

New insight into the removal kinetic of acetone in nitrogen plasma

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Abstract: The removal of acetone (< 5000 ppm) in transient homogeneous nitrogen plasma is studied by gas chromatography and by coupling a FT-ICR mass spectrometer, making use of chemical ionization (Proton transfer reaction mass spectrometry), to a pre-ionized discharge at 0.46 bar. The quenching of the N₂ metastable states by the organic molecule leads to dissociate this molecule, with a rate constant equal to $1.1 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$. PTR-MS allows real-time analysis, showing very usefulness for detailed kinetic studies.

Keywords: Acetone, nitrogen, photo-triggered discharge, proton transfer reaction mass spectrometry.

1. Introduction

Acetone is one of the major pollutants in the earth atmosphere [1], impacting the chemistry of the troposphere [2], and the reduction of its emissions by human activities becomes more and more necessary. Like other VOCs [3, 4], the non-thermal plasma appears an interesting alternative technique to remove this pollutant at low concentration (< 1000 ppm) in an air flow coming from a fixed or mobile source, compared to others such as adsorption, thermal and catalytic oxidation. However the understanding of reactions involved in acetone abatement by the plasma at atmospheric pressure is a first step in order to optimize the process. Since the first work by T. Oda et al. [5], very few studies have been published about the conversion of acetone in dielectric barrier or corona discharges without assistance of packing materials or catalysts [6-8] (i.e. without influence of a surface modifying the mixture reactivity), and the knowledge about the gas phase kinetics of acetone in such complex filamentary plasmas of N₂/O₂ mixtures remains poorly known. Nevertheless it is well-known for a long time that the decomposition of acetone by oxidation reactions at low temperature is not that efficient compared to other VOCs [9]. This could explain the low efficiency of some plasma reactors, but no clear demonstration based on validated kinetic arguments has been yet provided.

In our work at the LPGP laboratory, we used a photo-triggered discharge [10] to study decomposition mechanisms of acetone, and other VOCs, in nitrogen and the effect of oxygen addition to the mixture [11, 12]. This pre-ionised discharge allows obtaining transient homogeneous plasmas, and species concentrations measurements can be compared to predictions of a self-consistent 0D-modelling coupling the discharge physics to the plasma chemistry. In this way new kinetic data can be proposed without making restrictive assumption about the electrical energy deposition into the discharge. We are particularly interested in the role of dissociation reactions of the organic molecule induced by electronic energy

transfer from metastable excited states of N₂ (quenching processes). Very recently, a compact FT-ICR mass spectrometer (BTrap) developed by the company AlyXan in collaboration with the LCP laboratory was coupled to the discharge in order to follow, in real-time, the concentration of acetone and to detect and to quantify as much as possible long live products following the decomposition of the molecule. This apparatus makes use of Chemical Ionization (CI), a soft and selective ionization technique using ion/molecule reactions such as charge or proton transfers. The most used CI precursor ion is H₃O⁺, which reacts with most VOCs with little fragmentation whereas it is nonreactive with the major components of the matrix, in the present experiment N₂. Consequently, a compound with a molecular mass M will be detected at mass M+1 corresponding to (VOC)-H⁺ ion. This technique is known as PTR-MS (Proton Transfer Reaction Mass Spectrometry) [14]. It has proved to be very effective for studies of VOCs removal by plasmas [15].

2. Experiment and modelling

A detailed description of the photo-triggered discharge reactor, hereinafter referred to as UV510, can be found in [11, 16, 17]. The total pressure of the studied mixtures is fixed to 0.46 bar in order to ensure a perfect homogeneity of the plasma. Two electrodes (spacing d=1 cm, flat profile of 1 cm width) are directly connected to an energy storage unit charged up to a voltage V₀ in some hundreds ns. Once V₀ is reached, the gas breakdown is achieved through photo-ionisation of the gas mixture by UV-photons produced by an auxiliary corona discharge; the applied reduced electric field at the time of the pre-ionisation pulse, (E/n)₀, is given by (E/n)₀=V₀/(d.n), where n is the total density. Then, the discharge current pulse (60 ns) develops itself and the field drops to zero at the end. The deposited energy in the discharge, E_D, equals the stored energy and the specific energy per current pulse is E_{SD} = E_D/V_D, where V_D is the plasma volume (50 cm³).

A compressor is used to produce a gas flow through the discharge gap, in a closed loop, and the discharge frequency, 1.0 Hz, is chosen such that the whole reactor volume, 500 cm³, is renewed between two discharges. The volume of the experimental device, V_T, equal about 9 litres which corresponds to the total volume of the gas mixture studied; it is much higher than the discharge one owing to the use of a tank in the loop. The FT-ICR mass spectrometer was placed in this gas loop.

The discharge model used for the kinetic interpretation of the experimental results has been described in detail previously [11, 16, 17]; kinetic data taken into account for N₂ can be found in same references. It couples (i) the solution of the Boltzmann equation for electrons, (ii) the kinetic equations describing the temporal evolution of the various species (molecular excited states, ions, atoms, radicals, and molecules), (iii) the electric circuit equations given by the Kirchhoff laws, (iv) the energy conservation equation giving the gas mixture temperature. All are solved in a self-consistent way for one discharge, i.e. for one current pulse. Moreover, a second model was developed assuming few simplifying hypothesis in order to simulate the closed-looped functioning of UV510 [17]; we later call this theoretical approach the ‘closed-looped model’. Needing only one run of the self-consistent model, it gives the evolution of molecule densities as functions of the number of discharges performed in the mixture, taking into account the dilution of gases contained in the electrode gap volume V_D into the total volume V_T.

All results presented here were obtained for ‘standard’ electrical parameters previously adopted for studies on other organic molecules [11, 16, 17]: (E/N)₀=200 Td and E_D=4.6 J, E_{SD}=92 J/l.

3. Kinetic data for acetone and its by-products

As it was the case for acetaldehyde [17], it can be shown that, for the chosen values of (E/N)₀ and E_{SD}, electrons and ions play a minor role in the conversion of acetone. Neutral kinetics appears much more important for the considered experimental conditions.

In our kinetic scheme, most of the data concerning the gas phase chemistry of CH₃COCH₃ and its by-products are coming from the NIST database [9]. On the other hand, there is few data about reactions of organic molecules with excited states of N₂ [18]. For acetone, only Clark and Setser [19] and more recently Suzuki et al. [20] gave values for the quenching rate constant, k₁, of the N₂(A³Σ⁺_u) metastable state, i.e. 1.1×10⁻¹⁰ cm³s⁻¹ and 2.2×10⁻¹⁰ cm³s⁻¹ respectively; but no exit route is proposed for such a reaction. For the present study we take into account dissociative quenching collisions for A³Σ⁺_u, and also for the group of singlets a¹Σ⁺_u, a¹Π_g, and w¹Δ_u. Collision partners are acetone, but also important molecules created in the plasma: H₂, CH₄, C₂H₆, CH₂O, CH₃CHO, and HCN. Main radicals coming from these molecules, which are taken into account in the kinetic, are H, CH₃, HCO, and CH₃CO; dissociations of radicals

through quenching of N₂ states are neglected. The complete set of several hundred of reactions considered for the N₂/CH₃COCH₃ mixture will be described in a forthcoming article [21].

4. Results

In Fig. 1 is plotted the acetone concentration, C_T, measured in the total volume of the reactor by the mass spectrometer and normalized to its initial value, C_{T0}, according to the number of current pulses, N, performed in the gas mixture and for four values of C_{T0}. The decrease of C_T follows roughly the exponential law given on the diagram, where N_c can be understood as a characteristic number of discharges. At low C_{T0}, 42 ppm, the decrease is mono-exponential, whereas a slope break appears when the initial concentration is increased, as it can be clearly seen for C_{T0}=505 ppm (break for C_T around 140 ppm).

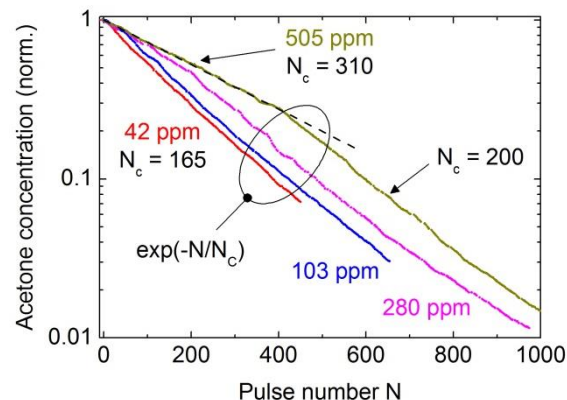
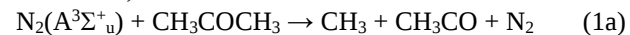


Fig. 1. Acetone concentration measured by PTR-MS in the total volume of the UV510.

This ‘breaking effect’ was not captured so clearly by our previous experimental work using the gas chromatography (GC) technique [13], and Fig. 1 emphasises the interest of using the BTrap apparatus to follow in real-time the acetone concentration; 320 data points were recorded for this example at C_{T0}=505 ppm, with a delay of about 3 s between each.

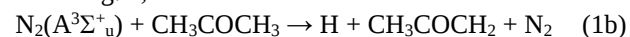
The measured value for N_c at low pulse number allow to determine the pollutant molecule concentration removed in the discharge volume, C_{RD}, for the first current pulse [17], to be then compared with prediction of the self-consistent modelling. Values of C_{RD} are plotted in Fig. 2 for C_{T0} up to 5000 ppm, the dashed line corresponding to C_{RD}=C_{T0} (all acetone molecules removed in the 50 cm³ of homogeneous plasma). Experimental points correspond to chromatographic measurements (GC-FID or GC-TCD) for C_{T0} > 450 ppm, and to PTR-MS for C_{T0} < 550 ppm; the data appear consistent as a whole. Fig. 3 shows an enlargement of Fig. 2 for the lowest values of initial concentration. Continuous lines are model predictions: ‘A’, with the coefficient k₁ taken from [20], and ‘B’, with k₁ from [19],

and considering that the quenching mechanism breaks the C-C bound, i.e.



and same reaction with same coefficient k_1 for the nitrogen singlet states.

A perfect agreement with experimental points is obtained for the B-case at C_{T0} lower than 500 ppm (Fig. 3), but the predicted value of C_{RD} is a little bit overestimated at C_{T0} higher than 1000 ppm (Fig. 2). However the agreement is better if ones consider that H-atoms are also produced by quenching of N_2 states, case 'C' in Fig. 2,



with quasi-equal branching ratios for (1a), 55%, and (1b), 45%.

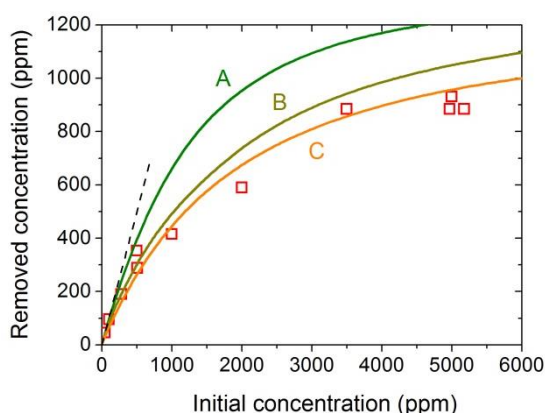


Fig. 2. Removed concentration of acetone in the discharge volume (50 cm³), for one current pulse. Lines A, B, C: model predictions (see text). Squares: measurements by PTR-MS ($C_{T0} < 550$ ppm) and by GC ($C_{T0} > 450$ ppm).

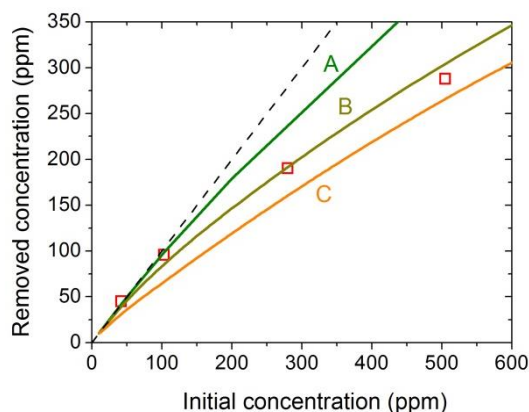


Fig. 3. Same as Fig. 2, with measurements by PTR-MS.

In order to achieve a more precise validation of the kinetic scheme proposed for the gas mixture, it is also of importance to compare predictions of the closed-looped model with measurements [17]. This allows describing the conversion of the pollutant molecule for a wide range of concentration values owing to the decrease of C_T in the mixture as the number of accumulated current pulses is

increased, with an increasing influence of other molecules coming from the conversion of the primary one. Then the model results are also sensitive to the chosen kinetics for these products. Experimental data obtained by PTR-MS are perfect candidate for such a comparison with model predictions. Fig. 4 presents results obtained for $C_{T0}=505$ ppm and case 'C' discussed above.

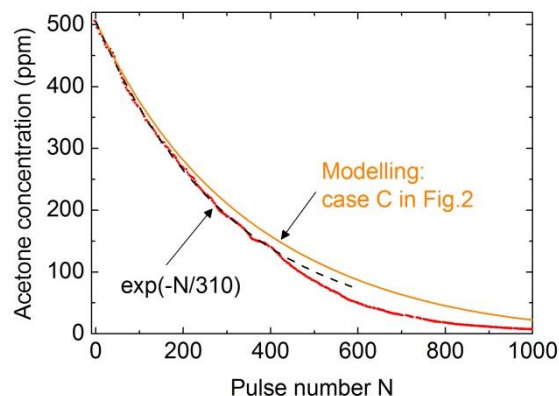


Fig. 4. Acetone concentration measured by PTR-MS in the total volume of the UV510 for $C_{T0}=505$ ppm, compared to model predictions.

The agreement appears satisfactory for C_T down to about 250 ppm, i.e. half of the initial acetone concentration. Model results are very close to the exponential decrease plotted in Fig. 1 with $N_C=310$ (dashed line). However the model clearly overestimates C_T for $N>400$, and do not explain the breaking effect captured by PTR-MS at that number of current pulses.

5. Main conclusions and prospects

Study of the acetone removal, in the homogeneous nitrogen plasma, shows that the quenching of the N_2 metastable states by the organic molecule leads to dissociate this molecule, with a rate constant equal to the value determined previously by Clark and Setser [19]. Two exit routes can be considered, producing either the hydrogen atom or the methyl radical. This analysis, previously discussed from GC measurements [13], is confirmed by the real-time tracking of acetone by PTR-MS, giving a new insight into the removal kinetic of this molecule. However the exact dissociation routes remain for the moment an open issue: concentrations of main by-products (H_2 , CH_4 , C_2H_6 , and CO detected by GC [13]) coming from the chemical reactivity of the plasma should be dependent upon these routes, as it was established previously for acetaldehyde [17]. Work is in progress to achieve a complete kinetics explaining the removal of acetone and the induced production of other molecules.

6. Acknowledgments

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7. References

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