RATE CONSTANTS FOR ADDITION OF TRIETHYLSILYL RADICALS TO SPIN TRAPS

R. G. Gasanov, L. V. Ivanova, UDC 541.127:543.422:541.515:547.245 and R. Kh. Freidlina

The securing of quantitative data on the unit steps of chemical processes, which are studied by the EPR method employing the technique of spin traps (ST) [1, 2], is of interest. To identify the  $Et_3Si$  radicals, which are widely used in chemical reactions, it is customary to use 2,4,6-(Me<sub>3</sub>C)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>NO (NB) [3] and PhCH=N(O)CMe<sub>3</sub> (PBN) [4], which form radicals (I) and (II), as the ST.

$$Et_{3}\dot{S}i + HB \xrightarrow{k \text{ add }} 2,4,6-(Me_{3}C)_{3}C_{6}H_{2}\dot{N}OSiEt_{3} (I)$$
(1)

$$Et_{3}\dot{S}i + PBH \xrightarrow{k^{2}add} PhCH(Et_{3}Si)N(\dot{O})CMe_{3} (II)$$
(2)

In the present paper the rate constants for the addition of  $Et_3 \dot{S}i$  radicals to NB and PBN were determined by the EPR method. Here we used the method of a competing rate (see, for example, [5]). As the competing reactions we selected either the cleavage of Cl

$$Et_{3}Si + RCl \xrightarrow{R_{cleav}} Et_{3}SiCl + R$$
(3)

or the addition of the C=O group to the O atom.

$$Et_{3}\dot{Si} + RR'CO \xrightarrow{k \text{ add}} RR'\dot{C}OSiEt_{3}$$
(4)

The  $k_{cleav}$  constants from RC1 were determined in [6], while the  $k_{add}$  constants were determined in [7].

The simultaneous identification by the EPR method of the spin adducts of the  $Et_3Si$  and R radicals with either PBN or NB permits determining the rate constant for the addition of these radicals to ST via Eq. (1)

$$k_{\text{add}}^{i} = k_{\text{cleav}} \frac{[\text{RCI}]_{0}}{[\text{ST}]_{0}} \cdot \frac{[\text{A}]}{[\text{B}]} \quad (i = 1, 2)$$

$$(1)$$

where [A] is the concentration of either radicals (I) or (II), and [B] is the concentration of the spin adducts of the  $\hat{R}$  radicals with either PBN nitroxyls (III) or NB (IV). It is obvious that

$$NB \xrightarrow{R^{*}} 2, 4, 6 - (Me_{3}C)_{3}C_{6}H_{2}N(O)R$$
(III)

$$PBN \xrightarrow{R} PhCHRN(\dot{O})CMe_{3}$$
(IV)

 $k_{add}^{1}$  can also be determined by the simultaneous identification via the EPR method of the radicals RR'COSiEt<sub>3</sub> (V) (see [4]) and either (I) or (II) in the reaction of Et<sub>3</sub>Si with RR'CO and either NB or PBN by using Eq. (2).

$$k_{\text{add}}^{i} = k_{\text{add}} \frac{[\text{RR'CO}]_{0}}{[\text{ST}]_{0}} \cdot \frac{[\text{A}]}{[\text{V}]}$$
(2)

The HFC constants of the (II) radicals, formed by the UV irradiation of  $(Me_3CO)_2$ ,  $Et_3SiH$ , and PBN solutions are given in Table 1 (expt. 1). In Table 1 are also given the parameters of the EPR spectra of the spin adducts of the R radicals with PBN; and of the (IV) radicals, which were obtained by the photochemical reaction of  $Et_3Si$  with RC1 (R = CCl<sub>3</sub>, PhCH<sub>2</sub>, Me<sub>3</sub>C) in the presence of PBN (expts. 3-5). The HFC constants found by us coincide with the corresponding constants for the spin adducts of the Me<sub>3</sub>Si, CCl<sub>3</sub>, PhCH<sub>2</sub>, and Me<sub>3</sub>C radicals with PBN [4, 8, 9]. From these results and the data in Table 2 it can be seen that at the selected [RC1] and

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TABLE 1. Parameters of EPR Spectra of Radicals  $2,4,6-(Me_3C)_3-C_6H_2NOSIEt_3$  (I), PhCH(Et\_3Si)N(0)CMe\_3 (II),  $2,4,6-(Me_3C)_3C_6H_2N-(0)R$  (III), PhCHRN(0)CMe\_3 (IV), and RC(Ph)OSIEt\_3 (V), Oe

Expt. No.	Radicals	Generation method	<sup>a</sup> N	a <sub>H</sub>
1 2 3 4 5 6 7	$ \begin{array}{c} (II) * \\ (I) \\ (I) + (IV) \\ (R = CCl_2) \\ (II) + (IV) \\ (R = PhCH_2) \\ (II) + (IV) \\ (R = Me_3C) \\ (I) + (III) \\ (R = PhCH_2) \\ (V) \\ (V) \\ (V) \end{array} $	A † B † A+CCl <sub>4</sub> A+PhCH <sub>2</sub> Cl A+Me <sub>3</sub> CCl B+PhCH <sub>2</sub> Cl Et <sub>3</sub> SiH+(Me <sub>3</sub> CO) <sub>2</sub> +(PhCO) <sub>2</sub> D + (PhCO) <sub>2</sub>	15,3 10,5 15,3; 13,8 15,3 14,0 15,3 14,1 10,6 13,7 -	$ \begin{array}{c} 6,1 \\ 2,1 \\ 2,1 \\ 1,5 \\ 6,1 \\ 2,6 \\ 6,1 \\ 2,6 \\ 6,1 \\ 2,2 \\ 2,1 \\ 14,9 \\ a_{p-H}=a_{o-H}=3,0; \\ a_{m-H}=1,1 \end{array} $
8	$(\mathbf{R}=\mathbf{PhCO})$	B+(PhCO) <sub>2</sub>	10,5	$a_{p-H} = a_{o-H} = 3,0$ $a_{m-H} = 1,1$

 $*\alpha_{29}S_{i} = 14.4.$ 

<sup>†</sup>A =  $E_{t_3}SiH$  + (Me<sub>3</sub>CO)<sub>2</sub> + PBN; B =  $E_{t_3}SiH$  + (Me<sub>3</sub>CO)<sub>2</sub> + NB. ‡From m-H of ST. \*\* $\alpha_{m-H}$  = 0.9 from hydrogen of trap.

 $[PBN]_{\circ}$  concentrations the (II) and (IV) radicals can be simultaneously recorded by the EPR method at 25°C. The concentrations of these radicals are given in Table 2. On the basis of these data and the k<sub>cleav</sub> values for CCl<sub>4</sub>, PhCH<sub>2</sub>Cl, and Me<sub>3</sub>CCl [6] (see Table 2) at known initial concentrations of PBN and RCl we used Eq. (1) to determine the rate constants for the addition of Et<sub>3</sub>Si radicals to PBN (see Table 2).\*

To determine the  $k_{add}$  constants for the addition of  $Et_3$ Si to NB we ran the competing reaction with NB and PhCH<sub>2</sub>Cl. The selection of PhCH<sub>2</sub>Cl, and not, for example, of either CCl<sub>4</sub> or Me<sub>3</sub>CCl as the Cl source, was due to the fact that in the case of CCl<sub>4</sub> the formed CCl<sub>3</sub> radicals, as is known [1, 3], are not fixed by NB, while in the case of Me<sub>3</sub>CCl the Me<sub>3</sub>C radicals should be obtained, whose spin adducts with NB have HFC constants that are close to the corresponding constants for the (I) radicals [3]. The HFC constants of the spin adducts of the PhCH<sub>2</sub> radicals, formed in the reaction of  $Et_3$ Si with PhCH<sub>2</sub>Cl, are given in Table 1 (expt. 6) and coincide with the corresponding constants for the (III) radicals (R = PhCH<sub>2</sub>) [3]. Having calculated the steady-state concentrations of radicals (I) and (III) from the obtained EPR spectra, by using Eq. (1) at known  $k_{cleav}$  values we obtain:  $k_{add}^1 = 1.4 \cdot 10^9$  liters/mole·sec (see Table 2, expt. 4).

The  $k_{add}^1$  value was also determined by studying the reaction of  $Et_3Si$  with NB in the presence of (PhCO)<sub>2</sub> (see Table 2, expt. 5).

When Et<sub>3</sub>Si is reacted with  $(PhCO)_2$ , the signals of the  $PhC(0)\dot{C}(Ph)OSiEt_3$  radicals are observed in the EPR spectrum, the values of whose HFC constants are given in Table 1 (expt. 7) and they coincide with the corresponding constants of these radicals, studied in [11]. When a solution of Et<sub>3</sub>SiH and  $(Me_3CO)_2$ , containing NB in  $(PhCO)_2$ , is irradiated with UV light the signals of radicals (I) and (V) (R = Ph, R' = PhCO) are observed in the EPR spectrum (Table 1, expt. 8). Substituting in Eq. (2) the concentrations of the identified radicals (see Table 1, expt. 8), and the initial concentrations of  $(PhCO)_2$  and ST when  $k_{add} =$  $3.3 \cdot 10^8$  liters/mole·sec [7], we obtain for  $k_{add}^1$  at 25°C:  $1.9 \cdot 10^9$  liters/mole·sec.

## EXPERIMENTAL

The EPR spectra were obtained on an RÉ-1306 spectrometer. The ampul with the solutions, which were degassed by the vacuum-freezing (at  $10^{-3}-10^{-4}$  mm) and thawing method (several cycles), were exposed to the UV light from a DRSh-500 lamp in the resonator of the spectrometer. When PBN was used as the spin trap the Et<sub>3</sub>Si radicals were generated by using Et<sub>3</sub>SiH and (Me<sub>3</sub>CO)<sub>2</sub> in a 1:1 volume ratio as the source of the radicals. In the case of NB we took 0.1 ml of Et<sub>3</sub>SiH in TBP in each experiment. We used C<sub>6</sub>H<sub>6</sub> as the solvent. The same

<sup>\*</sup>The rate constant for the addition of  $Et_3Si$  to PBN was determined in [10], which at 25°C is equal to  $(7.1 + 2.8) \cdot 10^7$  liter/mole•sec.

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RCI+A *	ccl₃	3,6.10-3	PBN, 0,1	2.10 <sup>9</sup> [6]	1	1,59	1	6,98	1	1,6-107
same	PhCH <sub>2</sub>	$3,2.10^{-2}$	*	2.107 [6]	ł	5,7	1	2,56	I	1,4.107
*	Me <sub>3</sub> C	5,5.10-1	*	1.107 [6]	1	2,7	1	2,53	ł	5,5.10
RCI+B *	PhCH <sub>2</sub>	0,89	[NB], 1,2.10 <sup>-2</sup>	2.107 [6]	3,6	1	3,6	)	I.	1,4.109
RC(0) Ph+B	PhCO	6.10-2 +	[ [NB ], 2,2·10- <sup>3</sup>	3,3.10 <sup>8</sup> [7]	0,72	1	1	1	6,08	1,9-10

\*A =  $Et_3SiH$  + ( $Me_3CO$ )<sub>2</sub> +  $PBN_*$  B =  $Et_3SiH$  + ( $Me_3CO$ )<sub>2</sub> + NB. † (PhCO)<sub>3</sub>. ratios of the reactants were also chosen in the experiments with  $(PhCO)_2$  when generating the  $PhC(0)C(Ph)OSiEt_3$  radicals. The concentrations of RCl and  $(PhCO)_2$  in the competing reactions are given in Table 2. As the standard for calculating the concentrations of the radicals we selected  $[2,2,6,6-Me_4-4-(PhCO)_2-C_6H_2NO]_0 = 3 \cdot 10^{-3}$  mole/liter.

## CONCLUSIONS

The rate constants for the addition of triethylsilyl radicals to  $\alpha$ -phenyl-N-tert-butylnitrone (k<sub>add</sub> = (11 ± 5)•10<sup>6</sup> liter/mole•sec) and 2,4,6-tri-tert-butylnitrosobenzene (k<sub>add</sub> = (1.5 ± 0.3)•10<sup>9</sup> liter/mole•sec) at ~20°C were determined by the EPR method.

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IONIC HYDROGENATION IN THE PRESENCE OF SURFACE-ACTIVE SUBSTANCES

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D. N. Kursanov\*, G. D. Kolomnikova, S. A. Goloshchapova, M. I. Kalinkin, and Z. N. Parnes

The rate of many chemical reactions depends on the presence of surface-active substances (SAS) in the reaction medium [1]. Frequently this is related to the formation of micelles, and in this case the accelerating effect of the SAS is called micellar catalysis. The vast majority of the data on micellar catalysis was obtained for aqueous solutions. Data on micellar catalysis in organic solvents is very scanty, although it is specifically such reactions that have interest for synthetic organic chemistry.

We studied the possible catalytic effect of the SAS in the ionic hydrogenation reaction [2]. The key step of this reaction is the formation of the carbocation, and consequently we used SAS which form micelles that are capable of stabilizing the intermediate carbenium ion, and specifically the Na salt of the diisooctyl ester of sulfosuccinic acid (I), poly(ethylene glycol 12-monolaurate) (II), and poly(ethylene glycol 10-oleate) (III). The substrates were olefins of variable structure and acetophenone, as the proton donor we used 68% HClO<sub>4</sub>,<sup>†</sup> the triethyl- and diphenylsilanes served as the hydride-ion donors, and the solvent was n-octane, in which (I)-(III) form micellar solutions [4]. It proved that all of the studied SAS substantially accelerate the ionic hydrogenation of branched olefins and acetophenone (Table 1).

From Table 1 it can be seen that the ionic hydrogenation rules, established using the standard silane:  $CF_3COOH$  system, are retained, and unbranched olefins, in particular cyclohexene, are not hydrogenated, while acetophenone is reduced to the hydrocarbon.

<sup>†</sup>The use of HClO<sub>4</sub> as the proton donor in ionic hydrogenation was shown in [3].

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<sup>\*</sup>Deceased.