



Direct kinetic measurements on reactions of atomic carbon, C (3 P), with O 2 and NO at temperatures down to 15 K

Delphine Chastaing, Sébastien D. Le Picard, and Ian R. Sims

Citation: The Journal of Chemical Physics **112**, 8466 (2000); doi: 10.1063/1.481448 View online: http://dx.doi.org/10.1063/1.481448 View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/112/19?ver=pdfcov Published by the AIP Publishing

Articles you may be interested in

Theoretical investigation of exchange and recombination reactions in O (P 3) + N O (Π 2) collisions J. Chem. Phys. **126**, 054304 (2007); 10.1063/1.2430715

Quantum real wave-packet dynamics of the N (S 4) + N O ($\tilde{X} \Pi 2$) \rightarrow N 2 ($\tilde{X} \Sigma g$ + 1) + O (P 3) reaction on the ground and first excited triplet potential energy surfaces: Rate constants, cross sections, and product distributions

J. Chem. Phys. 124, 174303 (2006); 10.1063/1.2186643

Ab initio ground potential energy surface (3 A ") for the O (3 P)+ N 2 O reaction and kinetics study J. Chem. Phys. **115**, 2540 (2001); 10.1063/1.1381010

Temperature dependent rate constants for the reactions of gas phase lanthanides with N 2 O J. Chem. Phys. **111**, 562 (1999); 10.1063/1.479336

H+N 2 O collision dynamics: Branching ratios for T–V energy transfer and the effect of N 2 O vibrational excitation on the reaction kinetics J. Chem. Phys. **107**, 4537 (1997); 10.1063/1.474815



Direct kinetic measurements on reactions of atomic carbon, $C({}^{3}P)$, with O₂ and NO at temperatures down to 15 K

Delphine Chastaing, Sébastien D. Le Picard, and Ian R. Sims School of Chemistry, The University of Birmingham, Edgbaston, Birmingham, B15 2TT, United Kingdom

(Received 22 February 2000; accepted 25 February 2000)

A CRESU (Cinétique de Réaction en Ecoulement Supersonique Uniforme) apparatus has been used to measure rate coefficients for the reactions of $C({}^{3}P)$ with O_{2} and NO at temperatures from 295 K down to 15 K. $C({}^{3}P)$ atoms were, for the first time in a kinetic study, monitored directly by vacuum ultraviolet laser-induced fluorescence. The rate coefficients for both reactions increase as the temperature is lowered, matching the expressions $k(C+O_{2})=(4.9\pm0.8)\times10^{-11}$ $(T/298 \text{ K})^{-(0.32\pm0.08)} \text{ cm}^{3}$ molecule⁻¹ s⁻¹ and $k(C+NO)=(1.5\pm0.4)\times10^{-10} (T/298 \text{ K})^{-(0.16\pm0.14)}$ cm³ molecule⁻¹ s⁻¹. © 2000 American Institute of Physics. [S0021-9606(00)01719-0]

INTRODUCTION

Ground state atomic carbon, $C(2p^{2} {}^{3}P_{J})$ has been detected in a wide range of astronomical environments, and is particularly abundant in dense interstellar clouds. Reactions of $C({}^{3}P)$ are thought to be important in the synthesis of long-chain carbon-containing radicals observed there, and so there is considerable interest in the measurement of the rate coefficients for $C({}^{3}P)$ reactions down to the temperatures prevailing in these dense clouds (10–50 K).

We recently performed the first ever measurements on the kinetics of $C({}^{3}P)$ reactions below room temperature, using an indirect chemiluminescence technique to follow the concentration of $C({}^{3}P)$ with time in a CRESU (reaction kinetics in uniform supersonic flow) apparatus.¹ Reaction rates were determined by observing the chemiluminescence from NO $(B^2\Pi)$ which is generated in the reaction between $C({}^{3}P)$ atoms and NO₂. As $C({}^{3}P)$ was not observed directly, it was not possible to confirm experimentally that any excited spin-orbit population formed in the photolysis was relaxed. It was argued that, as the spin-orbit splittings in $C({}^{3}P)$ are rather small, the ${}^{3}P_{1}$ and ${}^{3}P_{2}$ states lying 16.4 and 43.4 cm⁻¹, respectively, above the ground state ${}^{3}P_{0}$, relaxation would be very rapid. Furthermore, it was necessary to consider the possibility that other photolysis products of C₃O₂ were responsible for the observed signal. It was concluded that they were not. However, experimental confirmation of these points awaited the current work employing direct detection of atomic carbon. We had also hoped to measure the rate of reaction of $C({}^{3}P)$ with NO in our previous study, but this proved impossible owing to the reaction of NO with NO₂ present in excess as part of the chemiluminescence detection scheme.

Apart from the results published in our earlier paper, kinetic measurements on reactions of carbon atoms have been confined to room temperature or above. Husain and co-workers have performed kinetic measurements on the widest variety of reactions using atomic resonance absorption to detect $C({}^{3}P)$. Becker and co-workers are the only group to have used LIF detection, via a two-photon transition. Some dynamical studies have also been carried out us-

ing crossed molecular beams. References to these earlier studies may be found in our previous paper.¹

EXPERIMENTAL TECHNIQUE

In order to measure the rate of the prototypical atomdiatomic radical reaction between C and NO, as well as to confirm our earlier results, we sought to devise a scheme for directly detecting the relative concentration of $C({}^{3}P)$ formed in the CRESU flow, using one-photon vacuum ultraviolet (VUV) laser-induced fluorescence (LIF). We initially attempted to use a two-photon scheme first demonstrated by Bersohn and co-workers,² whereby a two-photon UV excitation is followed by VUV fluorescence. However, this proved impractical for kinetic measurements, as the precursor molecule, C₃O₂, was very effectively photolyzed by the probe laser, presumably via multiphoton absorption, resulting in a high and constant background signal. We therefore turned to one-photon VUV LIF employing the $(3s^{3}P-2p^{3}p)$ transitions around $\lambda = 166$ nm. One-photon VUV LIF detection of $C({}^{3}P)$ has been demonstrated previously,³ but never in a kinetic study. Generation of the required 166 nm radiation is not possible using standard frequency-tripling techniques in rare gas mixtures, and so we chose instead to employ twophoton resonant frequency mixing in xenon.⁴

The CRESU method, as applied to neutral-neutral reactions, has already been described in detail by Sims *et al.*⁵ Full specifications of the Birmingham CRESU apparatus have also been given recently by James *et al.*⁶ Here, we give a brief description of the CRESU apparatus, emphasizing the aspects peculiar to this study.

The heart of the CRESU apparatus is an axisymmetric Laval nozzle, mounted on a moveable reservoir within a vacuum chamber. All the temperatures (apart from 295 K) in the gas flows were achieved by the isentropic expansion of the gas mixture prepared in the reservoir through the nozzle and into the main chamber. This expansion generates a supersonic flow of gas in which the Mach number, the temperature, the density of the gas, the mole fraction of the co-reagent and the velocity of the gas stream are constant along the axis of the flow. A range of nozzles was employed

8466



FIG. 1. VUV LIF spectra of the $[3s {}^{3}P-2p {}^{3}P]$ transition in atomic carbon, observed in the CRESU flow at 295 K (upper spectrum) and 15 K (lower spectrum). The transitions are labeled according to the upper and lower spin–orbit levels involved (J', J'').

in the present work, each providing a particular temperature and density for the selected carrier gas. Experiments were carried out in He, Ar, and N_2 .

 $C({}^{3}P)$ atoms were created by the 10 Hz pulsed laser photolysis of carbon suboxide, $C_{3}O_{2}$, using the 193 nm radiation from an excimer laser (Lambda-Physik, Compex 102), which propagated through the throat of the Laval nozzle and along the axis of the flow. The fluence of the beam was about 50 mJ cm⁻² in the CRESU chamber. $C_{3}O_{2}$ was synthesized and used as before.¹

Detection of $C({}^{3}P)$ atoms was achieved using VUV LIF at wavelengths around 166 nm, corresponding to the $[3s {}^{3}P-2p {}^{3}P]$ electronic transition. 166 nm radiation was generated by two-photon resonant four-wave frequency mixing⁴ in xenon. A gas cell, with a path length of around 20 cm, was equipped with a quartz input lens (10 cm focal length) and a CaF₂ recollimation lens (10 cm focal length) at the output, leading directly into the CRESU chamber. Two tuneable dye laser beams were introduced into the cell, which contained 35 mbar of Xe. The first, at a wavelength 255.94 nm was the frequency-doubled output of a 355 nm Nd:YAG-pumped dye laser (LAS, LDL 205). The output energy was ~2 mJ. The UV frequency (ν_{UV}) was set to the Xe $5p-6p [2\frac{1}{2}, 2]$ two-photon resonance. Excitation of this

TABLE I. Rate coefficients k, for the reaction between $C({}^{3}P)$ atoms and O_{2} (in carrier gas M) measured over the temperature range 15–295 K.

<i>T</i> /K	М	$[M] / 10^{16}$ molecule cm ⁻³	$\begin{array}{c} [O_2]/10^{13}\\ molecule\\ cm^{-3} \end{array}$	No. of points	$k/10^{-11}$ cm ³ molecule ⁻¹ s ⁻¹
15	He	5.05	0-9.2	11	11.2 ± 0.7^{a}
27	He	4.65	0 - 7.2	10	12.2 ± 1.2
54	Ar	5.36	0 - 6.0	11	7.74 ± 0.84
83	N_2	4.88	0 - 0.8	11	7.27 ± 0.79
207	N_2	5.83	0 - 5.6	11	6.52 ± 0.33
295	Ar	17	0-23	11	4.09±0.16

^aErrors quoted as $\pm t\sigma$ statistical error, where *t* is the appropriate value of Student's *t* distribution for the 95% point.

resonance was ensured by monitoring the Xe⁺ multiphoton ionization signal in a separate cell. Another, visible dye laser beam (pulse energy ~ 20 mJ) at a wavelength of around 560 nm (corresponding to frequency v_{vis}) was generated in a second identical dye laser pumped by the same Nd:YAG laser (Spectra Physics, GCR 170), but at 532 nm, and combined and co-propagated into the Xe cell. VUV radiation resulted at a frequency $v_{\rm VUV} = 2 v_{\rm UV} - v_{\rm vis}$. Tuning the visible dye laser in the range $\lambda_{vis} = 560 - 565$ nm, corresponded to $\lambda_{VUV} = 165.44 - 165.88$ nm. The resultant VUV beam intersected the CRESU flow and the photolysis beam at the focus of an optically fast CaF2 condenser lens pair, which imaged any resulting fluorescence onto the photocathode of a VUV solar blind photomultiplier tube (Electron Tubes, type 9403) after passing through a VUV interference filter (Acton Research) centered at 159.8 nm (23.4 nm bandwidth).

Examples of VUV LIF spectra are shown in Fig. 1 at room temperature and at 15 K. Relaxation of the nascent spin-orbit distribution was seen at the lowest temperatures studied, and was observed to take place very rapidly (in $\sim 1-2 \ \mu$ s). Kinetic measurements were only started after this relaxation had taken place. Measurements of the actual rates of spin-orbit relaxation will be the subject of a future publication.

For each co-reagent concentration, a $C({}^{3}P)$ kinetic decay trace was recorded by systematically varying the time delay between the photolysis and probe laser pulses. Each decay consisted of 100 points, and was averaged for 6 laser shots per point. They were fitted to yield values of k_{1st} for each gas mixture on which experiments were carried out at a particular temperature. The flows of co-reagent (O₂, or NO; Air Products), and the carrier gas (He, Ar, or N₂; Air Products) were taken directly from the cylinders and regulated by means of mass flow controllers (MKS). Knowledge of the total gas density from Pitot-tube measurements and of the individual gas flows enabled the concentrations of the coreagent, and hence the corresponding second-order rate coefficient, to be calculated.

RESULTS AND DISCUSSION

Experiments to determine the kinetic behavior of carbon atom reactions with a reagent R ($R=O_2$ or NO) were performed both at room temperature in a subsonic flow, and at low temperatures ranging from 15 K to 204 K in He, Ar, or

TABLE II. Rate coefficients k, for the reaction between C(³P) atoms and NO (in carrier gas M) measured over the temperature range 15–295 K.

T/K	М	$[M] / 10^{16}$ molecule cm ⁻³	$[NO]/10^{13}$ molecule cm ⁻³	No. of points	$k/10^{-10}$ cm ³ molecule ⁻¹ s ⁻¹
15	He	5.05	0-4.6	11	$2.28 {\pm} 0.17^{a}$
27	He	4.65	0 - 1.8	14	2.01 ± 0.11
54	Ar	5.36	0 - 1.2	11	$2.50 {\pm} 0.08$
83	N_2	4.88	0 - 0.8	9	1.73 ± 0.26
207	N_2	5.83	0-4.9	10	1.69 ± 0.15
295	Ar	18	0-9.1	11	1.2 ± 0.09

^aErrors quoted as $\pm t\sigma$ statistical error, where *t* is the appropriate value of Student's *t* distribution for the 95% point.

 N_2 buffer gases, using a number of Laval nozzles. Results for $R=O_2$ and NO are summarized in Tables I and II, and the temperature dependences of the rate coefficients for these reactions of $C({}^{3}P)$ are displayed in Figs. 2 and 3. Table III compares previously measured values with the rate coefficients that have been determined in the present work at room temperature.

The new results for the reaction

$$C(^{3}P) + O_{2} \rightarrow CO + O \tag{1}$$

display a remarkably good agreement with our previous measurements using the indirect chemiluminescence detection technique. This lends confidence to both sets of measurements. An unweighted nonlinear least-squares fit to the combined data set yields the following temperature dependence: $k_1 = (4.9 \pm 0.8) \times 10^{-11}$ $(T/298 \text{ K})^{-(0.32 \pm 0.08)}$ cm³ molecule⁻¹ s⁻¹, with errors quoted as $\pm 2\sigma$, where σ is the standard error. This compared favorably with the temperature dependence determined previously $(k=4.7 \times 10^{-11})^{-11}$



FIG. 2. Rate coefficients *k* for the reaction of $C({}^{3}P)$ atoms with O_{2} plotted on a log–log scale against temperature. The filled symbols show the results of this work; circles (\bullet) denoting Ar carrier gas; squares (\blacksquare) N₂; and triangles (\blacktriangle) He. The open circles show the results of our previous measurements over the same temperature range with chemiluminescence detection (Ref. 1) and the solid line shows the result of a nonlinear least-squares fit to the combined data set, giving $k = (4.9 \pm 0.8) \times 10^{-11}$ (T/298K)^{$-(0.32\pm0.08)$} cm³ molecule⁻¹ s⁻¹. The room temperature results of Husain and Young (Ref. 12) and Becker *et al.* (Ref. 13) are shown as an open diamond (\diamond) and an open square (\Box), respectively.



FIG. 3. Rate coefficients k for the reaction of $C({}^{3}P)$ atoms with NO plotted on a log–log scale against temperature. The filled symbols show the results of this work: circles (\bullet) denoting Ar carrier gas; squares (\blacksquare) N₂; and triangles (\blacktriangle) He. The solid line shows the result of a nonlinear least-squares fit to this new data giving $k = (1.5 \pm 0.4) \times 10^{-10} (T/298 \text{ K})^{-(0.16 \pm 0.14)}$ cm³ molecule⁻¹ s⁻¹. The room temperature result of Braun (Ref. 10) is shown as an open circle (\bigcirc), that of Husain and Young (Ref. 12) as an open diamond (\diamondsuit), that of Becker *et al.* (Ref. 13) as an open square (\square), and that of Bergeat *et al.* (Ref. 15) as an open inverted triangle (\bigtriangledown).

 $(T/298 \text{ K})^{-0.34} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$. Possible explanations for the observed negative temperature dependence were discussed in our previous paper.¹

Our results for the reaction

$$C(^{3}P) + NO \rightarrow CN + O \tag{2a}$$

$$\rightarrow$$
CO+N (2b)

are in only fair agreement with the rather scattered results of previous studies at room temperature, as can be seen in Table III. An unweighted nonlinear least-squares fit over the temperature range 15–295 K yields the following temperature dependence for the overall rate coefficient: $k_2 = (1.5 \pm 0.4) \times 10^{-10} (T/298 \text{ K})^{-(0.16 \pm 0.14)} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, with errors quoted as before. The rapid rate at room temperature, combined with the mild negative temperature dependence, is characteristic of radical-radical or atom-radical reactions occurring on attractive potential surfaces.¹ In such cases,

TABLE III. Comparison of rate coefficients for the reactions of $C({}^{3}P_{j})$ with O_{2} and NO at room temperature from the present work with those from previous measurements.

$\frac{k_{\sim 300 \text{ K}}(\text{C}(^{3}P) + R \rightarrow \text{products})}{/10^{-10} \text{ cm}^{3} \text{ molecule}^{-1} \text{ s}^{-1}}$							
$R = O_2$	R = NO	Method ^a	Reference				
0.33	1.1	FP-VUVAb	10				
0.33 ± 0.15	0.73 ± 0.22	FP-VUVAb	11				
0.26 ± 0.03	$0.48 {\pm} 0.08$	FP-VUVAb	12				
0.47 ± 0.03	0.16 ± 0.02	PLP-LIF	13				
0.16 ± 0.02	0.27 ± 0.02	FT-CL	14				
0.25 ± 0.04	$0.54 {\pm} 0.08$	FT-RF	15				
$0.437 {\pm} 0.015$	_	PLP-CL	1				
0.409±0.016	1.20 ± 0.09	PLP-VUV LIF	This work				

^aFP, flash photolysis; VUVAb, vacuum ultraviolet absorption; PLP, pulsed laser photolysis; LIF, laser-induced fluorescence; FT, flow tube; CL, chemiluminescence; RF, resonance fluorescence; VUV LIF, vacuum ultraviolet laser-induced fluorescence.

This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP

some collisions may occur over surfaces that do not lead to thermodynamically accessible products. The observed mild negative temperature dependence may then result from an increase in the proportion of collisions which occur on surfaces that do lead to products. The ${}^{3}P_{1}$ and ${}^{3}P_{2}$ spin–orbit states of C(${}^{3}P$) lie at energies equivalent to 23 K and 62 K, respectively, above the ground state ${}^{3}P_{0}$. The populations in the individual spin–orbit states change markedly through the range of temperature covered in the present experiments. Therefore, if reaction is more probable from lower spin– orbit states this alone could lead to a negative temperature dependence, independent of the dynamics of the reactive collisions.⁷

In contrast to the reaction between C and O_2 , recent *ab* initio potential surface and rate coefficient calculations have been performed on the C+NO system. Beghin et al.⁸ employed the ACCSA method on a long range electrostatic/ dispersion potential, giving a rate coefficient at room temperature of 3.43×10^{-11} cm³ molecule⁻¹ s⁻¹, with a marked negative temperature dependence. Andersson et al.,9 in a very recent study, present quasiclassical trajectory calculations on a new ab initio potential surface. They obtain a rate coefficient of $\sim 8 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ at room temperature, and almost no temperature dependence. However, they took a constant correction factor of 1/9 to allow for the nonreactive collisions as explained above. At room temperature, and certainly below, this factor is temperature dependent, and fuller treatment could bring their results into agreement with our experimental data. Further comparisons with theoretical calculations, as well as with new crossed-beam measurements at very low collision energies being performed in Bordeaux by Costes and co-workers, will be the subject of a future paper.

ACKNOWLEDGMENTS

We are grateful to EPSRC for a substantial research grant to construct the CRESU apparatus. We thank the EU

(under its TMR program) for a studentship (DC) and postdoctoral fellowship (SDLP, as part of the Research Network on Astrophysical Chemistry). The EPSRC Laser Loan Pool at the Rutherford–Appleton Laboratory provided an Nd:YAG-pumped dye laser system, for which we express our thanks. We are also very grateful to Professor Ian W. M. Smith for valuable discussions, and to Stuart Arkless, Tony Rothin and Steve West for their skilled technical assistance.

- ¹D. Chastaing, P. L. James, I. R. Sims, and I. W. M. Smith, Phys. Chem. Chem. Phys. **1**, 2247 (1999).
- ²P. Das, G. Ondrey, N. Vanveen, and R. Bersohn, J. Chem. Phys. **79**, 724 (1983).
- ³M. Rowekamp, A. Goehlich, and H. F. Dobele, Appl. Phys. A: Solids Surf. **54**, 61 (1992).
- ⁴R. Hilbig and R. Wallenstein, IEEE J. Quantum Electron. **19**, 194 (1983).
- ⁵I. R. Sims, J. L. Queffelec, A. Defrance, C. Rebrion-Rowe, D. Travers, P. Bocherel, B. R. Rowe, and I. W. M. Smith, J. Chem. Phys. **100**, 4229 (1994).
- ⁶P. L. James, I. R. Sims, I. W. M. Smith, M. H. Alexander, and M. B. Yang, J. Chem. Phys. **109**, 3882 (1998).
- ⁷R. A. Brownsword, S. D. Gatenby, L. B. Herbert, I. W. M. Smith, D. W. A. Stewart, and A. C. Symonds, J. Chem. Soc., Faraday Trans. **92**, 723 (1996).
- ⁸A. Beghin, T. Stoecklin, and J. C. Rayez, Chem. Phys. **195**, 259 (1995).
- ⁹S. Andersson, N. Markovic, and G. Nyman, Phys. Chem. Chem. Phys. (in press).
- ¹⁰ W. Braun, A. M. Bass, D. D. Davis, and J. D. Simmons, Proc. R. Soc. London, Ser. A **312**, 417 (1969).
- $^{11}\mbox{D}.$ Husain and L. J. Kirsch, Trans. Faraday Soc. 67, 2025 (1971).
- ¹²D. Husain and A. N. Young, J. Chem. Soc., Faraday Trans. 2 71, 525 (1975).
- ¹³K. H. Becker, K. J. Brockmann, and P. Wiesen, J. Chem. Soc., Faraday Trans. 2 84, 455 (1988).
- ¹⁴G. Dorthe, P. Caubet, T. Vias, B. Barrere, and J. Marchais, J. Phys. Chem. 95, 5109 (1991).
- ¹⁵A. Bergeat, T. Calvo, G. Dorthe, and J. C. Loison, Chem. Phys. Lett. 308, 7 (1999).