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EPR SPECTROSCOPIC DETERMINATION OF ADDITION RATE CONSTANTS OF $\dot{C}Cl_3$ AND $Cl(CH_2)_2\dot{C}Cl_2$ RADICALS TO UNSATURATED COMPOUNDS

R. G. Gasanov and T. T. Vasil'eva

UDC 543.422.27:541.127:542.955:541.515

The reactivity determination of $\dot{C}Cl_3$ and $R\dot{C}Cl_2$ radicals (R = alkyl, aryl, and functional substituents) in additions to unsaturated compounds is of theoretical and practical interest because these reactions are widely used in organic synthesis and catalysis [1].

Absolute and relative addition rate constants for $\dot{C}Cl_3$ radicals have been determined for a small number of olefins [2-5] and the results reported by different authors differ significantly [2, 3]. Concerning the addition rate constants of $R\dot{C}Cl_2$ radicals to unsaturated compounds, they are not available in literature.

In this work we used EPR spectroscopy to determine the addition rate constants of $\dot{C}Cl_3$ and $Cl(CH_2)_2\dot{C}Cl_2$ radicals to the series of compounds represented by $CH_2{=}CHX$ [X = C_6H_5 (I), $COCH_3$ (II), $COOCH_3$ (III), CN (IV), OC_2H_5 (V), C_6H_{13} (VI), CH_2Cl (VII), $Si(CH_3)_3$ (VIII)] using nitrosodurol (ND) as a spin trap to fix the intermediate radicals. The chosen series of unsaturated compounds allowed us to trace the effect of the change in the nature of the substitutent at the vinyl group on its activity towards electrohilic $\dot{C}Cl_3$ and $Cl(CH_2)_2\dot{C}Cl_2$ radicals.

During photochemical irradiation at λ ∿ 366 nm of reaction mixtures containing $[Re_2(CO)_{10}]_0 = (1\text{-}3)\cdot10^{-3}$ mole/liter, $CH_2{=}CHX$ (M), ND, and $RCCl_3$ [R = Cl, $Cl(CH_2)_2$], the EPR spectra exhibited simultaneously the signals from spin adducts (SA) of $R\dot{C}Cl_2$ and $RCCl_2CH_2\dot{C}HX$ radicals with ND (Table 1). The formation of the identified radicals can be represented by the following scheme:

SCHEME

$$Re_2(CO)_{10} \rightarrow 2\dot{R}e(CO)_5$$
$$\dot{R}e(CO)_5 + RCCl_3 \rightarrow ClRe(CO)_5 + R\dot{C}Cl_2$$
$$R\dot{C}Cl_2 + ND \xrightarrow{k_1} RCCl_2N(\dot{O})Ar\ (A)$$
$$R\dot{C}Cl_2 + CH_2 = CHX \xrightarrow{k_2} RCCl_2CH_2\dot{C}HX\ (\dot{R})$$
$$\dot{R} + ND \xrightarrow{k_3} RCCl_2CH_2CHXN(\dot{O})Ar\ (B)$$
$$Ar = 2,3,5,6\text{-}(CH_3)_4C_6H.$$

The formation rate measurement for nitroxyls (A) and (B) made possible the determination of the addition rate constants of radicals $R\dot{C}Cl_2$ to unsaturated compounds with Eq. (1)

$$d[A]/d[B] = k_1/k_2\,\frac{[ND]_0}{[M]_0} \qquad (1)$$

(d[A] and d[B] are the concentration increment of radicals (A) and (B) with time). This equation is justified for chemical reactions described in the preceding scheme at a known addition rate constant of radicals $R\dot{C}Cl_2$ to ND [6].

Tables 2 and 3 show the increment ratios d[A]/d[B] for the addition of radicals $\dot{C}Cl_3$ and $Cl(CH_2)_2\dot{C}Cl_2$ to unsaturated compounds; these ratios depend linearly on $[ND]_0/[M]_0$ in

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A. I. Nesmeyanov Institute of Organometallic Compounds, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 4, pp. 800-804, April, 1989. Original article submitted January 12, 1988.

0568-5230/89/3804-0719$12.50

TABLE 1. Hyperfine Interaction Constants of Radicals $RCCl_2CH_2\dot{C}HXN(\dot{O})Ar$ ($R = Cl, Cl(CH_2)_2$), Obtained by Addition of $RCCl_3$ to $CH_2{=}CHX$*

a, E	C_6H_5	$COCH_3$	$COOCH_3$	CN	OC_2H_5	C_6H_{13}	CH_2Cl	$Si(CH_3)_3$
a_N	13,8	13,5	13,2	13,2	13,5	13,8	13,2	12,8
a_H	4,2	7,8	6,9	6,9	6,9	7,6	8,7	7,5

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*Together with the signals from radicals $RCCl_2CH_2CHXN(\dot{O})Ar$ we observed lines of radicals $CCl_3N(\dot{O})Ar$ ($a_N = 10.7$ and $a_{Cl} = 1.3$ Oe) in the case of CCl_4 and $Cl(CH_2)_2CCl_2N(\dot{O})Ar$ ($a_N = 11.5$ and $a_{Cl} = 2.2$ Oe) when using $Cl(CH_2)_2CCl_3$; Ar = 2, 3, 5, 6-$(CH_3)_4C_6H$.

TABLE 2. Addition Rate Constants of Radicals $\dot{C}Cl_3$ and $Cl(CH_2)_2\dot{C}Cl_2$ to $CH_2{=}CHX$ at 22°C

X	$[CH_2{=}CHX]$, mole/liter	$d[A]/d[B]$	$k_2 \cdot 10^{-3}$, liter/(mole·sec)	
			$\dot{C}Cl_3$	$Cl(CH_2)_2\dot{C}Cl_2$
C_6H_5	0,0494 [a] (0,0381) [b]	0,78±0,02 (4,0±0,8)	832±86	50±22
	0,1482 (0,0762)	0,28±0,01 (1,24±0,18)		
	0,247 (0,1524)	0,17±0,01 (0,79±0,28)		
	0,3952 (0,3048)	0,1±0,01 (0,58±0,22)		
$COCH_3$	0,198 [a] (0,0978) [c]	2,9±0,3 (3,0±0,5)	52±8	20±5
	0,396 (0,2222)	1,51±0,1 (1,4±0,3)		
	0,792 (0,2934)	0,67±0,4 (1,17±0,2)		
	2,4785 (0,4443)	0,25±0,2 (0,67±0,1)		
$COOCH_3$	0,7225 [d] (0,7225) [c]	1,29±0,16 (3,3±0,6)	42±3	3,1±1
	1,445 (1,445)	0,57±0,04 (1,4±0,4)		
	2,1675 (2,1675)	0,39±0,05 (1±0,3)		
	2,89 (3,6125)	0,31±0,02 (0,59±0,14)		
CN	1,1723 [e] (1,1723) [c]	1,86±0,1 (3,7±0,9)	12,8±0,1	1,66±0,01
	2,3445 (2,3445)	1,18±0,07 (1,8±0,4)		
	3,9075 (4,689)	0,52±0,04 (1±0,3)		
	(7,0332)	(0,49±0,01)		
OC_2H_5	2,8796 [f] (5,1833) [f]	1,7±0,15 (0,65±0,08)	4,8±0,2	1,3±0,2
	4,3194	1,05±0,08		
	7,199	0,77±0,05		

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[a] $[ND]_0 = 3.59 \cdot 10^{-3}$ mole/liter.

[b] The concentration of monomer in the reaction with $Cl(CH_2)_2 \cdot CCl_3$ was $[ND]_0 = 6.25 \cdot 10^{-3}$ mole/liter.

[c] $[ND]_0 = 4.35 \cdot 10^{-3}$ mole/liter.

[d] $[ND]_0 = 4.03 \cdot 10^{-3}$ mole/liter.

[e] $[ND]_0 = 4.23 \cdot 10^{-3}$ mole/liter.

[f] $[ND]_0 = 3.33 \cdot 10^{-3}$ mole/liter.

accordance with Eq. (1). The addition rate constants of radicals $\dot{C}CL_3$ and $Cl(CH_2)_2\dot{C}Cl_2$ to ND are equal to $9.1 \cdot 10^6$ and $1.3 \cdot 10^6$ liter/(mole·sec), respectively [6]. With the assumed values of k_1 and based on the found concentration increment ratios of radicals (A) and (B), we determined the addition rate constants (k_2) of radicals $\dot{C}Cl_3$ and $Cl(CH_2)_2\dot{C}Cl_2$ to $CH_2{=}CHX$ (Table 2).

We were not able to determine the formation rate of radicals (A) and (B) for the unsaturated compounds (VI)-(VIII) in the conditions chosen. They quickly reach steady-state concentrations, apparently as a result of their interaction with radicals $R\dot{C}Cl_2$ and $RCCl_2CH_2\dot{C}HX$. The addition rate constants k_2 can be determined using the following expression [6],

$$k_2 = \frac{k_1k_3[ND]_0 + k_1k_4([A]_{st} + [B]_{st})}{k_3[M]_0} \, \frac{[B]_{st}}{[A]_{st}} \qquad (2)$$

when radicals (A) and (B) have attained steady-state concentrations. We adopted $k_3 = 2 \cdot 10^7$ liter/(mole·sec) [6, 7] and $k_4 = 4 \cdot 10^8$ liter/(mole·sec) [8].

TABLE 3. Steady-state Concentration of Radicals $RN(\dot{O})Ar$ (A) and $RCH_2CHXN(\dot{O})Ar$ (B) and Addition Rate Constants (k_2) of Radicals $\dot{C}Cl_3(R^1)$ and $Cl(CH_2)_2\dot{C}Cl_2(R^2)$ to $CH_2{=}CHX$ at 22°C

X	$[CH_2{=}CHX]$, mole/liter	$[A]_{st}$		$[B]_{st}$		$k_2 \cdot 10^{-3}$, liter/(mole·sec)	
		10^5, mole/liter					
		(1) [a]	(2) [b]	(1)	(2)	R^1	R^2
C_6H_5	0,0494 [a] (0,0762) [c]	2,58	3,76	2,32	3,69	717±83	113±17
	0,1482 (0,1524)	1,91	2,74	4,43	4,05		
	0,247 (0,3048)	0,61	0,85	2,44	3,45		
	0,3952	0,39	–	3,17	–		
$COCH_3$	0,396 [b] (0,5331) [d]	0,71	0,35	0,63	0,66	85±6	23
	0,792 (0,4443)	1,04	0,12	1,96	0,26		15
	5,0	0,11	–	1,33	–		
$COOCH_3$	0,7225 [e] (1,445) [d]	1,14	0,68	0,54	1,0	29±9	8±2
	1,445 (2,1675)	1,11	0,72	1,09	1,39		
	2,1675 (0,7225)	0,64	0,75	1,31	1,0		
	2,89	1,21	–	1,83	–		
CN	2,3445 [f] (4,689) [d]	2,75	1,84	1,62	2,64	13±1	2,2
	3,9075 (7,0332)	1,46	0,66	1,72	2,11		2,9
	3,3075	2,22	–	2,22	–		
OC_2H_5	2,8796 [g] (3,4555) [g]	3,14	1,73	1,67	1,07	8,0±0,8	1,5
	4,3194 (5,1833)	2,61	0,83	2,6	1,09		0,9
	7,199	2,41	–	3,16	–		
C_6H_{13}	(4,9687) [h]	–	0,22	–	0,73	–	1,1
CH_2Cl	9,21 [i] (8,1722) [i]	1,04	1,63	1,79	0,77	2,0	0,1
$Si(CH_3)_3$	6,67 [i] (7,921) [i]	3,4	0,61	0,97	0,18	0,55	0,06

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[a] In radical (1) R = $\dot{C}Cl_3$; in (2) $Cl(CH_2)_2\dot{C}Cl_2$.

[b] $[ND]_0 = 3.59 \cdot 10^{-3}$ mole/liter.

[c] The concentration of monomer in the reaction with $Cl(CH_2)_2CCl_3$ was $[ND]_0 = 6.25 \cdot 10^{-3}$ mole/liter.

[d] $[ND]_0 = 4.35 \cdot 10^{-3}$ mole/liter.

[e] $[ND]_0 = 4.03 \cdot 10^{-3}$ mole/liter.

[f] $[ND]_0 = 4.23 \cdot 10^{-3}$ mole/liter.

[g] $[ND]_0 = 3.33 \cdot 10^{-3}$ mole/liter.

[h] $[ND]_0 = 1.15 \cdot 10^{-3}$ mole/liter.

[i] $[ND]_0 = 1.2 \cdot 10^{-3}$ mole/liter.

Table 3 gives the steady-state concentrations of radicals (A) and (B) found, as well as the addition rate constants of radicals $\dot{C}Cl_3$ and $Cl(CH_2)_2\dot{C}Cl_2$ to the series of $CH_2{=}CHX$ compounds. The obtained addition rate constants of radicals CCl_3 to styrene were close to those reported in [2, 9]. It follows from these data that the addition rate constants of radicals $Cl(CH_2)_2\dot{C}CL_2$ to $CH_2{=}CHX$ are 3-10 times smaller than the corresponding constants for radicals CCl_3.

The examined unsaturated $CH_2{=}CHX$ compounds can be arranged by their activity towards radicals CCl_3 and $Cl(CH_2)_2\dot{C}Cl_2$ in the following sequence: X = C_6H_5 > $COCH_3$ > $COOCH_3$ > CN ≥ OC_2H_5 ≃ C_6H_{13} > CH_2Cl > $Si(CH_3)_3$. The activity sequence for compounds (I)-(IV) towards radicals $RCCl_2$ found in this work agrees with the series obtained in [10] and other published works (see [10] and the cited references therein) for radicals C_6H_5S, C_6H_5COS, $C_6H_5SO_2$, and $(CH_3)_3CO$. Also, a linear dependence between the logarithm of the addition rate constant of radicals $RCCl_2$ to olefins with donor–acceptor properties (e) and the vinyl group substituents in $CH_2{=}CHX$ was observed [3]. These results speak in favor of that in the case of styrene vinylmethylketone, methylacrylate, and acrylonitrile their activity towards $RCCl_2$ radicals is determined by the polar effects of the substituents at the vinyl group. In the case of compounds (V)-(VIII) resonance effects also have a contribution in addition to the abovementioned effect.

EXPERIMENTAL

The EPR spectra were obtained with a RÉ-1306 spectrometer. The experimental methodology and the calculation of the concentration of nitroxyls are described in [11]. We chose

CH_2Cl_2 as the solvent. The starting concentrations of ND and $CH_2{=}CHX$ are given in Tables 2 and 3. The concentrations of the monomeric form of ND and $[M]_0$ were selected by considering the homopolymerization rate [3] in order to exclude the formation of telometric radicals.

The signal variations from the SA of radicals $R\dot{C}Cl_2$ and $RCCl_2CH_2\dot{C}HX$ with ND were linearly approximated by means of the least squares method. Table 2 gives the average values of d[A]/d[B] obtained from the results of three independent tests.

CONCLUSIONS

1. Radicals CCl_3 are added to vinyl monomers of type $CH_2{=}CHX$ (X = C_6H_5, $COCH_3$, $COOCH_3$ CN, OC_2H_5, C_6H_{13}, CH_2Cl, and $Si(CH_3)_3$) 3-10 times faster than radicals $Cl(CH_2)_2\dot{C}Cl_2$.

2. The reactivity of the vinyl groups in $CH_2{=}CHX$ towards radicals $\dot{C}Cl_3$ and $Cl(CH_2)_2\dot{C}Cl_2$ decreases by over an order of magnitude in the sequence X = C_6H_5, $COCH_3$, $COOCH_3$, CN.

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CONCENTRATION DEPENDENCE AND EFFECT OF OXYGEN ON THE PRIMARY PHOTOTRANSFORMATION PROCESSES OF KHINIFUR

N. K. Tatarskaya, M. A. Zhurav, S. M. Smirnov,
I. A. Degterev, V. F. Tarasov, Yu. E. Borisevich,
and G. E. Zaikov

UDC 541.141.7:547.722.5

The biological transformation of khinifur, a nitrofurane series preparation possessing anti-inflammatory and radiosensibilizing activities, as accompanied by its decolorization. This process is inhibited by oxygen [1]. Khinifur solutions are similarly decolorized by UV and visible light. It can be assumed that the phototransformation and biotransformation khinifur processes follow analogous mechanisms. The goal of this work was to examine the rules governing the photodecomposition of khinifur and the effect of oxygen on this decomposition.

EXPERIMENTAL

In a stationary photolysis process, khinifur (Kh) solutions were irradiated with filtered light of λ = 405 nm from a DRSh-1000 lamp with a combination of PS-13 and ZhS-10 filters. The measurements were carried out in 2-10 mm thick quartz cuvettes. The initial optical density of the solutions amounted to no more than 0.3 optical units. The absorption spectra

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N. N. Semenov Institute of Chemical Physics, Academy of Sciences of the USSR, Moscow.
Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 4, pp. 804-809, April, 1989. Original article submitted December 8, 1987.