76. Observation of the Neophyl Radical Rearrangement by Electron Spin Resonance Spectroscopy

by **Edwin J. Hamilton, Jr.** and **Hanns Fischer**
Physikalisch-Chemisches Institut der Universität, CH-8001 Zürich

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Summary. The rearrangement of the 2-methyl-2-phenylpropyl (or neophyl) radical **1** to the 1-methyl-1-benzylethyl radical **2** is observed by ESR. spectroscopy during photolysis of di-*t*-butylperoxide in *t*-butylbenzene at 270–360 K. The energy of activation of the rearrangement is determined to be (43 ± 9) kJ mol^{-1}.

Since the discovery [1] of the rearrangement of the 2-methyl-2-phenyl-propyl (or neophyl) radical **1** to the 1-methyl-1-benzylethyl radical **2**, this and similar radical rearrangements *via* 1,2-aryl migration have reveived considerable mechanistic study[1]. These investigations have relied on the analysis of product distributions under conditions of competition between radical rearrangement and radical scavenging. The direct observation of the radicals during such a rearrangement by electron spin resonance (ESR.) spectroscopy has not been previously reported[2].

We wish to report the ESR. observation of the neophyl rearrangement (**1** → **2**) and the determination of its activation energy. Both **1** and **2** have been separately observed by others [4, 5] and show classical structures. Further, the rearrangement has been found to be not significantly reversible [6].

Solutions of di-*t*-butylperoxide ($^1/_6$ by volume) in *t*-butylbenzene were photolyzed in the cavity of an ESR. spectrometer using the quartz flow cell and irradiation system [7] previously described. Fig. 1 shows ESR. spectra obtained at different temperatures. Below 270 K, the observed spectrum is due to **1**. On increasing the temperature, the spectrum becomes a superposition of the spectra of **1** and **2**, while above 360 K, only **2** is observed. In almost all spectra, lines due to methyl (**3**) are present, their intensities being greater at higher temperature. These observations show that the rearrangement of **1** to **2** is occuring and that the higher the temperature, the more radicals rearrange during the average radical lifetime (which is determined by second-order termination). Radical **2** was also observed on photolysis of di-*t*-butylperoxide in isobutylbenzene; at ≃ 310 K and lower temperatures, **1** was not present, in agreement with the expected irreversibility of the rearrangement. High-resolution ESR. spectra of **1** and **2** are shown in Fig. 2, and the spectral parameters are given in the Table. They agree with those previously reported [4, 5]. The similarity of the β-CH$_2$ coupling constant of **2** to that of the *t*-pentyl radical indicates that the former has the same lowest energy rotamer as that known for the latter [8], *i.e.*, the one with the β-carbon to γ-carbon bond eclipsing the half-filled 2p orbital. Thus substitution of a β-phenyl group for a β-methyl does not change the lowest energy rotamer, as is also the case for *n*-propyl [9, 10] and 2-phenylethyl [4b, 8, 10].

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[1] See [2] and references therein.

[2] Other free-radical rearrangements have been observed by ESR., see [4b] [3].

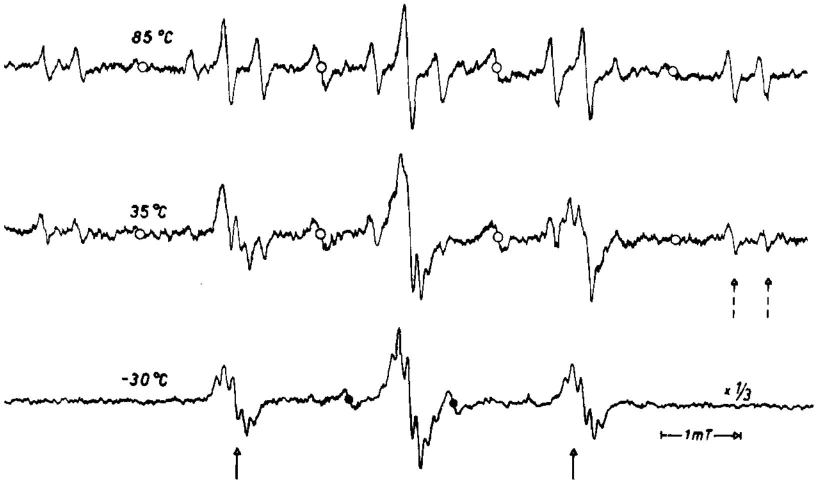

Fig. 1. *Spectra obtained during photolysis of di-*t*-butylperoxide in* t*-butylbenzene.* Open circles denote lines due to methyl radical **3**; solid circles denote lines due to unidentified species; solid arrows denote lines used for determination of S_1; dashed arrows denote the same for S_2. Outer lines of **2** are not shown.

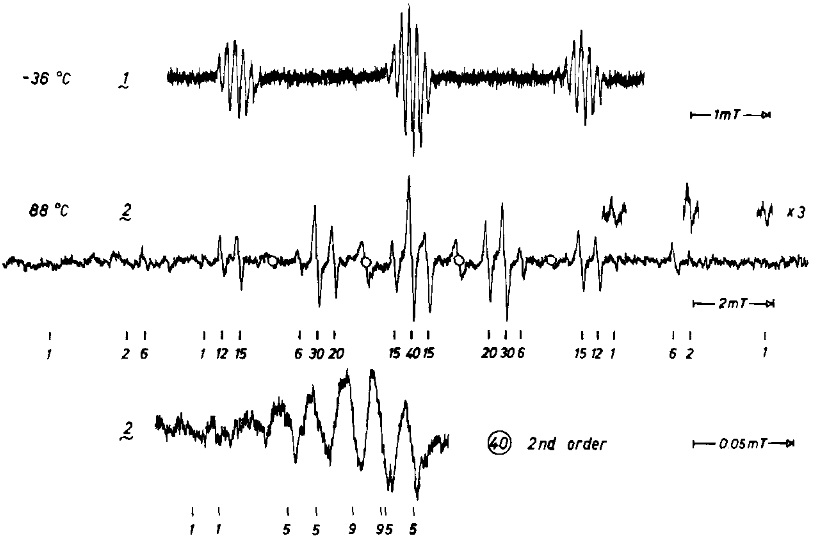

Fig. 2. *ESR. spectra of* **1** *and* **2**. Open circles denote lines due to methyl radical **3**

Table. *Coupling Constants* [mT] *and* g-*Factors*

	$a_H(\alpha)$	$a_H(\beta, CH_3)$	$a_H(\beta, CH_2)$	$a_H(\gamma)$	g	T(K)
1 = $C_6H_5C(CH_3)_2\dot{C}H_2$[a])	2.185(2)			0.102(2)	2.00266(8)	237
2 = $C_6H_5CH_2\dot{C}(CH_3)_2$[b])		2.287(2)	1.880(6)		2.00274(8)	363
$CH_3CH_2\dot{C}(CH_3)_2$[c])		2.28	1.89			253

[a]) Line width ~0.04 mT [b]) Line width ~0.014 mT [c]) From [8].

The observed radicals are consistent with the scheme:

$$(CH_3)_3COOC(CH_3)_3 \xrightarrow{h\nu} 2\,(CH_3)_3C\dot{O} \qquad (1)$$

$$(CH_3)_3C\dot{O} \longrightarrow (CH_3)_2CO + \underset{\mathbf{3}}{\dot{C}H_3} \qquad (2)$$

$$(CH_3)_3C\dot{O} + C_6H_5C(CH_3)_3 \longrightarrow (CH_3)_3COH + \underset{\mathbf{1}}{C_6H_5C(CH_3)_2\dot{C}H_2} \qquad (3)$$

$$\underset{\mathbf{1}}{C_6H_5C(CH_3)_2\dot{C}H_2} \xrightarrow{k_r} \underset{\mathbf{2}}{C_6H_5CH_2\dot{C}(CH_3)_2} \qquad (4)$$

$$\mathbf{i} + \mathbf{j} \xrightarrow{k_{ij}} \text{products } (\mathbf{i}, \mathbf{j} = \mathbf{1}, \mathbf{2}, \mathbf{3}) \qquad (5)$$

Because of the fast rates expected [11] for (2) and (3), second-order termination of *t*-butoxy radicals should be unimportant under our conditions. With the usual assumption for the cross-termination rate constants, $k_{ij} = 2(k_{ii}k_{jj})^{1/2}$ for $\mathbf{i} \neq \mathbf{j}$ [12], kinetic analysis of (1)–(5) under conditions of steady-state irradiation yields

$$\frac{[\mathbf{2}]}{[\mathbf{1}]} = \frac{k_r}{2k_{22}(I + J)^{1/2}} \qquad (6)$$

where I equals the rate of production of **1** by reaction (3), and J equals the rate of production of **3** by reaction (2).

In order to determine the activation energy E_r of k_r, we now consider the temperature dependences of the various quantities in (6). The sum I + J is just twice the rate of disappearance of peroxide in (1). That this rate should be nearly constant in the temperature range 290–340 K, may be shown as follows: Extrapolation of viscosity data for *t*-butylbenzene ($\eta = 2.1$ cp at 263 K [13]) using an assumed *Arrhenius* energy for viscosity of 8 kJ mol^{-1} [14] gives $\eta \simeq 1.5$ cp at 290 K, and 0.9 cp at 340 K. Then, using these viscosities, interpolation of data for the cage effect (f) in di-*t*-butylperoxide photolysis as a function of viscosity [15], with temperature correction using the relation $(f^{-1}-1) \sim T^{1/2}$ [16], gives $f \simeq 0.31$ at 290 K, and $f \simeq 0.24$ at 340 K for *t*-butylbenzene as solvent; thus I + J is in fact nearly constant. The temperature dependence of the radical termination reactions (5) is expected to be determined by that of the solvent viscosity, which gives $\simeq 8$ kJ mol^{-1} for the energy of activation of k_{22} [14]. From these assumptions and (6) we obtain

$$\log_{10}\left(\frac{[\mathbf{2}]}{[\mathbf{1}]}\right) = -\frac{E_r - 4}{2.3\,RT} + \text{const.} \qquad (7)$$

Since $\log_{10}([\mathbf{2}]/[\mathbf{1}]) = \log_{10}(a\,[\mathbf{2}]/[\mathbf{1}]) - \log_{10} a$, where a is an arbitrary constant, eq. (7) shows that an *Arrhenius* plot of any quantity which can be taken from the spectra and which is proportional to the ratio [**2**]/[**1**] will give E_r. The line shape of each of the three radicals **1**, **2** and **3** was essentially invariant with temperature. Therefore, ratios of signal heights (corrected for a small temperature dependence of the saturation behavior of **2**) are proportional to [**2**]/[**1**].

Fig. 3 shows a plot of the logarithm of the ratio of signal heights S_2/S_1, corrected as above, against T^{-1}. The slope $(-2.0 \cdot 10^3$ K) combined with (7) gives $E_r = 43$ kJ mol^{-1}. We estimate the accuracy as $\pm$ 9 kJ mol^{-1}.

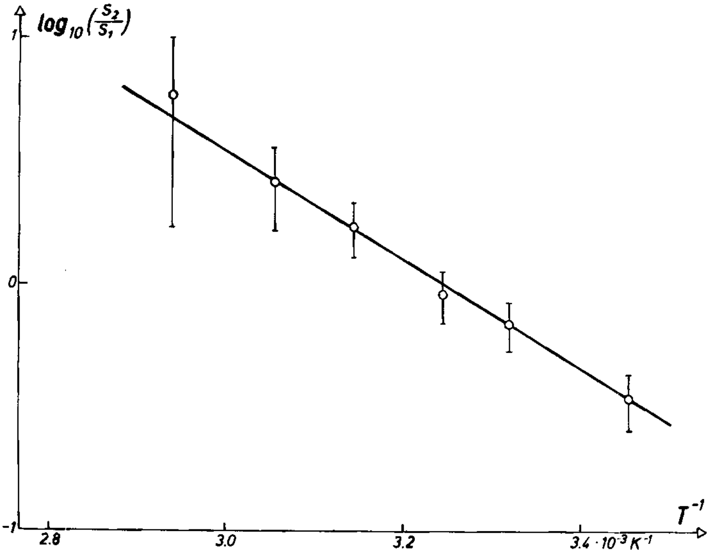

Fig. 3. *Plot of signal height ratios as a function of temperature*

Further, an approximate double integration and saturation correction of the ESR. signals showed that the concentration of **3** is less than about 10% of the total radical concentration, and that multiplication of S_2/S_1 by about 0.6 gives [**2**]/[**1**].

The activation energy agrees well with an estimate derived from literature data as follows: *Rüchardt* [17] has given accurate rate constant ratios for the decarbonylation of β-phenylisovaleraldehyde in 1,2-dichlorobenzene at $\simeq$ 410 K. His data yield a value of 15.5 kJ mol^{-1} for the difference between E_r and E for the reaction ($X = C_6H_5$):

$$XC(CH_3)_2\dot{C}H_2 + XC(CH_3)_2CH_2CHO \rightarrow XC(CH_3)_3 + XC(CH_3)_2CH_2\dot{C}O.$$

Taking E as equal to that for the same reaction with X = H in the gas phase, which is 27.2 kJ mol^{-1} [12], one obtains $E_r \simeq 42.7$ kJ mol^{-1}. Also, the observed irreversibility of the rearrangement is in accord with expectation since **1** → **2** is estimated to be exothermic by $\simeq$ 33 kJ mol^{-1} from the dissociation energies D(*neo*-C_5H_{11} – H) = 418 kJ mol^{-1} and D(*t*-C_4H_9 – H) = 385 kJ mol^{-1} [18], and the negligible difference in the standard enthalpies of formation for *t*-butylbenzene and isobutylbenzene [19].

From the value of E_r, it is clear that **1** → **2** does not proceed by simple dissociation and recombination, because **1** is estimated to be $\simeq$ 142 kJ mol^{-1} less energetic than phenyl + isobutene [18, 19]. More information about the rearrangement mechanism could be obtained from absolute measurement of k_r. From radical lifetimes in other chemical systems measured previously under similar conditions [7], we estimate the order of magnitude of k_r as 10^3 s^{-1} at 290 K. Experiments to measure k_r directly using time-resolved ESR. spectroscopy are in progress.

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77. Studies on the Constituents of Capsicum. Part 3[1]

A Quantitative Determination of Olefinic and Saturated Components by NMR. and of *trans*-Components by IR. Spectroscopy in a Capsaicinoid Mixture from Natural Source

by **Anneliese Müller-Stock, R. K. Joshi** and **J. Büchi**
Pharmazeutisch-chemische Abteilung des Pharmazeutischen Institutes der
Eidgenössischen Technischen Hochschule, Clausiusstrasse 25, 8006 Zürich (Schweiz)

(12. I. 73)

Introduction. – The crystalline pungent principle of *Capsicum annuum* is the mixture of capsaicin, dihydrocapsaicin and their homologs [1] [2]. We have already described the separation of these components by gas-chromatography [2] and their quantitative estimation in the mixture [3]. In the present work we report appropriate

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[1] For part 1 & 2 see [2] & [3].