THE DISTRIBUTION OF ENERGY IN
BIMOLECULAR CHEMILUMINESCENT REACTIONS
INVOLVING HYDROGEN ATOMS

Progress Report

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TECHNICAL PROGRESS REPORT

ABSTRACT OF PROGRESS REPORT

The final stages of development of a crossed molecular beam apparatus for the study of bimolecular chemiluminescent reactions involving hydrogen atoms are described. A stable, high-intensity, high-energy source of H atoms is operating and its intensity has been estimated by two different methods to be $\sim 10^{15}$ H atoms/cm²-sec at 1 meter. The determination of the velocity distribution of H atoms from this source is the only remaining major project planned prior to observation of chemiluminescence. Other aspects of the apparatus, e.g., the exemplary performance of the photon counting system, are also discussed. Related theoretical and non-beam spectroscopic work to further understanding of the first chemiluminescing molecule sought, LiH, and of the first total reactive system, Li₂H, is noted.

Bimolecular chemiluminescent reactions of the form

will be studied in a molecular beam apparatus; *indicates electronic excitation, A and B are atoms or simple groups. A high-intensity, high-energy (up to $\sim 3\text{eV}$) velocity-selected source of H atoms has been developed and is now being characterized. This H atom beam will be crossed with a relatively slow AB beam of low internal energy. The photons emitted by HA* will be analyzed and counted, thus providing the final distribution of energy into translation, electronic, vibrational and rotational degrees of freedom, assuming the spectrum of HA* has been analyzed and the total initial energy and bond strengths are known. The initial case under study is AB = Li₂, the simplest experimentally feasible system for which *ab initio* potential energy surfaces can be (and are being) accurately calculated. These experiments will provide definitive examples of simple chemical reactions where the complete final distribution

of energy has been determined and will begin to answer the fundamental question: How is energy redistributed in a chemical reaction? Moreover, this high information content will in turn provide a much greater challenge to theories seeking to explain the microscopic dynamics of chemical reactions.

For convenience, this progress report will be divided into four sections dealing with progress in the following areas:

- A. The development and characterization of the hydrogen atom source.
- B. The development and characterization of the crossed beam source of Li_2 .
- C. The photon detection and analysis for LiH .
- D. The theoretical understanding of $\text{H} + \text{Li}_2$ collisional processes.

The actual observations of chemiluminescence for $\text{H} + \text{Li}_2$ are expected in the next few months once the H atom velocity distribution (see A below) has been characterized.

A. The Development and Characterization of the Hydrogen Atom Source

The supersonic plasma-arc source of Knuth et al (Rev. Sci. Instrum. 40, 1346 (1969)) previously used with argon and helium has been used with minor modification to produce an intense, high-energy beam of hydrogen atoms for use in the present chemiluminescence experiments. The modifications include:

- a. installation of a water-cooled stabilizing electromagnet around the source to improve cooling
- b. striking the arc with argon and then changing over to hydrogen (the arc cannot be struck with pure hydrogen)
- c. development of readily-replacable copper (and also molybdenum) nozzles so that the nozzle can be replaced when erosion is significant (many runs - one as long as eight hours straight - have however been carried out and always without nozzle failure)

The arc has been found to be quite stable over a range of operating conditions: 25 - 150 torr source pressure, 50 - 200 amps DC arc current (usually with a voltage of 30 - 35). However, for convenience we shall usually consider a standard arc of 50 torr source pressure and 125 amps arc current. Thus, a stable supersonic plasma-arc source of H atoms has been developed and successfully operated for over a year. It remains only to characterize the beam (absolute intensity, composition, velocity distribution) and then use it in the chemiluminescent experiments.*

The absolute intensity of this hydrogen atom beam has been estimated using a platinum bolometer sensitive to the heat generated by H atom recombination and similar to that described by Fluendy (Rev. Sci. Instrum. 35, 1606 (1964)) and previously used by the principal investigator (J. Chem. Phys. 51, 2287 (1969)). The intensity of the standard beam described above (which varied somewhat from experiment to experiment for a variety of reasons) is estimated to be 50 - 400 times that found with a thermal tungsten oven hydrogen atom source (W. C. Stwalley, Ph.D. thesis, Harvard Univ. 1968) or $\sim 0.5 - 4 \times 10^{15}$ atoms/cm²-sec at one meter. No bolometric estimate of the amount of H₂ present is of course possible.

In October, the UTI 100C quadrupole mass filter (purchased on this year's budget) was installed in the molecular beam apparatus. After some initial problems were overcome (e.g., by replacing diffusion pump oil), this mass filter was used to analyze the standard beam. A preliminary hydrogen atom intensity of $\sim 0.8 \times 10^{15}$ atoms/cm²-sec was determined, based on the UTI ion source ionization efficiency of 5.5×10^{-6} ions/neutral for argon (T. C. English and

*There are, of course, many other applications of this source and the following individuals have contacted the principal investigator with plans to use this H atom source: A. Kupperman (Caltech), J. Polanyi (Toronto), S. Wexler (Argonne), H. Haberland (Freiburg), G. Kwei (SUNY - Stony Brook). J. Wilson (Univ. of London) is developing a similar source.

J. C. Pernicka, Rev. Sci. Instrum. 44, 230 (1973)) and ratio of 5 for the $\sigma_1(\text{Ar})/\sigma_1(\text{H})$ (L. J. Kieffer and G. H. Dunn, Rev. Mod. Phys. 38, 1 (1966)). The amount of H_2 present in the beam is difficult to determine because of background H_2 pressure, but H_2 seems to be the dominant species in the preliminary experiments with the standard beam. Further experiments with higher arc current and presumably higher H atom fluxes are planned for the near future.

The velocity distribution of the H atom beam has not yet been characterized. Knuth et al (Rev. Sci. Instrum. 40, 1346 (1969) and subsequent private communications) report temperatures up to 15000°K and thermal efficiencies of 15 - 40% in work with rare gases for the present plasma-arc. At an H_2 flow rate of $\sim 10^{-3}$ moles/sec (consistent with present runs), 15 - 40% efficiency corresponds to $4000 - 14000^\circ\text{K}$, assuming complete H_2 dissociation.

Two separate approaches have been taken toward obtaining the velocity distribution. A time-of-flight experiment using the quadrupole mass filter was carried out using thermal and arc-heated argon beams and a phase-shift was observed. Unfortunately the chopping motor bearings gave out and the ordered replacement motor will not be here for several months. The velocity-selecting magnet was calibrated and installed last summer, but a serious short developed in the magnet coil and prevented an H atom beam velocity distribution determination such as previously carried out for a thermal H atom source (W. C. Stwalley, Ph.D. thesis, Harvard Univ., 1968). The magnet coils have recently been reinsulated, and the magnet reassembled and recalibrated. Its reinstallation in the molecular beam apparatus is in progress, and thus it will probably provide the first direct measure of the H atom velocity distribution in the near future.

Finally, a combustible gas alarm was purchased in this year's budget and installed.

In summary, a stable hydrogen atom source of relatively high intensity and energy is in operation; its experimentally estimated absolute intensity is sufficient for the proposed chemiluminescent experiments (see C below) and it is quite likely that its energy will prove to be sufficient for the photon-producing processes expected in the $H + Li_2$ system.

B. The Development and Characterization of the Cross Beam of Li_2

A cross beam oven for production of a mixed Li/Li_2 beam by supersonic expansion has been designed and constructed. Since this oven is similar in design to others, e.g., that used by Gordon, Lee and Herschbach (J. Chem. Phys. 54, 2393 (1971)), no particular problems are anticipated. It will be tested when the H atom velocity distribution experiments are complete and the mass filter can be used for its primary function of monitoring the cross beam.

A secondary apparatus^{*} for characterization of the Li/Li_2 cross beam (and future cross beams) is being assembled. Equipped with an $E-H$ balance (B. Baderson, Advan. Chem. Phys. 10, 1 (1966)) and a Bendix 12-101 time-of-flight mass spectrometer[†], this will provide the composition of the cross beam, e.g., how much Li , $Li_2(^1\Sigma_g^+)$, $Li_2(^3\Sigma_u^+)$, Li_3 , Li_4 , etc.? The stable high voltage power supply for the E field of the $E-H$ balance has been purchased in this year's budget.

Finally a 200 liter liquid nitrogen tank has been purchased in this year's budget and has been provided with an automated fill system to the two apparatus liquid nitrogen traps.

In summary, a supersonic oven for producing an Li/Li_2 beam is ready to use in chemiluminescence experiments when the H atom velocity distribution experiments are complete. The precise characterization of this beam will

*The major components (pumps, stand, bell jar) were generously contributed by Prof. R. Carlson of the Univ. of Iowa Physics Dept.

†The mass spectrometer was made available for inclusion in this apparatus by Prof. E. D. Cater of the Univ. of Iowa Chemistry Dept.

be carried out on the secondary apparatus at a later date.

C. The Photon Detection and Analysis for LiH^+

The photons produced at the scattering center by the collision of H and Li_2 will be focused at a 0.5 meter spectrometer and counted with an SSR photon counting system employing a channeltron photomultiplier.

The number of counts per second with the photomultiplier directly over the scattering center (rather than at the spectrometer exit) has been determined to be 2 - 3 with the arc off and $10^5 - 10^6$ with the arc on. When the beam defining slits are in place, geometrical arguments indicate the arc-on counts should be reduced by a factor of 6×10^{-5} ; this will be directly tested in the near future. Moreover, this includes all frequencies, so the contribution of arc photons in say a $1\text{\AA}$ wavelength interval will be negligible* compared to the 2 - 3 arc-off counts mentioned above. In a velocity-selected experiment with no direct path for arc photons through the magnetic velocity-selector into the scattering center, these photons should, of course, be even more negligible. In order to obtain a signal equivalent to the noise level (2 - 3 counts/sec) given the present estimated (non-velocity-selected) H atom intensity, one needs only a cross section of $\sim 10^{-21} \text{ cm}^2$ for production of photons of a given frequency.

The analysis of the expected LiH photons as to what initial electronic, vibrational and rotational states produced them (and with what intensity) is an important question. Although the LiH electronic spectrum has been much studied, there are still gaps. In particular, the emission spectrum has not previously been analyzed and the upper vibrational levels ($v > 3$) of the ground

†Work on LiH theory and non-beam spectroscopy discussed in this section is also supported by the Donors of the Petroleum Research Fund, administered by the American Chemical Society.

*Except possibly at a few H atom lines such as Balmer α .

state have not been observed. Thus some effort has been devoted to obtaining LiH emission spectra with a hollow cathode lamp, but this has not yet proven successful. This work is continuing and is incidentally being used for calibration of the spectrometer.

The levels and spectra (including intensity) can also be predicted theoretically. Along these lines, improved potential energy curves for the $X^1\Sigma^+$, $A^1\Sigma^+$ and $B^1\Pi$ states have been obtained from experimental spectroscopic energy levels of the isotopic lithium hydrides by the RKR method, with extrapolations based on the *ab initio* potentials of Docken and Hinze (J. Chem. Phys. 57, 4928 (1972)) and the long-range potentials calculated by the principal investigator into the regions not defined by the observed energy levels. Some calculations of energy levels and intensities have been carried out; however, it is hoped in particular that a more accurate ground state potential will soon be available once LiH emission* is seen to the higher vibrational levels of the ground state. Two manuscripts (including extremely accurate values for LiH bond strengths) have resulted from this theoretical work:

K. R. Way and W. C. Stwalley, J. Chem. Phys. 59, 5298 (1973)
and W. C. Stwalley, K. R. Way and R. Velasco, "The Dissociation
Energies of ^7LiD ", COO-2326-2, submitted to J. Chem. Phys (1974).

In summary, the photon counting system has been shown to perform quite acceptably. Theoretical and non-beam spectroscopic work on LiH is progressing so that the analysis of the beam chemiluminescence will be relatively straightforward.

*R. Velasco, Institute of Optics, Madrid, Spain is also attempting to obtain LiH emission spectra.

D. The Theoretical Understanding of H + Li₂ Collisional Processes

The collision of H + Li₂ with initial energy of $\leq 3\text{eV}$ leads to the possibility of many reactive and inelastic processes, including the following electronic excitation (and thus photon producing) processes:

A sketch of some of the appropriate potential surfaces has been given (Y. T. Lee, R. J. Gordon and D. R. Herschbach, J. Chem. Phys. 54, 2410 (1971)).

To attempt to understand the photon-producing processes, some attention has been and will continue to be focused on *ab initio* calculations of the appropriate potential energy surfaces. Fortunately, a collaborative effort along these lines with Dr. A. C. Wahl's group at Argonne National Laboratory has been initiated. This group is well known for its theoretical work on a wide variety of diatomic and triatomic potentials. Dr. Peter Bertoncini at Argonne has the primary responsibility for work in this area and has carried out diatomic calculations to test the adequacy of the proposed basis set (similar to that used by P. Bertoncini, G. Das and A. C. Wahl, J. Chem. Phys. 52, 5112 (1970)). Sample configuration interaction calculations for the Li₂H ground and excited states will be carried out in the next few months.

The problem of surface-hopping and breakdown of the Born-Oppenheimer approximation is also being explored.

In summary, progress toward an accurate theoretical understanding of the potential surfaces of Li₂H has begun. It is anticipated that this close contemporaneous collaboration between theory and experiment will be quite fruitful.

PERSONNEL*

1. William C. Stwalley, principal investigator and Associate Professor of Chemistry, University of Iowa. Supervised all aspects of the project. Will continue. 1/3 time during 2 summer months 1973; 16% time academic year (thus far and for remainder of contract).
2. Warren Zemke, postdoctoral assistant during summer and Assistant Professor of Chemistry, Wartburg College, Waverly, Iowa. Worked on C. and D., especially programming including eigenvalue and RKR calculations, with AEC support summer 1973. Will continue full-time summer only.
3. Sze Yang, postdoctoral assistant. Worked mainly on A. and also on B. (secondary apparatus assembly) with AEC support from August 1, 1973. Will continue full-time at least through April 30, 1975.
4. Kermit Way, graduate assistant. Worked mainly on A., but also on B. (Li/Li₂ oven) and C. (photon counting, LiH theory), with a Phillips Fellowship through August 1973 and AEC support since. Will continue full-time until Ph.D. expected Spring 1975.
5. Kwong Li, graduate assistant. Worked mainly on C. (LiH theory and non-beam spectra; photon counting and spectrometer calibration) with PRF support through June 1973, AEC support summer 1973, and Sloan Foundation support since. Will continue full-time until Ph.D. expected Spring 1975.

*The collaborative effort (D.) with Drs. A. C. Wahl and P. Bertonecini, Argonne National Lab, should also be noted, although they were not directly supported by this contract.

Annual List of Publications for AT(11-1)-2326, January 1974

COO-2326-1. W. C. Stwalley, Initial Summary for AT(11-1)-2326.

COO-2326-2. W. C. Stwalley, K. R. Way and R. Velasco, "The Dissociation Energies of ^7LiD ", submitted to J. Chem. Phys.