

Kinetics of Cyclopropyl Radical Reactions. 1. Absolute Rate Constants for Some Addition and Abstraction Reactions¹

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Abstract: The reactions of cyclopropyl radicals produced in the photodecomposition of bis(cyclopropylformyl) peroxide have been examined with the use of laser flash photolysis techniques. For example, the reactions with styrene, β -methylstyrene, 1,4-cyclohexadiene, and carbon tetrachloride have rate constants in benzene at 298 K of $(1.5 \pm 0.3) \times 10^7$, $(2.0 \pm 0.5) \times 10^6$, $(7.9 \pm 0.3) \times 10^6$, and $(1.5 \pm 0.2) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$, respectively. In the case of carbon tetrachloride, a study of the temperature dependence of the kinetics (1:4 benzene:CF₂ClCFCl₂) in the 0 to 68 °C range yields $\log(k_{14}/\text{M}^{-1} \text{ s}^{-1}) = (8.7 \pm 0.4) - (3.5 \pm 0.6)/\theta$, where $\theta = 2.3RT \text{ kcal/mol}$. For addition reactions, the kinetics at 298 K follow the order Ph· > c-C₃H₅· > RCH₂CH₂·. For H-atom abstractions the reactivities of Ph· and c-C₃H₅· do not follow a simple relationship, though both are more reactive than RCH₂CH₂· radicals.

There is a large and rapidly growing body of absolute rate data for a wide variety of radical-molecule reactions in solution.³ The rotating-sector method has been applied to polymerization reactions and has yielded extensive results for the addition of carbon-centered macroradicals to vinyl monomers.⁴⁻⁷ However, there are surprisingly few absolute rate data for addition and abstraction reactions of "small" (nonpolymeric) carbon-centered radicals, less even than for many heteroatom-centered radicals.^{3,7} Phenyl is the only "small" carbon-centered radical for which there are reasonably extensive and directly measured rate data for its addition and abstraction reactions.⁸ There is also a small but significant body of data for primary alkyl radicals⁹ which has been based on the radical-clock concept,¹⁰ with the clock being provided by the known rate of cyclization of the 5-hexenyl radical.¹¹ In the present paper we provide the first absolute kinetic data for the interesting and highly reactive cyclopropyl radical.

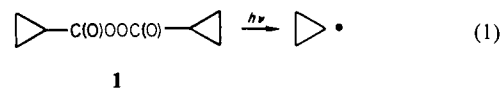
Current knowledge about the cyclopropyl radical has been summarized recently by Walborsky in an outstanding review.¹² The relative reactivities of quite a variety of molecules toward cyclopropyl have been measured, e.g., olefins,¹³ aromatics,¹⁴ and

tetrahalogenated methanes,¹⁵ and it has been concluded¹² that "the cyclopropyl radical behaves as a rapidly inverting σ radical of high reactivity (low selectivity) and low nucleophilicity". Of course, a high reactivity for cyclopropyl had not actually been demonstrated prior to the present work because there were no absolute rate data by which its reactivity could be compared with that of other carbon-centered radicals. However, the estimated C-H bond strength in cyclopropane, viz.,¹⁶ $D[\text{c-C}_3\text{H}_5\text{-H}] = 106 \text{ kcal/mol}$, would suggest a radical less reactive than phenyl, $D[\text{C}_6\text{H}_5\text{-H}] = 111 \text{ kcal/mol}$,¹⁶ but more reactive than a primary alkyl, $D[\text{RCH}_2\text{CH}_2\text{-H}] = 100 \text{ kcal/mol}$.^{17,18} Our results support this suggestion.

We have utilized the laser flash photolytic method to measure absolute rate constants for cyclopropyl radical-molecule reactions. Essentially the same procedures were employed as those used previously to generate and monitor the phenyl radical.^{8a} Most measurements were made at ambient temperatures, but for carbon tetrachloride measurements were made over a range of temperatures in order to make this compound a more useful absolute kinetic "standard" for any future competitive studies of cyclopropyl radical reactivity. An attempt to estimate the relative rate of decarboxylation of the cyclopropylformyloxy radical by an EPR method was not successful.

Results

Laser Flash Photolytic Experiments. Cyclopropyl radicals were generated by photolysis of bis(cyclopropylformyl) peroxide (**1**) with 308 nm light pulses from an excimer laser. Under these conditions any acyloxy radicals produced in the photoinitiated bond cleavage decarboxylate sufficiently rapidly that they do not interfere with measurements of the subsequent reactions of the cyclopropyl radicals, i.e.,



Evidence that cyclopropyl radical is the only transient of interest

(1) Issued as NRCC No. 23555.

(2) NSERC Postdoctoral Fellow 1983-1984.

(3) For a comprehensive listing of absolute rate data on all types of free-radical reactions in solution see: "Radical Reaction Rates in Liquids"; Fischer, H., Ed.; Springer-Verlag: Berlin, 1983; Landolt-Börnstein, New Series, Group II, Vol. 13.

(4) Walling, C. "Free Radicals in Solution"; Wiley: New York, 1957; Chapter 3.

(5) Bamford, C. H.; Barb, W. G.; Jenkins, A. D.; Onyon, P. F. "The Kinetics of Vinyl Polymerization by Radical Mechanisms"; Academic Press: New York, 1958.

(6) North, A. M. "International Encyclopedia of Physical Chemistry and Chemical Physics, Topic 17, Macromolecules"; Bawn, C. E. H., Ed.; Pergamon Press: Oxford, 1960; Vol. 1.

(7) Ingold, K. U. In "Free Radicals"; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 1, Chapter 2.

(8) (a) Scaiano, J. C.; Stewart, L. C. *J. Am. Chem. Soc.* **1983**, *105*, 3609-3614. (b) See also: Madhavan, V.; Schuler, R. H.; Fessenden, R. *Ibid.* **1978**, *100*, 888-893.

(9) See e.g.: (a) Schmid, P.; Ingold, K. U. *J. Am. Chem. Soc.* **1978**, *100*, 2493-2500. (b) Jenkins, C. L.; Kochi, J. K. *Ibid.* **1972**, *94*, 843-855. (c) Citterio, A.; Minisci, F.; Porta, O.; Sesana, G. *Ibid.* **1977**, *99*, 7960-7968. (d) Citterio, A. *Tetrahedron Lett.* **1978**, 2701-2704. (e) Citterio, A.; Arnoldi, A.; Minisci, F. *J. Org. Chem.* **1979**, *44*, 2674-2682. (f) Russell, G. A.; Tashtoush, H. *J. Am. Chem. Soc.* **1983**, *105*, 1398-1399. (g) Luszyk, J.; Maillard, B.; Lindsay, D. A.; Ingold, K. U. *Ibid.* **1983**, *105*, 3578-3580.

(10) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1980**, *13*, 317-320.

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(12) Walborsky, H. M. *Tetrahedron* **1981**, *37*, 1625-1651.

(13) Stefani, A. P.; Chuang, L.-Y. Y.; Todd, H. E. *J. Am. Chem. Soc.* **1970**, *92*, 4168-4173. Stefani, A. P.; Todd, H. E. *Ibid.* **1971**, *93*, 2982-2986.

(14) (a) Shono, T.; Nishiguchi, I. *Tetrahedron* **1974**, *30*, 2183-2190. (b) Clerici, A.; Minisci, F.; Porta, O. *J. Chem. Soc., Perkin Trans. 2* **1974**, 1699-1701.

(15) Herwig, K.; Lorenz, P.; Rüdhardt, C. *Chem. Ber.* **1975**, *108*, 1421-1436.

(16) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493-532.

(17) Reference 16 gives 98 kcal/mol which appears to be too low.¹⁸

(18) Castelhana, A. L.; Griller, D. *J. Am. Chem. Soc.* **1982**, *104*, 3655-3659.

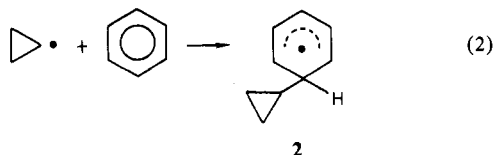
Table I. Rate Constants for the Reactions of Cyclopropyl Radicals with Various Substrates at 298 ± 2 K

entry	substrate	solvent	Δ^\bullet	method ^a	$k, ^b \text{M}^{-1} \text{s}^{-1}$
1	β -methyl styrene	C_6H_6	1	D(A)	$(2.0 \pm 0.5) \times 10^6$
2	β -methyl styrene	$\text{CF}_2\text{ClCFCl}_2$	1	D(A)	$(1.8 \pm 0.4) \times 10^6$
3	α -methyl styrene	C_6H_6	1	D(S)	$(1.4 \pm 0.3) \times 10^7$
4	styrene	C_6H_6	1	D(S)	$(1.5 \pm 0.3) \times 10^7$
5	styrene	$(t\text{-BuO})_2/\text{Et}_3\text{SiH}^c$	c- $\text{C}_3\text{H}_3\text{Br}$ (10%) ^d	D(S)	$(1.1 \pm 0.2) \times 10^7$
6	styrene	$(t\text{-BuO})_2/\text{Et}_3\text{SiH}^c$	c- $\text{C}_3\text{H}_3\text{Br}$ (20%) ^d	D(S)	$(1.3 \pm 0.2) \times 10^7$
7	toluene	C_6H_6	1	D(S), D(A)	$(7.9 \pm 1.5) \times 10^5$
8	<i>p</i> -xylene	C_6H_6	1	D(S)	$(1.6 \pm 0.4) \times 10^6$
9	benzene	C_6H_6	1	<i>e</i>	$\leq 2.7 \times 10^4$
10	1,4-cyclohexadiene	C_6H_6	1	D(A)	$(7.9 \pm 0.3) \times 10^6$
11	cyclohexene	C_6H_6	1	P(A)	$(1.3 \pm 0.3) \times 10^6$
12	tetrahydrofuran	C_6H_6	1	P(A)	$(5.5 \pm 1.0) \times 10^5$
13	benzhydrol	C_6H_6	1	D(S)	$(1.1 \pm 0.2) \times 10^6$
14	2-propanol	C_6H_6	1	P(A)	$(3.7 \pm 0.9) \times 10^5$
15	CCl_4	C_6H_6	1	P(A)	$(1.5 \pm 0.2) \times 10^6$
16	CBrCl_3	C_6H_6	1	P(S)	$(2.8 \pm 0.5) \times 10^9$
17	TEMPO ^f	C_6H_6	1	P(A)	$(1.2 \pm 0.3) \times 10^9$
18	benzenethiol	C_6H_6	1	D(S)	$(4.1 \pm 0.8) \times 10^9$

^a Monitoring procedure: D = direct detection, P = probe technique with β -methylstyrene; (S) = substrate concentration changed by its stepwise addition to a single solution of reactants, (A) = substrate concentration changed by using a new and separate sample of reactants for each concentration. ^b Total rate constant for the reaction, including all paths and reaction sites. ^c 1:1, v/v. ^d By volume. ^e Extrapolated, see text. ^f 2,2,6,6-Tetramethylpiperdin-1-oxyl.

that is produced by photolysis of **1** on the time scale of our experiments will be presented in the next section.

Irradiation of a benzene solution of **1** by the laser produced a weak transient signal (λ 323 nm) which we attribute to the cyclohexadienyl radical, **2**. Addition of styrene or α - or β -me-



thylstyrene gave a transient (λ_{max} 322 nm) which can be attributed to the benzylic radical formed by cyclopropyl addition at the double bond, e.g.,

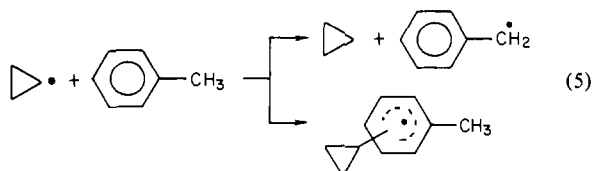


The growth of these benzylic radicals after the laser pulse could be monitored directly. A number of other substrates also gave transients having absorptions in the UV-vis region that were sufficiently strong for transient growth to be monitored directly, e.g., 1,4-cyclohexadiene (cyclohexadienyl, $\lambda_{\text{max}} \sim 323$ nm) and Ph_2CHOH (Ph_2COH , λ_{max} 540 and 330 nm).

The kinetic analysis for systems which yield radicals that can be directly detected is straightforward and has been described in detail.^{8a} Briefly, transient growth follows first-order kinetics and analysis of the growth trace yields k_{exptl} , the experimental first-order rate constant. This is related to k_X , the bimolecular rate constant for reaction of the cyclopropyl radical with the substrate X by the equation

$$k_{\text{exptl}} = k_0 + k_X[\text{X}] \quad (4)$$

where k_0 includes all first-order decay processes other than reaction with X. Of course k_X corresponds to the sum of all reactions of cyclopropyl regardless of which produces the observed signal.¹⁹ With toluene, for example, the reaction monitored is probably a combination of H-atom abstraction and ring addition,



(19) Chatgililoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 5119–5123.

The probe technique²⁰ was applied to substrates that did not yield optically detectable signals. In this technique, a probe, Y, that yields an observable signal is added to the system. Growth of the transient from Y can be represented by

$$k_{\text{exptl}} = k_0 + k_X[\text{X}] + k_Y[\text{Y}] \quad (6)$$

which at constant [Y] reduces to

$$k_{\text{exptl}} = k'_0 + k_X[\text{X}] \quad (7)$$

As our probe molecule we used β -methylstyrene, which we have also employed previously to monitor phenyl radical reactions.^{8a}

Kinetic results are summarized in Table I; more detailed kinetic data are available as Supplementary Material. The agreement between individual experiments was quite satisfactory for most substrates. However, the rate constants measured for cyclopropyl reaction with xylene showed a certain irreproducibility that we could neither eliminate nor explain. Similar problems were encountered previously for the reaction of phenyl radicals with toluene and cumene.^{8a}

The rate constant for the reaction of cyclopropyl radical with benzene was too slow to measure directly (which is one reason why benzene was chosen as solvent). However, k_X for benzene can be estimated from k_0 because the latter rate constant should primarily reflect the reaction of cyclopropyl with the benzene solvent.²¹ After extrapolation to zero light intensity (to eliminate second-order contributions) a typical value for k_0 (or k_{exptl} in the absence of a substrate) is $3 \times 10^5 \text{ s}^{-1}$, and since neat benzene is 11.2 M we can put an upper limit on $k_{\text{C}_6\text{H}_6}$ of ca. $2.7 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$.

Cyclopropyl or Cyclopropylformyloxy Radicals? Several lines of evidence which indicate that cyclopropylformyloxy radicals are not intermediates on the time scale of our photochemical experiments are summarized below:

(i) An acyloxy radical would not be expected to abstract halogen or otherwise react with CCl_4 or CBrCl_3 (see entries 15 and 16 in Table I).

(ii) In the reaction with CCl_4 , the intensity of the benzyl radical signal derived from the β -methylstyrene probe should follow a

(20) Paul, H.; Small, R. D., Jr.; Scaiano, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4520–4527.

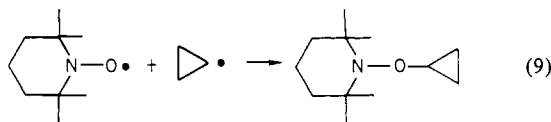
(21) The only other "side" reactions are attack on **1** (which is present at only 0.2 M) and the bimolecular self-reaction. Neither reaction is likely to be important relative to the attack on benzene under our experimental conditions. Ring opening of cyclopropyl to form the allyl radical can also be discounted as this reaction has a remarkably high activation energy. See: Beckwith, A. L. J.; Ingold, K. U. In "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 1, Essay No. 4.

Stern-Volmer type of relationship if the same radical is reacting with both the probe and CCl_4 . That is, the following relationship should be obeyed:

$$\frac{1}{\Delta\text{OD}} = \alpha + \alpha \frac{k_{\text{CCl}_4}[\text{CCl}_4]}{k'_0} \quad (8)$$

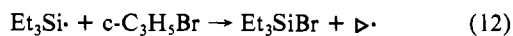
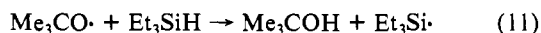
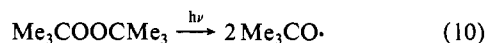
where ΔOD is the transient optical density at 322 nm before significant decay has occurred and α is a constant that incorporates a number of experimental parameters, it being assumed that the only species absorbing at this wavelength are derived from the probe. A plot of $1/\Delta\text{OD}$ vs. $[\text{CCl}_4]$ yielded $k_{\text{CCl}_4}/k'_0 = 2.46 \text{ M}^{-1}$, which agrees rather well with a value of 2.33 M^{-1} derived from the slope/intercept ratio in a plot of k_{exptl} vs. $[\text{CCl}_4]$. The radical which reacts with CCl_4 and decreases the signal ΔOD is therefore the same as that which produces the signal from β -methylstyrene.

(iii) The very high rate constant for the reaction with TEMPO (see entry 17 in Table I) is consistent with the trapping of a carbon-centered radical by this aminoxyl radical.²²

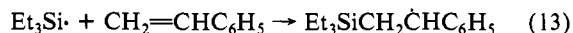


Since compounds of the type $\text{R}_2\text{NOOC(O)R}'$ appear to be unknown, it is highly improbable that the reaction being monitored could involve the trapping of cyclopropylformyloxyl by TEMPO.

(iv) The source of the cyclopropyl radical does not change the measured rate constant for the reaction with styrene (see entries 4, 5, and 6 in Table I). Photolysis of solutions of cyclopropyl bromide in di-*tert*-butyl peroxide/triethylsilane (1:1, v/v) containing various concentrations of styrene gave signals that can safely be attributed to a benzylic radical. Although this radical could not have been produced by the addition of cyclopropylformyloxyl to the styrene, the measured rate constants for its growth (viz. 1.1 and $1.3 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ for 10% and 20% $\text{c-C}_3\text{H}_5\text{Br}$ by volume, respectively) are in very satisfactory agreement with the rate constant measured with use of the peroxide **1** as the cyclopropyl radical source (viz. $1.5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$). The overall reaction sequence can be represented by:



The possibility that the signal being monitored in the cyclopropyl bromide systems is due to the addition of the triethylsilyl radical to the styrene, i.e.,



can be discounted on both qualitative and quantitative grounds. The qualitative argument rests on the fact that the measured rate constants are essentially independent of the $\text{c-C}_3\text{H}_5\text{Br}$ concentration. The quantitative argument rests on the known rate constant for reaction 12, viz.,^{23a} $3.4 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, and for reaction 13, viz.,^{23b} $2.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, and the two concentrations of $\text{c-C}_3\text{H}_5\text{Br}$ employed, viz., 1.1 and 2.2 M, compared with the maximum concentration of styrene used in these experiments, viz., 0.25 M. It is clear that no appreciable fraction of the $\text{Et}_3\text{Si}\cdot$ radicals could have reacted directly with the styrene.²⁴

(22) See Ingold, K. U. in ref 3, Vol. 13c, pp 184-186.

(23) (a) Chatgialloglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 5123-5127. (b) Chatgialloglu, C.; Ingold, K. U.; Scaiano, J. C. *Ibid.* **1983**, *105*, 3292-3296.

(24) The lifetime of *tert*-butoxyl will be less than 70 ns and will not interfere with the much slower kinetics examined here. In the case of $\text{Et}_3\text{Si}\cdot$, over 87% of these radicals will be scavenged by cyclopropyl bromide at the lowest concentration of this compound employed (1.1 M) and at the highest (0.25 M) styrene concentration. The situation will be even more favorable in all other cases.

Table II. Rate Constants for the Reaction of Cyclopropyl Radicals with Carbon Tetrachloride at Various Temperatures^a

temp, K	$k, \text{M}^{-1} \text{s}^{-1}$	temp, K	$k, \text{M}^{-1} \text{s}^{-1}$
272.4	$8.1_2 \times 10^5$	311.9	$1.5_9 \times 10^6$
272.9	$7.8_6 \times 10^5$	325.6	$1.9_3 \times 10^6$
281.0	$8.7_2 \times 10^5$	341.3	$2.5_1 \times 10^6$ ^b
294.8	$9.6_8 \times 10^5$		

^aTechnique A: probe, β -methylstyrene; 1:4 benzene: $\text{CF}_2\text{ClCFCl}_2$ v/v. ^b1:1 benzene: $\text{CF}_2\text{ClCFCl}_2$.

Table III. Comparison of the Absolute Rate Constants for Reaction of Cyclopropyl, Phenyl, and Primary Alkyl Radicals with Various Substrates at $298 \pm 2 \text{ K}$

substrate	$k, \text{M}^{-1} \text{s}^{-1}$		
	$\text{c-C}_3\text{H}_5$ ^a	C_6H_5 ^b	RCH_2CH_2 ^c
α -methylstyrene	1.4×10^7		5.9×10^4 ^c
β -methylstyrene	2.0×10^6	3.0×10^7	
styrene	1.5×10^7	1.1×10^8	1.2×10^5 ^d
toluene	7.9×10^5	1.7×10^6	
<i>p</i> -xylene	1.6×10^6	2.4×10^6	
benzene	$\leq 2.7 \times 10^4$	4.5×10^5	58 ^e
cyclohexene	1.3×10^6	2.8×10^8	
tetrahydrofuran	5.5×10^5	4.8×10^6	
benzhydrol	1.1×10^6	2.0×10^7	
2-propanol	3.7×10^5	1.4×10^6	
CCl_4	1.5×10^6	7.8×10^6	1.2×10^4 ^f
benzenethiol	4.1×10^9		1.8×10^8 ^g

^aThis work. Solvent is benzene. ^bReference 8a. Solvent is $\text{CF}_2\text{ClCFCl}_2$. ^cReference 9e. The value quoted in this reference of $8.9 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ at 69°C has been corrected to $1.7 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ at this temperature on the basis of the revised value for the rate constant for 5-hexenyl cyclization ($k_c = 9.8 \times 10^5 \text{ s}^{-1}$ at 69°C , ref 11) and has then been converted to 25°C with use of an A factor of $10^{8.33} \text{ M}^{-1} \text{ s}^{-1}$, the value reported for addition to styrene (ref 9e). ^dReference 9e. The value quoted in this reference of $5.4 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ at 25°C has been corrected on the basis of the revised value for the rate constant for 5-hexenyl cyclization ($k_c = 2.2 \times 10^5 \text{ s}^{-1}$ at 25°C , ref 11). A rate constant of $9.3 \times 10^4 \text{ s}^{-1}$ has been reported for *n*-heptyl addition to styrene at 25°C . See: Citterio, A.; Minisci, F.; Arnoldi, A.; Pagano, R.; Parravicini, A.; Porta, O. *J. Chem. Soc., Perkin Trans. 2* **1978**, 519-524. ^eReference 9c. Based on a competitive study of the addition of *n*-butyl radical to benzene vs. protonated and unprotonated 4-methylpyridine which gave $k(\text{C}_6\text{H}_6) = 3.8 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ at 79°C , the value of $k(4\text{-methylpyridine})$ having been determined for the protonated compound with use of the 5-hexenyl cyclization clock reaction. Revision of the rate constant for cyclization ($k_c = 1.3 \times 10^6 \text{ s}^{-1}$ at 79°C , ref 11) gives $k(\text{C}_6\text{H}_6) = 6.9 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ at 79°C . This value has been converted to 25°C by using $\log A_c/A(4\text{-methylpyridine}) = 1.6$, i.e., assuming $\log A(\text{C}_6\text{H}_6) = 10.37 - 1.6 = 8.77 (\text{M}^{-1} \text{ s}^{-1}) = \log A(4\text{-methylpyridine})$. ^fFor the $\text{C}_6\text{H}_5\text{C}(\text{CH}_3)_2\text{CH}_2$ radical: Lindsay, D. A.; Luszyk, J.; Ingold, K. U. *J. Am. Chem. Soc.*, in press. ^gReference 9f. Value given multiplied by 2.2 to fit revised k_c for 5-hexenyl cyclization (ref 11).

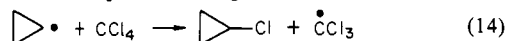
(v) The main procedure used to generate cyclopropyl radical in this work, i.e., photolysis of **1**, is the same as the main procedure previously used to generate phenyl radical, i.e., photolysis of benzoyl peroxide.^{8a} Rate constants for the reactions of all RCO_2 radicals would be expected to be almost independent of the nature of the R group (provided that the RCO_2 radicals have been formed in the same electronic state).²⁵ The fact that the rate constants measured in the present work are not the same as those measured previously for the phenyl radical^{8a} (see Table III) provides a strong argument that neither set of data refer to the corresponding RCO_2 radical.

On the basis of the five arguments outlined above, we conclude that cyclopropylformyloxyl radicals are not of importance under our experimental conditions and thus our laser-flash-derived kinetic data refer to the cyclopropyl radical. The cyclopropylformyloxyl radicals may be very short lived, or may not be discreet intermediates under laser-flash conditions,²⁶ or may be formed in some

(25) There is evidence that RCO_2 radicals may react in more than one electronic state, see: Skell, P. S.; May, D. D. *J. Am. Chem. Soc.* **1983**, *105*, 3999-4008.

electronically²⁵ or vibrationally excited state which encourages cleavage to cyclopropyl and CO₂. The behavior of thermally generated cyclopropylformyloxy radicals cannot be inferred from the laser-flash results (vide infra).

Effect of Temperature on the Cyclopropyl/CCl₄ Reaction. This reaction was chosen for detailed kinetic investigation for two main reasons: (1) Carbon tetrachloride yields a product, c-C₃H₅Cl, that is readily distinguishable from the product of an H-atom abstraction reaction, c-C₃H₆, or an addition reaction. (ii) The reactivity of CCl₄ is neither too great nor too small, so it can be utilized as a fairly general "standard" reagent in future competitive kinetic studies of cyclopropyl radical reactivity. Experimental data obtained in the temperature range 0–68 °C for the reaction

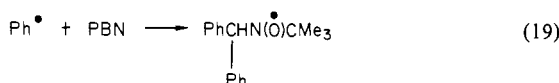
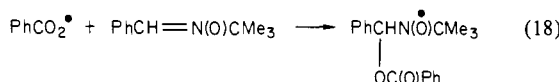
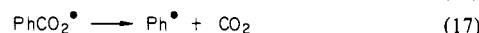
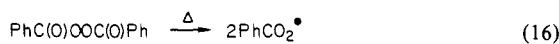


are given in Table II. The rate data can be represented by

$$\log(k_{14}/\text{M}^{-1} \text{s}^{-1}) = (8.7 \pm 0.4) - (3.5 \pm 0.6)/\theta \quad (15)$$

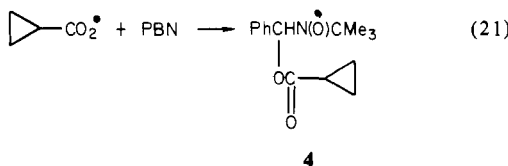
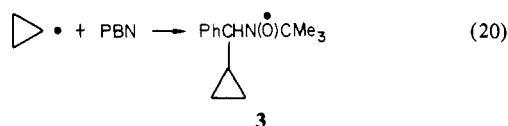
where $\theta = 2.3RT$ kcal/mol.

Attempted Spin-Trapping Study of Thermally Generated Cyclopropylformyloxy Radicals. When benzoyl peroxide is thermally decomposed in the presence of phenyl-*tert*-butyl nitron (PBN), both the benzoyloxy and phenyl spin adducts can be observed by EPR spectroscopy under suitable experimental conditions.²⁷



This general procedure can be employed to determine the rate constant ratio k_{17}/k_{18} .^{27,28}

When **1** was photolyzed in the presence of PBN in CH₂ClCFCl₂ as solvent in an EPR cavity at ambient temperatures, a complex EPR spectrum was obtained. Thermal decomposition of **1** in the same solvent at temperatures in the range 40–55 °C gave the cyclopropyl spin adduct, **3**, plus a radical having the hyperfine splittings characteristic^{27–29} of an RCO₂/PBN spin adduct, presumably **4**.



With 2.9×10^{-2} M **1** the total rate of formation of the spin adducts, **3** + **4**, at 52 °C was found to be independent of the concentration of PBN in the range 0.02–0.12 M (see Table IV). However, the rate of formation of **3** did not decrease with an increase in the PBN concentration, nor did the rate of formation

(26) A referee has pointed out that it is still not generally recognized that photolysis and thermolysis of acyl and aroyl peroxides are not equivalent. In particular, the photo-yield of RCO₂· (if any) from a particular peroxide appears to be smaller than the thermal yield, see, e.g.: Kitamura, A.; Sakuragi, H.; Yoshida, M.; Tokumaru, K. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1393–1398 and references cited.

(27) Janzen, E. G.; Evans, C. A.; Nishi, Y. *J. Am. Chem. Soc.* **1972**, *94*, 8236–8238. See also: Janzen, E. G.; Evans, C. A. *Ibid.* **1975**, *97*, 205–206.

(28) L. Grossi, unpublished results from this laboratory.

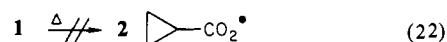
(29) Janzen, E. G.; Blackburn, B. J. *J. Am. Chem. Soc.* **1969**, *91*, 4481–4490.

Table IV. "Spin Trapping" of c-C₃H₅· and c-C₃H₅CO₂· by PBN in CF₂ClCFCl₂ at 52 °C^a

[PBN], M	d[3]/dt ^{b,c}	d[4]/dt ^{a,d}	(d[3]/dt) + (d[4]/dt) ^c
0.02	0.32	0.48	0.80
0.05	0.26	0.53	0.79
0.09	0.33	0.49	0.82
0.12	0.29	0.46	0.75

^a[1] = 0.029 M. ^bc-C₃H₅·/PBN spin adduct. ^cRates in arbitrary units (signal height/s). ^dc-C₃H₅CO₂·/PBN spin adduct.

of **4** increase (see Table IV). Both of these changes would have to occur if reaction 21 was in competition with the decarboxylation of the c-C₃H₅CO₂· radical, i.e., if the equations describing the thermal decomposition of **1** in the presence of PBN were the same as those which describe the thermal decomposition of benzoyl peroxide in the presence of PBN.^{27,28} We conclude that the thermal decomposition of **1** is not as straightforward as has heretofore been assumed,^{30,31} at least when the decomposition is carried out in CF₂ClCFCl₂ and in the presence of PBN. That is, the thermal decomposition of **1** in our experiments does not involve a simple one-bond cleavage to form two c-C₃H₅CO₂· radicals.



Discussion

Entries 1 and 2 in Table I show that the reactivity of the cyclopropyl radical is essentially identical in CF₂ClCFCl₂ and in benzene. It therefore appears justified to compare the reactivity of this radical in the latter solvent with that of phenyl radical in the former solvent. Such a comparison is shown in Table III together with some of the limited data available for primary alkyl radicals, RCH₂CH₂·, in various solvents.

Radical reactivities for substrates for which the principal mode of reaction must be an addition follow the expected order Ph· > c-C₃H₅· > RCH₂CH₂·, with Ph· being about 10 times as reactive as cyclopropyl (cf. β-methylstyrene, styrene, and benzene). For substrates for which the principal mode of reaction is presumed to be an H-atom transfer there is no simple relation between the reactivities of Ph· and c-C₃H₅·, though both are more reactive than RCH₂CH₂·. Thus, Ph· and c-C₃H₅· have very similar reactivities toward toluene and *p*-xylene, but Ph· is much more reactive than c-C₃H₅· toward tetrahydrofuran, cyclohexene, and benzhydrol. We do not rule out unsuspected errors in our measurements of one or more of the c-C₃H₅· or Ph· rate constants (particularly in view of the problems encountered with alkyl benzenes), and it was partly for this reason that the rate constants for the c-C₃H₅·/CCl₄ reaction were so carefully measured over a range of temperatures. We hope these data will encourage research workers who do not have access to equipment suitable for time-resolved kinetic studies to undertake measurements of the relative reactivity toward CCl₄ and other substrates of the cyclopropyl radical. Such information should help to put our own absolute rate data on a firmer foundation.

There are few results in the literature with which we may compare our own rate constants. We note only the following: $k_{\text{CCl}_3\text{Br}}/k_{\text{CCl}_4} = 278$ for cyclopropyl at 110 °C;¹⁵ toluene has about the same reactivity for cyclopropyl addition as benzene at 100 °C,^{14a} but chlorine atom abstraction from CCl₄ by the 2-phenylcyclopropyl radical is purported to be 9 times faster than H-atom abstraction from toluene at this temperature.^{14a}

Finally, the behavior of **1** during its thermal decomposition in the spin-trapping experiments is not, with hindsight, entirely surprising. It is well-established that the thermal decomposition of diacyl peroxides, RC(O)OOC(O)R', in which one or both R's are secondary or tertiary alkyl, involves a concerted scission of at least two bonds.^{32–34} If the thermal decomposition of **1** gave

(30) Hart, H.; Wyman, D. P. *J. Am. Chem. Soc.* **1959**, *81*, 4891–4896.

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both one-bond scission, i.e., two $c\text{-C}_3\text{H}_5\text{CO}_2\cdot$ radicals, and two-bond scission, i.e., $c\text{-C}_3\text{H}_5\cdot$, CO_2 , and $c\text{-C}_3\text{H}_5\text{CO}_2\cdot$, then the results in Table IV could be accommodated provided the decarboxylation of thermalized $c\text{-C}_3\text{H}_5\text{CO}_2\cdot$ radicals was slower than that of thermalized $\text{PhCO}_2\cdot$ radicals^{27,28} (assuming that these two radicals add to PBN at the same rate). That $c\text{-C}_3\text{H}_5\text{CO}_2\cdot$ should decarboxylate more slowly than $\text{PhCO}_2\cdot$ not only seems rather improbable but it would also contradict a report³⁵ that at 125 °C the $c\text{-C}_3\text{H}_5\text{CO}_2\cdot$ radical decarboxylates 41 times faster than the $\text{PhCO}_2\cdot$ radical. A more reasonable explanation for our results is that ionic processes are involved in spin adduct formation. That is, there is ample evidence that secondary (including cyclobutyl),³³ tertiary, and unsymmetrical $\text{RC}(\text{O})\text{OOC}(\text{O})\text{R}'$ decompose by a mixture of radical and ionic pathways, possibly involving a common rate-determining transition state.^{32-34,36-38} If the cyclopropylcarboxylate anion, $c\text{-C}_3\text{H}_5\text{CO}_2^-$, is produced (even transiently) during the thermal decomposition of **1**, it could yield the same adduct radical with PBN as that which would have been produced by spin trapping the $c\text{-C}_3\text{H}_5\text{CO}_2\cdot$ radical.³⁹

Experimental Section

Materials. Bis(cyclopropylformyl) peroxide (**1**) was prepared from cyclopropanecarboxylic acid and hydrogen peroxide by using a literature method⁴⁰ and was purified by recrystallization from pentane. Benzene

was refluxed over CaH_2 and then distilled. $\text{CF}_2\text{ClCFCl}_2$ was refluxed over CaCO_3 and fractionally distilled. Diphenylmethanol was doubly sublimed. All other substrates were purified by recrystallization or distillation. PBN was precipitated from a chloroform solution by addition of hexane. Di-*tert*-butyl peroxide and triethylsilane were passed through alumina.

Laser Flash Photolysis Experiments. Samples (1 or 2 mL, 0.2 M **1** in benzene) were contained in $7 \times 7 \text{ mm}^2$ (308 nm) or $3 \times 7 \text{ mm}^2$ (337 nm) cells made of Suprasil tubing and were deoxygenated by purging with oxygen-free nitrogen. For static experiments (technique S) the same sample was used for each concentration of substrate. For technique A a fresh sample was used for each substrate concentration in order to minimize problems due to a transient absorption jump directly after the laser pulse. A Lumonics TE-860-2 excimer laser (Xe-HCl-He mixture) with pulses at 308 nm ($\sim 4 \text{ ns}$, up to 80 mJ/pulse) was used for sample excitation except for the experiments with cyclopropyl bromide for which a Moletron UV-24 nitrogen laser with pulses at 337 nm ($\sim 8 \text{ ns}$, up to 10 mJ/pulse) was used. Further details on the laser-flash apparatus have been given elsewhere.⁴¹

EPR Experiments. $\text{CF}_2\text{ClCFCl}_2$ solutions of **1** (0.029 M) and varying concentrations of PBN were degassed by several freeze-pump-thaw cycles, and ~ 30 torr of nitrogen was added. The production of the spin adducts was followed on a Varian E104 EPR spectrometer at ~ 50 °C. DPPH was used for absolute radical concentration measurements.

Acknowledgment. Thanks are due to S. E. Sugamori for technical assistance.

Registry No. **1**, 1607-29-0; TEMPO, 2564-83-2; PBN, 3376-24-7; $c\text{-C}_3\text{H}_5\cdot$, 2417-82-5; $c\text{-C}_3\text{H}_5\text{CO}_2\cdot$, 28149-39-5; CCl_4 , 56-23-5; CBrCl_3 , 75-62-7; β -methylstyrene, 637-50-3; α -methylstyrene, 98-83-9; styrene, 100-42-5; toluene, 108-88-3; *p*-xylene, 106-42-3; benzene, 71-43-2; 1,4-cyclohexadiene, 628-41-1; cyclohexene, 110-83-8; tetrahydrofuran, 109-99-9; benzhydrol, 91-01-0; 2-propanol, 67-63-0; benzenethiol, 108-98-5.

Supplementary Material Available: Tables V–XLI giving detailed kinetic data (39 pages). Ordering information is given on any current masthead page.

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