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A Plausible Mechanism for the Chemiexcitation of Cyclic Hydrazides. The "Double-Crossing" Model

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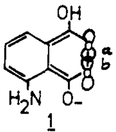
Abstract: The model suggested by Michl to rationalize the chemiexcitation in cyclic hydrazides is investigated in detail in light of recent experimental findings. An extended model is presented that identifies the decisive factors governing the mode and efficiency of chemiexcitation of these hydrazides. In addition, the role of the substituent in promoting or suppressing chemiluminescence is scrutinized.

In his discussion of the chemiluminescence of luminol Michl[1] suggested the endoperoxide **1** as the immediate precursor to the light-emitting phthalate ion and presented qualitative arguments as to why the rupture of the O–O bond should provide for an efficient mechanism of chemiexcitation. In Michl's model the endoperoxide **1** was assumed to result from a retro-Diels–Alder reaction from the alleged,[2] long assumed but never really detected, intermediate **3**.



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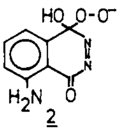

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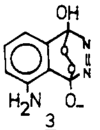

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Experiments in our laboratories[3] indicate, however, that **3** is really not a stable species at all and that it is rather a distorted variety of it which constitutes the transition state in the decomposition of the hydroperoxide **2**. Thus a direct reaction path from **2** to **1** is consistent with experiment. Experiment also clearly shows that the existence of the precursor **1** is plausible if it can be presumed to have a lifetime of no more than 10^{-6} s.

The present work will delve into the possible stability of the suggested endoperoxide **1** with respect to O–O bond stretching. From the point of view of electronic configuration the endoperoxide may be conceived of as a kind of vibrationally excited state of a doubly excited electronic state of the dicarboxylate. We shall, therefore, find it of interest to estimate the probability of a nonadiabatic transition concomitant with the O–O stretching.

In particular the question will be raised as to how the emitting state can be reached from the original doubly excited nonemitting state. It will be suggested that an orbital correlation featuring a double intersection of orbitals is essential for chemiluminescence to take place.

Detailed Presentation of the Michl Model

The principles of the simple Michl model are most clearly demonstrated with reference to a qualitative molecular orbital corelation diagram (Figure 1). In the endoperoxide, the orbital a + b is bonding while a − b is antibonding and has a much higher energy. It is therefore empty in the ground state. When the O–O distance is increased, the energies of the two orbitals will approach each other. In a rapid nonadiabatic reaction, the electrons would not have sufficient time to rearrange but would simply "slide" along the correlation curves. This would result in an empty a − b orbital while the LUMO would be doubly occupied; i.e., we would end up in a doubly excited state. This state would then be expected to decay into the corresponding singly excited state by a radiationless transition. The transition from the singly excited state to the ground state would finally be registered as chemiluminescence. Figure 2 shows the corresponding state correlation diagram. Since the ground state of the endoperoxide correlates with the doubly excited state of the 3-aminophthalate ion while the ground state of the latter correlates with a doubly excited state of the peroxide, these two curves will cross. Both of these curves are diabates since they represent a slow variation of the electronic state. Due to the noncrossing rule, the corresponding adiabatic curves will avoid each other. Thus, as Figure 2 shows, in a slow adiabatic process the endoperoxide will be converted into the ground state of the 3-aminophthalate ion while, in a rapid process, the system will instead follow the diabate, giving rise to a doubly excited state.

In order to obtain guidance regarding a possible extension and quantification of the Michl model quantum chemical calculations were carried out. For molecules of this size anything but a semiempirical method is, of course, out of the question. The method actually employed in these studies was HAM/3[4,5] (hydrogenic atoms in molecules), a novel semiempirical method that has yielded particularly promising results for ionization and excitation energies. This is, of course, of paramount importance in the construction of MO correlation diagrams. Since this method may still be fairly unknown to the general public, a short presentation may be in order.

The HAM/3 Method

The close connection between HAM and Hartree–Fock theory is described in ref 5. The main feature that distinguishes HAM from the usual semiempirical methods based on Hartree–Fock theory[6] is the addition of a term of the form

$$\tfrac{1}{2}\mathrm{Tr}[(P^2 - P)A] \qquad (1)$$

to the usual Hartree–Fock (energy) expectation value of the many-electron Hamiltonian. P is the density operator that projects onto the space spanned by the doubly occupied molecular orbitals and the operator A is defined by its matrix elements in the atomic orbital basis:

$$A_{\mu\nu} = S_{\mu\nu}[(\mu\mu|\mu\mu) + (\nu\nu|\nu\nu)] \qquad (2)$$

The added term will not change the expectation value of the energy since it is equal to zero for an idempotent projection operator, P, for which $P^2 = P$. Thus, the SCF wave function and the total energy will be invariant toward the addition of this term.

The one-electron or Fock operator, F, will, however, change and the molecular orbital functions will be slightly different The reason for this is that the Fock operator can be defined by the

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* Address Correspondence to Department of Physical Chemistry.

[1] J. Michl, *Photochem. Photobiol.*, **25**, 141 (1977).

[2] M. M. Rauhut, A. M. Semsel, and B. G. Roberts, *J. Org. Chem.*, **31**, 2431 (1966).

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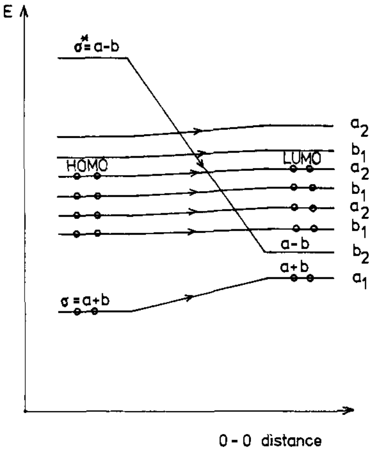


Figure 1. Qualitative MO correlation diagram of the endoperoxide–3-aminophthalate system.

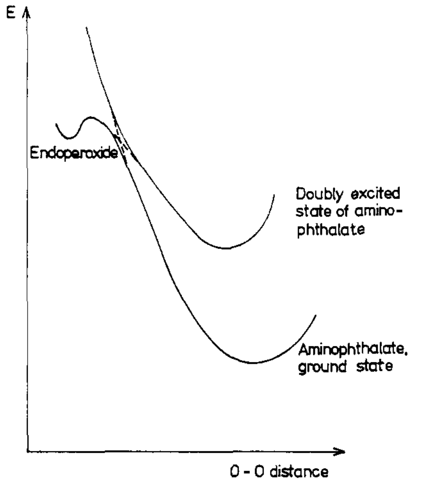


Figure 2. State correlation diagram of endoperoxide–3-aminophthalic acid according to the HAM/3 calculations.

following relation (this relation is true also in ordinary Hartree–Fock theory[6]) for the variation of the energy expectation value

$$\delta E = \delta\langle\psi_{\mathrm{SCF}}|H|\psi_{\mathrm{SCF}}\rangle = 2\sum_i^{\mathrm{occ}}(\langle\delta\psi_i|F|\psi_i\rangle + \langle\psi_i|F|\delta\psi_i\rangle) = \sum_{\mu\nu} F_{\mu\nu}\delta\rho_{\mu\nu} \equiv 2\mathrm{Tr}(\delta PF) \qquad (3a)$$

where $\rho_{\mu\nu}$ are elements of the traditional density matrix in the atomic orbital basis and P the corresponding operator (as a matter of fact, $\rho_{\mu\nu} = 2\langle\phi^{\nu}|P|\phi^{\mu}\rangle$, where the ϕ^{μ} are defined from the atomic orbitals ϕ_{ν} by the relation $\langle\phi^{\mu}|\phi_{\nu}\rangle = \delta_{\mu\nu}$):

$$P = \sum_i^{\mathrm{occ}}|\psi_i\rangle\langle\psi_i| \qquad (3b)$$

and

$$\delta P = \sum_i^{\mathrm{occ}}(|\delta\psi_i\rangle\langle\psi_i| + |\psi_i\rangle\langle\delta\psi_i|) \qquad (3c)$$

where ψ_{SCF} is a Slater determinant and the ψ_i are molecular orbitals. From this it follows[5] that

$$F_{\mu\nu} = \partial E/\partial\rho_{\mu\nu} \qquad (4)$$

Thus, the term $^1/_2\mathrm{Tr}[(P^2 - P)A]$ will give a nonzero contribution to F. The addition of this term has the interesting consequence of transforming the energy expression to a form where shielding efficiencies can be introduced analogous to those used by Slater in 1930. This formalism also permits the introduction of approximate pair correlation energies in a very natural way.

The results of HAM/3 calculations of ionization and excitation energies appear to be superior even to many results obtained by other methods with a much greater computational effort while the total electronic energy is usually less reliable. In view of the small energy differences involved the total energy data will mainly be used in a qualitative sense to support the theoretical interpretation.

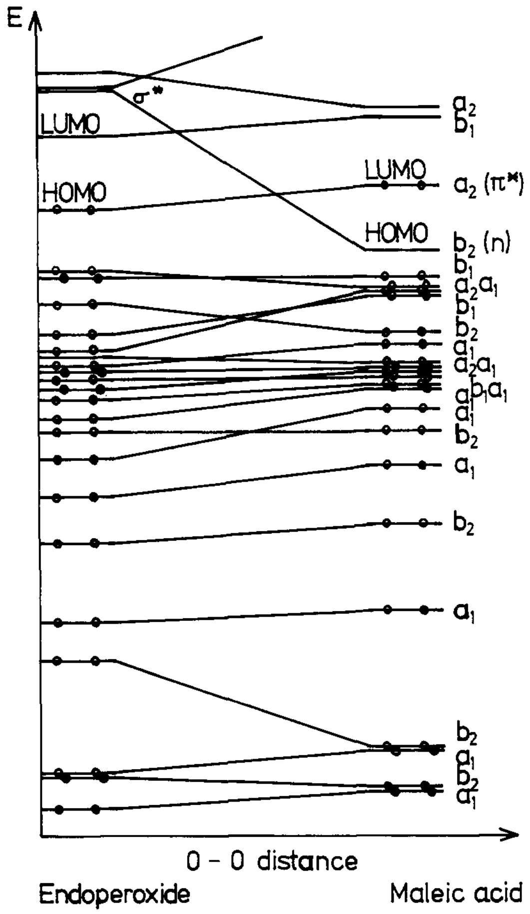
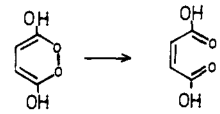


Figure 3. MO correlation diagram of the system endoperoxide–maleic acid according to the HAM/3 calculations.

In order to put the argument onto a somewhat more quantitative basis extensive HAM calculations were performed on the model system



i.e., maleic endoperoxide–maleic acid.

Computational Results

Figure 3 shows the molecular orbital correlation diagram of the system obtained from the HAM calculations when the coordinates were varied linearly from the values corresponding to the peroxide to those corresponding to maleic acid. The orbital energies shown in the diagram are those of the HAM orbitals and not of the localized orbitals usually employed in qualitative molecular orbital arguments. Since the HAM one-electron operator, F, is slightly different from the Hartree–Fock one-electron operator the molecular orbitals in HAM will not be exactly the same as in Hartree–Fock calculations. The difference is, however, as a rule, negligible for most intents and purposes.

The diagram of Figure 3 amplifies and confirms the qualitative picture of Figure 1. In particular, the σ^*(n) orbital, a − b, is easily recognizable. It has the symmetry b_2 in the C_{2v} group of the molecule. The qualitative shape of the n orbital is shown in Figure 4 together with the π^*-type orbital it crosses of symmetry a_2 (LUMO in the maleic acid). To abbreviate we will call these orbitals the i and a (n and π^*) orbitals, respectively. In a rapid adiabatic process the two electrons of the HOMO of the peroxide

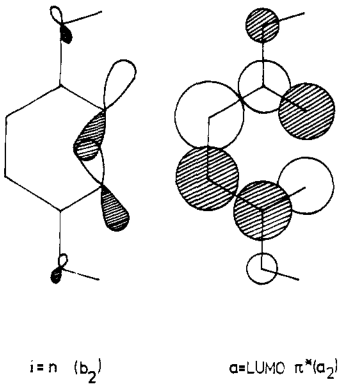


Figure 4. Shape of the n and π^* orbitals in the endoperoxide maleic acid system.

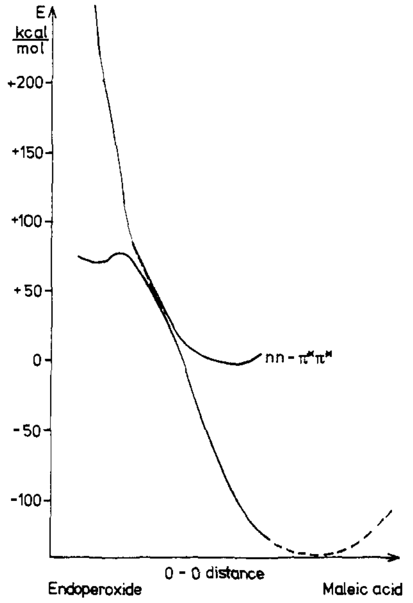


Figure 5. State correlation diagram of the endoperoxide–maleic acid system according to the HAM/3 calculations. A limited amount of configuration interaction has been applied.

will end up in the a (π^*) orbital. The transition between this orbital and the *n* orbital will be allowed since the direct product of the representations $a_2 \times b_2 = b_1$ contains the coordinate at right angles to the plane of the molecule. However, the oscillator strength will be low as is immediately obvious from the physical appearance of the orbitals. According to the HAM calculations the value of the oscillator strength would be no more than $f = 0.00153$. Since this is too small to compete with the radiationless transitions, no chemiluminescence will be observed with maleic hydrazide.

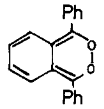
Figure 5 shows the state correlation diagram corresponding to the calculation presented in Figure 3. The adiabate that unites the ground states of the peroxide and maleic acid is pushed down by the amount $\langle\psi_0|H|\psi_{i\bar{i}\to a\bar{a}}\rangle$ where ψ_0 is the ground and $\psi_{i\bar{i}\to a\bar{a}}$ the doubly excited state, while the adiabate of the doubly excited state goes up by the same amount. For real-valued orbitals we have

$$\langle\psi_0|H|\psi_{i\bar{i}\to a\bar{a}}\rangle = K_{ia} \qquad (5)$$

where K_{ia} is the exchange integral which for the model substance was calculated to be 3.1 kcal/mol.

However, the most important result of the calculations is that there is actually a local energy minimum for the endoperoxide with a barrier height of 6 kcal/mol corresponding to a lifetime of approximatley 10^{-9} s. This is well consistent with the experimental findings.[3]

Some calculations on the model substance **5** were finally carried out in order to explain the unexpected stability of *o*-xylylene peroxide **4** observed as an intermediate by Schuster et al.[7] The lifetime estimated by these authors would require a barrier height for **4** that is much higher than 6 kcal/mol as calculated for the molecules reported above. Some rather incomplete HAM calculations actually indicated a barrier height above 12 kcal/mol for **5**.



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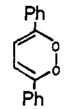

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The main reason for this difference in barrier heights between **1** and **5** seems to be that the replacement of the phenyl groups by OH increases the energy of the HOMO orbital by a few tenths of an electron volt while the energy of the σ^* orbital is lowered by approximately 1 eV. This produces a much greater configuration interaction between the ground and the doubly excited state which may lower the barrier by many kcal/mol.

Excitation Efficiencies

By use of the semiclassical Landau–Zener theory[8,9] it is possible to obtain an approximate estimate of the probability that a nonadiabatic transition to the doubly excited state of maleic acid will take place. According to this theory, the probability of a nonadiabatic transition between the two diabates corresponding to ψ_0 and $\psi_{i\bar{i}\to a\bar{a}}$ will be

$$P_{12} = \exp(-2\pi\alpha^2/h\dot{q}\Delta) \qquad (6)$$

where α is the matrix element

$$\alpha = |\langle\psi_0|H|\psi_{i\bar{i}\to a\bar{a}}\rangle| = K_{ia} \qquad (7)$$

and

$$\Delta = -\frac{\partial}{\partial q}(\langle\psi_0|H|\psi_0\rangle - \langle\psi_{i\bar{i}\to a\bar{a}}|H|\psi_{i\bar{i}\to a\bar{a}}\rangle) \qquad (8)$$

where q is the normal coordinate involving the O–O stretching vibration. As already pointed out, the matrix element α is equal to the exchange integral K_{ia} if the orbitals have real coefficients as is the case in HAM.

The value of Δ was easily obtained from the diagram setting q equal to the O–O distance. To obtain the velocity $\dot{q}$ it was assumed that $\dot{q} = 0$ at the top of the barrier with the energy E_b. We then obtain $\dot{q}$ at the energy, E_0, at the point of intersection as

$$\dot{q} = \sqrt{2(E_b - E_0)/M} \qquad (9)$$

where M is the reduced mass of the vibration. This formula presupposes that there is no attenuation of the vibration, which, of course, cannot be strictly true. If these data are inserted in the Landau–Zener formula, the probability of a nonadiabatic transition is found to be 24%, which yields an adequate population of the doubly excited state.

Some Problems in MO Theory

At this point it may be worthwhile to digress for a moment on some of the special problems associated with the construction of MO correlation diagrams for this type of processes. In the single-configuraiton SCF model each electron is assumed to move in the average field of the other electrons. When the HOMO and the LUMO intersect this average field will undergo an abrupt change from the point of view of the other electrons in the molecule. This means that the other molecular orbitals will also change abruptly if they are defined as solutions of the single-determinant SCF iteration. This may cause identification problems if the orbital energies are densely distributed, the whole concept of orbital correlation being based on the assumption of

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(7) J. P. Smith, A. K. Schrock, and G. B. Schuster, *J. Am. Chem. Soc.*, **104**, 1041 (1982).

(8) L. Landau, *Phys. Z. Sowjetunion* **2**, 46 (1932).

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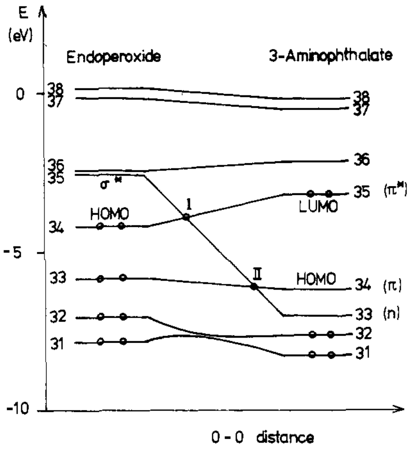

Figure 6. MO correlation diagram of the endoperoxide–3-aminophthalic acid system according to the HAM/3 calculations.

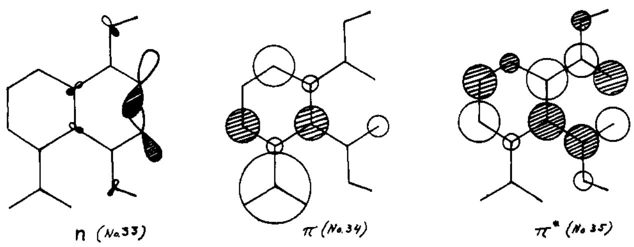

Figure 7. Shape of the n, π, and π^* orbitals in the endoperoxide–3-aminophthalic acid system.

a continuous variation of the orbitals and their energies with the reaction coordinate. In reality, the SCF calculations will, of course, diverge near the point of intersection unless configuration interaction is applied.

Second, even for symmetric molecules, the noncrossing rule has no meaning for canonical Hartree–Fock or HAM orbitals. The reason for this is that the canonical orbitals are in principle exact eigenfunctions of the Hartree–Fock (or HAM) one-electron operator. If we adhere to the view that the molecular orbitals are defined as the eigenfunctions of this operator, then the orbital concept will break down when we go beyond the Hartree–Fock approximation. Thus, further interaction will have to take place among configurations and not among orbitals.

This view is, of course, totally different from that usually employed in qualitative MO theory where the localized orbitals employed interact strongly and where the noncrossing rule plays an important part in keeping track of the correlation lines. **In** the Hartree–Fock or HAM orbitals this interaction has already taken place and further interaction is not possible. We may, however, sometimes see vestiges of this preceding interaction in the shape of the MO energy curves, which sometimes show an osculating behavior; i.e., the curves come close to each other but do not intersect. In such a case the electrons will not necessarily "slide" along the correlation lines in a nonadiabatic transition since the two osculating orbitals will exchange orbital character with one another.

It should, perhaps, also be pointed out that the Hartree–Fock canonical orbitals are the one-electron orbitals best suited for ionization purposes as was pointed out by Davidson.[10] This assumption is also the main content of the often misunderstood Koopmans theorem.[11]

The Double Crossing

In spite of the problems discussed above it was found possible to construct an orbital correlation diagram also for the endoperoxide–3-aminophthalate system. The orbitals relevant to our discussion of the chemiluminescence mechanism are shown in Figure 6. In addition, Figure 7 depicts the qualitative shapes of the three pertinent orbitals 33, 34, and 35 of 3-aminophthalate.

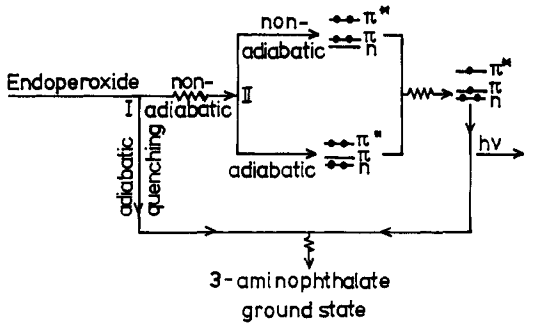

Figure 8. Paths leading from the endoperoxide to the radiating singlet state of 3-aminophthalate.

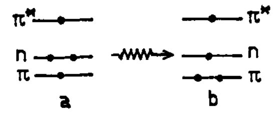

Figure 9. Nonradiating states in the absence of a second crossing.

The most interesting feature of the diagram in Figure 6 is that there is not only one intersection, I, with the HOMO orbital of the endoperoxide but also *another intersection*, II, with the HOMO orbital of the 3-aminophthalate ion. The probability of a nonadiabatic transition associated with intersection I is of the same order of magnitude as in the model substance, i.e., approximately 25%. By the same method of calculation the probability of a nonadiabatic transition associated with II is 99.5% for a single crossing. This would leave the orbital 34 filled and orbital 33 empty in 99.5% of the cases. This picture will, however, have to be modified for the following reason. The calculation above was based on the assumption of continuous undisturbed acceleration of the velocity $\dot{q}$ according to eq 9. Now, either this vibration must be strongly damped and the intersection II passed at a much lower velocity with an attendant higher yield of adiabatic transition or the representative point will swing back and forth many times, which would entail several passages of the intersection II, each passage yielding a contributing of 0.5% adiabatic transition.

In both cases the orbital no. 34 will be partially drained. There will, of course, also be more or less substantial drainage due to other radiationless transitions. If the orbital no. 34 is partially drained, this opens up the possibility of a radiating transition from the LUMO, no. 35, to the orbital 34. This transition has a high oscillator strength of $f = 0.327$ in contrast to the transition 33 $\leftarrow$ 35 which has only $f = 0.0018$ as calculated without configuration interaction. It would thus seem that a double intersection (I and II) is a necessary prerequisite for chemiluminescence to take place. We will refer to this mechanism as the "*double-*crossing *model*".

In passing it should be mentioned that due to the shape of the π^* orbital (no. 35) the emitting state will be rather rigid with respect to rotation around the C–COOH bond. This rigidity has been invoked[3] to rationalize the protonation state of the chemiexcited species.

We may, of course, take a somewhat more global view of the subsequent transition to the radiating single state as depicted in Figure 8. In a semiclassical picture[12] this probability is determined by the matrix element $\dot{q}\langle D|\partial/\partial q_i|S\rangle$, where D and S are the adiabatic electronic eigenfunctions at a fixed position of the nuclei of the doubly and singly excited states, respectively, and q_i is a normal vibrational coordinate.

A pseudosymmetry argument shows that, e.g., the reaction coordinate, q, will give a nonzero matrix element for this transition. Furthermore, such a transition may in principle take place at any value of the reaction coordinate. This transition may, in addition, occur irrespective of whether the passage of the crossing II is

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(10) E. R. Davidson, *J. Chem. Phys.*, **57**, 1999 (1972).

(11) T. A. Koopmans, *Physica (Amsterdam)* **1**, 104 (1933).

(12) C. Galloy and J. C. Lorquet, *J. Chem. Phys.*, **67**, 4672 (1977).

adiabatic or nonadiabatic, i.e., whether it is the π or the n orbital that is empty in the doubly excited state as illustrated in Figure 8.

From this point of view the main importance of the second crossing rests in the fact that if it does not occur then the n level will lie above the π level in the orbital diagram. The corresponding singly excited $\pi\pi^*$ state, Figure 9a, will then suffer a rapid radiationless transition in the sense of Kasha's rule[13] to the $n\pi^*$ state, Figure 9b. Due to the low oscillator strength of the $n \rightarrow \pi^*$ transition the latter state will rapidly decay into the ground state, presumably by intersystem crossing before radiation can take place. According to the HAM calculation the transition 34 ← 35 of 3-aminophthalate should correspond to a wavelength of 416 nm, which compares very favorably with the observed value of 425 nm, the wavelength of maximum fluorescence in aqueous solutions. Similarly the radiative lifetime of the singlet is calculated to be 7.9 ns, which compares well with 18 ns as estimated from the quantum yield[14] and measured lifetime[15] of the fluorescence of 3-aminophthalate.

Since the second intersection, II, appears to be essential for the chemiluminescence to take place, we should expect that upon interchanging the amino group for other substituent groups only those molecules will chemiluminesce whose MO correlation diagrams contain a second intersection. This is, in fact, predicted for the OH-substituted molecule. On the other hand, e.g., the H- or CH_3-substituted molecules should not luminesce since their MO correlation diagrams like those of the model substance contain only a single intersection. All this is in agreement with experimental facts.[16]

As far as the quantitative aspect is concerned, the quantum chemical calculations are, of course, much too approximate to allow a reliable estimate of the efficiency of chemiexcitation exhibited by individual molecules. It is, however, easy to discern some of the decisive factors that determine this yield. Such a factor is the probability of a nonadiabatic transition at the first intersection, I. This probability depends in part on the exchange integral K_{ia} and in part on the rate $\dot{q}$ at which the crossing is passed. These two factors are dependent on the forms and energies of the orbitals i and a and may vary slightly but perhaps significantly from case to case.

In one of their publications, White et al.[17] have noticed a negative correlation between the efficiency with which the emitting state is populated and the energy gap between the HOMO and the LUMO of the corresponding phthalate. Such a dependence is easy to explain from the present model. An increase of the LUMO energy in the substituted phthalate would obviously force the first crossing point, I, to move to the left in the diagram toward lower O–O distances. The system velocity, $\dot{q}$, at the intersection point would then be lower with an attendant decrease in the probability of a nonadiabatic transition. The probability P_{12} of a nonadiabatic transition is, in fact, highly sensitive to a change in $\dot{q}$. If $\dot{q}$ is halved, P_{12} will, e.g., decrease from 24 to 5.76%. It is, however, too early to say whether this effect alone is sufficient to explain the negative correlation between the HOMO–LUMO gap and the chemiexcitation efficiency observed by the above authors or if this correlation is partly due also to other accompanying changes of the molecular properties not necessarily related to the HOMO–LUMO gap.

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Carbon-14 Kinetic Isotope Effects and Mechanisms of Addition of 2,4-Dinitrobenzenesulfenyl Chloride to Substituted Styrenes-*1*-^{14}C and Styrenes-*2*-^{14}C[1]

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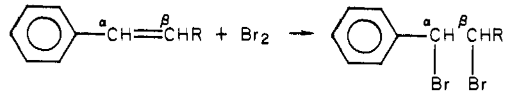
Abstract: As the first reported examples of carbon isotope effects in simple electrophilic addition reactions we have measured the carbon-14 kinetic isotope effects in the addition of 2,4-dinitrobenzenesulfenyl chloride to a series of para-substituted α- and β-labeled styrenes in acetic acid at 30.1 °C: for para substituents Cl, H, and CH_3 the $k/^{14}k$ values for α labeling are 1.027, 1.022, and 1.004, and the $k/^{14}k$ values for β labeling are 1.035, 1.032, and 1.037, all $\pm\sim 0.004$. The kinetics of the reaction were measured for the p-CH_3O, p-CH_3, unsubstituted, p-Cl, and m-NO_2 styrenes; electron-donating groups strongly accelerate the reaction, and electron-withdrawing groups retard it. The Hammett plot is curved with ρ^+ values ranging from about −4.6 at the electron-donating group (EDG) end to about −1.8 at the electron-withdrawing group (EWG) end. Both the isotope effect and kinetic data, and related data from the literature, are interpreted in terms of a changing mechanism, with the activated complexes of the rate-determining steps having much open carbenium ion (ion pair) character for EDG-substituted styrenes and much cyclic thiiranium ion (ion pair) character for EWG-substituted styrenes.

We have been puzzled for many years[2] about the reported[3] lack of a carbon kinetic isotope effect in the addition of bromine to $^{\alpha}$C and $^{\beta}$C carbon-14 labeled styrene and methyl cinnamate (eq 1 and 2).



(1)

$$^{12}k/^{14}k \text{ for } ^{\alpha}\text{C and } ^{\beta}\text{C} = 1.00^{3} \qquad (2)$$

All of the mechanisms proposed for these electrophile addition reactions involve substantial bonding changes at $^{\beta}$C and (perhaps—see below) at $^{\alpha}$C in the rate-determining steps, and these changes should be reflected in carbon isotope effects. Since the main action involved is bond formation, it might be anticipated

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[1] Presented in part at the 184th American Chemical Society meeting, Kansas City, Missouri, September 14, 1982, and in a preliminary communication: Kanska, M.; Fry, A. *J. Am. Chem. Soc.* **1982**, *104*, 5512–5514.

[2] Fry, A. In "Isotope Effects in Chemical Reactions"; Collins, C. J., Bowman, N. S., Eds.; Van Nostrand-Reinhold: New York, 1970; pp 364–414.

[3] Ropp, G. A.; Raaen, V. F.; Weinberger, A. J. *J. Am. Chem. Soc.* **1953**, *75*, 3694–3697.

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