mechanism," since the latter mechanism should not be concerned with the "acidity" of the sensitive protons.

There have been other observations on the deshielding effect of a phosphoryl group on the proton chemical shifts through space. In a recent paper, Lira and Huffman[65] have reported a deshielding influence of a phosphonate group upon H-8 in N^9-bis(β-chloroethyl)-β-adenin-9-yl ethyl phosphonate. These authors suggested that the deshielding arose as a result either of the P=O anisotropy or hydrogen bonding of H-8 to the phosphoryl oxygen. More direct evidence for the phosphate deshielding effect is forthcoming from the data on arabinosylcytosine 2′,5′-cyclic phosphate in which the phosphate anion is held in a position very close to H-3′.[66] It is found that the δ H-3′ of this cyclic phosphate is about 0.5 ppm to lower field than in arabinosylcytosine 5′-phosphate. In view of the mechanism discussed above, it would be of interest to examine the rate of hydrogen–deuterium exchange of this H-3′ proton.

It should be strongly emphasized here that, although we favor the proposal of the electrostatic field effect of the 5′-phosphate on the sensitive protons in order to cause the deshielding phenomenon, we do not mean that the phosphate group is strongly influenced by these protons such as by formation of a hydrogen bond to the phosphoryl oxygen atom. We view that our data and our proposal are in essential agreement with the conclusion of Phillips, *et al.*[67] They have studied the pK_a of the secondary phosphate group of various 5′-nucleoside mono-, di-, and triphosphates by potentiometric titration. They found that the pK_a of the secondary phosphate is not very sensitive to the nature of the bases attached to the nucleotides and concluded that there is no "ring–chain interaction" in nonmetal complexed mononucleotides. As a corollary, we do not consider that this phosphate–proton interaction provides much of the stabilization energy for the *anti* conformation. To the best of our knowledge from the X-ray data[35,37] and ORD data,[45] the nucleosides and the corresponding 3′-nucleotides and 5′-nucleotides all have the same *anti* conformation.

Regardless of the nature of the mechanism for this specific deshielding effect of the 5′-phosphate on the H-8 (purine) or H-6 protons (pyrimidine), the results of this pmr study strongly indicate that the 5′-nucleotides are in an *anti* conformation. This specific shielding effect of the 5′-phosphate has also been found in the dinucleoside monophosphates.[68] This effect can be used for purposes of identification to distinguish the resonance signal arising from the 3′-linked nucleoside (more shielded) from that arising from the 5′-linked nucleoside. This observation also infers that the 5′-linked nucleosides in the dinucleoside monophosphate are in an *anti* conformation.[69]

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(65) P. Lira and C. W. Huffman, *J. Org. Chem.*, 31, 2188 (1966).

(66) Dr. W. Wechter, Upjohn Co., private communication.

(67) R. Phillips, S. J. P. Eisenberg, P. George, and R. J. Rutman, *J. Biol. Chem.*, 240, 4393 (1965).

(68) M. P. Schweizer, P. O. P. Ts'o, and D. P. Hollis, unpublished data.

(69) NOTE ADDED IN PROOF. We wish to thank Drs. S. S. Danyluk and F. E. Hruska of Argonne National Laboratory for sending their preprint to one of us (P. O. P. T.) on Jan 5, 1968. In this paper, which will appear in the March issue of *Biochemistry*, they have examined the pD dependence of the chemical shifts of the base protons and H-1′ proton of the nucleotides of adenosine, guanosine, xanthosine, and thymidine and have reached a conclusion similar to ours, *i.e.*, the 5′-nucleotides are in an *anti* conformation.

Communications to the Editor

The Kinetics of the Reduction of *t*-Butyl Chloride and *t*-Butyl Bromide by Organotin Hydrides[1]

Sir:

Kuivila and coworkers have shown[2] that the reduction of an organic halide, RX, with an organotin hydride, R'_3SnH, proceeds by a free-radical chain reaction. A reasonable reaction scheme is given by eq 1–6. Although the relative reactivities of a number of halides with some tin hydrides have been measured,[2] the kinetics of the reaction have not previously been reported.

Initiation

$$\longrightarrow R\cdot \qquad (1)$$

Propagation

$$R\cdot + R'_3SnH \longrightarrow RH + R'_3Sn\cdot \qquad (2)$$

$$R'_3Sn\cdot + RX \longrightarrow R'_3SnX + R\cdot \qquad (3)$$

Termination

$$\left.\begin{array}{ll} R\cdot + R\cdot \longrightarrow & (4) \\ R\cdot + R'_3Sn\cdot \longrightarrow & (5) \\ R'_3Sn\cdot + R'_3Sn\cdot \longrightarrow & (6) \end{array}\right\} \text{inactive products}$$

We have examined the reaction of *t*-butyl chloride and bromide with tri-*n*-butyltin hydride and triphenyltin hydride in cyclohexane at 25°. The reaction was initiated photochemically at wavelengths above 3600 Å with the light from a filtered 200–250-V, 250-W ME/D B.T.H. ultraviolet lamp. α,α'-Azobis(cyclohexylnitrile) (ACHN) was used as the photoinitiator. The reaction was monitored by following the rate of heat evolution in the reaction. The apparatus has been described previously.[3] The rates of reaction were estimated from the heat of the over-all process

$$R'_3SnH + RX \longrightarrow R'_3SnX + RH + \Delta H$$

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(1) Issued as N.R.C. No. 9987.

(2) H. G. Kuivila, L. W. Menapace, and C. R. Warner, *J. Am. Chem. Soc.*, 84, 3584 (1962); L. W. Menapace and H. G. Kuivila, *ibid.*, 86, 3047 (1964).

(3) D. J. Carlsson and K. U. Ingold, *ibid.*, 89, 4885, 4891 (1967).

Table I. Kinetics for the Reduction of *t*-Butyl Halide by Organotin Hydride in Cyclohexane at 25°

		Reaction order				Concentration range, M			
RX	R'_3SnH	[ACHN]	I[a]	[RX]	[R'_3SnH]	[ACHN] × 10^3	[RX]	[R'_3SnH]	[RX]/-[R'_3SnH]
t-BuBr	Ph_3SnH	0.54 ± 0.1	0.58 ± 0.05	0 ± 0.1	0.95 ± 0.1	0.7–3.4	2.41–8.7	0.03–0.25	10–70
t-BuCl	Ph_3SnH	0.40 ± 0.05	0.52 ± 0.05	0.90 ± 0.05	0 ± 0.1	0.7–11.0	0.35–7.5	0.08–0.60	2.5–25
t-BuBr	*n*-Bu_3SnH			0 ± 0.1	0.87 ± 0.1		0.42–2.8	0.03–0.25	2.2–90
t-BuCl	*n*-Bu_3SnH		0.60 ± 0.10	See text	See text		0.41–9.0	0.07–0.44	1.7–130

[a] Light intensity.

ΔH was found to be $-(40 \pm 4)$ kcal/mole for each of the four reactions studied.

The kinetics are summarized in Table I. Chain termination is bimolecular since the over-all rates are proportional to (light intensity)$^{1/2}$ at constant ACHN concentration and to [ACHN]$^{1/2}$ at constant light intensity. The kinetics show an interesting dependence on the nature of both the halide and the hydride. In the case of *t*-butyl bromide, reaction 2 is rate determining with both hydrides, and termination occurs by reaction 4. For the reaction of *t*-butyl chloride with triphenyltin hydride, reaction 3 is rate determining and termination occurs by reaction 6. However, with *t*-butyl chloride and tri-*n*-butyltin hydride, reactions 2 and 3 are of comparable rate. The kinetics are estimated to deviate from approximately first order in [chloride] and zero order in [hydride] at [chloride]/[hydride] ratios above about 5 to zero order in [chloride] and first order in [hydride] at ratios below about 80. Termination can therefore occur by reactions 4, 5, or 6. The predominant mode of termination depends on the relative concentration of the two reactants.

The absolute rate constants of these reactions are given in Table II. They have been determined by the rotating sector method.[3] Rates of chain initiation were determined both by the inhibitor method and by comparison of the rates of photoinitiated and thermal-initiated reactions.[3] At an ACHN concentration of 3.4×10^{-2} M and with full light intensity the rate of initiation was about 3.5×10^{-8} M sec^{-1}. Under these typical conditions chain lengths were in the range (3×10^2)–(5×10^3).

Table II. Absolute Rate Constants for the *t*-Butyl Halide–Tin Hydride Reaction in Cyclohexane at 25°

Reaction	Rate constant, M^{-1} sec^{-1}
t-Bu· + Ph_3SnH	5×10^6
t-Bu· + *n*-Bu_3SnH	3×10^6
Ph_3Sn· + *t*-BuCl	3×10^4
n-Bu_3Sn· + *t*-BuCl	1.5×10^4
t-Bu· + *t*-Bu·	2×10^9
Ph_3Sn· + Ph_3Sn·	3×10^9
n-Bu_3Sn· + *n*-Bu_3Sn·	1.5×10^9
t-Bu · + *n*-Bu_3Sn ·	2×10^9

The rate constants for chain termination are consistent with essentially diffusion-controlled processes. The over-all reaction is rapid because the propagation steps are extremely fast.

This work will be described in more detail at a later date.

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[4] National Research Council Postdoctorate Fellow, 1965–1967.

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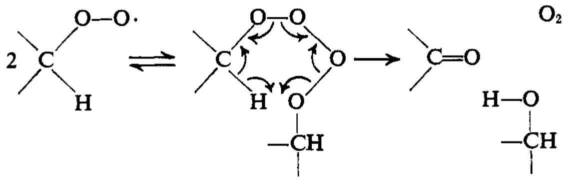
The Self-Reaction of *sec*-Butylperoxy Radicals. Confirmation of the Russell Mechanism[1,2]

Sir:

Rate constants for chain termination in the oxidation of hydrocarbons giving primary or secondary peroxy radicals are generally considerably faster than for hydrocarbons giving tertiary peroxy radicals.[3] About 10 years ago Russell proposed[4] that the self-reaction of secondary peroxy radicals involved a cyclic transition state. The recent discovery that di-*t*-butyl tetroxide is a stable species below −85°[5] supports Russell's suggestion[4] that "I may actually be an intermediate that is formed rapidly and reversibly and which decomposes slowly in an irreversible manner." The decomposition of I will not violate the Wigner spin-conservation rule if the oxygen is eliminated in the singlet state,[6] either $^1\Sigma_g^+$ or $^1\Delta_g$.[7] Alternatively, the oxygen could be eliminated in its triplet ground state, $^3\Sigma_g^-$, if the ketone is also formed in its excited triplet state.[8] We have now identified singlet oxygen in the



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(1) Absolute Rate Constants for Hydrocarbon Oxidation. IX. For part VIII see J. A. Howard, K. U. Ingold, and M. Symonds, *Can. J. Chem.*, in press.

(2) Issued as N.R.C. No. 9992.

(3) J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **45**, 793 (1967).

(4) G. A. Russell, *J. Am. Chem. Soc.*, **79**, 3871 (1957).

(5) P. D. Bartlett and G. Guaraldi, *ibid.*, **89**, 4799 (1967).

(6) The present experiments were started after this point was brought to the authors' attention by Professor Russell.

(7) The over-all reaction is exothermic by over 100 kcal/mole (Russell[4] estimates 157 kcal/mole) and there is therefore plenty of energy available to form either electronically excited singlet state of oxygen. The $^1\Sigma_g^+$ state is 37.5 kcal and the $^1\Delta_g$ state is 22.5 kcal above the triplet ground state.

(8) Organic materials undergoing autoxidation luminesce very weakly with a maximum emission generally in the range 420–450 mμ.[9] The emitter of this bluish luminescence appears to be an electronically excited carbonyl compound (n,π^*).[9] Transitions from both the triplet and singlet states are observed in the oxidation of methyl ethyl ketone