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An Experimental Study of the Intersystem Crossing and Reactions of $C_2(X^1\Sigma_g^+)$ and $C_2(a^3\Pi_u)$ with O_2 and NO at Very Low Temperature (24−300 K)[†]

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A low-temperature gas-phase kinetics study of the reactions and collisional relaxation processes involving $C_2(X^1\Sigma_g^+)$ and $C_2(a^3\Pi_u)$ in collision with O_2 and NO partners at temperatures from 300 to 24 K is reported. The experiments employed a CRESU (Cinétique de Réaction en Ecoulement Supersonique Uniforme) apparatus to attain low temperatures. The C_2 species were created using pulsed laser photolysis at 193 nm of mixtures containing C_2Cl_4 diluted in N_2, Ar, or He carrier gas. $C_2(X^1\Sigma_g^+)$ molecules were detected via pulsed laser-induced fluorescence in the $(D^1\Sigma_u^+ \leftarrow X^1\Sigma_g^+)$ system, and $C_2(a^3\Pi_u)$ molecules were detected via pulsed laser-induced fluorescence in the $(d\,^3\Pi_g \leftarrow a\,^3\Pi_u)$ system. Relaxation of $^3C_2$ by intersystem crossing induced by oxygen was measured at temperatures below 200 K, and it was found that this process remains very efficient in the temperature range 50−200 K. Reactivity of $C_2(X^1\Sigma_g^+)$ with oxygen became very inefficient below room temperature. Using these two observations, it was found to be possible to obtain the $C_2(X^1\Sigma_g^+)$ state alone at low temperatures by addition of a suitable concentration of O_2 and then study its reactivity with NO without any interference coming from the possible relaxation of $C_2(a^3\Pi_u)$ to $C_2(X^1\Sigma_g^+)$ induced by this reagent. The rate coefficient for reaction of $C_2(X^1\Sigma_g^+)$ with NO was found to be essentially constant over the temperature range 36−300 K with an average value of $(1.6 \pm 0.1) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. Reactivity of $C_2(a^3\Pi_u)$ with NO was found to possess a slight negative temperature dependence over the temperature range 50−300 K, which is in very good agreement with data obtained at higher temperatures.

Introduction

The C_2 molecule is ubiquitous in the universe. It has been observed in widely differing environments ranging from cold regions such as interstellar clouds,[1,2] circumstellar envelopes,[3] and comets[4] to hot media such as hydrocarbon flames,[5] plasmas,[6,7] and stellar atmospheres.[8,9] Although not yet detected in outer planetary atmospheres, it is also implicated in the photochemical models of these environments.[10−16] Understanding its chemistry and more specifically the temperature dependence of rate coefficients for reactions with other reagents is therefore of major interest. To date, most of the available experimental data, however, have been obtained at room temperature and essentially concern the reactivity of C_2 with hydrocarbons.[17−22] While studies have also been carried out at higher temperatures,[21,23−31] no measurements have been performed below 300 K in the gas phase.

One of the peculiarities of the C_2 species resides in the very low energy of its first excited electronic state, $a^3\Pi_u(v=0)$ (hereafter $^3C_2$), which is only separated by 610 cm^{-1} (i.e. ∼880 K)[32] from the electronic ground state $X^1\Sigma_g^+(v=0)$ (hereafter $^1C_2$). In cold environments such as those mentioned above, the C_2 molecule exists mainly in its ground state $X^1\Sigma_g^+$, and therefore kinetic data are required for this level. From an experimental point of view, however, present available techniques for the production of C_2 generate both states together. Although some methods based on the use of scavengers are available to eliminate the singlet state[33,34] and then study the fate of the triplet state alone, to date it has not been possible to isolate the singlet state from the triplet state. In previous studies of the reaction kinetics of $^3C_2$ with various reagents, the measured rate coefficient was generally considered as a *total removal rate coefficient* which included reactivity with the reagent on the one hand and possible relaxation to the singlet state on the other hand. Therefore, in some cases, the presence of $^3C_2$ could act as a source of $^1C_2$ resulting in underestimated measures for the reaction rate coefficients of the ground state with the reagent of consideration. A review of the available literature clearly indicates that the reactivity of the triplet state has been much more studied than that of the singlet state mainly for this reason.

Very few studies are available concerning collisional relaxation of $^3C_2$. The principal work relating to this topic was carried out 25 years ago by Reisler et al.[18] and Mangir et al.,[33] who measured the collision induced intersystem crossing rate coefficient of the $^1C_2/^3C_2$ system for a variety of partners including atoms (Ar, Kr, and Xe) and molecules (N_2, CO_2, CF_4, and O_2). More recently, Huang et al.[34] published a study related to molecular oxygen only. These studies, only performed at room temperature, showed that molecular oxygen was the most efficient quencher, by far. The rate coefficient for the $^3C_2 + O_2$ relaxation process was determined experimentally under conditions in which $^1C_2$ was removed much more rapidly than $^3C_2$.[33,34] In these studies, hydrocarbons or C_2Cl_4 were used as scavengers of $^1C_2$. Mangir et al.[33] found a rate coefficient of $(2.7 \pm 0.3) \times$

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10^{-11} cm^3 molecule^{-1} s^{-1}, which was confirmed by Huang et al.,[34] who obtained (1.58 ± 0.15) × 10^{-11} cm^3 molecule^{-1} s^{-1}. Although the measured rate coefficient was interpreted as the total removal of $^3C_2$ in the presence of O_2, it can be mostly considered as being the contribution of collision induced intersystem crossing. A large number of experiments, indeed, have been carried out, in which the triplet and/or the singlet state were probed in the presence of O_2.[17,19,23,24,26,35,36] In these studies, it was found that both states were removed at the same rate, leading to the conclusion that the measured rate coefficient corresponded to the reaction of an equilibrated $^1C_2/^3C_2$ population. At room temperature, the rate coefficient was found to be rather low (3 × 10^{-12} cm^3 molecule^{-1} s^{-1}), which indicated that the true reaction rate coefficient of $^1C_2$ and $^3C_2$ with O_2 is very small as this value has to be considered as an upper limit for this process. Equilibration of the two states can be understood if the intersystem crossing induced by O_2 between the two states is much faster than reaction with O_2. Every loss of $^1C_2$ by reaction with O_2 is then immediately compensated by relaxation/excitation in the $^1C_2/^3C_2$ system thus maintaining initial equilibrium. This assumption was experimentally verified since the quenching rate coefficient for $^3C_2$ was found to be about 1 order of magnitude higher than the reaction rate coefficient as previously mentioned.

At room temperature and above, addition of oxygen can then be employed to equilibrate the $^3C_2$ and $^1C_2$ populations, permitting the measurement of joint reaction rate coefficients under well-defined conditions. At lower temperatures, where the available thermal energy becomes much smaller than the energy gap between singlet and triplet states and provided that relaxation of $^3C_2$ is as efficient as at room temperature, O_2 could be a good candidate to remove entirely the $^3C_2$ thus enabling the measurement of “pure” $^1C_2$ rate coefficients.

The objective of this paper is to study the removal of both $^1C_2$ and $^3C_2$ by O_2 and NO in the temperature range 24−300 K using the CRESU technique that will be briefly described in the next section. Results showed that the expected decoupling of the $^1C_2/^3C_2$ system occurs and that the triplet state is efficiently removed by O_2 in the temperature range 50−200 K. This efficient quenching was then employed to enable the study of the reactivity of “pure” $^1C_2$ and $^3C_2$ with NO.

Experimental Section

The CRESU technique and its adaptation to the study of neutral−neutral reactions via pulsed laser photolysis-laser induced fluorescence technique (PLP-LIF) has been described in detail elsewhere.[37] Only a short description will be given here, drawing attention to those aspects of the experiments which relate to measurements of the reaction involving both $^1C_2$ and $^3C_2$ with O_2 and NO.

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 (typically 400 μs). 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.

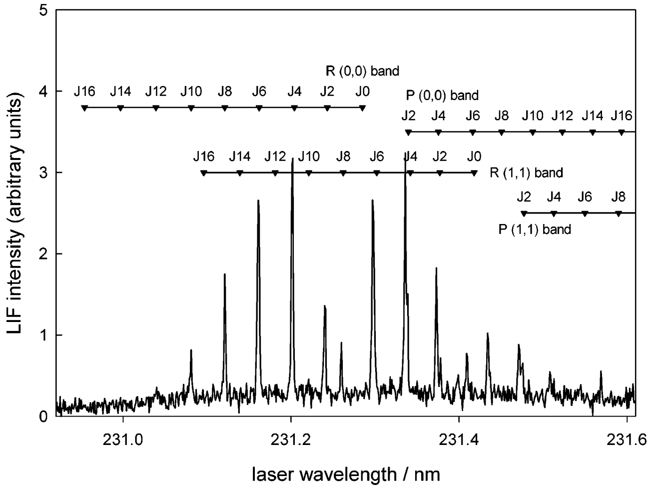

Figure 1. LIF spectrum of $C_2(X^1\Sigma_g^+)$ at 49 K in He, taken at a delay time between photolysis and probe lasers of 100 μs. Line assignments are indicated above the spectrum.

C_2 radicals have been produced in the past by using photodissociation techniques such as, CO_2 IR multiphoton dissociation of C_2H_3CN,[18,33,35,36,38] C_2H_4[35,38] or C_2HCl_3,[18,33] UV excimer laser photolysis of F_3CCCCF_3,[17,23,29,30] C_2H_2,[19,23] C_6H_6,[30] C_2Cl_4,[20,22,25,34,35,39] and C_3O_2/argon mixtures or C_4F_6/argon mixtures,[21] and laser ablation of graphite.[40,41] In the current work C_2 molecules have been obtained by UV photolysis of C_2Cl_4 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. Tetrachloroethylene C_2Cl_4 (Aldrich, 99.9% HPLC grade) was placed in a glass vessel outside the CRESU chamber. The C_2Cl_4 vapor was entrained into the buffer gas flow by bubbling a controlled flow of He through liquid C_2Cl_4. The resultant mixture was passed through a stainless steel tube whose walls were temperature controlled, and then this small precursor flow was introduced into the reservoir by means of a PTFE line. The typical C_2Cl_4 concentrations in the supersonic flow were in the range 5−10 × 10^{12} molecule cm^{-3}. This concentration was high enough to produce a detectable quantity of C_2 but low enough to avoid destruction of the $^1C_2$ state by reaction with C_2Cl_4. This process, indeed, is known to proceed 430 times faster (2.6 × 10^{-10} cm^3 molecule^{-1} s^{-1})[18] than the reaction of C_2Cl_4 with the $^3C_2$ state.

Both states $^1C_2$ and $^3C_2$ were produced at the same time in the photolysis and have been observed directly via LIF using the Mulliken ($D^1\Sigma_u^+ \leftarrow X^1\Sigma_g^+$) system and the Swan ($d^3\Pi_g \leftarrow a^3\Pi_u$) system respectively using the strongest available rotational line at the temperature of the flow. The $^3C_2$ population was probed by exciting the ($d^3\Pi_g \leftarrow a^3\Pi_u$) (0,0) band at ∼516 nm and detecting LIF on the (0,1) band at ∼ 563 nm which was isolated with an interference filter centered at 561.4 nm (band pass: 9 nm fwhm, Andover Corp.), while $^1C_2$ was probed by exciting the ($D^1\Sigma_u^+ \leftarrow X^1\Sigma_g^+$) (0,0) band at ∼231 nm and collecting LIF on resonance using an interference filter centered at 228 nm (band pass: 11 nm fwhm, Corion). Typical spectra at 49 K for the singlet state and at 36 K for the triplet state are presented in Figures 1 and 2.

Probe laser radiation was provided by a dye laser (Laser Analytical Systems, LDL 20505) operating with Coumarin 460 (Exciton) or Coumarin 307 (Exciton) dye diluted in methanol to study $^1C_2$ and $^3C_2$, respectively. 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 for $^1C_2$ and 50 mJ for $^3C_2$ studies. For the detection of the singlet

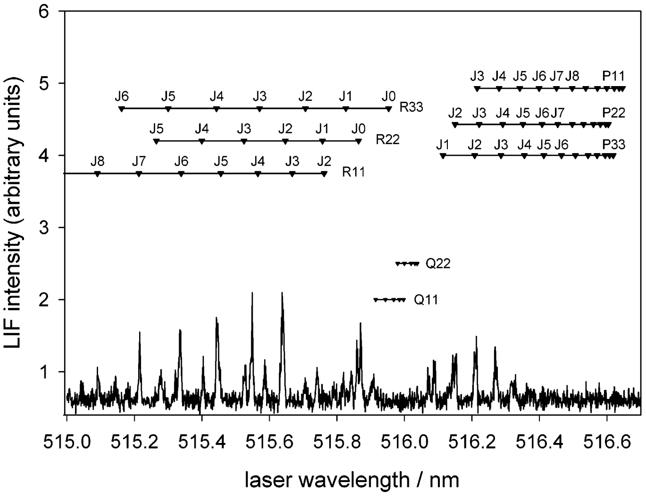

Figure 2. LIF spectrum of $C_2(a^3\Pi_u)$ at 36 K in He, taken at a delay time between photolysis and probe lasers of 100 μs. Line assignments are indicated above the spectrum.

state, the dye laser was frequency doubled using a BBO crystal to obtain the 231 nm wavelength (Laser Analytical Systems, LDL frequency mixer option).

The probe and the photolysis beams were combined on a dichroic mirror and were directed along the axis of the supersonic flow, entering the CRESU apparatus through a Brewster window, passing through another such window mounted on the back of the Laval nozzle reservoir and set at symmetric angle with respect to the first one to compensate for beam displacement. Then they copropagated out through the throat of the Laval nozzle and along the axis of the flow, before leaving the vacuum chamber via a third Brewster window. Laser induced fluorescence was collected at a known distance downstream of the Laval nozzle (usually 10 to 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 signals were accumulated, processed, and analyzed as described previously elsewhere.[37] The delay time between the photolysis and the probe laser was controlled by a digital delay generator (Stanford Research Systems DG 535). A typical LIF decay for the triplet state $^3C_2$ at 83 K is shown in Figure 3. As can be seen, a significant rise time was observed for the $^3C_2$ LIF signal. This was taken as resulting from collisional relaxation of $^3C_2$ formed in rotationally excited states. This was also observed for the singlet state LIF decays. In order to avoid contamination of the data, all nonlinear least-squares fits of the exponential decays of the $^{1,3}C_2$ LIF signals were commenced after this rise was complete. For a given temperature, LIF scans were then taken at differing reagent concentrations in the usual way in order to construct a kinetic plot from which the second-order rate coefficient could be extracted. Figures 4 and 5 show second-order plots for $^3C_2 + O_2$ at 49 K and $^1C_2 + O_2$ at 145 K, respectively. Measurements at room temperature were performed in the CRESU apparatus as previously described.[37]

The flows of O_2 (from Air Liquide, 99.998%), NO (Air Liquide 99%), and carrier gas (N_2, He, and Ar; Air Liquide, 99.995%) were taken directly from cylinders and regulated by means of Tylan mass flow controllers. Knowledge of the total gas density along the flow, and of the individual gas flow rates, allowed the O_2 and NO concentrations in the supersonic flow to be calculated.

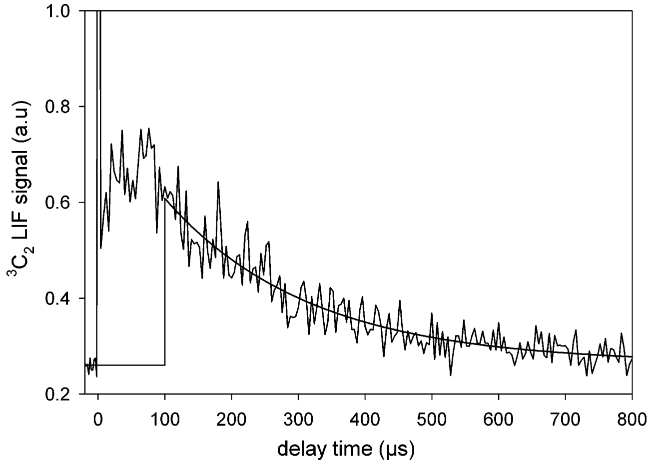

Figure 3. Decay of $C_2(a^3\Pi_u)$ LIF signal at 83 K in the presence of O_2 ($[O_2] = 1.7 \times 10^{14}$ molecule cm^{-3}) and N_2 buffer ($[N_2] = 4.88 \times 10^{16}$ molecule cm^{-3}), fit to a single-exponential function.

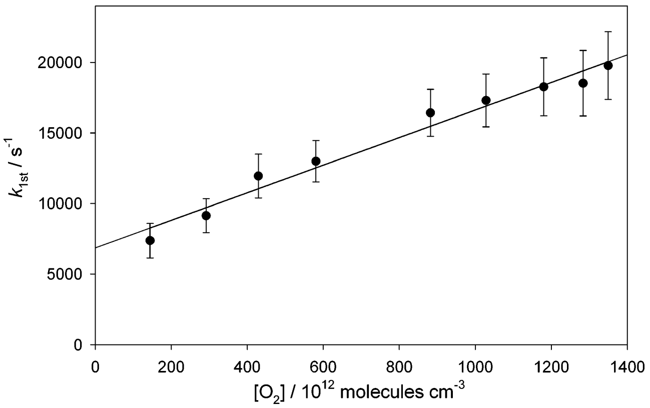

Figure 4. Second-order plot for the removal of $C_2(a^3\Pi_u)$ by O_2 at 49 K in He, yielding a value for the second-order rate coefficient of $k = (9.8 \pm 1.1) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.

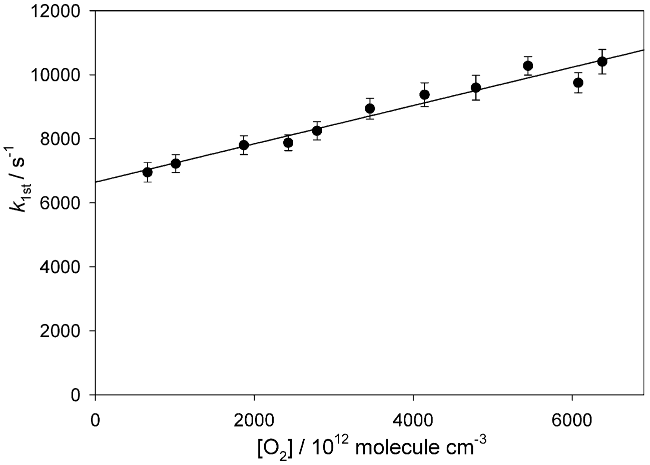

Figure 5. Second-order plot for the removal of $C_2(X^1\Sigma_g^+)$ by O_2 at 145 K in N_2, yielding a value for the second-order rate coefficient of $k = (0.6 \pm 0.1) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.

Results and Discussion

Impact of the Introduction of O_2 on the $^1C_2$ LIF Decays. As usual in this kind of study, LIF decays of the $^1C_2$ state were recorded for different O_2 concentrations added to the flow. These experiments showed that, as the O_2 concentration was increased,

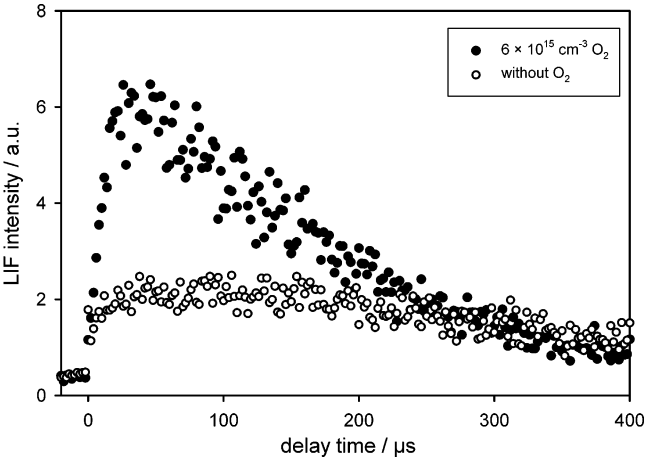

Figure 6. Dependence of the time-resolved $C_2(X^1\Sigma_g^+)$ LIF intensity upon O_2 concentration at 145 K in N_2 (at a density of 9.23×10^{16} molecule cm^{-3}).

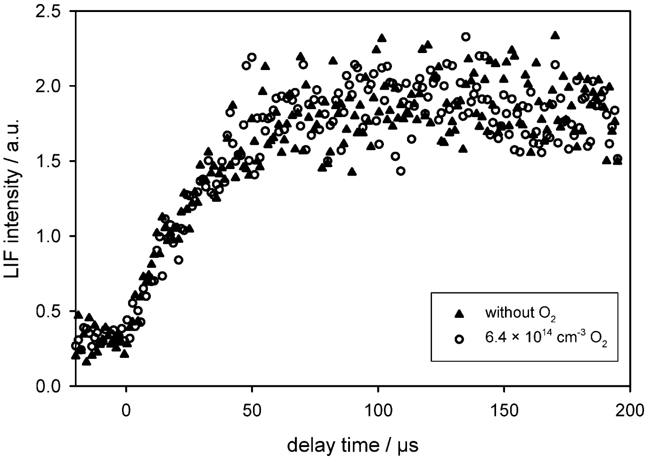

Figure 7. Dependence of the time-resolved $C_2(X^1\Sigma_g^+)$ LIF intensity upon O_2 concentration at 36 K in He (at a density of 5.28×10^{16} molecule cm^{-3}).

the LIF signal increased as well and the maximum of the signal moved to a shorter delay time while the level of the signal at long time delays was maintained almost unaffected, confirming a slow reactivity (see Figure 6). It is worth noting that, when the oxygen concentration is large enough, the maximum of the LIF signal does not increase any more indicating complete elimination of the $^1C_2$ source. This change in the LIF signal was interpreted as the existence of a source to the $^1C_2$ state which was thought to result from the relaxation of the $^3C_2$ state. This experiment was repeated for each temperature showing the same behavior for the $^1C_2$ LIF decay signals when O_2 was added except for the lowest temperatures, 36 and 24 K, in which the addition of O_2 did not change the LIF trace profile (see Figure 7).

This observation opened up the possibility of completely removing $^3C_2$ from the flow while maintaining $^1C_2$ (except at the very lowest temperatures of 24 and 36 K where O_2 had no effect) and therefore merited a detailed kinetic study of the removal of both states in the presence of O_2 and as a function of temperature.

Removal of $^1C_2$ and $^3C_2$ by O_2. Experiments have been carried out in the temperature range 24−300 K. However, the reactivity of $^1C_2$ has been found to be too low to be measured in the CRESU apparatus below 145 K, and therefore data were obtained at 145, 200, and 300 K only. Similarly, the measured rate coefficient at 24 K for the triplet state has to be considered as an upper limit. A synthetic view of all second-order rate coefficients measured for $^1C_2$ and $^3C_2$ is displayed in Table 1. Only statistical errors are quoted. Some systematic errors due to flow control inaccuracies or inaccuracies in the determination of the buffer gas total density should also be taken into account. Every effort was made however to minimize these additional errors which, we estimate, do not exceed 15%. Figure 8 presents these results along with previous experimental measurements performed at higher temperatures. Most of the earlier kinetic studies also probed the LIF decay of the triplet or/and singlet states of C_2. Fontijn et al.,[25] however, probed the CO molecules produced in the reaction of $^{1,3}C_2$ with O_2 via chemiluminescence in the VUV (fourth positive system ($A^1\Pi-X^1\Sigma$)) or in the visible.

As it can be appreciated from Figure 8, at room temperature our measured rate coefficients and almost all rate coefficients from previous studies for the removal of $^1C_2$ and $^3C_2$ are identical. As explained before, this situation corresponds to the removal of an equilibrated population of triplet and singlet states. However, there are two previous experimental studies in which the total removal of the triplet state has been measured.[33,34] The rate coefficients obtained for the total removal of the $^3C_2$ are much higher than those measured for the equilibrated states revealing the predominance of the collisionally induced intersystem crossing process.

At high temperatures ($T > 300$ K), the rate coefficients for the removal of $^1C_2$ and $^3C_2$ are still found to be identical, indicating that the rate coefficients measured also correspond to the reaction of O_2 with an equilibrated $^1C_2/^3C_2$ population.

In contrast, our work at low temperatures ($T < 300$ K) shows a different behavior. As the temperature decreases, the rate coefficients for the removal of $^1C_2$ and $^3C_2$ with oxygen start to diverge from each other, leading to the conclusion that the two states are now becoming decoupled. The rate coefficient for the removal of $^3C_2$ with O_2 becomes much higher than that for the singlet state.

Connecting these results to the $^1C_2$ LIF decay signal observations, it is now possible to conclude that O_2 is an efficient quencher of the $^3C_2$ state in the temperature range from 200 to 50 K whereas pure reactivity of $^1C_2$ with O_2 becomes (or remains) definitively negligible. It is worth mentioning that the marked decay of the relaxation rate coefficients of $^3C_2$ below 50 K suggests the possible presence of an activation energy barrier in the collisionally induced intersystem crossing process. At 36 K and even more at 24 K, error bars are very large because the hydrodynamic time of both nozzles is rather short to perform slow rate coefficient measurements.

Finally it is also worth noting that, from a theoretical point of view, nothing is presently available with respect to this process. It is our hope that the present results will encourage timely theoretical examinations of the relaxation of $^3C_2$ in the presence of O_2.

To conclude, oxygen addition provides an ideal situation to study the reactivity of $^1C_2$ with another partner without having any interference from $^3C_2$. This property was then used in further experiments where O_2 was systematically introduced in the flow in addition to the reagent of interest. In this paper, we have used this opportunity to study the reactivity of NO with $^1C_2$. Results will also be presented in the next section for the total removal of $^3C_2$ by NO.

Reactivity of $^1C_2$ and $^3C_2$ with NO. The second-order rate coefficients measured for the total removal of $^1C_2$ and $^3C_2$ with NO in the temperature range from 24 to 300 K are displayed in

TABLE 1: Rate Coefficients Measured at Different Temperatures for the Kinetic Study of $^1C_2$ and $^3C_2$ with O_2

			O_2			
			$^1C_2$		$^3C_2$	
T/K	buffer gas	[buffer] 10^{16} molecule cm^{-3}	$[O_2]$ 10^{12} molecule cm^{-3}	k_{2nd} 10^{-12} cm^3 molecule^{-1} s^{-1}	$[O_2]$ 10^{12} molecule cm^{-3}	k_{2nd} 10^{-12} cm^3 molecule^{-1} s^{-1}
300	N_2	10.4−10.9	134−695	3.6 ± 0.7^a	650−6100	3.1 ± 0.2
200	N_2	4.8	510−3150	2.1 ± 0.3	50−1600	4.8 ± 0.5
145	N_2	9.2	200−6750	0.6 ± 0.1	375−3250	11.1 ± 0.4
83	N_2	4.9			90−850	13.3 ± 1.3
49	He	10.4			150−1350	9.8 ± 1.1
36	He	5.3			200−2300	1.6 ± 1.2
24	He	18.3			22−300	1.1 ± 5.4

[a] Uncertainties are $\pm t\sigma$ where σ is the standard error obtained from the fit of the second-order plot and t is the appropriate value of the Student's t distribution for the 95% confidence interval.

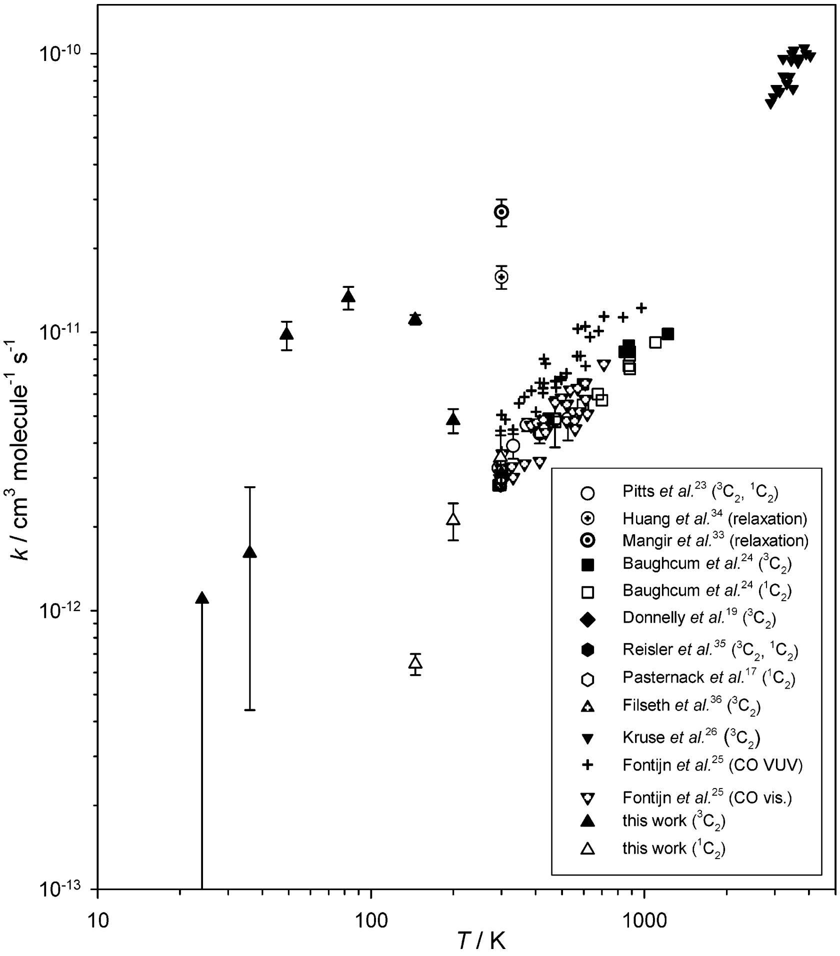

Figure 8. Second-order rate coefficients k for the reaction and/or relaxation of $C_2(X^1\Sigma_g^+)$ and $C_2(a^3\Pi_u)$ with O_2 measured at temperatures between 24 and 300 K, compared to the results of earlier studies at temperatures of 300 K and above.

Table 2, and Figure 9 presents these results along with previous experimental studies performed at higher temperatures.

As can be seen in Figure 9, the rate coefficient for the reaction of $^1C_2$ with NO in the temperature range from 200 to 36 K can be considered almost constant and close to 1.8×10^{-10} cm^3 molecule^{-1} s^{-1} while at 24 K there is an apparent decrease in reactivity. A possible explanation may be that at this temperature (where O_2 is ineffective as a relaxant and therefore not used) the $^1C_2$ and $^3C_2$ states are present together as noted above and as suggested by Reisler et al.[18] $NO(X^2\Pi)$ may induce fast intersystem crossing because this process is spin allowed for a doublet state. The resultant cascading would result in measuring underestimated rate coefficients for the $^1C_2$ state that would explain the observed decrease of its rate coefficient at 24 K. As the measured rate coefficient for removal of $^3C_2$ by NO at 24 K is about one-third the value of the observed value for $^1C_2$ (see below), in the worst case where this corresponds to relaxation of $^3C_2$ to $^1C_2$ rather than reaction, we estimate that the observed depression of the rate constant could be due to the effects of this cascading. Another explanation of the decrease of the $^1C_2$ + NO rate coefficient at 24 K could be that at $T <$ 36 K a small energy barrier to the reaction reduces reactivity, but as we cannot rule out the former explanation at the current time, we prefer to quote the values determined for the $^1C_2$ + NO rate coefficient at both 36 and 24 K in the absence of O_2 relaxant as lower limits. However, we would point out that no apparent depression of the $^1C_2$ rate constant occurred at 36 K despite the same He buffer gas and absence of O_2 also at this

TABLE 2: Rate Coefficients Measured at Different Temperatures for the Kinetic Study of $^1C_2$ and $^3C_2$ with NO in the Presence of an Optimized Concentration of O_2

			NO				
			$^1C_2$			$^3C_2$	
T/K	buffer gas	[buffer] 10^{16} molecule cm^{-3}	[O_2] 10^{16} molecule cm^{-3}	[NO] 10^{12} molecule cm^{-3}	k_{2nd} 10^{-11} cm^3 molecule^{-1} s^{-1}	[NO] 10^{12} molecule cm^{-3}	k_{2nd} 10^{-11} cm^3 molecule^{-1} s^{-1}
300	N_2	11.2−10.8	0.6	66−211	12.6 ± 2.1[a]	60−250	6.2 ± 0.5
200	N_2	4.8	0.3	10−52	18.8 ± 3.5	1−455	7.9 ± 0.7
145	N_2	9.2	0.4	20−170	16.2 ± 1.8	90−1000	9.0 ± 0.5
83	N_2	4.9	0.1	10−55	17.6 ± 3.2	40−425	11.0 ± 0.7
53	Ar	20.2				30−300	11.6 ± 0.5
49	He	10.4	0.3	20−160	17.2 ± 2.8		
36	He	5.3		12−125	18.7[b] ± 3.0	65−650	7.0 ± 0.7
24	He	18.3		20−380	10.6[b] ± 0.5	45−400	3.6 ± 0.6

[a] Uncertainties are $\pm t\sigma$ where σ is the standard error obtained from the fit of the second-order plot and t is the appropriate value of the Student's t distribution for the 95% confidence interval. [b] The values of the rate constant for $^1C_2 + NO$ at 24 and 36 K must be considered as lower limits owing to the possibility of cascading effects at these temperatures in this system, as explained in the text.

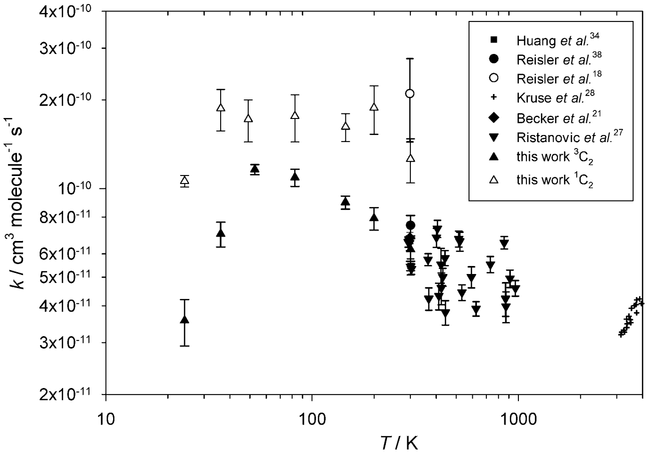

Figure 9. Second-order rate coefficients k for the reaction and/or relaxation of $C_2(X^1\Sigma_g^+)$ and $C_2(a^3\Pi_u)$ with NO measured at temperatures between 24 and 300 K, compared to the results of earlier studies at temperatures of 300 K and above.

temperature. We thus conclude that any cascading effects are likely to be rather small.

The only previous experimental study on $^1C_2 + NO$ was performed by Reisler et al.[18] at 300 K. They measured a rate coefficient of $(2.10 \pm 0.33) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, which is in a reasonable agreement with our value within the 2σ error bars presented in Figure 9.

In the case of the triplet state, the rate coefficients measured for the total removal by NO are significantly smaller that those for the reactivity of the singlet (typically a factor of 2 lower).

At room temperature our value lies in between all previous experimental data, and our results in the range of temperatures from 300 to 53 K follow the negative temperature dependence trend displayed by previous experimental data at $T \leq 1000$ K. It can be noted also in Figure 9 that, at even higher temperatures, the experiments performed by Kruse et al.[28] gave a positive temperature dependence which was explained by the opening of new exit channels, $C_2N + O$, $C_2O + N$ (see below).

To complete the discussion of our results, it can be seen that at 36 and 24 K there is a significant decrease of the rate coefficients. This may be due to the presence of a small energy barrier to the reactivity. More data at lower temperatures could help to explain and confirm this behavior. However, several attempts to study the reactivity of C_2 at 15 K were unsuccessful as it proved impossible to detect the $^{1,3}C_2$ molecule under these conditions.

Although our experimental study does not provide any information about products, some data are available in the literature. An extensive study of Reisler et al.[38] at room temperature suggested the following products for the $^3C_2 + NO$ reaction:

$$C_2(a^3\Pi_u) + NO(X^2\Pi) \rightarrow CN(A^2\Pi) + CO \qquad \Delta_r H_0^\ominus = -501.0 \text{ kJ mol}^{-1}$$

$$\rightarrow CN(B^2\Sigma^+) + CO \qquad \Delta_r H_0^\ominus = -303.2 \text{ kJ mol}^{-1}$$

Reisler et al.[18] studied the reactivity by following the formation of products by chemiluminescence of $CN(A^2\Pi)$ and $CN(B^2\Sigma^+)$ and also performed a direct LIF measurement of the removal of $^3C_2$ obtaining the same rate coefficient: $(7.3 \pm 0.3) \times 10^{-11}$, $(7.5 \pm 0.3) \times 10^{-11}$, and $(7.3 \pm 0.9) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, respectively). Later on they found that the removal rate of $^1C_2$ by NO was three times faster than the removal rate of $^3C_2$.[18] Taking into account these observations they concluded that the $CN(A^2\Pi)$ and $CN(B^2\Sigma^+)$ were predominantly formed by reaction with the $^3C_2$ state. These results were in agreement with the crossed molecular beams study performed by Krause,[42] who measured the chemiluminescence of the $CN(B^2\Sigma^+)$ state and based on an adiabatic correlation diagram approach claimed that this state could only be produced from reaction of $^3C_2 + NO$. By contrast, Kruse et al.[28] studied the reaction in a shock tube obtaining results for a high-temperature range (3150 K $< T <$ 3950 K). The extrapolation of these results to room temperatures gave a value 6 orders of magnitude lower than that of Reisler et al.,[18] suggesting that a change in mechanism for the reaction occurs. This was confirmed by the results obtained in the O, N, and CN product formation measurements, which led to the conclusion that at these temperatures the main product channels are

$$C_2 + NO \rightarrow C_2N + O \quad 70\% \quad \Delta_r H_0^\ominus = -122.3 \text{ kJ mol}^{-1}$$

$$\rightarrow C_2O + N \quad 30\% \quad \Delta_r H_0^\ominus = -168.8 \text{ kJ mol}^{-1}$$

The CN + CO channel was found to be negligible, in contrast to the results at room temperature.

Ristanovic et al.[27] studied the reaction in the temperature range 292 K $< T <$ 968 K, and the results that they obtained at the lowest temperatures were in excellent agreement with the results of Reisler et al.[18] Linear extrapolation of their results crosses the results of Kruse et al.,[28] which, however, show a major positive activation barrier and a larger preexponential factor. By comparing their *k*(T) expressions one can draw the conclusion that there is a change in mechanism with temperature and the total rate coefficient for the $^3C_2$ + NO reaction must pass through a minimum between temperatures of 1000 and 3100 K.

From a theoretical point of view very little information is available; however, ab initio calculations have been performed very recently by Wei et al.[43] confirming that CN + CO is expected to be the major channel at low temperatures and C_2N + O the major channel at higher temperatures. No pathway was found to the C_2O + N channel which disagrees with the experimental results of Kruse et al.[28]

Conclusions

The present study demonstrates that relaxation of $^3C_2$ by intersystem crossing induced by oxygen can be measured at temperatures below 200 K and that this process remains very efficient in the temperature range 50−200 K. On the other hand, the reactivity of $^1C_2$ with oxygen becomes very inefficient below room temperature. This is therefore an ideal situation where it is possible to produce the $^1C_2$ state alone and then study its reactivity with another reagent without any interference coming from the possible relaxation of $^3C_2$ to $^1C_2$ induced by this reagent. Adding an optimized concentration of O_2 in the flow, we were then able to study the reactivity of the singlet state of C_2 with NO. The rate coefficient has been found to be essentially constant in the temperature range 36−300 K with an average value of $(1.6 \pm 0.1) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}. The rate coefficient for the $^1C_2$ + NO reaction below 36 K shows an apparent decrease which may be due either to a small activation barrier or to cascading effects. Measurements at lower temperatures would certainly be of great interest to confirm this behavior, but present attempts failed in detecting the C_2 molecule at 15 K. Reactivity of the triplet has been found to follow a different trend; a slight negative temperature dependence has been found in the temperature range 50−300 K, which is in very good agreement with data obtained at higher temperatures. Below 50 K a stronger decrease has been observed probably revealing the presence of a small energy barrier.

The present work sheds more light on these two processes for which experimental data are now available over a wide temperature range (24−4000 K for both $C_2 + O_2$ and C_2 + NO systems). This should encourage future theoretical studies to improve our knowledge of the mechanisms involved in both processes.

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