An experimental study of the reaction kinetics of $C_2(X^1\Sigma_g^+)$ with hydrocarbons (CH_4, C_2H_2, C_2H_4, C_2H_6 and C_3H_8) over the temperature range 24–300 K: Implications for the atmospheres of Titan and the Giant Planets

André Canosa [a,*], Alejandra Páramo [a,b], Sébastien D. Le Picard [a], Ian R. Sims [a]

[a] *Laboratoire PALMS, UMR CNRS-Université no. 6627, Equipe "Astrochimie Expérimentale," Campus de Beaulieu, Bât. 11C, Université de Rennes 1, 35042 Rennes Cedex, France*
[b] *School of Chemistry, University of Birmingham, Edgbaston B15 2TT, Birmingham, UK*

Abstract

The reactivity of $C_2(X^1\Sigma_g^+)$ with simple saturated (CH_4, C_2H_6 and C_3H_8) and unsaturated (C_2H_2 and C_2H_4) hydrocarbons has been studied in the gas phase over the temperature range 24–300 K using the CRESU (Cinétique de Réaction en Ecoulement Supersonique Uniforme or Reaction Kinetics in a Uniform Supersonic Flow) technique. All reactions have been found to be very rapid in this temperature range and the rate coefficients are typically $\geqslant 10^{-10}$ cm³ molecule⁻¹ s⁻¹ with the exception of methane for which the rate coefficient is one order of magnitude lower: $\sim 10^{-11}$ cm³ molecule⁻¹ s⁻¹. These results have been analyzed in terms of potential destruction sources of $C_2(X^1\Sigma_g^+)$ in the atmospheres of Titan and the Giant Planets. It appears that the rate coefficient of the reaction $^1C_2 + CH_4$ should be updated with our new data and that reactions with C_2H_2, C_2H_4 and C_2H_6 should also be included in the existing photochemical models.
© 2006 Elsevier Inc. All rights reserved.

Keywords: Experimental techniques; Jovian planets; Titan; Organic chemistry

1. Introduction

Methane has been found to be present in all Giant Planet atmospheres (Flasar et al., 2004; Taylor et al., 2004; Encrenaz, 2005). Furthermore it is a major component in the nitrogen atmosphere of Titan (Coustenis, 2005) as well. In Pluto and Triton it has been detected in its solid state and, although weakly or not yet spectroscopically identified in the gas phase of these nitrogen atmospheres, it is strongly expected to be present as well (Cruikshank, 2005). It is now widely admitted that the destruction of methane is mostly driven by photodissociation from the solar Ly-α radiation at 121.6 nm although catalytic dissocia-

tion following photodissociation of acetylene is also considered (Strobel, 2005). The former process represents the cornerstone of a rich hydrocarbon photochemistry in all these environments. Thanks to several successful spacecraft missions (Voyager, Galileo, Cassini), Earth-orbiting satellites such as ISO (Infrared Space Observatory) and HST (Hubble Space Telescope) and also ground-based IR and mm telescopes, a large number of hydrocarbon molecules have been detected in these environments (Encrenaz, 2005; Coustenis, 2005) including all those of interest in the present study. This has led to the development of photochemical models in order to try to reproduce all these observations. Models have been developed for Jupiter (Gladstone et al., 1996; Moses et al., 2005), Saturn (Moses et al., 2000; Ollivier et al., 2000) and its satellite Titan (Yung et al., 1984; Toublanc et al., 1995; Lara et al., 1996; Lebonnois et al., 2001; Wilson and Atreya, 2004), Neptune (Romani et al., 1993; Bishop et al., 1998) and its satellites Triton (Krasnopolsky and

Cruikshank, 1995) and Pluto (Lara et al., 1997; Krasnopolsky and Cruikshank, 1999).

Probably due to the homonuclear nature of C_2, no evidence of detection of this radical in planetary atmospheres has been reported in the literature until now. In all photochemical models however, C_2 is clearly identified in the chemical scheme. It is expected to be essentially a product of acetylene photodissociation and it is considered to be a source of C_2H via its reaction with H_2 and CH_4 (see, for example, Moses et al., 2000; Lebonnois et al., 2001) with the exception of Triton, in which the destruction routes are via reactions with atoms: O or N (Krasnopolsky and Cruikshank, 1995). On Titan, C_2 is involved in the chemical cycle of C_4H_2 for which there is a lack of data as has been pointed out already by Yung in 1984 (Yung et al., 1984) who stressed: "*Our discussion reveals a number of deficiencies in our understanding of. . . the photochemistry of C_4H_2, the chemical kinetics of the radicals C_2 and C_4H. . . .*"

The C_2 radical, which is one of the simplest diatomic molecules, has two low lying electronic states, the ground state $C_2(X^1\Sigma_g^+)$ and the metastable triplet state $C_2(a^3\Pi_u)$ (hereafter $^1C_2$ and $^3C_2$, respectively). The energy difference between the lowest vibrational levels of these two states is only 610 cm^{-1} or 880 K. While many experimental studies have been carried out to measure the rate coefficients of the removal of $^3C_2$ by hydrocarbons (Donnelly and Pasternack, 1979; Reisler et al., 1979, 1980; Pasternack et al., 1980, 1981; Becker et al., 2000; Huang et al., 2004, 2005), data concerning the reactivity of $^1C_2$ are scarcer. These were obtained in the early eighties and were only available at room temperature (Pasternack and McDonald, 1979; Reisler et al., 1980) and above (Pitts et al., 1982). Modellers used the results from this latter study for the reactivity of $^1C_2$ with H_2 and CH_4 and extrapolated the given rate coefficient temperature dependences to the conditions reigning in planetary atmospheres. It is worth mentioning here that Pitts et al. found a positive temperature dependence, in the range 300–600 K, for both processes resulting in even lower extrapolated rate coefficients for the stratospheric conditions of planetary atmospheres. Furthermore, the reactivity of $^1C_2$ with other important small hydrocarbons such as C_2H_2, C_2H_4 (Reisler et al., 1980) and C_2H_6 (Pasternack and McDonald, 1979) was found to be very rapid at room temperature, close to the collisional limit. This was an indication that the rate coefficient at lower temperature could still remain fast. Connecting these elements together, we realized that reactions other than those with H_2 and CH_4 could be also of some importance in the destruction processes of $^1C_2$ in planetary atmospheres.

The main goal of the present study was then to determine experimentally the rate coefficient temperature dependences for the reactions of $^1C_2$ with CH_4, C_2H_2, C_2H_4, C_2H_6 and C_3H_8 in the temperature range 24–300 K and then analyze the possible consequences of our results for the chemistry of $^1C_2$ in planetary atmospheres with a special focus on Titan for which very recent data are now available from the Cassini–Huygens mission (Flasar et al., 2005; Waite et al., 2005; Shemansky et al., 2005).

2. Experimental technique

The CRESU technique which is now well established for the study of gas phase reaction kinetics at very low temperatures (Dupeyrat et al., 1985; Sims et al., 1994) has been used in the present study. CRESU is a French acronym standing for Cinétique de Réaction en Ecoulement Supersonique Uniforme which can be translated as Reaction Kinetics in a Uniform Supersonic Flow. Only a short description will be given here, drawing attention to those aspects of the experiments which relate to measurements of the reaction involving $^1C_2$ with CH_4, C_2H_2, C_2H_4, C_2H_6 and C_3H_8.

In the CRESU technique, low temperatures are achieved via the isentropic expansion of a buffer gas through a Laval nozzle. Each nozzle employed provides an axially and radially uniform supersonic flow at a particular temperature, density and velocity for a given buffer gas. The relatively high density of the supersonic flow (10^{16}–10^{17} cm^{-3}) ensures frequent collisions, thus maintaining thermal equilibrium. All these properties are conserved in the core of the supersonic flow over a typical distance of a few tens of centimeters along the flow corresponding to a hydrodynamic time of several hundreds of microseconds. The Laval nozzle is mounted on a reservoir kept at room temperature into which the buffer gas, the C_2 precursor molecule and the reagent gases were injected (see Fig. 1).

In the current work, C_2 molecules have been obtained by UV photolysis of C_2Cl_4 (Aldrich, 99.9% HPLC grade) using an ArF excimer laser (Lambda-Physik, LPX 210i) working at 193 nm with repetition frequency of 10 Hz and an exit energy ∼200 mJ per pulse.

The $^1C_2$ radical was observed by laser induced fluorescence (LIF) exciting the $(D^1\Sigma_u^+ \leftarrow X^1\Sigma_g^+)$ (0,0) transition at ∼231 nm (Mulliken bands) and collecting the LIF signal in resonance using an interference filter centred at 228 nm. Probe laser radiation was provided by a dye laser (Laser Analytical Systems, LDL 20505) operating with Coumarin 460 (Exciton) dye diluted in methanol. The dye was pumped by the third harmonic of a Nd:YAG laser (Spectra Physics, GCR 190, 10 Hz) at 355 nm working at an exit energy of about 30 mJ and frequency doubled using a BBO crystal to obtain the 231 nm wavelength.

The probe and the photolysis beams were combined on a dichroic mirror and were directed along the axis of the supersonic flow, LIF was collected at a known distance downstream of the Laval nozzle (usually 10–30 cm) using a UV-enhanced, optically fast telescope–mirror combination mounted inside the main vacuum chamber, focused through a slit and directed onto the photocathode of a UV-sensitive photomultiplier tube (Thorn EMI, 9813 QSB) after passing through a narrow band filter (see above) to reduce the scattered light from the photolysis laser. The LIF signals as a function of time were accumulated, processed and analyzed as described previously elsewhere (Sims et al., 1994) leading to the determination of a first-order rate coefficient proportional to the hydrocarbon reagent concentration. For a given temperature, LIF scans were then taken at differing reagent concentrations in order to construct a kinetic plot from which the second-order rate coefficient could be extracted. Measurements at room temperature were