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Semi-empirical molecular orbital calculations on the interaction between singlet oxygen and amines: modeling charge transfer quenching

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Abstract

Semi-empirical molecular orbital calculations were performed using MINDO/3 to examine the mechanism of quenching of singlet (excited) molecular oxygen by amines. Amines with reported ionization potentials and singlet oxygen quenching rate constants were modeled with singlet oxygen at various distances from the amine nitrogen, and the enthalpies of formation of the resultant supramolecules were graphed vs. the nitrogen–oxygen separation. Primary amines gave a distinct energy minimum at a nitrogen–oxygen separation of about 1.54 Å and a nitrogen–oxygen–oxygen "bond" angle of about 119°. The electron density at nitrogen and the distal oxygen in the minimum energy complex, relative to that in the individual molecules, indicated a substantial (approximately 0.3 esu) transfer of charge from nitrogen to oxygen, consistent with a charge transfer complex. Secondary amines showed a less distinct energy minimum at the same nitrogen–oxygen separation, whereas tertiary amines gave only an inflection point. Because a charge transfer quenching mechanism requires intersystem crossing (singlet to triplet) during complexation, the upper limit of the energy of the charge transfer complex was also calculated by specifying a triplet state. This was substantially higher in energy than the singlet complex in the case of primary and secondary amines, but slightly lower in energy for tertiary amines. This calculated upper limit for the enthalpy of activation of intersystem crossing (quenching) via a charge transfer complex correlated well ($r = -0.97$) with the logarithm of the quenching rate constant for a series of amines. The close proximity (1.54 Å) required between nitrogen and oxygen in the charge transfer complex explains the sensitivity to steric hindrance in the vicinity of nitrogen observed for singlet oxygen quenching rates by aliphatic amines. These data are consistent with a charge transfer mechanism of quenching of singlet oxygen by amines.

Keywords: Amines; Charge transfer; Exciplex; MINDO/3; Quenching mechanism; Singlet oxygen

1. Introduction

In 1981, Martin and Jefford [1] reported that the reaction of singlet oxygen with certain enamines involved a charge transfer mechanism, based on product studies and the interpretation of the effect of substituents on the reaction rate. In 1991, Allen et al. [2] reported that MINDO/3 calculations provided evidence of an intermediate charge transfer complex with a nitrogen–oxygen separation of 1.55 Å in the reaction of singlet oxygen with vinylamine. Vinylamine was chosen in Ref. [2] because it is the simplest enamine, thereby making it amenable to calculation. Because Dewar and Thiel [3] had also performed calculations on various other possible modes of reaction of vinylamine with singlet oxygen, values were available for comparison. However, Dewar and Thiel [3] had not considered a charge transfer interaction among the various mechanisms of reaction of singlet oxygen with vinylamine.

It has been known for many years that amines quench singlet oxygen [4,5]. 1,4-Diazabicyclo[2.2.2]octane (DABCO) is one of the most efficient physical quenchers of singlet oxygen [6]; it is often added to reaction mixtures to prevent singlet oxygen reactions. Foote [5] proposed that DABCO quenches singlet oxygen by a charge transfer mechanism. In 1970, Ogryzlo and Tang [7] reported that the logarithm of the singlet oxygen quenching rate constant for aliphatic amines correlated well ($r = -0.99$) with the ionization potential of the amine and suggested that a weakly bound charge transfer complex was involved. Subsequently, the quenching rate constants were re-determined by Furukawa and Ogryzlo [8]; the correlation between their revised rate constants and the reported ionization potentials was less satisfactory ($r = -0.91$, Fig. 1), but data were presented which still supported the charge transfer mechanism of quenching. In this paper, the term charge transfer refers to a partial shift of electron density as suggested by Young et al. [9,10], whereas the term electron transfer denotes complete

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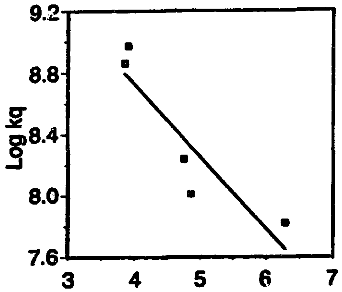


Fig. 1. Logarithm of the singlet oxygen quenching rate constant (k_q) vs. the ionization energy for some aliphatic amines [8].

transfer of an electron as suggested by Foote et al. [11] and Rehm and Weller [12]. The calculations reported in this paper were undertaken to examine the mechanism of singlet oxygen quenching by amines.

2. Experimental details

Calculations were performed using MINDO/3 (a semi-empirical molecular orbital calculation program found in AMPAC, a collection of programs by Dewar and coworkers [13–15]) using a VAX 11/785 computer. MINDO/3 was used in this research because it incorporates parameters for diatomic interactions and therefore models diatomic molecules such as O_2 well; indeed, the heat of formation of singlet oxygen calculated by MINDO/3 (22.8 kcal mol^{-1}) is quite close to the experimental value of 22.5 kcal mol^{-1} [16]. In contrast, MNDO and the subsequently developed AM1, two semi-empirical molecular orbital programs in AMPAC, gave calculated values of 12.2 and 0.7 kcal mol^{-1} respectively for singlet oxygen. Stewart's most recent semi-empirical parametrization PM3 (found in MOPAC [17]) gives a value of 18.4 kcal mol^{-1}. In addition to the better agreement between MINDO/3 calculations and the observed enthalpies, Dewar and Thiel [3] have examined the reactions of singlet oxygen with vinylamine and other electron donors using MINDO/3.

The structures of various amines were created graphically on a microcomputer using HyperChem (HyperCube, Inc.) in which the geometries were first optimized using molecular mechanics (MM+) and then MINDO/3 semi-empirical molecular orbital calculations. Diatomic singlet oxygen (optimized by MINDO/3) was then added to the minimum energy structure of the amine in the vicinity of the nitrogen. The structure of the amine–O_2 complex was saved in the appropriate file format, transmitted to the VAX 11/785 computer and edited to perform an AMPAC calculation. The keyword SINGLET was specified to ensure that only singlet electronic states were considered [18]. By default, the lowest energy singlet state is calculated; for dioxygen, this is the $^1\Delta_g$ state. This was ensured by specifying ROOT = 1 as a keyword. A reaction pathway calculation was performed in which the distance between the nitrogen atom and the proximal oxygen atom was varied stepwise, and energy optimizations were performed at each step. Prior to calculating the enthalpy of formation of the amine–singlet oxygen supramolecule as a function of the nitrogen–oxygen separation, the lowest energy orientation of the singlet oxygen molecule relative to the amine was determined as follows. A reaction pathway calculation was performed with the nitrogen–oxygen distance fixed at 1.55 Å (the distance of minimum energy in the published vinylamine–singlet oxygen calculation [2]) and the nitrogen–oxygen–oxygen bond angle held at 120°, with the carbon–nitrogen–oxygen–oxygen dihedral angle varied over 120° or 180° depending on the symmetry of the amine. The dihedral angle was varied initially in 2° increments, and then the process was repeated in 0.5° increments over a narrow (20°) range including the dihedral angle of minimum enthalpy. Next the carbon–nitrogen–oxygen–oxygen dihedral angle was fixed at the optimum value (that having the minimum enthalpy of formation) and the nitrogen–oxygen–oxygen bond angle was varied in 1° increments from 90° to 180°. Frontier molecular orbital theory [19] predicts a stabilizing HOMO–LUMO interaction between the amine and the vacant π^* orbital on oxygen (Fig. 2), and the axis of these orbitals is approximately 120° to the oxygen–oxygen bond axis. Our calculations reveal a minimum energy for amine–singlet oxygen complexes at a nitrogen–oxygen–oxygen bond angle of 119°.

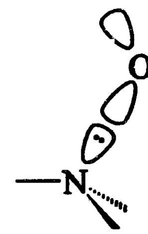


Fig. 2. Proposed frontier molecular orbital theory interaction between N_{nb} and O_{π}^{*}.

3. Results

An example of a calculated structure of the minimum energy complex between singlet oxygen and an amine (propylamine) is shown in Fig. 3. The nitrogen–oxygen separation for the propylamine–singlet oxygen complex is 1.54 Å, the nitrogen–oxygen–oxygen "bond" angle is 119° and the carbon$_1$–nitrogen–oxygen–oxygen dihedral angle is 179°. The enthalpies of formation of the analogous amine–singlet oxygen complexes for various aliphatic amines were calculated for several nitrogen–oxygen distances in the range 1.0–8.0 Å. Fig. 4 shows a graph of these data over a range of 1.2–

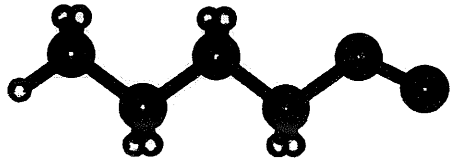


Fig. 3. MINDO/3 minimum energy structure of the propylamine–singlet oxygen complex.

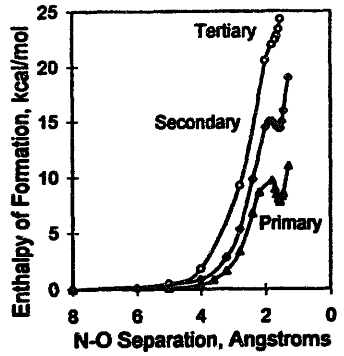


Fig. 4. Calculated relative enthalpy of formation vs. N–O separation for representative primary, secondary and tertiary amines interacting with singlet oxygen.

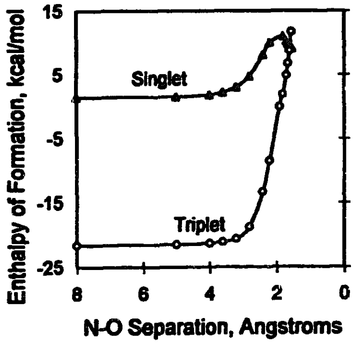


Fig. 5. Calculated enthalpies of formation of propylamine–singlet oxygen and propylamine–triplet oxygen complexes vs. N–O separation.

8.0 Å for representative primary, secondary and tertiary amines. In the case of primary amines (e.g. propylamine), a distinct enthalpy minimum was observed at a nitrogen–oxygen distance of 1.54 Å. A less distinct enthalpy minimum was observed at the same nitrogen–oxygen distance in the graphs of the secondary amines (e.g. dimethylamine). In the graph of most tertiary amines (e.g. trimethylamine), no distinct enthalpy minimum was evident; instead, an inflection point was observed midway between 1.5 and 1.6 Å. In order to confirm that this attractive interaction is unique to singlet oxygen, the calculations were repeated using TRIPLET as a keyword instead of SINGLET. Specifying TRIPLET ensures that a triplet electronic state will be calculated; by default, the lowest energy triplet state is considered. Fig. 5 shows a graph of the data for singlet and triplet dioxygen and propylamine. The curve marked "Singlet" shows the singlet oxygen–propylamine attractive interaction. The curve marked "Triplet" shows the calculation with ground state (triplet) oxygen and propylamine. Only repulsion is observed between the amine and ground state oxygen as the distance between them is decreased; this contrasts with the attractive interaction observed in the singlet curve.

Evidence of charge transfer is indicated by the increase in the positive character of the nitrogen in the various amines studied (Table 1) by 0.25–0.35 esu when the amine and oxygen are brought together to form the complex. Concomitantly, a partial negative charge of 0.24–0.35 esu develops on the distal oxygen, while the proximal oxygen remains essentially neutral. Two comments on the magnitude of charge calculated by MINDO/3 are appropriate. First, the concept of atomic charge in a covalent molecule is variously defined and poorly reproduced between the several available computational methods. Thus it is inappropriate to place much credence on small differences in the calculated charges. Second, the absence of an expected correlation between the calculated magnitude of the charge and the ionization energy may be related to the known sensitivity of the singlet oxygen quenching rate to steric hindrance in the vicinity of the nitrogen [20]. More highly substituted amines (e.g. tertiary) have lower ionization potentials and therefore might be expected to form a complex with singlet oxygen with a greater transfer of charge than less highly substituted amines (e.g. primary). However, the greater steric hindrance in tertiary amines prevents the close approach associated with a greater transfer of charge. Indeed, all the complexes have calculated nitrogen–oxygen distances of approximately 1.54 Å at the energy minimum, and the data in Table 1 suggest that the calculated magnitude of charge transfer correlates with a lack of steric hindrance.

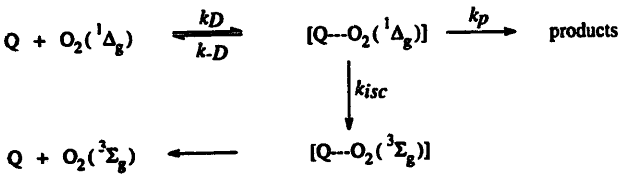
4. Discussion

The kinetics of quenching of singlet oxygen via a charge transfer complex (exciplex) have been analyzed as follows [21,22])

Table 1
Summary of the calculations of aliphatic and alicyclic amine–singlet oxygen complexes

Amine	Enthalpy of activation of intersystem crossing (kcal mol^{-1})	Ionization energy (eV) [a]	Log k_q^a	Δq_N	Δq_O
Methylamine	52.00	9.40	5.30	0.34	0.29
Propylamine	49.20	9.4 [b]	5.4 [b]	0.34	0.30
Dimethylamine	29.00	8.90	5.80	0.31	0.27
Diethylamine	24.70	8.40	6.30	0.32	0.27
Piperidine	25.10	8.7 [b]	6.8 [b]	0.30	0.27
Trimethylamine	19.00	8.30	6.50	0.25	0.24
DABCO	17.60	7.5 [c]	7.08	0.35	0.35

[a] Ref. [7].
[b] Ref. [20].
[c] Ref. [10].



where Q is the amine quencher, $O_2(^1\Delta_g)$ is singlet oxygen, $[Q—O_2(^1\Delta_g)]$ is the singlet oxygen–amine complex (exciplex), $[Q—O_2(^3\Sigma_g)]$ is the triplet oxygen–amine complex and $O_2(^3\Sigma_g)$ is triplet (ground state) oxygen.

Gorman et al. [21] employed the steady state approximation and the observation that the lifetime ($\tau_\Delta = k_d^{-1}$) of singlet oxygen ($^1\Delta_g$) is typically several orders of magnitude longer than the measured lifetimes of the exciplexes to obtain

$$k_d + k_D[Q] \ll k_{-D} + (k_{isc} + k_p) \quad (1)$$

which simplifies the kinetics, so that Eqs. (2) and (3) hold

$$k' = k_d + k_q[Q] \quad (2)$$

$$k_q = \frac{k_D(k_{isc} + k_p)}{k_{-D} + (k_{isc} + k_p)} \quad (3)$$

where k' is the first-order rate constant for the decay of $O_2(^1\Delta_g)$, k_d is the quencher-independent rate constant for singlet oxygen deactivation and k_q is the overall quenching rate constant. For quenchers which are fast ($k_{-D} \ll (k_{isc} + k_p)$) and those which are slow ($k_{-D} \gg (k_{isc} + k_p)$), these equations reduce to Eq. (4) (diffusion limit) and Eq. (5) (pre-equilibrium limit) respectively, where K is the equilibrium constant for charge transfer complex (exciplex) formation

$$k_q = k_D \quad (4)$$

$$k_q = K(k_{isc} + k_p) \quad (5)$$

No amines have reported quenching rate constants within an order of magnitude of the diffusion-limited value, and therefore Eq. (5) (but not Eq. (4)) is operative in this study. With few exceptions [20], amines are regarded as physical (not chemical) quenchers of singlet oxygen [21,23]. Therefore k_p is negligible relative to k_{isc} in Eq. (5), which reduces to Eq. (6)

$$k_q = K(k_{isc}) \quad (6)$$

The calculated relative enthalpies of the charge transfer complexes (compared with the isolated reactants) and their corresponding enthalpies of activation for charge transfer complex formation for amines with different degrees of substitution (primary, secondary and tertiary) are shown in Fig. 4. Primary amines quench singlet oxygen much less effectively than tertiary amines, and yet the calculations indicate that they form more stable charge transfer complexes (more favorable equilibrium constants) with faster rates. This apparent discrepancy can be explained by a mechanism involving rate-limiting intersystem crossing after rapid reversible formation of the singlet charge transfer complex.

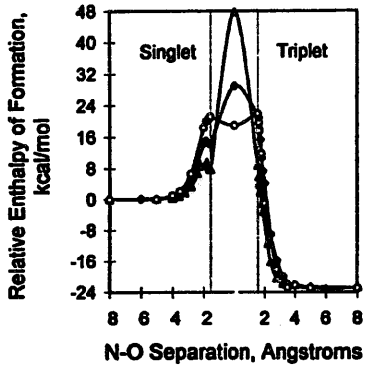


Fig. 6. Calculated relative enthalpy of formation vs. N–O separation for representative primary, secondary and tertiary amines quenching singlet oxygen by a charge transfer mechanism. The points between the broken lines represent single point calculations of the energy of the triplet complex having the same geometry as the singlet complex at 1.54 Å N–O separation.

Intersystem crossing should be facilitated by mixing of the singlet and triplet charge transfer states through spin–orbit coupling as suggested by Ogryzlo and Tang [7]. Although it is not possible using AMPAC to perform a calculation involving mixed singlet–triplet states, an estimate of the upper energy limit of this mixed state complex can be made by performing a single point triplet state calculation using the same geometry as the complex found at the minimum (or inflection point) of the singlet calculation. Fig. 6 summarizes the data obtained for representative primary, secondary and tertiary amines. It should be emphasized that this is a calculation for a triplet state having the geometry of the singlet complex and that it represents an upper limit of the energy, not the expected energy of the transition state; the actual energy of the "mixed" singlet–triplet state is expected to be substantially lower, as is the geometry optimized triplet state. Another reason for the unexpectedly high values of the enthalpy of the triplet state is that the calculations are performed assuming a vacuum; solvent effects on the stabilization of charged species are of course considerable, but are not included in these calculations. For tertiary amines, this calculated upper limit is slightly lower in energy than the singlet "complex" at the inflection point; this explains the observed rapid quenching by tertiary amines despite the higher energy of the singlet complex relative to less substituted amines. For tertiary amines, it appears that the large rate constant for intersystem crossing (k_{isc}) is the dominant term in Eq. (6) leading to a large k_q value. For primary and secondary amines, the energy of the triplet state complex is substantially higher than any point on the singlet reaction coordinate (Fig. 6), and therefore the rate constant for intersystem crossing (k_{isc}) is much less than that for tertiary amines. We define the difference between the sum of the energies of the non-interacting ground state amine and singlet oxygen (separated by 8 Å) and the highest energy point on the singlet to triplet reaction profile in Fig. 6 as $\Delta H^{\#}_{isc}$, the calculated upper limit of the enthalpy of activation of intersystem crossing. When the calculated value of $\Delta H^{\#}_{isc}$ for a series of simple aliphatic amines is plotted against the reported values of log k_q, a

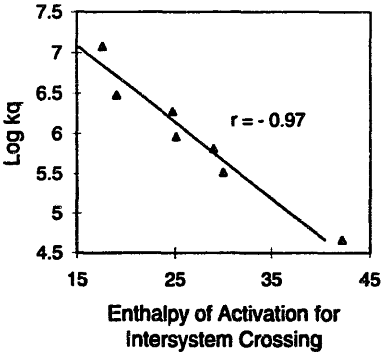


Fig. 7. Logarithm of the singlet oxygen quenching rate constant (k_q) vs. the calculated enthalpy of activation for intersystem crossing for some aliphatic and alicyclic amines and oxygen.

straight line ($r = -0.97$) is obtained (Fig. 7). This excellent correlation suggests that quenching may in fact occur by rate-limiting intersystem crossing following the rapid reversible formation of a charge transfer complex, as discussed by Gorman et al. [21] and Clennan et al. [23], although other quenching mechanisms cannot be excluded.

The singlet charge transfer complexes have an energy minimum at a nitrogen–oxygen separation of 1.54 Å. The charge transfer mechanism for intersystem crossing requires this close approach between oxygen and nitrogen in order to maximize orbital overlap, thus allowing spin–orbit coupling and mixing of the singlet and triplet states, and thereby providing a lower energy pathway for intersystem crossing [7,10]. The close approach between singlet oxygen and the amine nitrogen atom is also consistent with the observed sensitivity of the singlet oxygen quenching rate to steric hindrance in the vicinity of the nitrogen in a series of α-alkyl-substituted piperidines [20]. Lastly, the calculated nitrogen–oxygen distance in the complex is consistent with the formation of a "weakly bound collision complex" as suggested by Ogryzlo and Tang [7] and Young et al. [10,24].

5. Conclusions

In 1981, Martin and Jefford [1] reported that the reaction of singlet oxygen with certain enamines involved the intermediacy of a charge transfer complex, based on the interpretation of the effect of aryl ring substituents on the reaction rate and product studies. Allen et al. [2] used MINDO/3 calculations to demonstrate how vinylamine and singlet oxygen may react by the initial formation of a charge transfer complex. Aliphatic amines are known to be effective quenchers of singlet oxygen, and several workers have proposed a charge transfer mechanism for the quenching process. MINDO/3 calculations on amine–singlet oxygen interactions indicate that weak charge transfer complexes may indeed be formed, but that the rate-limiting step for quenching is not the formation of the charge transfer complex, but the subsequent intersystem crossing. This conclusion is supported by the experimental evidence summarized by Gorman et al. [21]. Spin inversion during intersystem crossing is facilitated by mixing of the singlet and triplet states in the charge transfer complex (exciplex) owing to spin–orbit coupling which is favored by amines with low ionization potentials. Efficient spin–orbit coupling requires close approach of the interacting molecules to maximize orbital overlap. This requirement is consistent with the observed sensitivity of the quenching rate constant to steric hindrance in the vicinity of the nitrogen and the short calculated nitrogen–oxygen distance (1.54 Å) in the charge transfer complex.

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