0.02:1:6. The reaction mixture was degassed as described above and the sealed ampul was held in the bath for 1 h at 100°C. After the ampul was opened, the reaction mixture was analyzed directly.

c. Reactions Carried Out with TFP. Iron pentacarbonyl, DMF, benzyl bromide, and VTMS were charged into an ampul. The mixture was degassed as described above, and then TFP was condensed into the ampul through a special dosing system, and the ampul was sealed. The ratio of the reagents was the same as in the pair analyses.

All the compounds formed in the reaction mixtures were analyzed by comparison with authentic samples, or by chromato-mass spectrometry [1], while their content in the reaction mixture was determined from the data of GLC analysis using the internal normalization method.

COTELOMERIZATION OF BENZYL BROMIDE WITH ACRYLONITRILE AND VTMS

A 2.9 g portion (0.0148 mole) of $Fe(CO)_5$, 3.2 g (0.0438 mole) of DMF, 25.0 g (0.146 mole) of benzyl bromide, 73.3 g (0.731 mole) of VTMS and 7.8 g (0.147 mole) of acrylontrile were charged in a nitrogen atmosphere into a rotating autoclave with glass lining. The autoclave was heated to 140°C and was held at this temperature for 1 h. After the end of the reaction, the mixture was treated similarly as in the ampul experiments initiated by $Fe(CO)_5$ + DMF. After the distillation of the reaction mixture, 9.8 g of benzyl bromide remained, and its conversion was 60.8%. A fraction was obtained with bp 90-156°C (1 mm Hg, 0.9 g) containing according to the GLC data 32.6% of $T_2^{CN,SiMe_3}$, and also a fraction with bp 156-166°C (1 mm

Hg, 4.2 g) containing 80.4% of $T_2^{CN,SiMe_3}$. The overall yield of $T_2^{CN,SiMe_3}$ was 7.7%. Repeated distillation of the latter fraction gave a pure compound $C_6H_5CH_2CH_2CH(CN)CH_2CHBrSiMe_3$ ($T_2^{CN,SiMe_3}$), bp 150-151°C (1 mm Hg), n_D^{20} = 1.5238, d_4^{20} = 1.1324. ^{13}C NMR spectrum (δ, ppm, $^1J_{C-H}$, Hz): 33.4, 32.5 ($-\underline{C}H_2-Ph$); 32.9, 30.6 ($-CH_2-$); 31.2 29.2, $^1J_{C-H}$ = 130 ($\underline{C}H-CN$); 35.6, 34.8 ($-CH_2-$); 40.5, 38.6, $^1J_{C-H}$ = 137 (Br−CH−Si) [5]; 120.5, 121.3 (CN) [6]; −3.7 (CH_3-Si); 139.6 cl, 128.1, 127.9, 125.9 (Ph).

MASS SPECTRA OF THE REACTION PRODUCTS

The masses of ions (*m/z*) are given for the ^{79}Br isotope. Given are: compound, type of ion, *m/z*, in brackets the relative intensity with respect to the maximal signal (in %), number of bromine atoms:

$C_6H_5CH_2CH_2CH(CN)CH_2CHBrSiMe_3$, $M^{+\cdot}$ 323(0), 1 Br; $[M-Me]^+$ 308(1.3), 1 Br; $[M - Me - HBr]^+$ 228(2.5), $-[M - CN - HBr]^+$ 217(2.7), −; Me_2BrSi^+ 137(8.0), 1 Br; $C_6H_5CH_2CH_2^+$ 105(2.3), −; $C_6H_5CH_2^+$ 91(27.3) −; Me_3Si^+ 73(50.6), −.

$C_6H_5CH_2CH_2CH(CN)CH_2CHBrSiMe_3$, diastereomer.

$C_6H_5CH_2CH_2CH(CO_2Me)CH_2CHBrSiMe_3$, $M^{+\cdot}$ 356(0), 1 Br; $[M - Me]^+$ 341(2.1), 1 Br; $[M - OMe]^+$ 325(0.6), 1 Br; $[M - C_6H_5CH{=}CH_2]^+$ 252(2.5), 1 Br; $[M - Br - C_6H_5CH{=}CH_2]^+$ 159(100), −; Me_2BrSi^+ 137(7.6), 1 Br; $C_6H_5CH{=}CH_2^{+\cdot}$ 104(6.3), −; $C_6H_5CH_2^+$ 91(45.0), −, Me_3Si^+ 73(54.2), −.

$C_6H_5CH_2CH_2CH(CO_2Me)CH_2CHBrSiMe_3$,

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REFERENCES

1. T. T. Vasil'eva, S. I. Gapusenko, C. V. Vitt, and A. B. Teretn'ev, *Izv. Akad. Nauk, Ser. Khim.*, No. 2, 442 (1992).
2. R. Kh. Freidlina, F. K. Velichko, S. S. Zlotskii, D. L. Rakhmankulov, and A. B. Terent'ev, *Radical Telomerization* [in Russian], Khimiya, Moscow (1988), p. 17.
3. B. Giese, J. He, and W. Mehl, *Chem. Ber.*, **121** No. 11, 2063 (1988).
4. R. G. Gasanov, T. T. Vasilieva, S. I. Gapusenko, and Y. A. Borisov, *Mendeleev Commun.*, No. 3, 111 (1991).
5. T. T. Vasil'eva, L. F. Germanova, V. I. Dostovalova, B. V. Nelyubin, and R. Kh. Freidlina, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 4, 896 (1985).
6. A. B. Terent'ev, V. I. Dostovalova, and R. Kh. Freidlina, *Org. Magn. Reson.*, **9**, No. 6, 301 (1977).