The electronic spectrum of **2** measured in aqueous solution showed peaks at 258 (ϵ(M^{-1} cm^{-1}) = 20000), 300(sh, 7500), 450(sh, 750), 636(630), 900(sh, 86), and 1150 nm (260).

The most remarkable feature of **2** is its high stability to acid (up to 1 M HCl) and atomospheric oxygen. It should be noted that all Fe_4S_4 and $MoFe_3S_4$ cluster compounds so far reported[10] are decomposed by acids to give hydrogen sulfide, while oxygen-bridged di-,[11a] tri-,[11b] and tetranuclear[11c] $Mo^{III/IV}$ compounds are readily air oxidized.

A cyclic voltammogram of **2** (0.8 mM in 0.1 M $HClO_4$) shows two quasi-reversible, one-electron waves (Figure 2). The controlled potential Coulometry of **2** at 0.50 V (vs. SCE) in 0.1 M $HClO_4$ and at −0.40 V (vs. SCE) in 0.5 M KCl gave an electron stoichiometry of 0.25e per molybdenum. The reversibility indicates that one electron is added to or removed from **2** without drastic change in structure. The large comproportionation constant (K = 7.3 × 10^{11}) for the following equilibrium

$$[Mo_4S_4(edta)_2]^{4-} + [Mo_4S_4(edta)_2]^{2-} \rightleftharpoons 2[Mo_4S_4(edta)_2]^{3-}$$

indicates that the trivalent anion is the overwhelmingly dominant species in solution.

Recently the oxidized and reduced species, $[Mo_4S_4(edta)_2]^{2-}$ and $[Mo_4S_4(edta)_2]^{4-}$, have been successfully isolated as single crystals in combination with appropriate cations. Comparisons of the structure and property of **2** with those of $[Mo_4S_4(edta)_2]^{2-}$ and $[Mo_4S_4(edta)_2]^{4-}$ will disclose the electronic structure for each of the $Mo_4S_4{}^{n+}$ cores.

Acknowledgment. We are grateful to Dr. I. Kinoshita of Osaka City University for his help in the cyclic voltammometry measurement.

Supplementary Material Available: Lisitng of atomic coordinates, thermal parameters, and bond angles and electronic spectrum (4 pages). Ordering information is given on any current masthead page.

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(10) Lippard, S. J. In "Mixed-Valence Compounds"; Brown, D. B., Ed.; Reidel: Dordrecht, Holland, 1979; "Polymetalic Centers in Biology", p 427.

(11) For example: (a) Shibahara, T.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **1978**, 95. (b) Richens, D. T.; Sydes, A. G. *Inorg. Chem.* **1982**, *21*, 418. (c) Shibahara, T.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **1978**, 100.

"Hyperconjugation Transitions" in Radical Cation Optical Spectra

Stephen F. Nelsen,* Mark F. Teasley, Daniel L. Kapp,
Carl R. Kessel, and Loretta A. Grezzo

S. M. McElvain Laboratories of Organic Chemistry
Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706

Received July 11, 1983

Murrell has stated that alkyl substituents are spectroscopically rather inert and only produce a large change in the absorption spectrum of a molecule when the shape of the absorbing group is appreciably changed by the substitution.[1] In contrast, when *tert*-butyl cation was believed to show a strong absorption band at 290–295 nm,[2] the absorption was attributed to charge-transfer configurations caused by electron transfer from the methyl groups toward the central carbon, which bears a formally empty 2p orbital. This band was called the "hyperconjugation transition", and approximate MO calculations agreed fully with this rationalization.[3] When Olah and co-workers prepared a purer sample of *tert*-butyl cation, the 290–295 nm band was shown to be absent, and Olah, Pittman, and Symons concluded that "the theory that the "hyperconjugation transitions" can contribute to the optical spectra is, therefore returned to the realm of fancy: apparently possible, they do not seem to have been detected experimentally".[4] The strained σ bonds in three- and four-membered rings, which have high p character relative to unstrained σ bonds, are known to provide significant σ,π interactions leading to interesting spectral and chemical behavior,[5] but we are not aware of previous observations of such transitions involving unstrained alkyl groups. We report here the observation of bands involving unstrained alkyl group interactions with both olefin radical cations (1-electron, 2-atom π orbitals) and hydrazine radical cations (1-electron, 2-atom π^* orbitals).

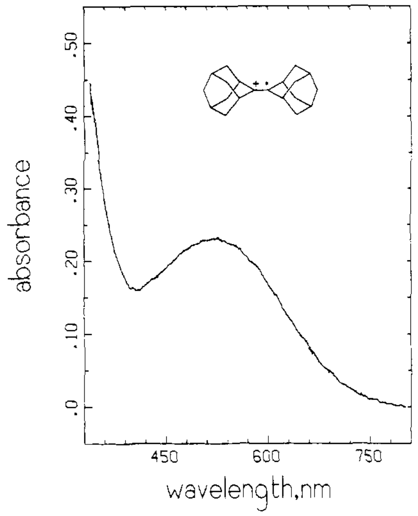
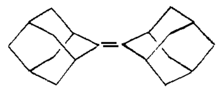


Figure 1. Visible spectrum of $1^{+\cdot}$ in CH_2Cl_2, −78 °C.

Monoolefins **1** and **2** give radical cations that are long-lived on the cyclic voltammetry time scale at room temperature[6] because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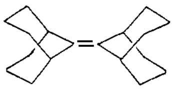
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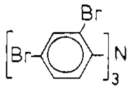

3

they are "Bredt's Rule" protected—their α hydrogens are held near the nodal plane of the formally spin-bearing π system. We have found that both $1^{+\cdot}$ and $2^{+\cdot}$ are colored. We had considerable difficulty generating solutions of these species that last for minutes, because low temperatures are required and their oxidation potentials are rather high. This problem was solved by employing tris(o,p-dibromophenyl)aminium hexachloroantimonate ($3^{+\cdot}$ $SbCl_6{}^-$),[7] a powerful enough oxidant that the electron transfer gives the olefin radical cation (cyclic voltammetry shows the electron transfer is 1.5 kcal/mol exothermic with **1** at −78 °C in methylene chloride, and under the conditions of the experiment, 10^{-2} M **1**, 10^{-3} M $3^{+\cdot}$ initially, the electron transfer is over 99% complete at equilibrium). Solutions of $1^{+\cdot}$ are deep purple, and the color lasts for tens of minutes at −78 °C, at millimolar concentration. The ESR spectrum of $1^{+\cdot}$ fades as the purple color fades upon warming. Because $1^{+\cdot}$ disappears more rapidly at higher concentration as well as at higher temperature, we believe that it is destroyed by self-electron-transfer disproportionation. The second oxidation wave of **1** is totally irreversible at all scan rates in cyclic voltammetry experiments, indicating a very short lifetime for the dication. The visible spectrum of $1^{+\cdot}$ shows a very broad absorption centered at λ_m ca. 530 nm (Figure 1). The

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(1) Murrell, J. N. "The Theory of the Electronic Spectra of Organic Molecules"; Wiley: New York, 1963; p 238.

(2) (a) Rosenbaum, J.; Symons, M. C. R. *Proc. Chem. Soc.* **1959**, 92; (b) *Mol. Phys.* **1960**, *3*, 205.

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(4) Olah, G. A.; Pittman, C. U., Jr.; Symons, M. C. R. In "Carbonium Ions"; Olah, G. A., Schleyer, P. v. R., Eds.; Interscience: New York, 1968; Vol. 7, pp 197–203.

(5) See: Jorgenson, W. L.; Borden, W. T. *J. Am. Chem. Soc.* **1973**, *95*, 6649 and references therein.

(6) Nelsen, S. F.; Kessel, C. R. *J. Am. Chem. Soc.* **1979**, *101*, 2503.

(7) Schmidt, W.; Steckhan, E. *Chem. Ber.* **1980**, *113*, 577.

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Table I. Absorption Maxima for Olefin and Hydrazine Radical Cations

species	λ_m, nm (ϵ)
$1^{+\cdot a}$	530 (>970)
$2^{+\cdot a}$	450 (>750)
$4^{+\cdot b}$	340 (4000), ca. 260 sh (1300)
$5^{+\cdot b}$	338 (3200), ca. 250 (1300)
$6^{+\cdot b}$	331 (5000), 236 (2500)

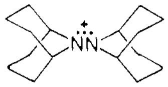
[a] CH_2Cl_2, −78 °C. [b] CH_3CN, room temperature; sh, shoulder.

absorption band for **1**$^{+\cdot}$ (λ(half-maximum absorption) = 635 nm) is even broader than that of the three-electron σ-bonded species 1,6-diazabicyclo[4.4.4]tetradecane radical cation, for which Alder and Sessions[8] report λ_m = 480, λ(half maximum absorption) = 575 nm. Assuming a 100% yield of **1**$^{+\cdot}$ and no decomposition, ε(530) is about 970; the true ε is doubtless somewhat larger than this. The short wavelength side of this very broad **1**$^{+\cdot}$ absorption is obscured by the tail of the neutral **3** absorption, which rises rapidly below about 380 nm, but there probably is shorter wavelength absorption maximum for **1**$^{+\cdot}$ as well.

The color of **1**$^{+\cdot}$ can only reasonably arise from σ,π^+ transitions. Large σ,π^+ interaction in **1**$^{+\cdot}$ is also indicated by the surprisingly facile oxidation of **1** ($E^{\circ\prime}$ for **1** is about the same as that of 1,2-benzanthracene, which as 18 π electrons), the unusually large long-range proton ESR splitting constants of **1**$^{+\cdot}$, and its anomalously large *g* factor for a hydrocarbon radical cation.[9]

2 behaves in a completely analogous fashion to **1**,[10] but **2**$^{+\cdot}$ is brownish peach color (λ_m = ca. 450 nm, see Table I). Although the 80-nm blue shift between **1**$^{+\cdot}$ and **2**$^{+\cdot}$ is initially surprising, perhaps it should not be considered so. The lack of the bridging CH_2 groups in **2** compared to **1** is known to cause flattening of the six-membered rings, and since the transition involves the upper σ orbitals of these rings, substantial differences in σ,π^+ interaction can occur. This is also borne out by the rather large differences in ^1H hyperfine coupling constants for **1**$^{+\cdot}$ and **2**$^{+\cdot}$ (principally a much larger $a(H_{\delta_{eq}})$ value for **1**$^{+\cdot}$, 6.05 vs. 3.20 G, but a smaller $a(H_{\gamma_{eq}})$ value, 3.27 vs. 3.70 G[9]).

We also suggest that "hyperconjugation transitions" are observed in the UV region for hydrazine radical cations **4**$^{+\cdot}$–**6**$^{+\cdot}$.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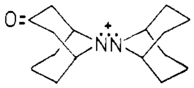
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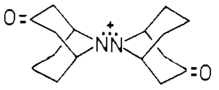
6⁺

They show intense $\pi^* \leftarrow \pi$ absorption bands for the three-electron π bond and also a less intense, shorter wavelength band, which overlaps greatly with the $\pi^* \leftarrow \pi$ absorption and appears only as a shoulder for **4**$^{+\cdot}$ (see table). Because these cations are isolably stable and were crystallized to analytical purity, we believe it is unreasonable to contend the short-wavelength absorptions are caused by impurities. Neutral **5** and **6** show σ coupled charge-transfer bands due to nitrogen lone pair, carbonyl group overlap through the intervening σ bonds.[11] Although one might be tempted to try to attribute the 260–236 bands in their radical cations to such a phenomenon, this is not reasonable. The radical cations must have considerably stabilized nitrogen lone pairs (the nitrogens are formally half-positive), which would increase the lone pair, carbonyl π^* energy gap considerably and shift the band out of the near UV. More conclusively, **4**$^{+\cdot}$ shows a similar absorption but has no carbonyl groups. Although **4**$^{+\cdot}$ is expected to be nearly isostructural with **3**$^{+\cdot}$, it is not isoelectronic; the "hole" in **4**$^{+\cdot}$ is in the π_{NN}^* antibonding orbital, while that in **2**$^{+\cdot}$ is in the π_{CC} bonding orbital. Despite the fact that the more electronegative nitrogens of **4**$^{+\cdot}$ will stabilize both its π and π^* orbitals relative to those of **2**$^{+\cdot}$, the large energy difference between the π and π^* orbitals ensures that the σ orbital, singly occupied π orbital energy gap of **4**$^{+\cdot}$ is larger than that for **2**$^{+\cdot}$, and we assign the 260-nm shoulder in the UV spectrum of **4**$^{+\cdot}$ to the "hyperconjugation transition". The blue shift observed upon successive carbonyl substitution in **5**$^{+\cdot}$ and **6**$^{+\cdot}$ is consistent with this assignment, as the electron-withdrawing C=O groups should stabilize the σ combination orbitals.[12]

Registry No. **1**$^{+\cdot}$, 70535-07-8; **2**$^{+\cdot}$, 79684-47-2; **3**$^{+\cdot}$$SbCl_6^-$, 58047-17-9; **4**$^{+\cdot}$, 62781-95-7; **5**$^{+\cdot}$, 74773-86-7; **6**$^{+\cdot}$, 74773-87-8.

Supplementary Material Available: Visible spectrum of **2**$^{+\cdot}$ in CH_2Cl_2 (−78 °C) and UV spectra of **4**, **5**, **6**, **4**$^{+\cdot}$, **5**$^{+\cdot}$, and **6**$^{+\cdot}$ (all in CH_3CN, room temperature) (7 pages). Ordering information is given on any current masthead page.

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(8) (a) Alder, R. W.; Sessions, R. B. *J. Am. Chem. Soc.* **1979**, *101*, 3651. (b) We thank Dr. Alder for a reproduction of the spectrum from the Thesis of R. B. Sessions.

(9) Gerson, F.; Lopez, J.; Nelsen, S. F.; Akaba, R. *J. Am. Chem. Soc.* **1981**, *103*, 7045.

(10) Since $E^{\circ\prime}$ is higher for **2** than for **1**, the electron-transfer equilibrium with **3**$^+$ is significantly less exothermic, only 0.5 kcal/mol at −78 °C in methylene chloride. Nevertheless, with a 10× excess of **2** over **3**$^+$, the electron transfer is over 96% complete at −78 °C, allowing the experiment to be done.

(11) Nelsen, S. F.; Kessel, C. R.; Grezzo, L. A.; Steffek, D. J. *J. Am. Chem. Soc.* **1980**, *102*, 5482.

(12) We gratefully acknowledge the support of this work by the National Science Foundation, the National Institutes of Health, and the Wisconsin Alumni Research Foundation. We are also grateful to Prof. R. C. West of this department for the use of his low-temperature optical spectral equipment.

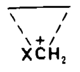
Corner Bromination of Cyclopropane

Joseph B. Lambert,*[1] William J. Schulz, Jr.,
Paul H. Mueller, and Keiji Kobayashi

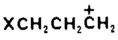
Department of Chemistry, Northwestern University
Evanston, Illinois 60201

Received October 13, 1983
Revised Manuscript Received December 10, 1983

Electrophilic opening of cyclopropanes involves two points of attack, so that there are four stereospecific extremes (inversion/inversion, etc.), as well as a nonstereospecific continuum.[2] Possible intermediates include corner attack by X^+ (**1**), edge attack (**2**), and open carbocations (**3**). In most[3] but not all[2] cases open


1


2


$XCH_2CH_2\overset{+}{C}H_2$

3

carbocation intermediates are required by the observation of loss of stereochemistry, in contrast to analogous reactions of alkenes. All these examples involved substituted cyclopropanes, in which the open carbocation was secondary or tertiary. Apparently such carbocations normally are more stable than their bridged analogues when the electrophile is bromine. It is less likely that a primary carbocation (**3**) would be more stable than the bridged alternatives (**1** and **2**). Only unsubstituted cyclopropane forms primary carbocations as the sole open-chain possibility.

Deno and Lincoln[4] showed that cyclopropane reacts sluggishly with bromine in the dark, more facilely in the presence of $FeBr_3$ catalyst, to produce 1,3-dibromopropane, among other products. They suggested intermediates of the types **1**–**3** but made no mechanistic distinctions. Because unsubstituted cyclopropane seems an excellent candidate for bridged or pentavalent carbon intermediates in bromination,[5] we have carried out experiments

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(1) This work was supported by the National Science Foundation (Grant CHE80-25601). We thank the Southern New England NMR Facility for a 500-MHz spectrum.

(2) DePuy, C. H. *Fortschr. Chem. Forsch.* **1973**, *40*, 73–101.

(3) Lambert, J. B.; Black, R. D. H.; Shaw, J. H.; Papay, J. J. *J. Org. Chem.*, **1970**, *35*, 3214–3216. Lambert, J. B.; Iwanetz, B. A. *Ibid.* **1972**, *37*, 4082–4086. LaLonde, R. T.; Debboli, A. D., Jr. *Ibid.* **1973**, *38*, 4228–4232. Day, J. C.; Shea, K. J.; Skell, P. S. *J. Am. Chem. Soc.* **1973**, *95*, 5089–5090. Skell, P. S.; Day, J. C.; Shea, K. J. *Ibid.* **1976**, *98*, 1195–1204.

(4) Deno, N. C.; Lincoln, D. N. *J. Am. Chem. Soc.* **1966**, *88*, 5357–5358.

(5) Such intermediates have been found in protonation reactions of cyclopropanes.[2,6]

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