REPORT DOCUMENTATION PAGE

Form Approved
OMB NO. 0704-0188

1. AGENCY USE ONLY (Leave Blank)

2. REPORT DATE 1 March 2002

3. REPORT TYPE AND DATES COVERED
FINAL: 21 Sept 1998 - 20 Sept 2000

4. TITLE AND SUBTITLE
Electronically Excited Oxygen

5. FUNDING NUMBERS
DAAG55-98-1-0515

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8. PERFORMING ORGANIZATION REPORT NUMBER 2000-1

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)
U. S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSORING / MONITORING AGENCY REPORT NUMBER
37298-EL
.1

11. SUPPLEMENTARY NOTES
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13. ABSTRACT (Maximum 200 words)

The specific aim of this research project was to explore the role of electronically excited oxygen in a variety of processes: combustion, spontaneous ignition, cool flames, and unusual structural forms of oxygen. The results show that electronically excited oxygen participates in cool flame combustion through a chain mechanism involving a manifold of electronically excited molecular species. At elevated temperatures of 600 K that are much lower than normal combustion temperatures, electronically excited oxygen reacts with hydrocarbons (for instance, through ene-reactions) at rates that are 10-20 times faster than quenching of the excited state. The significance of this result is that the oxygen excitation process can be exploited to enhance the fuel burning properties of internal combustion engines and that the spontaneous oxidation (combustion) of liquid fuels can be explained. A further result is that a valence bond analysis of assemblies of oxygen molecules provides insight into their electronic structure. The significance of this result is in explaining the nature of bonding between oxygen atoms in an extended molecular system.

14. SUBJECT TERMS
electronic excitation, oxygen, combustion, molecular structure

15. NUMBER OF PAGES
3

16. PRICE CODE

17. SECURITY CLASSIFICATION OR REPORT	18. SECURITY CLASSIFICATION ON THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

NSN 7

Standard Form 298 (Rev.2-89)
Prescribed by ANSI Std. 239-18
298-102

20030605 099

Enclosure 1

REPORT DOCUMENTATION PAGE (SF298)
(Continuation Sheet)

Final Report: Electronically Excited Oxygen – 37298-EL – DAAG55-98-1-0515
Period: 21 September 1988 – 20 September 2000

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(A) Statement of the problem studied

The problem studied in this research project was the inefficiency in the combustion process in a normal diesel engine. The question posed was what is the role of electronically excited oxygen in the combustion process? Can electronically excited oxygen be used to improve the performance of a diesel engine? A further problem studied was the electronic structure of extended molecular systems containing oxygen, especially as pertaining to electronically excited oxygen.

(B) Summary of the most important results

The results show that electronically excited oxygen, $O_2(^1)_g)$, participates in cool flame combustion through a chain mechanism involving a manifold of electronically excited molecular species. The chain reaction consists of the following three processes:

$$R_a + O_2\left(^1\Delta_g\right) \xrightarrow{k_1} R_aO_2 \quad (1)$$

$$R_aO_2 \xrightarrow{k_2} {}^{3,1}R_bCO^* + R_cCO \quad (2)$$

$${}^{3,1}R_bCO^* + O_2\left(^3\Sigma_g^-\right) \xrightarrow{k_3} {}^{1,3}R_bCO + O_2\left(^1\Delta_g\right) \quad (3)$$

The first of these reactions (k_1) is a spin allowed reaction of an organic molecule (fuel) R_a forming an organic peroxide, hydroperoxide or endoperoxide, R_aO_2, depending on the composition of R_a, steric factors and conditions. As an example, the reaction of singlet delta excited oxygen with olefins is a 1,2 cycloaddition process[1-3] forming dioxetanes. These dioxetanes are thermally unstable and decompose (k_2) into organic carbonyls, ketones and aldehydes, where one of the product carbonyl species, represented by ${}^{3,1}R_bCO^*$, is found in an excited electronic state with triplet or singlet spin and the other is in the ground state, symbolically R_cCO. The excited carbonyl molecule undergoes an energy transfer reaction (k_3) with excitation of ground state oxygen to regenerate singlet delta excited oxygen. This energy transfer reaction has been seen to be efficient for both triplet and singlet excitation of the carbonyl[1,4-12]. The enhancement of methane and ethylene cool flames by the photoexcitation of formaldehyde[13] can be explained through energy transfer excitation of oxygen to the singlet delta state, as in k_3, followed by the chain, k_1 to k_3.

The chain reaction is vulnerable to termination through both radiative and radiationless degradation modes

$$R_bCO^* + M \xrightarrow{k_4} R_bCO + M \quad \{+h\nu\} \quad (4)$$

$$O_2\left({}^1\Delta_g\right) + M \xrightarrow{k_5} O_2\left({}^3\Sigma_g^-\right) + M \;\; \{+h\nu\} \qquad (5)$$

The production of excited carbonyl products (k_2) in the decomposition of the organic peroxides leads to the formaldehyde-like chemiluminescence (k_4) of these reactions[1,4-11]. The radiative emission of the carbonyl (k_4) has been measured[14,15] as 10^{-6} photons per excited R_xCO^*, implying both a weak emission and the possibility of a reasonable chance for the chain-sustaining reaction with ground state oxygen. Quenching[16-19] of the singlet delta excited oxygen (k_5) can occur with a number of possible collision partners, M, where $O_2(^1)_g)$ itself is one of the more efficient quenchers[20-22]. However, the $O_2(^1)_g)$ - $O_2(^1)_g)$ dimole radiation at 0.633 : is not prominent in cool flames, probably because the concentration of $O_2(^1)_g)$ is low relative to other species. This suggests perhaps a reasonable probability of reaction with the starting hydrocarbon, which is initially in greater abundance. The radiationless processes are expected to be relatively slower.

At elevated temperatures of 600 K that are much lower than normal combustion temperatures, electronically excited oxygen reacts with hydrocarbons in reaction (1) above (for instance, through ene-reactions[23]) at rates that are 10-20 times faster than quenching[24] of the excited state in reaction (5) above. This is an indication that the linear chain mechanism of reactions (1)-(3) above is a realistic and viable possibility for cool flame combustion processes.

Thermodynamic conditions within a diesel cylinder leading to significant reduction in ignition delay are consistent with cool flame spontaneous ignition. The significance is that reduction in ignition delay is accompanied by a reduction in the amount of fuel burned in the pre-mixed combustion phase and an increase in the mixing-controlled phase, thus leading to improvement in diesel performance (less knock and soot). The research involved investigating methods of gaining control of this process through the infusion of energy during the diesel cycle to excite oxygen to its electronically excited singlet spin state, $O_2(^1)_g)$.

A further result is that a valence bond analysis[25-26] of assemblies of oxygen molecules provides insight into their electronic structure. The significance of this result is in explaining the nature of bonding between oxygen atoms in an extended molecular system.

(C) Listing of all publications and technical reports supported under this grant or contract

Technical reports submitted to ARO:
Interim Report 1998-1, 24 April 1999
Interim Report 1999-1, 31 March 2000

(D) List of all participating scientific personnel showing any advanced degrees earned by them while employed on the project

David M. Silver, PhD

(E) Report of Inventions (by title only)

none

(F) Bibliography

1. Turro, N. J. *Modern Molecular Photochemistry;* Benjamin/Cummings: Menlo Park, California, 1978; Chap. 14.
2. Kearns, D. R. *Chem. Rev.* **1971**, *71*, 395-427.

3. Kearns, D. R. *J. Am. Chem. Soc.* **1969**, *91,* 6554-6563.
4. Schaap, A. P., ed. *Singlet Molecular Oxygen;* Halsted Press, Wiley: New York, 1976.
5. Wasserman, H. H.; Murray, R. W., Eds. *Singlet Oxygen;* Academic Press: New York, 1979.
6. Frimer, A. A., Ed. *Singlet O_2 Volume I: Physical-Chemical Aspects, Volumes II and III: Reaction Modes and Products, Parts 1 and 2;* CRC Press: Boca Raton, Florida, 1985.
7. Khan, A. U.; Kasha, M. *J. Am. Chem. Soc.* **1966**, *88,* 1574-1576.
8. Wayne, R. P. *Advan. Photochem.* **1969**, *7,* 311-371.
9. Ogryzlo, E. A. In ref. 5, pp. 35-58.
10. Khan, A. U. In ref. 6, Volume I, pp. 39-79.
11. Wilson, T. In ref. 6, Volume II, pp. 37-65.
12. Gorman, A. A.; Rodgers, M. A. J. *J. Am. Chem. Soc.* **1989**, *111*, 5557-5560.
13. Norrish, R. G. W.; Patnaik, D. *Nature* **1949,** *163,* 883-885.
14. Day, R. A.; Pease, R. N. *J. Am. Chem. Soc.* **1940**, *62*, 2234-2237.
15. Topps, J. E. C.; Townend, D. T. A. *Trans. Faraday Soc.* **1946**, *42*, 345-353.
16. Foote, C. S. In ref. 5, pp. 139-171.
17. Matheson, I. B. C.; Lee, J.; Yamanashi, B. S.; Wolbarsht, M. L. *J. Am. Chem. Soc.* **1974**, *96,* 3343-3348.
18. Schmidt, R. *J. Am. Chem. Soc.* **1989**, *111*, 6983-6987.
19. Mikkelsen, K. V.; Xgren, H. *J. Phys. Chem.* **1990**, *94*, 6220-6227.
20. Khan, A. U.; Kasha, M. *J. Am. Chem. Soc.* **1970**, *92*, 3293-3300.
21. Matheson, I. B. C.; Lee, J.; Yamanashi, B. S.; Wolbarsht, M. L. *Chem. Phys. Letters* **1974**, *27*, 355-358.
22. Fisk, G. A.; Hays, G. N. *Chem. Phys. Letters* **1981**, *79*, 331-333.
23. Heidner, R.F.; Gardner, C.E., El-Sayed, T. M., Segal G. I., Kasper, J. V. V. *J. Chem. Phys.* **1981**, *74*, 5618.
24. Ashford, R. D.; Ogryzlo, E. A.*J. Am. Chem. Soc.* **1975**, *97*, 3604.
25. Silver, D. M. *J. Am. Chem. Soc.* **1974,** *96*, 5959-5967.
26. Silver, D. M.; Karplus, M. *J Am. Chem. Soc.* **1975,** *97,* 2645-2654.

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CONTRACT/GRANT NUMBER: 37298-EL

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