Model GC-12A apparatus equipped with a flame ionization detector and a 25 m × 0.2 mm Shimadzu capillary column of OV-1 (carrier gas N_2; carrier gas pressure 1.3 kg/cm^2; column temperature 240 °C; injector temperature 250 °C).

The ESR spectra were measured at 77 K with an ESR spectrometer, JEOL ME-3X, equipped with 100-kHz magnetic field modulation.

Cyclic voltammograms were obtained on a potentiostat (Nikko Keisoku NPOT-2501) with a potential sweeper (Nikko Keisoku NPS-2A) or a BAS 100 instrument by using a glassy carbon working electrode, a platinum foil counter electrode, and a saturated calomel reference electrode (SCE). The working electrode was polished with alumina powder prior to use, followed by washing with twice-distilled water in an ultrasonic bath. All measurements were carried out at 25 °C.

Other analyses were identical with those reported in the previous paper.[31]

Photoreactions. As reported in the previous paper,[31] distilled TEA (0.5 mL), acetonitrile (AN) (2.0 mL), a methanolic solution of $Co^{III}L_1$ (0.5 mL, 5×10^{-3} M), and 10 mg of OPP-3 were placed in a Pyrex tube (8 mm in diameter). After the mixture was purged with CO_2 gas, the tube was closed off with a gum stopper and then irradiated under magnetic stirring at $\lambda > 290$ nm using a 500-W high-pressure mercury arc lamp. For homogeneous runs, the AN solution of OPP-3 (3×10^{-3} M) was used. The gaseous and liquid products were analyzed by GLC and HPLC.

Laser Flash Photolysis. An AN solution containing OPP-3 and TEA (1 M) was placed in a quartz cell and then degassed; [OPP-3] = 1.0×10^{-5} M. Measurements were conducted by means of an excimer laser under conditions similar to those reported.[31]

ESR Measurements. A mixture of an AN solution of OPP-3 (3 mM, 2 mL), a methanolic solution of $Co^{III}L_1$ (10 mM, 0.5 mL), and TEA (0.5 mL) was prepared, and 1 mL of the solution was pipetted into each of two Pyrex ESR tubes. The solution in one tube was saturated with CO_2, and the tube was sealed. The other tube was sealed under vacuum. Two pairs of the above samples were irradiated with a high-pressure 100-W Hg lamp ($\lambda > 290$ nm). Spectra of frozen sample solutions were recorded at liquid-nitrogen temperature in intervals of 5-s irradiation at room temperature or after 5-min irradiation at room temperature. The ESR spectrum in the presence of TEOA was obtained similarly by substituting TEOA for TEA. In order to maintain a nearly identical sensitivity, the same ratio-frequency power of 8 mW incident on the cavity and the same modulation amplitude of 16 G were used throughout. For the measurement of g values, a Mn–MgO probe was employed.

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Copper(I)/(*t*-BuOOH)-Induced Activation of Dioxygen for the Ketonization of Methylenic Carbons

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Abstract: In acetonitrile/pyridine bis(bipyridine)copper(I) [$Cu^I(bpy)_2^+$] activates HOOH and *t*-BuOOH for the selective ketonization of methylenic carbons. With 5 mM $Cu^I(bpy)_2^+$/100 mM HOOH(Bu) the conversion efficiencies [product per 2HOOH(Bu)] for c-C_6H_{12} are 31% (HOOH) and 59% (*t*-BuOOH, argon atmosphere) and for $PhCH_2CH_3$ are 24% (HOOH) and 64% (t-BuOOH, argon). With 5 mM $Cu^I(bpy)_2$ and 10 mM *t*-BuOOH under argon the conversion efficiency for c-C_6H_{12} is 10% and for $PhCH_2CH_3$ is 140%. However, in the presence of O_2 (1 atm, 7 mM) the conversion efficiency for c-C_6H_{12} increases to 67%, and for $PhCH_2CH_3$ to 440% [all PhC(O)Me (22 mM)], respectively. The latter result represents a $Cu^I(bpy)_2^+$/*t*-BuOOH-induced *autoxygenation* with at least 2.2 O_2/catalyst turnovers. In acetonitrile the bis(bipyridine)cobalt(II) [$Co^{II}(bpy)_2^{2+}$] complex in combination with *t*-BuOOH also activates O_2 for the ketonization of methylenic carbons but is about one-half as efficient as the $Cu^I(bpy)_2^+$/*t*-BuOOH combination.

A recent paper[1] summarizes the reaction efficiencies and product selectivities for a group of ML/HOOH(or *t*-BuOOH)/hydrocarbon–substrate systems (ML = seven iron complexes and one cobalt complex) that ketonize methylenic carbons via the initial formation of a hydroperoxide(or *t*-BuOO)–substrate intermediate.[2,3] The reaction efficiencies [product per two HOOH(or *t*-BuOOH) range from 10–80% and usually are greater with *t*-BuOOH. Because the $Co^{II}(bpy)_2^{2+}$ and $Fe^{II}(bpy)_2^{2+}$ complexes provide unique selectivities and good conversion efficiencies,[1,4] we initiated an evaluation of other bipyridine complexes of transition metals (Cu, Mn, Cr, V, Mo, and Ru).

Although copper(II) salts in pyridine activate hydrogen peroxide for the ketonization of methylenic carbons, the reaction efficiencies for all conditions were less than 12% (product per two HOOH molecules).[5] Here we report (a) that bis(bipyridine)copper(I) [$Cu^I(bpy)_2^+$] in acetonitrile/pyridine [4:1 mol-ratio] activates HOOH and *t*-BuOOH for the selective ketonization of methylenic carbons [closely similar to the $Co^{II}(bpy)_2^{2+}$/HOOH(Bu) system][1,4] and (b) that the 1:1 $Cu^I(bpy)_2^+$/*t*-BuOOH combination activates O_2 for the direct ketonization of methylenic carbons.

Experimental Section

Equipment. The reaction products were separated and identified with a Hewlett-Packard 5880A series gas chromatograph equipped with an HP-1 capillary column (cross-linked methyl silicone gum phase, 12 m × 0.2 mm i.d.) and by gas chromatography–mass spectrometry (Hewlett-Packard 5790A Series gas chromatograph with a mass-selective detector).

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A three-electrode potentiostat (Bioanalytical Systems Model CV-27) with a Houston Instruments Model 200 XY recorder was used to record the voltammograms. The experiments were conducted in a 15-mL electrochemical cell with provision to control the presence of O_2 with an argon-purge system. The working electrode was a Bioanalytical Systems glassy-carbon inlay (area, 0.09 cm^2), the auxiliary electrode a platinum wire, and the reference electrode an Ag/AgCl wire in an aqueous tetramethylammonium chloride solution that was adjusted to give a potential of 0.00 V vs SCE. The latter was contained in a Pyrex tube with a cracked soft-glass tip, which was placed inside a luggin capillary.[6] A Hewlett-Packard Model 8450A diode-array spectrophotometer was used for the UV-visible measurements.

Chemicals and Reagents. The reagents for the investigations and syntheses were the highest purity commercially available and were used without further purification. Burdick and Jackson "distilled in glass" grade acetonitrile (MeCN, 0.004% H_2O) and pyridine (py, 0.014% H_2O) were used as solvents. High-purity argon gas was used to deaerate the solutions. All compounds were dried in vacuo over $CaSO_4$ for 24 h prior to use. 2,2′-Bipyridine (bpy, 99+%) was obtained from Aldrich, hydrogen peroxide (50% H_2O) from Fisher, and *t*-BuOOH (5.5 M, in 2,2,4-trimethylpentane) from Aldrich. The organic substrates included cyclohexane (Aldrich, anhydrous, 99+%), cyclohexane-d_{12} (Aldrich, 99.5 atom % D), ethyl benzene (Kodak, 99.8%), toluene (Burdick and Jackson, 0.005% H_2O), cyclohexane (Fisher, 99%), 1,4-cyclohexadiene (Aldrich, 96%), adamantane (Aldrich, 99+%), and *cis*-stilbene (Aldrich, 97%).

$[Cu^{I}(MeCN)_4](ClO_4)$. The $[Cu^{I}(MeCN)_4](ClO_4)$ complex was prepared by dissolution of Cu_2O with $HClO_4$ (0.2 M) in MeCN.[7]

Copper(I) Bis(2,2′-bipyridine) and Cobalt(II) Bis(2,2′-bipyridine) Solutions. The $Cu^{I}(bpy)_2^{+}$ and $Co^{II}(bpy)_2^{2+}$ complexes were prepared in situ by mixing $[Cu^{I}(MeCN)_4](ClO_4)$ and $[Co^{II}(MeCN)_4](ClO_4)_2$ in MeCN with stoichiometric ratios of bipyridine.

Methods. The investigations of HOOH and *t*-BuOOH activation by the $Cu^{I}(bpy)_2^{+}$ and $Co^{II}(bpy)_2^{+}$ complexes (5–10 mM) used solutions that contained 1.0 M substrate in 3–5 mL of MeCN/py (4:1 mol-ratio or MeCN). Hydrogen peroxide (50%) or *t*-BuOOH (5.5 M) was injected to give 5–200 mM HOOH(Bu-*t*). After 3–8 h with constant stirring at room temperature (22 ± 2 °C) under argon or O_2 (1 atm), samples of the reaction solutions were injected into a capillary-column gas chromatograph for analysis. In some cases, the reaction was quenched with water, and the product solution was extracted with diethyl ether. Product species were characterized by GC–MS. Reference samples were used to confirm product identifications and to produce standard curves for quantitative assays of the product species.

The kinetic isotope effect [K] was determined with a 1:1 cyclohexane/cyclohexane-d_{12} mixture (0.5 M/0.5 M) as the substrate; the k_H/k_D values were calculated from the product ratios of cyclohexanone/cyclohexanone-d_{10}, cyclohexanol/cyclohexanol-d_{11}, and c-C_6H_{11}OOBu-*t*/c-C_6D_{11}OOBu-*t*. Similar measurements were made for *t*-BuOOH was the oxidant in the absence and presence of O_2.

The experiments were designed to be limited by HOOH and *t*-BuOOH in order to (a) evaluate the reaction efficiency with respect to oxidant, (b) minimize secondary reactions with the primary products, and (c) minimize catalyst deactivation by product water.

Results

The reaction efficiencies and product profiles for the activation of HOOH and *t*-BuOOH by $Cu^{I}(bpy)_2^{+}$ for reaction with c-C_6H_{12} and $PhCH_2CH_3$ are summarized in Table IA. With 5 mM $Cu^{I}(bpy)_2^{+}$/100 mM HOOH in MeCN/py (4:1 mol-ratio) the conversion efficiency [ketone/2HOOH and ROH/HOOH] (a) for 1 M c-C_6H_{12} is 31% (ketone/ROH ratio, 1.7) and (b) for 1 M $PhCH_2CH_3$ is 24% [PhC(O)Me only product], and the yields and product profiles are unaffected by the absence or presence of O_2 in the reaction media. In contrast, the 5 mM $Co^{II}(bpy)_2^{2+}$/100 mM HOOH system exhibits conversion efficiencies of 40% for 1 M c-C_6H_{12} [c-C_6H_{10}(O) only product] and 41% for 1 M $PhCH_2CH_3$ [product >99% PhC(O)Me].[1]

The 5 mM $Cu^{I}(bpy)_2^{+}$/100 mM *t*-BuOOH system (under argon) with 1 M c-C_6H_{12} is 59% efficient [14 mM c-C_6H_{10}(O), 13 mM/ROOBu-*t*, and 5 mM ROH] and with 1 M $PhCH_2CH_3$ is 64% efficient [9 mM PhC(O)Me and 23 mM ROOBu-*t*]. In contrast, the 5 mM $Co^{II}(bpy)_2^{2+}$/100q *t*-BuOOH system is essentially unreactive with 1 M c-C_6H_{12} (2% reaction efficiency) and much less reactive with 1 M $PhCH_2CH_3$ [37% reactive efficiency, 6 mM PhC(O)Me and 12 mM ROOBu-*t*].[1]

In sharp contrast to HOOH, the presence of dioxygen (1 atm O_2, 7 mM) in the 5 mM $Cu^{I}(bpy)_2^{+}$/100 mM *t*-BuOOH system has a major effect. With 1 M c-C_6H_{12} the conversion efficiency is 62% [25 mM c-C_6H_{10}(O), 1 mM ROOBu-*t*, and 10 mM ROH], and with 1 M $PhCH_2CH_3$ the conversion efficiency is 208% [103 mM PhC(O)Me and 1 mM ROOBu-*t*]. Even more impressive results occur with (a) 5 mM $Cu^{I}(bpy)_2^{+}$ and 5 mM *t*-BuOOH (1 atm O_2) [1 M $PhCH_2CH_3$ yields 12 mM PhC(O)Me (480% conversion efficiency)] and (b) 5 mM $Cu^{I}(bpy)_2^{+}$/10 mM *t*-BuOOOH (1 atm O_2) [1 M $PhCH_2CH_3$ yields 22 mM PhC(O)Me (440% efficiency)]. For the latter system, four increments of 10 mM *t*-BuOOH (added sequentially at 15-min intervals) produce 80 mM PhC(O)Me and 3 mM ROOBu-*t* (415% efficiency). The presence of O_2 causes the reaction stoichiometry for $PhCH_2CH_3$ to be at least one PhC(O)Me formed per *t*-BuOOH (200% conversion efficiency), and for 10 mM *t*-BuOOH more than four turnovers per $Cu^{I}(bpy)_2^{+}$ occur and at least two of these do not involve *t*-BuOOH. With 100 mM *t*-BuOOH, 5 mM $Cu^{I}(bpy)_2^{+}$, and 1 M $PhCH_2CH_3$ there are at least 20 catalyst turnovers to produce 103 mM PhC(O)Me. Although the $Co^{II}(bpy)_2^{2+}$/*t*-BuOOH/MeCN system also activates O_2 for the ketonization of methylenic carbon centers, it is much less efficient than the $Cu^{I}(bpy)_2^{+}$/*t*-BuOOH system (Table IA).

Table IB summarizes the product profiles from the oxygenation of several substrates by the $Cu^{I}(bpy)_2^{+}$/*t*-BuOOH/O_2 system. The limited reaction with methyl groups is evident, which confirms that this system is especially selective for methylenic carbons. The relative extent for $PhCH_2Me$/c-C_6H_{10}/c-C_6H_{12} to form ketones is 4/3/1, which correlates with their respective C–H bond dissociation energies (ΔH_{DBE}: 85, 87, and 95.5 kcal mol^{-1}).[8]

With adamantane ($C_{10}H_{16}$) the $Cu^{I}(bpy)_2^{+}$/*t*-BuOOH/O_2 system (Table IB) is 23% efficient and yields a secondary versus tertiary product ratio of 0.3 [C^2/C^3; 6/4 for $C_{10}H_{16}$], which is in sharp contrast with the 4% reaction efficiency and C_2/C_3 value of 0.7 for the $Cu^{II}(ClO_4)_2$/HOOH/py system.[5] The $Fe^{II}(PA)_2$/HOOH/$(py)_2$HOAc system (PA, anion of picolinic acid) is 30% efficient and gives a C_2/C_3 ratio of 0.7; with *t*-BuOOH the system is 72% efficient and the C_2/C_3 ratio is 0.15.[1] These data confirm that the present system produces unique reactive intermediates that result from the combination of $Cu^{I}(bpy)_2^{+}$, *t*-BuOOH, and O_2.

Note: Although the solvent of the *t*-BuOOH reagent, 2,2,4-trimethylpentane, contains a CH_2 group; for the conditions of Table IB its concentration is about 100 mM, which, on the basis of the reactivity for 1 M c-C_6H_{12}, should yield less than 0.4 mM product (none is detected).

The kinetic isotope effect ([K], Table I) for the reaction of c-C_6H_{12} with $Cu^{I}(bpy)_2^{+}$/HOOH to form ketone is 2.5 [the same [K] value as for the $Fe^{II}(PA)_2$/HOOH system][1] and to form c-C_6H_{11}OH is 1.4 (8.4 for $Fe^{II}(PA)_2$/*t*-BuOOH).[1] The [K] value for c-C_6H_{12} with the $Cu^{I}(bpy)_2^{+}$/*t*-BuOOH system to form c-C_6H_{11}OOBu-*t* is 7.3 and to form c-C_6H_{11}OH is >7. The $Cu^{I}(bpy)_2^{+}$/*t*-BuOOH system with O_2 (1 atm) has a [K] value of 8.8 for the formation of ketone, and a [K] value >8 for the formation of c-C_6H_{11}OH.

The relative reactivity per methylenic carbon (CH_2) of $PhCH_2CH_3$ and c-C_6H_{12} [{R} = $PhC(O)CH_3$ product/(c-C_6H_{10}(O) product/6)] provides insight to the reactive intermediate for the ketonization process. With the $Fe^{II}(PA)_2$/HOOH/$(py)_2$HOAc system the {R} value is 5 and is believed to result from $[(PA)_2Fe^{IV}(OOH)(OH)]$ as the reactive intermediate.[1] Here the {R} value for the $Cu^{I}(bpy)_2^{+}$/HOOH/(MeCN/py) system is 6. With *t*-BuOOH the respective {R} values for the production of ROOBu-*t* are 24 (Fe) and 13 ± 2 (Cu). In the presence of O_2 (1 atm) the $Cu^{I}(bpy)_2^{+}$/*t*-BuOOH system gives an {R} value of 24 ± 1 for ketonization, and the formation of ROOBu-*t* is suppressed.

When $PhCH_2CH_3$ is the substrate, it forms an O_2 adduct with $Cu^{I}(bpy)_2^{+}$ that sustains an autoxygenation cycle with one-to-three *t*-BuOOH-independent turnovers (the estimated {R} value for the

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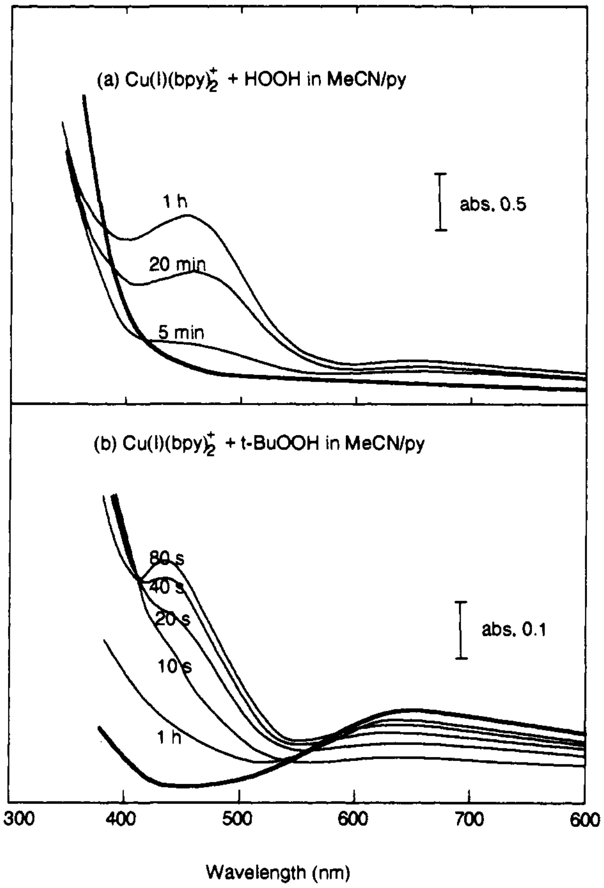

Figure 1. UV-visible spectra of (a) 1 mM $Cu^I(bpy)_2^+$ (—) plus 20 mM HOOH at different times (—); (b) 1 mM $Cu^I(bpy)_2^+$ plus 20 mM *t*-BuOOH at different times (—) and 1 mM $Cu^{II}(bpy)_2^{2+}$ (—) in MeCN/py (4:1 mol-ratio).

latter process is 60 ± 20). Hence, for the $Cu^I(bpy)_2^+$/*t*-BuOOH system there are three different reactive intermediates, with the one that couples with O_2 able to sustain an autoxygenation with $PhCH_2CH_3$ for 1-2 cycles.

Essentially the same results (Table I) are obtained when $Cu^{II}(bpy)_2^{2+}$ is used as the catalyst. Electrochemical and spectrophotometric measurements confirm that excess HOOH(Bu-*t*) reduces $Cu^{II}(bpy)_2^{2+}$ at diffusion-controlled rates. In contrast, the rate of reaction between $Cu^I(bpy)_2^+$ and HOOH (or *t*-BuOOH) is 10–100 times slower. Although $Cu^I(bpy)_2^+$ is slowly oxidized by O_2 in pure acetonitrile, in MeCN/py it remains reduced. In the absence of substrate the final product from the $Cu^I(bpy)_2^+$/HOOH combination is $(bpy)_2^+Cu^{II}OOH$ [$E_{1/2}$, –0.10 V vs SCE; 460 nm (ϵ 2000) and 650 nm (ϵ 180)].

Characterization of the Reactive Intermediates. Figure 1a (heavy line) illustrates the absorption spectrum for $Cu^I(bpy)_2^+$ and the effect over time after adding a 20-fold excess of HOOH. The final spectrum after 1 h is identical to that for $(bpy)_2^+$-$Cu^{II}OOH$(λ_{max}, 460 nm). When a 20-fold excess of *t*-BuOOH is added to $Cu^I(bpy)_2^+$, an entirely different sequence of spectral changes occurs with a transient intermediate observed during the first 20 min after mixing (Figure 1b, λ_{max} at 438 nm with maximum absorbance 80 seconds after mixing). Again, the final solution has a spectrum that is closely similar to that for $Cu^{II}(bpy)_2^{2+}$.

The electrochemistry of the $Cu^I(bpy)_2^+$ complex in MeCN/py is illustrated by the cyclic voltammogram of Figure 2a [$(E_{1/2})_{ox}$, +0.15 V vs SCE; $E_{p,c}$, –1.4 V]. When 5 mM $Cu^I(bpy)_2^+$ is combined with 50 mM *t*-BuOOH in MeCN/py (under argon), the resulting solution during the first 20 min after mixing exhibits diffuse irreversible reductions [$E_{p,c}$, –0.4 V vs SCE and –0.8 V] and an irreversible one-electron oxidation ($E_{p,a}$, +0.9 V) (Figure 2b). Scan reversal after the –0.4-V peak yields a two-electron irreversible oxidation ($E_{p,a}$, +1.15 V) that produces $Cu^{II}(bpy)_2^{2+}$ and O_2. Analogous electrochemistry is observed when 1 M $PhCH_2CH_3$ is present, but it persists for a longer period (at least 2 h). In the case of 5 mM $Cu^I(bpy)_2^+$, 10 mM *t*-BuOOH, O_2 (1 atm), and 1 M $PhCH_2CH_3$ a similar pair of irreversible reductions occurs during the first hour of reaction, but the oxidation peak at +1.0 V is smaller.

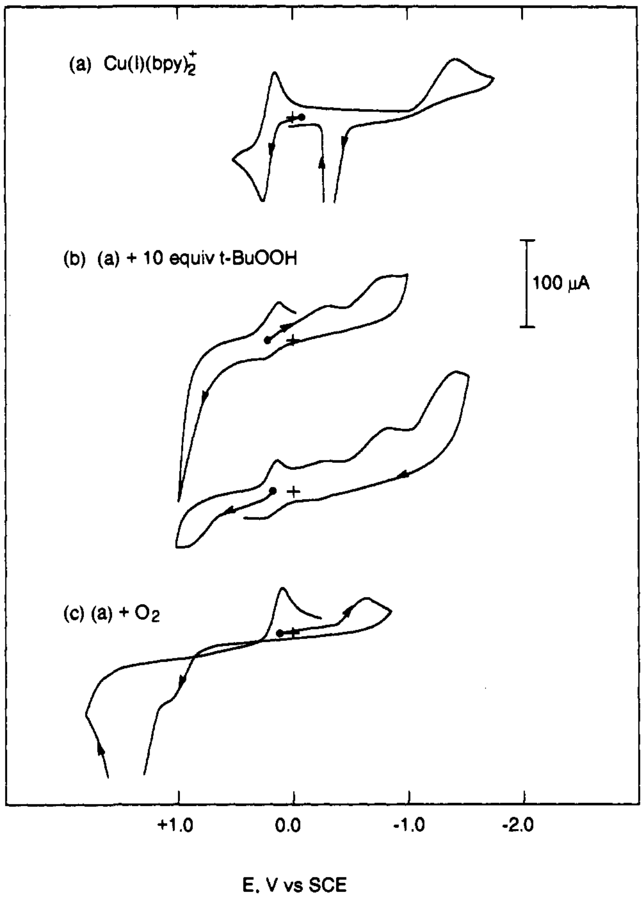

Figure 2. Cyclic voltammograms in MeCN/py [0.1 M $(Et_4N)ClO_4$] for (a) 5 mM $Cu^I(bpy)_2^+$; (b) (a) plus 50 mM *t*-BuOOH; and (c) (a) plus 1 M $PhCH_2CH_3$ under 1 atm of O_2 (7 mM). Scan rate, 0.1 V s^{-1}; GCE (0.09 cm^2); SCE vs NHE, +0.242 V.

The reduction of $Cu^I(bpy)_2^+$ in the presence of O_2 and $PhCH_2CH_3$ is illustrated by the cyclic voltammogram of Figure 2c. The reduction at –0.6 V yields a copper oxide film that upon scan reversal is stripped at +1.5 V. An initial positive scan yields the reversible oxidation couple for free $Cu^I(bpy)_2^+$.

In contrast, when 5 mM $Cu^I(bpy)_2^+$ is combined with 10 mM *t*-BuOOH and 7 mM O_2 (1 atm) the oxidation couple for $Cu^I(bpy)_2^+$ is absent and is replaced by a broad irreversible one-electron oxidation peak at +1.0 V and a drawn out irreversible reduction at –0.45 V (Figure 3a; scan reversal after this peak results in the enhancement of the peak current for the +1.0-V oxidation). The combination of 5 mM $Cu^I(bpy)_2^+$, 100 mM *t*-BuOOH, and 1 M $PhCH_2CH_3$ under an argon atmosphere has essentially the same electrochemical characteristics (Figure 3b) as the $Cu^I(bpy)_2^+$/*t*-BuOOH/O_2 system (Figure 3a), but for the latter the reduction current at –0.45 V is much larger.

Discussions and Conclusions

The results of Table I provide compelling evidence that the $Cu^I(bpy)_2^+$ complex catalyzes the reaction of *t*-BuOOH with methylenic carbon centers, for example.

$$PhCH_2CH_3 + 2t\text{-}BuOOH \xrightarrow[MeCN/py]{Cu^I(bpy)_2^+} PhCH(OOBu\text{-}t)CH_3 + t\text{-}BuOH + H_2O \quad (1)$$

With 5 mM $Cu^I(bpy)_2^+$ and 100 mM *t*-BuOOH the reaction is

Table I. $Cu^{I}(bpy)_2^+$/HOOH(Bu-*t*)-Induced and $Co^{II}(bpy)_2^{2+}$/*t*-BuOOH-Induced Oxygenation of Hydrocarbons[a]

A. HOOH(H) vs *t*-BuOOH(Bu)

			products (mM, ±5%)						
			$c-C_6H_{12}$ (1 M)				$PhCH_2CH_3$ (1 M)		
$Cu^{I}(bpy)_2^+$ (mM) (MeCN/py)	HOOH(Bu-*t*) (mM)	$[O_2]$ (mM)	reac[b] effncy, %	$c-C_6H_{10}(O)$ [K][c]	ROOBu-*t* [K]	ROH [K]	reac[b] effncy, %	PhC(O)Me {R}[d]	ROOBu-*t* {R}[d]
5	100 (H)	0	31	12 [2.5]		7 [1.4]	24	12 {6}	
5	100 (H)	7	31	12 [2.4]		7 [1.1]	24	12 {6}	
5	100 (Bu)	0	59	14 [8.6]	13 [7.3]	5 [>7]	64	9 {4}	23 {11}
5	100 (Bu)	7	62	25 [8.8]	1	10 [>8]	208	103 {25}	1
10	100 (Bu)	7	79	34	<1	10	190	94 {17}	1
5	5 (Bu)	0	0	0	0	0	180	4	<1
5	5 (Bu)	7	<40	<1	0	0	480	12 {>72}	0
5	10 (Bu)	0	10	0	0	1	140	6	1
5	10 (Bu)	7	67	3	0	<1	440	22 {44}	0
5	4 × 10 (Bu)	7					415	80	3
5	20 (Bu)	0	60	3	3	0	110	8 {16}	3 {6}
5	20 (Bu)	7	60	6	0	0	280	28 {28}	0

			products (mM, ±5%)							
			$c-C_6H_{12}$ (1 M)				$PhCH_2CH_3$ (1 M)			
$Co^{II}(bpy)_2^{2+}$ (mM)	[MeCN]	$[O_2]$ (mM)	reac[b] effncy, %	$c-C_6H_{10}(O)$	ROOBu-*t*	ROH	reac[b] effncy, %	PhC(O)Me {R}[d]	ROOBu-*t*	ROH
5	5 (Bu)	0	24	0.5	0	0.2	94	1.4	0.7	0.5
5	5 (Bu)	8	22	0.5	0	0.1	206	4.6	0	1.1
10	10 (Bu)	0	29	1.0	0	0.9	120	4.0 {24}	1.6	0.8
10	10 (Bu)	8	35	1.3	0	0.9	204	9.2 {42}	0	2.0

B. 5 mM $Cu^{I}(bpy)_2^+$/100 mM *t*-BuOOH/O_2 (1 atm, 7 mM)

substrate (1 M)	reac[b] effncy, %	products (mM, ±2)
$c-C_6H_{12}$	62	$c-C_6H_{10}(O)$ (25), $c-C_6H_{11}OOBu$-*t* (1), $c-C_6H_{11}OH$ (10)
$c-C_6H_{10}$	199	$c-C_6H_8(O)$ (74), $c-C_6H_9OOBu$-*t* (25),[e] $c-C_6H_9OH$ (1)
1,4-cyclohexadiene	108	PhH (76), PhOH (16)
adamantane ($C_{10}H_{16}$) (0.1 M)	23	$C_{10}H_{14}(O)$ (4), 1-$C_{10}H_{15}OH$ (15)
$PhCH_2CH_3$	208	PhC(O)Me (103), PhCH(Me)OOBu-*t* (1)
$PhCH(Me)_2$	183	PhC(O)Me (54), PhC(OOBu-*t*)$(Me)_2$ (2),[f] $PhC(OH)(Me)_2$ (70), $PhC(Me)=CH_2$ (1)
$PhCH_3$	16	PhCH(O) (8)[g]
$c-C_6H_{11}OH$	78	$c-C_6H_{10}(O)$ (78)
$CH_3(CH_2)_4CH_2OH$	38	$CH_3(CH_2)_4CH(O)$ (38)
$PhCH(OH)CH_3$	66	PhC(O)Me (66)
$PhCH_2OH$	100	PhCH(O) (100)
$PhCH_2NH_2$	208	$PhCH_2N=CHPh$ (104)

[a] Substrate and $Cu^{I}(bpy)_2^+$ combined in 3–5 mL of MeCN/py (4:1 mol-ratio), [or $Co^{II}(bpy)_2^{2+}$ combined in 3–5 mL of MeCN], followed by the slow addition of 17.6 M HOOH (50% in H_2O) or 5.5 M *t*-BuOOH (in 2,2,4-trimethylpentane) to give the indicated HOOH(Bu-*t*) concentrations. The product solutions were analyzed by capillary-column gas chromatography and GC-MS after a reaction time of 3 h at 24 ± 2 °C. [b] Reaction efficiency; 100% represents one ketone or ROOBu-*t* per two HOOH(Bu-*t*) molecules and/or one alcohol per HOOH(Bu-*t*). [c] $[K] = k_{c-C_6H_{12}}/k_{c-C_6D_{12}}$, kinetic isotope effect. [d] $\{R\} = [k_{PhCH_2Me}/(k_{c-C_6H_{12}}/6)]$, relative reactivity per (CH_2) for $PhCH_2Me$ vs $c-C_6H_{12}$.

64% efficient relative to *t*-BuOOH, with the remainder transformed to O_2 and *t*-BuOH

$$2t\text{-BuOOH} \xrightarrow{Cu^{I}(bpy)_2^+} O_2 + 2t\text{-BuOH} \qquad (2)$$

When HOOH is used in place of *t*-BuOOH the reaction with $PhCH_2CH_3$ is similar but much less efficient (24%) with most of the HOOH consumed by disproportionation ($2HOOH \rightarrow O_2 + 2H_2O$).

When an atm of O_2 is present, the primary product shifts from ROOBu-*t* (eq 1) to the ketone of the substrate and the amount of alcohol product increases. For example, with the 5 mM $Cu^{I}(bpy)_2^+$/100 mM *t*-BuOOH/O_2 (1 atm) system the yield of ketone from $c-C_6H_{12}$ increases to 25 mM (from 14 mM) and the yield of alcohol doubles (Table IA)

$$2c\text{-}C_6H_{12} + t\text{-BuOOH} + O_2 \xrightarrow[MeCN/py]{Cu^{I}(bpy)_2^+} c\text{-}C_6H_{10}(O) + c\text{-}C_6H_{11}OH + H_2O + t\text{-BuOH} \qquad (3)$$

With $PhCH_2CH_3$ this system enhances the yield of $PhC(O)CH_3$ from 9 mM in the absence of O_2 to 103 mM [the yield of ROOBu-*t* decreases from 23 mM (no O_2) to 1 mM].

A new catalytic autoxygenation cycle occurs with 1:1 or 1:2 $Cu^{I}(bpy)_2^+$/*t*-BuOOH combinations in O_2-saturated solutions of substrate with weak methylenic C–H bonds [e.g., Ph(Me)CH–H, ΔH_{DBE} = 87 kcal mol^{-1} and $c-C_6H_9$–H (allylic), ΔH_{DBE} = 85 kcal mol^{-1}].[8]

$$PhCH_2CH_3 + O_2 \xrightarrow{Cu^{I}(bpy)_2^+, t\text{-BuOOH}} PhC(O)CH_3 + H_2O \qquad (4)$$

With the 5 mM $Cu^{I}(bpy)_2^+$/10 mM *t*-BuOOH/1 M $PhCH_2CH_3$ system the yield of ketone is 22 mM (Table IA), which requires a minimum of 2.2 turnovers via an autoxygenation cycle (eq 4) in addition to two turnovers of the coupled *t*-BuOOH/O_2 process (eq 3). This autoxygenation cycle does not occur with aliphatic hydrocarbons ($c-C_6H_{12}$; ΔH_{DBE} = 95.5 kcal mol^{-1}).

Although the $Co^{II}(bpy)_2^{2+}$/*t*-BuOOH/MeCN system exhibits a similar stimulation of O_2 reactivity with methylenic carbon centers (eq 3), it is less effective than $Cu^{I}(bpy)_2^+$ and does not facilitate an autoxygenation cycle (eq 4) with $PhCH_2CH_3$ (Table IA).

The results of Table I and Figures 1–3 indicate that the $Cu^{I}(bpy)_2^+$/HOOH(Bu-*t*) activation system initially forms a reactive intermediate via nucleophilic addition by HOOH(Bu-*t*) (**1**, Scheme I), which is analogous to the primary step for the $Fe^{II}(PA)_2$/HOOH(Bu-*t*) systems (PA, anion of picolinic acid)[1] and consistent with the nucleophilic character of HOOH(Bu-*t*).[8] The transient absorption band at 438 nm for the $Cu^{I}(bpy)_2^+$/

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(8) Lide, D. R., Ed. CRC *Handbook of Chemistry and Physics*, 71st ed.; CRC Press: Boca Raton, FL, 1990; pp 9-86–90.

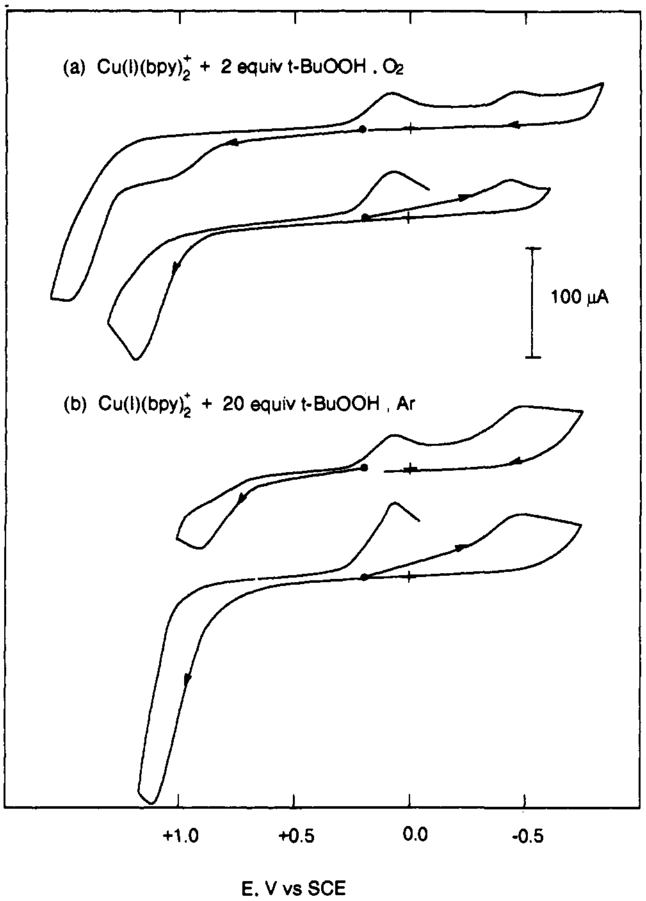


Figure 3. Cyclic voltammograms MeCN/Py [0.1 M $(Et_4N)ClO_4$] for (a) 5 mM $Cu^I(bpy)_2^+$ plus 10 mM *t*-BuOOH under 1 atm of O_2 (7 mM) and (b) 5 mM $Cu^I(bpy)_2^+$ with 100 mM *t*-BuOOH and 1 M $PhCH_2CH_3$ under argon. Scan rate, 0.1 V s^{-1}; GCE (0.09 cm^2); SCE vs NHE, +0.242 V.

BuOOH system (Figure 1b) may be due to species **1** [the $(Hbpy)^+(bpy)_2Cu^IOH$ complex has a closely similar absorption at 438 nm (ϵ 5900 $M^{-1}\ cm^{-1}$)]. With excess HOOH(Bu-*t*) **1** reacts via path A of Scheme I to form an intermediate {possibly $(bpy)_2Cu^{III}(OH)[OOH(Bu\text{-}t)]$ (**3**)} that facilitates the disproportionation of HOOH(Bu-*t*) to O_2 and HOH(Bu-*t*). The broad reduction at −0.4 V (Figures 2b and 3) appears to be for a $[\mathbf{1}(O_2)]$ adduct that yields a product (eq 5)

$$[(bpy)_2(BuOO)Cu(O_2) + pyH^+] + 2e^- \xrightarrow{-0.4\ V} (bpy)_2Cu^I(OOBu)(OOH)^- + py \quad (5)$$

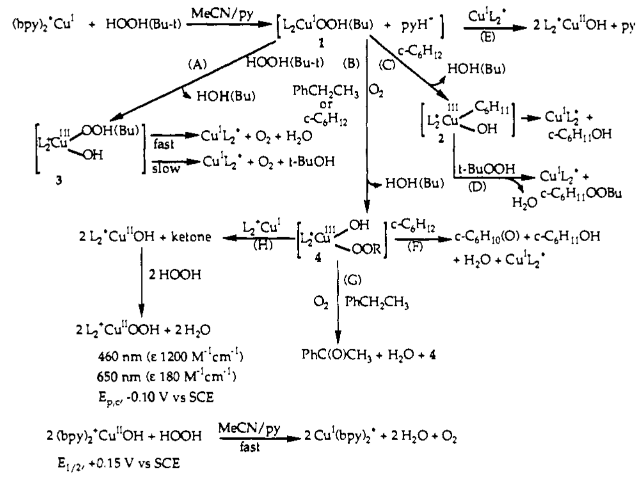
which is oxidized at +0.9 V via a multielectron process to give $(bpy)_2{}^+Cu^{II}OH$ and O_2 (eq 6)

$$(bpy)_2Cu^I(OOBu)(OOH)^- + H_2O + py \xrightarrow[+0.9\ V]{-3e^-} (bpy)_2{}^+Cu^{II}OH + 2O_2 + t\text{-}BuOH + pyH^+ \quad (6)$$

Although we proposed recently that the iron analogues of species **3** {e.g., $(PA)_2Fe^{IV}(OH)[OOH(Bu)]$} react with RH substrates to form ROOH(Bu-*t*),[1] this appears unreasonable for the present system. If species **3** of Scheme I were the reactive intermediate for the production of ROOH(Bu-*t*) from $c\text{-}C_6H_{12}$(RH) and $PhCH_2CH_3$, then the [K] values and {R} values for HOOH and *t*-BuOOH should be closely similar. However, the respective [K] values are 2.5 and 7.3 and the respective {R} values are 6 and 11.

With low HOOH(Bu-*t*)/$Cu^I(bpy)_2^+$ ratios most hydrocarbon substrates react with species **1** to give some alcohol via path C and intermediate **2** (with bound substrate) of Scheme I. For cyclohexane the kinetic isotope effect [K] for alcohol production is 1.4 with HOOH (the [K] value for $Fe^{II}(bpy)_2^{2+}$ is 1.4)[1] and >7 with *t*-BuOOH [the [K] value for $Fe^{II}(bpy_2^{2+}$ is 4.8]. In contrast, with a large *t*-BuOOH/$Cu^I(bpy)_2^+$ ratio under argon the system transforms hydrocarbon substrates (RH) via path C (intermediate **2**) and path D (Scheme I) to give ROOBu-*t* {for $c\text{-}C_6H_{12}$ the [K] value is 7.3 [with $Fe^{II}(bpy)_2^{2+}$ the [K] value is 5.4],[1] and the relative reactivity per CH_2 group of $PhCH_2CH_3$ and $c\text{-}C_6H_{12}$, {R} (Table I), is 11 [with $Fe^{II}(bpy)_2^{2+}$ the {R} value is 9]}.[1] The enhanced [K] and {R} values relative to those for alcohol production indicate that species **1** and path C precede the production of ROOBu-*t* via species **2**.

Scheme I. $Cu^I(bpy)_2^+$/HOOH(Bu-*t*)-Induced Activation of O_2



In the presence of O_2 (1 atm) species **1** appears to form $\mathbf{1}(O_2)$ (see Figure 3) prior to reaction with hydrocarbon substrates (RH) via path B to give a peroxy adduct $[(bpy)_2Cu^{III}(OH)(OOR), \mathbf{4}]$. The latter reacts with a second RH via path F to give ketone (for *t*-BuOOH [K] = 8.8 and {R} = 25) and alcohol ([K] >8). Intermediate **4** also can react (a) with $Cu^I(bpy)_2^+$ via path H to give ketone and two $(bpy)_2{}^+Cu^{II}OH$ and (b) with the $PhCH_2CH_3/O_2$ combination via path G to give $PhC(O)CH_3$ and **4** in an autoxygenation cycle ({R} = 44). The results of Table I indicate that $c\text{-}C_6H_{12}$ (with its larger C–H bond energy, 95.5 kcal mol^{-1})[8] is not reactive via path G. When the reaction efficiency is >100% paths B/F and B/H must be dominant, and when it is >200% the reaction cycle of path B/G must occur {turnovers ≥ [(% reaction efficiency)/200] − 1}.

In accord with the proposed reaction pathways for the $Cu^I(bpy)_2^+$/*t*-BuOOH system, an O_2-free reactor should not yield any ketone (pathway B is precluded). However, with large *t*-BuOOH/$Cu^I(bpy)_2^+$ ratios under argon substantial amounts of ketone are produced (Table IA). This must be due to the internal generation of O_2 via path A [e.g., a substrate-free solution of 100 mM *t*-BuOOH/5 mM $Cu^I(bpy)_2^+$ generates the equivalent of 50 mM O_2 over a 1 h period (O_2 solubility at 1 atm, 7 mM)]. Such internal generation and incorporation of O_2 to form ketone has been demonstrated in a recent elegant study of an $Fe^{III}Cl_3$/HOOH/adamantane ($C_{10}H_{16}$) system.[10]

The presence of an O_2 atmosphere (7 mM) with the $Cu^I(bpy)_2^+$/*t*-BuOOH system causes path B to be dominant at the expense of paths A, C, and D and enhances the yield of ketone at the expense of ROOBu-*t* production. For example, the 5 mM $Cu^I(bpy)_2^+$/100 mM *t*-BuOOH system and 1 M $c\text{-}C_6H_{12}$ (a) under argon yields 14 mM ketone, 13 mM ROOBu-*t*, and 5 mM ROH and (b) under O_2 (1 atm) yields 25 mM ketone, 1 mM ROOBu-*t*, and 10 mM ROH. The same system with 1 M $PhCH_2CH_3$ (a) under argon yields 9 mM $PhC(O)CH_3$ and 23 mM ROOBu-*t* and (b) under O_2 (1 atm) yields 103 mM $PhC(O)CH_3$ and 1 mM ROOBu-*t*.

The ability of the 5 mM $Cu^I(bpy)_2^+$/10 mM *t*-BuOOH/7 mM O_2/1 M $PhCH_2CH_3$ system to produce 22 mM $PhC(O)CH_3$ is clear evidence for a $Cu^I(bpy)_2^+$/*t*-BuOOH-induced autoxygenation of a hydrocarbon with at least 2.2 O_2/catalyst turnovers. We

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believe that this is a unique example of metal/*t*-BuOOH-induced catalytic activation of O_2 for useful chemistry (four 10-mM-*t*-BuOOH increments yield 80 mM PhC(O)Me). Although this appears to be a radical-induced process, the electrochemical results (Figure 3) and the selectivity ({R} = 44) indicate that the dioxygen adduct of species **1** [**1**(O_2)] is the initiator rather than an oxy-radical.

Note Added in Proof. Closely similar results have been obtained for several iron(II) complexes;[11] e.g., in py/HOAc the 5 mM $Fe^{II}(PA)_2$/100 mM *t*-BuOOH, O_2/1 M c-C_6H_{12} system yields 46 mM c-C_6H_{10}(O) [without O_2, it yields 19 mM (c-C_6H_{11})py, 11 mM c-C_6H_{10}(O), and 7 mM c-C_6H_{11}OOBu-*t*] versus 25 mM c-C_6H_{10}(O) for the comparable $Cu^{I}(bpy)_2$[7] system (Table IA).

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Origin of the Stability of Carbon Tetrafluoride: Negative Hyperconjugation Reexamined

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Abstract: The energetic preference for multiple fluorine substitution at carbon has been examined theoretically. Both the stabilization and bond shortening with increasing fluorine substitution may be attributed to Coulombic interactions between the negatively charged fluorines and the increasingly more positively charged carbon. This conclusion leads to the prediction that multiple silyl substitution should also lead to stabilization, and it was confirmed by calculations. Conversely, FCH_2SiH_3, in which the carbon will be close to neutral because of the opposing electron demand of the substituents, has negligible stabilization. Multiple cyano substitution leads to destabilization, and this may be attributed to Coulombic interactions between the positively charged carbons of the cyano groups and the increasingly more positively charged central carbon. The same is found with multiple nitro substitution. Multiple chlorine substitution has little effect, in accord with the smaller difference in electronegativity between carbon and chlorine. The question of negative hyperconjugation in carbon tetrafluoride was explored by the calculation of delocalization indices for the fluorine lone pairs, and no significant interactions were found. Deformation density plots also were examined and showed that increasing fluorine substitution led to reduction in charge density only at the backside of the C–F bonds, as expected for electron polarization due to the increasing positive charge at carbon. A case in which negative hyperconjugation is more likely to be important ((fluoromethyl)amine) also was examined, and some evidence for nitrogen lone pair donation was found.

Introduction

The thermochemical stability of carbon tetrafluoride has been the subject of considerable discussion.[1-11] The basic observation is that the isodesmic reaction

$$CF_4 + 3CH_4 \rightarrow 4CH_3F$$

is endothermic by 53 kcal/mol, indicating that carbon prefers to be multiply substituted by fluorine. A similar preference is found in the corresponding fluoromethyl radicals and anions, in which multiple fluorine substitution also leads to a synergistic stabilization.[9] The stability of carbon tetrafluoride as compared to methyl fluoride has commonly been discussed in terms of negative hyperconjugation, using no bond–double bond resonance structures,[1,3,9] or in MO terms via delocalization of the fluorine lone pairs into adjacent C–F-bond σ^* orbitals.[4] Recently Salzner and Schleyer[12] have presented a detailed analysis in these terms making use of the Weinhold–Reed NBO formalism.[13] Here the molecular orbitals are localized, and it is found that there are significant off-diagonal elements between the lone pairs and the partially occupied C–F σ^* localized orbitals. These terms are attributed to negative hyperconjugation. Their effect was estimated by removing the off-diagonal elements and performing one SCF cycle to evaluate the energy of the altered Fock matrix. The stabilization energy thus calculated was 15.7 kcal/mol per F lone pair–σ^* CF interaction. There are 12 such interactions leading to a total stabilization of 188 kcal/mol!

Hyperconjugation is a well-established phenomenon.[14] In the *tert*-butyl carbocation the C–H bond orbitals may interact with the empty p orbital, transferring some charge density to the latter. The electrons find themselves in a region of lower potential energy,

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