

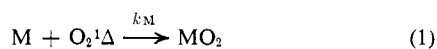
# Photoperoxidation of Unsaturated Organic Molecules. XIV. O<sub>2</sub><sup>1</sup>Δ<sub>g</sub> Acceptor Properties and Reactivity

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**Abstract:** O<sub>2</sub><sup>1</sup>Δ<sub>g</sub> reactivity indices (β) measured for naphthalene, anthracene, 1,2-benzanthracene, naphthacene, 1,2,5,6-dibenzanthracene, pentacene, and/or certain derivatives vary by six orders of magnitude in benzene at 25°. An orbital correlation through the transition state is presented for anthracene as a model acceptor in an attempt to identify those acceptor properties which contribute to the activation energy for O<sub>2</sub><sup>1</sup>Δ<sub>g</sub> addition insofar as this largely controls acceptor reactivity. It is shown that the π-relocalization energy L<sub>π</sub><sup>±</sup> provides a satisfactory reactivity parameter for unsubstituted acceptors if this is estimated as the difference in π-electron energy of the acceptor and of those odd-alternant fragments which provide electron localization at the site of O<sub>2</sub><sup>1</sup>Δ<sub>g</sub> addition, with a value of -36 kcal for the bond integral. Electron donating substituents at the site of O<sub>2</sub><sup>1</sup>Δ<sub>g</sub> addition increase acceptor reactivity in the order H < C<sub>6</sub>H<sub>5</sub> < CH<sub>3</sub>O ~ CH<sub>3</sub>, each methyl substituent producing an increase in reactivity by a factor of ~13 for anthracene.

The reactivity index β = k<sub>Δ</sub>/k<sub>M</sub> for the addition of O<sub>2</sub><sup>1</sup>Δ<sub>g</sub> to an acceptor M (process I) may be evalu-



ated directly from measurements of the quantum yield γ<sub>MO<sub>2</sub></sub> (or relative yield) of photoperoxidation as a function of acceptor concentration [M] using expression I

$$\gamma_{MO_2}([M]) = \gamma_\Delta \{k_M[M]/(k_\Delta + k_M[M])\} \quad (I)$$

in which the quantum efficiency of O<sub>2</sub><sup>1</sup>Δ<sub>g</sub> formation, γ<sub>Δ</sub>, is independent of acceptor concentration. β-Values reported for olefinic and aromatic hydrocarbon acceptors in a number of solvents range over some five orders of magnitude<sup>1</sup> and reflect variations in both k<sub>M</sub> and k<sub>Δ</sub> which in turn depend on solvent (k<sub>M</sub> and k<sub>Δ</sub>) and acceptor (k<sub>M</sub>).

Following recent determinations of the O<sub>2</sub><sup>1</sup>Δ<sub>g</sub> lifetime τ<sub>Δ</sub> (=k<sub>Δ</sub><sup>-1</sup>) in various solvents by Merkel and Kearns<sup>2</sup> and by Young and coworkers,<sup>3</sup> reactivity indices may now be converted to absolute values of the addition rate constant k<sub>M</sub> which is some three orders of magnitude lower than the diffusion-limited value even for the most reactive acceptors. Thus for rubrene (β = 10<sup>-3</sup> M) in benzene (τ<sub>Δ</sub> = 24 μsec) the addition rate constant of

$$k_M = (\beta\tau_\Delta)^{-1} = 4.2 \times 10^7 M^{-1} \text{ sec}^{-1}$$

may be compared with that of

$$k_{O_2} = 3.1 \times 10^{10} M^{-1} \text{ sec}^{-1}$$

for the oxygen quenching of the rubrene singlet state in the same solvent.<sup>4</sup>

From the data presented in part X<sup>5</sup> it is concluded that the solvent dependence of β for typical aromatic acceptors is largely accommodated by changes in τ<sub>Δ</sub>, there being little variation in k<sub>M</sub> with solvent viscosity for this bimolecular process of low encounter efficiency

(1) C. S. Foote, *Accounts Chem. Res.*, **1**, 104 (1968).

(2) P. B. Merkel and D. R. Kearns, *J. Amer. Chem. Soc.*, **94**, 7244 (1972).

(3) R. H. Young, D. Brewer, and R. A. Keller, *J. Amer. Chem. Soc.*, **95**, 375 (1973).

(4) B. Stevens and B. E. Algar, *J. Phys. Chem.*, **72**, 2582 (1968).

(5) B. Stevens and S. R. Perez, *Mol. Photochem.*, **6**, 1 (1974).

as anticipated; moreover, the relative insensitivity of k<sub>M</sub> to changes in dielectric constant of the reaction medium suggests little change in dipole moment of the reacting system along the reaction coordinate in support of a concerted addition mechanism. In this contribution, orbital and state correlations are used to define the reaction free energy profile in an attempt to identify those acceptor properties which determine reactivity toward O<sub>2</sub><sup>1</sup>Δ<sub>g</sub> addition.

## Experimental Section

β-Values for the reactive acceptors rubrene and 9,10-dimethylanthracene (DMA) were estimated directly from measurements of relative quantum yields of acceptor consumption<sup>6</sup> using a form of eq I. In each case the acceptor was excited directly (rubrene at 546 nm and DMA at 365 nm) to act as its own sensitizer and the change in its concentration was limited to ~2% of the dissolved oxygen concentration which may be assumed constant as required for use of eq I; no reaction was observed in the absence of oxygen. The subsequent use of rubrene as a reference acceptor necessitated the determination of its reactivity with relatively high precision; to this end Pyrex cylindrical cells of 1-, 2-, 5-, 10-, and 20-mm path length (and 2-cm diameter) from Precision Cells, Inc., were used for solution of different initial concentrations to provide a uniform initial optical density and so avoid Beer-Lambert conversions of relative rates to relative quantum yields.

For less reactive acceptors of higher solubility, or those which exhibit photodimerization when excited directly, β-values were estimated by competitive methods<sup>7</sup> with rubrene (R) as a reference acceptor, excited selectively at 546 nm. The dynamic competition technique is based on measurements of the initial rate of rubrene consumption as a function of competitor concentration [M] expressed by eq II, where use of the same (initial) rubrene concentra-

$$-d[R]/dt = I_a\gamma_\Delta \{k_R[R]/(k_\Delta + k_R[R] + k_M[M])\} \quad (II)$$

tion ensures invariance of the initially absorbed light intensity I<sub>a</sub>, and the reactivity index β<sub>M</sub> of the additive is obtained from a plot of reciprocal rate against additive concentration as

$$\text{intercept/slope} = \beta_M(1 + [R]/\beta_R)$$

together with known values of the concentration and β-value of the reference acceptor rubrene; the use of rubrene concentrations [R] ≪ β<sub>R</sub> where possible minimizes the overall error in β<sub>M</sub>.

A "static" competition technique<sup>7</sup> was adopted for the estimation of β-values for the less reactive acceptors, 1,4-dimethylnaphthacene, 1,2-benzanthracene, and 1,2,5,6-dibenzanthracene, using anthracene

(6) B. Stevens and B. E. Algar, *J. Phys. Chem.*, **72**, 3468 (1968).

(7) T. Wilson, *J. Amer. Chem. Soc.*, **88**, 2898 (1966).

**Table I.** Reactivity Indices ( $\beta$ ), Rate Constants ( $k_M$ ), and Relative Activation Energies ( $E_F^\ddagger$ ) for  $O_2^1\Delta_g$  Addition in Benzene at 25°

Acceptor	$10^3\beta$ (M)	$10^{-6}k_M^a$ ( $M^{-1} \text{sec}^{-1}$ )	$E_F^\ddagger^b$ (kcal/mol)
1,4-Dimethylnaphthalene <sup>c</sup>	3400 ± 1400 <sup>e</sup>	0.012	7.6
Anthracene (A)	270 ± 50 <sup>e</sup> (570, <sup>h</sup> 420 <sup>i</sup> )	0.15	6.1
9-Phenyl-A	100 ± 20 <sup>e</sup>	0.42	5.5
9,10-Diphenyl-A	35 ± 10 <sup>e</sup> (45, <sup>h</sup> 47, <sup>i</sup> 40 <sup>j</sup> )	1.2	4.9
9-Methyl-A	13 ± 3 <sup>e</sup>	3.2	4.3
9,10-Dimethyl-A	2.0 ± 0.5 <sup>d</sup> (0.3 <sup>k</sup> )	21	3.1
9-Methoxy-A	17 ± 5 <sup>e</sup>	2.5	4.5
9,10-Dimethoxy-A	3.0 ± 0.8 <sup>f</sup>	14	3.4
1,2-Benzanthracene (BA)	870 ± 250 <sup>e</sup>	0.048	6.7
9,10-Dimethyl-BA	3.0 ± 1.0 <sup>f</sup> (0.7 <sup>k</sup> )	14	3.4
Naphthacene	3.4 ± 0.9 <sup>f</sup> (1.7 <sup>k</sup> )	12	3.5
Rubrene	1.0 ± 0.1 <sup>d</sup> (1.7, <sup>i</sup> 0.3 <sup>k</sup> )	42	2.8
1,2,5,6-Dibenz-A <sup>c</sup>	4400 ± 1600 <sup>e</sup>	0.0095	7.8
Pentacene	0.010 ± 0.002 <sup>m</sup>	4200	0.0
DPBF <sup>l</sup>	0.060 ± 0.005 <sup>f</sup> (0.041 <sup>n</sup> )	700	1.1

<sup>a</sup> Calculated from  $\beta$  using value<sup>2</sup> for  $\tau_\Delta = 24 \mu\text{sec}$ . <sup>b</sup> Relative to the value for pentacene. <sup>c</sup> Solvent cyclohexane. <sup>d</sup> Directly from eq I. <sup>e</sup> From eq II with rubrene as a reference acceptor. <sup>f</sup> From eq III with rubrene as a reference acceptor. <sup>g</sup> From eq III with anthracene as a reference acceptor. <sup>h</sup> R. Livingston and V. S. Rao, *J. Phys. Chem.*, **63**, 794 (1959). <sup>i</sup> E. J. Bowen and D. W. Tanner, *Trans. Faraday Soc.*, **51**, 475 (1955). <sup>j</sup> From  $\gamma_{MO_2}$  ( $[O_2]$ ) ref 15. <sup>k</sup> From  $\gamma_{MO_2}$  ( $[O_2]$ ) ref 14. <sup>l</sup> 1,3-Diphenylisobenzofuran. <sup>m</sup> From eq IIIa with DPBF as a reference acceptor and  $p\beta = 4 \times 10^{-6} M$ . <sup>n</sup> In benzene:methanol (4:1).<sup>3</sup> <sup>o</sup> From eq III with naphthacene as a reference acceptor.

as a secondary reference acceptor. This relies on the use of the integrated form (III) of the combined rate expressions

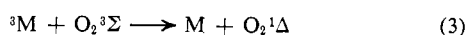
$$\log \left( \frac{[M]_0/[M]_t}{[R]_0/[R]_t} \right) = (\beta_R/\beta_M) \log \left( \frac{[R]_0/[R]_t}{[M]_0/[M]_t} \right) \quad (\text{III})$$

$$-d[M]/dt = k_M[M][O_2^1\Delta]$$

$$-d[R]/dt = k_R[R][O_2^1\Delta]$$

where initial  $[ ]_0$  and subsequent  $[ ]_t$  concentrations of reference acceptor R and competitor M are computed from electronic absorption spectra of the mixed solution before and after irradiation. Since this technique does not require controlled exposure, it is useful for dilute solutions of relatively unreactive acceptors and for acceptors of low solubility (pentacene) or available in small quantities (9,10-dimethoxyanthracene); it is, however, limited to pairs of acceptors which differ in reactivity by no more than an order of magnitude for which reason it was necessary to use 1,3-diphenylisobenzofuran (DPBF) as a reference acceptor for pentacene as described below.

**1,3-Diphenylisobenzofuran (DPBF).** Following Wilson's observation<sup>7</sup> that the self-sensitized photoperoxidation of DPBF cannot be completely inhibited by 2,3-dimethylbutene-2, Olmsted and Akashah<sup>8</sup> have shown that the quantum yield of the uninhibited reaction becomes independent of DPBF concentration when this is reduced to  $\lesssim 10^{-6} M$  and suggest that this results from direct addition of the unexcited oxygen molecule to the excited singlet state of DPBF. This behavior has been confirmed and interpreted<sup>9</sup> in terms of a reencounter reaction of  $O_2^1\Delta$  and acceptor molecules generated in the same triplet-triplet annihilation act (eq 3) with a



probability,  $p$ , which leads to an additional term  $p\beta$  in the quantum yield expression. Equation I now becomes<sup>9</sup>

$$\gamma_{MO_2}([M]) = \gamma_T \{ [M] + p\beta \} / \{ [M] + \beta \} \quad (\text{Ia})$$

where  $\gamma_T$ , the quantum yield of triplet state formation, is equal to  $\gamma_\Delta$  if oxygen quenching of the triplet state (process 3) is complete, and for benzene at 25°  $p\beta$  has a value of  $4 \times 10^{-6} M$  which is independent of acceptor ( $p$  varies as the reaction probability per encounter which is inversely proportional to  $\beta^9$ ); this term becomes significant therefore only in dilute solutions of acceptor undergoing direct excitation. Accordingly the reactivity index  $\beta_{DPBF}$  in benzene was measured relative to that for rubrene (at  $10^{-4} M$ ) by selective excitation of rubrene (R) at 546 nm; the value of  $\beta_R/\beta_{DPBF} = 16.5 \pm 1.5$  obtained using eq III compares favorably with that of 17.3 reported for these acceptors in pyridine<sup>7</sup> in support of the con-

clusion<sup>5</sup> that  $k_M$  (process 1) is essentially independent of solvent for a given acceptor.

**Pentacene (P)** undergoes rapid bleaching when exposed to light in air-saturated solutions at low concentrations where photodimerization is expected to be insignificant but is photochemically stable to visible light in the absence of oxygen.<sup>10</sup> Control experiments showed that pentacene consumption in air-saturated benzene solutions is negligible (<1%) during a dark period of ten reaction half-lives, indicating that autoperoxidation does not contribute significantly to the observed photochemical reaction rate.<sup>11</sup> Qualitative observations that pentacene ( $10^{-6} M$ ) inhibits the photoperoxidation of DPBF excited at 410 nm indicate that pentacene reacts with  $O_2^1\Delta_g$  and the ability of pentacene to sensitize the photoperoxidation of DPBF (see below) demonstrates that pentacene is a photochemical source of  $O_2^1\Delta_g$ . However, process 3 is almost certainly endothermic in this case,<sup>12</sup> and although oxygen quenches the pentacene triplet state with a rate constant of  $1.66 \times 10^9 M^{-1} \text{sec}^{-1}$  in benzene,<sup>13</sup> the possibility remains that this does not involve energy transfer and that the pentacene singlet state is the direct precursor<sup>7</sup> of  $O_2^1\Delta_g$ .

The reactivity of pentacene toward  $O_2^1\Delta_g$  addition was estimated relative to that of DPBF in benzene from recordings of the absorption spectrum of a mixed solution in a 10-cm cell before and after various exposures to light absorbed by pentacene only; control experiments confirmed that DPBF consumption was negligible in the absence of pentacene under otherwise identical conditions. Since the initial concentration of pentacene ( $1.0 \times 10^{-6} M$ ) estimated from the published absorption spectrum<sup>10</sup> is less than the value of the reencounter term  $p\beta$  in this solvent, the appropriate form of eq III is

$$\ln \left( \frac{[P]_0 + p\beta_P}{[P]_t + p\beta_P} \right) = \frac{\beta_{DPBF}}{\beta_P} \ln \left( \frac{[DPBF]_0}{[DPBF]_t} \right) \quad (\text{IIIa})$$

under the conditions employed,  $[DPBF]_0 \sim 10^{-6} M \ll \beta_{DPBF} = 6 \times 10^{-6} M$ . The mean of six independent determinations of  $\beta_{DPBF}/\beta_P = 6 \pm 1$  is used to obtain the value of  $\beta_P$  reported in Table I.

With the exception of 9-methoxy- and 9,10-dimethoxyanthracene donated by Dr. Henri Bouas-Laurent, the acceptors used were of the highest purity available from commercial sources. All measurements were made on air-saturated solutions of benzene (MCB spectroquality reagent) at  $25 \pm 1^\circ$  except for 1,4-dimethylnaphtha-

(10) C. Hellner, L. Lindquist, and P. C. Roberge, *J. Chem. Soc., Faraday Trans. 2*, **68**, 1928 (1972).

(11) We appreciate the suggestion by a referee that this possibility, together with the use of DPBF as a reference acceptor in view of ref 8, be examined.

(12) N. E. Geacintov, J. Burgos, M. Pope, and C. Strom, *Chem. Phys. Lett.*, **11**, 504 (1971), conclude that the pentacene triplet state energy is  $6500 \text{ cm}^{-1}$  in a doped naphthacene crystal.

(13) O. L. J. Gijzeman, F. Kaufman, and G. Porter, *J. Chem. Soc., Faraday Trans. 2*, **69**, 708 (1973).

(8) J. Olmsted III, and T. Akashah, *J. Amer. Chem. Soc.*, **95**, 6211 (1973).

(9) B. Stevens, J. A. Ors, and M. L. Pinsky, *Chem. Phys. Lett.*, **27**, 157 (1974).

lene and 1,2,5,6-dibenzanthracene where relative  $\beta$ -values measured in cyclohexane (MCB spectroquality) are assumed to be independent of solvent.<sup>6</sup>

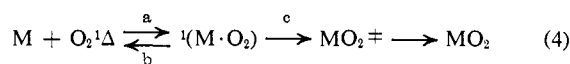
## Results

Reactivity indices,  $\beta$ , for the aromatic acceptors indicated are listed in Table I together with corresponding values for the rate constant  $k_M$  computed from the reported value of 24  $\mu\text{sec}$  for  $\tau_\Delta$  in benzene;<sup>2</sup> activation energies for  $\text{O}_2^1\Delta_g$  addition relative to that for pentacene are also tabulated on the assumption of a constant entropy term. For certain acceptors, notably rubrene and 9,10-dimethylantracene, the reported  $\beta$ -values exceed by a factor of  $\geq 3$  those previously obtained indirectly<sup>14</sup> from measurements of  $\gamma_{\text{MO}_2}$  as a function of dissolved oxygen concentration at a single acceptor concentration; this is attributed to the insensitivity of the term in  $[M]$  (eq I) on acceptor concentration when this differs appreciably from  $\beta$  since excellent agreement is found for the  $\beta$ -value of 9,10-diphenylantracene estimated directly and indirectly<sup>15</sup> from  $\gamma_{\text{MO}_2}([\text{O}_2])$  at a concentration of  $\beta/2$ . The relative reactivities of 9,10-dimethylantracene (1.0), 9,10-diphenylantracene (0.06), rubrene (2.0), and DPBF (33.3) are in fair agreement with those of 1.0:0.2:2.25:38.5 reported for these compounds in pyridine solution.<sup>7</sup>

The following points are noted in connection with the data tabulated: (a) reactivities and rate constants vary by almost six orders of magnitude, (b)  $k_M$  increases with substitution of electron-releasing groups at the sites of  $\text{O}_2$  addition in the order  $\text{H} < \text{C}_6\text{H}_5 < \text{CH}_3 \sim \text{OCH}_3$  reflecting the electrophilic nature of  $\text{O}_2^1\Delta_g$ , (c) the effect of one or two identical substituents at the reaction sites on the logarithm of the rate constant  $k_M$  (for anthracene), or the activation energy, is approximately additive, consistent with the concerted nature of the reaction.

## Discussion

The relatively low encounter efficiency of  $\text{O}_2^1\Delta_g$  addition is accommodated by a reversible formation of the initial complex  $^1(\text{MO}_2)$  in the detailed reaction sequence (4) proposed by Koch<sup>16</sup> which leads to expression



IV for the experimental rate constant if  $k_c \ll k_b$  and

$$k_M = k_a k_c / (k_b + k_c) \sim K_{ab} k_c \quad (\text{IV})$$

$K_{ab}$  ( $=k_a/k_b$ ) describes the formation of a weak encounter complex ( $\Delta H_{ab} \sim 0$ ). If this complex has the appropriate configuration for formation of the peroxide  $\text{MO}_2$  via the transition state  $\text{MO}_2^\ddagger$ , the activation entropy  $\Delta S^\ddagger$  will be close to zero and eq IV may be formulated thermodynamically as

$$k_M = (ekT/h) \exp(\Delta S_{ab}/R) \exp(-E_F^\ddagger/RT) \quad (\text{V})$$

where  $e$ ,  $k$ ,  $h$ , and  $R$  have their usual significance and  $E_F^\ddagger$  is an activation energy. From an analysis of the temperature dependence of  $\beta$ , Koch<sup>16</sup> finds that the entropy term  $\Delta S_{ab}$  is approximately constant at  $-15.6 \pm 1.0$  eu for a series of five cyclic conjugated dienes (Table 5 of ref 16) which form transannular

peroxides ( $\Delta S_{ab}$  varies from  $-12$  to  $-18$  eu if hydroperoxide forming acceptors are included) and attributes the variation in  $\beta$  to differences in activation energy. We therefore proceed on the tentative assumption<sup>17</sup> that  $E_F^\ddagger$  is the dominant factor in determining the magnitude of the rate constant  $k_M$  for aromatic acceptors in order to identify those acceptor properties which influence their reactivity toward  $\text{O}_2^1\Delta_g$  addition. To this end the reaction energy profile is sketched from thermodynamic data, following which orbital correlations are presented and the transition state energy estimated as the sum of doubly-occupied orbital energies in the assumed configuration using anthracene as a model acceptor.

**The Reaction Energy Profile.** The standard heats of formation of anthracene and its transannular peroxide have reported values of 30 and 20 kcal/mol, respectively,<sup>18</sup> in which case, since  $\text{O}_2^1\Delta_g$  lies at 23 kcal/mol above its (standard)  $\text{O}_2^3\Sigma_g^-$  ground state, the overall reaction enthalpy is given by

$$-33 \text{ kcal/mol} = \Delta H = E_F^\ddagger - E_R^\ddagger$$

The activation energy  $E_R^\ddagger$  for the reverse dissociation of peroxide to anthracene and  $\text{O}_2^1\Delta_g$  must exceed the O-O bond energy of  $\sim 34$  kcal/mol<sup>19</sup> by at least  $\sim 4$  kcal/mol since rupture of the peroxide bond is the dominant mode ( $\geq 99\%$ ) of anthracene peroxide decomposition.<sup>20</sup>  $E_F^\ddagger$  is therefore estimated to be at least  $\sim 5$  kcal/mol consistent with the experimental limit of  $E_F^\ddagger \geq 6.1$  kcal/mol (Table I).

**Orbital Correlations.** It is assumed that the encounter complex  $^1(\text{M}\cdot\text{O}_2)$  and transition state  $\text{MO}_2^\ddagger$  configurations are identical and indistinguishable from that of the transannular peroxide  $\text{MO}_2$  except that the benzene rings are coplanar. All three species then belong to the  $C_{2v}$  point group. However, the orbital correlations are examined at two levels of symmetry as follows.

Of the 14  $\pi_C$  orbitals of anthracene, 12 are converted to  $\pi_C$  orbitals of two benzene rings and do not participate in localized  $\sigma$ -bond formation; if these are treated in the full  $D_{2h}$  symmetry of the anthracene  $\pi$ -electron system, the anthracene  $\pi$ -orbitals  $\psi_1$  to  $\psi_6$  and  $\psi_9^*$  to  $\psi_{14}^*$  correlate smoothly with the 12 symmetry-adapted linear combinations of benzene orbitals  $\psi_1^\pm$  to  $\psi_3^\pm$  and  $\psi_4^{*\pm}$  to  $\psi_6^{*\pm}$  (the asterisk denotes antibonding), leaving  $\psi_7$  (HOMO) and  $\psi_8^*$  (LUMO) of anthracene available for interaction with  $\text{O}_2^1\Delta_g$ . This redistribution of 12  $\pi_C$  electrons contributes a term to the reaction enthalpy (VI) where  $L_\pi$  is the paraloocalization energy used by

$$\Delta H_\pi = 2E_\pi(\text{C}_6\text{H}_6) - E_\pi(\text{C}_{14}\text{H}_{10}) + 2E_\pi(\psi_7) = L_\pi + 2E_\pi(\psi_7) \quad (\text{VI})$$

Brown<sup>21</sup> to describe the acceptor dependence of equilibrium constant for maleic anhydride addition. Chalvet, *et al.*,<sup>17</sup> have shown that  $L_\pi$  is not a satisfactory parameter for the interpretation of substituent effects on the site of  $\text{O}_2^1\Delta_g$  attack which must reflect changes in

(17) O. Chalvet, R. Daudel, C. Ponce, and J. Rigaudy, *Int. J. Quantum Chem.*, **2**, 521 (1968).

(18) J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds," Academic Press, New York, N. Y., 1970.

(19) K. S. Pitzer, *J. Amer. Chem. Soc.*, **70**, 2140 (1948).

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(21) R. D. Brown, *J. Chem. Soc.*, 1955 (1951).

(14) B. E. Algar and B. Stevens, *J. Phys. Chem.*, **74**, 3029 (1970).

(15) B. Stevens and L. E. Mills, *Chem. Phys. Lett.*, **15**, 381 (1972).

(16) E. Koch, *Tetrahedron*, **24**, 6295 (1968).

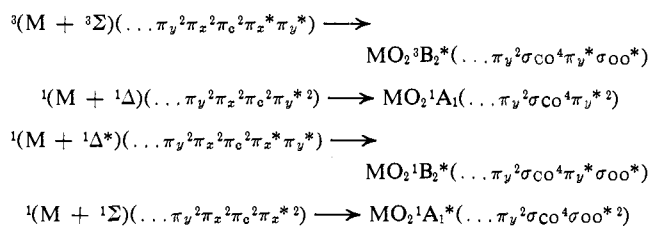
$E_F^\ddagger$  and  $k_M$ ; accordingly the contribution of  $\pi_C$  redistribution to the overall activation energy is given as

$$E_F^\ddagger = L_\pi^\ddagger + 2E(\psi_7) \quad (\text{VII})$$

where  $L_\pi^\ddagger$  is the energy required to localize two  $\pi$  electrons in  $\psi_7$  at the site of  $O_2^1\Delta_g$  attachment as discussed later.

The orbital correlation diagram for  $O_2^1\Delta_g$  addition to anthracene is constructed in the reduced  $C_{2v}$  symmetry of this system. The orbitals of interest and their transformation properties are  $\psi_7$  ( $b_1$ ) and  $\psi_8^*$  ( $a_1$ ) of anthracene together with the  $\sigma_{OO}$  ( $a_1$ ),  $\sigma_{OO}^*$  ( $b_1$ ),  $\pi_x$  ( $a_1$ ),  $\pi_y$  ( $b_2$ ),  $\pi_x^*$  ( $b_1$ ), and  $\pi_y^*$  ( $a_2$ ) orbitals of oxygen and symmetry-adapted linear combinations  $\sigma_{CO} \pm \sigma_{CO}$  ( $a_1, b_1$ ) and  $\sigma_{CO}^* \pm \sigma_{CO}^*$  ( $a_1, b_1$ ) of  $\sigma_{CO}$  orbitals in the peroxide (and transition state). The following points are noted in connection with the  $\sigma$  orbital correlation diagram shown in Figure 1. (a) The lifting of the  $\pi_{x,y}^*$  orbital degeneracy in the encounter complex is shown as an increase in the  $\pi_x^*$  orbital energy with that of  $\pi_y^*$  unchanged (Kearns case I<sup>22</sup>) since  $\pi_y^*$  and  $\pi_C$  belong to different symmetry species. (b) Orbital energies in units of the resonance integral  $K^{23}$  are obtained from simple Huckel MO calculations based on the following parameters<sup>21,22</sup>:  $J_0 = J_C + 1.5K_{CC}$ ;  $K_{OO}(\pi) = K_{CC}$ ;  $K_{OO}(\sigma) = 1.5K_{CC}$ .  $K_{CO}$  and  $K_{CO}^\ddagger$  are treated as adjustable parameters. (c) Application of the noncrossing rule leads to the ultimate correlation of  $\pi_x^*$  ( $b_1$ ) with  $\sigma_{OO}^*$  ( $b_1$ ) rather than with  $\sigma_{CO}^*$  ( $b_1$ ).

If the behavior of the low-lying electronic states of molecular oxygen in the encounter complex is described in terms of nondegenerate  $\pi_{x,y}^*$  orbital occupancy,<sup>22</sup> these complexes correlate with different electronic states of the peroxide as follows



where electronic configurations are included parenthetically. As in the case of nonaromatic acceptors,<sup>22</sup> only  $(M + O_2^1\Delta_g)$  correlates (exothermically) with the peroxide  $^1A_1$  ground state and since  $O_2^1\Delta_g$  is distinguishable from  $O_2^1\Delta_g^*$  only in complex formation,  $k_M$  must include an orbital statistical factor<sup>24</sup> of  $1/2$ . The inclusion of this factor in eq V leads to the experimental rate constant  $k_M$  tabulated for the most reactive acceptor (pentacene) with  $E_F^\ddagger = 0$  and  $\Delta S_{ab} = -15.6$  eu, and, since  $-\Delta S_{ab}$  is unlikely to be significantly lower than 15.6 eu, we conclude that  $E_F^\ddagger$  is close to zero for pentacene and that the relative activation energies tabulated for the less reactive acceptors are close to the true values. In this respect it is noted that Koch<sup>16</sup> finds that  $E_F^\ddagger = 0.7$  kcal/mol for DPBF although his reported  $\beta$ -value for this acceptor at 20° is two orders of magnitude larger than that reported here and

(22) D. R. Kearns, *J. Amer. Chem. Soc.*, **91**, 6554 (1969).

(23) To avoid confusion with the reactivity parameter  $\beta$ ,  $J$ , and  $K$  are used here to denote coulomb and resonance integrals.

(24) On the assumption that complex  $(M \cdot ^1\Delta_g)$  and  $(M \cdot ^1\Delta_g^*)$  are formed with equal encounter probability from  $M + O_2^1\Delta_g$ .

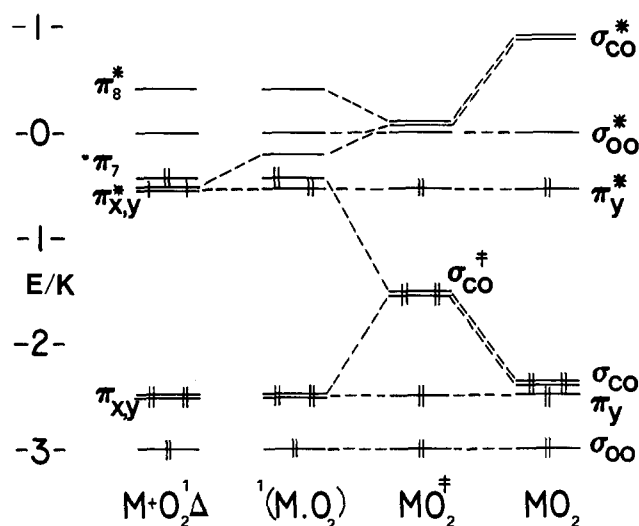


Figure 1.  $\sigma$ -Orbital correlation diagram for  $O_2^1\Delta_g$  addition to anthracene via transition state  $MO_2^\ddagger$  ( $C_{2v}$  symmetry with twofold  $x$  axis).

elsewhere,<sup>2,25</sup> whereas Wilson<sup>26</sup> finds that  $E_F^\ddagger$  is on the order of 1 kcal/mol for rubrene if it may be assumed that  $\tau_\Delta$  is temperature independent.

The orbital occupancies indicated in Figure 1 for the formation of the  $MO_2^1A_1$  ground state from anthracene and  $O_2^1\Delta_g$  permit the computation of the corresponding contributions to the reaction enthalpy and activation energy as the difference in closed-shell orbital energies of initial, final, and transition states; these are

$$\Delta H_\sigma = 4\sigma_{CO} - 2\pi_x - 2E_\pi(\psi_7) - E_\Delta \quad (\text{VIII})$$

$$E_\sigma^\ddagger = 4\sigma_{CO}^\ddagger - 2\pi_x - 2E_\pi(\psi_7) - E_\Delta \quad (\text{IX})$$

which in combination with eq VI and VII provide the following relationships for the overall quantities

$$\Delta H = \Delta H_\pi + \Delta H_\sigma = L_\pi + 4\sigma_{CO} - 2\pi_x - E_\Delta \quad (\text{X})$$

$$E_F^\ddagger = E_\pi^\ddagger + E_\sigma^\ddagger = L_\pi^\ddagger + 4\sigma_{CO}^\ddagger - 2\pi_x - E_\Delta \quad (\text{XI})$$

$$E_R^\ddagger = L_\pi^\ddagger - L_\pi + 4(\sigma_{CO}^\ddagger - \sigma_{CO}) \quad (\text{XII})$$

where  $E_\Delta$  is the energy of  $O_2^1\Delta_g$  relative to  $O_2^3\Sigma_g^-$ .

The HMO  $\pi$ -electron energies for anthracene (19.314K) and benzene (8.000K) provide a paralogalization energy of 3.314K, or with the value  $K = -36$  kcal adopted from the variation of Diels-Alder equilibrium constant with  $L_\pi$ <sup>27</sup> eq X reduces to

$$\Delta H = 0.346K - E_\Delta \approx -35 \text{ kcal/mol}$$

when  $K_{CO}$  is assigned a value of  $1.2K_{CC}$  close to that of  $1.3K_{CC}$  previously used.<sup>17,22</sup> Chalvet, *et al.*,<sup>17</sup> have examined a transition state in which the  $\pi_x^*$  orbitals of molecular oxygen provide an extension of the acceptor  $\pi$ -electron system and successfully predict the position of  $O_2^1\Delta_g$  attachment to a particular acceptor as that which provides the largest calculated magnitude of the extended delocalization energy  $\Delta\epsilon_{id}^\ddagger$ ; however, this parameter alone fails to describe the relative reactivities of different acceptors in that the rate constant ratio

(25) R. H. Young, K. Wehrly, and R. L. Martin, *J. Amer. Chem. Soc.*, **93**, 5774 (1971).

(26) T. Wilson, *J. Amer. Chem. Soc.*, **91**, 2387 (1969).

(27) E.g., A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1961, p 433.

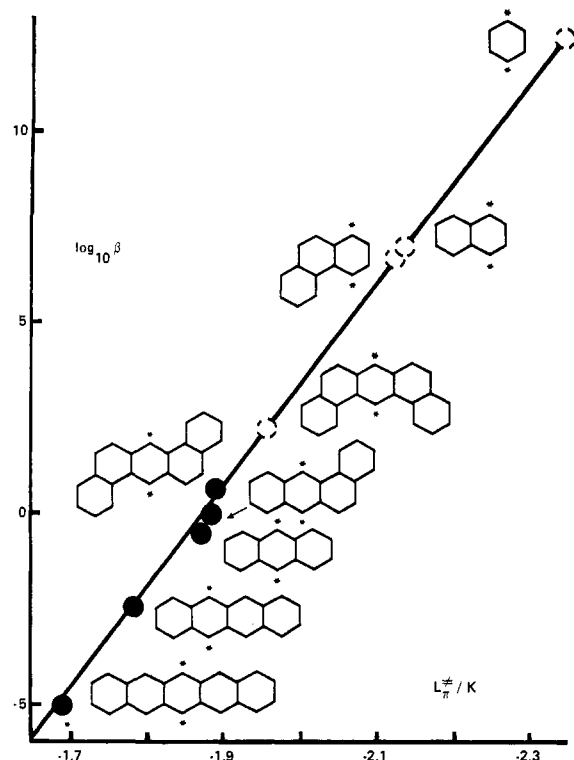


Figure 2. Plot of  $\log \beta$  against relocation energy  $L_{\pi}^{\ddagger}$  computed for  $O_2^1\Delta_g$  addition at sites indicated by asterisks: ●, experimental; ○, predicted values of  $\beta$ . Solid line drawn according to eq XIII with resonance integral  $K = -36$  kcal.

100:10:1 predicted for 9,10-dimethoxyanthracene:9,10-dimethylantracene:rubrene is at variance with the values reported here, neither does use of the paralogization energy  $L_{\pi}$  itself as a reactivity parameter account for the 250-fold difference in reactivity of the isomers naphthalene and 1,2-benzanthracene.

We examine here the approach of Dewar<sup>28</sup> in the estimation of  $L_{\pi}^{\ddagger}$  as the difference in  $\pi$ -electron energy between that of the acceptor and that of the odd-alternant radicals R and S which provide electron localization at the sites of  $O_2^1\Delta_g$  addition, *viz.*

$$L_{\pi}^{\ddagger} = E_{\pi}^R + E_{\pi}^S - E_{\pi}$$

In the case of anthracene with  $R \equiv S \equiv$  benzyl this leads to the value

$$L_{\pi}^{\ddagger} = 2(8.721)K - 19.314K = -1.872K$$

which with eq XI and XII gives

$$E_F^{\ddagger} = -0.812K - E_{\Delta} = 6.7 \text{ kcal/mol}$$

$$E_R^{\ddagger} = -1.158K \approx 42 \text{ kcal/mol}$$

if  $K_{CO}^{\ddagger}$  is adjusted to  $0.15K_{CC}$ .<sup>29</sup>

(28) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969, Chapter 6.

Insofar as the  $\sigma_{CO}^{\ddagger}$  orbital energy is constant for unsubstituted acceptors it is apparent that  $L_{\pi}^{\ddagger}$  is the major acceptor-dependent term contributing to  $E_F^{\ddagger}$ . In this case eq XI reduces to

$$E_F^{\ddagger} = L^{\ddagger} + 1.685K$$

and with eq V provides the expression (including the orbital statistical factor of  $1/2$ )

$$\log \beta = (L^{\ddagger} + 1.685K)/2.3RT - \log(ekT\tau_{\Delta}/2h) - \Delta S_{ab}/2.3R = (L^{\ddagger} + 1.685K)/2.3RT - 4.92 \quad (\text{XIII})$$

for an association entropy  $\Delta S_{ab} = -15.6$  eu with  $\tau_{\Delta} = 24 \mu\text{sec}$  in benzene<sup>2</sup> at 25°. The solid line drawn in Figure 2 according to eq XIII with a value of  $-36$  kcal for the resonance integral  $K$ , fairly describes the experimental data for unsubstituted hydrocarbons shown as solid circles and provides a basis for estimating reactivity indices for less reactive acceptors benzene ( $\beta_{\text{calcd}} \sim 10^{12} M$ ), naphthalene, and phenanthrene ( $\beta_{\text{calcd}} \sim 10^7 M$ ) shown as broken circles in Figure 2.

An examination of eq XI in the form

$$E_F^{\ddagger} = E_{\pi}^R - E_{\pi}^S - E_{\pi} + 4\sigma_{CO}^{\ddagger} - 2\pi_{OO} - E_{\Delta}$$

indicates that substituent effects on acceptor reactivity may reflect changes in  $L_{\pi}^{\ddagger}$  ( $=E_{\pi}^R + E_{\pi}^S - E_{\pi}$ ) or  $\sigma_{CO}^{\ddagger}$  or both depending on the position of the substituent relative to  $O_2^1\Delta_g$  attack, in addition to its inductive and conjugative properties. Since a variation of  $0.04K$  in  $E_F^{\ddagger}$  is sufficient to produce an order of magnitude change in  $\beta$ , a quantitative estimate of substituent effects on the energy terms contributing to  $E_F^{\ddagger}$  must await the accumulation of more experimental data. However, it may be noted that each phenyl group at the site of  $O_2^1\Delta_g$  attack on anthracene reduces the activation energy by  $0.6$  kcal/mol whereas each methyl or methoxy group leads to a reduction in  $E_F^{\ddagger}$  of  $\sim 1.5$  kcal/mol. Moreover the site of  $O_2^1\Delta_g$  addition may be predicted from estimates of  $L_{\pi}^{\ddagger}$ ; thus for 1,4-addition to anthracene,  $L_{\pi}^{\ddagger}$  (with  $R \equiv \beta$ -naphthylmethyl and  $S \equiv$  allyl) is  $\sim 3.3$  kcal/mol greater than  $L_{\pi}^{\ddagger}$  for 9,10-addition ( $R \equiv S \equiv$  benzyl), but if this reduced by  $\sim 3$  kcal/mol in the 1,4-dimethyl derivative both sites are equally reactive as evidenced by the formation of both isomeric peroxides at approximately the same rate.<sup>17</sup>

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(29) This may be compared with  $K_{CO}^{\ddagger} = 0.3K_{CC}$  adopted by Chalvet, *et al.*,<sup>17</sup> in their calculations of extended localization energies and used by Kearns<sup>22</sup> to account for ring strain in dioxetane formation.