Attempts to isolate Cu(tet b)$(O_2)^+$ have been frustrated by the base-induced decomposition that occurs when excess O_2^- is present and the lack of solvents for Cu(tet b)X_2 that are compatible with O_2^-. Having established that this approach is a suitable general strategy for synthesis of mononuclear copper dioxygen complexes, however, we are investigating the reactions of other copper macrocyclic complexes with superoxide with the expectation that complexes of this type can be synthesized which are more stable and more amenable to isolation and crystallization.

Acknowledgments. This work was supported by grants from the Charles and Johanna Busch Memorial Fund (to J.S.V.), an NSF grant CHE78-08122 (to J.S.V.), and an NIH grant AM-16412 (to H.J.S.). M.N. is the recipient of a graduate fellowship from Allied Chemical Foundation and J.S.V. of a NIH Research Career Development Award.

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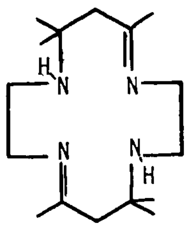
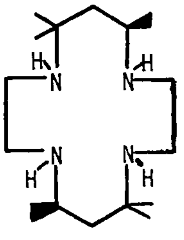


4,11-diene



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(17) A relatively weak band appears in the visible spectrum at ~410 nm when Cu(tet b)$^{2+}$ is reacted with O_2^- in Me_2SO, with OH^- in Me_2SO or CH_3CN, and with F^- in Me_2SO but not in CH_3CN. At this point, we cannot be certain whether this band is due to the anion complex or is the result of a small amount of base-induced decomposition or deprotonation of the N_4 macrocycle.

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Mario Nappa, Joan S. Valentine,* Andrew R. Miksztal
Harvey J. Schugar,* Stephan S. Isied
Departments of Chemistry
Busch Campus and Douglass College
Rutgers, the State University
New Brunswick, New Jersey 08903

Received August 17, 1979

Chemical Generation of Excited-State Radicals: Succinimidoyl

Sir:

Skell and co-workers[1] have proposed that two electronic states of the succinimidoyl radical, the π ground state and a σ_N excited state,[2] may be chemically generated. We have used MNDO semiempirical molecular orbital theory[3,4] to investigate the mechanism of generation of these two radicals from *N*-chlorosuccinimide (NCS). Our results show that the electronic state of the product succinimidoyl radical is dependent on the nucleophilicity or electrophilicity of the generating radical.

N-Chlorosuccinimide is calculated to be slightly nonplanar at MNDO[5] with a heat of formation of −63.3 kcal mol^{-1}, which is reasonable in view of the experimental heat of formation of −85.6 kcal mol^{-1} for crystalline NCS.[6] There is some question as to the ordering of the molecular orbitals in NCS. Worley et al.[7] have interpreted the PE spectral band at 10.29 eV as being due to both the n_{CO}^- and the n_{CO}^+ orbitals. MNDO, on the other hand, predicts the HOMO to be the π_{NCl}^* orbital shown in Figure 1. This conclusion is supported by a single-point RHF/STO-3G calculation on the MNDO optimum geometry for NCS. The original PES assignment[7] is based on the vibrational structure observed for the band at 10.29 eV, compared with the relatively sharp band at 11.12 eV. The n_{CO}^- band in succinimide,[7] however, does not show the same type of vibrational structure as that found for the 10.29-eV band in NCS, suggesting that this is a new type of band. Furthermore, the n_{CO}^-/n_{CO}^+ splitting in 1,3 diketones has been shown to be independent of the twist angle between the carbonyls,[8] so that they are unlikely to be almost degenerate in NCS. The calculated (MNDO, Koopman's theorem) ionization potentials for NCS (10.92, 11.32, and 12.32 eV) are also in accord with the experimental values (10.29, 11.12, and 12.32 eV). The exact ordering of the occupied and unoccupied MO's in NCS is, however, for the purpose of this paper, unimportant. What is important is that the highest occupied and lowest unoccupied molecular orbitals *with significant contributions at N and Cl* are the orbitals shown in Figure 1,[9] which are calculated to be HOMO and LUMO at MNDO.[10] These orbitals are both N-Cl antibonding and, equally significantly, correspond to the SOMO's of the π and σ_N succinimidoyl radicals, respectively.

The π and σ_N succinimidoyl radicals have calculated heats of formation of −30.4 and −16.6 kcal mol^{-1}, respectively, so that any reaction which leads to the latter must be kinetically controlled. Skell[1] has speculated that alternative in- and out-of-plane modes of attack may lead to the two different radical electronic states. Interaction of the HOMO and the LUMO of NCS with the SOMO of an attacking radical shows how this is possible.

The SOMO of an electrophilic radical will interact most strongly with the NCS HOMO. The preferred interaction is shown in Scheme I (a), and leads to attack from above the NCS plane. Further reaction yields the new Cl-Cl bonding orbital and the SOMO of the π succinimidoyl radical.

If, on the other hand, the SOMO of the attacking radical is high lying (i.e., the radical is nucleophilic), it will interact strongly with the NCS LUMO, as shown in Scheme I (b). The

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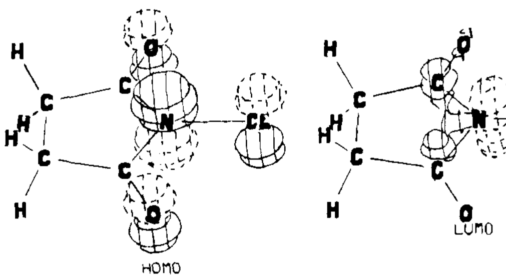


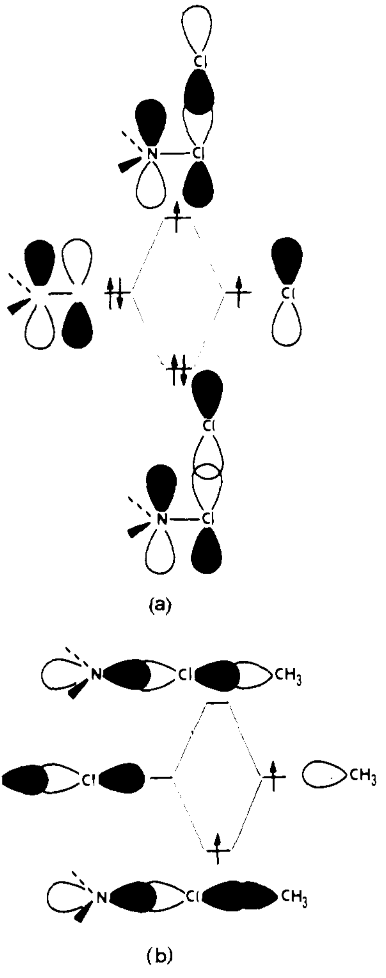
Figure 1. The frontier orbitals of *N*-chlorosuccinimide.

preferred direction of attack is colinear with the NCl bond and further reaction leads to formation of the σ_N succinimidoyl radical via involvement of the lower lying σ_{NCl} orbital.

MNDO reaction path calculations confirm these predictions. A chlorine atom gives initial attack from above the NCS molecule, practically on a line from chlorine perpendicular to the mean molecular plane. This reaction yields the π radical and is calculated to be exothermic by 14.6 kcal mol^{-1}, with an activation energy of 7.2 kcal mol^{-1}. The methyl radical, however, gives initial attack colinear with the NCl bond, yielding σ_N succinimidoyl in a reaction which has an activation energy of 14.6 kcal mol^{-1} and which is exothermic by 0.8 kcal mol^{-1}.

Reaction paths calculated using initial attack by $CH_3\cdot$ perpendicular to the NCS plane collapsed to the colinear attack path. When Cl approaches from exactly the line of the NCl bond, an electronic state which correlates with the σ_O succinimidoyl radical is obtained. This approach leads to a steep increase in energy but no reaction. If the Cl· atom is initially placed slightly away from the N–Cl axis, the reaction path collapses to one identical with that calculated for initial attack perpendicular to the plane.

Scheme I



The orbital situation outlined above is by no means uncommon, so that Skell's suggestion[1] that there may be more cases of excited-state radical generation is almost certainly correct. The search for further examples can, however, be greatly facilitated by preliminary screening of likely precursors by molecular orbital theory.

Acknowledgments. The author thanks Professor P. v. R. Schleyer for support and encouragement and Dr. J. Chandrasekhar and Dr. P. Hofmann for helpful discussions. This work was facilitated by the cooperation of the staff of the Regionales Rechenzentrum Erlangen.

Supplementary Material Available: Summaries of MNDO results for NCS and the two succinimidoyl radicals (3 pages). Ordering information is given on any current masthead page.

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(10) At RHF/STO-3G the NCS LUMO is a π^*_{CO} combination with very little contribution at N and Cl. This orbital is, however, close in energy to the σ^*_{NCl}, as it is at MNDO. The HOMO and LUMO discussed here refer to the orbitals shown in Figure 1. The order of the π^*_{CO} and σ^*_{NCl} orbitals has no effect on the arguments presented in the mechanistic discussion.

(11) The half-electron method is not well suited for the calculation of excited-state radicals, and this is not usually possible with our present version of the MNDO program. In this case, however, the σ_N radical can be obtained by use of a suitable starting geometry.

Timothy Clark
Institut für Organische Chemie
der Friedrich-Alexander-Universität Erlangen-Nürnberg
D-8520 Erlangen, West Germany

Received June 27, 1979

The Carbenoid, CCl_3Li, Eschews Tetrahedral Structures

Sir:

Both reactivity[1,2] and matrix isolation studies[3,4] suggest the carbenoid, CCl_3Li, to exist in more than one isomeric form. Our calculations on the prototype carbenoid, CH_2FLi, revealed three separate minima (isomers),[5] none of which conforms to conventional structural rules for organic molecules. We have now continued our quest for unusual geometries of carbon compounds[6] by investigating CCl_3Li by ab initio molecular orbital theory.[7] Our results indicate the *triply bridged* species (**1**), with lithium situated on the "wrong side" of the molecule, to be the most stable form of CCl_3Li!

Geometry optimization of a $Cl_2C{:}ClLi$ complex of C_s symmetry, analogous to one of the minima of H_2CFLi,[5] led to **1** (C_{3v}). The most stable form of CH_2FLi[5] has its counterpart in **2**. **3**, a $Cl_2C{:}LiCl$ complex, is the third local minimum on the potential energy surface at both the minimal basis STO-3G[8] and split-valence basis 4-31G[9] levels. The geometry of the

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