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Absolute Rate Constants for the Reactions of Some Carbon-Centered Radicals with 2,2,6,6-Tetramethylpiperidine-*N*-oxyl[1]

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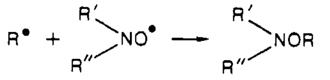
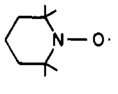
A time-resolved, laser flash photolysis study of the reaction of a variety of carbon-centered radicals with Tempo (2,2,6,6-tetramethylpiperidine-*N*-oxyl) at room temperature is reported. Some of the radicals examined and the corresponding measured rate constants ($M^{-1}\ s^{-1}$) are $CH_3(CH_2)_7\dot{C}H_2$, 1.2×10^9; $(CH_3)_3C^\bullet$, 7.6×10^8; $C_6H_5\dot{C}H_2$, 4.9×10^8; $C_6H_5\dot{C}(CH_3)_2$, 1.2×10^8; $(C_6H_5)_2\dot{C}CH_3$, 4.6×10^7. Arrhenius parameters have also been determined for the *n*-nonyl and benzyl radicals.

The reactions of a variety of carbon-centered radicals with numerous dialkyl nitroxides are known to be rapid.[3]



(1)

Direct, time-resolved measurements of the rate constants for reaction 1 appear to be confined to studies using pulse radiolysis in water as solvent,[3] under which conditions k_1 generally lies in the range $2\text{–}8 \times 10^8\ M^{-1}\ s^{-1}$. However, nitroxides have a large dipole moment[4,5] and their EPR nitrogen hyperfine splittings show that they must be rather strongly solvated in water.[6-8] There have been many different types of indirect measurements of k_1 in nonaqueous systems using various carbon-centered radicals and various nitroxides which have relied on some form of competitive kinetics.[3,9] In view of the growing use of stable nitroxides both to trap and, frequently, to identify carbon-centered radicals formed in nonaqueous systems[11-13,18-21] we decided to measure some absolute rate constants for these reactions in an alkane solvent at ambient temperatures by the direct, time-resolved technique of nanosecond laser flash photolysis. In most of this work, we have employed Tempo, **1**, as the nitroxide trap. A few measurements have also been made with 1,1,3,3-tetramethylisoindoline-*N*-oxyl,[22] **2**, which is becoming increasingly important as a trap in mechanistic studies.



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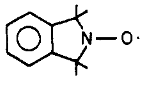

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Results

The carbon-centered radicals were generated by laser flash photolysis (LFP) of appropriate precursors. These included symmetrically substituted ketones (eq 2), diacyl peroxides (eq 3), and di-*tert*-butyl peroxide in the presence of a hydrogen donating substrate (eq 4 and 5). Rate

$$R_2CO \xrightarrow{h\nu} 2R^\bullet + CO \qquad (2)$$

$$(RCO_2)_2 \xrightarrow{h\nu} 2R^\bullet + 2CO_2 \qquad (3)$$

$$Me_3COOCMe_3 \xrightarrow{h\nu} 2Me_3CO^\bullet \qquad (4)$$

$$Me_3CO^\bullet + RH \rightarrow Me_3COH + R^\bullet \qquad (5)$$

constants for reaction 1 were measured in the usual manner by monitoring the "quenching" (increased rate of decay) of the $R^\bullet$ radical produced in the laser pulse by the addition of known concentrations of the nitroxide. The decay of $R^\bullet$ follows pseudo-first-order kinetics and the experimental rate constant is given by

$$k_{\text{exp}} = k_0 + k_1[\text{nitroxide}]$$

where k_0 represents the sum of the rate constants for all first- and pseudo-first-order decay processes of $R^\bullet$ except for its reaction with the nitroxide. For those radicals having a measurable absorption in the 290–800 nm range,

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[3] For a comprehensive survey of these rate constants, see: Ingold, K. U. *Landolt-Börnstein. New Series. Radical Reaction Rates in Liquids*: Fischer, H., Ed.; Springer-Verlag: Berlin, 1984; Vol. 13, Part c, pp 181–200.

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[8] For a compilation of nitroxide EPR parameters, see: Forester, A. R. *Landolt-Börstein. New Series. Magnetic Properties of Free Radicals*; Fischer, H., Hellewege, K.-H., Eds.; Springer-Verlag: Berlin, 1979; Vol. 9, Part c1, Chapter 6.

[9] For example, by using as the competing reaction of free radical "clock"[10] in which $R^\bullet$ rearranges at a known rate to form a different carbon-centered radical,[11-13] by using as the competing reaction the addition of $R^\bullet$ to a nitroso or nitrone spin-trap,[14] by using the competition with the reaction of $R^\bullet$ with O_2,[15] etc. The only time-resolved study in a nonaqueous medium was of the reaction of the cyclopropyl radical with Tempo in benzene[16] and it must be admitted that even in this case β-methylstyrene was used as a "probe"[17], i.e., there was a competition between Tempo and the β-methylstyrene for the cyclopropyl radicals.

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Table I. Absolute Rate Constants for Reactions of Some Carbon-Centered Radicals with Nitroxides in Isooctane at 20 ± 2 °C

precursor of $R^\bullet$	precursor concn (M)	LFP wavelength (nm)[a]	monitoring wavelength (nm)	method[b]	radical $R^\bullet$	nitroxide[c]	$10^{-7}k_1$ ($M^{-1}\ s^{-1}$)[d]
$(RCO_2)_2$	0.10	308	329	P	$CH_3(CH_2)_7\dot{C}H_2$	1	123 ± 26
$(RCO_2)_2$	0.10	308	329	P	$(CH_3)_3C\dot{C}H_2$	1	96 ± 22
R_2CO	0.05	308	317	D	$(CH_3)_3C^\bullet$	1	76 ± 16
R_2CO	0.05	308	317	D	$(CH_3)_3C^\bullet$	2	88 ± 12
R_2CO	0.01	308	317	D	$C_6H_5\dot{C}H_2$	1	49 ± 8
R_2CO	0.01	308	317	D	$C_6H_5\dot{C}H_2$	2	55 ± 5
$Me_3CO^\bullet$ + RH	3.3[e,f]	308	320	D	$C_6H_5\dot{C}HCH_3$	1	16 ± 4
$Me_3CO^\bullet$ + RH	3.2[e,g]	308	322	D	$C_6H_5\dot{C}(CH_3)_2$	1	11.8 ± 0.1
R_2CO	0.005	308	320	D	$(C_6H_5)_2\dot{C}H$	1	4.63 ± 0.02
$Me_3CO^\bullet$ + RH	0.5[e,h]	308	320	D	$(C_6H_5)_2\dot{C}CH_3$	1	4.58 ± 0.47
$Me_3CO^\bullet$ + RH	0.1[e,h]	308	335	D	$(C_6H_5)_3C^\bullet$	1	<0.1
$Me_3CO^\bullet$ + RH	2.8[e,h]	337	366	D	1-$C_{10}H_7\dot{C}H_2$[i]	1	8.2 ± 0.2
$Me_3CO^\bullet$ + RH	0.50[e,h]	337	380	D	2-$C_{10}H_7\dot{C}H_2$[j]	1	5.7 ± 1.8

[a] A Lumonics E-860-2 excimer laser (Xe–HCl–He mixture) was employed for 308-nm LFP (~4 ns, up to 80 mJ/pulse) and a Molectron UV-24 nitrogen laser for 337-nm LFP (~8 ns, up to 10 mJ/pulse). [b] P = probe; radical's addition to 0.12 M $[CH_2{=}C(C_6H_5)]$ was monitored. D = direct; radical's own absorption was monitored. [c] **1** = Tempo. **2** = 1,1,3,3-tetramethylisoindoline-*N*-oxyl. [d] Errors correspond to 95% confidence limits but include only random errors. [e] RH concentration. [f] [Di-*tert*-butyl peroxide] = 0.82 M. [g] [Di-*tert*-butyl peroxide] = 0.55 M. [h] [Di-*tert*-butyl peroxide] = 1.1 M. [i] 1-Naphthylmethyl. [j] 2-Naphthylmethyl.

viz., *tert*-butyl, benzyl, and all other aralkyl radicals, the quenching was monitored directly, i.e., by following the change with time in the intensity of the radical's absorption. Primary alkyl radicals do not have an absorption in the above-mentioned spectral region and it was therefore necessary to employ the "probe" technique of Scaiano and co-workers[17] with these radicals. As the probe we chose 1,1-diphenylethylene, to which a primary alkyl radical such as *n*-nonyl adds to produce a 1,1-diphenylalkyl radical

$$CH_3(CH_2)_7\dot{C}H_2 + CH_2{=}C(C_6H_5)_2 \rightarrow CH_3(CH_2)_9\dot{C}(C_6H_5)_2 \quad (6)$$

which has a strong absorption at ca. 330 nm.[23] The experimental rate constant that is obtained by monitoring at this wavelength can be represented by

$$k_{exp} = k_0 + k_6[CH_2{=}C(C_6H_5)_2] + k_1[\text{nitroxide}]$$

By working with a variable concentration of the probe and no nitroxide it is simple to measure k_6 from a plot of k_{exp} vs. $[CH_2{=}C(C_6H_5)_2]$ (see Figure 1). In this way, we obtained with the *n*-nonyl radical a value for $k_6 = (2.97 \pm 0.01) \times 10^5\ M^{-1}\ s^{-1}$ at 20 °C.[24] Of more importance, by working with a constant concentration of probe and a variable concentration of nitroxide it is simple to determine k_1 from a plot of k_{exp} vs [nitroxide].

Values of k_1 in isooctane at 20 °C were measured for various carbon-centered radicals as described above. They are summarized in Table I together with information regarding the source of the radical, the wavelength that was monitored, etc.

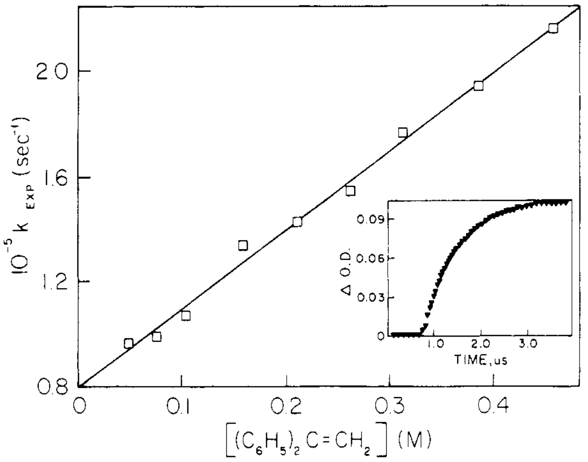

Figure 1. Bimolecular "quenching" plot for addition of the *n*-nonyl radical to 1,1-diphenylethylene. The rate constant, k_6, for this process is obtained from the slope, $k_{exp}/[(C_6H_5)_2C{=}CH_2]$. The main inset shows a representative single exponential growth of the $CH_3(CH_2)_9\dot{C}(C_6H_5)_2$ radical monitored at 329 nm after 308-nm LFP of 0.1 M decanoyl peroxide in isooctane containing 0.12 M diphenylethylene.

Discussion

The direct determination of the absolute rate constants for the reaction of carbon-centered radicals with nitroxides was possible only because of the high rates of these processes. These high rates allowed very low concentrations of nitroxides **1** and **2** to be used in the quenching experiments, which was crucial because both nitroxides have strong UV-vis absorptions[28] and it is important that the laser pulse be absorbed principally by the $R^\bullet$ precursor.[29]

Before considering the kinetic data summarized in Table I it must be emphasized that reaction 1 is known to be reversible even at ambient temperatures when $R^\bullet$ is a resonance-stabilized radical.[15] Unfortunately, there are no truly reliable kinetic or thermodynamic data regarding

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(23) 1,1-Diphenylethylene is not suitable as a probe for carbon-centered radicals generated by reaction 5 because *tert*-butoxyl radicals also add rapidly to this olefin.

(24) This rate constant would appear to be in general agreement with Fischer et al.'s[25] time-resolved measurements of the rate constant for the addition of the *tert*-butyl radical to styrene, viz.,[25] $1.3 \times 10^5\ M^{-1}\ s^{-1}$ at 300 K. However, there can be little doubt that an indirect estimate of the rate constant for the addition of the *tert*-butyl radical to 1,1-diphenylethylene by Pedulli and co-workers[26] is badly in error. These workers give an upper limit for this rate constant of 400 $M^{-1}\ s^{-1}$ at 370 K.[26] Even if the revised kinetic data for the neophyl rearrangement[27] (employed as a "clock" by Pedulli) is used, this upper limit rises only to $2.6 \times 10^3\ M^{-1}\ s^{-1}$.

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(28) Note that Tempo abstracts hydrogen from hydrocarbons on photoexcitation, see: Johnston, L. J.; Tencer, M.; Scaiano, J. C. *J. Org. Chem.* **1986**, *51*, 2806–2808.

(29) Under such conditions, i.e., low nitroxide concentrations and high photon flux, there is always a potential danger that the substrate which is in low concentration will be seriously depleted by even a single laser pulse. In the present instance, blank experiments showed that with 3×10^{-3} M Tempo up to 8 laser pulses did not deplete the nitroxide significantly and so the results obtained with 8 pulses could be, and generally were, signal-averaged.

the extent to which reaction 1 is (or is not) reversible for a specific $R^{\bullet}$ structure. What evidence there is[15] suggests that even the 1,1-diphenylalkyl radical/Tempo adduct[15a] will decompose very slowly at 20 °C.[30] However, k_{-1} may become important at this temperature for $R^{\bullet}$ = triphenylmethyl.

The rate constants for reaction 1 decrease as the thermodynamic stabilities of the $R^{\bullet}$ radicals[31] increase. That is, k_1 for reaction with Tempo decreases along the series $R^{\bullet} = CH_3(CH_2)_7\dot{C}H_2 > (CH_3)_3C\dot{C}H_2 > (CH_3)_3\dot{C} > C_6H_5\dot{C}H_2 > C_6H_5\dot{C}HCH_3 > C_6H_5\dot{C}(CH_3)_2 > C_{10}H_7\dot{C}H_2 > (C_6H_5)_2\dot{C}H \sim (C_6H_5)_2\dot{C}CH_3 > (C_6H_5)_3\dot{C}$. The present data do not reveal how much of the difference in k_1 values between, for example, $R^{\bullet} = CH_3(CH_2)_7\dot{C}H_2$ and $(CH_3)_3\dot{C}$ or between $R^{\bullet} = C_6H_5\dot{C}H_2$ and $C_6H_5\dot{C}(CH_3)_2$ is due to steric factors and how much is due to the greater thermodynamic stabilization of the tertiary radicals relative to the primary. However, the k_1 values for the benzyl (4.9×10^8 M^{-1} s^{-1}) and 1-naphthylmethyl radicals (8.2×10^7 M^{-1} s^{-1}) indicate that thermodynamic factors play some role since the latter radical has ca. 4.5 kcal/mol greater resonance stabilization than the former,[32] while steric effects would be expected to be similar for these two radicals.

Even the most reactive carbon-centered radicals such as *n*-alkyl ($k_1 = (1.23 \pm 0.26) \times 10^9$ M^{-1} s^{-1}, Table I) or cyclopropyl ($k_1 = (1.2 \pm 0.3) \times 10^9$ M^{-1} s^{-1})[16] are trapped by Tempo at a rate which is roughly 1 order of magnitude smaller than the rate of a diffusion-controlled process. The barrier to a reaction which, at first sight, would appear to be a straightforward radical–radical coupling appears to be due to an unfavorable entropy of activation rather than to an unfavorable enthalpy of activation. Thus, a few measurements of k_1 for the reactions of nonyl radicals and benzyl radicals with Tempo were made over a range of temperatures. There was little change in k_1 and the data could be represented by

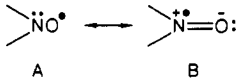
$$CH_3(CH_2)_7\dot{C}H_2 + \mathbf{1} \ (T = -3\ ^{\circ}C \text{ to } 44\ ^{\circ}C)$$

$$\log (k_1/M^{-1}\ s^{-1}) = (10.4 \pm 0.6) - (1.8 \pm 0.9)/\theta$$

$$C_6H_5\dot{C}H_2 + \mathbf{1} \ (T = -40\ ^{\circ}C \text{ to } 33\ ^{\circ}C)$$

$$\log (k_1/M^{-1}\ s^{-1}) = (9.3 \pm 0.40) - (0.88 \pm 0.49)/\theta$$

where $\theta = 2.3RT$ (kcal/mol) and the errors correspond to two standard deviations. These two preexponential factors lie between the preexponential factors that have been measured for the bimolecular self-reactions (combination and disproportionation) of carbon-centered radicals in solution, viz.[33] ca. $10^{11.5 \pm 0.5}$ M^{-1} s^{-1}, and the preexponential factors found for the additions of carbon-centered radicals to carbon–carbon double bonds, viz.[36] ca. $10^{8.5 \pm 0.5}$ M^{-1} s^{-1}. The magnitude of the *A* factors for reaction 1 can perhaps be rationalized in terms of the major contribution (perhaps nearly 50%)[5] that the dipolar, double-bonded canonical structure, B, makes to the A ↔ B nitroxide resonance hybrid.


A B

Finally, we will compare the kinetic data given in Table I with some of the more reliable results obtained by other workers.[37] Beckwith and Bowry[13] have utilized the free radical "clock"[10] method to measure k_1 for the reaction of a variety of primary alkyl radicals with **2** in cyclohexane. They also employed conventional competitive kinetics to study the reaction of **1** and **2** with the $CH_3CH_2^{\bullet}$ radical (generated by thermal decomposition of propionyl peroxide at 80 °C). For the ethyl radical they obtained $k_1(\mathbf{2})/k_1(\mathbf{1}) = 1.05 \pm 0.08$, which suggests that **2** may be slightly more reactive than **1**—an idea that is supported by our own kinetic data for the reactions of *tert*-butyl and benzyl radicals with these two nitroxides. Selecting just Beckwith and Bowry's results with the 5-hexenyl radical (the cyclization of which to the cyclopentylmethyl radical is certainly the most studied and best calibrated radical "clock") gives[38]

$$CH_2{=}CH(CH_2)_3\dot{C}H_2 + \mathbf{2}$$

$$\log (k_1/M^{-1}\ s^{-1}) = 9.7 - 0.9/\theta$$

$$k_1 = 1.07 \times 10^9\ M^{-1}\ s^{-1} \text{ at } 20\ ^{\circ}C$$

Both the preexponential factor and the activation energy are in very satisfactory agreement with the values obtained for $CH_3(CH_2)_7\dot{C}H_2 + \mathbf{1}$ in the present work. The same is even more true for the calculated values of k_1 for reaction of a primary alkyl radical with **1** at 20 °C, viz., ca. $1.07 \times 10^9/1.05 = 1.02 \times 10^9$ M^{-1} s^{-1}, cf. our direct measurements which gave 1.23×10^9 M^{-1} s^{-1} for this quantity.

Time-resolved, pulse radiolytic studies on the trapping of carbon-centered radicals by nitroxides in water at room temperature[3] suggest that k_1 values may be about half as large in this solvent as in hydrocarbon solvents. Comparison with the present data is not easy as Tempo has not been employed and most of the radicals, which were derived from alcohols, would themselves be strongly hydrogen-bonded. The closest comparison would be for reaction 8, for which Asmus et al.[39] give $k_8 = (4.0 \pm 0.4) \times 10^8$ M^{-1} s^{-1} at room temperature. Our own results for the


(8)

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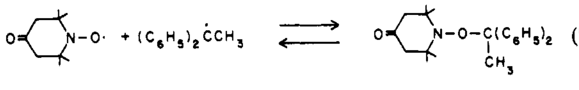
(30) The most complete data on reversibility is contained in ref 15a and refers to reaction 7. Over the temperature range 38 to 100 °C measurements were made which yielded $\Delta H^{\circ} \approx -21.4$ kcal/mol and $\Delta S^{\circ} \approx -36$ cal/mol K, and over a temperature range from 20 to 50 °C decomposition of the hydroxylamine in the presence of oxygen yielded the equation $\log (k_{-7}/s^{-1}) = 14.8 - 5348/T$. From these data, we calculate that at 20 °C $k_{-7} = 3.5 \times 10^{-4}$ s^{-1} and $k_7 = 4.4 \times 10^4$ M^{-1} s^{-1}. (A slightly different set of data gave $k_7 = 5 \times 10^4$ M^{-1} s^{-1} at 30 °C.[15a]). Our present results imply that Howard and Tait's[15a] value for k_7 is as much as 3 orders of magnitude less than the true value (cf. $(C_6H_5)_2\dot{C}CH_3$ in Table I). The origin of the error in the earlier work[15a] is not apparent to us, but it may lie in incomplete scavenging of the $(C_6H_5)_2\dot{C}CH_3$ radicals by O_2.


(7)

(31) (a) As measured by R–H bond strength,[31b] for example. (b) McMillen, D. F.; Golden, D. M. *Ann. Rev. Phys. Chem.* **1982**, *33*, 493–532.

(32) Peyman, A.; Mickl, E.; Beckhaus, H.-D. *Chem. Ber.* **1987**, *120*, 713–725.

(33) For example, for the *tert*-butyl + *tert*-butyl reaction in *n*-alkane solvents, $\log (A/M^{-1}\ s^{-1})$ lies in the range 11.6 – 12.0 depending on the hydrocarbon[34] and for the benzyl + benzyl reaction $\log (A/M^{-1}\ s^{-1}) = 10.7$ in cyclohexane and 11.9 in toluene.[35]

(34) Schuh, H.; Fischer, H. *Int. J. Chem. Kinet.* **1976**, *8*, 341–356. For additional data in other solvents, see: Schuh, H.-H.; Fischer, H. *Helv. Chim. Acta* **1978**, *61*, 2130–3164, 2463–2481.

(35) Lehni, M.; Schuh, H.; Fischer, H. *Int. J. Chem. Kinet.* **1979**, *11*, 705–713.

(36) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley-Interscience: New York, 1976.

(37) The great abundance of (purported) measurements of k_1 for a variety of carbon-centered radicals and a number of nitroxides[3] in no way reflects the reliability of most of these measurements!

(38) Results obtained for the reaction of **2** with a tertiary alkyl radical could be represented by $\log (k_1/M^{-1}\ s^{-1}) = 9.1 + 0.3/\theta$.[13] Since the activation energy for this reaction cannot be negative the calibration of this "clock" is probably somewhat unreliable and hence the results should not be compared with our value of k_1 for $(CH_3)_3\dot{C}$ + **2**.

(39) Asmus, K.-D.; Nigam, S.; Willson, R. L. *Int. J. Radiat. Biol.* **1976**, *29*, 211–219.

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reactions of the *n*-nonyl and *tert*-butyl radicals with Tempo would suggest a value for k_1 of ca. 8–9 × 10^8 M^{-1} s^{-1} for the reaction of the cyclopentyl radical with Tempo in hydrocarbon solvents.

Experimental Section

All reagents and solvents used in this work were of the highest purity available commercially (>98%). They were either used as received or were further purified by standard procedures.

The lasers that were used are described in footnote a of Table I. The laser flash photolysis apparatus has been adequately described in earlier publications from this laboratory.[40,41] In a typical experiment, 2 mL of a solution of Tempo [(1×10^{-5})–(5×10^{-3}) M] in isooctane containing the precursor of the radical of interest was placed in a 7 × 7 mm^2 Suprasil quartz tube and was deoxygenated by purging for ca. 2–5 min with oxygen-free nitrogen. Up to 8 pulses from the laser were employed per sample, the results being signal-averaged. In all cases examined, identical results were obtained in these "static" systems as in systems in which fresh reagents flowed continuously through the cell.

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Registry No. 1, 2564-83-2; **2**, 80037-90-7; $CH_3(CH_2)_7CH_2\bullet$, 32757-65-6; $(CH_3)_3CCH_2\bullet$, 3744-21-6; $(CH_3)_3C\bullet$, 1605-73-8; $PhCH_2\bullet$, 2154-56-5; $PhMeCH\bullet$, 2348-51-8; $PhMe_2C\bullet$, 4794-07-4; $Ph_2CH\bullet$, 4471-17-4; $Ph_2MeC\bullet$, 51314-23-9; $Ph_3C\bullet$, 2216-49-1; 1-$C_{10}H_7CH_2\bullet$, 7419-60-5; 2-$C_{10}H_7CH_2\bullet$, 7419-61-6.

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Kinetics of the Coupling Reactions of the Nitroxyl Radical 1,1,3,3-Tetramethylisoindoline-2-oxyl with Carbon-Centered Radicals

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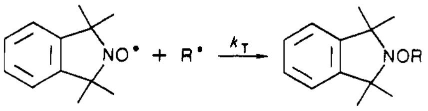
Radical clocks have been used to study the kinetics of the coupling of the nitroxyl radical 1,1,3,3-tetramethylisoindoline-2-oxyl (T) in cyclohexane or benzene with a variety of carbon-centered radicals including simple unhindered primary, secondary, and tertiary radicals (**1**, **2**, **3**, **4**, **5**, **8**, and **9**), neopentyl radicals (**6** and **7**), an alkoxyalkyl radical (**10**), an acyl radical (**11**), and alkoxycarbonyl radicals (**12** and **13**). The reaction rates are slower than expected for diffusion control. Within the limits of experimental error the coupling rate constant, k_T, for each radical is ca. 1 × 10^9 M^{-1} s^{-1} and is given by log $k_T = 9.7 - 0.9/\theta$. Tempo couples with carbon-centered radicals at similar rates. The coupling reaction can be used as a kinetic probe. By this means discrepancies in existing data for some clocks have been resolved and the cyclopropylmethyl–butenyl radical rearrangement has been recalibrated (log $k_r = 13.3 - 7.4/\theta$).

Introduction

Stable nitroxides are very efficient radical scavengers or traps and as such have been used to investigate the mechanisms of reactions involving putative free radical intermediates. This paper describes a reaction and analysis technique designed to extend the use of nitroxide radical coupling from a qualitative mechanistic probe to a reliable method for evaluating the kinetic parameters and stereochemistry of radical reactions.

1,1,3,3-Tetramethylisoindoline-2-oxyl (T)[1] and similar species[2] couple with carbon-centered radicals (R•), but not with oxygen-centered radicals, to give stable alkoxyamine products (RT).[3-8] Solomon and his co-workers[4] have used this selective coupling reaction to trap and identify reactive intermediates in the initial stages of free radical polymerizations of commercial and theoretical importance.



T RT

By analogy with other radical–radical termination processes, the rate constant, k_T, for nitroxide coupling has been assumed to be at or near the diffusion-limited value.[5] For example, Robbins and Eastman[6] used an estimated value of 10^{10} M^{-1} s^{-1} for the rate constant for coupling of the phenylacetyl radical with Tempo (2,2,6,6-tetramethylpiperidineoxyl) in their determination of the rate of decarbonylation (**11** → **11′**) of the former. More recent literature data suggest a lower value. Schmid and Ingold[7] found the rate constants for coupling of *n*-hexyl radical with various nitroxides in benzene to be 3–5 × 10^8 M^{-1} s^{-1} at 40 °C and these values agree well with the results of pulse radiolysis studies on reactions in water.[8] A laser flash photolysis study[9] of the coupling of cyclopropyl radical

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