

Comparison of the cross-sections and thermal rate constants for the reactions of C(³P_J) atoms with O₂ and NO

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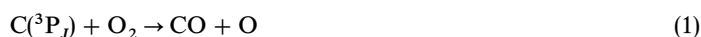
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We report the results of two sets of experiments on each of the reactions



and



In low temperature (15–295 K) kinetic experiments performed in a CRESU (Cinétique de Réaction en Ecoulement Supersonique Uniforme) apparatus, the rate constants for these two reactions were found to fit the following expressions:

$$k_1 = (4.9 \pm 0.8) \times 10^{-11} (T/298 \text{ K})^{-(0.32 \pm 0.08)} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

and

$$k_2 = (1.5 \pm 0.4) \times 10^{-10} (T/298 \text{ K})^{-(0.16 \pm 0.14)} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

In crossed beam experiments, relative cross-sections for products of the two reactions [CO from (1) and CN from (2a)] in specific vibrational levels were measured at collision energies (ϵ_{tr}) between *ca.* 4 and 100 meV. The cross-sections are proportional to $(\epsilon_{\text{tr}})^{-0.94}$ for reaction (1) and to $(\epsilon_{\text{tr}})^{-0.72}$ for reaction (2a). Both sets of results demonstrate that these reactions proceed over potential energy surfaces with no barrier on the path from reactants to products. If the reaction cross-sections are independent of the rotational energy level of the reagents and of the distribution of C(³P_J) atoms over spin–orbit states, and if they exhibit the same dependence on relative translational energy below 4 meV as above, integration of the excitation functions leads to the rate constants exhibiting temperature dependences of $k_1(T)$ proportional to $T^{-0.44}$ and $k_{2a}(T)$ proportional to $T^{-0.22}$, in reasonable agreement with the direct measurements of the rate constants for reactions (1) and (2). The two sets of experimental results are also compared with theoretical calculations, based on the adiabatic capture centrifugal sudden approximation (ACCSA) model. The calculations correctly predict the temperature dependence of the rate constants for both reactions. The consistency of these three data sets is discussed.

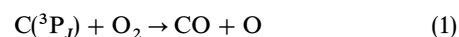
Introduction

Although the relationship between the excitation function for a chemical reaction, *i.e.*, how the cross-section varies with relative translational energy, and its thermal rate constant is well known,¹ because reactive scattering measurements are generally limited to only a few relative translational energies, it has rarely been tested experimentally. What is required are measurements of reaction cross-sections (σ_{reac}) over a wide range of relative translational energy (ϵ_{tr}) and of thermal rate constants (k) over a wide range of temperature (T). If the reaction cross-section is independent of the internal states of the reagents, the relationship between the excitation function, $\sigma_{\text{reac}}(\epsilon_{\text{tr}})$, and the rate constant is given by¹

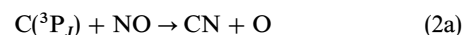
$$k(T) = \left(\frac{1}{\pi\mu}\right)^{1/2} \left(\frac{2}{k_{\text{B}}T}\right)^{3/2} \int_0^\infty \sigma_{\text{reac}}(\epsilon_{\text{tr}}) \epsilon_{\text{tr}} \times \exp(-\epsilon_{\text{tr}}/k_{\text{B}}T) d\epsilon_{\text{tr}} \quad (i)$$

where μ is the reduced mass for the reagents and k_{B} is the Boltzmann constant. To measure $\sigma_{\text{reac}}(\epsilon_{\text{tr}})$, one requires a crossed molecular beam apparatus in which the relative translational energy can be varied, preferably continuously and over a wide range. Then the rate constants calculated from eqn. (i) can be compared with those measured directly under thermally equilibrated conditions over a range of temperatures.

The present paper reports the results of such a comparison for two fast exothermic reactions of C(³P_J) atoms:

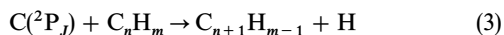


and



Carbon atoms in their (2p² ³P_J) electronic ground state are particularly abundant in interstellar clouds (ISCs),² and the

need to confirm that some of their reactions with neutral molecules are rapid at low temperatures, and are therefore important in ISCs, has inspired our collaboration. For example, the reaction of $C(^3P_J)$ with O_2 may be a source of CO,³ which is the second most abundant molecule in ISCs. Most of the recent experiments on the reactions of $C(^3P_J)$ atoms have emphasised their reactions with unsaturated hydrocarbons. Indeed, such neutral–neutral reactions have been identified by Bettens and Herbst⁴ as potentially of great importance in the synthesis of large carbon-containing species in ISCs, through successive insertion-elimination reactions of the type



Following the room temperature measurements of Husain and co-workers⁵ on the kinetics of the reactions of $C(^3P_J)$ with a huge range of unsaturated hydrocarbons, the theoretical work of Clary *et al.*⁶ indicated that such reactions were likely to remain very rapid at the temperatures of ISCs. Crossed molecular beam studies of a number of such reactions have been performed by Kaiser *et al.*⁷ They used mass spectrometry to identify scattered species and their experiments are therefore especially valuable in identifying reaction products. However, their dynamical findings are not directly relevant to the conditions in dense ISCs, since all their experiments have been performed at relative translational energies between 90 and 460 meV, equivalent to mean kinetic energies ($\langle \epsilon_{tr} \rangle = \frac{3}{2}k_B T$) of thermal Maxwell–Boltzmann distributions at temperatures between 700 and 3500 K.

Our main purpose in the present paper is to compare the temperature dependences of the thermal rate constants for reactions (1) and (2), which were measured at temperatures down to 15 K, with those which can be inferred from the variation of the reaction cross-section for the two reactions at low kinetic energies. Such a comparison parallels that made previously on the reaction between $Al(^2P_J)$ atoms and O_2 .^{8,9} Rate constants for both reactions have been measured directly over a wide range of temperature, 15–295 K, in the CRESU (Cinétique de Réaction en Ecoulement Supersonique Uniforme) apparatus in Birmingham.¹⁰ Relative cross-sections for the production of molecular reaction products in specific states, *i.e.*, CO from reaction (1)¹¹ and CN from reaction (2a), have been determined in Bordeaux by crossed beam experiments over the relative translational energy range 4.4–100 meV. In addition, rate constants have been calculated in Bordeaux using the adiabatic capture theory of Clary.¹²

The next section gives only brief description of each set of experiments, since fuller descriptions can be found elsewhere.^{8,10,13,14} The results from both experiments and from theory are presented in the third section of the paper. Finally, we compare all the results, identifying those factors which might make the three sets of rate constants differ in respect of their dependence on temperature.

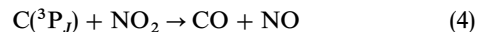
Experimental

(a) Low temperature experiments in the CRESU apparatus

The rate constants for the $C(^3P_J) + O_2$ and $C(^3P_J) + NO$ reactions were measured in the Birmingham CRESU apparatus¹⁰ at temperatures down to 15 K.¹⁴ In a CRESU apparatus, low temperatures are achieved by isentropic expansion of a gas mixture, consisting predominantly (typically >99.9%) of a carrier gas (He, Ar or N_2) through an axisymmetric, convergent–divergent, Laval nozzle. A supersonic flow of gas is generated in which the Mach number, the temperature, the total pressure of the gas and the mole fractions of the components of the mixture are all uniform along the flow. In all the experiments referred to here, a small concentration of C_3O_2 was included in the flow and $C(^3P_J)$ atoms

were generated by pulsed laser photolysis of this precursor at 193 nm,^{13–15} using an excimer laser operating on ArF.

For the $C(^3P_J) + O_2$ reaction, two sets of measurements were carried out, differing in the methods used to monitor the progress of reaction. In the first experiments, the results of which have already been published,¹³ a small concentration of NO_2 was included in the flowing gas mixture. The reaction



produces NO in its $A^2\Sigma^+$ and $B^2\Pi$ excited electronic states, and also in its $X^2\Pi$ ground state. The chemiluminescence in the $B^2\Pi \rightarrow X^2\Pi$ (0, 8) band was isolated with a filter centred at 320 nm and detected by a photomultiplier tube. Since $NO(B^2\Pi, v=0)$ has a short radiative lifetime ($\tau = 2.0 \mu s$)¹⁶ compared with the reaction time, it acts as a marker for C atoms with the intensity of the chemiluminescence proportional to the concentration of $C(^3P_J)$ atoms. Using different Laval nozzles, rate constants for the $C(^3P_J) + O_2$ reaction were measured at eight temperatures between 295 and 15 K in the presence of three carrier gases (He, Ar or N_2).¹³ Because NO and NO_2 might combine at low temperatures, no results for the reaction between $C(^3P_J)$ and NO were obtained using this chemiluminescent technique.

In more recent CRESU experiments, data were obtained for the reactions of $C(^3P_J)$ atoms with both O_2 and NO by directly monitoring the kinetic decays of the $C(^3P_J)$ atomic concentration using resonant vacuum-ultraviolet laser-induced fluorescence (VUV-LIF), that is, with both excitation and observation of the fluorescence on the $(2s^2 2p^3s^3P_J - 2s^2 2p^2^3P_J)$ transition of atomic carbon. Pulses of VUV laser radiation were generated using four-wave mixing in Xe. The method is described in some detail elsewhere.^{14,17} Briefly, dye laser radiation was tuned to 255.94 nm in order to excite Xe in a two-photon transition to its $5p^5 6p[2\frac{1}{2}, 2]$ state. A second pulsed dye laser could be tuned through the wavelength range between 560 and 565 nm to generate VUV radiation between 165.9 and 165.4 nm. LIF spectra of the $(2s^2 2p^3s^3P_J - 2s^2 2p^2^3P_J)$ transition were recorded and confirmed that spin–orbit relaxation within the electronic ground state was achieved on a time-scale which was short relative to that for reaction.¹⁴ Earlier measurements in the Birmingham CRESU apparatus¹⁰ had established that spin–orbit and rotational relaxation in NO (and presumably rotational relaxation in O_2) would be much faster than reaction under the conditions of the present experiments so that the rate constants that are measured correspond to those for entirely thermalised conditions.

For kinetic measurements, the VUV probe laser was set at the wavelength of the $(2s^2 2p^3s^3P_{J=1} - 2s^2 2p^2^3P_{J=0})$ transition at 165.69 nm and LIF signals were recorded as the time delay between the pulses from the photolysis and probe lasers was systematically varied. The recorded traces of LIF signal *vs.* time accurately fitted single exponential decays yielding pseudo-first-order rate constants (k_{1st}). Second-order rate constants for reaction at a particular temperature were obtained by measuring values of k_{1st} , with different concentrations of the co-reagent added to the flowing gas mixture, and plotting k_{1st} *vs.* $[O_2]$ or $[NO]$.

(b) Crossed beam experiments

The beam apparatus in Bordeaux uses skimmed, differentially pumped, pulsed molecular beams. Carbon atoms were produced by laser ablation from a graphite rod and entrained into the supersonically expanded carrier gas (Ar or Ne) which originated from a first pulsed nozzle. The co-reagent beam (O_2 or NO) originated from a second pulsed nozzle. Both beams were crossed with an intersection angle which can be varied between 22.5° and 90°, allowing the relative translational energy for both reactions to be continuously scanned between

ca. 4 and 100 meV. Since results were reported¹¹ for $C(^3P_J) + O_2$, improvements have been made in the C-atom beam source in order to reduce any C_2 and C_3 in the beam and hence background¹⁸ to the LIF signals from CN. The results reported here for the $C(^3P_J) + NO$ reaction were obtained using this improved source and the beam characteristics listed in Table 1.

$C(^3P_J)$ atoms, the NO reagent for reaction (2) and molecular products of both reactions [CO from reaction (1) and CN from reaction (2a)] were all probed by LIF within the volume where the two pulsed beams crossed. $C(^3P_J)$ atoms were detected using a two-photon LIF scheme and tunable dye laser radiation near 280 nm. Excitation in the $(2s^22p^3\ ^3P_J \leftarrow 2s^22p^2\ ^3P_J)$ transition is followed by successive emissions in the infrared $(2s^22p^3\ ^3P_J \rightarrow 2s^22p^3s\ ^3P_J)$ and in the VUV $(2s^22p^3s\ ^3P_J \rightarrow 2s^22p^2\ ^3P_J)$.¹⁴ The VUV photons were detected by a solar blind photomultiplier tube. Excitation spectra demonstrated that relaxation among the spin-orbit levels of the $C(^3P_J)$ electronic ground state was efficient in both Ne and Ar carrier gases with the population distribution corresponding to a temperature of ca. 35 K. The NO internal state distribution was characterised by LIF on transitions in the $A\ ^2\Sigma^+ - X\ ^2\Pi$ system around 220 nm. The rotational energy was found to be less than 1 meV, corresponding approximately to a temperature of <12 K. The O_2 internal state distribution was not determined, but, by analogy with that measured in the NO beams under similar operating conditions, could be assumed to be very cold. CO produced in the $C(^3P_J) + O_2$ reaction was observed by exciting LIF in the $\Delta v = -9$ band sequence of the $A\ ^1\Pi - X\ ^1\Sigma^+$ system between 229 and 234 nm. The resultant fluorescence at wavelengths <190 nm was observed with the solar blind photomultiplier tube. CN radicals produced from the $C(^3P_J) + NO$ reaction were detected by LIF using the $\Delta v = -2$ band sequence of the $B\ ^2\Sigma^+ - X\ ^2\Sigma^+$ system between 450 and 461 nm. Fluorescence was observed on the $\Delta v = 0$ sequence around 380 nm through a Schott UG1 filter.

In a typical $C(^3P_J) + NO$ experiment, LIF signals from CN averaged over 16 laser pulses were recorded at 46 intersection angles between intersection angles $\theta = 90^\circ$ and 22.5° . Relative values of the cross-sections were obtained by dividing the averaged signal intensities by the relative velocities of the reagents.¹⁹ The excitation functions displayed in Fig. 2 are averages over four separate runs.

Results

(a) Low temperature rate constants

Experiments using the chemiluminescent method to follow the rate of reaction (1) have been described in detail previously.¹³ In brief, at a given temperature provided by a selected Laval nozzle, a series of experiments were performed on gas mixtures containing (a) the same small concentrations of C_3O_2 (estimated to be ca. 10^{12} molecule cm^{-3}) and NO_2 (ca. 10^{14} molecules cm^{-3}), and (b) different concentrations of O_2 up to ca. 1.3×10^{14} molecule cm^{-3} . Measurements were made for

supersonic expansions from several nozzles (in He, Ar and N_2 carrier gases), providing temperatures between 15 and 204 K, and also in a subsonic flow at 295 K.

The intensity of the chemiluminescence from $NO(B\ ^2\Pi, v = 0)$ formed in the reaction between $C(^3P_J)$ atoms and NO_2 was proportional to the concentration of $C(^3P_J)$ atoms and decayed exponentially providing values of k_{1st} for removal of carbon atoms. A plot of these pseudo-first-order rate constants against the concentration of O_2 , i.e., $[O_2]$, included in the reaction mixture yields the second-order rate constant, k_1 , for reaction (1) at the selected temperature. Possible sources of error in these indirect measurements were considered at length in a previous paper.¹³ The results of these experiments fit the expression:

$$k_1(T) = (4.7 \pm 1.0) \times 10^{-11} (T/298\text{ K})^{-(0.34 \pm 0.10)} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

with errors quoted as $\pm 2\sigma$, where σ is the standard error.

In more recent experiments,¹⁴ we observed $C(^3P_J)$ atoms directly using VUV-LIF as described above. Again, $C(^3P_J)$ atoms were generated by pulsed laser photolysis of C_3O_2 at 193 nm and, in a given set of experiments, $[C_3O_2]$ was held constant and $[O_2]$ varied. The values of k_1 derived from these experiments, in which the kinetic decays of $[C(^3P_J)]$ were observed directly, are shown by the filled symbols in Fig. 1(a), where the open symbols represent the earlier data obtained by the chemiluminescent method.

The results of the two sets of experiments on reaction (1) are clearly in excellent agreement, dispelling any doubts about the efficacy of the chemiluminescent method. Fitting the latest data, obtained by VUV-LIF detection of C-atom decays, yields

$$k_1(T) = (5.1 \pm 1.5) \times 10^{-11} (T/298\text{ K})^{-(0.30 \pm 0.13)} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

A least squares fit to both sets of data yields the expression

$$k_1(T) = (4.9 \pm 0.8) \times 10^{-11} (T/298\text{ K})^{-(0.32 \pm 0.08)} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

where the errors in both cases again correspond to $\pm 2\sigma$.

For the reason stated earlier, measurements on the reaction between $C(^3P_J)$ and NO were only made using the direct VUV-LIF technique for observing concentrations of $C(^3P_J)$. The method was the same as that outlined above for $C(^3P_J) + O_2$. The derived values of k_2 are displayed in Fig. 1(b). Again, $\log[k_2(T)/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}]$ varies linearly with $\log(T/K)$ and a least squares fit to the data yields the expression

$$k_2(T) = (1.5 \pm 0.4) \times 10^{-10} (T/298\text{ K})^{-(0.16 \pm 0.14)} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

where again the errors correspond to $\pm 2\sigma$.

(b) Reaction cross-sections measured at low collision energies

Relative state-to-state cross-sections have been measured as a function of relative translational energy for the production of

Table 1 Characteristics of the molecular beams for the experiments on the $C(^3P_J) + NO$ reaction

Gas mixture	$v/m\text{ s}^{-1a}$	$\Delta v/v^b$	$\Delta t/\mu\text{s}^c$	$J = 0, 1, 2^d$
<i>C-atom source—</i>				
Ne	1050	0.09	10	0.43, 0.43, 0.14
Ar	820	0.07	13	0.38, 0.45, 0.17
<i>NO source—</i>				
NO : He = 0.33 : 0.67	1080	<0.08	20	
Neat NO	820	<0.08	17	

^a Velocity at the peak, uncertainty on v determination is $\pm 2\%$. ^b Velocity spread half-width at $1/e$ (HWE). ^c Pulse width (HWE) at the crossing point. ^d Spin-orbit population.

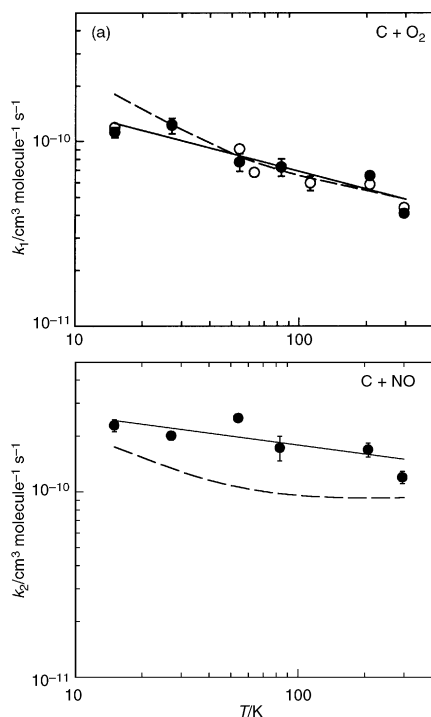
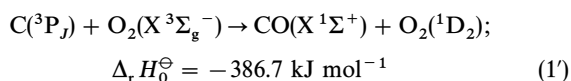


Fig. 1 Rate coefficients for the reactions of (a) $C(^3P_J)$ with O_2 and (b) $C(^3P_J)$ with NO plotted on a log-log scale against temperature. The open circles (\circ) in (a) show the results of experiments in which chemiluminescence from $C(^3P_J) + NO_2$ was used to follow the kinetics, the filled circles (\bullet), in (a) and (b), are the results of experiments in which kinetic decays of $C(^3P_J)$ atoms were recorded using VUV-LIF. The solid lines show the results of non-linear least squares fits in (a) to the combined chemiluminescent and VUV-LIF data, yielding $k_1 = (4.9 \pm 0.8) \times 10^{-11} (T/298 \text{ K})^{-(0.32 \pm 0.08)} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, and in (b) to the VUV-LIF data, yielding $k_2 = (1.5 \pm 0.4) \times 10^{-10} (T/298 \text{ K})^{-(0.16 \pm 0.14)} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, with errors quoted as $\pm 2\sigma$, where σ is the standard error. The dashed lines show the temperature-dependent ACCSA rate coefficients, calculated according to the methods outlined in the text.

$CO(v = 15, 16 \text{ and } 17)$ in reaction (1) between $C(^3P_J)$ atoms and O_2 . The data have been reported previously,¹¹ so only the main features will be emphasised here to allow for comparison with the kinetics results.

The measurements on $CO(v = 17, J = 10-11)$ yielded an excitation function showing clear evidence of a threshold for the formation of CO in this vibrational level at a relative translational energy of *ca.* 45 meV. With support from earlier infrared chemiluminescence experiments,²⁰ this observation suggests that the observed reaction pathway is



for which $v = 16$ is the highest vibrational level accessible at low relative translational energies.

The measurements on $CO(v = 15, J = 10-11)$ and $CO(v = 16, J = 10-11)$ exhibit a different behaviour. Both cross-sections show a similar dependence on relative translational energy, characteristic of a barrierless process: σ_{reac} decreases monotonically with increasing kinetic energy. Fitted independently to expressions of the form $\log(\sigma_{\text{reac}}/\text{arbitrary units}) = \alpha \log(\epsilon_{\text{tr}}/\text{meV})$, the experimental data yield $\alpha = -1.14$ for $CO(v = 16, J = 10-11)$ and $\alpha = -0.94$ for $CO(v = 15, J = 10-11)$. The latter result is more likely to be representative of the excitation function as a whole since (a) the branching into the $v = 15$ is less sensitive to the relative translational energy than that into $v = 16$, the highest accessible vibrational level in most of these experiments if reaction proceeds exclusively to $CO(X^1\Sigma^+) + O(^1D_2)$, and (b) the detectivity does depend on the kinetic energy released into the products which

will be less dependent on the initial relative translational energy for levels furthest below the energetic limit.

Relative state-specific cross-sections were measured as a function of relative translational energy for the production of CN in reaction (2a) between $C(^3P_J)$ and NO . Two sets of experiments were performed.

Firstly, the laser was tuned to the wavelengths of the $B^2\Sigma^+ - X^2\Sigma^+$ (0, 2), (1, 3) and (2, 4) bandheads, *i.e.*, probing the ($v = 2, N = 17-20$), ($v = 3, N = 18-20$) and ($v = 4, N = 18-21$) states, yielding the excitation functions displayed in Fig. 2(a). The fits of $\log(\sigma_{\text{reac}}/\text{arbitrary units})$ *vs.* $\log(\epsilon_{\text{tr}}/\text{meV})$ within the range $\epsilon_{\text{tr}} = 8-50$ meV all gave straight lines with similar gradients, corresponding to $\alpha = -0.68, -0.71$ and -0.68 , respectively. It therefore seems likely that the measured cross-sections are representative of the total cross-section for the reaction $C(^3P_J) + NO \rightarrow CN + O$. It should be noted that reaction (2a) is considerably less exothermic than reaction (1'), $\Delta_r H_0^\ominus = -120.8 \text{ kJ mol}^{-1}$ as against $\Delta_r H_0^\ominus = -386.7 \text{ kJ mol}^{-1}$, so that the highest energetically accessible level of CN is $v = 5$.

Second [see Fig. 2(b)], results have been gathered for the production of $CN(X^2\Sigma^+, v = 4, N = 18-21)$ with different beam conditions, LIF signals from the (2, 4) bandhead displaying the highest signal-to-noise ratio. Fits of these data in the common energy domain (*i.e.*, 8–50 meV) yielded $\alpha = -0.68, -0.72$ and -0.71 . A global fit of all the data in this energy domain gave $\alpha = -0.72$, allowing all the results to be normalised. Indeed, all the data in the entire range of kinetic energy from 4.5 to 101 meV are well represented by this value of α .

(c) Theoretical calculations

A theoretical study of the kinetics of reactions (1) and (2) was also performed at Bordeaux using the adiabatic capture centrifugal sudden approximation (ACCSA) method derived by Clary.¹² When this method was recently applied to the $Al(^2P_J)$

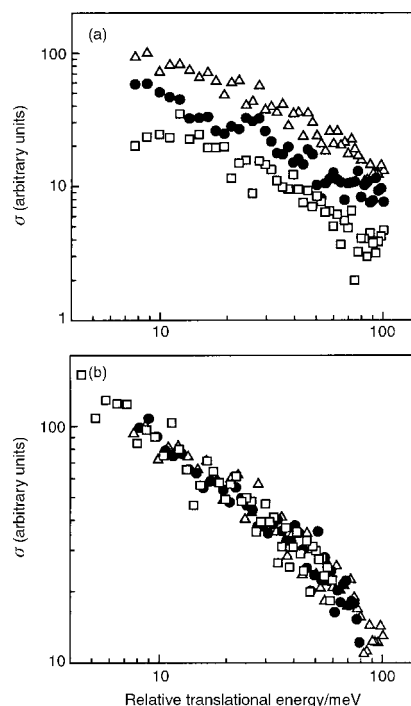


Fig. 2 Excitation function for the $C(^3P_J) + NO$ reaction from observation of CN : (a) in the ($v = 2, N = 17-20$) (\square), ($v = 3, N = 18-20$) (\bullet) and ($v = 4, N = 18-21$) (Δ) states; $v_C = 1050 \text{ m s}^{-1}$ and $v_{NO} = 1080 \text{ m s}^{-1}$; (b) in the ($v = 4, N = 18-21$) states for different beam conditions: $v_C = 1050 \text{ m s}^{-1}$ and $v_{NO} = 1080 \text{ m s}^{-1}$ (Δ), $v_C = 1050 \text{ m s}^{-1}$ and $v_{NO} = 820 \text{ m s}^{-1}$ (\bullet), $v_C = 820 \text{ m s}^{-1}$ and $v_{NO} = 820 \text{ m s}^{-1}$ (\square).

Fig. 3 Calculated (ACCSA) excitation functions for the reactions of (a) $C(^3P_0)$ with $O_2(X^3\Sigma_g^-)$ and (b) $C(^3P_0)$ with $NO(X^2\Pi_{1/2})$ showing the influence of the rotational level N of the molecular reagent.

+ O_2 reaction,⁹ it gave good agreement between theory and experiments.

Long-range potentials made up of the sum of the dipole–quadrupole, quadrupole–quadrupole, dispersion and spin–orbit contributions were used. The experimental data necessary to evaluate these long-range potentials were taken from previous work.^{9,21–23} For each system, the matrix elements of the potential were calculated in the spin–orbit basis set of the impinging atom and the corresponding matrix diagonalised. The lowest root was used to calculate the coupling between the rotational states of the diatomic molecule and then to obtain the rotationally adiabatic potential energy curves. The capture hypothesis was then applied and the corresponding cross-section and rate constant computed.

The rate constant for the $C(^3P_J) + O_2$ reaction, $k_1^{ACCSA}(T)$, was derived from the excitation function calculated on the ground surface ($^1\Sigma^+$ in $C_{\infty v}$ or $^1A'$ in C_s symmetry): see the correlation diagram for this reaction given by Chastaing *et al.* (Fig. 8 in ref. 13). Assuming that the reactivity is similar on all three singlet surfaces [$^1\Sigma^+$ and $^1\Pi$ in $C_{\infty v}$ or $^1A'(2)$ and $^1A''$ in C_s symmetry) allowed the thermal rate constant to be estimated as

$$k_1(T) = P_1(T) \times k_1^{ACCSA}(T) \quad (ii)$$

where $P_1(T)$ stands for the probability of initiating reaction on these surfaces. This factor is calculated from the relevant

Table 2 Temperature dependence of the detailed rate constants ($k/cm^3 \text{ molecule}^{-1} \text{ s}^{-1}$) for the $C(^3P_J) + O_2$ and $C(^3P_J) + NO$ reactions in the limit of zero temperature, as a function of the spin–orbit state of the carbon atom

	$O_2(X^3\Sigma_g^-)$	$NO(X^2\Pi_{1/2})$
$C(^3P_0)$	$1.73 \times 10^{-10} T^{1/6}$	$1.71 \times 10^{-10} T^{1/6}$
$C(^3P_1)$	$4.01 \times 10^{-11} T^{1/10}$	4.05×10^{-11}
$C(^3P_2)$	$4.51 \times 10^{-11} T^{1/10}$	4.31×10^{-11}
$k(T = 15 \text{ K})$	1.82×10^{-10}	1.75×10^{-10}

The last entry is a Boltzmann averaging of detailed rate constants.

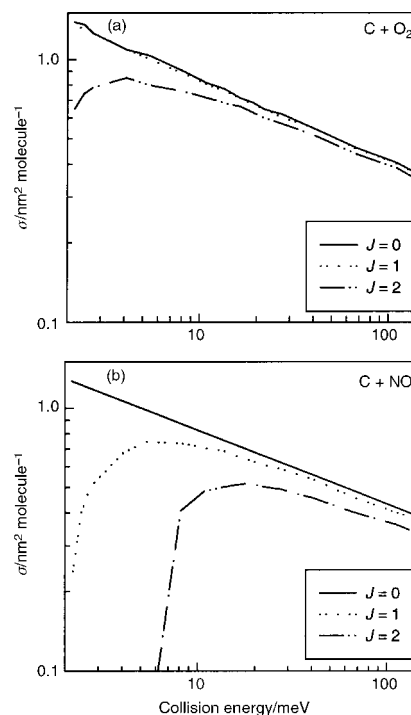


Fig. 4 Calculated (ACCSA) excitation functions for the reactions of (a) $C(^3P_J)$ with $O_2(X^3\Sigma_g^-, N=1)$ and (b) $C(^3P_J)$ with $NO(X^2\Pi_{1/2}, N=0)$ showing the influence of the C-atom spin–orbit state, J (for $J=1, 2$, an average of each sub-level is plotted as there is no significant variation between these sub-levels).

electronic partition functions, Q_{elec} , of the reactants and the adiabatic potential energy surfaces on which reaction can take place:

$$P_1(T) = Q_{elec}^{\dagger}\{CO_2[^1A'(2) + ^1A'']\}/[Q_{elec}(C^3P_J) \times Q_{elec}(O_2^3\Sigma_g^-)] \approx 1/[Q_{elec}(C^3P_J)] \quad (iii)$$

when one considers that $Q_{elec}^{\dagger}[CO_2(^1A', ^1A'')] \approx Q_{elec}(O_2^3\Sigma_g^-) = 3$ and

$$Q_{elec}(C^3P_J) = 1 + 3 \exp(-23.6/T) + 5 \exp(-62.4/T) \quad (iv)$$

Such calculations were also presented in a previous paper concerning the $C + NO$ reaction.²³ In that work, the lowest electronic state of the CNO reaction intermediate was erroneously assumed to be a $^2\Sigma$ state. The $^2\Pi$ state, which is close in energy to the $^2\Sigma$ state, is in fact the lowest state.²⁴ A CASSCF²⁵ calculation of the spin–orbit splitting between the $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ state of CNO was performed using the Breit Pauli Hamiltonian in a valence-double-zeta Gaussian basis set of Dunning²⁶ with the MOLPRO²⁷ code. The splitting obtained is 108.71 cm^{-1} , which is close to the splitting in NO (119.82 cm^{-1}). We then assume that the spin–orbit population of the intermediate is a direct consequence of the initial spin–orbit population of NO. If one further assumes that the reaction proceeds on this single $^2\Pi$ surface, the thermal factor reads:

$$P_2(T) = Q_{elec}^{\dagger}(CNO^2\Pi)/[Q_{elec}(C^3P_J) \times Q_{elec}(NO^2\Pi)] \approx 1/Q_{elec}(C^3P_J) \quad (v)$$

when one considers that $Q_{elec}^{\dagger}(CNO^2\Pi) \approx Q_{elec}(NO^2\Pi)$. New calculations were run using the latter thermal factor for this system.

The capture cross-sections for both reactions are presented in Fig. 3, for several different rotational quantum numbers of the diatomic reagent. These diagrams clearly show that the $C + O_2$ capture cross-section is a function of the rotation of O_2 , whereas the $C + NO$ cross section is found to be almost

independent of the rotational state of NO. As can be seen in Fig. 1, the calculated rate constants for both reactions agree fairly well with the experimental values insofar as the temperature dependence is concerned. The adiabatic capture results are, however, lower than experiment in the case of the C + NO reaction, which can be ascribed to the thermal factor, $P_2(T)$. ACCSA values of the rate constant, which do not include the thermal factor, would be higher than the experimental values, as is usually the case. As can be seen in Fig. 1, the adiabatic capture rate constant of the C + O₂ reaction is lower than its C + NO counterpart at 300 K, in agreement with experiment. Conversely, for the lowest temperatures, the rate coefficient of C + O₂ is found to be slightly above its C + NO counterpart. In order to check this result we also calculated the law of variations of the rate constant as a function of temperature in the limit of zero temperature using the equation given in a recent study.²⁸ The results of this approach are presented in Table 2 and are consistent with the low temperature values (*i.e.*, those at 15 K).

This simple approach shows that the reactivities of the $J = 0$ and $J = 2$ spin-orbit states of the carbon atom should differ by a factor of four in the limit of zero temperature for both reactions. On the other hand, the reactivities of the $J = 1$ and $J = 2$ states are almost the same. The open shell nature of the reactant is then expected to play a significant role in the temperature dependence of the rate constant even at higher temperature. In order to assess this hypothesis, we also calculated the capture cross-sections obtained when using the potential energy surface correlating with the excited spin-orbit states of C atoms. We can see in Fig. 4 that again the two reactions studied exhibit a slightly different behaviour. However, the rate constants for both depend on the spin-orbit state of the C atom. This point is discussed further in the next section.

Discussion

As shown in Fig. 1(a), the rate constants for reaction (1) between C(³P_{*J*}) atoms and O₂ compare remarkably well with those obtained previously in the Birmingham CRESU apparatus using the chemiluminescent technique.¹³ The present room temperature data for both reactions are compared in Table 3 with a number of previous measurements.^{29–32} The present values of $k_1(T = 298\text{ K})$ and $k_2(T = 298\text{ K})$ are larger than those measured previously with the exception of the value of $k_1(T = 298\text{ K})$ reported by Becker *et al.*³⁰ The relative values of $k_1(T = 298\text{ K})$ and $k_2(T = 298\text{ K})$ are generally in fair agreement except, curiously, in the case of the measurements of Becker *et al.* Their value of $k_2(T = 298\text{ K})$ is almost an order of magnitude lower than ours, so that, in the case of their measurements, the ratio $k_2(T = 298\text{ K}) : k_1(T = 298\text{ K})$ is much lower than that from any other single set of measurements. We can offer no explanation for this large discrepancy.

The excitation function for C(³P_{*J*}) + O₂ is that reported earlier.¹¹ The cross-sections reported here for C(³P_{*J*}) + NO can be compared with those deduced from experiments performed in the earlier crossed beam apparatus in Bordeaux which used fixed beam sources.³³ As in the present work, beams of C(³P_{*J*}) atoms were generated by laser ablation from a graphite rod and subsequent entrainment in rare gases

expanding supersonically from a fast pulsed valve, and relative cross-sections were determined by observing CN product using LIF in the B²Σ⁺–X²Σ⁺ band system. However, in these earlier experiments, variation of the relative translational energy was achieved by changing the laboratory beam velocities, rather than by rotating one beam source as in the present work. With this procedure, it was possible to measure cross-sections at relative translational energies between 38 and 163 meV, overlapping the current range of kinetic energies but not reaching the very low energies achieved in the present experiments. In all, nine different NO beams and eight different C atom beams were used. However, to calculate the excitation function from those measurements, it was necessary to assume that there was no variation in the cross-section with relative translational energies for normalisation points between $\epsilon_{\text{tr}} = 200$ and 290 meV. Based on this assumption, a value of $\alpha = -0.33$ was derived. In view of the present measurements which yield $\alpha = -0.72$, it appears that this assumption was invalid.

The main thrust of the present work was to compare the temperature dependences of the rate constants measured for reactions (1) and (2) with those derived from the dependence of the reaction cross-sections on relative translational energy. Because the crossed beam experiments only determine *relative* cross-sections at different collision energies, it was not possible to compare *absolute* values of the rate constants. Moreover, the comparison of the temperature dependences has to be based on a simple integration of eqn. (i) using the form of $\sigma_{\text{reac}}(\epsilon_{\text{tr}})$ determined in the crossed beam experiments. According to this operation, the parameters α , which describes the energy dependence of the cross-sections according to $\sigma_{\text{reac}}(\epsilon_{\text{tr}}) \propto (\epsilon_{\text{tr}})^\alpha$, and n , representing the temperature dependence of the rate constants according to $k(T) \propto T^n$, are connected by the simple relationship

$$n = \alpha + \frac{1}{2} \quad (\text{vi})$$

If this equation was obeyed, based on the excitation functions n would have the values of -0.44 for the C(³P_{*J*}) + O₂ reaction and -0.22 for C(³P_{*J*}) + NO. These values of n compare remarkably well with those of -0.33 and -0.16 , respectively, determined directly from the CRESU experiments.

Of course, there are several reasons why the two values of n for these reactions might differ, and we now examine these. First, it has to be recognised that the CRESU experiments measure rate constants for the overall reactions between C(³P_{*J*}) atoms and O₂ and NO, whereas the crossed beam experiments measure the variation of cross-section for production of one product of these reactions in particular rovibronic levels. For these two measurements to be directly related, it is necessary that the branching ratio into the particular monitored product is independent of relative translational energy. In the case of reaction (1) between C(³P_{*J*}) and O₂, excitation functions have been measured for the production of CO($v = 15, J = 10-11$) and CO($v = 16, J = 10-11$). In the previous section, we presented arguments to support the conclusion that the yield of CO($v = 15$), in particular, will be representative of the cross-section for production CO(X¹Σ⁺) + O(¹D₂) in the reaction between C(³P_{*J*}) atoms and O₂. There remains the questions of whether, at least at low temperatures, eqn. (1') represents reaction (1) in its

Table 3 Rate constants ($k/10^{-11}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$) at 298 K for the C(³P_{*J*}) + O₂ and C(³P_{*J*}) + NO reactions^a

	Husain and Young ²⁹	Becker <i>et al.</i> ³⁰	Dorthe <i>et al.</i> ³¹	Bergeat <i>et al.</i> ³²	CRESU (this work)
$k_1(\text{C} + \text{O}_2)$	2.6 ± 0.3	4.7 ± 0.3	1.6 ± 0.3	2.5 ± 0.4	4.8 ± 0.5
$k_2(\text{C} + \text{NO})$	4.8 ± 0.8	1.6 ± 0.2	2.7 ± 0.3	5.4 ± 0.8	15 ± 4
k_2/k_1	$1.8_5 \pm 0.4$	0.34 ± 0.05	1.7 ± 0.4	2.2 ± 0.5	2.9 ± 0.8

^a Note that the error limits are those given in the original papers and do not correspond to the same levels of uncertainty.

entirety, or whether the electronic branching ratio depends on the kinetic energy or temperature, if a significant fraction of reaction forms $\text{CO}(\text{X}^1\Sigma^+) + \text{O}(\text{P}_J)$.

Chastaing *et al.*¹³ have previously analysed the low temperature rate data for reaction (1) in the light of the spin and orbital correlation rules, which connect the reactants to products *via* adiabatic potential surfaces (see Fig. 8 in ref. 13). Within the adiabatic approximation, crossings would not occur between such surfaces and only collisions on adiabatic potential surfaces leading to a thermodynamically accessible product would contribute to the thermal rate constant. Chastaing *et al.* pointed out that the $^3\text{P}_1$ and $^3\text{P}_2$ spin-orbit states of $\text{C}(\text{P}_J)$ lie at energies 2.0 and 5.4 meV (equivalent to 23.6 and 62.4 K) above the $^3\text{P}_0$ ground state and that the populations in these spin-orbit levels change markedly through the range of temperature between 298 K ($N_{J=2} : N_{J=1} : N_{J=0} = 4.1 : 2.8 : 1.0$) and 15 K ($N_{J=2} : N_{J=1} : N_{J=0} = 0.08 : 0.65 : 1.0$). If reaction occurs only from specific spin-orbit states, then this factor alone could lead to a significant negative dependence on temperature. Such effects are often allowed for by a factor, equivalent to the thermal factor $P(T)$ introduced into the ACCSA calculations [eqn. (iii)], that is inversely proportional to the product of the electronic partition functions (Q_{elec}) for the reagents.

For $\text{C}(\text{P}_J)$ atoms, the value of $Q_{\text{elec}}(\text{C } ^3\text{P}_J)$ falls from 7.84 at 298 K to 1.70 at 15 K in the temperature-range of the CRESU experiments. Consequently, if this effect alone was responsible for the temperature dependence of k_1 , then the rate constants should increase by a factor of 4.5 from 298 to 15 K, whereas the experiments show that $k_1(T = 15 \text{ K})$ is only *ca.* $2.2 \times k_1(T = 298 \text{ K})$. Furthermore, the molecular beam experiments were conducted with a constant distribution over the $\text{C}(\text{P}_J)$ spin-orbit levels, corresponding to $T \approx 35 \text{ K}$ and $Q_{\text{elec}}(\text{C } ^3\text{P}_J) \approx 3.4$.

Another interesting question in regard to reaction between $\text{C}(\text{P}_J)$ atoms and O_2 is the electronic states of the products. As stated above, the experimental evidence,^{11,20} regarding the highest populated vibrational level in $\text{CO}(\text{X}^1\Sigma^+)$, indicates that the major products are $\text{CO}(\text{X}^1\Sigma^+) + \text{O}(\text{D}_2)$, although the products $\text{CO}(\text{X}^1\Sigma^+) + \text{O}(\text{P}_J)$ cannot be ruled out. Including all spin-orbit terms of the reactants, 27 states in all correlate with $\text{C}(\text{P}_J) + \text{O}_2(\text{X}^3\Sigma_g^-)$. Only three of these surfaces ($2^1\text{A}' + 1^1\text{A}''$) lead adiabatically to $\text{CO}(\text{X}^1\Sigma^+) + \text{O}(\text{D}_2)$, whereas two triplet surfaces ($^3\text{A}' + ^3\text{A}''$) correlate to $\text{CO}(\text{X}^1\Sigma^+) + \text{O}(\text{P}_J)$. The capture rate was evaluated

assuming that reaction only occurs on the three singlet surfaces. The good agreement with the CRESU results, even at 298 K where the value of $P_1(T)$ is only $(1/7.84)$, gives some support to this assumption. The corresponding ACCSA rate constant (on a single surface) is fairly large, $k_1^{\text{ACCSA}}(T = 298 \text{ K}) = 3.8 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [see eqn. (ii)], reflecting a fairly high value of the mean capture cross-section (*ca.* 0.4 nm^2) at the mean relative translational energy of 40 meV for 298 K.

For $\text{C}(\text{P}_J) + \text{NO}(\text{X}^2\Pi_a)$, the situation with respect to electronic correlations is even more complicated. Now 36 states ($3^2\text{A}' + 3^2\text{A}'' + 3^4\text{A}' + 3^4\text{A}''$) correlate with the reagents. Fig. 5 shows the correlation diagram for reaction to both $\text{CN} + \text{O}$ and $\text{CO} + \text{N}$ products. (For some surfaces, the complex will be able to dissociate to both sets of products.) Despite the larger number of surfaces correlating with $\text{C}(\text{P}_J) + \text{NO}(\text{X}^2\Pi_a)$ compared with $\text{C}(\text{P}_J) + \text{O}_2(\text{X}^3\Sigma_g^-)$, a higher fraction of the surfaces lead adiabatically to exothermic products; indeed, as many as 18 states ($2^2\text{A}' + 2^2\text{A}'' + 4^4\text{A}' + 2^4\text{A}''$) correlate with $\text{CN}(\text{X}^2\Sigma^+) + \text{O}(\text{P}_J)$, and the same number to the weakly exothermic products $\text{CN}(\text{A}^2\Pi) + \text{O}(\text{P}_J)$. This may be why the rate constants for reaction (2) are approximately three times those for reaction (1). As pointed out earlier, the cross-sections for production of $\text{CN}(\text{X}^2\Sigma^+)$ in levels $v = 2, 3$ and 4 show the same dependence on relative translational energy, within experimental error. Furthermore, as $v = 5$ is the highest accessible level, it is certain that the experiments provide a good measure of the overall excitation function for the $\text{CN}(\text{X}^2\Sigma^+) + \text{O}(\text{P}_J)$ product channel. Bergeat *et al.*³² measured the branching ratio for production of $\text{N}(\text{D}) + \text{N}(\text{S})$ relative to $\text{O}(\text{P}_J)$ as 1.5 ± 0.3 at 298 K. It is impossible from our measurements to infer whether there is any change in the branching ratio into different chemical and electronic product states as the relative translational energy or temperature is altered.

The ACCSA rate constants $k_2(T)$, calculated with the thermal factor $P_2(T)$ given by eqn. (v), are lower than those measured in the CRESU experiments. This might indicate that reaction (2) proceeds on other potential energy surfaces besides the lowest one ($\text{CNO } ^2\Pi$). In this case, the thermal factor should take into account all the surfaces involved. In an attempt to address this problem, the capture cross-sections on each of the spin-orbit surfaces were computed (see Fig. 4). Whereas the $\text{C}(\text{P}_0) + \text{NO}(\text{X}^2\Pi_{1/2})$ surface has no barrier and yields a regular behaviour, *i.e.*, a $(\epsilon_{\text{tr}})^{\alpha}$ functionality for the

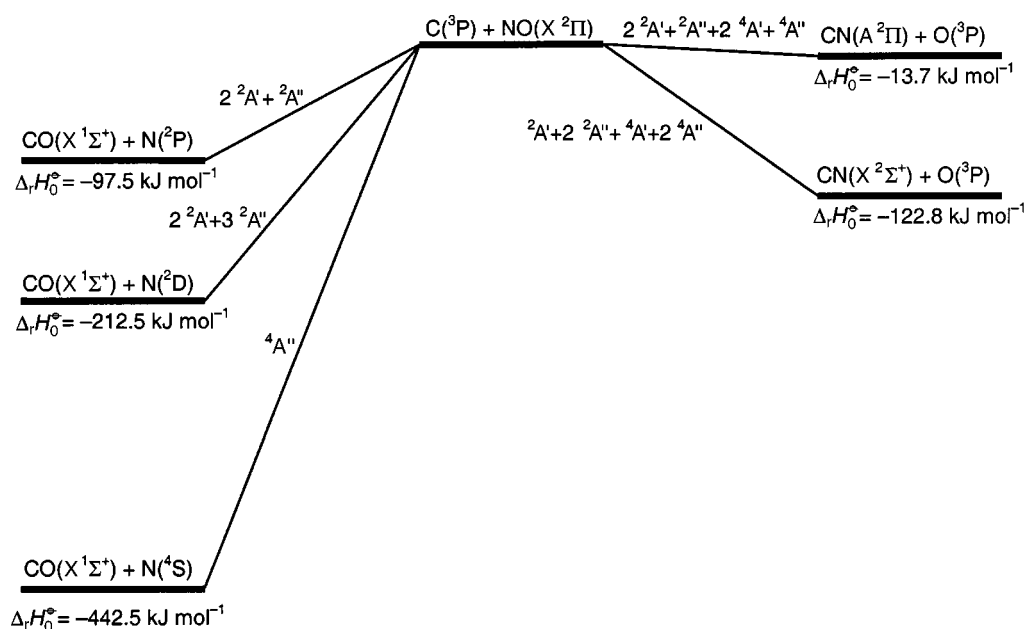


Fig. 5 Spin and orbital correlation diagram for $\text{C}(\text{P}_J) + \text{NO}(\text{X}^2\Pi_a)$.

capture cross-section, the other attractive surfaces originating from $C(^3P_1)$ or $C(^3P_2)$ have a weakly repulsive nature yielding excitation functions which exhibit a kinetic energy threshold in the 2–5 meV range. Two difficulties prevent us from calculating the rate constant $k_2(T)$ as an average of those on different spin–orbit surfaces. First, the usual capture functionality, $\sigma_{\text{reac}}(\epsilon_{\text{tr}}) \propto (\epsilon_{\text{tr}})^\alpha$, is valid only on the lowest surface, and second, the extent of non-adiabatic coupling between the different spin–orbit surfaces is unknown.

We note that the excitation function calculated for reaction on the $C(^3P_0) + \text{NO}(X^2\Pi_{1/2})$ surface exhibits a $(\epsilon_{\text{tr}})^{-1/3}$ functionality which differs from the $(\epsilon_{\text{tr}})^{-0.72}$ dependence found experimentally for the channel leading to $\text{CN}(X^2\Sigma^+) + \text{O}(^3P_J)$. However, it should be recalled that the crossed beam results were obtained with a constant $C(^3P_J)$ spin–orbit state distribution, and that capture results do not distinguish $\text{CN} + \text{O}$ and $\text{CO} + \text{N}$ product channels. A marked difference is nonetheless not expected, especially if one considers the fair agreement between the experimental kinetic and dynamic results.

In addition to differing in the distributions over the spin–orbit levels of the $C(^3P_J)$ atoms, the beam experiments and those performed at low temperatures in the CRESU apparatus differ in the distributions of the molecular reagent, O_2 or NO , over rotational levels. As stated earlier, LIF measurements of the NO rotational state distribution in the beam experiments showed that the rotational temperature over the lowest levels was < 12 K, and a similar distribution would be expected in beams containing O_2 . On the other hand, the reagent rotational distributions in the CRESU experiments were equilibrated with the translational temperature within each gas flow.

Overall, when capture rate coefficients are averaged over the appropriate Boltzmann rotational distributions, rotational effects are expected to give rise to a negative-temperature dependence, especially when the long-range attraction arising from dispersion forces and electrostatic forces between the non-symmetric charge distributions on the reagents is not dominant at all temperatures. For reactions (1) and (2), the mild temperature dependence observed for $k(T)$ and the agreement between the form of $k(T)$ which is determined in the kinetic experiments and that inferred from the beam experiments suggests that capture is dominated by the long-range forces and that, for reactions (1) and (2), there is no strong dependence of the rotationally selective rate constants on the rotational level N of the molecular reagent. This is indeed what was found in the ACCSA calculations presented in part (c) of the Results section and illustrated in Fig. 3.

The third and final factor that must be taken into account when considering the measured temperature dependence of $k(T)$ and that derived from the excitation functions is the lack of information about the reaction cross-sections at relative translational energies below *ca.* 4 meV. In integrating eqn. (i), it has been assumed that the values of the cross-sections continue to depend on $(\epsilon_{\text{tr}})^\alpha$, with the same values of α below 4 meV as above. For an excitation function that varies as $(\epsilon_{\text{tr}})^{-1}$, half of the contribution to the thermal rate constant, $k(T)$, would come from collisions with energies below $k_B T \ln 2$. Put another way, for a minimum relative translational energy of 4 meV, more than half of the contribution to the thermal rate constants comes from relative translational energies below 4 meV at temperatures ≤ 67 K.

Adiabatic capture theories suggest that, as the temperature approaches zero, capture is determined by the limiting long-range attraction between the two reagents. If this potential varies as R^{-6} , where R is the separation between the two species, then the cross-section for capture varies as $(\epsilon_{\text{tr}})^{-1/3}$ and the rate constant for capture varies as $T^{1/6}$. Certainly, one would expect the increase in the cross-section as the relative translational energy decreases to decelerate as the relative

translational energy falls towards zero. If the cross-sections for reactions (1) and (2) at low kinetic energies do actually vary in this way, then the rate constants derived making the assumption that the excitation function varies as $(\epsilon_{\text{tr}})^\alpha$ all the way to $\epsilon_{\text{tr}} = 0$ would be overestimated most at low temperatures. As a result the extent of the negative temperature dependence would be overestimated. This agrees with what is found but one must recall the absence of any allowance for the changing Boltzmann populations in the spin–orbit states of $C(^3P_J)$ and the rotational levels of O_2 and NO as the temperature is changed.

Summary and conclusions

This paper reports a comparison between the thermal rate constants for the reactions between $C(^3P_J)$ atoms and O_2 and NO measured between 298 and 15 K in a CRESU apparatus, and the excitation functions for the same two reactions measured at collision energies between *ca.* 4 and 100 meV in a crossed beam apparatus with rotatable pulsed beam sources. The excitation functions for both reactions are found to be accurately fitted by expressions of the form, $\sigma_{\text{reac}} \propto (\epsilon_{\text{tr}})^\alpha$, with $\alpha = -0.94$ for production of CO from reaction (1') between $C(^3P_J)$ and O_2 , and with $\alpha = -0.72$ for production of CN from reaction (2a) between $C(^3P_J)$ and NO . Using the simplest relationship between reaction cross-sections and thermal rate constants, the results of the molecular beam experiments were used to derive the temperature dependence of the rate constants, yielding $k_1(T) \propto T^{-0.44}$ and $k_{2a}(T) \propto T^{-0.22}$, results which are in fair agreement with the temperature dependence of the overall rate constants, k_1 and k_2 , obtained from the kinetic experiments.

The results of both sets of experiments demonstrate that these reactions occur across potential energy surfaces lacking any barrier between reagents and products. The assumptions underlying the use of eqn. (i) to relate reaction cross-sections to rate constants were carefully examined. Adiabatic capture calculations are also consistent with these experimental results. This agreement is attributed to the open-shell nature of the reactants. There remains, however, a major uncertainty, which we hope will prompt theoretical work in this area, *viz.*, the role of the spin and orbital correlation rules and electronic adiabaticity, when the reagents and products of reactions correlate with a multiplicity of potential energy surfaces.

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