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Stability of $PhCH_2CH_2\dot{C}HX$ (X = H, CF_3, Me, CO_2Me) Radicals

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Using EPR spectroscopy, β-fragmentation of the radicals $PhCH_2CH_2\dot{C}HX$ (R^1, X = H; R^2, X = CF_3; R^3, X = Me; R^4, X = CO_2Me) accompanied by C—C bond cleavage has been found and studied, and the activation energy of this reaction has been calculated, thus permitting us to determine the rate constants for fragmentation of R^1 ($k_{3a} = 3.9(\pm 0.2) \times 10^4\ s^{-1}$, R^2 ($k_{3b} = 6.5(\pm 0.4) \times 10^3\ s^{-1}$ and to evaluate the value of this rate constants for radical R^3 and R^4 ($k_3 = 10^2\ s^{-1}$) at 22 °C.

The stability of adduct-radicals formed by the radical reactions addition and telomerization plays an important role in explaining the reactivity of radicals and in directing them to unsaturated compounds for addition. The present communication gives an EPR spectroscopic analysis and calculation of the activation energy for β-fragmentation of the adduct-radicals $PhCH_2CH_2\dot{C}HX$ (R^1, X = H; R^2, X = CF_3; R^3,

$PhCH_2CH_2CHXY$

1; X = H, Y = Br
2; X = CF_3, Y = Br
3; X = Me, Y = I
4; X = CO_2Me, Y = Br

Table 1 Hfs constants for the spin-adducts of radicals R^1–R^4 with spin trap,[a] formed during the reaction of $Re_2(CO)_{10}$ with compounds **1–4**

Compound	Identified radical	a_N/G^b	$a_{\beta\text{-H}}/G^b$
1[c]	$Ph\dot{C}H_2$ (R^5)	13.7	8.1
	$PhCH_2CH_2\dot{C}H_2$ (R^1)	13.7	10.9
2[c]	$Ph\dot{C}H_2$ (R^5)	13.7	8.1
	$PhCH_2CH_2\dot{C}HCF_3$ (R^2)	12.49	1.85 ($a_F = 5.25$)
3	$PhCH_2\dot{C}HMe$ (R^3)	13.5	6.1
4	$PhCH_2CH_2\dot{C}HCO_2Me$ (R^4)	13.2	8.7

[a] Hfs constants for the identified radicals coincide with those observed for species obtained by us previously[4] and with analogous radicals covered in refs. 6–8. [b] $G = 10^{-4}$ T. [c] When 2-methyl-2-nitrosopropane was used, signals from the radicals $PhCH_2N(\dot{O})CMe_3$ ($a_N = 14.6$ and $a_{\beta\text{-H}} = 7.3$ G), $Ph(CH_2)_3N(\dot{O})CMe_3$ ($a_N = 15.1$ and $a_{\beta\text{-H}} = 10.7$ G) and $PhCH_2CH_2CH(CF_3)N(\dot{O})CMe_3$ ($a_N = 13.41$, $a_{\beta\text{-H}} = 2.06$ and $a_F = 2.62$ G) were observed.

X = Me; R^4, X = CO_2Me). Radicals R^1–R^4 were generated by halogen abstraction from compounds **1–4** respectively. Compounds **1**, **2** and **4** were obtained by addition of benzyl bromide to ethylene, 3,3,3-trifluoroprop-1-ene and methyl acrylate respectively on initiation with the $Fe(CO)_5$–*N*,*N'*-dimethylformamide (DMF) system; their structure and purity were confirmed by ^{13}C NMR, mass spectral and elemental analysis data. Compound **3** was obtained by replacing Cl with I in $PhCH_2CH_2CHClMe$, produced previously.[1]

During photochemical reactions of compounds **1–4** with $Re_2(CO)_{10}$, the spin-adducts (SAs) of radicals R^1–R^4 with spin traps (STs) were identified by EPR spectroscopy in the presence of the ST, nitrosodurol (ND) (2,3,5,6-tetramethyl-1-nitrosobenzene) [eqn. (1)] (R = 2,3,5,6-Me_4C_6H, Me_3C;

$$R^i + ST \xrightarrow{k_1} \underset{\textbf{A}}{R^iN(\dot{O})R} \tag{1}$$

i = 1–4) (see Table 1). In addition to the signals due to the SAs of radicals R^1 and R^2, signals due to SAs of radical $PhCH_2(R^5)$ were observed in the reactions of **1** and **2** [eqn. (2)]. The

$$R^5 + ST \xrightarrow{k_2} \underset{\textbf{B}}{R^5N(\dot{O})R} \tag{2}$$

formation of these SAs may be explained in terms of β-fragmentation of radicals R^1 and R^2 with cleavage of a C—C bond [eqns. (3a) and (3b)].

$$PhCH_2CH_2\dot{C}H_2 \xrightarrow{k_{3a}} Ph\dot{C}H_2 + C_2H_4 \tag{3a}$$

$$PhCH_2CH_2\dot{C}HCF_3 \xrightarrow{k_{3b}} Ph\dot{C}H_2 + CH_2{=}CHCF_3 \tag{3b}$$

Simultaneous identification of the SAs of radicals R^1, R^2 and R^5 with STs allows the determination of the rate constants for fragmentation of radicals R^1 and R^2 using EPR spectroscopy and eqn. (4). The dependence of the ratio Y on the concentration of the spin trap ND (1.11×10^{-2}–3.1×10^{-3} mol dm^{-3}) was processed by the least-squares method, yielding

$$Y = d[\textbf{A}]/d[\textbf{B}] = k_1/k_3[ST] \tag{4}$$

a linear dependence of Y on ST concentration (correlation coefficient > 0.99) in full compliance with eqn. (4) at $k_1/k_{3a} = 774(\pm 47)$ and $k_1/k_{3b} = 604(\pm 40)$.

With regard to the data on hyperfine splitting (hfs) constants for the radicals $PhCH_2\dot{C}H_2$ ($a_{\alpha\text{-H}} = 22.10$; $a_{\beta\text{-H}} = 30.94$ G)† and $Me(CH_2)_2CH_2$ ($a_{\alpha\text{-H}} = 21.94$; $a_{\beta\text{-H}} = 29.72$ G),[2] R^1 may be regarded as a primary alkyl radical, for which the rate constant of addition to ND has been determined previously.[3] Making allowance for the dependence of this constant on temperature[3] we assumed a value for k_1 of 3×10^7 mol^{-1} dm^3 s^{-1} for R^1 addition. Under these conditions, the rate constant k_{3a} for radical fragmentation of R^1 is $3.9(\pm 0.2) \times 10^4$ s^{-1}. Assuming that constant k_1 for the rate of addition of R^2 radicals to ND is 3.9×10^6 mol^{-1} dm^3 s^{-1},[4] we derived from the results obtained values for $k_{3b} = 6.5(\pm 0.4) \times 10^3$ s^{-1} and $k_{3a}/k_{3b} = 6$.

Calculation of the activation energy of reaction (3) for radicals R^1–R^4 was performed by the Dewar method.[5] This allows us to propose the following series $R^1(18.7) < R^2(19.9) < R^3(21.6) < R^4$(21.4 kcal mol^{-1}).† The series obtained correlates with the experimental data obtained by EPR spectroscopy. Assuming that the fragmentation of radicals R^1–R^4 is characterized by equal values of the preexponential factors, then the ratio of the rate constants for fragmentation of the radicals will be determined by $\exp(\Delta E/RT)$, where ΔE is the difference between the calculated values of the thermal effect for radicals R^1–R^4. Under these conditions, $k^{3a}/k_{3b} = 8$, consistent with the experimental data, while the constants for fragmentation of radicals R^3 and R^4 at 22 °C will be in the region of 10^2 s^{-1}.

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† 1 G = 10^{-4} T; 1 cal = 4.184 J.