$C_{60}^{\bullet +}$ and C_{60}^{2+} were both observed to add $H^\bullet$ (and $D^\bullet$) rapidly, with addition occurring upon at least 10% of the collisions at 0.4 Torr of helium. The primary products were also observed to react further according to reactions 2 and 3. Reaction 2 occurs for

$$C_{60}H_n^{+} + H^\bullet \rightarrow C_{60}H_{n+1}^{+} \qquad (2)$$

$$C_{60}H_n^{2+} + H^\bullet \rightarrow C_{60}H_{n+1}^{2+} \qquad (3)$$

$n = 1$, 2, and possibly 3 (a tentative identification of $C_{60}D_4^{+}$ was made), while reaction 3 occurs for at least $n = 1$–3. At high flows of D atoms, the major product peak seen for the sequence of reactions initiated by C_{60}^{2+} was at m/z 364, corresponding to $C_{60}D_4^{2+}$: we are unable to deduce whether the "buildup" of this signal is due to the low reactivity of $C_{60}D_4^{2+}$ with $D^\bullet$ or due to the occurrence of a rapid D atom transfer reaction of type 1 involving $C_{60}D_5^{\bullet 2+}$ and $D^\bullet$. The addition reactions of $C_{60}^{\bullet +}$ and C_{60}^{2+} with $H^\bullet$ and $D^\bullet$ are extraordinarily rapid; they are at least as efficient as any ion/$H^\bullet$ atom addition reactions which have been reported previously.[20] This can be rationalized in terms of the long collision complex lifetime expected for a species as large as $(C_{60}H^{+})^{*}$, resulting in a high probability of collisional stabilization instead of complex dissociation. Indeed, the fullerene ions are sufficiently large and have enough internal modes of energy dispersal that radiative stabilization of the collision complex is also feasible.[21]

Ion signals obtainable for $C_{70}^{\bullet +}$ and C_{70}^{2+} were about 1 order of magnitude lower in intensity than the signals obtainable for $C_{60}^{\bullet +}$ and C_{60}^{2+}. For this reason, it was not possible to quantify the extent of reaction of $C_{70}^{\bullet +}$ and C_{70}^{2+} with $H^\bullet$ and with $D^\bullet$. At moderate H/D atom flows, however, the decrease in the m/z 840 and 420 ion signals appeared to parallel the decrease seen for m/z 720 and 360, so that we can suggest that the reactivity of the C_{70} monocation and dication is analogous to that of their C_{60} counterparts.

Rapid reactions of fullerene cations with $H^\bullet$ are likely to play a significant role in the chemistry of sooting flames, especially in view of the nonreactivity of $C_{60}^{\bullet +}$ with closed-shell species.[22] Conversion of $C_{60}^{\bullet +}$ to $C_{60}H^{+}$ is likely to enhance the production of neutral C_{60} as shown in the reaction sequence 4–6. Proton

$$C_{60}^{\bullet +} + H^\bullet \rightarrow C_{60}H^{+} \qquad (4)$$

$$C_{60}H^{+} + M \rightarrow MH^{+} + C_{60} \qquad (5)$$

$$C_{60}H^{+} + e \rightarrow C_{60} + H^\bullet \qquad (6)$$

transfer from $C_{60}H^{+}$ to a species of high PA (such as cyclopropenylidene, which is easily formed within flames)[26] and dissociative recombination of protonated C_{60} are likely to be more efficient processes within sooting flames than are charge transfer from $C_{60}^{\bullet +}$ (since C_{60} has a lower IE than most smaller hydrocarbon species)[27] and the recombination reaction $C_{60}^{\bullet +}$ + e (which may not have any accessible fragmentation product channels).[28] The reactivity of $C_{60}^{\bullet +}$, and C_{60}^{2+}, with $H^\bullet$ can be of similar significance to interstellar chemistry, as we shall discuss elsewhere.[29] The reactivity of $H^\bullet$ with $C_{60}H^{+}$ to regenerate $C_{60}^{\bullet +}$, and thus the possible role of $C_{60}^{\bullet +}$ as a catalyst for the recombination of H atoms, remains to be explored. Also, since neutralization may proceed by the electron–ion recombination and proton-transfer reactions 7 and 8, the observations reported here clearly point toward the possible presence of slightly hydrogenated fulleranes in interstellar and circumstellar gases. These fulleranes may then provide a signatures for the corresponding fullerenes which are being sought spectroscopically in these regions.[10]

$$C_{60}H_n^{2+} + e\ (M) \rightarrow C_{60}H_{n-x}^{+} + xH\ (MH^{+}) \qquad (7)$$

$$C_{60}H_n^{+} + e\ (M) \rightarrow C_{60}H_{n-x} + xH\ (MH^{+}) \qquad (8)$$

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A Stable Crystalline (Alkylperoxy)iodinane: 1-(*tert*-Butylperoxy)-1,2-benziodoxol-3(1*H*)-one

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(Alkylperoxy)iodinanes have not been synthesized probably because of their high tendency to decompose.[1] Milas and Plesnicar reported the reaction of iodosylbenzene with *tert*-butyl hydroperoxide in dichloromethane and proposed the in situ generation of [bis(*tert*-butylperoxy)iodo]benzene, which decomposes even at −80 °C to *tert*-butyl peroxy radical and iodobenzene.[2,3] This ready decomposition of the (alkylperoxy)iodinane will be attributed to the small dissociation energy of the apical hypervalent peroxy–iodine(III) bond and be facilitated by conjugative overlap of the breaking hypervalent bond with π-orbitals of the aromatic nucleus.[4] Thus, it appears that fixation of an apical hetero ligand and an equatorial aromatic ligand on iodine(III) by the formation of five-membered heterocycles such as an iodoxolone, which makes

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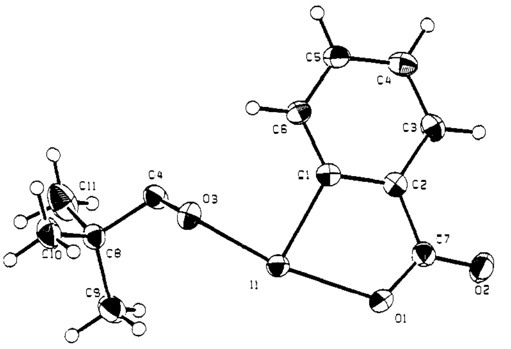
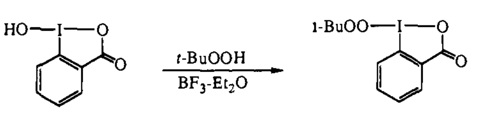


Figure 1. ORTEP representation of the peroxyiodinane **2**.

this destabilizing orbital interaction very difficult, will lead to enhanced stability of the (alkylperoxy)iodinanes.[5] We report the synthesis and characterization of the first stable crystalline (alkylperoxy)iodinane, 1-(*tert*-butylperoxy)-1,2-benziodoxol-3-(1*H*)-one (**2**).



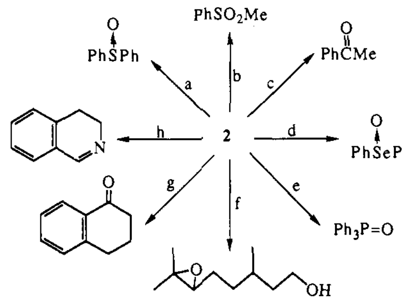
1 2

In marked contrast to the facile reaction of *tert*-butyl hydroperoxide with iodosylbenzene at −80 °C, no ligand exchange was observed in the reaction with 1-hydroxy-1,2-benziodoxol-3(1*H*)-one (**1**) even at room temperature, and the iodinane **1** was recovered unchanged. However, activation of **1** with Lewis acids makes possible the ligand exchange of the hydroxy group with a *tert*-butylperoxy group; thus, treatment of **1** with *tert*-butyl hydroperoxide (1.1 equiv) in the presence of $BF_3 \cdot Et_2O$ (1 equiv) in chloroform at room temperature for 6 h afforded the (alkylperoxy)iodinane **2** in 85% yield. The peroxyiodinane **2** was isolated by recrystallization from ethyl acetate–hexane as colorless plates, mp 128–129 °C dec, and fully characterized by spectral analysis.

The structure of **2** was established by a single-crystal X-ray analysis. The ORTEP representation of Figure 1 clearly illustrates that the *tert*-butylperoxy group occupies an apical position of distorted trigonal-bipyramidal geometry around the iodine. There are two primary hypervalent I–O bonds: a considerably ionic endocyclic bond (2.181 (5) Å) to the ring oxygen and a short exocyclic bond (2.039 (5) Å) to the peroxide oxygen.[5b,6] The O3–O4 bond length of 1.459 (7) Å is somewhat shorter than a standard bond length of 1.48 Å for dialkyl peroxides, but comparable to that in anhydrous hydrogen peroxide (1.453 (7) Å).[7] The I1–O3–O4–C8 torsional angle of 109.9 (5)° is markedly smaller than the C–O–O–C torsional angle in di-*tert*-butyl peroxide (165.8°).[8]

The peroxyiodinane **2** is stable in the solid state and can be safely stored at room temperature for an indefinite period of time. In chloroform solution (0.03 M), however, **2** decomposes at room temperature with a half-life of 4 days and affords, through ligand exchange, 1-chloro-1,2-benziodoxol-3(1*H*)-one (74%), identical to the material prepared by the reaction of **1** with HCl.[9] On heating at 140 °C without solvent, **2** decomposes explosively yielding a mixture of 1,2-diiodobenzene (46%), iodobenzene (6%), *o*-iodobenzoic acid (14%), and acetone (43%). This thermal reaction probably involves a cleavage of the weak hypervalent peroxy–iodine(III) bond and generates a *tert*-butylperoxy radical and a 9-I-2[10] σ-iodinanyl radical.[11]

Scheme I[a]



4

[a] Reaction details: (a) PhSPh, CH_2Cl_2, 0 °C (2 h) then 25 °C (26 h); (b) PhSMe, CH_2Cl_2, 25 °C (11 h); (c) 2-methyl-2-phenyl-1,3-dithiane (3), $MeCN$–H_2O (9:1), 25 °C (3 min); (d) PhSePh, CH_2Cl_2, 0 °C (2 h) then 25 °C (18 h); (e) Ph_3P, CH_2Cl_2, 0 °C (30 min); (f) citronellol, CH_2Cl_2, 25 °C (7 days); (g) 1,2,3,4-tetrahydronaphthalene, K_2CO_3, CH_2Cl_2, 25 °C (41 h); (h) 1,2,3,4-tetrahydroisoquinoline, K_2CO_3, CH_2Cl_2, 25 °C (18 h).

The versatility of the peroxyiodinane **2** as an oxidizing reagent is noteworthy, and the reactions shown in Scheme I illustrate the broad range of the utility. Oxidation of diphenyl sulfide at room temperature afforded diphenyl sulfoxide (84%), in which **2** was reduced to a mixture of *o*-iodobenzoic acid (86%), *tert*-butyl alcohol (54%), and acetone (27%).[12] The attempted oxidation of diphenyl sulfide with either **1** or *tert*-butyl hydroperoxide under the same reaction conditions recovered the sulfide. Using 2.5 equiv of **2**, thioanisole was oxidized to methyl phenyl sulfone (94%). Deprotection of the dithioacetal **3** proceeded smoothly, yielding acetophenone (69%). Reaction with triphenylphosphine illustrates that **2** can oxidize 2 mol of the substrate. Oxidation of citronellol afforded the epoxide **4** (36%). Benzylic oxidation of 1,2,3,4-tetrahydronaphthalene gave α-tetralone (61%). Furthermore, 3,4-dihydroisoquinoline was obtained in 83% yield by the oxidation of 1,2,3,4-tetrahydroisoquinoline.

Thus, the present study provided the first synthesis of (alkylperoxy)iodinanes. The versatility of the peroxyiodinane **2** as an oxidizing reagent was also established.

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Supplementary Material Available: Synthetic details for the preparation of **2**, ^1H and ^{13}C NMR spectra of **2**, and tables of crystallographic details, positional and thermal parameters, general temperature factor expressions, bond distances, bond angles, and torsional angles of **2** (17 pages). Ordering information is given on any current masthead page.

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