Photoelectron and Chemielelectron Spectroscopy of Metal Oxides of Atmospheric Importance

Prof J.M.Dyke

Department of Chemistry
University of Southampton
Southampton SO9 5NH, England

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; Distribution unlimited

13. ABSTRACT (Maximum 200 words)

The contractor has characterized some chemionization reactions of Group II metals with atmospheric oxidants using electron spectroscopy and mass spectrometry. The contractor has measured the valence ionization energies of LiO, NaO and KO produced from the reactions of appropriate Group I metals with N2O and O3.

17. SECURITY CLASSIFICATION OF REPORT

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Principal Investigator: Prof. J.M. Dyke
Dept. of Chemistry
The University
Southampton S09 5NH
U.K.

Title: Photoelectron and Chemielectron Spectroscopy of Metal Oxides of Atmospheric Importance
Products of the gas-phase reactions M + N₂O and M + O₃, where M=Na or K, have been investigated with u.v. photoelectron spectroscopy and the observed bands have been assigned with the assistance of results from ab initio molecular orbital calculations.

For the M + N₂O reactions, the observed products were MO + N₂. Measurement of the photoelectron bands associated with the metal monoxide, MO, allowed determination of the first adiabatic ionization energies (AIEs) of NaO and KO. The values obtained were AIE [NaO(X²Σ⁺)] = (7.1 ± 0.1) eV and AIE [KO(X²Σ⁺)] = (6.9 ± 0.1) eV. A similar study of the Li + N₂O reaction gave AIE [LiO(X²Σ⁺)] = (7.6 ± 0.2) eV.

The reactions M + O₃ with M = Na or K, were observed to give MO + O₂ as the major reaction products. However, for each reaction a band was observed which was assigned to the first ionization energy of the secondary reaction product, MO₂. From the spectra obtained, the first adiabatic ionization energies of NaO₂ and KO₂ were measured as

AIE [NaO₂(X²A₁)] = (6.2 ± 0.2) eV and

AIE [KO₂(X²A₁)] = (5.7 ± 0.1) eV.

For both the M + N₂O and M + O₃ reactions, production of MO A²Σ⁺ was found to be favoured relative to production of the MO X²Σ⁻ state, a result which has important implications in understanding the sodium night-glow in the mesosphere.

The ionization energy values determined in this work allow determination of ground state ionic dissociation energies. For example, for NaO⁺ and KO⁺ in their ground states, Dₒ has been derived as (0.60 ± 0.31) and (0.15 ± 0.14) eV respectively.

Reaction enthalpies can also be derived from the thermodynamic values derived in this work, for ion-molecule reactions of the type

MO + O₂⁺ → MO⁺ + O₂  .................................................. (1)

M⁺ + O₃ → MO⁺ + O₂  .................................................. (2)

For example for M = Na, ΔH₁ and ΔH₂ can be derived as -(4.98 ± 0.11) and (0.23 ± 0.44) eV respectively.

Work performed under this part of the contract, involving the study of Group I metals with oxidants, has been written up for publication and will soon be submitted to Journal of Chemical Physics. A preprint of this work is enclosed.

As part of an on-going experimental programme in chemionization using chemielectron and chemion spectroscopy, the ionization chamber of an electron spectrometer has been modified to allow ions and electrons to be sampled from the same reaction cell under a given set of experimental conditions simply by choosing the sign and magnitude of the extraction voltage on the cell. This experimental arrangement has been used to study the reaction of the group II metals (calcium, strontium and barium) with the oxidants O₂(X²Σ⁺), O₃(a¹Δₓ) and O(³P). The results have been interpreted in terms of a simple thermodynamic model that is consistent with these reactions proceeding via long lived collision intermediates. The electron energy distributions have been interpreted in terms of a simple potential energy model, and the possibility
of the inclusion of an associative ionization reaction into a kinetic model of metal chemistry in the upper atmosphere has been considered. This work will soon be written up for publication.

Taking the $\text{Ba} + O_2(X^3\Sigma_g^{-})$, $\text{Ba} + O_2(a^1\Delta_g)$ and $\text{Ba} + O(3\Pi)$ reactions as examples, the electron energy distributions and ions seen in the $\text{Ba} + O_2(X^3\Sigma_g^{-})$ case can be interpreted in terms of the following processes:

$$\text{Ba} + O_2(X^3\Sigma_g^{-}) \rightarrow \text{BaO}_2^* \quad \text{(3)}$$

$$\text{BaO}_2^* + \text{Ba} \rightarrow \text{Ba}_2\text{O}_2^* + e^- \quad \text{(4)}$$

Adding $O_2(a^1\Delta_g)$ to the $\text{Ba} + O_2(X^3\Sigma_g^{-})$ reaction mixture reduces the ion and electron yield by removing Ba atoms via the neutral reaction

$$\text{Ba} + O_2(a^1\Delta_g) \rightarrow \text{BaO}^* + O \quad \text{(4)}$$

Chemionization can, however, occur via

$$\text{BaO}^* + \text{Ba} \rightarrow \text{Ba}_2\text{O}^* + e^- \quad \text{(5)}$$

On adding $O(3\Pi)$ to the system, $\text{BaO}$ is produced via

$$\text{Ba} + O(3\Pi) \rightarrow \text{BaO}^* \quad \text{(6)}$$

which then undergoes chemionization via reaction (5)

The new apparatus proved very useful in distinguishing between primary and secondary ions via the saturation current method, and in associating a given primary ion to an observed chemielectron band. The high kinetic energy offsets of the experimental chemielectron bands were used to estimate the exothermicities of the observed chemionization reactions. Negative ion formation, a competing process to electron production in chemionization, has also been investigated for the Group II metal plus oxidant reactions and in each case negative ion production has been found to be a minor channel.
REPORT DOCUMENTATION PAGE

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PROFESSOR J. M. DYKE

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University of Southampton
Department of Chemistry
Highfield
Southampton SO9 5NH, UK

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The contractor has measured the valence ionization energies of LiO, NaO and KO produced from the reactions of appropriate Group I metals with N2O and O3.

The results of both investigations are documented in a final report which has been delivered at the end of the contract.

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## SECTION I - SUBJECT INVENTIONS

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## SECTION II - SUBCONTRACTS (Containing a "Patent Rights" clause)

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