solution of 0.0025 mol of alkyl chloroglyoxalate in 3.0 ml of CCl_4 (or CCl_3Br) was added dropwise over a period of 10 min. Pyridine hydrochloride began precipitating immediately. When addition was complete, the ice bath was removed and the solution stirred for 15 min. The mixture was filtered into a 10-ml volumetric flask, and the reaction flask and precipitate were rinsed with CCl_4 (or CCl_3Br) which was added to the volumetric. An iodometric assay was run on the sample (which was theoretically 0.25 *M*) and generally showed the peroxide concentration to be 0.23–0.24 *M*.

Warning! Isolation of alkyl *tert*-butylperoxyglyoxalates is dangerous, and it is recommended that the compounds be prepared and reacted only in dilute solutions.

Decomposition of samples in sealed ampoules was carried out at 95° for 4, 6, and 9 min, and the reported yield is the average (which varied only 1–2%) determined by GLC.

Structures were assigned by comparison of retention times and NMR spectra with those of known materials. Assignment of structure to 2,2-dimethylcyclohexyl chloride was based on its NMR spectrum, principally the CHCl quartet at δ 3.7 which was reduced to a singlet upon irradiation of the signals at δ 1.2–2.0, and elemental analysis.

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Wavelength Dependence of the Photoionization of Phenolic Compounds

Sir:

Phenolic compounds are known to photodissociate with production of the characteristic phenoxyl radical.[1,2] In a flash photolysis study of neutral aqueous solutions of tyrosine, Feitelson and Hayon[3] showed that hydrated electrons are produced, supporting the photoionization mechanism

$$\begin{aligned}\text{Ty-OH} &\rightarrow \text{TyOH}^+ + e^-_{aq}\\ \text{TyOH}^+ &\rightarrow \text{TyO}\cdot + \text{H}^+\end{aligned} \qquad (I)$$

On the grounds of quenching experiments, they further proposed triplet tyrosine as a precursor of the reaction.[3,4]

Results obtained in our laboratory confirmed these views but showed a linear dependence of the yield of TyO· radical on the flash intensity, in contradiction with the quadratic law reported by Feitelson et al.[5] The flash duration and energy were quite comparable in both works (10 μsec; 1500–2000 J) but the spectral distributions of the flash lamps were not necessarily identical. We therefore investigated the intensity dependence of the photoionization yield for various spectral ranges of the exciting flash.

The following filter solutions were used: for excitation at $220 < \lambda < 360$ nm, $CoSO_4$ (240 g/l.) in water (this filter presents a low transmittance in the visible); for excitation at $\lambda > 270$ nm, carbon tetrachloride; for $240 < \lambda < 270$ nm, cyanine perchlorate[6] (0.4 g/l.) in water.

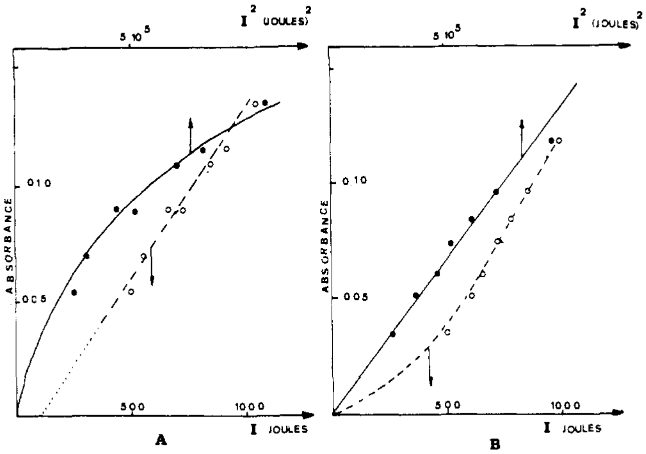

Figure 1. Absorbance of tyrosinyl radical as a function of the flash intensity: (A) excitation wavelengths, $240 < \lambda < 270$ nm; (B) excitation wavelengths, $\lambda > 270$ nm.

In each wavelength range, the flash output was proportional to the square of the applied voltage.

Upon flashing N_2 saturated solutions of tyrosine (2.5 10^{-4} mol/l.) at pH 6, the results were the following. (I) Suppression of most visible light did not appreciably affect the amount of [TyO] radical formed. (II) For an excitation restricted to the long wavelength side of tyrosine ($270 < \lambda < 300$ nm) a quadratic dependence of [TyO·] on the flash intensity is observed (Figure 1B). (III) Figure 1A shows that the tyrosine radical formation strongly deviates from a I^2 law for excitation wavelengths shorter than 270 nm. Due to experimental uncertainties and since the low intensity region cannot be explored in flash photolysis, it cannot be decided whether the linear plot in Figure 1A goes through the origin (in fact, the regression line does not).

Assuming triplet–triplet (TT) absorption to be responsible for the biphotonic ionization,[4] visible TT bands are seen to be inefficient in fluid solution. The quadratic law is obeyed only for $\lambda > 270$ nm. However, by monitoring the [OH·] adduct to tyrosine[3] formed upon conversion of e^-_{aq} by N_2O, we found a constant ratio: $[\text{TyO}\cdot]/[e^-_{aq}]$. This result suggests that the same reaction (I) is operating following long or short wavelength excitation, eliminating in the latter case the possibility of a direct O–H bond rupture.

$$\text{TyOH} \rightarrow \text{TyO}\cdot + \text{H}\cdot \qquad (II)$$

Bent and Hayon[7] recently reported the TT absorption spectrum of tyrosine excited at 265 nm by a 15-nsec laser pulse. As an argument supporting the biphotonic mechanism, the authors mention that TyO· radicals are only formed during the exciting pulse. However, this observation does not exclude a one-photon ionization from a nonrelaxed singlet state. The existence of a true one-photon pathway at short wavelength, in addition to a biphotonic mechanism has been demonstrated for the β-bond cleavage of durene in a rigid matrix.[8] The fluorescence method allowed the investigation of the durene system at low light levels. In contrast to flash photolysis experiments the formation of bityrosine has been studied at low excitation rates by monitoring its fluorescence. Shimizu[9] concludes to a monophotonic process, in the case of an excitation at 275 nm. However, his work refers to air-saturated solutions and the conclusion should be applied with caution to our case since oxygen might be implied in a direct reaction with the tyrosine triplet state.[5]

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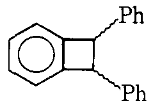
Stereochemistry of Retroelectrocyclic Reactions of Anion Radicals. Preferred Conrotation in a Cyclobutene System

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 $\mathbf{1}\cdot^-$ 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.



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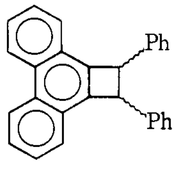

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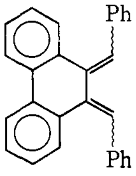

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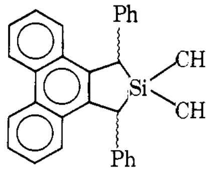

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The model cyclobutene derivatives *cis*- and *trans*-**2** were the specific subjects of the experimental study. The OCD's connecting $\mathbf{2}\cdot^-$ and $\mathbf{3}\cdot^-$ are not depicted but parallel in every essential those of the parent system. In particular, neither the dis- nor the conrotatory cleavage is allowed. The HOMO in $\mathbf{3}\cdot^-$ 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*-$\mathbf{2}\cdot^-$ 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