Scheme I

$$\begin{tikzcd}
\mathrm{RON{=}NOR} \arrow[r, "\Delta"] & {[\mathrm{RO}\cdot\uparrow + \mathrm{N_2} + \mathrm{RO}\cdot\downarrow]} \arrow[r, "k_s"] \arrow[d, harpoon, shift left, "\text{fast}"] & \mathrm{ROH} + \mathrm{R'R''CO}\ (^{\circ}\mathrm{S}) \\
 & {[\mathrm{RO}\cdot\uparrow + \mathrm{N_2} + \mathrm{RO}\cdot\uparrow]} \arrow[r, "k_t"] \arrow[u, harpoon, shift left] & \mathrm{ROH} + \mathrm{R'R''CO}\ (^{3}\mathrm{T})
\end{tikzcd}$$

The triplet yields in *tert*-butylbenzene are presented in Figure 1 as a function of the gas-phase exothermicities of the alkoxyl disproportionations to give *ground state* products.[15,16] The use of a log scale for the ordinate is a matter of convenience, and the points are not corrected for the cage effect (ca. 30–70%)[13,17] or solvation energies. A linear relation may be assumed *tentatively*, since the error in ΔH_r is at least ±1 kcal/mol. The plot is consistent with our qualitative observation that methyl hyponitrite ($-\Delta H_r^\circ = 79$ kcal) gives much less light than the other esters. Linear extrapolation of the four points leads to a prediction of a quantum efficiency of about 0.5 above $-\Delta H_r \cong 92$ kcal, an exothermicity accessible with suitable derivatives now under synthesis.

The ordering of triplet yields in Figure 1 is interesting for two reasons. First, the quantum yields do not appear to be a function of triplet energies of the excited-state carbonyl species formed or of the exothermicities of triplet production. Thus IIa, giving acetophenone ($E_T = 74.0$ kcal/mol,[18] $-\Delta H_{r,\text{triplet}} = 15.5$ kcal/mol), is at the opposite end of the scale from IId, which gives benzaldehyde ($E_T = 71.0$ kcal/mol,[18] $-\Delta H_{r,\text{triplet}} = 14.9$ kcal/mol). Second, an exothermicity relationship of the sort shown in Figure 1 would be consistent with larger activation energies for rate constants k_t than k_s (Scheme I) as the source of the differences in quantum yields. The activation energies, obtained by temperature-jump methods for DBA-enhanced chemiluminescence from IId, IIc, and IIa were 20.4 ± 1.1, 23.3 ± 0, and 21.5 ± 0.6 kcal/mol, respectively. The respective activation energies for disappearance of hyponitrite ester were 26.0 ± 0.4, 27.1 ± 0.0, and 25.2 ± 0.0 kcal/mol in the same solvent system. The differences of −5.6 ± 1.2, −3.8, and −3.7 kcal/mol increase in the opposite direction than expected and are largely due to an activation energy of about −4 kcal/mol for DBA fluorescence.[3]

It is possible that the anticipated differences (≅3 kcal/mol) are overwhelmed by an increase of solvent fluidity with temperature, which would decrease the fraction of alkoxyl pairs that undergo cage reaction.[19] Such an explanation, however, would require us to assume that cage escape for benzyloxyl pairs increases to a greater extent with fluidity than for the other radical pairs.

A more promising explanation may be in quantum-mechanical tunneling[20] of the H atom in II′, particularly if the thickness of the tunneling barrier for k_t resembled k_s and the resemblance were more so with increasing exothermicity of the latter process.

The following experiments indicate that the CL from hyponitrites arises from the mechanism of Scheme I and not from a related or adventitious process: (a) *tert*-butyl hyponitrite, which lacks α-protons, does not give significant CL under our conditions, (b) the extrapolated yield of triplets from 10^{-3} M benzyl hyponitrite in *tert*-butylbenzene with DBA was unchanged in the presence of 0.02 M 2,6-di-*tert*-butyl-4-methylphenol, a free radical scavenger, and (c) the decay of CL from solutions of hyponitrite and fluorescers at elevated temperatures gave the same first-order rate constants as those determined by following the loss of the hyponitrite by HPLC.[13a]

These results may have implications for the mechanism of hydrocarbon oxyluminescence, which heretofore has been ascribed almost exclusively to excited states from peroxyl radical termination.[11,21]

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[15] For the calculations we assumed $DH^\circ(\mathrm{RO{-}H}) = 103$ kcal/mol, from which the equation $\Delta H_r = \Delta H_f^\circ(\mathrm{R'R''CO}) - \Delta H_f^\circ(\mathrm{ROH}) - 102$ can be derived. The heat of formation of 1-phenylethanol was estimated from group additivity[15b] while values for other compounds were taken from the literature.[15c] (b) Benson, S. W. "Thermochemical Kinetics"; Wiley: New York, 1968; p 23. (c) Cox, J. D.; Pilcher, G. "Thermochemistry of Organic and Organometallic Compounds"; Academic Press: New York, 1970.

[16] A marked solvent effect was noted in 95% ethanol, which reduced Φ_{triplet} from IIa to 1.9×10^{-5}. The measurements of Φ_{CL} in $\mathrm{CClF_2CFCl_2}$ and in *tert*-butyl alcohol was frustrated by the insolubility of DBA and in isooctane by nonlinear Stern–Volmer plots.

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Thermal Generation of the [16]Annulene Anion Radical from the [8]Annulene Anion Radical

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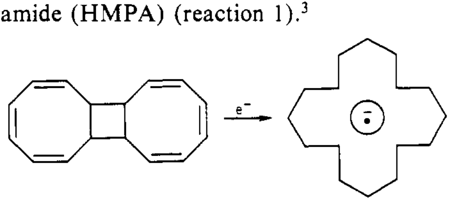
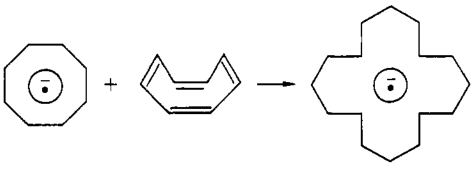
The anion radical of [16]annulene was first generated by Schröder and co-workers[1] via the reduction of the neutral molecule with alkali metal. Later Vincow and Concepcion[2] found that this anion radical could be generated without the laborious synthesis of neutral [16]annulene by simply reducing the (2 + 2) dimer of [8]annulene in tetrahydrofuran (THF) or in hexamethylphosphoramide (HMPA) (reaction 1).[3]



(1)

We now wish to report the generation of the [16]annulene anion radical directly from that of [8]annulene (COT). This reaction represents the first example of a (2 + 2) anion radical–neutral molecule combination.

The high reactivity of electron-rich alkenes with electron-deficient alkenes in the (2 + 2) cycloaddition reaction has been of synthetic importance for a number of years (for example, tetrafluoroethylene preferentially adds to cyclopentadiene in the 2 + 2 mode rather than the 4 + 2 mode).[4] The present work indicates that the very electron-rich COT anion radical reacts readily with the electron-deficient [8]annulene to yield the anion radical of [16]annulene (reaction 2).



(2)

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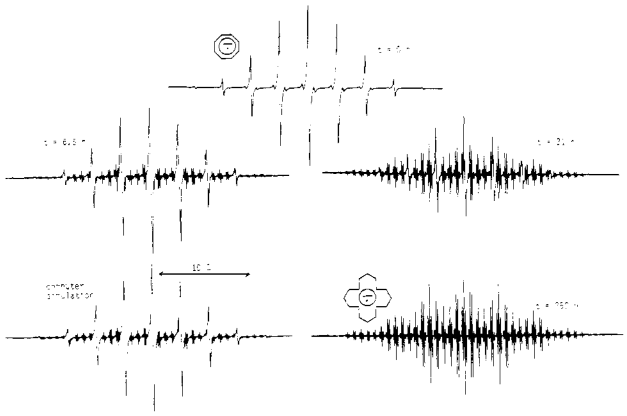


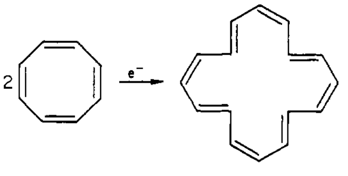
Figure 1. ESR spectra taken at various times for a 0.3 M COT solution in HMPA in the presence of the COT anion radical. The computer simulation was generated for a 1/6.0 ratio of [16]annulene$^{-}\cdot$ to COT$^{-}\cdot$. Line widths of 0.05 and 0.15 G were used for the anion radicals of [16]annulene and COT, respectively. Spectra were recorded at 25 °C at the times indicated on the spectra. The first spectrum exhibits the presence of the COT anion radical only. The last (recorded after 250 h) shows only the anion radical of [16]annulene.

The reduction of COT (0.1–1 M) in HMPA with a very deficient (by at least 2 orders of magnitude) amount of sodium metal (under conditions where ion association is absent[5]) results in a solution that yields the familiar nine-line ESR spectrum of the COT anion radical. After several hours at 25 °C, the ESR spectrum of this same solution shows the presence of the anion radical of [16]annulene (Figure 1). Over a period of several days, the anion radical of COT is gradually replaced with that of [16]annulene. Quantitative aspects of this unusual reaction were followed with the use of computer simulations.

Unfortunately, the rate law for this reaction seems to be very complex, and the actual rate constants could not be obtained. Part of the problem involves the fact that the anion radicals of both [16]annulene and COT disproportionate to form the dianions and neutral molecules. Thus there are six species, which are all kinetically connected, in solution simultaneously. Despite this problem, it is clear that the rate of anion radical–neutral molecule combination is very thermally dependent. In a typical reaction, the time that it takes for the concentrations of the two anion radicals to become equal (half-life for COT$^{-}\cdot$) is about 11 h at 35 °C, 41 h at 25 °C, and 520 h at 0 °C.

The thermal dimerization of COT to yield the (2 + 2) dimer does not take place at room temperature at an observable rate (this reaction takes several days at 100 °C).[6] After 3 days at room temperature, a solution of COT in the presence of COT$^{-}\cdot$ shows only the anion radical of [16]annulene upon ESR analysis. However, when a portion of this same solution was kept from contact with the sodium metal for 2 weeks and then touched to the metal surface, only COT$^{-}\cdot$ was immediately observed. Thus, the formation of [16]annulene involves the anion radical of COT and does not involve any previously formed dimer that may have existed in the solution.

Thermal (2 + 2) anion radical–neutral molecule combination reactions have synthetic potential that is well-worth exploring. This is especially true since many anion radical systems readily disproportionate, and both the newly generated anion radical and its dianion can be easily oxidized to form the neutral products. For the example described here, the anion radical product disproportionates to form the [16]annulene neutral molecule, and reaction 3 must result to some extent. However, the accumulation of a sufficient amount of neutral [16]annulene for isolation has not yet been realized.



(3)

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Registry No. [8]Annulene radical anion, 34510-85-5; [8]annulene, 629-20-9; [16]annulene radical anion, 37552-62-8.

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Spatially Isolated Redox Orbitals: Evidence from Low-Temperature Voltammetry

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The purpose of this report is to provide additional evidence for the concept of spatially isolated redox orbitals and to present some unusual cyclic voltammetric results.

The concept of spatially isolated orbitals was originally postulated[1-3] to explain the occurrence of multiple-state emission[3] from $[Rh(bpy)_2phen]^{3+}$ and $[Rh(phen)_2bpy]^{3+}$, compounds that exhibited two distinct $\pi\pi^*$ emissions, one characteristic of the bpy portion of the molecule and the other of the phen. Consequently, it was suggested that the parent compounds, $[Rh(bpy)_3]^{3+}$ and $[Rh(phen)_3]^{3+}$, also possess excited states deriving from excitation into a single chelate ring. The spectroscopy of $[Ru(bpy)_3]^{2+}$ and $[Os(bpy)_3]^{2+}$ would by analogy be expected to involve excited states such as $[Ru^{III}(bpy)_2(bpy^{-})]^{2+}$ resulting from the presence of spatially isolated optical orbitals. While the analogous mixed-ligand complexes ($[Ru(bpy)_2phen]^{2+}$) did not produce direct spectroscopic evidence[4] for a spatially isolated redox orbital, the cyclic voltammetric pattern observed for the d^6 tris bpy Ir(III)[5] and other Ru(II) complexes[6] and bis diimine complexes enabled us[3,5] to postulate that spatially isolated (single chelate ring) orbitals also exist for the Ru(II) parent molecule as well as for the mixed ligand species. For the $[Ir(bpy)_3]^{3+}$ ion, a pattern of three closely spaced one-electron waves was followed by a gap of 0.6 V and three more closely spaced waves. Our model placed the first three electrons each in an orbital on a single chelate ligand[11] and the next three reversible one-electron waves corresponded to pairing up of the first three electrons.

Subsequently, this prediction for the optical orbital of $[Ru(bpy)_3]^{2+}$ has been supported by observation of high-resolution photoselection spectra[7] for $[Ru(bpy)_3]^{2+}$ and by the observation

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