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Turbulent ion flow tube experiments on the charge transfer reaction O2+ C8H10 (ethylbenzene) >O2 + C8H10+ and the subsequent competition between collisional stabilization of excited C8H10+ and its fragmentation to CH3+C7H7+ (benzylium or tropylium) has been analyzed quantitatively by statistical rate theory and a master equation analysis of energy transfer. Charge transfer is shown to proceed by a resonant process or through complex-formation, accompanied by differing distributions of vibrational energy generated in the excited ions. Calibrating collisional stabilization against measured fragmentation rates, collisional energy transfer of excited ions is shown to proceed at the ion-molecule collision rate with average energies removed by collision which are close to the corresponding values for excited neutral molecules. Benzylium vs tropylium yields were measured and analyzed quantitatively by statistical rate theory. The project provided ample information required for the understanding of the behaviour of molecular ions under high temperature/high pressure combustion conditions.

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Abstract

Turbulent ion flow tube experiments on the charge transfer reaction $O_2^+ + C_8H_{10}$ (ethylbenzene) $\rightarrow O_2 + C_8H_{10}^+$ and the subsequent competition between collisional stabilization of excited $C_8H_{10}^+$ and its fragmentation to $CH_3 + C_7H_7^+$ (benzylium or tropylium) has been analyzed quantitatively by statistical rate theory and a master equation analysis of energy transfer. Charge transfer is shown to proceed by a resonant process or through complex-formation, accompanied by differing distributions of vibrational energy generated in the excited ions. Calibrating collisional stabilization against measured fragmentation rates, collisional energy transfer of excited ions is shown to proceed at the ion-molecule collision rate with average energies removed by collision which are close to the corresponding values for excited neutral molecules. Benzylium vs tropylium yields were measured and analyzed quantitatively by statistical rate theory. The project provided ample information required for the understanding of the behaviour of molecular ions under high temperature/high pressure combustion conditions.

1. Introduction

This project started in fall 2002 by defining the list of priorities in the planned collaboration. It was decided to start working on the analysis of experimental results for the pressure and temperature dependence of ion-molecule reactions such as they may be of use in accelerated ignition schemes for advanced hydrocarbon-fuelled airbreathing propulsion systems. Work at Hanscom AF laboratory on reactions of O_2^+ with various aromatic hydrocarbons in turbulent ion flow tubes had given information on charge transfer, hydrocarbon cation stabilization and fragmentation pathways. The reaction $O_2^+ + C_8H_{10}$ (ethylbenzene) $\rightarrow O_2 + C_8H_{10}^+$ and subsequent processes like the fragmentation $C_8H_{10}^+ \rightarrow C_7H_7^+ + CH_3$ or the collisional stabilization of $C_8H_{10}^+$ were of primary interest as a prototype. The identification of the isomeric nature of $C_7H_7^+$, the quantitative understanding of the $C_7H_7^+$ or $C_8H_{10}^+$ yields, and the possibilities to predict rates of pyrolysis of molecular ions were special aspects of the project. As anticipated, the approach required an advanced understanding of the collisional processes in terms of a master equation analysis, of statistical unimolecular rate theory for describing intramolecular processes, and of electronic structure calculations. The collaboration immediately led into unknown territory. A considerable amount of new information and new methodology was derived which is of exemplary value for other systems. The transfer of theoretical into practical results was always of primary importance.

The collaboration was characterized by excellent combination of forces, intense information exchange by email, and on visits to Hanscom and various conferences. Apart from the PI, Drs.V. Ushakov, E. Dashevskaya, E. Nikitin, and I. Litvin contributed and were part-time paid from the grant. In addition, the interaction with Ph.D. students at Goettingen University proved most helpful.

2. Results

The results of this project have been described in two articles which have been cleared and submitted for publication in the Journal of Physical Chemistry. The first article deals with a quantitative analysis of the product yields and reaction rates at various pressures and temperatures of the reaction $O_2^+ + C_8H_{10}$. It was discovered that at least two pathways of charge exchange must be operating, one of near-resonant character and one involving an O_2^+-C_8H_{10} addition complex. By statistical rate theory the energy distribution in the generated $C_8H_{10}^+$ ions was derived.

The subsequent fate of highly excited $C_8H_{10}^+$ ions was described by a combination of a master equation treatment for stepwise collisional stabilization of $C_8H_{10}^+$ with advanced unimolecular reaction rate theory describing the fragmentation of $C_8H_{10}^+$. At this stage, fragmentation rates could be taken from recent experiments, but the theoretical modelling provides a rational approach to this and other systems as well. This theory is really new, as it replaces available older theories such as RRKM or phase space theory, which are commonly used in ion-molecule kinetics but prove to be inapplicable in reality. The work on the theory of fragmentation of molecular ions is of so basic importance and wide practical application that it will continue over the next time.

The analysis of the pressure dependence of stabilization vs fragmentation rates led to step sizes of collisional deactivation of highly excited molecular ions. These important quantities could not be derived before as reliably as this was possible here. It was found that overall rates for collisional energy transfer of excited ions are well represented by Langevin-type collision rates and that average energies transferred per collision are surprisingly close to the corresponding quantities in excited neutral molecules. This information on energy transfer is an obligatory input parameter for calculating thermal dissociation rates of molecular ions in hot gases.

In a second collaborative work with the Hanscom group and the group of T. Fridgen and T. McMahon, the nature of the $C_7H_7^+$ fragment of $C_8H_{10}^+$ fragmentation was

clarified. It was found that benzylium ions are the dominant fragments, but that also tropylium ions are formed. The energy dependence of the tropylium vs benzylium yields could be studied by employing a series of different charge exchange ions. At low energies, the tropylium yield decreases with increasing energy before it increases at higher energies. The latter effect was attributed to secondary isomerization of excited benzylium arising from the primary fragmentation. By a combination of electronic structure calculations and RRKM unimolecular rate theory, the modelling could be fitted to the experimental observations.

The two mentioned articles are attached to this report as Annexes.

3. Declarations

The contractor hereby declares that, to the best of his knowledge and belief, the technical data delivered herewith under Award No. F49620-03-1-0012 are complete, accurate, and complies with all requirements of the contract.

DATE 10/25/2003
Name and Title of Authorized Official: Juergen Troe

"I certify that there were no subject inventions to declare during the performance of this contract"

DATE 10/25/2003
Name and Title of the Authorized Official: Juergen Troe