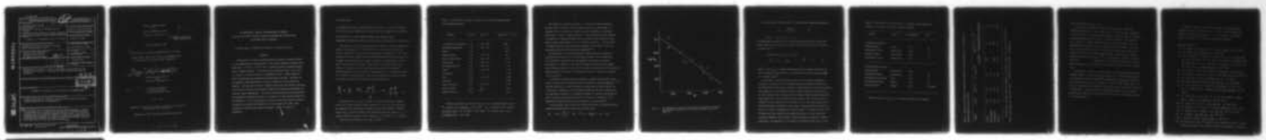
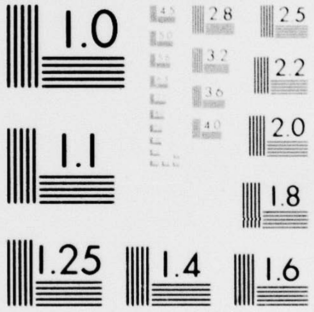
AD-A076 571   BOSTON UNIV MASS DEPT OF CHEMISTRY   F/G 13/8
THE QUENCHING OF BIACETYL PHOSPHORESCENCE BY ALKENES. A DISSECT--ETC(U)
JUL 79   G JONES, M SANTHANAM , S CHIANG   N00014-76-C-0442

UNCLASSIFIED   NL

1 OF 1
AD
A076571



END
DATE
FILMED
12-79
DDC



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS 1963-A

AD A076571

DDC FILE COPY

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

B.S.

REPORT DOCUMENTATION PAGE	READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER Technical Report No. 8 ✓	2. GOVT ACCESSION NO.
3. RECIPIENT'S CATALOG NUMBER	
4. TITLE (and Subtitle) The Quenching of Biacetyl Phosphorescence by Alkenes. A Dissection of Rate Effects on Exciplex Formation and Exciplex Decay for Ketone Triplet Quenching.	5. TYPE OF REPORT & PERIOD COVERED Technical, 10/1/77-2/28/79
	6. PERFORMING ORG. REPORT NUMBER ----
7. AUTHOR(s) G. Jones, II, M. Santhanam, and S.-H. Chiang	8. CONTRACT OR GRANT NUMBER(s) N00014-76-C-0442
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry, Boston University Boston, Massachusetts 02215	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 051-574/9-26-75 (472)
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research 800 North Quincy Street Arlington, Virginia 22217 DODAAD Code N00014	12. REPORT DATE July 1, 1979
	13. NUMBER OF PAGES 9
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	15. SECURITY CLASS. (of this report) Unclassified
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

451 003

LEVEL

16. DISTRIBUTION STATEMENT (of this Report)

Reproduction in whole or in part is permitted for any purpose of the United States Government. Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

DDC RECEIVED OCT 10 1979 E

18. SUPPLEMENTARY NOTES

Prepared for publication in the Journal of Photochemistry

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Ketone phosphorescence quenching, electron donor-acceptor exciplexes, biacetyl photochemistry and photophysics

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Rate constants for the quenching of biacetyl phosphorescence by alkenes at room temperature in benzene have been measured. Quenching constants correlate with the ionization potentials of the alkenes. Rate data from phosphorescence quenching for a number of ketones are compared and trends associated with formation and decay of electron donor-acceptor complexes of excited ketone triplets and alkene quenchers.

DD FORM 1473, 1 JAN 73 EDITION OF 1 NOV 65 IS OBSOLETE

S/N 0102-014-6601

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

79 10 09 135

OFFICE OF NAVAL RESEARCH

(15)

(12) 15

Contract N00014-76-C-0442

Project No. NR 051-574

(9) Technical rept. no. 8,
1 Oct 77-28 Feb 79,

TECHNICAL REPORT NO. 8

(6) THE QUENCHING OF BIACETYL PHOSPHORESCENCE BY ALKENES - A DISSECTION OF RATE EFFECTS ON EXCIPLEX FORMATION AND EXCIPLEX DECAY FOR KETONE TRIPLET QUENCHING.

by

(10) Mahalingam Sheau-Hwa
Guilford [redacted] Jones, II, [redacted] Santhanam [redacted] Chiang

Prepared for Publication
in the
Journal of Photochemistry

(11) 1 Jul 79

Department of Chemistry
Boston University
Boston, Massachusetts 02215

July 1, 1979

401 003

THE QUENCHING OF BIACETYL PHOSPHORESCENCE BY ALKENES
A DISSECTION OF RATE EFFECTS ON EXCIPLEX FORMATION AND EXCIPLEX DECAY FOR KETONE TRIPLET QUENCHING

Guilford Jones, II, Mahalingam Santhanam, and Sheau-Hwa Chiang

ABSTRACT

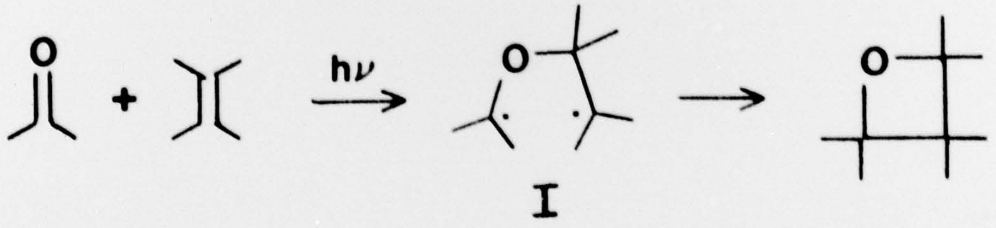
The quenching of biacetyl phosphorescence by alkenes in benzene solution at room temperature has been observed. Stern-Volmer quenching constants which range from 1×10^4 to 1×10^7 M^{-1} sec^{-1}, correlate with the ionization potentials of alkene quenchers. The slope of the correlation line ($\Delta \log k_q/\Delta IP$) is -1.90 eV^{-1}, a value similar to IP dependences found in other studies of ketone fluorescence and phosphorescence quenching by alkenes. Constants for the quenching of phosphorescence of several ketones by a given alkene are compared. The data, which include relatively low values for biacetyl quenching, do not reflect electron donor-acceptor properties of ketones and quenchers but show more complex dependences. The results are consistent with the formulation of the empirical quenching constant as a product of an equilibrium constant for the formation of an excited complex of ketone triplet and alkene (a constant relatable to the mutual polarizability of the encounter pair) and a rate constant for exciplex decay (which represents a number of competing processes).

Preliminary Note

THE QUENCHING OF BIACETYL PHOSPHORESCENCE BY ALKENES. A DISSECTION OF RATE EFFECTS ON EXCIPLEX FORMATION AND EXCIPLEX DECAY FOR KETONE TRIPLET QUENCHING

GUILFORD JONES, II,* MAHALINGAM SANTHANAM, AND SHEAU-HWA CHIANG
Department of Chemistry, Boston University, Boston, Massachusetts 02215 (U.S.A.)

The quenching of ketone phosphorescence by alkenes has been the subject of a number of investigations.[1] The relationships of structure and reactivity for the interaction of ketone triplets and alkenes are important to the understanding of the well known oxetane ring-forming Paterno-Buchi reaction (eqn 1).[2] A number of ketone/alkene pairs appear to undergo cycloaddition by a triplet path.[3] Biacetyl has been shown to participate in the Paterno-Buchi cycloaddition in competition with a photochemical ene addition to alkenes;[4] a triplet mechanism including diradical intermediates (e.g., I) has been suggested.[5] We wish to report results concerning the quenching of biacetyl triplets by alkenes including those important in photocycloaddition.



(1)

The quenching by a series of alkenes of steady-state biacetyl phosphorescence in nitrogen-purged or degassed benzene solutions at room temperature was analyzed using conventional procedures (Perkin Elmer MPF44A instrument). Values of $k_q\tau_0$ from Stern-Volmer plots along with quenching constants k_q, calculated assuming a biacetyl triplet lifetime (τ_0) of 0.46 ms[6] and including data from the literature, are shown in Table 1.

Table 1. Stern-Volmer Constants for Quenching of Biacetyl Phosphorescence by Unsaturated Compounds

Quencher	IP_v(eV)[a]	$k_q\tau_o(M^{-1})$	$k_q(M^{-1}sec.^{-1} \times 10^{-5})$
2,5-dimethyl-2,4-hexadiene	7.84	3.66×10^5	7960.
hexamethyldewarbenzene	7.90	1.04×10^3	22.6
indole	7.92	----	129.[b]
N-methylpyrrole	7.95	1.25×10^3	27.2
trans-1-phenylpropene	8.28	4.84×10^2	10.5
dihydropyran	8.34	9.06×10^1	1.97
tetramethylethylene	8.42	7.00×10^1	1.52
indene	8.63	1.24×10^2	2.70
cyclohexene	8.72	----	1.00[c]
furan	8.89	3.15×10^1	0.68
norbornene	8.95	----	0.24[d]
ethyl vinyl ether	9.07	2.63×10^1	0.57
trans-2-hexene	9.16	4.60	0.10
methacrylonitrile	10.39	< 0.5	< 0.01

---

[a] Ionization potentials from the literature, most from photoelectron spectra. [b] E. Fujimori, Mol. Photochem., 6, 91 (1974). [c] H.L.J. Backstrom and K. Sandros, Acta Chem. Scand., 14, 48 (1960). [d] R.R. Sauers, P.C. Valenti, and E. Tauss Tetrahedron Lett., 3129 (1975).

The pattern of quenching constants as a function of alkene structure was most readily related to electron donor properties of the alkenes. A reasonable fit of the data with alkene ionization potentials (correlation coefficient = 0.939) is shown in Figure 1. The unusually effective quencher, 2,5-dimethyl-2,4 -hexadiene (DMH) was not included in the correlation since energy transfer from biacetyl (E_T = 56 kcal/mol) to DMH (E_T < 56 kcal/mol[7]) is probably important (energy transfer quenching of dicarbonyl triplets by conjugated dienes has been previously documented[6,8]).

The dependence of quenching constant on alkene ionization potential is consistent with the behavior of other ketone triplets[1] and is reminiscent of relationships established for the quenching of alkanone and alkanal fluorescence. A summary of data (Table 2) shows the nearly uniform dependence of emission quenching rate for n,π^* carbonyl excited states on the electron donor properties of alkenes. The slopes of IP plots ($\Delta \log k_q/\Delta$ IP) average -1.78 ± 0.38 eV^{-1}.

In studies of carbonyl emission quenching, apparent donor-acceptor interaction has been usually associated with the formation of excited complexes.[1,9-12] Although exciplexes of simple ketones and alkenes have not been directly detected, their intermediacy (in fluorescence quenching) has been inferred from the temperature dependence of quenching constants.[9] Deviant Stern-Volmer behavior has been associated with reversible formation of exciplexes in the quenching of glyoxal phosphorescence by alkenes in the gas phase.[13]

For bimolecular decay of biacetyl triplets and alkenes, reversible exciplex formation and deactivation involve the following steps

$$^3\mathrm{BI} + \mathrm{ALK} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} {}^3\mathrm{EXC} \xrightarrow{k_2} \mathrm{PRODUCT} + \mathrm{BI} + \mathrm{ALK}$$

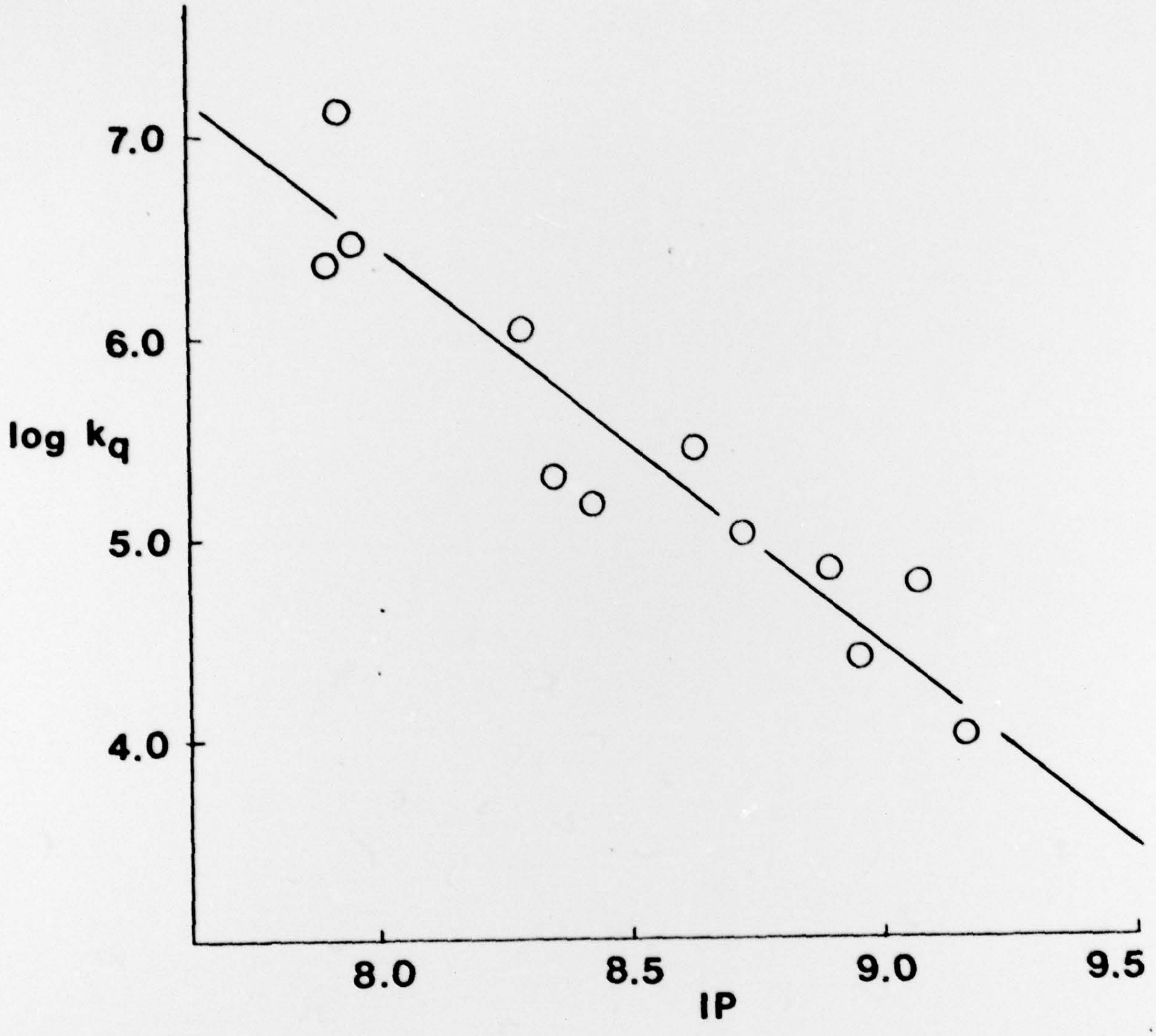


Figure 1. The dependence of biacetyl phosphorescence quenching constant on the ionization potential (eV) of alkene quenchers (data from Table 1).

For this simple kinetics scheme, the phosphorescence quenching constant is

$$k_q = \frac{k_1 k_2}{k_{-1} + k_2} \qquad (3)$$

and $k_q = K_1 k_2$ if $k_{-1} >> k_2$

The dependence of quenching rate on alkene ionization potential follows from proportionalities associated with charge transfer within sensitizer-quencher encounter pairs.[14]

$$\log k_q \propto \log K_1 \propto \Delta G_{ct} \propto E_{ox} \propto IP$$

$$\Delta G_{ct} = E_{ox} - E_{red} - E_T - \frac{e^2}{\varepsilon r} - T\Delta S \qquad (4)$$

where E_{ox} and E_{red} are standard redox potentials for alkenes and biacetyl in their electronic ground states, E_T is the biacetyl excitation energy and $\frac{e^2}{\varepsilon r}$ is a coulombic term.[15]

Loutfy and his coworkers[1] have used eqn 4 in an extensive treatment of reversible exciplex kinetics for alkene quenching of ketone phosphorescence. The implication of this work is that for a given ketone and a series of quenchers $\log k_q \propto \log K_1$ is the important relation, whereas structural effects on k_2 are less important and not related to the principal donor-acceptor interaction represented by K_1. (For acetone and donor alkenes a 200 fold range was calculated for K_1 as opposed to 20 fold change in k_2 in the opposite direction.[1]) We have paid special attention to the change in phosphorescence quenching constant for a series of ketones with a single alkene. The sample of data (Table 3) taken from other studies and including our biacetyl results shows that structural changes in ketone lead to large variations in quenching constants. Importantly, the dependence is not readily associated with the redox driving

Table 2. The Quenching of Emission from n,π* Carbonyl Excited States by Alkenes as a Function of Quencher Ionization Potential

System	Solvent	IP Dependence[a]	Ref
Fluorescence quenching			
acetone/alkenes	hexane	-1.28	9
acetone/enol ethers	acetonitrile	-2.10	10
biacetyl/alkenes	acetonitrile	-2.10	11
biacetyl/enol ethers	acetonitrile	-2.70	11
Phosphorescence quenching			
acetone/alkenes	acetonitrile	-1.66	1
acetone/enol ethers	acetonitrile	-1.50	10
benzophenone/enol ethers	freon	-1.65	10
butyrophenone/alkenes	benzene	-1.09	12
biacetyl/alkenes	benzene	-1.90	this work

[a] Slopes of plots of log k_q vs IP (ionization potentials of alkenes).

Table 3. Ketone Triplet Energies and Reduction Potentials and Rate Constants for the Quenching of Ketone Phosphorescence by Alkenes

Ketone	E_T (eV)	E_{red}[a] (V)	$E_T + E_{red}$ (eV)	$k_q (M^{-1} sec^{-1}) \times 10^{-6}$		
				enol ether	tetramethylethylene	norbornene
Acetone	3.38	-2.31	1.07	340[b]	51	43
Butyrophenone	3.13	-2.03	1.10		460	37
Benzophenone	2.94	-1.84	1.10	1100[b]	895	40
Biacetyl	2.42	-1.22	1.20	0.20[c]	0.15	0.024

[a] Polarographic half-wave reduction potentials (vs Ag/AgCl, CH_3CN); ref 1 and G.A. Russell and S.A. Weiner, J. Am. Chem. Soc., 89, 6623 (1967). [b] 1-Ethoxy-2-methyl propene. [c] Dihydropyran

force for the ketones (E_{red} + E_T).

Since exciplex formation constants are expected to be similar for different ketones and a single quencher (ΔG_{ct} is almost constant, suggesting similar values for K_1 assuming common coulombic and entropy factors), relative quenching rates may reflect changes in exciplex decay rate. The makeup of k_2 is complex; it includes rate constants for product formation as well as parameters for unproductive decay to ketone and starting alkene. One factor that is likely to be important is the ketone excitation energy (the most important driving force for mounting decay barriers) revealed in the general diminished reactivity of biacetyl [6,16]. If the sequence, ^{3}ketone → ^{3}exciplex → ^{3}diradical is important,[17] then diradical stability (which along with E_T determines the exothermicity of diradical formation) will be reflected in k_2.

For diradical formation the effectiveness of the presumed reactive center (carbonyl oxygen) in alkene attack may be decisive. The delocalized nature of the non-bonding orbitals of biacetyl[18] (compared with monoketones) matches the much reduced reactivity of the dicarbonyl triplet.[19] Other factors may be important in determining the rate of direct exciplex decay (not involving diradical intermediates), including rotational and other motion away from an exciplex geometry which affects spin-orbit coupling and the rate of intersystem crossing to the ground state.[21]

We thank the donors of the Petroleum Research Fund administered by the American Chemical Society and the U.S. Office of Naval Research for support of (postdoctoral associate)   M.S. and the U.S. Department of Energy for support of S.C. through a research assistantship.

References and Notes

(1) R.O. Loutfy, S.K. Dogra, and R.W. Yip, Can. J. Chem., 57, 342 (1979).

(2) D.R. Arnold, Adv. In Photochem., 6, 301 (1968).

(3) See, for example, L.A. Singer, R.E. Brown, and G.A. Davis, J. Am. Chem. Soc., 95, 8638 (1973); (b) N.C. Yang, M. Kimura and W. Eisenhardt, ibid., 95, 5058 (1973); (c) H.A.J. Carless, J.C.S. Perkin II, 834 (1974); (d) N.J. Turro, et al., Accounts Chem. Res., 5, 92 (1972).

(4) H.-S. Ryang, K. Shima, and H. Sakurai, J. Org. Chem., 38, 2860 (1973).

(5) H.-S. Ryang, K. Shima, and H. Sakurai, J. Am. Chem. Soc., 93, 5270 (1971).

(6) N.J. Turro and R. Engel, J. Am. Chem. Soc., 91, 7113 (1969).

(7) R.E. Kellogg and W.T. Simpson, J. Am. Chem. Soc., 87, 4230 (1965).

(8) (a) A.W. Jackson and A.J. Yarwood, Mol. Photochem., 8, 255 (1977), (b) F.B. Wampler and R.C. Oldenborg, Int. J. Chem. Kinetics, 10, 1225 (1978).

(9) N.C. Yang, M.H. Hui, D.M. Shold, N.J. Turro, R.R. Hautala, K. Dawes, and J.C. Dalton, J. Am. Chem. Soc., 99, 3023 (1977).

(10) N.E. Schore and N.J. Turro, J. Am. Chem. Soc., 97, 2482 (1975).

(11) B.M. Monroe, C.-G. Lee, and N.J. Turro, Mol. Photochem., 6, 271 (1974).

(12) I.E. Kochevar and P.J. Wagner, J. Am. Chem. Soc., 94, 7512 (1972).

(13) J.T. Yardley, J. Am. Chem. Soc., 94, 7283 (1972).

(14) D. Rehm and A. Weller, Israel J. Chem., 8, 259 (1970).

(15) The slopes of IP plots for carbonyl emission quenching are small relative to values expected if full electron transfer from quencher to excited ke-

tone is rate determining (maximum slope = $\Delta \log k_q / \Delta G_{ct}$ = 1/2.3 RT = 17 eV^{-1}, assuming $\Delta G_1^{\neq}$ is a monotonous function of ΔG_{ct}[14]). For modest donor-acceptor interaction in quenching, the ΔG_{ct} function is best understood as an indicator of the mutual polarizability of excited states and quenchers (the mixing of locally excited and charge transfer configurations) rather than an association with outright electron transfer.

(16) J.C. Scaiano, *J. Photochem.*, **2**, 81 (1973/74).

(17) We will provide in another publication additional evidence that diradicals are formed on interaction of biacetyl triplets and alkenes. The evidence will include the observation of nearly complete loss of stereochemistry for photoaddition of biacetyl and 1,2-dimethoxyethene.

(18) E. Drent and J. Kommandeur, *Chem. Phys. Lett.*, **14**, 321 (1972).

(19) For relatively "slow" reactions of ketone triplets and alkenes we do not exclude a path of direct attack to give diradicals and not involving exciplexes (although arguments can be made against this route[20]). The IP correlation for phosphorescence quenching then would be understood as the result of semipolar radical attack by electrophilic carbonyl triplets. Another complicating feature in slow triplet quenching is the intervention of hydrogen abstraction as a competitor to the path which leads to cycloadducts. H abstraction may be direct or also involve an exciplex and have semi polar characteristics as well.

(20) I.E. Kochevar and P.J. Wagner, *J. Am. Chem. Soc.*, **94**, 3859 (1972).

(21) (a) N.D. Epiotis and S. Shaik, *J. Am. Chem. Soc.*, **100**, 29 (1978);
(b) N.J. Turro and V. Ramamur thy, *Mol. Photochem.*, **8**, 239 (1977).

TECHNICAL REPORT DISTRIBUTION LIST

No. Copies

Office of Naval Research
Arlington, Virginia 22217
Attn: Code 472 2

Office of Naval Research
Arlington, Virginia 22217
Attn: Code 102IP 1 6

ONR Branch Office
536 S. Clark Street
Chicago, Illinois 60605
Attn: Dr. Jerry Smith 1

ONR Branch Office
715 Broadway
New York, New York 10003
Attn: Scientific Dept. 1

ONR Branch Office
1030 East Green Street
Pasadena, California 91106
Attn: Dr. R. J. Marcus 1

ONR Branch Office
760 Market Street, Rm. 447
San Francisco, California 94102
Attn: Dr. P. A. Miller 1

ONR Branch Office
495 Summer Street
Boston, Massachusetts 02210
Attn: Dr. L. H. Peebles 1

Director, Naval Research Laboratory
Washington, D.C. 20390
Attn: Code 6100 1

The Asst. Secretary of the Navy (R&D)
Department of the Navy
Room 4E736, Pentagon
Washington, D.C. 20350 1

Commander, Naval Air Systems Command
Department of the Navy
Washington, D.C. 20360
Attn: Code 310C (H. Rosenwasser) 1

No. Copie

Defense Documentation Center
Building 5, Cameron Station
Alexandria, Virginia 22314 12

U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, N.C. 27709
Attn: CRD-AA-IP 1

Naval Ocean Systems Center
San Diego, California 92152
Attn: Mr. Joe McCartney 1

Naval Weapons Center
China Lake, California 93555
Attn: Head, Chemistry Division 1

Naval Civil Engineering Laboratory
Port Hueneme, California 93041
Attn: Mr. W. S. Haynes 1

Professor O. Heinz
Department of Physics & Chemistry
Naval Postgraduate School
Monterey, California 93940 1

Dr. A. L. Slafkosky
Scientific Advisor
Commandant of the Marine Corps (Code RD-1
Washington, D.C. 20380 1

Office of Naval Research
Arlington, Virginia 22217
Attn: Dr. Richard S. Miller 1

TECHNICAL REPORT DISTRIBUTION LIST

No. Copies

Dr. M. A. El-Sayed
University of California
Department of Chemistry
Los Angeles, California 90024 1

Dr. M. W. Windsor
Washington State University
Department of Chemistry
Pullman, Washington 99163 1

Dr. E. R. Bernstein
Colorado State University
Department of Chemistry
Fort Collins, Colorado 80521 1

Dr. C. A. Heller
Naval Weapons Center
Code 6059
China Lake, California 93555 1

Dr. M. H. Chisholm
Princeton University
Department of Chemistry
Princeton, New Jersey 08540 1

Dr. J. R. MacDonald
Naval Research Laboratory
Chemistry Division
Code 6110
Washington, D.C. 20375 1

No. Copies

Dr. G. B. Schuster
University of Illinois
Chemistry Department
Urbana, Illinois 61801 1

Dr. E. M. Eyring
University of Utah
Department of Chemistry
Salt Lake City, Utah 1

Dr. A. Adamson
University of Southern California
Department of Chemistry
Los Angeles, California 90007 1

Dr. M. S. Wrighton
Massachusetts Institute of Technology
Department of Chemistry
Cambridge, Massachusetts 02139 1

Dr. M. Rauhut
American Cyanamid Company
Chemical Research Division
Bound Brook, New Jersey 08805 1