

Neutral–neutral reactions at the temperatures of interstellar clouds: Rate coefficients for reactions of atomic carbon, C(³P), with O₂, C₂H₂, C₂H₄ and C₃H₆ down to 15 K

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A CRESU (Cinétique de Réaction en Ecoulement Supersonique Uniforme) apparatus has been used to measure rate coefficients for the reactions of ground-state carbon atoms, C(³P), with C₂H₂, C₂H₄, C₃H₆ and O₂ at temperatures from 295 down to 15 K. C(³P) atoms were generated by photolysis of C₃O₂ at 193 nm using an ArF excimer laser and reaction rates were determined by observing the chemiluminescence from NO(B ²Π) which is generated in the reaction between C(³P) atoms and NO₂. The rate coefficients for all four reactions increase as the temperature is lowered, and those for reactions with the unsaturated hydrocarbons exceed $2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at all temperatures below 300 K. The results confirm that C(³P) atoms, like C₂H radicals and CN radicals, react rapidly with unsaturated hydrocarbons at very low temperatures. It therefore seems likely that these reactions—and similar ones involving C(³P) atoms and other hydrocarbons—play an important role in forming species with long carbon chains in dense interstellar clouds.

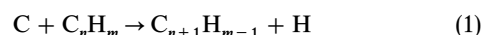
Introduction

Carbon is believed to be the fourth commonest element in the universe, with an abundance relative to hydrogen of $(2.4 \pm 0.5) \times 10^{-4}$.¹ Ground state atomic carbon, C(2p² ³P_J), has been detected in a wide range of astronomical environments, and is particularly abundant in dense interstellar clouds (ISCs).^{2–4} Dense by interstellar standards, where the average gas density is $\sim 1 \text{ cm}^{-3}$, these clouds correspond to the laboratory equivalent of an ultra high vacuum, with gas densities of the order of 10^4 cm^{-3} . They are also extremely cold, with temperatures in the range 10–50 K. However, owing to their great size, they may contain typically the equivalent of 10–100 times the mass of our Sun, and it is within these clouds that the richest variety of interstellar molecules has been observed, including many carbon-containing radicals. The largest confirmed interstellar molecule is HC₁₁N,⁵ but it is highly probable that much larger species such as polyaromatic hydrocarbons (PAHs) and fullerenes exist as well.

Astrophysical chemists have attempted to assemble reaction networks in order to simulate the synthesis of these interstellar molecules under the extreme conditions of temperature and density prevailing in dense ISCs. On the whole, attention has been focused in these simulations on ion–molecule reactions,^{6–8} as these have been shown to be very rapid down to extremely low temperatures. However, in recent years, the importance of rapid neutral reactions has been recognised, in part as a result of our own work on rate coefficients at extremely low temperatures for reactions of CN,^{9–13} OH,^{14–16} CH^{17–21} and, most recently, C₂H.²² Herbst and co-workers have been at the forefront of recognising the importance of neutral–neutral reactions in the chemistry of dense ISCs, and have found that their inclusion in cloud chemistry models has a profound effect on predicted abundances of important interstellar species.^{23–25}

Neutral–neutral reactions of atomic carbon with various hydrocarbon species have been identified by Herbst and co-workers as potentially of great importance in the *synthesis* of

larger carbon-containing species, employing successive insertion–elimination reactions of the type:²⁶



Following the kinetic measurements of Husain and co-workers on reactions of atomic carbon with a wide range of hydrocarbon species at room temperature,^{27–32} the theoretical work of Clary and co-workers³³ has pointed to the continued rapidity of such reactions down to the temperatures prevailing in dense ISCs.

A further impetus to the study of atomic carbon reactions has been the elegant and detailed dynamical studies carried out by Kaiser *et al.*, employing the crossed molecular beam scattering technique.^{34–41} Identification of the products of these reactions was possible, providing a major advantage over kinetic measurements based on monitoring the disappearance of atomic carbon. However, as they themselves recognise,³⁷ the minimum collision energy they were able to access corresponds to a translational temperature of $\sim 700 \text{ K}$, and the extrapolation of their results—showing rising cross-sections as the collision energy falls—to interstellar temperatures as low as 10–100 K depends on the absence of even small barriers. Kinetic studies down to such temperatures are therefore highly desirable.

Crossed molecular beam experiments on reactions of C(³P), employing detection of reaction products by laser-induced fluorescence, have also been performed by Reisler and co-workers.^{42–46} However, these were performed at rather high collision energies, for example *ca.* 2 eV in a recent study on endoergic reactions of C(³P) with CH₄ and C₂H₂,⁴⁶ and so these studies are not particularly relevant to interstellar temperatures and energies.

Very recently, Costes and Naulin⁴⁷ have measured cross-sections for the reaction of C(³P) with O₂ in a crossed molecular beam apparatus with rotatable sources at collision energies as low as 4.4 meV, corresponding to translational temperatures of $\sim 30 \text{ K}$, providing a useful comparison with kinetic studies at extremely low temperatures.

Despite their importance, there have been, to our know-

ledge, no studies of the kinetics of atomic carbon reactions below room temperature, let alone down to 10–100 K. Our principal motivation in this current work has been, therefore, to measure the rates of reactions of atomic carbon with a range of species, including hydrocarbons, at extremely low temperatures in order to ascertain their importance in chemical synthesis within dense ISCs. In addition, a study of the kinetics of reactions of $C(^3P)$ with species such as O_2 provides an opportunity to examine the behaviour of a fundamentally interesting class of reaction between atoms and radicals down to extremely low temperatures. Such studies should provide a challenging test bed for modern reaction rate theories.

Our studies of the kinetics of neutral–neutral reactions at extremely low temperatures are conducted in the Birmingham CRESU apparatus, one of only two such facilities world-wide which enable accurate rate coefficients for such reactions to be measured down to the temperatures prevailing in dense ISCs. CRESU is a French acronym standing for ‘*Cinétique de Réaction en Ecoulement Supersonique Uniforme*’ or ‘*Reaction Kinetics in Uniform Supersonic Flow*.’ The technique was originally developed by Rowe and co-workers for the study of ion–molecule reactions,^{48,49} and adapted for the measurement of neutral–neutral reaction rates by the use of the pulsed laser photolysis–laser induced fluorescence (PLP-LIF) technique in a fruitful collaboration between our group and that of Rowe and co-workers in Rennes, France.

The majority of the kinetic measurements on elementary reactions at ultra-low temperatures which have been reported so far have been performed in collaboration between our two groups on the CRESU apparatus at Rennes.^{10,11,13–21,50,51} Recently, however, a new CRESU apparatus has been constructed at the University of Birmingham, and used initially to study energy transfer at extremely low temperatures.^{52–54} Very recently, we have focused our efforts on the study of reactions of interstellar interest, commencing with measurements of the kinetics of the C_2H radical with O_2 , C_2H_2 , C_2H_4 and C_3H_6 down to 15 K.²² The extension of these measurements to the highly significant reactions of atomic carbon are the subject of this article.

Previous kinetic investigations of carbon atom reactions have employed a range of techniques. The experiments of Husain and co-workers^{27–33,55–57} referred to earlier employed time-resolved atomic resonance absorption spectroscopy to monitor the $C(^3P)$ concentration directly *via* the $(3s\ ^3P-2p\ ^3P)$ resonant transition at 166 nm. Carbon atoms were created in the reaction cell by VUV photolysis ($\lambda \leq 160$ nm) of carbon suboxide (C_3O_2) using a coaxial flash lamp. The authors report rapid room temperature rates for reactions with unsaturated hydrocarbons, NO and O_2 .

Becker and co-workers⁵⁸ used the PLP-LIF technique to study kinetics of the reactions of atomic carbon with NO and O_2 in a flow cell at room temperature. Ground state carbon atoms were produced by multiphoton dissociation of CH_2Br_2 using the focused output of a KrF excimer laser at 248 nm. The temporal variation of the carbon atom concentration was monitored by two-photon laser induced fluorescence at 143.5 nm ($^3P_2-^3D_3$ transition).

Dortche *et al.*⁵⁹ conducted fast flow studies of atomic carbon kinetics at room temperature. In these experiments, ground state atomic carbon was produced by the microwave dissociation of CO, and the kinetic removal of $C(^3P_j)$ by reaction with various molecules was monitored by an indirect chemiluminescent method involving addition of a constant excess of OCS to the reaction vessel. The pseudo-first-order decay of atomic carbon was determined from the decay of CS ultra-violet chemiluminescence produced by the $C + OCS$ reaction. This chemiluminescence was ascribed to the spin allowed pathway:



However, the electronically excited CS is relatively long lived ($\tau \approx 16$ ms), since relaxation occurs *via* a spin forbidden transition ($a\ ^3\Pi-X\ ^1\Sigma^+$). Therefore, in such flow experiments, for a rigorous determination of the pseudo-first-order reaction rate constants it was necessary to solve the differential continuity equation of the decaying reactive species in the flow.

Direct detection of $C(^3P)$ by VUV absorption at 166 nm is difficult to implement within the CRESU apparatus owing to limited potential path lengths, and so we have also chosen to use a chemiluminescent marker technique in the CRESU apparatus to study the reactions of atomic carbon. This will be described in the next section.

Experimental technique

The CRESU method, as applied to neutral–neutral reactions, has already been described in detail by Sims *et al.*¹³ Full specifications of the Birmingham CRESU apparatus have also been given recently by James *et al.*⁵² Here, after a brief explanation of the CRESU method, we will emphasise those features of our experiments specific to kinetic experiments on the reactions of atomic carbon.

The heart of the CRESU apparatus is an axisymmetric Laval nozzle. It is mounted on a reservoir equipped with a perforated Teflon disc to ensure laminar flow and good mixing of the gas streams entering the reservoir. Although the gas reservoir is jacketed, permitting cryogenic cooling,^{52,54} this facility was not used in the present experiments. All the temperatures 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 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 . All of the nozzles were characterised by impact-pressure measurements.¹³ In addition, the temperatures provided by some nozzles were confirmed by recording the spectra of bands in the $A\ ^2\Sigma^+-X\ ^2\Pi$ system of NO and matching these with simulated spectra.⁵² The temperature determined from the relative intensities of the rotational lines agreed with the values inferred from the impact-pressure measurements. Room temperature measurements were performed as before, in a subsonic flow obtained by drastically reducing the pumping speed and monitoring the chamber pressure (and hence total gas density) using a capacitance manometer.

$C(^3P)$ atoms were created by the pulsed laser photolysis of carbon suboxide, C_3O_2 , using the 193 nm radiation from one of two similar excimer lasers (Lambda-Physik, Compex 102 or Compex 202), equipped with unstable resonator optics to give the required low-divergence beam, and operating on ArF at a repetition frequency of 10 Hz. The beam from this laser entered the CRESU apparatus through a Brewster angle window, passed through another such window mounted on the back of the reservoir, and then propagated through the throat of the Laval nozzle and along the axis of the flow, before leaving the vacuum chamber *via* a third Brewster angle window. The laser power output was typically ~ 150 mJ per pulse, but after reduction in beam size and reflection from steering optics, it was estimated that only about 5–10 mJ reached the observation zone. Fig. 1 shows a schematic diagram of the CRESU apparatus, as used for the study of the kinetics of $C(^3P)$ reactions.

C_3O_2 was synthesised *via* the dehydration of bis(trimethylsilyl) malonate (Aldrich),⁶⁰ and stored in a collection vessel. When required, the collection vessel was surrounded by an acetone–dry ice slush. The C_3O_2 has a vapour

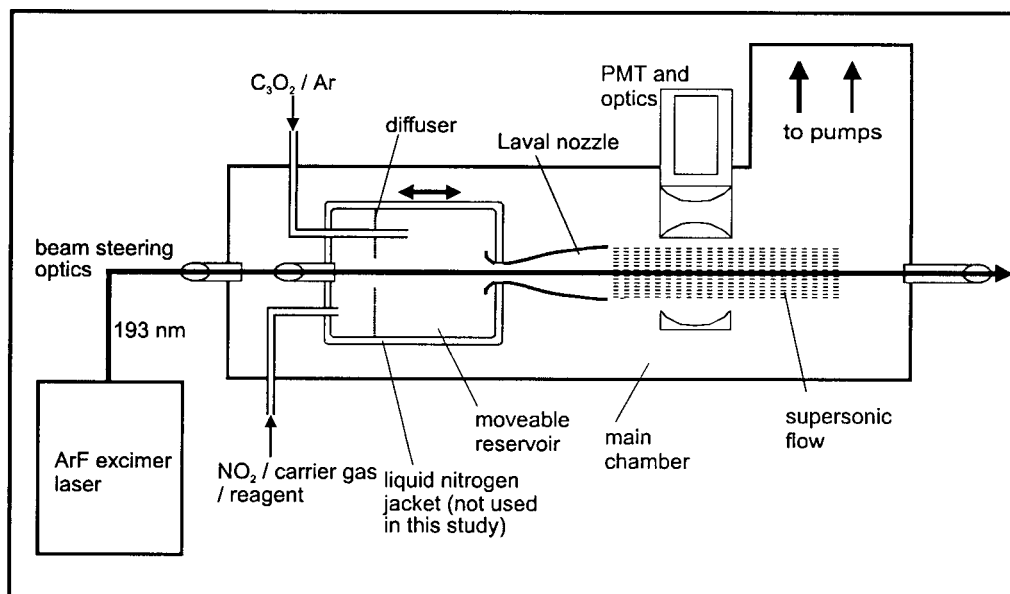
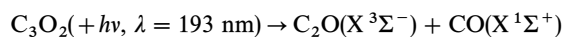


Fig. 1 Schematic diagram of the CRESU apparatus at the University of Birmingham, adapted for the study of $C(^3P)$ kinetics by the PLP-CL method.

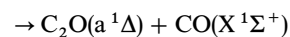
pressure of approximately 20 Torr at this temperature (-60°C). A cylinder of high purity argon (Air Products) provided a regulated flow ($\sim 10\text{--}100$ standard $\text{cm}^3 \text{min}^{-1}$) of buffer gas, which bubbled through the liquid C_3O_2 and was saturated with C_3O_2 vapour. The absolute concentration of

C_3O_2 within the CRESU flow was estimated to be *ca.* 10^{12} molecules cm^{-3} .

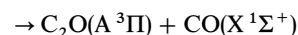
Carbon suboxide can be photodissociated into five thermodynamically open channels at a photolysis energy of 620 kJ mol^{-1} ($\equiv 193 \text{ nm}$):⁶¹



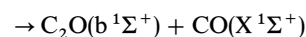
$$\Delta H^0 \approx 359 \text{ kJ mol}^{-1} \quad (3.1)$$



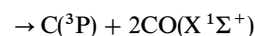
$$\Delta H^0 \approx 443 \text{ kJ mol}^{-1} \quad (3.2)$$



$$\Delta H^0 \approx 497 \text{ kJ mol}^{-1} \quad (3.3)$$



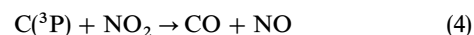
$$\Delta H^0 \approx 510 \text{ kJ mol}^{-1} \quad (3.4)$$



$$\Delta H^0 \approx 577 \text{ kJ mol}^{-1} \quad (3.5)$$

The channel represented by reaction (3.5), used in our experiments to generate $C(^3P)$ atoms, has been found to have a relative yield of not more than 6%.⁶²

The progress of reaction was monitored by a chemiluminescent marker technique, resembling that used in our study of the kinetics of C_2H radical reactions in the CRESU apparatus.²² In each series of experiments, a constant concentration of NO_2 was added to the CRESU flow, along with the C_3O_2 precursor, and appropriate reagent and buffer gases. $C(^3P)$ atoms produced in the photolysis then reacted at a constant rate with the NO_2 , which was in large excess over the C_3O_2 :



Dorthe *et al.*⁶³ observed chemiluminescence resulting from both $NO(B^2\Pi)$ and $NO(A^2\Sigma^+)$ products from this reaction. The chemiluminescence was gathered in the CRESU apparatus by an optically fast collection arrangement,¹³ and the (0, 8) β -band $NO(B^2\Pi-X^2\Pi)$ emission isolated using an interference filter centred at 320 nm (10 nm FWHM), before being imaged on to the photocathode of a sensitive photomultiplier tube (Electron Tubes, type 9125 MgFIB). The radiative lifetime of $NO(B^2\Pi; v' = 0)$ is short (2.0 μs)⁶⁴ relative to the lifetime of the kinetic decays, and so its concentration rapidly reached a steady state value which was directly proportional

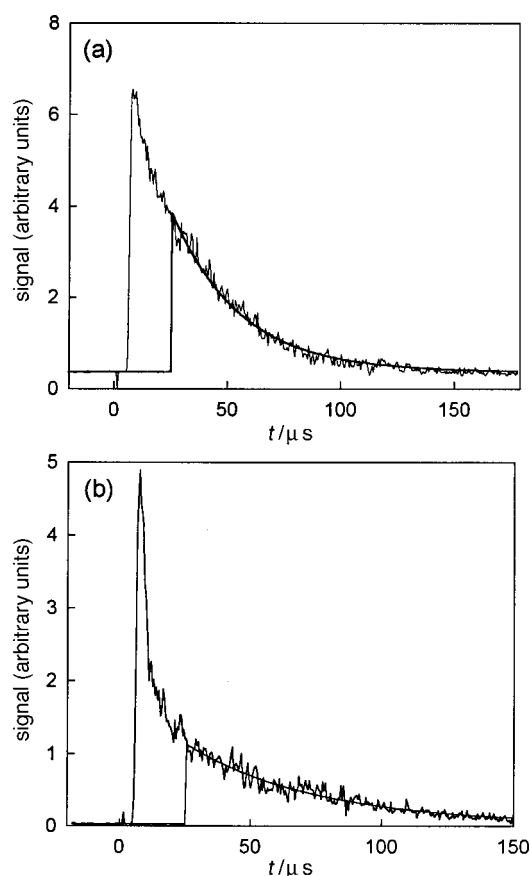


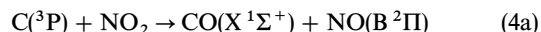
Fig. 2 Traces of chemiluminescence intensity *vs.* time with background subtraction. As scattered light was not removed in all cases by this subtraction, a short delay was introduced before fitting to a single exponential decay (smooth curves). Experimental conditions: (a) $T = 27 \text{ K}$, $[He] = 4.65 \times 10^{16} \text{ molecule cm}^{-3}$, $[NO_2] = 6.79 \times 10^{13} \text{ molecule cm}^{-3}$, $[C_2H_2] = 5.60 \times 10^{13} \text{ molecule cm}^{-3}$; (b) $T = 15 \text{ K}$, $[He] = 5.05 \times 10^{16} \text{ molecule cm}^{-3}$, $[NO_2] = 1.38 \times 10^{14} \text{ molecule cm}^{-3}$, $[O_2] = 7.63 \times 10^{13} \text{ molecule cm}^{-3}$.

both to the intensity of the emission and to the concentration of the carbon atoms (see below for a full discussion). The resulting signal was transferred *via* an appropriate load resistor to a 200 MHz digital oscilloscope (Tektronix, model TDS350), which averaged emission traces from 128 laser shots before the resultant data were transferred to a PC. Typically, this procedure was repeated four times, so that the traces that were analysed were the result of 512 individual experiments. In addition, under some conditions it was necessary to perform a background subtraction to allow for the effects of scattered light. The background trace was recorded by omitting NO₂ from the gas mixture, leaving all other conditions the same. Fig. 2 shows two typical chemiluminescent decay traces.

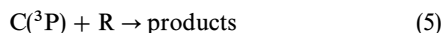
The flows of NO₂ (SIP Gases), the co-reagent (O₂, C₂H₂, C₂H₄ or C₃H₆; Air Products), and the carrier gas (He, Ar or N₂; Air Products) were taken directly from the cylinders and regulated by means of mass flow controllers (MKS). The C₂H₂ was passed through a trap immersed in cooled methanol at -40 °C to remove any residual acetone resulting from the storage method. Knowledge of the total gas density from Pitot-tube measurements and of the individual gas flows enabled the concentrations of the minor gases in the supersonic flows, which are needed to determine the rate coefficients, to be calculated. In all cases, fractional photodissociation of reagent gases was estimated to be less than ~0.5% at the laser fluences employed.

Results

Experiments to determine the kinetic behaviour of carbon atom reactions with a reagent R (R=O₂, C₂H₂, C₂H₄ or C₃H₆) were performed both at room temperature in a subsonic flow, and at low temperatures ranging from 15 to 204 K in He, Ar or N₂ buffer gases, using a number of Laval nozzles. The flows contained a small concentration of C₃O₂ (estimated to be *ca.* 10¹² molecule cm⁻³), a constant concentration of NO₂ (~10¹⁴ molecule cm⁻³), and a variable concentration of reagent, R (ranging up to ~10¹⁴ molecule cm⁻³), in a buffer gas of density in the approximate range 10¹⁶–10¹⁷ molecule cm⁻³. A small fraction of the C₃O₂ was photodissociated by the 193 nm photolysis laser pulse, yielding C(³P) as a minor product. The C(³P) atoms then reacted both with the NO₂, yielding NO(B²Π) as one product:



and with the reagent, R:



We observed the intensity of the (0,8) band of the NO (B²Π–X²Π) chemiluminescence as a function of time. Fig. 2 shows two typical traces. The kinetics of this emission in experiments of this kind have been discussed by Van Look and Peeters.⁶⁵ In brief, the intensity is proportional to the instantaneous concentration of NO(B²Π), which rapidly reaches a value determined by the steady-state equation:

$$k_{4a}[\text{C}(\text{}^3\text{P})][\text{NO}_2] = k_{\text{rad}}[\text{NO}(\text{}^2\Pi)] \quad (\text{I})$$

because the mean radiative lifetime of NO(B²Π, *v*'=0), that is 1/*k*_{rad}, is only 2.0 μs.⁶⁴ When the concentrations of NO₂ and R are much greater than the concentration of C(³P), the latter can be written as

$$[\text{C}(\text{}^3\text{P})]_t = [\text{C}(\text{}^3\text{P})]_0 \exp(-k_{1st}t) \quad (\text{II})$$

where *k*_{1st} = *k*₄[NO₂] + *k*₅[R]. The variation of the chemiluminescent intensity, *I*_{CL}(*t*), may then be expressed as:

$$I_{\text{CL}}(t) \propto [\text{NO}(\text{}^2\Pi)]_t = (k_{4a}[\text{NO}_2]/k_{\text{rad}})[\text{C}(\text{}^3\text{P})]_0 \exp(-k_{1st}t) \quad (\text{III})$$

*I*_{CL}(*t*) decays exponentially with a pseudo-first-order rate coefficient which depends on the concentrations of NO₂ and R. The traces of chemiluminescent intensity shown in Fig. 2, like all others which we have recorded, exhibit this predicted behaviour. They were fitted, using a non-linear least squares algorithm, to yield values of *k*_{1st} for each gas mixture on which experiments were carried out at a particular temperature.

Values of the second-order rate coefficients *k*_R were established by series of experiments in which [R] was varied whilst [NO₂] was kept constant. The results of two such experiments are displayed in Fig. 3, where *k*_{1st} is plotted against [R] for R=C₂H₄ and C₂H₂ with [NO₂] constant at temperatures of 54 and 15 K. The gradients of these lines yield the values of *k*_R. The intercepts on these plots correspond principally to loss of C(³P) *via* the reaction with NO₂ [used to monitor the C(³P) concentration], combined with a much smaller contribution from diffusive loss. Both of these effects remain constant across the range of reagent concentrations employed.

Complete results for R=C₂H₂, C₂H₄, C₃H₆ and O₂ are summarised in Tables 1–4, and the temperature-dependence of the rate coefficients for these reactions of C(³P) are displayed in Fig. 4–7.

Our use of chemiluminescence from NO to monitor changes in the concentration of C(³P) atoms indirectly requires us to verify that the signal we see is indeed due only to reaction of ground state, thermalised C(³P) atoms. There are two possible complications: first, that the signal may arise from some reaction of another photodissociation product of C₃O₂, in particular the radical C₂O, with NO₂; and second, that the C(³P) atoms are produced with a non-equilibrium distribution over spin-orbit states, which may not relax rapidly on the time scale of the experiment.

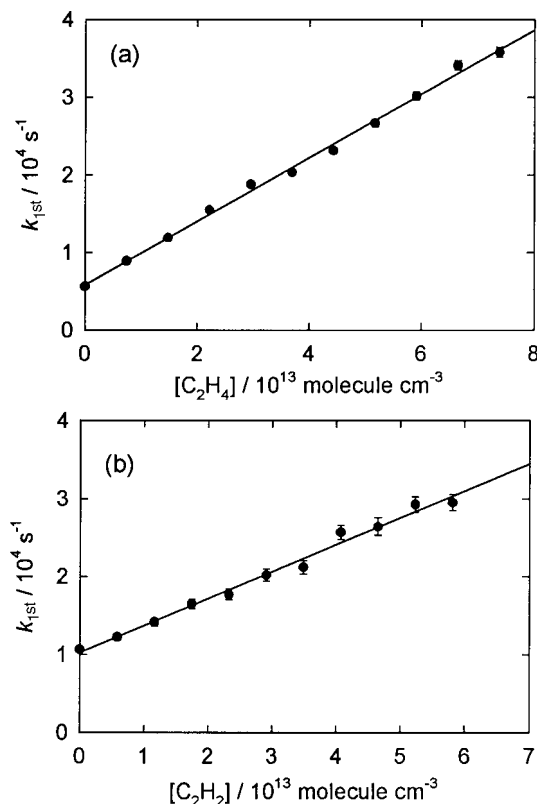


Fig. 3 Plots of pseudo-first-order decay constants, *k*_{1st}, *vs.* reagent concentration [R], at (a) *T* = 54 K, [Ar] = 5.37 × 10¹⁶ molecule cm⁻³ and [NO₂] = 9.13 × 10¹³ molecule cm⁻³, R = C₂H₄; (b) *T* = 15 K, [He] = 5.05 × 10¹⁶ molecule cm⁻³ and [NO₂] = 1.03 × 10¹⁴ molecule cm⁻³, R = C₂H₂. In each case the gradient of the line yields the second order rate constant, *k*, for the reaction of C with R.

Table 1 Rate coefficients, k , for the reaction between $C(^3P)$ atoms and C_2H_2 measured over the temperature range 15–295 K

T/K	M	$[M]/10^{16}$ molecule cm^{-3}	$[NO_2]/10^{13}$ molecule cm^{-3}	$[C_2H_2]/10^{13}$ molecule cm^{-3}	No. of points	$k/10^{-10} cm^3$ molecule $^{-1} s^{-1}$
15	He	5.05	10.33	0–5.81	11	3.46 ± 0.23^a
27	He	4.72	6.90	0–5.60	10	3.69 ± 0.22
54	Ar	5.37	9.13	0–7.70	12	3.59 ± 0.12
63	He	2.08	9.28	0–1.92	10	3.22 ± 0.37
83	N ₂	4.88	6.33	0–2.67	11	3.31 ± 0.16
112	Ar	2.78	4.55	0–3.83	11	3.07 ± 0.13
207	N ₂	5.83	8.22	0–4.86	8	3.05 ± 0.08
295	Ar	21.71	62.86	0–21.2	9	2.82 ± 0.08

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

The photodissociation of C_3O_2 at 193 nm produces not only $C(^3P)$ atoms and CO molecules, but also C_2O radicals, as indicated by reactions (3.1)–(3.5). We must consider the possibility that the observed chemiluminescence signal arises from reaction of C_2O in one of the various electronic states in which it is formed. Rosenfeld and co-workers have studied the photolysis of C_3O_2 at 193 nm and 248 nm, detecting the $CO(X^1\Sigma^+)$ product in a state-specific fashion.^{61,66} At 193 nm, they postulated a rapid internal conversion of the photo-excited C_3O_2 to the ground state surface, followed by dissociation from a bent geometry on a barrier-free surface to give $C_2O(a^1\Delta)$ and $CO(X^1\Sigma^+)$ as the primary photo-products.

Owing to the correlation of $C_2O(a^1\Delta)$ and $CO(X^1\Sigma^+)$ to stable C_3O_2 , we believe that the addition of CO will rapidly

quench any $C_2O(a^1\Delta)$ formed, with a rate coefficient of at least $10^{-11} cm^3 molecule^{-1} s^{-1}$, by analogy with the quenching of $O(^1D)$ by $N_2(X^1\Sigma_g^+)$.⁶⁷ Becker *et al.*⁶⁸ comment on the unique ability of CO to quench singlet excited C_2O via the formation of a transient C_3O_2 molecule, and observed a large increase in ground state $C_2O(X^3\Sigma^-)$, as detected by LIF after photolysis, when they added CO to their C_3O_2 /buffer gas system. They also found the quenching rate coefficient for $C_2O(A^3\Pi)$ by CO to be $2.8 \times 10^{-11} cm^3 molecule^{-1} s^{-1}$,⁶⁸ presumably again because of the possibility of quenching via the formation of a transient C_3O_2 molecule.

We therefore performed rate coefficient measurements for reaction with O_2 both with and without CO, both at room temperature and at low temperature. In all cases, the rate

Table 2 Rate coefficients, k , for the reaction between $C(^3P)$ atoms and C_2H_4 measured over the temperature range 15–295 K

T/K	M	$[M]/10^{16}$ molecule cm^{-3}	$[NO_2]/10^{13}$ molecule cm^{-3}	$[C_2H_4]/10^{13}$ molecule cm^{-3}	No. of points	$k/10^{-10} cm^3$ molecule $^{-1} s^{-1}$
15	He	5.05	22.04	0–4.46	9	3.40 ± 0.41^a
27	He	4.72	6.82	0–5.44	11	3.83 ± 0.15
54	Ar	5.37	9.13	0–7.39	10	4.10 ± 0.15
63	He	2.08	4.58	0–1.67	10	3.50 ± 0.35
83	N ₂	4.88	6.33	0–5.13	11	3.16 ± 0.08
112	Ar	2.78	9.09	0–3.69	11	3.24 ± 0.14
207	N ₂	5.83	8.22	0–4.66	8	3.22 ± 0.07
295	Ar	21.86	62.86	0–20.29	9	2.8 ± 0.08

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

Table 3 Rate coefficients, k , for the reaction between $C(^3P)$ atoms and C_3H_6 measured over the temperature range 15–295 K

T/K	M	$[M]/10^{16}$ molecule cm^{-3}	$[NO_2]/10^{13}$ molecule cm^{-3}	$[C_3H_6]/10^{13}$ molecule cm^{-3}	No. of points	$k/10^{-10} cm^3$ molecule $^{-1} s^{-1}$
15	He	5.05	22.05	0–1.37	9	2.88 ± 0.60^a
27	He	4.72	6.69	0–3.03	9	4.82 ± 0.27
54	Ar	5.37	17.91	0–3.62	11	2.59 ± 0.07
112	Ar	2.78	4.51	0–2.05	9	3.18 ± 0.14
295	Ar	19.5	56.4	0–16.5	11	2.69 ± 0.05

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

Table 4 Rate coefficients, k , for the reaction between $C(^3P)$ atoms and O_2 measured over the temperature range 15–295 K

T/K	M	$[M]/10^{16}$ molecule cm^{-3}	$[NO_2]/10^{13}$ molecule cm^{-3}	$[O_2]/10^{13}$ molecule cm^{-3}	No. of points	$k/10^{-11} cm^3$ molecule $^{-1} s^{-1}$
15	He	5.05	13.79	0–9.54	11	11.87 ± 0.16^a
27	He	4.72	6.72	0–9.28	10	12.31 ± 0.37
54	Ar	5.37	9.12	0–12.6	12	9.10 ± 0.39
63	He	2.08	4.58	0–3.11	11	6.79 ± 0.23
83	N ₂	4.88	6.33	0–8.74	11	7.25 ± 0.25
112	Ar	2.78	9.11	0–6.28	11	5.96 ± 0.42
207	N ₂	5.83	8.21	0–11.35	10	5.85 ± 0.21
295	Ar	21.57	5.91	0–85.5	10	4.37 ± 0.15

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

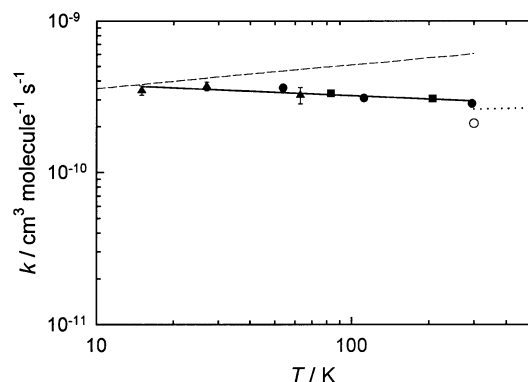


Fig. 4 Rate coefficients k for the reaction of $C(^3P)$ atoms with C_2H_2 plotted on a log-log scale against temperature. The filled symbols show the results of this work: circles (●) denoting Ar carrier gas; squares (■) N_2 ; and triangles (▲) He. The room temperature result of Haider and Husain²⁸ is shown as an open circle (○). The solid line shows the result of a non-linear least-squares fit to the data giving $k = 2.9 \times 10^{-10} (T/298 \text{ K})^{-0.08} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The dashed line (---) shows the results of a capture calculation performed by Liao and Herbst,⁷⁵ while the dotted line (·····) represents the VRRKM calculation of Guadagnini *et al.*⁷⁴

coefficients determined were unchanged within the estimated experimental error limits. For example, at room temperature, the addition of $4 \times 10^{15} \text{ molecule cm}^{-3}$ of CO resulted in a change of less than 5% in the measured rate coefficient for the

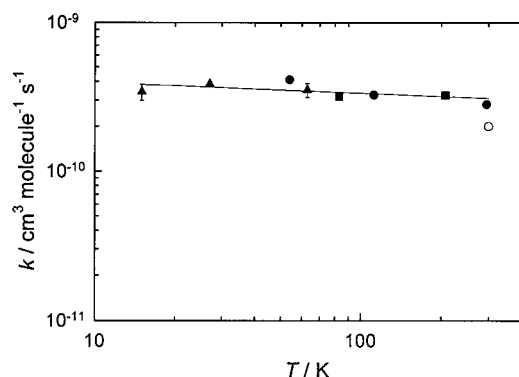


Fig. 5 Rate coefficients k for the reaction of $C(^3P)$ atoms with C_2H_4 plotted on a log-log scale against temperature. The filled symbols show the results of this work: circles (●) denoting Ar carrier gas; squares (■) N_2 ; and triangles (▲) He. The room temperature result of Haider and Husain²⁸ is shown as an open circle (○). The solid line shows the result of a non-linear least-squares fit to the data giving $k = 3.1 \times 10^{-10} (T/298 \text{ K})^{-0.07} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

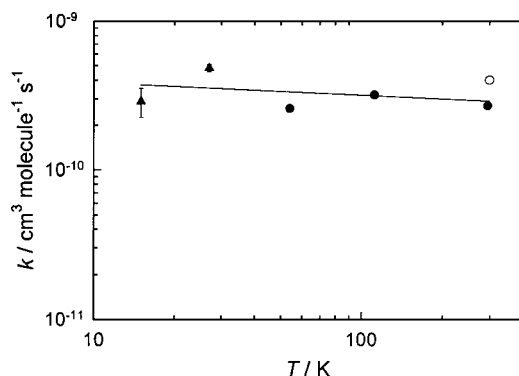


Fig. 6 Rate coefficients k for the reaction of $C(^3P)$ atoms with C_3H_6 plotted on a log-log scale against temperature. The filled symbols show the results of this work: circles (●) denoting Ar carrier gas; and triangles (▲) He. The room temperature result of Haider and Husain²⁹ is shown as an open circle (○). The solid line shows the result of a non-linear least-squares fit to the data giving $k = 2.9 \times 10^{-10} (T/298 \text{ K})^{-0.08} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

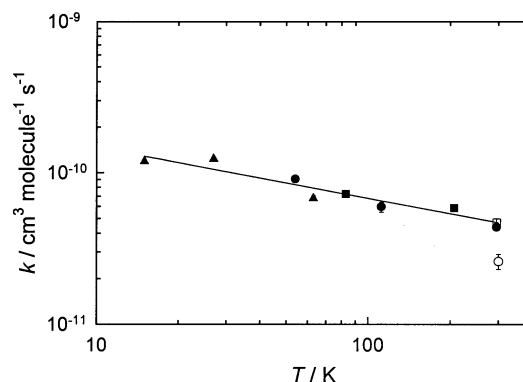


Fig. 7 Rate coefficients k for the reaction of $C(^3P)$ atoms with O_2 plotted on a log-log scale against temperature. The filled symbols show the results of this work: circles (●) denoting Ar carrier gas; squares (■) N_2 ; and triangles (▲) He. The room temperature results of Husain and Young⁵⁵ and Becker *et al.*⁵⁸ are shown as an open circle (○) and an open square (□) respectively. The solid line shows the result of a non-linear least-squares fit to the data giving $k = 4.7 \times 10^{-11} (T/298 \text{ K})^{-0.34} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

$C + O_2$ reaction. Under these conditions, CL (chemiluminescence) decays were observed over periods of the order of 100 μs , while quenching of $C_2O(a^1\Delta)$ by the added CO would be expected to take place with a decay time of $\approx 25 \mu\text{s}$ (assuming a conservative estimate of $1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the quenching rate coefficient). We therefore conclude that reaction of $C_2O(a^1\Delta)$ with NO_2 is not responsible for the observed CL signal. Furthermore, given the high efficiency of CO in quenching excited states of C_2O , we can also rule out the participation of other electronically excited states of C_2O .

It is possible, however, that any electronically excited C_2O would be quenched to ground state $C_2O(X^3\Sigma^-)$ on the time scale of the experiment, even in the absence of added CO: indeed, Pitts *et al.*⁶⁹ found a quenching rate for $C_2O(A^3\Pi)$ by Ar of $1.95 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, which would yield a decay time of $\sim 10 \mu\text{s}$ at a typical Ar density of $5 \times 10^{16} \text{ molecule cm}^{-3}$. We must therefore consider the possibility that our signal arises from the reaction of ground state $C_2O(X^3\Sigma^-)$ with NO_2 . Fortunately, the observed decays of signal upon addition of C_2H_2 and C_2H_4 corresponded at room temperature to rate coefficients of $\sim 3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ in each case, with CL signals dropping rapidly and exponentially back to the baseline. If the reaction of $C_2O(X^3\Sigma^-)$ with NO_2 had been responsible for all or part of the signal, this would not have been the case, as Donnelly *et al.*, in their PLP-LIF study of reaction rates of $C_2O(X^3\Sigma^-)$, observed no reaction with either C_2H_2 or C_2H_4 , within their measurement limits (*i.e.*, $k < 1 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$).⁷⁰ We can, therefore, safely conclude that our signal does not arise from $C_2O(X^3\Sigma^-)$, leaving the known reaction (4a) of $C(^3P)$ with NO_2 to give CO and $NO(B^2\Pi)$ as the source of our signal, as discussed above.

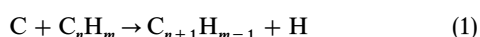
The use of chemiluminescence detection precluded direct observation of the relaxation of any excited spin-orbit population of $C(^3P)$ formed in the photolysis. However, the spin-orbit splittings in $C(^3P)$ are rather small, the 3P_1 and 3P_2 states lying 16.4 and 43.4 cm^{-1} respectively above the ground state 3P_0 . Lavendy *et al.*⁷¹ have computed rate coefficients for excitation of $C(^3P_J)$ states by He for astrochemical purposes. They quote an excitation rate coefficient at $T = 20 \text{ K}$ for $J = 0 \rightarrow 2$ of $7.67 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, giving a corresponding relaxation rate coefficient for $J = 2 \rightarrow 0$ of $3.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Under typical conditions within the CRESU flow ($[He] \approx 5 \times 10^{16} \text{ molecule cm}^{-3}$), this would indicate a lifetime of only $\sim 0.6 \mu\text{s}$. In experimental studies, Ar has been shown to be less efficient than He at quenching spin-orbit excitation, but only by a factor of 2–4,^{72,73} while N_2 is more

efficient. Thus we conclude that, on the time scale of our measurements, any non-equilibrium distribution over spin-orbit states in $C(^3P_J)$ would be fully thermalised.

Discussion

Rate coefficients for the reactions of ground state carbon atoms with C_2H_2 , C_2H_4 , C_3H_6 and O_2 have been measured several times before at room temperature by a variety of methods. Table 5 compares these previously measured values with the rate coefficients that have been determined in the present work at room temperature, using the pulsed laser photolysis (PLP)-chemiluminescence (CL) technique. For $R=O_2$, C_2H_2 and C_2H_4 , our results are somewhat higher than those of Husain and co-workers, while our result for $R=C_3H_6$ is lower. While we have no explanation for these discrepancies, we note that the results are within $\sim 30\%$ of each other, and furthermore that the only other laser-based study by Becker *et al.*⁵⁸ gave a result for the rate coefficient for $C + O_2 \rightarrow CO + O$ at room temperature which is in much better agreement with our own. The result of Dorthé *et al.*⁵⁹ for the same reaction is much lower than any of the other studies, including this one. However, they used a flow-tube method, combined with detection of $C(^3P)$ by observing long-lived CS ($a^3\pi_r \rightarrow X^1\Sigma^+$) chemiluminescence from the fast $C + OCS$ reaction. Possible complications resulting from this method include wall reactions, and the use of a long-lived species to monitor time-resolved behaviour.

The magnitudes of the rate coefficients for the reactions of carbon atoms with C_2H_2 , C_2H_4 and C_3H_6 , and their very slight increase as the temperature is lowered, are consistent with the initial formation of an energised complex in which the radical attacks a π -orbital in the unsaturated hydrocarbon with a rate which is determined by capture on a potential energy surface (or potential energy surfaces) with no barrier. This mechanism is supported by the crossed molecular beam experiments of Kaiser *et al.*^{35,37–39,41} who report the explicit identification (under single collision conditions) of the reaction products corresponding to carbon atom insertion followed by rapid hydrogen elimination, *i.e.* C_3H (from C_2H_2), C_3H_3 (from C_2H_4) and C_4H_5 (from C_3H_6). The overall reactions may be represented as:



As our experiments are not capable of determining reaction products, we refer interested readers to the articles of Kaiser *et al.*^{35,37–39,41} for a full discussion of product channels and exothermicities. It is worth noting, however, that the lifetime with respect to dissociation to products of any intermediate complexes formed (such as C_3H_2 from $C + C_2H_2$) will be very short compared to the time between collisions under the experimental conditions reported here.

Atomic carbon has, as noted above, three closely spaced spin-orbit states. $C(^3P_1)$ lies 16.4 cm^{-1} ($\equiv 23 \text{ K}$) above the

ground state 3P_0 , and the upper spin orbit state, 3P_2 , lies 43.4 cm^{-1} ($\equiv 62 \text{ K}$) above ground. At room temperature, all of these states will have an appreciable population. However, at the lowest temperatures of the present experiments, only the lowest 3P_0 state will be appreciably populated. Thus, the electronic partition function q_{elec} has a value 7.84 and 1.73 at $T = 298$ and 15 K respectively [*i.e.* $1 + 3 \exp(-23 \text{ K}/T) + 5 \exp(-62 \text{ K}/T)$]. The rate data for the reactions of carbon atoms with alkenes and alkynes can be analysed using conventional transition state theory, but allowing for the fact that reaction may occur over more than one potential energy surface. As the temperature is lowered, the electronic partition function of atomic carbon will decrease, which would lead to an overall increase in the thermal rate coefficient unless the change in the electronic partition function of the reagents is matched by a similar decrease in that of the transition state.

A strong negative temperature dependence for such reactions would suggest that collisions between reactant and carbon atoms in the lowest spin-orbit state are more likely to lead to reaction than collisions between reactant and carbon atoms in the higher spin-orbit states. However, these reactions show only a very slight temperature dependence, which suggests that the electronic partition function for the transition state species, Q_{elec}^\ddagger , also decreases as the temperature is lowered, or equivalently that reaction can occur with similar probabilities from all spin-orbit states. Furthermore, the magnitude of the rate coefficients suggests that reaction occurs essentially on every collision.

The reaction of $C(^3P)$ with C_2H_2 has been the subject of two recent theoretical studies, employing differing but complementary techniques. Guadagnini *et al.*⁷⁴ performed high-level *ab initio* calculations along the minimum-energy reaction path, and then calculated rate coefficients in the range $T = 300\text{--}1000 \text{ K}$ using the variational RRKM (VRRKM) method. They obtained a value for the rate coefficient at room temperature of ($k = 2.6 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$), in very good agreement with the result from this present study. Furthermore, they found essentially no temperature dependence up to 1000 K .

Liao and Herbst⁷⁵ performed capture calculations using the ACCSA approach of Clary and co-workers^{76–81} and obtained rate coefficients which, while they are too large at higher temperatures, do converge with experiment at the lowest end of the temperature range. Capture theories based on long-range potentials would be expected to work best at the lowest temperatures, and this is also in accord with findings for CN reactions. The products of this reaction are almost certainly $C_3H + H$. Both cyclic and linear forms of C_3H are seen in the cold, dark cloud TMC-1,^{82–85} and this reaction may be responsible for their abundance. Clearly, direct measurements of product branching ratios at ultra-low temperatures are required.

The finding that carbon atoms react rapidly with simple unsaturated hydrocarbons lends strong support to the proposal that such reactions could play an important role in the

Table 5 Comparison of rate coefficients for the reactions of $C(^3P_J)$ with C_2H_2 , C_2H_4 , C_3H_6 and O_2 at $T \approx 300 \text{ K}$ from the present work with those from previous measurements

$k_{\approx 300 \text{ K}} [C(^3P) + R \rightarrow \text{products}]/10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$					
$R=O_2$	$R=C_2H_2$	$R=C_2H_4$	$R=C_3H_6$	Method ^a	Ref.
0.33	—	—	—	FP-VUVA	93
0.33	—	—	—	FP-VUVA	55
—	—	2.0	4.0	FP-VUVA	29
—	2.1	2.0	—	FP-VUVA	28
0.47	—	—	—	PLP-LIF	58
0.16	—	—	—	FT-CL	59
0.437	2.82	2.80	2.69	PLP-CL	This work

^a FP, flash photolysis; PLP, pulsed laser photolysis; FT, flow tube; VUVA, vacuum ultraviolet absorption; CL, chemiluminescence; LIF, laser induced fluorescence.

chemistry of cold interstellar clouds. The ability of free radicals to add to unsaturated hydrocarbons has been discussed in the past^{22,86} in terms of a high electron affinity of the radical and low ionisation energy of the molecule facilitating reaction. As longer chain alkynes have lower ionisation energies than C_2H_2 ,⁸⁷ it seems reasonable to suppose that their reactions with carbon atoms will also be rapid at ultra-low temperatures. Experimental confirmation of this suggestion is one future aim of work in the CRESU laboratory.

The synthesis of carbon-rich hydrocarbon radicals in the interstellar medium *via* reactions of type (1) appears to represent a more realistic route than the previously postulated ion-molecule reaction networks. The much higher concentrations of neutral species compared to ions⁸⁸ would more than compensate for the somewhat greater rate coefficients of ion-molecule reactions at the temperatures of dense ISCs.

The rate coefficients for the reaction of ground state atomic carbon with the diradical O_2 ($X^3\Sigma_g^-$) are lower than those for the reactions of $C(^3P)$ with the unsaturated hydrocarbons and display a stronger, though still slight, negative temperature dependence ($T^{-0.34}$). This behaviour is characteristic of radical-radical reactions occurring on attractive potential surfaces.^{13,17,22,89,90} The results can be analysed with regard to the spin and orbital correlation rules, which connect the reactants to products *via* adiabatic potential surfaces. Fig. 8 shows the correlation diagram for $C(^3P_j) + O_2(X^3\Sigma_g^-)$. In the reaction $C(^3P_j) + O_2(X^3\Sigma_g^-)$, both reagents have a spin $S = 1$ (hence triplet states). The overall spin can take values from $|S_1 + S_2|$ to $|S_1 - S_2|$, and so collisions may occur on singlet, triplet or quintet surfaces. The symmetry of these surfaces is determined from orbital correlation tables.⁹¹ Within the adiabatic approximation, crossing does not occur between potential surfaces and only collisions occurring on an adiabatic potential surface leading to a thermodynamically accessible product will contribute to the thermal rate coefficient.

It can be seen from the correlation diagram that some collisions may occur over surfaces that do not lead to thermodynamically accessible products. The negative temperature dependence of the reaction of carbon atoms with O_2 may be because, as the temperature is lowered, more collisions occur on surfaces that *do* lead to products. The 3P_1 and 3P_2 spin-orbit states of $C(^3P)$ lie at energies equivalent to 23 K and 62 K respectively above the ground state 3P_0 . As shown above, the populations in the individual spin-orbit states changes markedly through the range of temperature covered in the present experiments. Therefore, if reaction is more prob-

able from lower spin-orbit states this alone could lead to a negative temperature-dependence, independent of the dynamics of the reactive collisions.^{89,90}

The only published calculation of rate coefficients for the reaction between $C(^3P)$ atoms and O_2 , to our knowledge, is the 1977 study of Kinnersly and Murrell.⁹² They derived an analytical form for the relevant potential surfaces, and performed classical trajectory calculations to obtain the rate coefficient over the temperature range 300–800 K. They obtained a result in reasonable agreement with experiment at room temperature ($k = 1.92 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$), but predicted a mild positive temperature dependence, in disagreement with our results extrapolated to higher temperatures. Clearly, it would be interesting to compare our results with calculations performed on *ab initio* potential surfaces calculated using the latest methods.

Summary and conclusions

We have measured rate coefficients for the reactions of ground-state carbon atoms, $C(^3P)$, with C_2H_2 , C_2H_4 , C_3H_6 and O_2 at temperatures from 295 down to 15 K in a CRESU apparatus, using a combination of pulsed laser photolysis to generate, and a chemiluminescence marker technique to follow the concentration of, $C(^3P)$ atoms. The rate coefficients for all four reactions increase as the temperature is lowered, and those for reactions with the unsaturated hydrocarbons exceed $2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at all temperatures below 300 K. These reactions would appear to proceed *via* an addition-elimination mechanism, resulting in an increase in carbon chain length, and must take place on potential surfaces without significant barriers to initial complex formation. It therefore seems likely that these reactions—and similar ones involving $C(^3P)$ atoms and other hydrocarbons—play an important role in forming species with long carbon chains in dense interstellar clouds.

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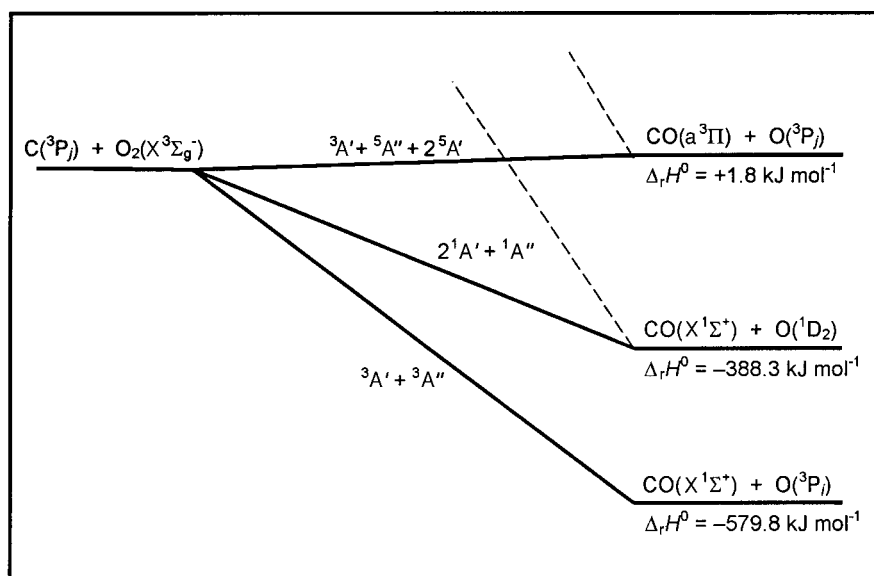


Fig. 8 Orbital correlation diagram for $C(^3P_j) + O_2(X^3\Sigma_g^-)$.

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