The change of kinetics around 270 nm can be explained as well by assuming a lifetime shortening of the triplet precursor due to an increased ionization efficiency at shorter wavelengths. According to Pilloff and Albrecht[10] the order of reaction may be as low as unity when ionization by the second photon becomes the main depletion channel of the triplet state. The light flux in our experiments was of the order of $\simeq 3$ mEinsteins cm^{-2} sec^{-1} in the 240-270-nm region. The triplet-triplet molecular extinction coefficient is not known for tyrosine, but ϵ_T values >20,000 are typical of many organic molecules.[11]

Using tentatively this value, the rate constant for the second photon absorption would be $K_a \simeq 1.38 \times 10^5$, which is comparable to the rate constant for the triplet decay (at 2.5×10^{-4} M l.$^{-1}$), $K_T = 1.4\ 10^5$ sec^{-1}.[1] Since the triplet absorbance is roughly twice as intense at 250 nm than at 300 nm,[7] we must conclude that a true biphotonic mechanism cannot be excluded either.

In conclusion our results show, if necessary, the difficulty of comparing kinetic flash photolysis studies when the spectral output of the exciting flash is not specified. The exact nature of the ionization mechanism of tyrosine in fluid solution is only partly understood. Whether ionization below 270 nm is due to a nonrelaxed singlet state or to TT absorption could be decided, as in the case of β-naphtholate,[12] by future experiments monitoring the radical (or e^-_{aq}) formation during a laser pulse shorter than the singlet state lifetime.

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References and Notes

(1) E. J. Land, G. Porter, and E. Strachan, *Trans. Faraday Soc.*, **57**, 1885 (1961).
(2) G. Dobson and L. I. Grossweiner, *Trans. Faraday Soc.*, **61**, 708 (1965).
(3) J. Feitelson and E. Hayon, *J. Phys. Chem.*, 77, 10 (1973).
(4) J. Feitelson and E. Hayon, *Photochem. Photobiol.*, **17**, 265 (1973).
(5) J. Feitelson, E. Hayon, and A. Treinin, *J. Am. Chem. Soc.*, **95**, 1025 (1973).
(6) M. Kasha, *J. Opt. Soc. Am.*, **38**, 929 (1948).
(7) D. V. Bent and E. Hayon, International Conference on Excited States of Biological Molecules, Lisbon, in press.
(8) F. P. Schwartz and A. C. Albrecht, *Chem. Phys. Lett.*, **9**, 163 (1971).
(9) O. Shimizu, *Photochem. Photobiol.*, **18**, 125 (1973).
(10) H. S. Pilloff and A. C. Albrecht, *J. Chem. Phys.*, **49**, 4891 (1968).
(11) D. Lavalette, R. Bensasson, B. Amand, and E. J. Land, *Chem. Phys. Lett.*, **10**, 331 (1971).
(12) C. R. Goldschmidt and G. Stein, *Chem. Phys. Lett.*, **6**, 299 (1970).

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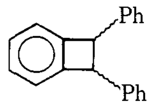
Stereochemistry of Retroelectrocyclic Reactions of Anion Radicals. Preferred Conrotation in a Cyclobutene System

Sir:

Two methods have been recommended for rationalizing the stereochemistry of electrocyclic transformations, viz., the highest occupied molecular orbital (HOMO)[1] and orbital correlation diagram (OCD)[2,3] methods. The former is exceedingly simple and general and, although a sound theoretical basis for it has apparently not been provided, Woodward and Hoffmann have asserted its validity, stating that "The sense of orbital symmetry control can *always* be determined through inspection of the behavior of the highest occupied molecular orbital in the reacting system, ..."[4] Nevertheless, a recent report from this laboratory describes an electrocyclic reaction of **1**$\cdot^-$ in which HOMO and OCD blatantly disagree.[5] The experimental result coincides with the OCD prediction. Subsequently, further examples have emerged which serve to uncouple HOMO and OCD and find HOMO to generate erroneous predictions.[6] Thus HOMO, as a general principle, is *not* valid and its use in radical reactions is particularly to be avoided. To make matters worse, OCD, presumably a more reliable device, takes an equivocal position on most such reactions. Both modes of electrocyclic reaction of acyclic odd alternant hydrocarbon radicals, such as the allyl-cyclopropyl transformation, are viewed as forbidden, and the preferred route is not identified. The same is true in general for the reactions of anion (and cation) radicals of the even alternant systems, e.g., the butadiene-cyclobutene anion radical transformation. No pertinent experimental data are available. MINDO/2 calculations on the allyl-cyclopropyl transformation, however, predict disrotation and thus also contradict HOMO.[7] Determination of the preferred stereochemistry for a model butadiene-cyclobutene anion radical transformation has now been accomplished and is described below. These results together with INDO calculations elucidate several important aspects of the electrocyclic reactions of radicals.

The model cyclobutene derivatives *cis*- and *trans*-**2** were the specific subjects of the experimental study. The OCD's connecting **2**$\cdot^-$ and **3**$\cdot^-$ are not depicted but parallel in every essential those of the parent system. In particular, neither the dis- nor the conrotatory cleavage is allowed. The HOMO in **3**$\cdot^-$ is symmetrical; therefore HOMO predicts disrotation. *trans*-**2** was already known:[8] mp 195-197°; NMR ($CDCl_3$) τ 1.25-1.42 (m, 2 H), 2.33-2.58 (m, 6 H), 2.87 (s, 10 H), 6.5 (s, 2 H). The cis isomer was prepared via lithium aluminum hydride-aluminum chloride reduction of the dibromide obtained from the action of *N*-bromosuccinimide on *trans*-**2**: mp 158-160°; NMR ($CDCl_3$) τ 1.25-1.42 (m, 2 H), 2.35-2.6 (m, 6 H), 3.13 (s, 10 H), 4.9 (s, 2 H); mass spectrum *m/e* 356 (M). Isomerization of *cis*- to *trans*-**2** occurred in *tert*-butoxide-tetrahydrofuran at room temperature. Reduction of *cis*-**2** at −78° with potassium, sodium, or lithium biphenyl anion radical gave *cis*-2$\cdot^-$: ESR (THF) 4.22 G (4 H, 2p + 2 saturated methines), 2.85 (2 H, *o*), 0.48 (4 H, *m*). The identity of this species is established by comparison of its hfs with those of the anion radicals of *cis*-1,2,3,4-tetraphenylcyclobutene,[9] 1,2-diphenylcyclobutene,[10] and phenanthrene. After total reduction, *cis*-**2** was regenerated in 80% yield by aqueous quenching. *cis*-**2**$\cdot^-$ is indefinitely stable at −78° and resists decomposition up to about 0°. In significant contrast, *trans*-2 gave no detectable paramagnetic species even at −78°. The mode of decomposition of transient *trans*-2$\cdot^-$ was identified as electrocyclic



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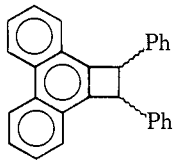

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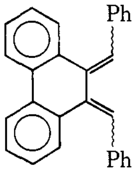

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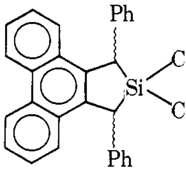

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by quenching the reduction product with aqueous ammonium chloride. An 84% yield of 9,10-dibenzylphenanthrene was obtained. Dimethyldichlorosilane quenching gave **4**. The ultimate reduction product of *trans*-**2** is thus $\mathbf{3}^{2-}$. Even at −78° this dianion underwent rapid $Z,E \rightleftarrows E,E$ equilibration, thus invalidating the silane quench as a mechanistic probe.[5] The dramatically different rates of cleavage of *cis*- and *trans*-$\mathbf{2}\cdot^-$, nevertheless, form the basis for a relatively secure assignment of reaction stereochemistry, as follows. Despite the greater thermodynamic stability of *trans*- than *cis*-**2**, *trans*-$\mathbf{2}\cdot^-$ cleaves far more rapidly. This phenomenon is familiar in the conrotatory cleavages of neutral 3,4-diphenylcyclobutene derivatives[11-13] and is understood on the basis of strong steric repulsion in the Z,E diene isomer, formed conrotatorily from the *cis*-cyclobutene. The trans > cis rate order may thus be considered diagnostic for conrotation in such systems.

INDO/MO calculations were carried out for the parent cyclobutene-1,3-butadiene anion radical cleavage using as initial and final geometries those of the corresponding neutral substrates.[14] Intermediate state geometrics were calculated assuming a linear relationship between C_3–C_4 bond stretching and rotation. This assumption was validated by more extensive studies on the neutral cyclobutene system. The initial (cyclobutene anion radical) and final (butadiene anion radical) state binding energies thus calculated were −4.0519 and −4.0232 hartrees, respectively. For the conrotatory cleavage, ten intermediate calculations fixed the transition state at $\theta = 45°$, binding energy −3.9901. The smaller activation energy is thus 0.0331 hartree or 20.8 kcal/mol. The disrotatory maximum also occurred at $\theta = 45°$, $E = -3.9233$, the smaller, activation energy being 0.0989 hartree or 62.1 kcal/mol. The *conrotatory* mode is clearly predicted. Incidentally, the perpendicular state corresponding to a "diradical" mechanism has $E = -3.9714$ hartrees, and this mechanism is thus also favored over the dis mode. The parent benzocyclobutene anion radical, the electrocyclic cleavage of which is ideally allowed,[5] was also investigated using INDO. The initial and final state energies are −8.1140 (benzocyclobutene anion radical) and −7.8846 hartrees (*o*-xylylene anion radical). For the conrotatory mode the transition state (again at $\theta = 45°$) has energy −7.8838, corresponding to a barrier of only *0.0008 hartree* or *0.5* kcal/mol. In the dis mode, the smaller activation energy is 0.0378 hartree or 23.7 kcal/mol. These results emphatically concur with OCD and with experiment in foreseeing a favored and ideally allowed con mode for this radical. One notes also that the unfavorable interaction between the termini of the *o*-xylylene system in the conrotatory mode envisioned by HOMO is not manifested in the calculation, since virtually no activation barrier exists. Thus not only is the predominance of HOMO's single interaction questioned but even its quantitative importance.

The available facts are consistent with the generalization that ideally allowed electrocyclic reactions of radicals have extremely low barriers and that, in the more numerous instances where neither mode is allowed, both have substantial barriers. In the cyclobutene–butadiene anion radical system the preferred mode is the same as for the neutral cyclobutene system, viz., conrotation.

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References and Notes

(1) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395 (1965).
(2) H. C. Longuet-Higgins and E. W. Abrahamson, *J. Am. Chem. Soc.*, **87**, 2045 (1965).
(3) R. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.*, **87**, 2046 (1965).
(4) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, Weinheim, Germany, 1970, p 44.
(5) N. L. Bauld, C.-S. Chang, and F. R. Farr, *J. Am. Chem. Soc.*, **94**, 7164 (1972).
(6) The naphtho[*b*]cyclobutene and acenaphthylene anion radicals also have allowed electrocyclic modes which are incorrectly treated by HOMO.
(7) M. J. S. Dewar and S. Kirshner, *J. Am. Chem. Soc.*, **93**, 4290 (1971).
(8) M. P. Cava and D. Mangold, *Tetrahedron Lett.*, 1751 (1964).
(9) N. L. Bauld, F. R. Farr, and C. E. Hudson, *J. Am. Chem. Soc.*, **96**, 5634 (1974).
(10) I. B. Goldberg, *Org. Magn. Reson.*, **5**, 29 (1973).
(11) Diphenylbenzocyclobutene: R. Huisgen and H. Seidel, *Tetrahedron Lett.*, 3381 (1964).
(12) Tetraphenylcyclobutene: H. H. Freedman, G. A. Doorakian, and V. R. Sandel, *J. Am. Chem. Soc.*, **87**, 3019 (1965).
(13) 3,4-Diphenylcyclobutene: H. Shechter, W. J. Link, and G. V. D. Tiers, *J. Am. Chem. Soc.*, **85**, 1601 (1963).
(14) Interatomic Distances Supplement, *Chem. Soc., Spec. Publ.*, **No. 18**, M109s (1965).

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Oxidation State Properties of Delocalized, Ligand-Bridged Metal Complexes. $[\mathrm{Ru_3O(CH_3CO_2)_6L_3}]^{n+}$ and the Pyrazine-Bridged, Cluster–Cluster Dimer, $[\mathrm{Ru_3O(CH_3CO_2)_6(py)_2}]_2\mathrm{pyz}^{m+}$

Sir:

Spencer and Wilkinson[1] have investigated the redox properties of the triangular cluster system $[\mathrm{Ru_3O(CH_3CO_2)_6L_3}]^{n+}$ (L is a neutral ligand, e.g., H_2O, pyridine) using chemical and electrochemical experiments. They found that the cluster units remain intact for $n = 0$ and +1 (eq 1) but that a two-electron reduction of the neutral cluster gave a compound formulated as $\mathrm{Ru_3(CH_3CO_2)_6L_3}$, in which the bridging oxide ion is lost. Cotton and Norman[2] have determined the structure of the mixed-valence cluster $[\mathrm{Ru_3}^{\mathrm{II,III,III}}\mathrm{O(CH_3CO_2)_6(PPh_3)_3}]$ by X-ray methods (Figure 1). Since the ruthenium ions are crystallographically equivalent, they have suggested that substantial electron delocalization occurs within the Ru_3O framework and have proposed a qualitative MO scheme to describe the electronic structure of the cluster system.

$$[\mathrm{Ru_3O(CH_3CO_2)_6L_3}]^+ \xrightleftharpoons[-e^-]{+e^-} [\mathrm{Ru_3O(CH_3CO_2)_6L_3}]^0 \qquad (1)$$

Because of our general interest in the chemical and electronic properties of polymetallic systems, including oxo-bridged compounds,[3] we have investigated the redox properties and some aspects of the synthetic chemistry of the triangular ruthenium cluster systems. In Figure 2a is shown a cyclic voltammogram for the system $\mathrm{Ru_3O(CH_3CO_2)_6(py)_2(pyz)}$ (py is pyridine, pyz is pyrazine)[4] which demonstrates that the clusters have an extensive oxidation state chemistry.[5] The four electrochemically reversible[6] one-electron waves in the voltammogram indicate that the cluster system remains intact in five discrete molecular oxidation states, $[\mathrm{Ru_3O(CH_3CO_2)_6(py)_2(pyz)}]^{+3,+2,+1,0,-1}$.

Ruthenium ESCA[7] experiments have been carried out on a series of the cluster systems including the mixed-valence pyridine cases, $[\mathrm{Ru_3}^{\mathrm{II,III,III}}\mathrm{O(CH_3CO_2)_6(py)_3}]$ and $[\mathrm{Ru_3}^{\mathrm{III,III,IV}}\mathrm{O(CH_3CO_2)_6(py)_3}]^{2+}$, and $[\mathrm{Ru_3}^{\mathrm{III,III,III}}\mathrm{O(CH_3CO_2)_6(py)_3}]^+$ (PF_6^- salts). The +2 system was prepared from the +1 system by either chemical (using Cl_2) or electrochemical (at +1.2 V vs. SSCE; $n = 1.2$) oxidation in CH_2Cl_2.[8] The ESCA results reinforce the idea that the clusters are delocalized and that the observed redox properties are carried by valence orbitals delocalized over all three