

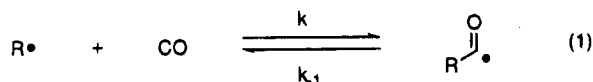
Rate Constants for Addition of a Primary Alkyl Radical to Carbon Monoxide

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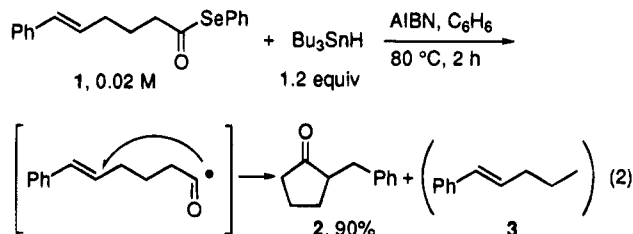
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The addition of a radical to carbon monoxide is an important key step in free-radical carbonylation.¹ The absence of kinetic data for this process in organic solvents^{2,3} may have constituted one of the main reasons for the long-delayed development in this promising synthetic area. In this paper, we wish to disclose approximate rate constants for addition of a primary alkyl radical to carbon monoxide, which was calibrated by employing a well-established radical clock system.⁴



Since the CO trapping of alkyl radicals is reversible, there is the necessity of taking into account the rate of the backward decarbonylation reaction (eq 1). Unfortunately, the only known kinetic data for decarbonylation of acyl radicals to give primary alkyl radicals and CO were those measured in the gas phase and were varied from 10^2 to 10^4 at 80 °C.⁵ This led us to employ a "decarbonylation free" system comprising the sequential CO trapping of an alkyl radical followed by the rapid 5-exo cyclization of the resulting acyl radical onto a styryl terminus. The decarbonylation possibility was checked beforehand. Thus, 6-phenyl-5-hexenoyl phenyl selenide (1) and nonanoyl phenyl selenide, for comparison, were exposed to tin hydride mediated free-radical reaction conditions (0.02 M, 80 °C, 2 h), respectively. Nonanoyl radical yielded significant amounts of octane (36%), decarbonylation product, together with nonanal (60%).⁶ In contrast, reaction of 1 under identical condi-

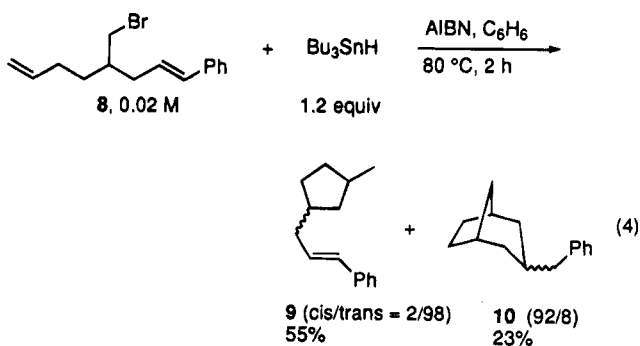
tions yielded 2-(phenylmethyl)cyclopentanone (2) in high yield (90%) with no detectable amount of decarbonylation product 3 (by GC (<1:150)) (eq 2).⁷ When the reaction of 1 was conducted at 100 °C, only a trace amount of decarbonylation product 3 was detected.



Scheme 1 summarizes our plan to estimate the rate constant for the addition of a primary alkyl radical to carbon monoxide. Two paths are available from the key radical 4, cyclization to produce a cyclopentylmethyl radical 6 proceeding with a known rate constant (k_{5-exo}) versus addition to carbon monoxide to give 5 proceeding with a rate constant of k_{CO} . In the latter case, the resulting acyl radical 5 would be trapped efficiently by the styryl terminus to furnish stable benzyl type radical 7. Thus, from the ratio of (products B arising from 7)/ (products A arising from 6), the ratio of rate constants (k_{CO}/k_{5-exo}) could be calculated using eq 3.

$$\frac{d[B]}{d[A]} = \frac{k_{CO}[CO]}{k_{5-exo}} \quad (3)$$

As a prelude to the kinetic CO studies, the tin hydride mediated cyclization of 8 was carried out under a nitrogen atmosphere. This experiment yielded a mixture of cyclization product 9 and a tandem cyclization product 10 (eq 4). It is important to point out that no



direct reduction or cyclization onto the styryl unit of the primary radical 4 was detected.

Kinetic studies of the carbonylation of radical 4 in benzene solution were performed over the temperature range of 60–118 °C at 34–107 atm using V-65 (2,2'-azobis(2,4-dimethylvaleronitrile)), V-40 (1,1'-azobis(cyclohexane-1-carbonitrile)), and AIBN as radical initiators. In one experiment, 2-methyl-2-propanol was employed as the solvent to ensure that solvent effects on the kinetics of the radical carbonylation would be minor.⁸

(7) The same acyl radical cyclization starting with the corresponding acyl methyl selenide was reported by Curran and Schwartz to give a high yield of 2; see: (a) Schwartz, C. E.; Curran, D. P. *J. Am. Chem. Soc.* **1990**, *112*, 9272. Also see the carbonylation route: (b) Ryu, I.; Kusano, K.; Hasegawa, M.; Kambe, N.; Sonoda, N. *J. Chem. Soc., Chem. Commun.* **1991**, 1018.

(1) Selected work on free-radical carbonylation: (a) Ryu, I.; Kusano, K.; Ogawa, A.; Kambe, N.; Sonoda, N. *J. Am. Chem. Soc.* **1990**, *112*, 1295. (b) Ryu, I.; Yamazaki, H.; Kusano, K.; Ogawa, A.; Sonoda, N. *J. Am. Chem. Soc.* **1991**, *113*, 8558. (c) Ryu, I.; Hasegawa, M.; Kurihara, A.; Ogawa, A.; Tsunoi, S.; Sonoda, N. *Synlett* **1993**, 143. (d) Ryu, I.; Nagahara, K.; Yamazaki, H.; Tsunoi, S.; Sonoda, N. *Synlett* **1994**, 643. (e) Tsunoi, S.; Ryu, I.; Sonoda, N. *J. Am. Chem. Soc.* **1994**, *116*, 5473. (2) (a) Carvert, J. G.; Gruver, J. T. *J. Am. Chem. Soc.* **1958**, *80*, 1313. (b) Watkins, K. W.; Thompson, W. W. *Int. J. Chem. Kinet.* **1973**, *5*, 791. (c) Watkins, K. W.; Ward, W. W. *Int. J. Chem. Kinet.* **1974**, *6*, 855. (d) Anastasi, C.; Maw, P. R. *J. Chem. Soc., Faraday Trans. 1* **1982**, *78*, 2423.

(3) Very recently, two reports concerning rate constants for addition of methyl radical and cyclohexyl radical to CO in different solvents appeared. (a) Methyl radical/CO/water ($2.0 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$, 25 °C): Bakac, A.; Espenson, J. H. Young, V. G., Jr. *Inorg. Chem.* **1992**, *31*, 4959. (b) Cyclohexyl radical/CO/cyclohexane ($1.2 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$, 50 °C): Boese, W. T.; Goldman, A. S. *Tetrahedron Lett.* **1992**, *33*, 2119.

(4) For reviews on radical clocks, see: (a) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1980**, *13*, 317. (b) Newcomb, M. *Tetrahedron* **1993**, *49*, 1151.

(5) (a) Kerr, J. A.; Lloyed, A. C. *Trans. Faraday Soc.* **1967**, *63*, 2480. (b) Cadman, P.; Dodwell, C.; Trotman-Dickenson, A. F.; White, A. J. *J. Chem. Soc. A* **1970**, 2371. (c) Cadman, P.; Dodwell, C.; Trotman-Dickenson, A. F.; White, A. J. *J. Chem. Soc. A* **1970**, 3189. Also see ref 2b,c and a recent review: (d) Brown, C. E.; Neville, A. G.; Rayner, D. M.; Ingold, K. U.; Luszytyk, J. *Aust. J. Chem.* **1995**, *48*, 363. Cf.: ref 11.

(6) Pfenninger, J.; Heuberger, C.; Graf, W. *Helv. Chim. Acta* **1980**, *63*, 2328.

Scheme 1

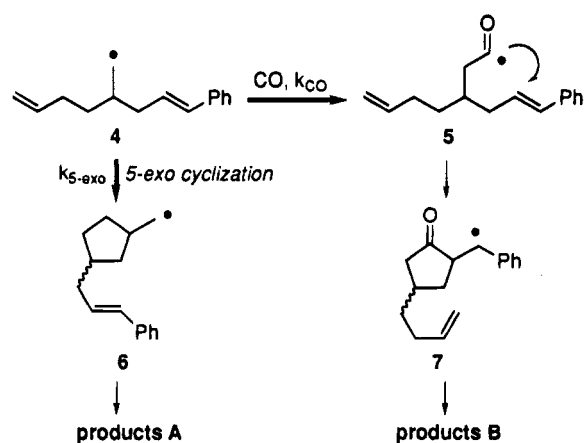
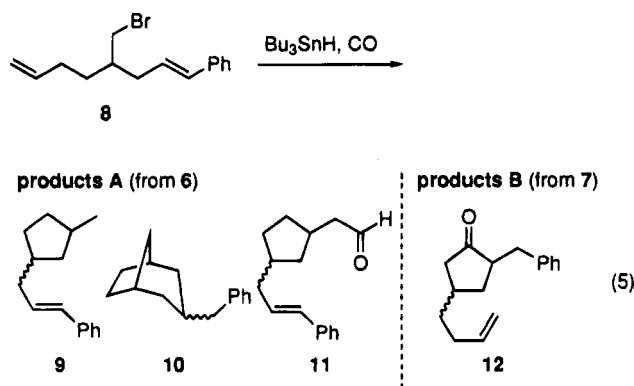


Table 1. Rate Data for Addition of a Primary Alkyl Radical to Carbon Monoxide at Various Temperatures

temp (°C)	$k_{5\text{-exo}}^a$ (s ⁻¹)	CO (atm)	[CO] ^b (M)	B/A	k_{CO} (M ⁻¹ s ⁻¹)
60	2.1×10^6	97	0.82	0.150	3.9×10^5
		96	0.81	0.130	3.4×10^5
		93	0.78	0.120	3.2×10^5
70	2.7×10^6	96	0.81	0.125	4.2×10^5
		93	0.78	0.132	4.6×10^5
		88	0.74	0.115	5.6×10^5
80	3.6×10^6	106	0.89	0.158	6.4×10^5
		99	0.83	0.161	7.0×10^5
		34	0.28	0.053	6.7×10^5
		107	0.90	0.142	9.2×10^5
100	5.8×10^6	107	0.90	0.155	1.0×10^6
		97	0.81	0.113	8.0×10^5
		107	0.89	0.137	1.3×10^6
118	8.6×10^6	107	0.89	0.137	1.3×10^6
		93	0.78	0.120	1.3×10^6
80 ^c	3.6×10^6	99	0.89	0.148	6.4×10^5

^a Reference 9. ^b See ref 10. ^c 2-Methyl-2-propanol was used as a solvent.

When the radical reaction was performed under CO pressures two carbonylation products **11** and **12** were obtained together with uncarbonylated products **9** and **10** (eq 5). Aldehyde **11** arises from carbonylation of the



cyclized radical **6**, and ketone **12** arises from carbonylation and cyclization of **4**. Thus, the ratio of B/A corresponds to the ratio of **12**/(**9** + **10** + **11**). These results are summarized in Table 1.

Rate constants for CO trapping of a primary radical **4** at the different temperatures were calculated from the

experimentally obtained values of B/A along with known values of $k_{5\text{-exo}}$ and with postulated CO concentrations. The $k_{5\text{-exo}}$ values used as the radical clock were obtained from the reported value by Beckwith for 2-methyl-5-hexenyl radical cyclization.⁹ The CO concentrations in benzene were calculated by multiplying the CO pressures used times the reported value for [CO] under atmospheric pressure.¹⁰

The calculated k_{CO} values gave the Arrhenius function shown in eq 6. Equation 6 leads to the Arrhenius

$$\ln k_{\text{CO}} = 21.8 - (3.0 \times 10^3)/T \quad (6)$$

parameters $E_a = 6.0$ kcal/mol and $\log A = 9.5$. The calculated rate constant for addition of the primary radical **4** to CO at 80 °C is approximately 6.0×10^5 M⁻¹ s⁻¹.

During the course of previous synthetic work in our laboratory, we frequently observed that primary alkyl radicals were more efficiently carbonylated than secondary and tertiary alkyl radicals.^{1b,c} However, the obtained rate constant for a primary radical in this study (2.7×10^5 M⁻¹ s⁻¹ at 50 °C; a converted value for comparison) is similar to the rate constant for addition of cyclohexyl radical to CO (1.2×10^5 M⁻¹ s⁻¹ at 50 °C)^{3b} which was reported by Goldman and Boese recently. Very recently, Chatgililoglu and co-workers estimated approximate decarbonylation rates of primary, secondary, and tertiary acyl radicals.¹¹ According to the report, the rate constant for decarbonylation of a secondary acyl radical is 30 times faster than that for decarbonylation of a primary acyl radical at 80 °C. Hence, we consider that the superiority in carbonylation of primary alkyl radicals over secondary radicals can result from slow backward decarbonylation reaction rather than from CO trapping process.

In summary, the present work has provided the first kinetic data for addition of a primary alkyl radical to carbon monoxide.¹² We hope that the present data will serve as a useful guide in the planning of free-radical reactions of CO.

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Supporting Information Available: Characterization data for compounds **9–12** and experimental details for the syntheses of those products and their precursors (16 pages).

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(10) [CO] = [CO]_{1atm} × (CO pressure); [CO]_{1atm} = 0.0084 M (in benzene, 60 °C); [CO]_{1atm} = 0.0090 M (in *t*-BuOH, 50 °C). Taken from: Fogg, P. G. T.; Gerrard, W. *Solubility of Gases in Liquids*; Wiley: New York, 1991; p 274.

(11) The approximate rate constants for decarbonylation of dodecanoyl radical (1.3×10^4 s⁻¹) and 2-ethylhexanoyl radical (3.9×10^5 s⁻¹) were recently estimated (in *tert*-butylbenzene, 80 °C); see: Chatgililoglu, C.; Lucarini, M. *Tetrahedron Lett.* **1995**, *36*, 1299. Chatgililoglu, C.; Ferreri, C.; Lucarini, M.; Pedrielli, P.; Pedulli, G. F. *Organometallics* **1995**, *14*, 2672. Cf.: Applequist, D. E.; Kaplan, L. J. *Am. Chem. Soc.* **1965**, *87*, 2194.

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