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Rate Coefficients for H^+ Ions in n-Butanol Gas

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Abstract:

In this work we show predictions for the low energy cross sections and transport properties for the H^+ ions in n-Butanol gas. These data are needed for modelling in numerous applications of technologically importance. Appropriate gas phase enthalpies of formation for the products were used to calculate scattering cross section as a function of kinetic energy. Calculated cross sections can be used to obtain rate coefficients as a function of E/N (E -electric field strength; N-gas density) for H^+ in n-Butanol gas.

Keywords*: Monte Carlo Simulations; Positive ions; n-Butanol gas.*

1. Introduction

n-Butanol (C_4H_9OH) also known as 1-butanol or bio-butanol has a 4 carbon straight-chain structure, with the –OH at the terminal carbon. It is an important chemical feedstock used to produce solvents (butyl acetate, butyl glycol ethers) [1,2], polymers (butyl acrylate, butyl methacrylate) [3] and plastics. But the recent interest in n-Butanol is mostly due to its application as a biofuel for use in engines, as an alternative to conventional gasoline and diesel fuels [4-7]. Biofuels are attracting great interest as transportation fuels because they are renewable, can be locally produced, less polluting, more biodegradable, and reduce net greenhouse gas emissions [8]. n-Butanol, like ethanol, can blend with gasoline very well and could be a future option for blending with diesel. Butanol consists more oxygen content compared with biodiesel, leading to further reduction of the soot. n-Butanol occurs naturally as a minor product of the fermentation of sugars and other carbohydrates and is present in many foods and beverages as well as in a wide range of consumer products. Although most volatile organic compounds can be detected by fast methods such as ion mobility spectroscopy, precise determination is possible only if reaction of specific ions with targeted compound is well known.

n-Butanol is produced by alcoholic fermentation of the biomass feedstock [9-12] which include sugar beet, sugar cane, corn, wheat, and other various plant crops containing cellulose that could not be used for food and would otherwise go waste. Recently, the use of generically enhanced bacteria has also increased the fermentation process productivity.

The goal of this work is to calculate transport parameters of fragment ions of n-Butanol. Mechanical properties can also be modeled, i.e. elastic modulus [13] and mechanical impedance [14]. We employ Denpoh-Nanbu's theory (DNT) [15] to calculate transport cross section sets for H^+ ions scattering on n-Butanol appropriate for low energies of H^+ ions. By using Monte Carlo technique that properly takes into account thermal collisions [16] we calculated transport parameters as a function of *E/N*.

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2. Calculation on the cross sections set

The calculation of cross sections would include the determination of the potential energy surface of the ion-neutral interaction, followed by quantum-mechanical calculations of ion-neutral scattering processes [17]. All these tasks can be performed only if a certain level of approximation is introduced. There is another approach where it is possible to use some statistical theory [18] where the specific reaction rate for a single molecular reaction can be used to obtain the cross section for each particular process [15,19].

The scattering cross sections of H^+ on n-Butanol are calculated by using the DNT [15] separating elastic from reactive collisions. The induced dipole polarizability of 8.9×10^{-24} cm^3 [20] is used for the n-Butanol target. In resemblance with our recent work [21] DNT method is used to separate elastic from reactive endothermic collisions by accounting for the thermodynamic threshold energy and branching ratio according to the Rice-Rampsperger-Kassel (RRK) theory [22]. Within the RRK theory the internal energy is being distributed among an empirical number of ***s*** equivalent effective modes of the complex selected from the total number of atoms involved in the complex.

Appropriate gas phase enthalpies of formation for the products [23] (Table I) were used to calculate thermodynamic thresholds. The cross-section for the exothermic reaction (EXO) forming a molecular ion H^+ in n-Butanol is commonly represented by ion capture cross-section:

$$\sigma_{exo} = \beta\sigma_L , \qquad (1)$$

where σ_L is the orbiting cross-section [17] and β is the probability of a specific exothermic reaction.

In this calculation, in the absence of resonant exothermic reactions, we assumed that the probability of exothermic reactions is zero ($\beta = 0$). At the low energy limit, the cross sections are similar due to the dominant polarization of the target. At higher energies, reactive collisions, including non-conservative collisions, become efficient for various possible processes.

It is well known that the swarm method [24,25] can be used to modify the cross section for the transmission of an elastic impulse if the transport parameters are known. Thus, an elastic pulse transmission cross section can be obtained if some initial, approximate cross section is available. Transport parameters are not available for n-Butanol transport [19]. We have separated the endothermic and exothermic processes by using the enthalpies from Ref. [23].

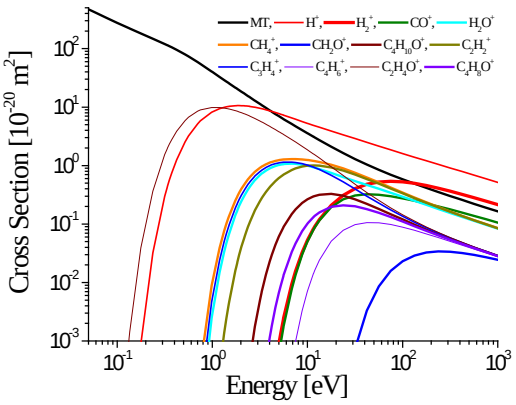

Fig. 1. Cross sections for H^+ ions in n-Butanol.

In this paper there are 20 exothermic processes. Exothermic process with lowest excess energy (H^+ + n-butanol→$C_3H_3OH^+$+C_3H_4 +H) has 0.118 eV excess energy while lowest endothermic threshold (H^++n-butanol→ $C_2H_4O^+$+C_2H_2+2H_2+H) is 0.061 eV. Therefore we have assumed in this work that exothermic processes are non-resonant, and neglected their effect on transport properties. With assumed product ions we have selected 47 endothermic processes with thermodynamic thresholds up to about 11 eV. In the reaction of H^+ in n-Butanol the product can be observed ion and the remaining particles in the collision are grouped in different ways. That number is indicated in parentheses next to the ion. If the number in parentheses is greater than 1 the cross sections are summed and shown as one in Fig. 1 next to the ion designation formed.

Tab. I Heats of formation $\Delta_f\mathbf{H^0}$ at 298 K (kJ/mol).

Species	$\mathbf{\Delta H_f^+}$ **ion**	$\mathbf{\Delta H_f^0}$ **neutral**
H_2	1488.3	0
CO	1241.59	-393.51
CO_2	935.4	-393.51
CH_2O	940.5	-108.7
H_2O	975.0	-241.83
CH_4	1132	-74.5
C_2H_4	1066	52.2
C_2H_6	1028	-84.0
C_3H_6	959	20.2
C_3H_8	227.5	951.5
C_4H_8	924	-0.4
C_4H_{10}	889	-126.5
CH_4O	845.3	-201.6
C_2H_6O	775.4	-234.8
C_3H_8O	731	-254.8
C_2H_2	1327.9	228.0
C_3H_4	1186.2	186.6
C_4H_6	1033	162.3
C_2H_4O	821.1	-165.8
C_3H_6O	772.9	-187.4
C_4H_8O	742	-207.5

3. Results and Discussion

A precise treatment for obtaining ion transport parameters of higher accuracy in the E/N function would be to follow the solution of the generalization of the Boltzmann equation [26]. The non-equilibrium regime in discharges can be well represented under a broad range of conditions by using the Boltzmann kinetic equation or by following individual evolutions of all ions with Monte Carlo technique [27,28].

The transport properties of species in gas plasma are of great importance for understanding the nature of molecular and ionic interactions in gas mixtures [29,30]. These properties include mean energy, drift velocity, diffusion coefficients, ionization and chemical reaction coefficients, ion chemical reaction coefficients and rarely excitation coefficients, and are very useful in the chemical industry for the design of many types of transport and process equipment. Swarm parameters, which are functions of the reduced electric field E/N (E-electric field strength, N-gas density) in direct electric fields are usually used for plasma modeling and simulation.

In this work we have used a Monte Carlo code that properly takes into account the thermal collisions [16,19]. The code has passed all the tests and the benchmarks that were covered in our earlier studies [19,31]. Calculations are performed for the gas pressure 1 Torr and gas temperature of 300 K.

In Fig. 2 we show results for mean energy as a function of reduced electric field *E/N*. The mean energy cannot be directly measured in experiments but a map of mean energy versus *E/N* may be used directly to provide the data in fluid models especially when the local field approximation fails. The Monte Carlo code gives good results in which for all n-Butanol gas the mean energy converges to the thermal mean energy 3/2 kT = 0.0388 eV.

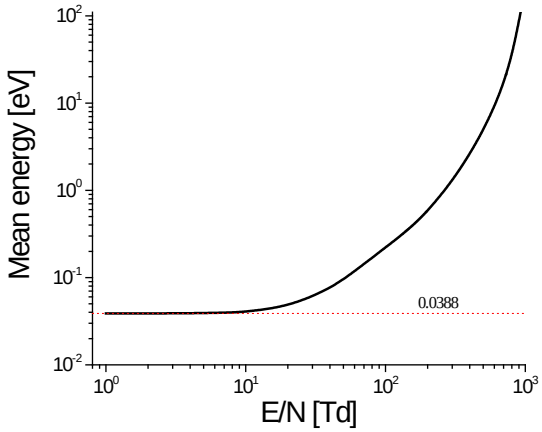

Fig. 2. Mean energy as a function *E/N* for H^+ ions in n-Butanol.

The flux and bulk drift velocities [28] for H^+ in n-Butanol gas as a function of *E/N* are given in Fig. 3. The drift velocities obtained by the Monte Carlo simulation are calculated in real space (bulk) and in velocity space (flux) values which are obtained as $\langle v \rangle$ and $d\langle x \rangle/dt$, respectively. As *E/N* increases, the high-energy ions from the distribution function increasingly have non-conservative collisions in which the H^+ ions disappear, shifting the center of mass of the swarm backward, resulting in a bulk velocity less than the flux.

In Fig. 4 we show the results of Monte Carlo simulation for reduced mobility as a function of *E/N*. The mobility *K* of an ion is a quantity defined as the velocity attained by an ion moving through a gas under the unit electric field strength. One often exploits the reduced or standard mobility defined as:

$$K_0 = \frac{v_d}{N_0 E} N \qquad (2)$$

where v_d is the drift velocity of the ion, N is the gas density at elevated temperature T, N_0= $2.69 \cdot 10^{25}$ m^{-3} and E is the electric field strength. Due to reactive collisions bulk and flux values of reduced mobility are separated.

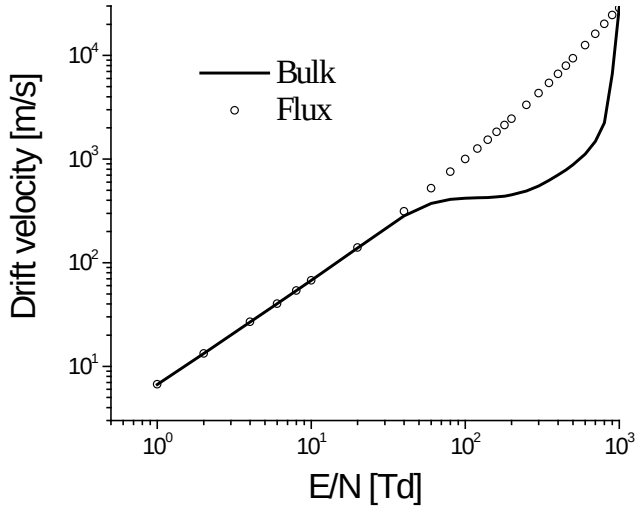

Fig. 3. Bulk and flux velocity as a function *E/N* for H^+ ions in n-Butanol.

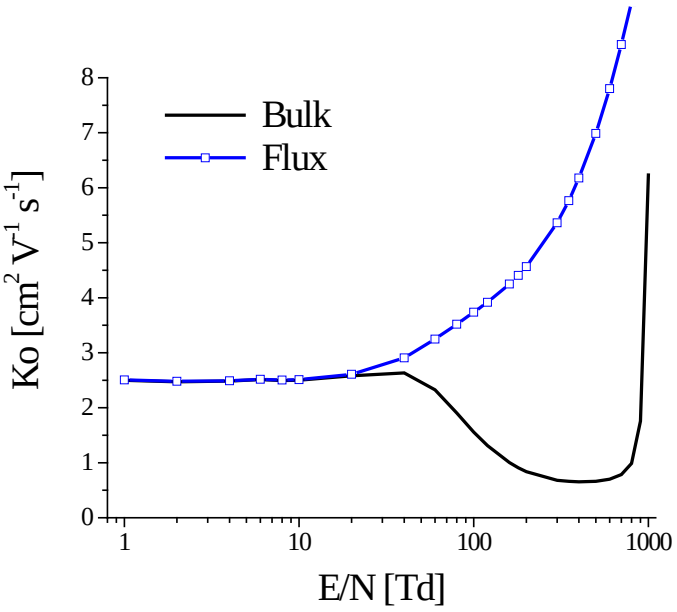

Fig. 4. Reduced mobility as a function *E/N* for H^+ ions in n-Butanol.

In Fig. 5 we show rate coefficients for reactions of H^+ ions with n-Butanol gas at T = 300 K. Rate coefficients are important for applications of the global model to n-Butanol gas. We present formation of H_2^+(8), CO^+(4), H_2O^+(3), CH_4^+(3), CH_2O^+(1), $C_4H_{10}^+$(1), $C_2H_2^+$(3),

$C_3H_4^+(1)$, $C_4H_6^+(1)$, $C_2H_4O^+(1)$, $C_4H_8O^+(1)$. The products of a) light ions, b) medium ions and c) heavy ions are also presented in Fig. 5.

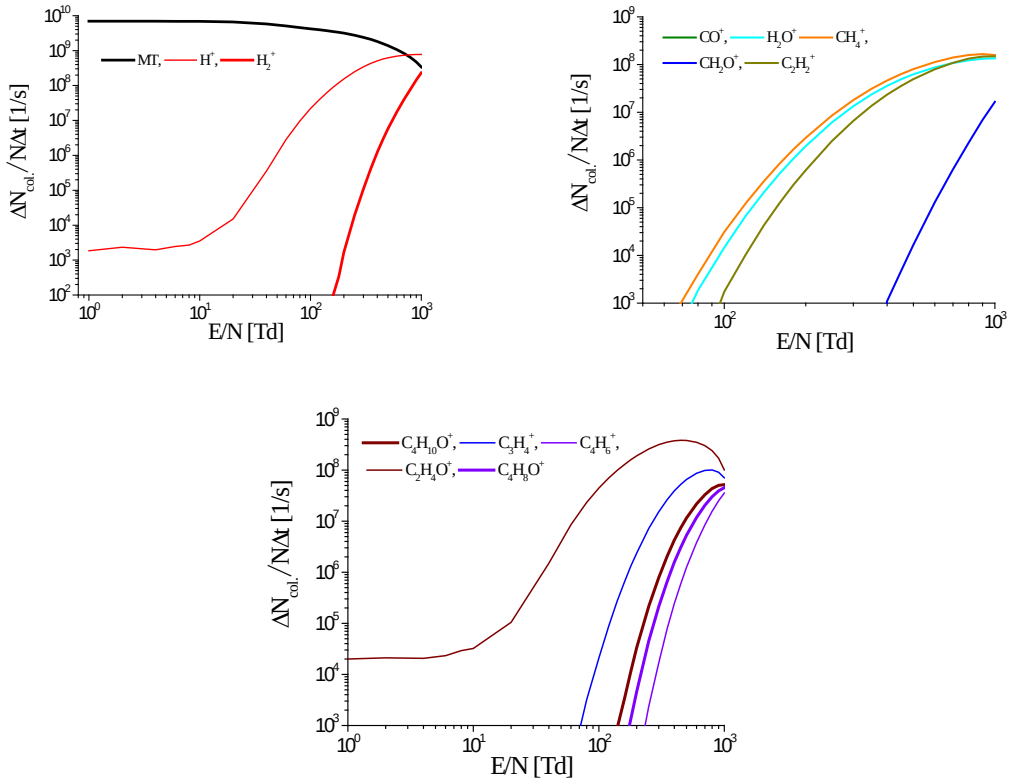

Fig. 5. Rate coefficients of a) light ions, b) medium ions and c) heavy ions as a function *E/N* in n-Butanol.

4. Conclusion

In this paper we show transport properties for the H^+ ions in n-Butanol gas. The cross section set has been determined by extending Denpoh-Nanbu's method.

The Monte Carlo technique was applied to carry out calculations of the mean energy, drift velocity, reduced mobility and specially rate coefficients as a function of reduced DC electric field. The results are believed to be a good base for modeling, which could be further improved when measured values of transport coefficients become available and then we could perform this analysis again.

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Сажетак: *У овом раду предлажемо сет пресека за јоне H^+ у гасу n-Бутанол на ниским енергијама и њима придружене транспортне параметре. Ови подаци су потребни за моделовање у бројним технолошки важним применама. За израчунавање пресека за судare у функцији кинетичке енергије коришћене су одговарајуће енталпије формирања гасне фазе за производе реакција. Израчунати попречни пресеци су коришћени за добијање коефицијената брзине у функцији E/N (E – јачина електричног поља; N– густина гаса) за јоне H^+ у гасу n-Бутанол.*

Кључне речи*: Монте Карло Симулације, позитивни јони, n-Бутанол гас.*