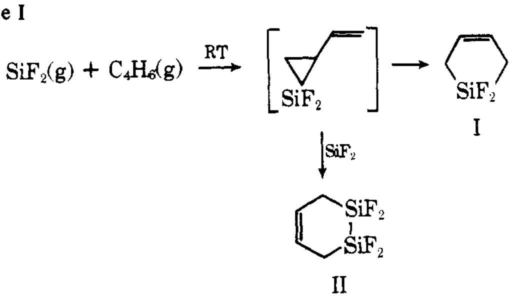
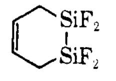
**Scheme I**



various reaction conditions are so far rather similar.

In all cases the results showed that thermally generated $SiF_2$ is indeed reactive toward butadiene in gas phase. The total yield of reaction products based on recovered butadiene was estimated to be at least 30%. The products were isolated from $SiF_4$ and excess starting material by prolonged pumping through a trap at −96 °C, and were identified unequivocally by means of mass spectrometry and IR and NMR spectroscopy. The major product was found to be 1,1-difluorosilacyclopent-3-ene (I). The existence of a small amount of 1,1,2,2-tetrafluoro-1,2-disilacyclohex-4-ene (II) was also indicated by mass spectral data. In the case of experimental condition iii, II was isolated by passing the product mixture through a trap at −45 °C and characterized by spectroscopic methods. The relative yields of I and II in all cases were estimated to be ≥20:1.

I



II

It is interesting to note that, although Thompson and Margrave[9] have reported that the products in cocondensation of $SiF_2$-$C_4H_6$ were II and $H_2C{=}C{=}CHCH_2SiF_2SiF_2CH_2CH_2CH{=}CH_2$ (III), we do find a small amount of I in a repeated cocondensation experiment. The relative quantity of I is only 1 ~ 2%; however, it is mechanistically significant.

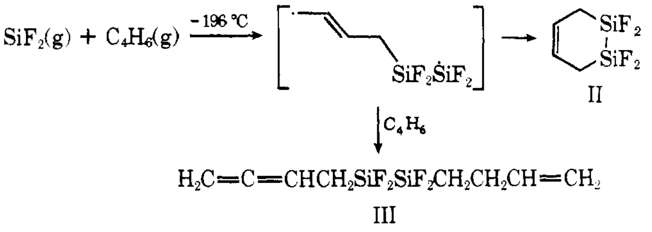
Since on condensation only a negligible amount of $SiF_2$ was left over in the present work, it seems very likely that monomeric $SiF_2$ reacts directly with 1,3-butadiene, perhaps via an initial formation of silirane as suggested by Seyferth,[7] followed by either intramolecular rearrangement to form I or reaction with another molecule of $SiF_2$ to form II (Scheme I).

Comparing the results from gas-phase and cocondensation experiments, it is obvious that the major reaction occurring in gas phase is the monomeric $SiF_2$ reaction just like the case of recoiled $^{31}SiF_2$ reactions, whereas, in the case of cocondensation, the diradical mechanism seems to be important for the formation of volatile products (Scheme II).

The small quantity of I found in cocondensation reaction is very likely a result from the gas-phase reaction prior to condensation. On the other hand, since no polymeric material was observed when the gas-phase reaction mixture was condensed, it is evident that the formation of II had occurred in gas phase. (In cocondensation experiments the formation of II is accompanied by the formation of a large amount of polymers.) While the formation of II in Scheme I seems reasonable, a possible alternative is that II was formed from a small amount of $Si_2F_4$ which existed in the gas mixture. Margrave and Perry in a recent correspondence discussed the possible existence of $F_2Si{=}SiF_2$ under such conditions.[10]

Thus the results from this study suggest that $SiF_2$ reacts similarly to carbene species in gas phase, but in low-temperature cocondensations it may proceed via different pathways. It is perhaps premature to draw any further conclusion at this stage; nonetheless, the significance of the $SiF_2$ chemistry in gas phase, i.e., the potential to provide genuine insights into the reaction mechanisms comparable with those in the development of carbene chemistry, is evident. Gaspar predicted in a review article[11] "in view of the poor Si-Si π interaction and the relative weakness of Si-Si single bond, it is very likely that characteristic reaction of $SiF_2$ other than polymerization will be found in the near future". This study demonstrates a true difluorosilylene chemistry.

**Scheme II**



**Acknowledgment.** The work has been financially supported by the Chinese National Science Council. One of us (T.L.H.) thanks the Institute of Nuclear Energy Research for a research fellowship.

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## Mechanisms of Photooxygenation. 1. Substituent Effects on the [2 + 2] Cycloaddition of Singlet Oxygen to Vinyl Ethers

*Sir:*

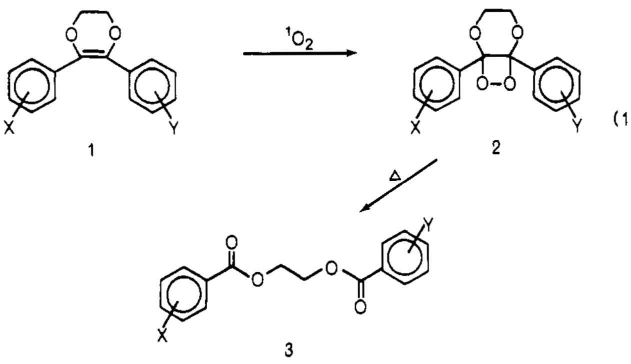
The mechanism of [2 + 2] cycloaddition of singlet molecular oxygen to olefins and its relationship to the ene and [2 + 4] cycloaddition modes has been of interest for some time.[1] A wide variety of mechanisms has been proposed but conclusive evidence is, in general, lacking. Moreover, there is disagreement among theoreticians regarding the formulation of this process[2]—a controversy which has recently been enlivened.[3] We now present the results of a study of the addition of singlet molecular oxygen ($^1O_2$) to a series of substituted vinylene diethers, which strongly restrict the mechanistic possibilities.

The 2,3-diaryl-1,4-dioxenes **1** undergo photooxidation to yield initially the dioxetanes **2** which thermolyze smoothly to the diesters **3** in 90–95% isolated yield (eq 1). Competitive experiments show formation of **2** to be an authentic $^1O_2$ reaction.[4] Relative reactivities are unaffected by choice of sensitizer, presence of radical inhibitor, addition of the $^1O_2$

Table I. Rates of Reaction ($k$) with Singlet Oxygen and Oxidation Potentials of Olefins **1**

| olefin | substituent X | substituent Y | $k^a \times 10^{-7}$ ($M^{-1}\,s^{-1}$) | photooxygenation solvent | $E_{1/2}{}^b$ (V vs. SCE) | $\Delta G^c$ for electron transfer, kcal/mol |
|---|---|---|---|---|---|---|
| **1a** | $p$-NMe$_2$ | $p$-NMe$_2$ | 37.3 | $Me_2CO^d$ | $0.314^e$ | ≤2.1 |
| **1b** | $p$-OH | $p$-OH | 6.48 | $Me_2CO^d$ | 0.677 | 10.5 |
| **1c** | $p$-OMe | $p$-OMe | 4.80 | $Me_2CO$ | 0.726 | 11.6 |
| **1c** | | | 12.6 | $MeCN^d$ | | |
| **1d** | $p$-Me | $p$-Me | 2.93 | $Me_2CO$ | 0.836 | 14.2 |
| **1e** | $p$-NHAc | $p$-NHAc | 1.53 | $Me_2CO^{d,f}$ | 0.795 | 13.2 |
| **1f** | H | H | 1.59 | $Me_2CO$ | 0.928 | 16.3 |
| **1g** | $m$-OMe | $m$-OMe | 1.03 | $Me_2CO$ | 0.937 | 16.5 |
| **1h** | $p$-Cl | $p$-Cl | 0.749 | $Me_2CO$ | 1.000 | 18.0 |
| **1h** | | | 1.94 | MeCN | | |
| **1i** | $m$-Cl | $m$-Cl | 0.355 | $Me_2CO$ | 1.075 | 19.7 |
| **1j** | $p$-NMe$_2$ | H | 7.54 | $Me_2CO^d$ | 0.512 | 6.7 |
| **1k** | $p$-NMe$_2$ | $p$-CN | 2.34 | $Me_2CO^d$ | 0.591 | 8.5 |
| **1l** | $p$-OMe | H | 2.73 | $Me_2CO$ | 0.824 | 13.9 |

[a] Rates from competitive kinetics of **1** against tetramethylethylene ($k = 5.46 \times 10^7\ M^{-1}\,s^{-1}$ in acetone and $10.8 \times 10^7\ M^{-1}\,s^{-1}$ in acetonitrile, from $\beta$ values). [b] Oxidation half-wave potentials.[14] [c] Calculated for electron transfer from **1** to $^1O_2$; see text. [d] Deuterated solvent. [e] This is a two-electron oxidation. Two separate waves are, however, found in $CH_2Cl_2$. [f] Contained 5% $Me_2SO$-$d_6$.

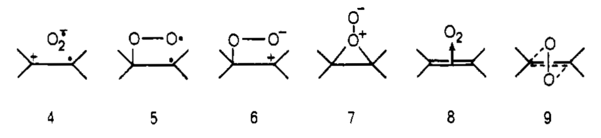


(1)

quencher, 1,4-diazabicyclo[2.2.2]octane,[5] or presence of the reactive competitive inhibitor, tetramethylethylene. Competition kinetics with the latter yield absolute rate constants for reaction of **1** with $^1O_2$.[6] Although **2** could result from rearrangement of an initially formed endoperoxide, we were unable to observe any endoperoxide in low-temperature experiments, even though we have successfully observed and isolated one in a closely related system.[9] We conclude, therefore, that dioxetanes **2** which have been characterized by $^{13}C$ and $^1H$ NMR spectroscopy and chemiluminescence behavior[10] are the initially formed products. The relevant kinetic data are summarized in Table I. Also included in Table I are the results of an electrochemical study of the reversible one-electron oxidation of the olefins **1**.

Among the suggestions for the [2 + 2] cycloaddition mechanism of $^1O_2$ is that of Mazur[11] and Foote[12] implicating a rate-limiting electron-transfer process with the formation of olefin$^{+\cdot}$ and $O_2^{-\cdot}$ (Chart I, **4**). The relationship between the rate and the free energy ($\Delta G$) of electron-transfer reactions has been delineated by Rehm and Weller.[13] For electron transfer that is endothermic by 5 kcal/mol or more, a plot of the logarithm of the rate constant against the free energy of reaction assumes a numerically maximal slope of −0.73 mol/kcal (−16.9 $V^{-1}$) at 25 °C. Figure 1 shows such a plot for olefins **1**. $\Delta G$ for electron transfer from **1** to $^1O_2$ is calculated from the Weller equation[13] ($\Delta G = 23.06\,[E(\mathbf{1}/\mathbf{1}^{+\cdot}) - E(O_2^{-\cdot}/O_2) - e^2/\epsilon a] - \Delta E_{0,0}$) using olefin oxidation potentials determined in acetonitrile[14] [$E(\mathbf{1}/\mathbf{1}^{+\cdot})$], the reduction potential of ground-state oxygen in the same solvent (−0.82 V vs. SCE),[15] the excitation energy of $^1\Delta_g$ molecular oxygen (7882.39 $cm^{-1}$),[16] and a radical-ion separation of 6 Å.[13] Table I shows that only slight accelerations in oxidation rate are observed in acetonitrile relative to acetone, permitting rates obtained in the latter solvent to be used in Figure 1. The slope of −0.11 mol/kcal (−2.4 $V^{-1}$) is only ~14% of the limiting slope expected for full electron transfer and is comparable with values obtained in related studies.[17] Although similar slopes have been found for endothermic *irreversible* electron transfer,[18] experiments[19] with chemically generated $\mathbf{1}^{+\cdot}$ and $O_2^{-\cdot}$ suggest that an electron-transfer reaction of **1** and $^1O_2$ would be *reversible*. Therefore, the present data indicate that the reaction of $^1O_2$ with **1** does not involve electron transfer, a conclusion emphasized by the rate constant observed for **1i** which is 10 orders of magnitude higher than predicted for electron transfer. Inspection of Figure 1 indicates that electron transfer may be competitive for substituents more electron donating than $p$-NMe$_2$. Preliminary results suggest this may be the case for the $p$-O$^-$ group. In the following paper, we shall provide evidence that electron transfer can be a viable mechanism for oxidation of olefins **1**, albeit without direct involvement of $^1O_2$.

Chart I



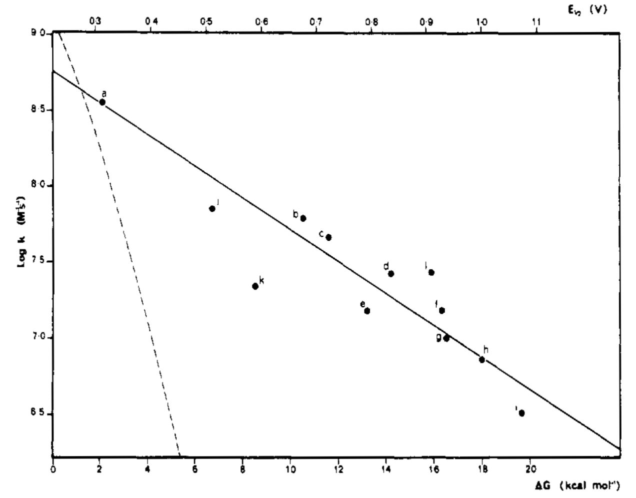
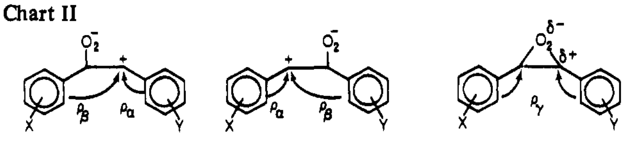


Figure 1. Plot of the logarithm of the photooxidation rate constant for olefins **1** against the free energy of electron transfer from **1** to $^1O_2$ (lower scale) and against oxidation half-wave potentials of **1** (upper scale). The broken line represents the expected relationship for full electron transfer.[13]

**Chart II**



10a 10b 11

Other mechanisms proposed for cycloaddition involve radical **5**,[2j,3a] zwitterionic **6**,[20] or peroxirane **7**[2a-c,21] intermediates, and cyclization via a charge-transfer complex **8**[2c,22] or by a concerted $[{}_\pi 2_s + {}_\pi 2_a]$ process **9**[23] (Chart I). These remaining mechanisms fall into two categories: those involving bonding in the transition state at only one terminus of the double bond (**5** and **6**) and those requiring bonding at both termini, in other words a symmetrical transition state (**7**–**9**). The two classes can be distinguished by the dependence of rate on the symmetry of substitution in the olefin **1**.

Symmetrically substituted olefins **1** show a linear Hammett relationship with $\sigma$ having a slope of $-1.66$. That this represents the effect of substitution on the transition state rather than on the ground state is suggested by a lack of correlation with $\sigma$ of ground-state olefin charge densities as measured by $^{13}$C chemical shifts.[24] In the case of one bound terminus, two values of a reaction constant $\rho$ are required, one ($\rho_\alpha$) representing interaction with charge $\alpha$ to the aryl ring, the second ($\rho_\beta$) with charge $\beta$ to the other aryl ring (Chart II, **10a** and **10b**). $\rho_\beta$ may be estimated from $\rho_\beta = f\rho_\alpha$ where $f$ is an attenuation factor due to interposition of a carbon atom. $f$ is not known with certainty but is unlikely to exceed 0.5.[25] Typical examples are 0.49 for ionization of $Ar(CH_2)_nCO_2H$[26] and 0.3 for stilbene bromination[27] where CHBr is interposed next to a carbonium ion. The overall reaction rate is the sum of the reaction rates at each of the two possible sites, which separately obey the Hammett equation. The relative overall rates are given by $k_{XY}/k_{HH} = 0.5 \times 10^{-1.66(\sigma_x + f\sigma_y)/(1+f)} + 0.5 \times 10^{-1.66(\sigma_y + f\sigma_x)/(1+f)}$.[28] For a symmetrical transition state **11**, only a single $\rho$ value is required ($\rho_\gamma$) and substituent effects are additive so that $k_{XY}/k_{HH} = 10^{-1.66(\sigma_x + \sigma_y)/2}$. For each representation, the relative rate of a suitable, unsymmetrically substituted olefin may be calculated and compared with the experimental value to determine the correct formulation. For olefin **1k** (X = $p$-NMe$_2$, Y = $p$-CN), its rate relative to the parent **1f** is predicted for the unsymmetrical case **10** to be 3.4 ($f$ = 0.3) or 2.1 ($f$ = 0.5), but 1.4 for the symmetrical case **11**. The experimental value of 1.45 is consistent only with a symmetrical transition state.[29] As anticipated from this conclusion, a plot of the logarithm of the relative rate against the sum of $\sigma$ correlates all compounds including unsymmetrical examples ($r$ = 0.999) with a resultant $\rho_\gamma$ of $-0.82$ (Figure 2). These observations militate against the radical and zwitterionic mechanisms and point to symmetrical transition states such as **7**, **8**, or **9**. Although we have successfully restricted the mechanistic possibilities for the cycloaddition of $^1O_2$ to **1**, the different behavior of the 2-aryl-1,4-dioxenes[1b] indicates that these conclusions need not be general for all vinylene diethers. Furthermore, oxygenation by electron transfer is possible under appropriate conditions and is described in the following paper.

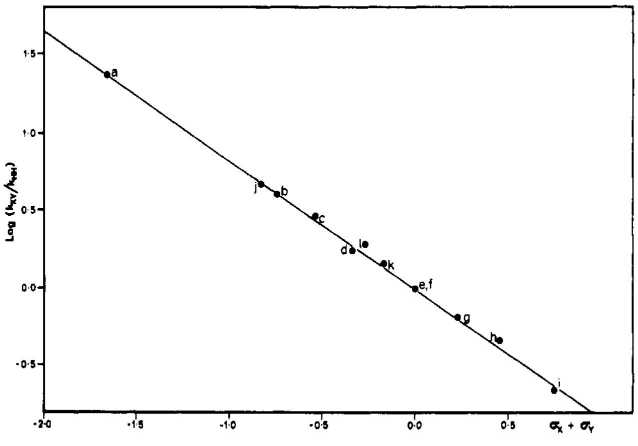


**Figure 2.** Plot of the logarithm of the relative rates for reaction of **1** with $^1O_2$ against the sum of the Hammett substituent constants $\sigma_x$ and $\sigma_y$.

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(29) *f* would have to assume the unrealistic value of 0.8 to predict a relative rate of 1.45 on the basis of a one-terminus mechanism.
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## Mechanisms of Photooxygenation. 2. Formation of 1,2-Dioxetanes via 9,10-Dicyanoanthracene-Sensitized Electron-Transfer Processes

*Sir:*

Electron-transfer quenching of singlet excited sensitizers by olefins has recently received considerable attention.[1] Radical-ion intermediates have been characterized by transient absorption spectroscopy[2] and CIDNP methods.[3] 9,10-Dicyanoanthracene (DCA) is a typical sensitizer for photogeneration of radical ions. Electron-transfer quenching of the fluorescence of DCA by a variety of substrates has been postulated from correlations of quenching rate constants and free energies of electron transfer,[4] from solvent dependent exciplex emissions,[4a] and on the basis of distinctive photochemistry.[5]

We now provide direct evidence for the photochemical formation of the DCA radical anion (DCA$^{-}\cdot$) with the observation of the ESR spectrum of this species upon irradiation of solutions of DCA and various quenchers in deoxygenated acetonitrile.[6] Figure 1 shows an ESR spectrum obtained with 1,1-diphenylethylene (**1**). The spectrum is identical with that reported by Brunner and Dörr for DCA$^{-}\cdot$ prepared by metal/ammonia reduction.[7] Under conditions of high modulation, the spectrum becomes similar to that obtained by Happ and Janzen following addition of cyanide ion to an air-saturated solution of 9-cyanoanthracene.[8] The ESR spectrum of DCA$^{-}\cdot$ was also obtained upon electrochemical reduction of DCA[9,10] or on irradiation of DCA in the presence of quenchers **2–6a–d** (Chart I), all of which can reduce singlet excited DCA exothermically.[11] Additionally, DCA$^{-}\cdot$ could be photogenerated in dichloromethane and acetone in the presence of **6a**.

The radical cation of the quencher should also be a primary product of electron transfer to singlet excited DCA (Scheme I, eq 3). We have characterized by ESR spectroscopy a variety of radical cations of the general structure **6** produced by electrochemical oxidation[12] or by chemical oxidation with tris(*p*-bromophenyl)ammoniumyl tetrafluoroborate (**7**).[13] Although ESR signals due to **6**$^{+}\cdot$ are readily detected, we have so far been unable to observe them upon irradiation of mixtures of DCA and **6**.[14] Flash experiments with 1,1-diphenylethylene (**1**) and the related sensitizer methyl *p*-cyanobenzoate[2] are, however, reported to result in a transient absorption ascribable to **1**$^{+}\cdot$.

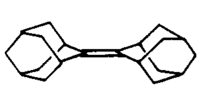
While the photochemical generation of DCA$^{-}\cdot$ is of general significance to electron-transfer quenching, it is particularly relevant to the mechanism of DCA-sensitized photooxygenation recently proposed by Foote.[5a] A related reaction had been described earlier by Farid.[5b,15] Foote observed carbonyl products suggestive of 1,2-dioxetane intermediates when olefins were photooxygenated under these conditions. We find that oxygenation of olefins of structure **6** using DCA or 9,10-dicyano-2-methylanthracene (MeDCA) as sensitizers leads to substantial yields of 1,2-dioxetanes.[16] Figure 2 shows the time evolution of the photooxygenation of **6a** using MeDCA in acetone. It is evident that, unless the MeDCA is efficiently quenched by the olefin, it sensitizes the cleavage of the 1,2-dioxetane[17] which can therefore escape observation. In another experiment **6a** yielded 45% dioxetane (characterized by $^{1}$H NMR spectroscopy and chemiluminescence[18]), whereas the yields were 53% with **6e** and 61% with **6f**. Pho-

**Chart I**

$(p\text{-MeOC}_6\text{H}_4)_2\text{C}{=}\text{CH}_2$ **2**

$\text{Ph}_2\text{S}$ **3**

$\text{Ph}_2\text{C}{=}\text{CPh}_2$ **4**



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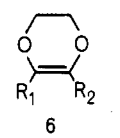


6

a, $R_1{=}R_2{=}\underline{p}\text{-MeOC}_6\text{H}_4$
b, $R_1{=}R_2{=}$2-naphthyl
c, $R_1{=}\text{H}$; $R_2{=}\text{C}_6\text{H}_5$
d, $R_1{=}\text{C}_6\text{H}_5$; $R_2{=}$2-(6-dimethylaminonaphthyl)
e, $R_1{=}R_2{=}\underline{m}\text{-MeOC}_6\text{H}_4$
f, $R_1{=}R_2{=}\underline{p}\text{-MeC}_6\text{H}_4$

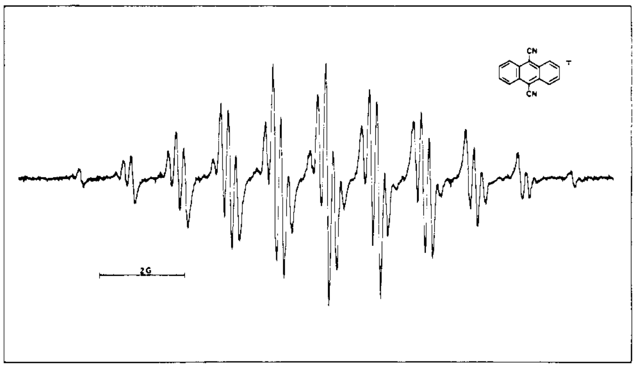
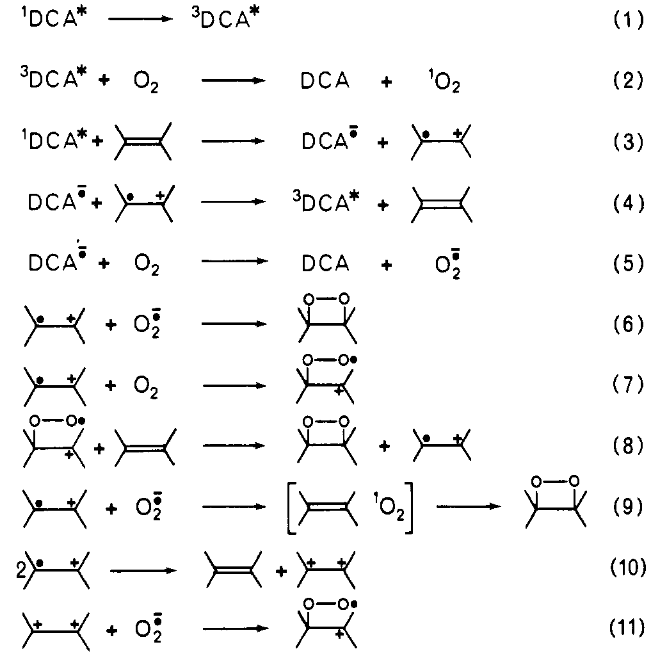


**Figure 1.** ESR spectrum of DCA$^{-}\cdot$ obtained by photolysis of a solution of DCA ($5 \times 10^{-4}$ M) and 1,1-diphenylethylene ($10^{-2}$ M) in dry acetonitrile under Ar.[6]

**Scheme I**



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