References

1. C. Tourné and G. Tourné, *Bull. Soc. Chim. Fr.*, 1969, 1124.
2. M. A. Fedotov, O. M. Ilinich, L. I. Kuznetsova, G. L. Semin, Yu. S. Vetchinova, and K. I. Zamaraev, *Catal. Lett.*, 1990, **6**, 417.
3. M. A. Fedotov, L. G. Detusheva, L. I. Kuznetsova, and V. A. Likholobov, *Zh. Neorg. Khim.*, 1993, **38**, 515 [*Russ. J. Inorg. Chem.*, 1993, **38**, 477].

Received August 10, 1995

A free-radical reaction of alkanoic acids with tetrachloroethylene

M. I. Dyusenov,[a]★ ***V. P. Engulatova,***[a] ***and G. I. Nikishin***[b]

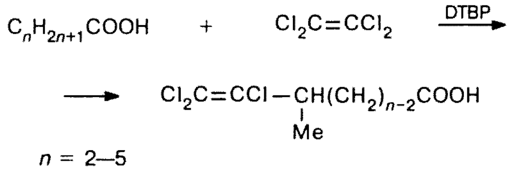
[a]*Institute of Oil Chemistry and Natural Salts, National Academy of Sciences of the Republic of Kazakhstan,*
1 ul. Lenina, 465002 Atyrau, Republic of Kazakhstan
[b]*N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,*
47 Leninsky prosp., 117913 Moscow, Russian Federation.
Fax: +7 (095) 135 5328

The di-*tert*-butyl peroxide-initiated free-radical reaction of C_3—C_6 alkanoic acids with tetrachloroethylene results in the formation of a mixture of isomeric (trichlorovinyl)alkanoic acids with the predominant isomer bearing the trichlorovinyl group at the ($\omega-1$) position.

Key words: free radical reaction, alkanoic acids, tetrachloroethylene, (trichlorovinyl)alkanoic acids.

Alkanoic acids add to alkenes *via* the radical mechanism with a high regioselectivity, and the reaction occurs at the α-C atom of the acid.[1] Esters of mono- and dialkanoic acids behave similarly: almost exclusively α-CH_2 groups of the acyl fragment participate in reactions with alkenes.[1] Unlike alkenes, under the action of peroxide initiators, tetrachloroethylene (TCE) reacts with esters, ethyl chloroacetate and dimethyl succinate, at the α-C—H bond of the alkoxyl fragment to form the products of substitution of the H atom for the trichlorovinyl group.[2]

In the present work, the reactions of C_3-, C_4-, C_5-, and C_6-alkanoic acids with TCE initiated by di-*tert*-butyl peroxide (DTBP) are carried out. It is established that the process occurs with the formation of 1 : 1 adducts: isomeric (trichlorovinyl)alkanoic acids (TCVA) bearing the trichlorovinyl group at various carbon atoms of the acid, but predominantly at the ω−1 position.



$$C_nH_{2n+1}COOH + Cl_2C{=}CCl_2 \xrightarrow{DTBP} Cl_2C{=}CCl-\underset{Me}{CH}(CH_2)_{n-2}COOH$$

n = 2–5

In propionic and butyric acids, the hydrogen atom is substituted for the trichlorovinyl group mainly in the CH_2 groups and to a lesser extent in the CH_3 group, while in pentanoic and hexanoic acids it is substituted almost exclusively in the CH_2 groups. The reaction conditions and the overall preparative yield of TCVA (a mixture of isomers isolated by distillation *in vacuo*) are presented in Table 1. The proportion of ($\omega-1$)-TCVA in the total amount of isomeric TCVA obtained from C_3—C_6-alkanoic acids is 65—70 % (Table 2).

The mechanism of the reactions of alkanoic acids with TCE is similar to that presented previously[2] for esters. The key stages are the addition of carbon-centered $C_nH_{2n}COOH]^{\bullet}$ radicals, which originate from the acid at the initiation and chain transfer stages, to TCE followed by the elimination of the chlorine atom from the adduct-radicals formed, and the chlorine atom continues the chain process.

$$C_nH_{2n}COOH\,]^{\bullet} + Cl_2C{=}CCl_2 \longrightarrow$$

$$\longrightarrow Cl_2\dot{C}{=}CCl_2C_nH_{2n}COOH \longrightarrow$$

$$\longrightarrow Cl_2C{=}CClC_nH_{2n}COOH + Cl^{\bullet}$$

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 4, pp. 1011—1013, April, 1996.

Table 1. DTBP-initiated reactions of alkanoic acids with TCE*

Initial acid	Reaction temperature/°C	Yield of TCVA (%)**
Propionic	130—140	35 (60)
Butyric	150—155	49 (65)
Pentanoic	155—160	52 (70)
Hexanoic	155—160	53 (70)

* The molar ratio of acid : TCE : DTBP was 10 : 1 : 0.4; the reaction time was 8 h.

** Calculated on the TCE taken (consumed in the reaction).

The formation of the (ω−1)-adducts is favored by the fact that the chain transferrer (chlorine atom) attacks alkanoic acids, according to the literature data,[3] preferably on the (ω−1)-C atom. The predominant formation of these TCBA is determined additionally by the manifestation of the polar interaction of more nucleophilic radicals $Me^{\bullet}CH(CH_2)_{n-2}COOH$ (compared to their isomers) with the electrophilic multiple bond of TCE. Isomeric radicals also add to TCE to form isomeric TCVA, but they can additionally generate (ω−1)-C radicals in the reaction with the initial acid.

A similar manifestation of the polar effect was observed in the radical reactions of esters of alkanoic acids with methyl maleate that resulted in the formation of noticeable amounts of 1 : 1 adducts due to the addition on the C=C bond of the (ω−1)-C-centered radicals generated from esters.[4]

The formation of 1 : 1 adducts from alkanoic acids and TCE is accompanied by the chlorination of the initial acids. With a molar ratio acid : TCE : DTBP = 10 : 1 : 0.4, the yield of chloroalkanoic acids is 2—3 % (calculated on the initial TCE). When the ratio changes to 5 : 1 : 0.4 (for example, for butyric acid), the yield increases three- to fourfold, and with a molar ratio of 3 : 1 : 0.4 it reaches ~18 %. This results in the formation of α-, β-, and γ-chlorobutyric acids in the ratio 2 : 3.6 :1 (GLC and ^{1}H NMR data), *i.e.*, the (ω−1)-isomer is also predominant. The yield of (trichlorovinyl)butyric acids decreases simultaneously from 49 % (see Table 1) to 10 %.

The structure of TCVA was established by IR and ^{1}H NMR spectroscopy (see Table 2) and mass spectrometry (Table 3) and confirmed by elemental analysis data (see Table 3), and for isomeric (trichlorovinyl)butyric acids it was also confirmed by ^{13}C NMR spectra. The characteristic distribution of intensities of the peaks of the molecular ions corresponding to the isotopic composition of chlorine is observed in the mass spectra. The ratio of TCVA isomers was determined by GLC and ^{1}H NMR from the integral intensity of the characteristic signals for the protons (see Table 2): for (trichlorovinyl)propionic acids **1** and **2**, protons of the CH_3 group (1.45 ppm) and the CH_2CH_2 fragment (2.13—3.1 ppm); for (trichlorovinyl)butyric acids **3**, **4**, and **5**, protons of the CH_3 groups (0.9 and 1.18 ppm) and the $(CH_2)_3$ fragment (1.6—2.2 ppm), respectively. The ^{13}C NMR spectrum of (trichlorovinyl)butyric acids contains signals corresponding to the C atom adjacent to the trichlorovinyl group in isomers **3**, **4**, and **5** (51.3, 35.6, and 32.0 ppm, respectively). The content of (ω−1)-isomers **8** and **9** in mixtures of (trichlorovinyl)valeric and -caproic acids was determined by GLC.

Thus, unlike alkenes, whose free-radical reactions with alkanoic acids result in the formation of α-alkylalkanoic acids (1 : 1 adducts), TCE and alkanoic acids form predominantly (ω−1)-TCVA under similar conditions.

Experimental

^{1}H NMR spectra were recorded on Varian DA 60 IL (60 MHz) and Tesla BS-497 (100 MHz) spectrometers in $CDCl_3$. ^{13}C NMR spectra were recorded on a Bruker-60 instrument (15.08 MHz) in CCl_4 using $SiMe_4$ as the internal

Table 2. IR and ^{1}H NMR spectra of (trichlorovinyl)alkanoic acids obtained and the relative content of their isomers

(Trichlorovinyl)alkanoic acid	IR, ν/cm^{-1}		^{1}H NMR ($CDCl_3$), δ*				Relative content of isomers**
	ν(C=C)	ν(COOH)	CH	CH_2	CH_3	COOH	
Cl_2=CCl(Me)CHCOOH (**1**)	1067	1721	4.18 (q)	—	1.45 (d)	12.3 (s)	70
Cl_2=CCl$(CH_2)_2$COOH (**2**)			—	2.23—3.1 (m)	—	12.3 (s)	30
Cl_2=CCl(Et)CHCOOH (**3**)			4.0 (t)	2.43 (quint)	0.9 (t)	11.9 (s)	21
Cl_2=CCl(Me)CHCH_2COOH (**4**)	1602	1713	3.64 (sext)	2.2—2.8 (m)	1.18 (d)	11.9 (s)	67
Cl_2=CCl$(CH_2)_3$COOH (**5**)			—	1.6—2.20 (m)	—	11.9 (s)	12
Cl_2=CCl(Pr)CHCOOH (**6**)			4.10 (t)	—			—
Cl_2=CCl(Et)CHCH_2COOH (**7**)			3.56 (quint)				—
Cl_2=CCl(Me)CH$(CH_2)_2$COOH (**8**)	1597	1713	3.33 (sext)	α 2.24 (t) β 1.74 (q)	1.1 (d)	11.9 (s)	65
Cl_2=CCl(Me)CH$(CH_2)_3$COOH (**9**)	1597	1714	3.1 (sext)	1.5—2.8 (m)	1.1 (d)	10.7 (s)	66

* The spectra of the mixtures of **1** and **2**; **3**, **4**, and **5**; **6**, **7**, and **8**; and of separate isomers **1**, **4**, **8**, and **9** were recorded.

** For compounds **1**—**5**, according to ^{1}H NMR and GLC data; for **8** and **9**, according to GLC data.

Table 3. Parameters of (trichlorovinyl)alkanoic acids

Compound	B.p./°C (*p*/Torr)	Mass spectrum*, $[M]^+$	$\frac{\text{Found}}{\text{Calculated}}$ (%)			Molecular formula
			C	H	Cl	
Acid **1**	112—135 (1)	202, 204, 206, 208	29.22 29.51	2.51 2.47	52.63 52.57	$C_5H_5Cl_3O_2$
Acid **4**	121—150 (1)	216, 218, 220, 222	33.10 33.13	3.18 3.24	49.10 48.90	$C_6H_7Cl_3O_2$
Acid **8**	135—165 (1)	230, 232, 234, 236	36.53 36.31	3.89 3.91	45.98 45.94	$C_7H_9Cl_3O_2$
Acid **9**	142—175 (1)	244, 246, 248, 250	39.53 39.20	4.28 4.51	44.05 43.31	$C_8H_{11}Cl_3O_2$

* Molecular ions are given for (ω—1)-isomers: compounds **1**, **4**, **8**, and **9**.

standard. Mass spectra (EI, 70 eV) were obtained on an MKh-1303 instrument with a direct inlet system. IR spectra were recorded on an UR-20 spectrophotometer in thin films, and for compound **1** they were recorded in pellets with KBr.

GLC analyses of the reaction mixtures were performed on an LKhM-8MD chromatograph (katharometer, helium as carrier gas, columns 3000×3 mm, silicone DC 500 and E 301 on Chromaton AW-DMCS and N-AW).

Reagents of "chemically pure" and "pure" grade were used.

Reaction of TCE with alkanoic acids (see Table 1). A solution of TCE and DTBP in 1/3 of the acid was added steadily with stirring over 5 h to alkanoic acid (2/3 of the total amount) at the temperature indicated in Table 1. The reaction mixture was heated for an additional 2 h, and the products of the decomposition of DTBP, unchanged acid, and TCE were distilled off. A mixture of isomers of (trichlorovinyl)alkanoic acid was isolated from the residue by distillation *in vacuo*. The boiling points, elemental analysis data of the mixtures of isomers, and the mass spectra (molecular ions) of (ω—1)-TCBA **1**, **4**, **8**, and **9** are presented in Table 3. Isomers **4**, **8**, and **9** were isolated from the mixtures by rectification *in vacuo* followed by additional chromatography on Al_2O_3. α-(Trichlorovinyl)propionic acid (**1**), m.p. 42—43 °C (from hexane), crystallized from the mixture of **1** and **2** on standing.

References

1. H.-H. Fogel, *Synthesis*, 1970, 99.
2. G. I. Nikishin, Yu. N. Ogibin, and V. N. Lebedev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1971, 1066 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1971, **20**, 980 (Engl. Transl.)].
3. N. C. Deno, in *Methods in Free-Radical Chemistry*, Ed. E. S. Huyser, Marcel Dekker, New York, 1972, **3**.
4. Yu. N. Ogibin, M. N. Elinson, and G. I. Nikishin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1980, 1842 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1980, **29**, 1320 (Engl. Transl.)].

Received October 31, 1995