biradical precursors produce intermediates with the same lifetime and reactivity toward PQ^{2+}. We propose that the same biradical is produced from the short- and long-lived precursors, which supports Wagner's proposal[3] that these are the syn and anti conformers of the ketone triplet. From Figure 1, we obtain $\tau_B = (300 \pm 40)$ ns[9] and $k_2 = (4.8 \pm 1.0) \times 10^9\ M^{-1}\ s^{-1}$. The curvature observed in the absence of diene probably reflects the breakdown of the assumption of very fast biradical generation at high PQ^{2+} concentrations under these conditions. In related systems[6c] we have established that this effect usually reflects the presence of a relatively long-lived triplet.[10]

In the region where the two lines in Figure 1 overlap, the yield of $PQ^{+}\cdot$ is proportional to the biradical input. From the ratio of radical-ion yields in the presence and absence of diene, we conclude that 23% of the biradicals are derived from the long-lived triplet in methanol as solvent.

The quantum yields of radical-ion formation increase with increasing PQ^{2+} concentration and $\Phi(PQ^{+}\cdot)^{-1}$ vs. $[PQ^{2+}]^{-1}$ gives a linear plot as can be expected from the mechanisms proposed.[6]

We have also examined the interaction of the biradical with oxygen, using the same techniques as described previously.[11] We found that the biradicals react with oxygen with a rate constant of $4.6 \times 10^9\ M^{-1}\ s^{-1}$; the value is in line with the reactivity of other biradicals[6,11] and typical free radicals.[12] This scavenging effect has been observed by Findlay and Tchir,[5] who attribute it to quenching of the triplet enol to produce ground-state enol; as a result, the quantum yield of the latter is increased. Further, they suggest[5] that the triplet enol is the species identified as the triplet ketone by Lindqvist et al.[2] While our results agree with those of Findlay and Tchir,[5] we believe that they can be explained by the intermediacy of biradicals in the same way as in the Norrish type II reaction, where the interaction of oxygen with the biradicals results in an enhancement of the quantum yields.[11,13] The effect is similar to that of polar solvents.[14] The lack of oxygen effect on the quantum yields[5] in polar solvents probably reflects the stabilization of the biradicals by alcohols which leaves little room for oxygen enhancement of the yields. In the case of *o*-alkyl-substituted benzophenones the effect of oxygen is not yet clear.[15]

In conclusion, the transient produced by intramolecular hydrogen abstraction in *o*-methylacetophenone has a lifetime of 300 ns, which most likely is determined by the rate of spin inversion;[6c] it reacts in the electron transfer to paraquat dications in the same manner as the biradicals produced in the Norrish type II reaction (e.g., from γ-methylvalerophenone).[6] The same biradical is apparently produced from both triplet states as required by Wagner's mechanism,[3] the long-lived triplet accounting for 23% of the biradicals produced in methanol. The biradical interacts with oxygen at nearly diffusion controlled rates.

Finally, a comment on the experimental technique seems pertinent. The method used has the obvious disadvantage that the transient of interest is not observed directly. However, as many as five transients are sometimes detected in this type of reactions.[17] In view of the complexity inherent to such a system, it is perhaps an advantage to use a technique which might be somewhat indirect but is specific for the only good electron donor involved.

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(4) Some authors have questioned the use of the term biradical for the product of reaction 1 which can also be described as the triplet state of the enol.[5] We have prefered to use the term "biradical" simply because it describes best the properties exhibited in this work.

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(7) In Lindqvist's mechanism[2] the biradicals would be produced with different multiplicity, which would be expected to lead to different biradical lifetimes.[6b,c]

(8) The radical ions, $PQ^{+}\cdot$ were fully characterized using transient spectroscopy, as well as generating concentrations of $\sim 10^{-5}$ M and examining the spectrum in a Cary 14 spectrophotometer. Triplet acetophenone and ground-state enols do not generate the radical ion.

(9) In experiments in the absence of PQ^{2+}, we observed a transient with decays with $\tau \sim 400$ ns and which has essentially the same spectroscopic properties as the species with $\tau \sim 1200$ ns reported by Lutz and Lindqvist.[2] The decay does not strictly follow first-order kinetics, probably reflecting the underlying absorbances of precursors and products. These experiments will be discussed in detail in a full paper.

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Electron Spin Resonance Spectrum of $[(MeO)_3B\cdot B(OMe)_3]^-$. A Novel σ Radical with a One-Electron Bond

Sir:

We wish to report the ESR detection and identification of the dimer radical anion of trimethyl borate. This radical is of more than cursory interest because it resembles the prototype species H_2^+ and the ethane positive ion $C_2H_6^+$ in having essentially a one-electron bond between two atoms or groups which are identical.[1,2] Moreover, we believe this is the first electron-deficient σ radical of this type to be characterized by ESR studies.[3] Although Kasai and McLeod[4] have reported the ESR spectrum of $B_2H_6^-$ which is isoelectronic with $C_2H_6^+$, the hyperfine parameters were found to be consistent with the retention of the bridged D_{2h} structure of the parent diborane molecule.[4,5]

Whereas previous work has shown that the BF_3^- radical anion is generated by γ irradiation of a *dilute* solid solution of BF_3 in tetramethylsilane at 77 K,[6] we now find that a paramagnetic color center (λ_{max} 550 nm) containing two equivalent boron atoms is produced by γ irradiation of *crystalline* $B(OMe)_3$ at the same temperature. Taken together with the finding that BF_3^- and the $B(OMe)_3$ dimer center are photobleachable under the same conditions, these preparative details strongly suggest that a dimer radical anion is formed as a result of the consecutive reactions

$$B(OMe)_3 + e^- \rightarrow B(OMe)_3^- \qquad (1)$$

$$B(OMe)_3^- + B(OMe)_3 \rightarrow [(MeO)_3B\cdot B(OMe)_3]^- \qquad (2)$$

reaction 2 being facilitated in the trimethyl borate crystal. Similarly, the dimer radical anion of acetonitrile is produced by γ irradiation of the upper crystalline phase of acetonitrile

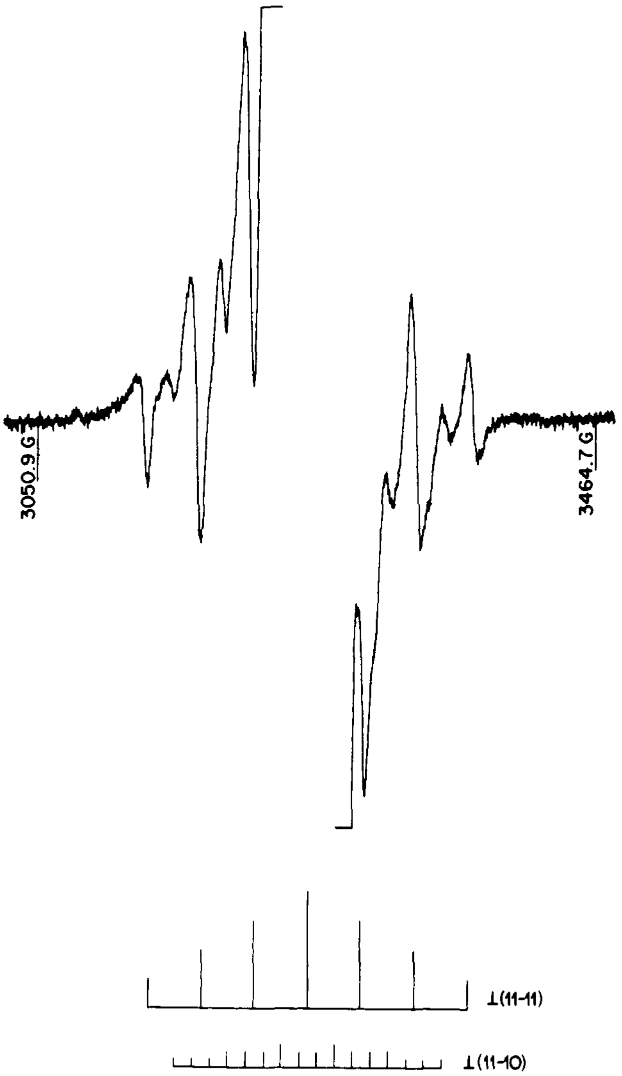

Figure 1. First-derivative ESR spectrum of γ-irradiated crystalline trimethyl borate at 82 K. The sample received a dose of 1 Mrad at 77 K and was oriented in the magnetic field (see text) to intensify the perpendicular components of the spectrum. The stick diagrams represent the perpendicular hyperfine patterns calculated for the $^{11}B^{11}B$ and the $^{11}B^{10}B$ species of the radical containing two equivalent borons. The center of the spectrum (see text and Figure 2) has been omitted for the sake of clarity.

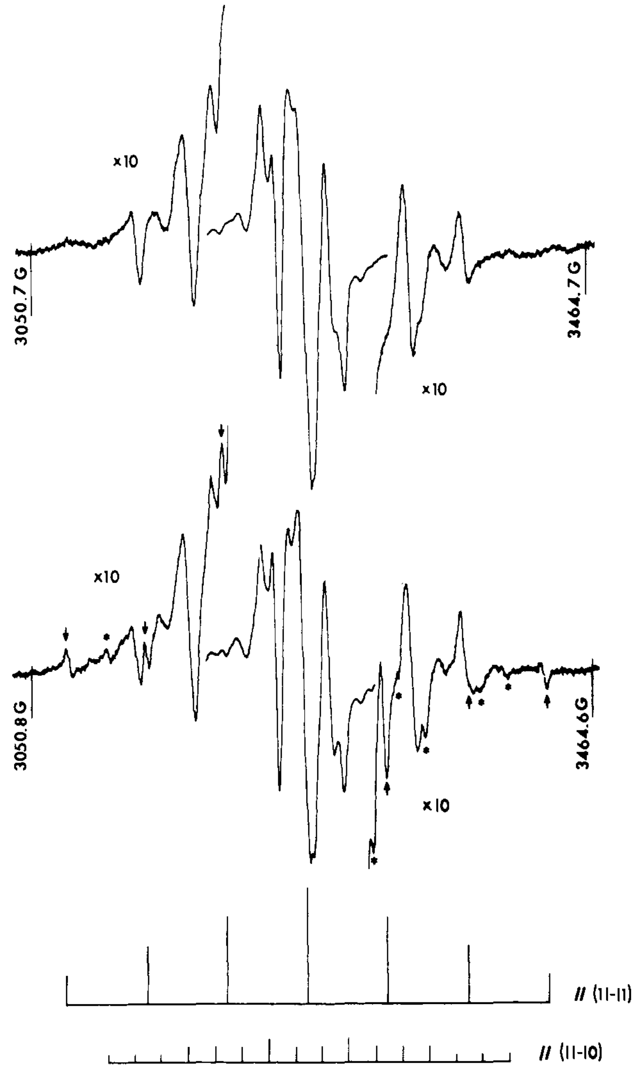

Figure 2. Orientation dependence of the ESR spectrum of γ-irradiated (2.4 Mrad) crystalline trimethyl borate at 84 K. The upper and lower spectra were obtained before and after an 80° rotation of the sample tube about its vertical axis. The stick diagrams represent the parallel components of the hyperfine patterns, which are strongly enhanced in the lower spectrum. The spectral features indicated by arrows are the $^{11}B^{11}B$ parallel features while the asterisks designate the corresponding $^{11}B^{10}B$ components.

at 77 K,[7] although the structure of the $(MeCN)_2^-$ species is quite different from the center described in the present report.

Outside the central region which is dominated by the spectrum of the radical formed by loss of a hydrogen atom, the ESR spectra of γ-irradiated trimethyl borate show several features having the characteristic line shapes of parallel and perpendicular components. The spectral analysis was aided by the use of crystalline samples possessing partial alignment,[8,9] this technique allowing the signal intensities of either the perpendicular or parallel features to be intensified relative to the other by optimizing the sample orientation in the magnetic field (vide infra). In this way, the complete set of outer features can be assigned to a radical containing two boron atoms which are equivalent and have cylindrically symmetric hyperfine tensors with parallel axes. As the relative abundance of the ^{11}B ($I = \frac{3}{2}$) and ^{10}B ($I = 3$) isotopes is $\approx$4:1, only the spectra of the $^{11}B^{11}B$ and $^{11}B^{10}B$ species contribute significantly to the hyperfine pattern. Thus, the strong lines in the perpendicular spectrum of Figure 1 are the six outer components of the 1:2:3:4:3:2:1 spectrum of the $^{11}B^{11}B$ species, while the two weaker lines situated just inside the $M_I = \pm 3$ wing components are the outermost lines of the $^{11}B^{10}B$ spectrum as indicated by the stick diagram.

The effect of sample orientation in enhancing the parallel features is shown in Figure 2. Although the perpendicular features are still present in the lower spectrum, all six outer components of the parallel $^{11}B^{11}B$ spectrum are visible together with several components of the corresponding $^{11}B^{10}B$ spectrum. The anisotropy of the spectrum was also established by single-crystal studies which yielded well-resolved spectra of both the $^{11}B^{11}B$ and $^{11}B^{10}B$ species with the magnetic field vector parallel and perpendicular to the principal axis.

From the spectra we obtain the parameters $A_\parallel(^{11}B) = 59.3$ G, $g_\parallel = 2.002\,0$, and $A_\perp(^{11}B) = 39.8$ G, $g_\perp = 2.004\,3$. The hyperfine tensor components yield values for the isotropic coupling constant $a(^{11}B) = 46.3$ G[10] and for the anisotropic parameter $B(^{11}B) = 6.5$ G. From these results and the ^{11}B atomic parameters $A_0 = 721$ G and $B_0 = 18.9$ G given by Morton,[11] the spin densities ρ_{2s} and ρ_{2p} on each boron atom are calculated to be 0.064 and 0.344, respectively. Thus, the total spin density in the orbitals of the two boron atoms is 0.82. Also, the ratio ρ_{2p}/ρ_{2s} of 5.3 can be used to calculate[12] that the angle between the B-OMe bonds and the plane normal to the

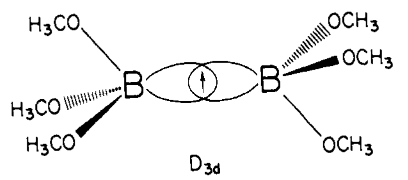

Figure 3. A D_{3d} structure for the dimer radical anion of trimethyl borate.

C_3 axis of each $B(OMe)_3$ unit is 15.7°.[13] This result may be compared with the optimum value of 10° predicted by theoretical calculations[2d] for the corresponding out-of-plane angle in the $^2A_{1g}$ ground state of $C_2H_6^+$. We conclude that, just as predicted for $C_2H_6^+$,[2] the unpaired electron in the dimer radical anion of trimethyl borate is largely concentrated in the σ-bonding orbital between two nonplanar $B(OMe)_3$ units, as represented in the D_{3d} structure for the species (Figure 3).

Acknowledgment. This work was supported by the Division of Physical Research, U.S. Energy Research and Development Administration (Document No. ORO-2968-110).

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Methylene Singlet-Triplet Separation. An ab Initio Configuration Interaction Study

Sir:

The energy separation between the two lowest states ($^3B_1$ and $^1A_1$) of the CH_2 radical has been thoroughly investigated both experimentally and theoretically. For a review up until 1974 we refer to a paper by Harrison.[1] Still the results are in conflict. While the most accurate theoretical calculations yield values between 9 and 14 kcal/mol for the energy separation, a recent spectroscopic measurement, based on photodetachment from CH_2^-, gives the value 19.5 ± 0.7 kcal/mol.[2]

The singlet-triplet separation has recently been studied by Meadows and Schaefer on the Hartree-Fock level.[3] Very large basis sets were used and the results can therefore be expected to be close to the Hartree-Fock limit. For the $^1A_1$ state they present results both from a one-configuration ($1a_1^2\ 2a_1^2\ 3a_1^2\ 1b_2^2$) and a two-configuration (including also $1a_1^2\ 2a_1^2\ 1b_1^2\ 1b_2^2$) treatment, which thus includes the effect of near degeneracy between the two lowest $^1A_1$ states. The adiabatic energy differences computed with these two wave functions are 24.8 and 10.9 kcal/mol, respectively. When the near-degeneracy effect has been accounted for, the primary remaining approximation is the neglect of the dynamical correlation for the electronic motion. Another effect, which was not accounted for by Meadows and Schaefer, is the contribution due to differences in zero-point vibrational energy between the two states.

To study these effects we have performed a series of CI[15] calculations around the equilibrium geometries of the two lowest electronic states of CH_2. The direct CI method as developed in the program system MOLECULE was used.[4] For the $^3B_1$ state UHF-CI calculations were performed, i.e., the reference state is an UHF determinant and the CI expansion includes all singly and doubly replaced determinants, however, without replacing the carbon 1s orbital. For the $^1A_1$ state MC-SCF calculations[5a] were first made with a wave function comprising the two above-mentioned $^1A_1$ configurations. Using the MC-SCF orbitals as the one-particle basis set, CI calculations were then performed with all singly and doubly replaced configurations with respect to the two reference configurations. Again the carbon 1s shell was left uncorrelated. These calculations were made with a new computer program in which the direct CI method has been extended to cover also the case of a multiconfigurational root function.[5b]

A contracted Gaussian basis set was used with the primitive set[6,7] (C/11, 7, 2), (H/6, 2) contracted to ⟨C/6, 4, 2⟩, and ⟨H/4, 2⟩. The orbital exponents of the two most diffuse carbon 2p orbitals and the carbon 3d and the hydrogen 2p orbitals were optimized—using direct energy minimization techniques—on the UHF level ($^3B_1$) and MC-SCF level ($^1A_1$), respectively. The overall effect of the exponent optimization was somewhat disappointing, with only a small energy gain on the CI level. Actually the CI energies reported by Lucchese and Schaefer,[8] with a somewhat smaller Gaussian basis set—they used only one p function on hydrogen—are lower than the corresponding values with our optimized basis set. There are several reasons for this rather strange result. First, optimization of the carbon 2p and the hydrogen 2p orbitals have a neglibible effect on the energy. This probably also means that the second p function on hydrogen is rather unimportant. Second, it seems to be necessary to optimize the carbon 3d orbital, which is much more energy sensitive, on the CI level. The optimal exponents on the SCF level actually gave less correlation energy than the original guessed exponents. However, the reason for performing the exponent optimization was not primarily to obtain the lowest possible energy, but rather to get an idea of the sensitivity of the $^3B_1$-$^1A_1$ separation energy to the basis set. Since the net result of the optimization is only a change of 0.3 kcal/mol for the excitation energy, it is not likely that there are any serious defects in the one-particle basis set. The adequacy of the basis set is also borne out by a comparison with the Hartree-Fock limit calculations by Meadows and Schaefer.[3] The energies obtained here for the $^1A_1$ state are for both the one- and the two-configuration calculations, only 1.8