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COLUMBIA UNIV NEW YORK DEPT OF CHEMISTRY  
METAL COMBUSTION PROCESSES AS STUDIED BY CHEMI-LUMINESCENCE AND--ETC(U)  
FEB 78 R N ZARE

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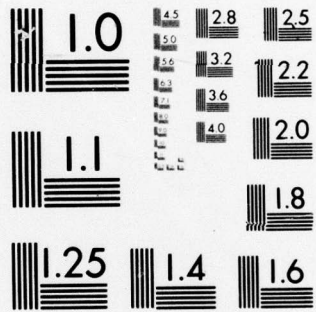
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FINAL TECHNICAL REPORT

Title: Metal Combustion Processes as Studied by Chemi-  
luminescence and Chemi-ionization.

Contract: DAAG 29-76-G-0208

Period: 5/1/76 to 6/30/77

Amount: \$50,000

Institution: The Trustees of Columbia University  
in the City of New York

Principal  
Investigator: Richard N. Zare  
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Department of Chemistry  
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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER 13785.8-C	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Metal Combustion Processes as Studied by Chemi-luminescence and Chemi-ionization	5. TYPE OF REPORT & PERIOD COVERED Final Report: 1 May 76 - 30 Jun 77	
	6. PERFORMING ORG. REPORT NUMBER	
7. AUTHOR(s) Richard N. Zare	8. CONTRACT OR GRANT NUMBER(s) DAAG29 76 G 0208	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Columbia University New York, NY 10027	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS	
11. CONTROLLING OFFICE NAME AND ADDRESS U. S. Army Research Office Post Office Box 12211 Research Triangle Park, NC 27709	12. REPORT DATE Feb 78	
	13. NUMBER OF PAGES 8	
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	15. SECURITY CLASS. (of this report) Unclassified	
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE	
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES The findings in this report are not to be construed as an official Department of the Army position, unless so designated by other authorized documents.		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Chemiluminescence Energy Chemi-ionization Metals Combustion Ions		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Metal combustion processes have been studied (1) by observing and spectroscopically analyzing visible emission; (2) by detecting "dark" states through their characteristic laser-induced fluorescence; and (3) by determining the nature and type of ionic products produced in some of these highly exothermic reactions. In the course of this work we seek general principals that can tell us about the various ways of disposing of excess reaction energy in the products.		

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I. PROBLEMS STUDIED

Metal combustion processes have been studied (1) by observing and spectroscopically analyzing visible emission; (2) by detecting "dark" states through their characteristic laser-induced fluorescence; and (3) by determining the nature and type of ionic products produced in some of these highly exothermic reactions. In the course of this work we seek general principals that can tell us about the various ways of disposing of excess reaction energy in the products.

## II. MAJOR RESULTS

The following Abstracts summarize the work performed during this contract period:

F. Engelke,\* R. K. Sander,† and R. N. Zare

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(Received 18 March 1976)

Chemiluminescence resulting from the reaction  $M + \text{ClO}_2$ ,  $M = \text{Mg, Ca, Sr, or Ba}$ , has been observed in crossed molecular beams. Two special features are found: (1) selective formation of  $\text{MO}^*$  in the  $A' {}^1\Pi$  state in preference to the isoenergetic  $A' {}^1\Sigma^+$  state; and (2) the formation of  $\text{MCl}^*$  in various electronic states. Although the  $\text{MCl}^*$  product results from attack of the central Cl atom in  $\text{ClO}_2$ , its cross section is comparable to that of  $\text{MO}^*$ . The cross section for chemiluminescence is a small fraction of the total reaction cross section, which is larger than gas kinetic. From the chemiluminescent spectra the relative electronic, vibrational, and rotational population distributions are derived and the following lower bounds are placed on the MO dissociation energies:  $D_0^0(\text{CaO}) \geq 109.7 \pm 3.5$  kcal/mole;  $D_0^0(\text{SrO}) \geq 107.7 \pm 3.5$  kcal/mole; and  $D_0^0(\text{BaO}) \geq 133.6 \pm 3.5$  kcal/mole. The reaction dynamics are discussed in terms of an electron transfer from M to the half-filled antibonding orbital of  $\text{ClO}_2$ .

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Received 16 February 1976

A study is made of the visible chemiluminescence resulting from the reaction of an atomic beam of barium with  $\text{I}_2$  under single-collision conditions ( $\sim 10^{-4}$  torr). The resulting spectrum consists of the  $\text{BaI } C {}^2\Pi_1 \rightarrow X {}^2\Sigma$  emission on top of an underlying "continuum". The variation of the BaI emission intensity with Ba and  $\text{I}_2$  flux is investigated, and it is concluded that the reaction is bimolecular. The total phenomenological cross section for barium atom removal is determined to be  $86 \text{ \AA}^2$ , which agrees well with the total reactive cross section calculated assuming an electron jump mechanism. The short wavelength cutoff is identified as the transition from the  $v' = 41$  level of the  $\text{BaI } C {}^2\Pi_{3/2}$  state to the  $v'' = 41$  level of the  $\text{BaI } X {}^2\Sigma$  state. A strict lower bound  $D_0^0(\text{BaI}) \geq 102 \pm 0.7$  kcal/mole for the ground state dissociation energy of BaI is obtained from this short wavelength cutoff. The value  $D_0^0(\text{BaI}) = 102 \pm 1$  kcal/mole is recommended, where the error estimate includes the possible contribution from the final relative translational energy of the products.

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Received 16 February 1976

The reactions  $\text{Ba} + \text{CH}_3\text{I} \rightarrow \text{BaI} + \text{CH}_3$  and  $\text{Ba} + \text{CH}_2\text{I}_2 \rightarrow \text{BaI} + \text{CH}_2\text{I}$  have been investigated by the method of laser-induced fluorescence. Excitation spectra are reported for BaI products formed under single-collision conditions in a "beam-gas" arrangement. The production of BaI for  $\text{Ba} + \text{CH}_2\text{I}_2$  is found to be a major reaction pathway with a cross section about twice that for  $\text{Ba} + \text{CH}_3\text{I}$ . The relative vibrational populations show for both reactions bell-shaped distributions peaking close to  $v = 21$  for  $\text{Ba} + \text{CH}_3\text{I}$  and  $v = 39$  for  $\text{Ba} + \text{CH}_2\text{I}_2$ . The corresponding average fraction of the total reaction exoergicity that appears as BaI vibration is  $\bar{f}_v = 0.18$  for  $\text{Ba} + \text{CH}_3\text{I}$  and  $\bar{f}_v = 0.29$  for  $\text{Ba} + \text{CH}_2\text{I}_2$ . In the case of  $\text{Ba} + \text{CH}_3\text{I}$ , an estimate for the average relative translational energy of the products, obtained from the primitive angular distribution measurements of Lin, Mims and Herm. can be combined with the average vibrational excitation of BaI to provide evidence that the internal excitation of the methyl radical exceeds that of BaI. A model is discussed which postulates an electron jump in the exit valley of the  $\text{Ba} + \text{CH}_3\text{I}$  reaction to account for this feature of the reaction dynamics.

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Received 15 September 1976

The reaction of the heavier Group IIA metal atoms Ba, Sr, and Ca with  $\text{S}_2\text{Cl}_2$  under crossed-beam conditions produces a chemiluminescent spectrum in which the  $\text{S}_2 \text{B}^3\Sigma_u^- - \text{X}^3\Sigma_g^-$  emission bands are the most prominent feature. In addition, chemiluminescence is also observed from excited states of the alkaline earth monochlorides and from a "pseudo-continuum" which is believed to originate from an excited polyatomic metal halide, probably the alkaline earth dichloride. More than 100 bands are assigned to the  $\text{S}_2 \text{B}-\text{X}$  band system; the vibrational levels of the  $\text{S}_2 \text{B}$  state are found to be populated by the reaction in a non-thermal manner. The reaction forming  $\text{S}_2^*$  is determined to be first order with respect to both the ground state metal atom and the disulfur dichloride molecule. Phenomenological cross sections for removal of metal atoms from the metal beam by  $\text{S}_2\text{Cl}_2$  are  $162 \pm 20 \text{ \AA}^2$  for Ba,  $105 \pm 20 \text{ \AA}^2$  for Sr, and  $92 \pm 20 \text{ \AA}^2$  for Ca, which is consistent with an electron jump model if the vertical electron affinity of  $\text{S}_2\text{Cl}_2$  is 3.25 eV. Absolute photon yield measurements indicate that less than 1% of the reaction products are  $\text{S}_2^*$  molecules that emit in the 2800–6000 Å region. From the single-collision chemiluminescence spectra the following dissociation energies are estimated:  $D_0^0(\text{Cl}-\text{S}_2\text{Cl}) = 44.2 \pm 5 \text{ kcal/mole}$  and  $D_0^0(\text{S}_2-\text{Cl}) = 54 \pm 5 \text{ kcal/mole}$ . A speculation is offered that most of the reaction exoergicity appears in the  $\text{S}_2^*$  product when the  $\text{S}_2\text{Cl}_2\text{M}$  collision complex passes through a nearly-planar, five-member ring structure in separating to form products.

HENRY U. LEE AND RICHARD N. ZARE

*Department of Chemistry, Columbia University, New York, New York 10027*

We have obtained the chemiluminescent spectra of YbF and YbCl from the reactions of ytterbium with fluorine and ytterbium with chlorine dioxide under beam-gas conditions and in a high-pressure (3 Torr) flow system. Much more extensive band systems are observed than hitherto reported, and a vibrational reanalysis of the ground and low-lying states is made. Although the *A-X* and *B-X* systems appear regular in YbCl, the *A*  $^2\Pi_1-X$   $^2\Sigma^+$  and *B-X* systems in YbF exhibit extensive vibrational perturbations. The interaction between molecular states arising from the separated atoms Yb(*5d*) + X(*np*) as well as Yb(*6p*) + X(*np*) is believed to cause these perturbations. An unassigned red-band system is observed in emission for both YbF and YbCl, suggesting that the lowest-lying excited state is not the *A* state.

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Received 23 June 1976

Revised manuscript received 10 November 1976

Large variations are observed in the chemi-ionization cross sections for the thermal reactions of Ca, Sr, Ba, and Yb atoms with various halogen and interhalogen molecules, as well as chlorine dioxide. While the alkaline earth metal atom reactions generally produce ion products, this is only true for Yb + F<sub>2</sub>. The absence of ions for the other Yb reactions is explained on energetic grounds. For the reaction of a metal atom (M) with a halogen (X<sub>2</sub>), the positive and negative ions are determined mass spectrometrically to be MX<sup>+</sup> and X<sup>-</sup>. For the interhalogens, both ion channels, MX<sup>+</sup> + Y<sup>-</sup> and MY<sup>+</sup> + X, are observed, the dominant channel being the one more exoergic. Absolute chemi-ionization cross sections are estimated to range from 0.001 to 1.6 Å<sup>2</sup>, with an uncertainty of ± 100%. These cross sections decrease in the order Ba > Sr > Ca > Yb for all oxidizer gases other than F<sub>2</sub>. For a given alkaline earth metal, the cross sections decrease in the order F<sub>2</sub> > Cl<sub>2</sub> > Br<sub>2</sub> > I<sub>2</sub>, the only exception being Ba + F<sub>2</sub>. These large cross sections indicate that for all the reactions discussed here, the chemi-ionization channel is much more important than the chemiluminescence pathway.



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ABSTRACT

The chemiluminescent intensity resulting from the reaction of Pb with  $F_2$  is studied under beam-gas conditions at  $F_2$  pressures of  $10^{-4}$  torr and in the presence of argon at  $\sim 7$  torr. A series of 133 red degraded bandheads belonging to the  $A(\Omega=\frac{1}{2}) - X_1 \ ^2\tilde{\Pi}_{1/2}$  system in the wavelength region of 400-540 nm are observed in the chemiluminescent spectrum obtained in the presence of argon. Since 69 of these bandheads are new, a vibrational reanalysis of the PbF A- $X_1$  system is made. Two new band systems in the 670-800 nm wavelength region are believed to result from emission between higher PbF states. Under beam-gas conditions, the variation of the chemiluminescent intensity as a function of metal flux and oxidant pressure shows that PbF\* results from the bimolecular reaction  $Pb + F_2 \rightarrow PbF^* + F$ . Energetic considerations based on the mass spectrometric value of  $D_0^0(PbF)$  and the short wavelength cutoff in the beam-gas chemiluminescent spectrum rule out the reaction  $Pb(^3P_0) + F_2$  as responsible for populating the PbF A state but suggest instead that it is the reaction of a metastable lead atom  $Pb(^3P_1)$  or  $Pb(^3P_2)$  with  $F_2$ , most likely the former.

III. LIST OF PUBLICATIONS

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2. C.R. Dickson, J.B. Kinney, and R. N. Zare, "Determination of  $D_0^0(\text{BaI})$  from the Chemiluminescent Reaction  $\text{Ba} + \text{I}_2$ " Chem. Phys. 15, 243 (1976).
3. P.J. Dagdigian, H.W. Cruse, and R.N. Zare, "Vibrational State Analysis of Unrelaxed BaI from the Reactions  $\text{Ba} + \text{CH}_3\text{I}$  and  $\text{Ba} + \text{CH}_2\text{I}_2$ " Chem. Phys. 15, 249 (1976).
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5. H. U. Lee, and R.N. Zare, "Chemiluminescent Spectra of YbF and YbCl," J. Mol. Spectrosc. 64, 233 (1977).
6. G. J. Diebold, F. Engelke, H. U. Lee, J. C. Whitehead, and R. N. Zare, "Chemi-Ionization Reaction of Ca, Sr, Ba, and Yb Atoms with the Halogen and Interhalogen Molecules," Chem. Phys. 20, 265 (1977).
7. C. R. Dickson and R.N. Zare, "Spectroscopic Study of  $\text{Pb} + \text{F}_2$  Chemiluminescence" Optica Pura y Aplicada (accepted for publication).
8. C. R. Dickson, "Study of Selected Diatomic Metal Oxides and Halides Using Chemiluminescence and Laser-Induced Fluorescence" Ph.D. thesis, Columbia University, 1976.

9. H. U. Lee, "Selected Studies on the Combustion of Organometallic Compounds and on the Chemiluminescent and Chemi-ionizing Reactions of Ytterbium" Ph.D. thesis, Columbia University, 1976.

IV. PARTICIPATING SCIENTIFIC PERSONNEL

R. N. Zare	Principal Investigator
C. R. Dickson	Graduate Student; received Ph.D. during contract period; now at Allied Chemical Co. Morristown, New Jersey
H. U. Lee	Graduate Student; received Ph.D. during contract period; now at Universität Stuttgart Stuttgart, Germany (West)
J. B. Kinney	Undergraduate Student Assistant (summer); now a graduate student at M.I.T.
F. Engelke	Postdoctoral Research Associate; now at Universität Bielefeld, Bielefeld, Germany (West)