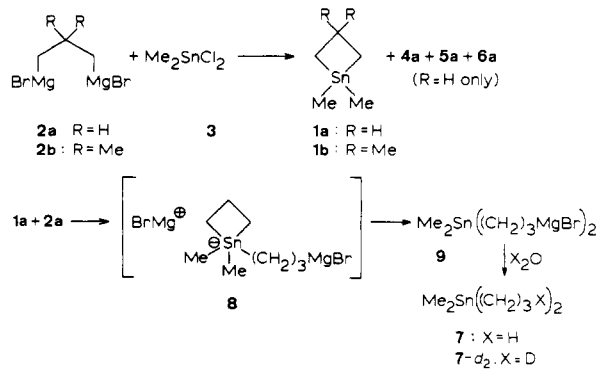
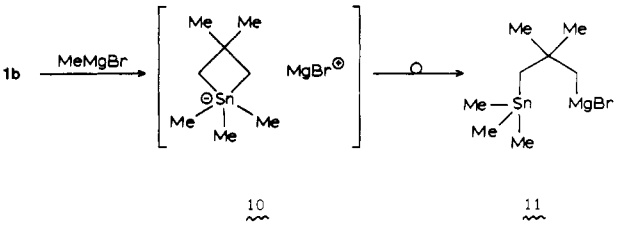
Scheme I



Scheme II



these conditions, **4a**, **5a**, and **6a** are not volatile; moreover, they are inert toward **2a**. Therefore, the formation of **7** can be explained only by the reaction of **1a** with **2a**; via the intermediate ate complex **8** the di-Grignard reagent **9** is formed, which with D_2O gives **7**-d_2. An analogous ring opening of 1,3-distannacyclobutanes with methyllithium has been observed by Seyferth and Lefferts.[3b]

More success was achieved in our efforts to directly identify and isolate **1b**, the 3,3-dimethyl derivative of **1a**. It was formed in 48% yield in the stoichiometric reaction of **2b** with **3** in diethyl ether (Scheme I). The yield was determined as follows: after 0.5 h at 25 °C, the volatile compounds were distilled in vacuo from the reaction mixture into a solution of methylmagnesium bromide in diethyl ether; presumably, **1b** reacted via the ate complex **10** to give **11** (Scheme II), which on hydrolysis gave (trimethylstannyl)neopentane (**12**), independently synthesized from neopentylmagnesium bromide and chlorotrimethylstannane; deuterolysis of **11** gave **12**-d_1.

The isolation of **1b** was achieved in the following way. First, the diethyl ether was removed from **2b** by addition of the high-boiling polyether bis(2-*n*-butoxyethoxy)methane and distillation of all low-boiling material in vacuo (a similar treatment of **2a** would lead to considerable decomposition due to β-hydride elimination[5]). To the remaining solution, **3** was added at room temperature, and after 0.5 h, **1b** was distilled in vacuo out of the reaction mixture into a liquid nitrogen trap. A colorless liquid of practically pure **1b** was thus obtained (5% isolated yield) and characterized by its spectral data.[8]

The properties of **1b** convincingly demonstrate its monomeric structure. Typical is its high volatility, in contrast to that of **4a**, and the fact that its molecular ion can be observed in the mass spectrum on electron impact ionization (70 eV), though with low intensity (1%). All other cyclic dimethyltin compounds reported here showed no detectable molecular ion under this condition, the highest mass ions observed being $[M - CH_3]^+$ or even smaller fragment ions. We believe this to be a consequence of the rapid cleavage of an endocyclic Sn–C bond in $\mathbf{1b}^{+\cdot}$ under relief of ring strain; the structure of the observed ion is therefore probably $Me_2{}^+SnCH_2CH_2CH_2{}^{\cdot}$.

Similarly unique and characteristic are the ^1H and ^{13}C NMR resonances of the 1-methyl groups of **1b**. They occur at much lower field (in dioxane-d_8: δ (^1H) 0.39 ($^2J_{SnH}$ = 53.1, 55.6 Hz); δ (^{13}C) 15.4) than those of the strain-free oligomers in $CDCl_3$: (**4a**) δ (^1H) 0.02 ($^2J_{SnH}$ = 48–50 Hz); δ (^{13}C) −11.8. Qualitatively, these low-field shifts can be understood as a consequence of the presumably rather small CH_2–Sn–CH_2 bond angle, imposed by the geometry of the four-membered ring. This increases the p character of the endocyclic bonds of the tin atom and in turn the s character and thus the electronegativity in its exocyclic bonds toward the methyl groups. The increased values of $^2J_{SnH}$ for the methyl groups of **1b** may also reflect this effect.

In view of the reported instability of stannacyclopentanes,[2] it was not surprising that **1b** was not stable at room temperature. With air, it reacted immediately under formation of a white precipitate of unknown composition (cf. the slow reaction of stannacyclopentanes with oxygen[2]). In solution **1a** and **1b** polymerized; **4–6** were not formed from **1**. The rate of polymerization of **1b** was strongly solvent dependent: at room temperature, $t_{1/2} \approx 30$ days in toluene-d_8 while in ethereal solvents such as dioxane-d_8, $t_{1/2} \approx 2$ days. Preliminary NMR results suggest that in the latter case, the solvent is also consumed to a certain extent, which indicates its active participation in the polymerization process.

Registry No. 1a, 85443-02-3; **1b**, 85443-03-4; **2a**, 62934-64-9; **2b**, 83528-98-7; **3**, 753-73-1; **4a**, 85443-04-5; **5a**, 85443-05-6; **6a**, 85443-06-7; **7**, 56535-52-5; **7**-d_2, 85443-07-8; **9**, 85452-92-2; **11**, 85443-08-9; **12**, 55204-72-3; **12**-d_1, 85443-09-0; MeMgBr, 75-16-1.

(7) **7**: ^1H NMR (90 MHz, $CDCl_3$) δ 0.00 (s, $^2J_{SnH}$ = 49.0, 51.0 Hz, 6 H, SnMe), 0.82 (t, $^3J_{HH}$ = 8.0 Hz, $^2J_{SnH} \simeq$ 50 Hz, 4 H, $SnCH_2$), 1.04 (t, $^3J_{HH}$ = 7.0 Hz, 6 H, Me), 1.35–1.75 (m, 4 H, CH_2CH_2Me); mass spectrum, *m/z* 236 (1) [M^+·, calcd for $C_8H_{20}Sn$ 236.0586, obsd 236.0589], 221 (6) [M − Me]$^+$, 193 (75), 151 (100).

(8) **1b**: ^1H NMR (90 MHz, dioxane-d_8) δ 0.39 (s, $^2J_{SnH}$ = 53.1, 55.6 Hz, 6 H, SnMe), 1.13 (s, 6 H, CMe), 1.54 (s, $^2J_{SnH}$ = 52 Hz, 4 H, CH_2); ^1H NMR (250 MHz, toluene-d_8) δ 0.25 (s, $^2J_{SnH}$ = 54 Hz, 6 H, SnMe), 1.25 (s, 6 H, CMe), 1.65 (s, $^2J_{SnH}$ = 52 Hz, 4 H, CH_2); ^{13}C NMR (62.89 MHz, dioxane-d_8) δ 15.4 (q, $^1J_{CH}$ = 126 Hz, SnMe), 34.5 (t, $^1J_{CH}$ = 125 Hz, $SnCH_2$), 35.6 (q, $^1J_{CH}$ = 125 Hz, C*Me*), 40.3 (s, *C*Me); ^{13}C NMR (62.89 MHz, toluene-d_8) δ −6.5 (q, $^1J_{CH}$ = 129 Hz, SnMe), 34.0 (t, $^1J_{CH}$ = 132 Hz, $SnCH_2$), 35.6 (q, $^1J_{CH}$ = 132 Hz, C*Me*), 40.2 (s, *C*Me); mass spectrum, *m/z* 220 (1) [M^+·, calcd for $C_7H_{16}Sn$ 220.0273, obsd 220.0263], 205 (6) [M − Me]$^+$, 150 (61), 135 (100).

Oxygenation of Chloroalkenes by Superoxide in Aprotic Media

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Although primary and secondary haloalkanes are readily oxidized by superoxide ion (O_2^-) in aprotic media via an S_N2 mechanism,[1-4] simple alkenes are unreactive.[5-7] In a recent study of polychloro hydrocarbons,[8] we observed that chloroethene and trichloroethene also did not react at significant rates with O_2^- in dimethyl sulfoxide. However, we now report that *cis*-1,2-dichloroethene, trichloroethene, and tetrachloroethene among others are rapidly oxygenated by O_2^- in dimethylformamide (DMF) or acetonitrile.

The extent of the reaction of electrogenerated O_2^- with chloroalkenes has been determined by cyclic voltammetry of O_2 in the presence of excess substrate.[8] The overall reaction and product stoichiometries for the degradation of the chloroalkene substrates

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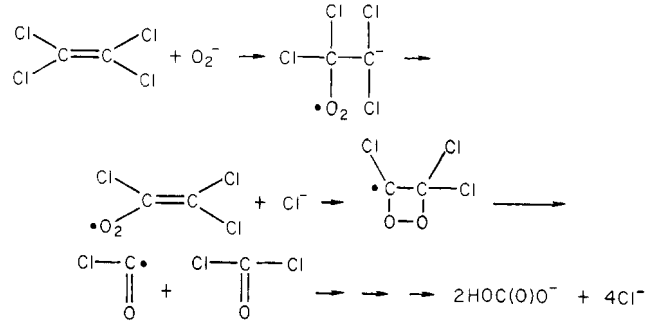
Table I. Reactions of Superoxide Ion with Chloroalkenes in Dimethylformamide[a]

substrate (S), 1–10 mM	O_2^-/S	Cl^- released/S	$HOC(O)O^-$ released/S	O_2 released/S	$k_1/[S]$, M^{-1} s^{-1}
cis-CHCl=CHCl	4.0 ± 0.4	2.0 ± 0.2	2.0 ± 0.2	0.0 ± 0.0	10.0 ± 3.0
CH_2=CCl_2	3.0 ± 0.3	2.0 ± 0.2	1.0 ± 0.1	1.0 ± 0.1	2.0 ± 0.6
CHCl=CCl_2	5.0 ± 0.5	3.0 ± 0.3	2.0 ± 0.2	1.5 ± 0.2	9.0 ± 2.7
CCl_2=CCl_2	6.0 ± 0.6	4.0 ± 0.4	2.0 ± 0.2	3.0 ± 0.3	15.0 ± 4.5
(*p*-ClPh)$_2$C=CCl_2 (DDE)	3.0 ± 0.3	2.0 ± 0.2	1.0 ± 0.1	1.0 ± 0.1	2.0 ± 0.6

[a] Overall reactions: (1) *cis*-CHCl=CHCl + $4O_2^- \xrightarrow{H_2O}$ $2HOC(O)O^- + 2Cl^- + 2H_2O_2$; (2) CH_2=CCl_2 + $3O_2^- \xrightarrow{H_2O}$ H_2C=O + $HOC(O)O^-$ + $2Cl^- + {}^1/_2H_2O_2 + O_2$; (3) CHCl=$CCl_2$ + $5O_2^- \xrightarrow{H_2O}$ $2HOC(O)O^- + 3Cl^- + 1.5H_2O_2 + 1.5O_2$; (4) CCl_2=CCl_2 + $6O_2^- \xrightarrow{H_2O}$ $2HOC(O)O^-$ + $4Cl^- + H_2O_2 + 3O_2$; (5) (*p*-ClPh)$_2$C=CCl_2 + $3O_2^- \xrightarrow{H_2O}$ (*p*-ClPh)$_2$C=O + $HOC(O)O^- + 2Cl^- + {}^1/_2H_2O_2 + O_2$.

Scheme I

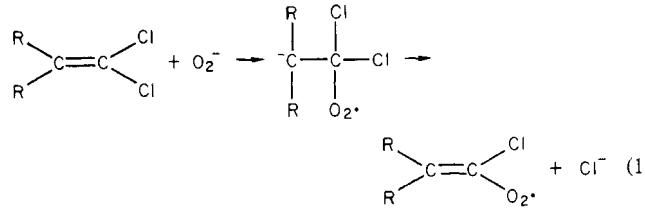


by O_2^- in DMF are summarized in Table I.[9] Within the limits of a reaction time of 10 min or less, 1-chloroethene, *trans*-1,2-dichloroethene, Aldrin,[10] and Dieldrin[10] are not oxidized by O_2^- in DMF.

The rates of reaction for the respective substrates with O_2^- have been measured by the rotating ring–disk voltammetric technique,[11] and the normalized pseudo-first-order rate constants ($k_1/[S]$) are summarized in Table I. Essentially the same apparent rate constants and reaction stoichiometries are observed when MeCN is used as the solvent, but in Me_2SO the apparent rate constants, $k_1/[S]$, are 10–100 times smaller.

A reasonable mechanism for these oxidations is an initial nucleophilic addition of superoxide to the chloroalkenes (e.g., tetrachloroethene (Scheme I)). Subsequent loss of chloride ion would give a vinyl peroxy radical, which can cyclize and decompose to a chloroacyl radical and phosgene.[12] These would undergo subsequent facile reactions with O_2^- to give bicarbonate and chloride ions.[13,14]

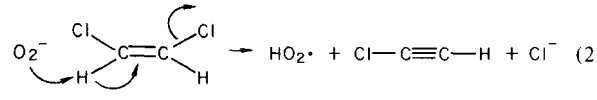
In the case of (*p*-ClPh)$_2$C=CCl_2(DDE) and 1,1-dichloroethene, addition of superoxide can only be followed by β-elimination of chloride if attack occurs on the carbon bearing the chlorine atoms (eq 1).[15] The apparent second-order rate constants for loss of



these two substrates are substantially smaller than those for the other systems, which is consistent with this restriction.

The apparent nonreactivity of *trans*-1,2-dichloroethene, and of Dieldrin and Aldrin, is not immediately explained by this mechanism in view of the facile reactivity of *cis*-1,2-dichloroethene. We suggest that the double bonds of the two bicyclic systems are sterically hindered, by the syn-chlorine on C_7, to the preferable exo attack of superoxide. Likewise, steric effects may account for the differential reactivities of *cis*- and *trans*-1,2-dichloroethene; addition of superoxide ion would be expected to relieve steric strain between the two chlorines in the cis isomer. However, this reactivity pattern also is consistent with base-catalyzed elimination reactions of these systems.[16]

Because of its nucleophilic character, superoxide acts as a strong Brønsted base.[17] The base-catalyzed elimination reaction of *cis*-1,2-dichloroethene (eq 2) is much more facile than that of the

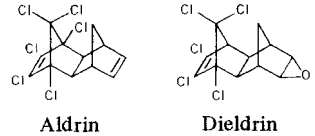


trans isomer because trans elimination can occur with the former but not the latter.[16] Subsequently, chloroethyne could react with superoxide ion via nucleophilic attack[18] to give the observed products (Table I). Both the nucleophilicity and basicity of O_2^- are leveled by Me_2SO (relative to DMF and acetonitrile),[19] which accounts for the slower reaction rates that are observed.

These observations indicate that in vivo superoxide could react with ingested chloroethenes. The proposed radical intermediates (vide supra) are likely toxins, and their reactivity with lipids may represent the mechanism for the cytotoxicity of cleaning solvents in the liver.[20]

(9) Stoichiometries were determined by incremental titration with substrate of a known amount of O_2^- (~4 mM, electrosynthesized), with the residual O_2^- determined by positive-scan voltammetry. The O_2 from the stoichiometric combination of substrate and O_2^- in a sealed cell was determined by cyclic voltammetry. The yield of Cl^- was determined by anodic cyclic voltammetry at +0.95 V vs. SCE (confirmed by $AgNO_3$ titration) and the yield of base (after dilution with H_2O) by titration with HCl (titration curves for the product solutions were identical with that for bicarbonate ion).

(10) Structures are as follows:



Aldrin Dieldrin

(11) A Pine Instruments Co. Model RPE 3 dual potentiostat in combination with a Pt–Pt ring–disk electrode was used for the kinetic studies. Oxygen was reduced at the disk to O_2^-, which traveled to the ring where it was oxidized to O_2. The ratio of currents, i_{ring}/i_{disk}, decreased when a reactive substrate (with O_2^-) was present in excess. Pseudo-first-order rate constants were determined for the O_2^--substrate reactions with 10-fold excess by use of analytical functions (Albery, W. J.; Hitcheman, M. L. "Ring-Disc Electrodes"; Clarendon Press: Oxford, 1971). These constants exhibit a first-order dependence on substrate concentration.

(12) (a) This chemistry of vinyl peroxy radicals has precedent.[12b] (b) Kochi, J. K. In "Free Radicals"; Kochi, J. K., Ed.; Wiley: New York, 1973; p 698.

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(14) Frimer[7] has reported that certain polynitro or polycyano substituted alkenes react with superoxide via initial electron transfer. Although nucleophilic addition of O_2^- to these alkenes was dismissed on the basis of ^{18}O labeling experiments, the possible presence of hydroxide makes these studies suspect.

(15) Further reaction of the vinyl peroxy radical would be analogous to that shown in Scheme I.[12] This sequence would lead to the ketones RC(O)R, which have been observed as products (see Table I).

(16) For example, see: Truce, W. E.; Boudakian, M. M.; Heine, R. F.; McManimie, R. J. *J. Am. Chem. Soc.* **1956**, *78*, 2743.

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(18) See: Miller, S. E.; Tanaka, R. *Sel. Org. Transform.* **1970**, *1*, 143.

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Registry No. *cis*-CHCl=CHCl, 156-59-2; CH_2=CCl_2, 75-35-4; CHCl=CCl_2, 79-01-6; CCl_2=CCl_2, 127-18-4; (*p*-ClPh)$_2$C=CCl_2, 72-55-9; superoxide ion, 11062-77-4; *trans*-1,2-dichloroethene, 156-60-5; chloroethene, 75-01-4; aldrin, 309-00-2; dieldrin, 60-57-1.

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Transient Absorption Study of the Intramolecular Excited-State and Ground-State Proton Transfer in 3-Hydroxyflavone and 3-Hydroxychromone

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Nano- and picosecond fluorescence studies provide the reaction kinetics and relaxation in the excited-state proton transfer of the hydrogen bonding system.[1-5] The mechanism of the excited-state proton transfer in 3-hydroxyflavone was proposed by Sengupta and Kasha.[6] Recently, Itoh et al.[7] have reported time-resolved and steady-state fluorescence studies of the excited-state proton transfer in 3-hydroxyflavone (3-HF) and 3-hydroxychromone (3-HC), which lacks a phenyl group in γ-pyrone ring of 3-HF. They demonstrated that the excited-state proton transfer from the normal form (N*) to the tautomer (T*) takes place more rapidly in 3-HC than in 3-HF and suggested that the phenyl group has a large effect on the excited-state proton transfer and relaxation process of 3-HF. We present here a transient absorption study of the mechanism for proton transfer in the excited state (N* → T*) as well as in the ground state (T → N) of 3-HF and 3-HC at room temperature.

As reported in the previous paper,[7] the 3-methylpentane (MP) solutions of 3-HF and 3-HC show no normal form fluorescence but only the long-wavelength fluorescence at 500–530 nm. The long-wavelength fluorescence was ascribed to the radiative transition from T* to the corresponding ground state (T). However, the existence of this type of ground-state tautomer as an intermediate from T* to the ground-state normal form (N) has never been evidenced. The present transient absorption study reveals the mechanism and kinetics of the processes of T* → T → N as well as the absorption bands of T and T*. Further, the ground-state reverse proton transfer (T → N) was observed to take place more rapidly in 3-HC than 3-HF.

The MP solution of 3-HF shows the strong absorption spectrum in the 300–360-nm region. The ground-state absorption bleaching and recovery were observed in the 337-nm excitation of the MP solution at room temperature by using a N_2 laser (Molectron UV 12) and a flash lamp (USSI 3CP-3) system.[8] A single-exponential recovery of the absorption with a lifetime of 3.1 μs was observed. This long time recovery can be ascribed to either the recovery through the excited-state proton transfer followed by the reaction

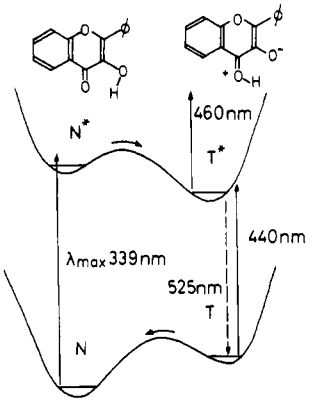

Figure 1. Schematic energy diagram of the proton transfer in 3-hydroxyflavone.

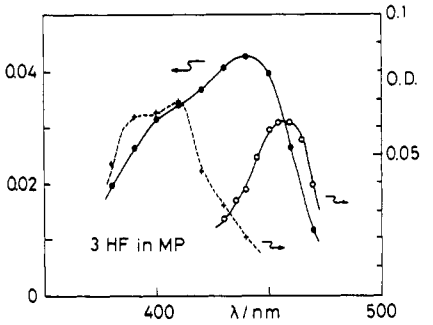

Figure 2. Time-resolved transient absorption spectra of the MP solution of 3-hydroxyflavone at room temperature: (●) depicted at 300-ns delay after a laser excitation; (○) at ~13-ns delay; (+) at ~50-ns delay.

processes shown in Figure 1 or the decay of the triplet species. However, it is confirmed that the former process is predominant in the recovery of the ground-state absorption by the consistent decay of the transient absorption of T, as will be mentioned later.

The time-resolved absorption spectra of the aerated MP solution of 3-HF at 360–500 nm were determined as shown in Figure 2. The rather broad band (λ_{max}440 nm) was observed at 300-ns delay after a laser excitation. Further, a very short time decay absorption was observed at λ_{max} 460 nm. The transient absorption at 440 nm exhibits a single exponential decay (τ = 2.9 μs), while the lifetime at 460 nm is approximately 1–2 ns. Both lifetimes are almost invariant in the deaeration of solution. Therefore, the long- and short-lifetime absorption bands are not ascribed to the triplet species. The long time absorption may be attributable to the ground-state tautomer (T), since the lifetimes of T* and N* were reported to be less than 2 ns and several 10 ps, respectively. The decay time of this transient shows a good consistency with the ground-state recovery time of N. These findings demonstrate the experimental evidence of the reaction scheme of the excited-state proton transfer and relaxation process (Figure 1). The decay times of the 460-nm absorption band (Figure 2) and of the T* fluorescence are in good consistency with each other within experimental error, though the determination of the absorption lifetime has less accuracy than that of the fluorescence lifetime. Therefore, the absorption band at 460 nm is ascribed to the $S_n \leftarrow S_1$ absorption of T*.

On the other hand, the aerated MP solution of 3-HF shows a transient absorption at 390–420 nm in addition to the T* and T absorption bands. The lifetime of ~200 ns remarkably increases in the deaeration of the solution by nitrogen gas bubbling. Therefore the absorption band at 400 nm may be attributable to the triplet–triplet absorption band. Hamanoue et al.[9] reported triplet absorption bands of flavone at 365–370 and 640–650 nm and suggested it as the lowest triplet state with a π,π^* character.[10]

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