Estimation of the stability of the exciplexes involving triplet oxygen

IVAN JURANIĆ and SVETOZAR R. NIKETIĆ

*Department of Chemistry, Faculty of Science,
University of Belgrade, Studentski trg 16, P.O.Box 550,
YU—11001 Belgrade, Yugoslavia*

An approximation to the excited state potential energy curve of the exciplexes involving triplet oxygen is proposed. It is constructed essentially as a superposition of the attractive electrostatic potential originating from exciplex charge transfer to oxygen and the ground state repulsion potential. It offers a simple semiquantitative explanation of the stability and reactivity of the exciplexes of triplet oxygen.

Light induced oxygenation of organic compunds has been a subject of extensive investigation over last 50 years.[1] The vast majority of the publications were concerned with the reactivity of singlet oxygen reactive species in photochemical reactions involving moleculaj oxygen.[1]

However, there is a number of examples[2-7] where oxygenation proceeds in such a manner that no singlet oxygen can be formed. One of the examples from everyday life is the formation of hydroperoxides in rubber and similar materials exposed to the air and sunlight. Other examples comprise many of the so called autooxidation processes.

One of us has investigated experimentally the photooxygenation of steroidal isoxazolidines[2,8,9] which is an example for such reaction. The products were identified as nitro and azoxy compounds originating from the primary formed hydroperoxides. A possible mechanism involves a formation of a loose complex between the triplet oxygen and the substrate.[5] The absorption of light cause the formation of a charge-transfer (CT) complex which then undergoes chemical transformation into the products:

$$O_2(T_0)\cdots X + h\nu \rightarrow [O_2^-\cdots X^+](T_1) \rightarrow \text{products}$$
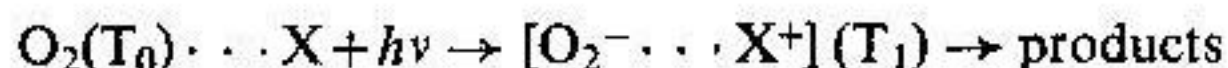
We have performed MNDO calculations on $O_2\cdots NH_3$ and $O_2\cdots NH_2X$ pairs of molecules.[10-12] It appears that there exists a shallow minimum on the ground state potential energy (PE) curve (Fig. 1).

The calculations of the excited state PE curve usually require excessive computational efforts. Nevertheless, there seems to be a simple way to estimate its approximate shape.
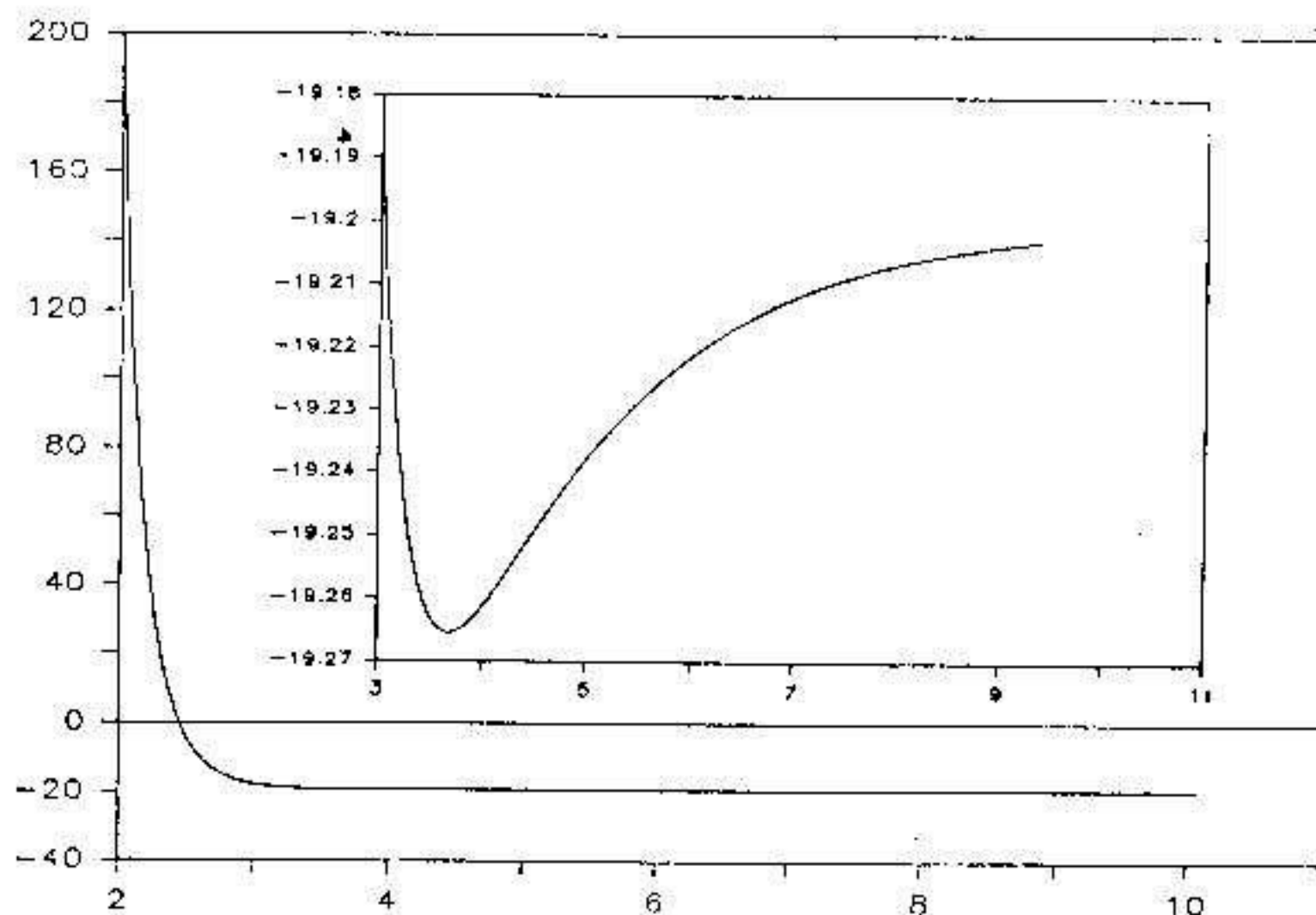
Fig. 1. The MNDO ground state potential energy curve for $O_2 \cdots NH_3$ interaction. A curve segment
expanded on the vertical scale (window) clearly shows the minimum.

Results of MNDO calculations for $O_2 \cdots NH_3$ interaction show that HOMO
is practically pure lone-pair orbital of ammonia and SOMO and LUMO orbitals
are localized on oxygen moiety (Fig. 2). The lowest energy electron transfer in-
volves HOMO-SOMO transition, $i.\,e.$, complete electron transfer from ammonia
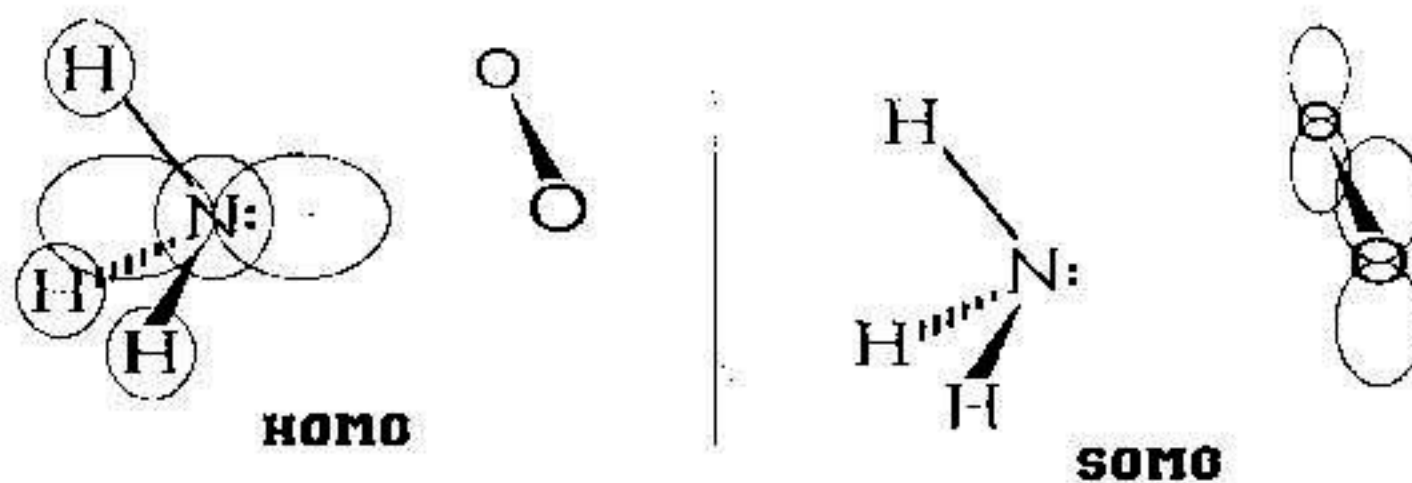to oxygen.

Fig 2. The MNDO MO shapes of the HOMO and the lowest SOMO orbital for $O_2 \cdots NH_3$ super-
molecule.

Due to the triplet state of oxygen the exciton resonance is not expected to con-
tribute to any extent to the binding energy between the two moieties.[13] The sole
attraction between oxygen and substrate moieties is due to the London forces.
The same considerations on repulsive forces can be applied to the excited state.
However, in the excited state of the oxygen-substrate complex there is substantial
charge transfer, and considerable electrostatic attraction between the two moieties
takes place.

The approximate shape of the excited state PE curve for varying distances
between oxygen and substrate can be constructed by a superposition of the attrac-
tive electrostatic potential and the ground state repulsive potential:

$$V_{excit}(r) = V_{ground}(r) + 1/r + D \quad \text{(in a. u.)}$$

This curve is, of course, shifted for the energy difference (D) between the electronic states. Certain refinements of the above relation can be made by taking into account different overlap between moieties at various distances. Closer inspection reveals that at the assumed equilibrium distance for the exciplex (ca. 0.25 nm) HOMO and SOMO LCAO coefficients differ very slightly from the corresponding coefficients at the ground-state equilibrium distance (ca. 0.43 nm). This result provides a further support for the validity of our approximation to the excited state PE curve.

On Fig. 3 the evaluated potential for the $O_2 \cdots NH_3$ exciplex is shown. This curve has a very deep minimum which can account for very high stability of the exciplex. The estimated depth of this minimum is over 400 kJ/mol. Therefore, it is very likely that the exciplex will relax through a chemical transformation giving hydroperoxides or other oxidation products.
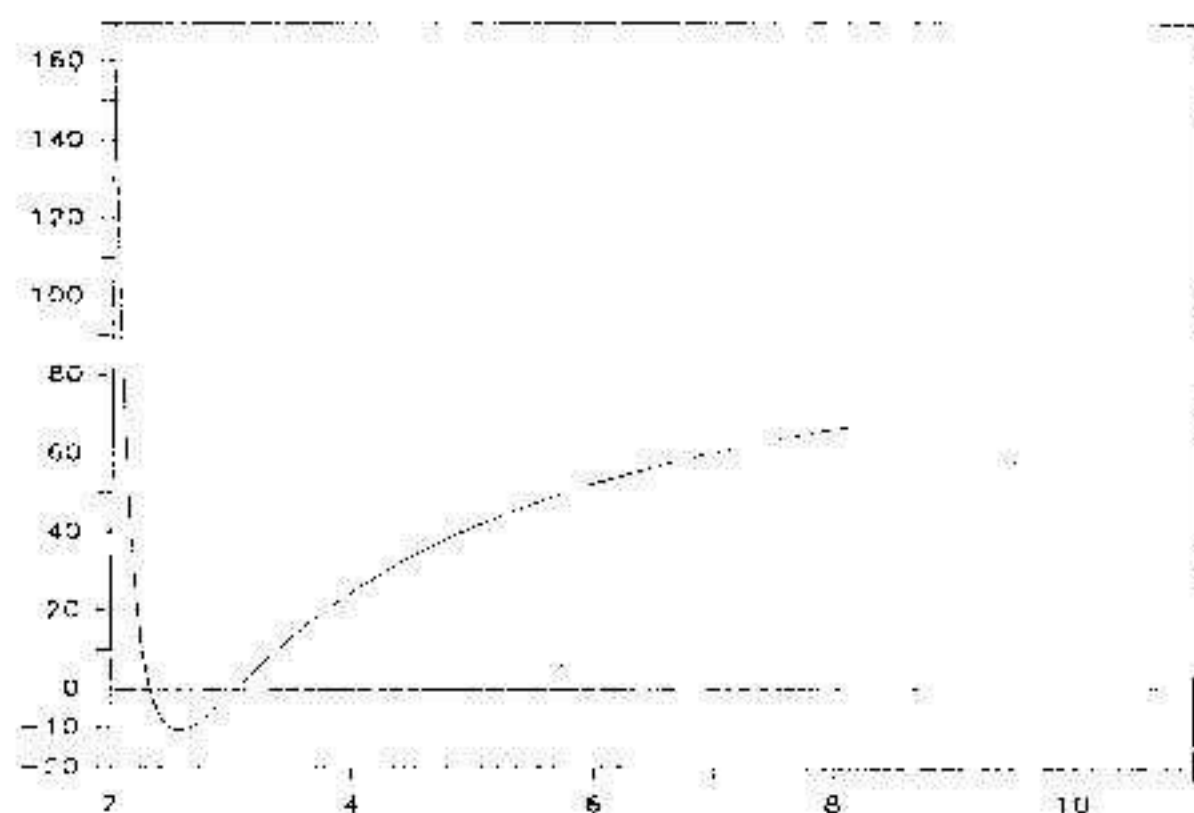

Fig 3. Estimated potential energy curve for the excited state of $O_2 \cdots NH_3$ complex.

Similar considerations can be applied to the oxygenation in the dark. If the energy of the HOMO of the substrate is shifted upwards (for example, when anion is formed) the ground-state CT PE curves may cross not very far from the ground-state equilibrium energy (Fig. 4). This can account for readiness of oxygenation in basic media.
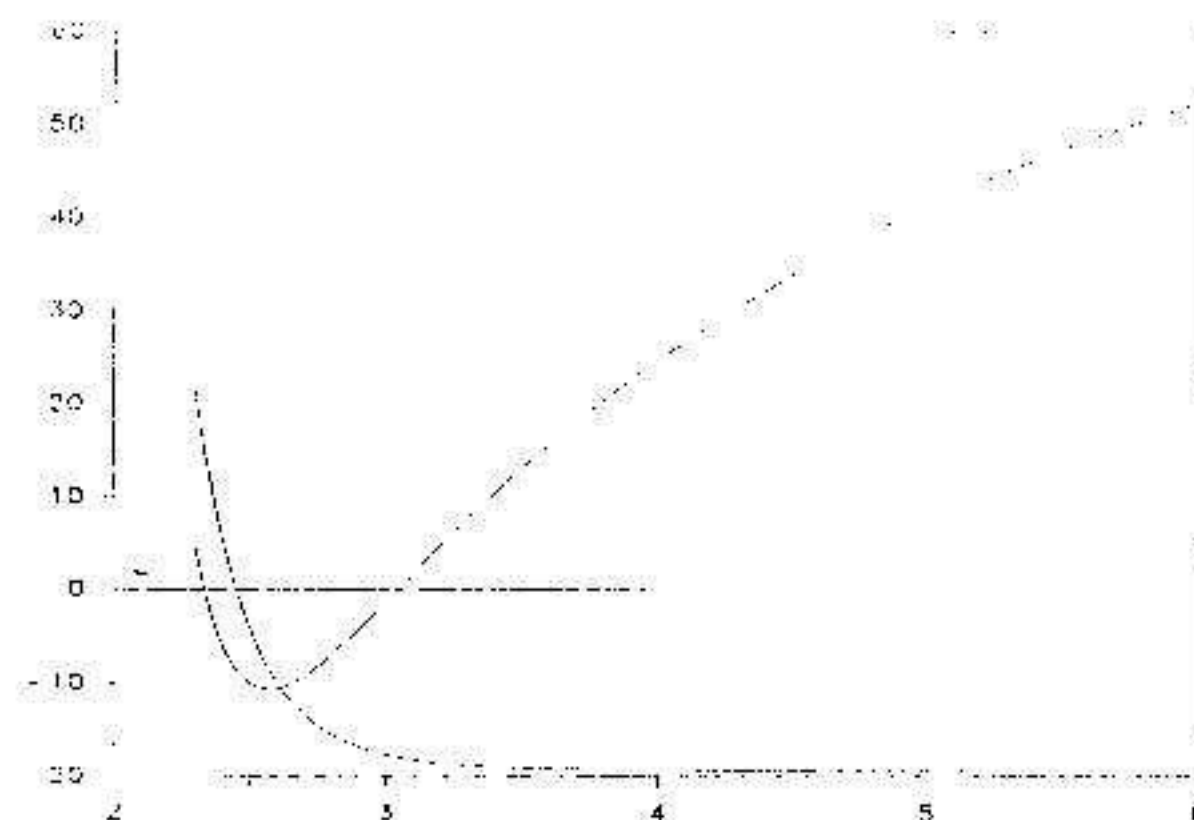

Fig 4. Crossing of the excited and ground state potential energy curves for $O_2 \cdots NH_3$ complex

ИЗВОД

ПРОЦЕЊИВАЊЕ СТАБИЛНОСТИ ЕКСЦИПЛЕКСА СА ТРИПЛЕТНИМ КИСЕОНИКОМ

ИВАН ЈУРАНИЋ и СВЕТОЗАР Р. НИКЕТИЋ

Хемијски инсшишуш, Хемијски факулшеш, ПМФ, Универзишеша у Беоїраду, Сшуденшски шрї 16, и. їр. 550, 11001 Беоїрад

Предложена је апроксимација за криву потенцијалске енергије за ексциплексе који садрже триплетни кисеоник. Она се у основи може конструисати као суперпозиција потенцијала електростатичког привлачења које настаје услед трансфера шарже на кисоеник, с једне стране, и потенцијала одбијања у основном стању, с друге стране. Ова апроксимација пружа једноставно семиквантитативно објашњење за стабилност и реактивност ексциплекса са триплетним кисеоником.

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