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Kinetic studies of atomic carbon, $C[2p^2(^3P_J)]$, with small sulfur-containing molecules by time-resolved atomic resonance absorption spectroscopy in the vacuum ultra-violet

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Abstract

We present a kinetic investigation of the reaction of atomic carbon in its electronic ground, $C[2p^2(^3P_J)]$, with the small sulfur-containing molecules H_2S, OCS, SO_2 and CS_2 by time-resolved atomic spectroscopy in the vacuum ultra-violet following the generation of $C(2^3P_J)$ by the pulsed photolysis of C_3O_2. Decay profiles for atomic carbon were derived from resonance absorption at $\lambda = 166$ nm (3^3P_J–2^3P_J) using repetitive pulsing techniques coupled with signal averaging. Absolute rate data for the collisional removal of $C(2^3P_J)$ by these gases were obtained as follows: k_R (cm^3 molecule^{-1} s^{-1}, 300 K)—H_2S $2.5 \pm 0.6 \times 10^{-10}$, OCS $5.6 \pm 0.2 \times 10^{-11}$, SO_2 $9.7 \pm 0.3 \times 10^{-11}$ and CS_2 $1.6 \pm 0.4 \times 10^{-10}$. Rate data for the reaction of atomic carbon with the photochemical precursor, necessary as an absolute kinetic standard, were obtained yielding $k(C_3O_2) = 1.8 \pm 0.3 \times 10^{-10}$, in full agreement with previous investigations. The rate data in general were compared, where possible, with those derived from fast flow techniques and molecular beams for the particular case of H_2S where overall insertion has been demonstrated with the detection of HCS and where H atom abstraction would be endothermic. The results in general are considered within the context of C atom reactions with sulfur-containing species in the interstellar medium.

Keywords: Atomic carbon reactions; Time-resolved atomic absorption spectroscopy; Vacuum ultra-violet measurements; Pulsed photolytic initiation; Absolute rate data

1. Introduction

Fundamental collisional investigations of the reactions of atomic carbon in its $C[2p^2(^3P_J)]$ ground state is a large area of study that has been developed in recent years and has been extensively reviewed by Kaiser [1], particularly in the context of the interstellar medium (ISM) [2]. Indeed, ground state atomic carbon has now been detected in a wide range of astronomical environments and is particularly abundant in dense interstellar cloud [3–5]. These observations have been made by radio frequency measurements on the magnetic dipole-allowed transitions at 809.3435 GHz ($^3P_2$–$^3P_1$), and 492.1611 GHz ($^3P_1$–$^1P_0$) [6–8]. More recently, the $^3P_2$–$^3P_1$ transition for carbon-12 has been characterised in absorption using terahertz spectroscopy and yielding a frequency of 809.34197 GHz [9] which has been combined with recent astronomical observations [10]. Recent kinetic methods for characterising rate data for ground state atomic carbon include time-resolved atomic resonance absorption spectroscopy [11–20], the 'CRESU' method for extending investigations to the low temperatures of interstellar clouds [21–29], molecular beams [30–33] and also fast flow measurements to be considered later.

A wide range of sulfur-containing species including H_2S, OCS and SO_2 have been detected in the interstellar medium [34] but the outcome of reaction models to reproduce observed abundances is still unresolved [35–40]. There is now ample evidence from the foregoing that a variety of neutral–neutral reactions, including those of atomic carbon, have no significant activation barriers and are sufficiently rapid at low temperatures to contribute to the chemistry of the ISM. Rate constants for some reactions of $C(2^3P_J)$ have been found to be characterised by cross-sections comparable with those of the Langevin cross-sections for ion–molecule reactions. Clary *et al.* [17] who

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have presented a systematic study of absolute rate data for the reaction of $C(2^3P_J)$ with a wide range of mono-olefins and mono-acetylenes and which are seen to be in sensible accord with classical capture theory where the dominant term in the potential for reaction is governed by the isotropic dispersion term described using the standard C_6 coefficient [41]. Hence, the investigation of $C(2^3P_J)$ with sulfur-containing molecules in the interstellar medium and species related to these are of fundamental importance to this aspect of sulfur chemistry.

Kaiser and co-workers carried out an extensive investigation of the reaction between ground-state carbon atoms and H_2S under single-collision conditions using crossed molecular beams [34,42,43]. That study suggested that the reaction proceeds through the addition of $C(^3P_J)$ at the sulfur atom to form a triplet CSH_2 van der Waals complex. This is followed by H atom migration on the singlet/triplet surface to form a thiohydroxycarbene intermediate, HCSH, which then decomposes through a tight exit transition state into $HCS(X^2A') + H(^2S_{1/2})$. Galland *et al.* studied the $C + H_2S$ reaction, at room temperature in a low-pressure fast flow reactor using atomic resonance fluorescence and coupled with *ab initio* studies [44]. The transition structure leading to triplet HCSH was found to be lower in energy than the reactants, in agreement with the measured rate constant, which was found to be close to the gas kinetic limit. Rate measurements of atomic carbon at room temperature with OCS, SO_2 and H_2S have been reported earlier by Dorthe *et al.* [45]. The pseudo-first-order decay profiles of atomic carbon were determined from the decay of CS ultra-violet chemiluminescence $CS(a^3\Pi{-}^1\Sigma^+)$ produced by the $C + OCS$ reaction [45,46]. In the present investigation, measurements of absolute rate data are described for the reaction of $C(^3P_J)$ with OCS, SO_2, H_2S and CS_2 by time-resolved atomic resonance absorption spectroscopy in the vacuum ultra-violet following pulsed irradiation of C_3O_2 for which rate data are also characterised and used as a standard [16–20]. The results are compared, where possible, with data derived from previous techniques.

2. Experimental

The experimental method involving time-resolved atomic resonance absorption spectroscopy with photoelectric monitoring of $C(2^3P_J)$ in the vacuum ultra-violet following the pulsed irradiation of C_3O_2 has been described hitherto [16–20]. $C(2^3P_J)$ was produced from the photolysis of C_3O_2 in the presence of excess helium buffer gas using a coaxial lamp and vessel with the common high purity quartz "Spectrosil" wall ($\lambda > 160$ nm). The vacuum ultra-violet absorption spectrum of this molecule has been extensively characterised by Roebber and co-workers [47–49]. The spectrum includes a strong absorption system whose maximum lies at $\lambda = 158.7$ nm and extending to *ca.* $\lambda = 172$ nm. Strauss *et al.* [50] have presented a detailed study of the photodissociation dynamics of C_3O_2 at $\lambda = 157.6$ nm using a F_2 excimer laser and reported the relative yields of $C(2^3P_J)$ and $C(2^3D_2)$ as 97 and 3%, respectively, using laser-induced fluorescence on the atomic carbon. Thus, the present system will essentially be free from collisional relaxation into $C(2^3P_J)$ from the higher lying ^1D state. Further, the spin–orbit splitting in the ground state is small compared with kT at room temperature ($J = 0 \rightarrow 1$, 16.4 cm^{-1}; $1 \rightarrow 2$, 27.1 cm^{-1}) [51] and hence the ^3P ground state can be considered as a single entity from the collisional viewpoint. Repetitive pulsing (0.2 Hz, $E = 88$ J) was employed (0.2 Hz, $E = 88$ J) for the purpose of signal averaging on a slow flow system, kinetically equivalent to a static system. The resulting $C(2^3P_J)$ was then monitored in absorption by means of a microwave-powered atomic emission resonance source at $\lambda = 166$ nm (3^3P_J–2^3P_J) in the vacuum ultra-violet [52,53]. The resulting photoelectric signals were then amplified without distortion using a current-to-voltage converter [54] prior to transfer to the data handling and analysis system.

The photoelectric output from the current-to-voltage converter, representing the decay profiles for $C(2^3P_J)$, was captured with a transient digitiser (Digital Storage Adaptor, Thurlby DSA 524) interfaced to a computer and triggered at 0.2 Hz by a thyratron pulsing system. The resonance absorption signals were analysed using the standard Beer–Lambert law

$$I_{\mathrm{tr}}\,(\lambda = 166\,\mathrm{nm}) = I_0\,\exp(-\varepsilon cl) \tag{1}$$

where the symbols have their usual meaning, given the difficulty of constructing a "curve-of-growth" for $C(2^3P_J)$ [55]. The value of I_0 is automatically recorded in the digital storage adaptor. The first-order decay of the ground state atom is given by:

$$[C(2^3P_J)]_t = [C(2^3P_J)_{t=0}\exp(-k't) \tag{2}$$

Hence, we may write the transmitted light signal in the form:

$$I_{\mathrm{tr}} = I_0\,\exp(-A\,\exp(-k't)) \tag{3}$$

and subject the profiles to a computerised fit ("Origin", OriginLab Corporation, Northampton, USA) of this form to avoid the use of logarithms at the low degrees of light absorption by $C(2^3P_J)$. Nevertheless, even using relatively low energy for pulsed photolysis in this system, degrees of light absorption by $C(2^3P_J)$ in the range 10–20% are routinely recorded and analysed. The overall first-order decay coefficient of the atom, k', is the object of the profile analysis and from which the appropriate collisional rate data are subsequently obtained. Graphical presentation of the profiles employed the commercial program "Grapher" display program (Golden Software Inc., CO, USA).

2.1. Materials

C_3O_2 was prepared as hitherto [16–20]. He (BOC, 99.999%) and Kr (BOC, 99.995%) for the repetitive pulsed coaxial lamp were used directly from cylinders. C_2H_2 for the atomic resonance source (2% in He) (cylinder BOC) was degassed at −196 °C and distilled from −78 to −196 °C. H_2S (Distillers MG, 99%), OCS (Matheson, 99%), SO_2 (Aldrich, 99.9%) and CS_2 (Aldrich, 98%) were obtained commercially and degassed by freeze–pump–thaw cycles before use. It may be stressed again that neither excessively high levels of purity nor consideration of low levels of photolytic fragments are critical in this investigation where reactions of $C(2^3P_J)$ are found to proceed at the order of the respective collision numbers.

3. Results and discussion

The first-order rate coefficients, k', for $C(2^3P_J)$ were obtained from computerised non-linear least squares analysis of the decay profiles using Eq. (3) as described previously above [18,20], namely,

$$k' = k_1 f_1 p_T + k_2 f_2 p_T + \frac{\beta}{p_T} \quad (4)$$

where k_1 and k_2 represent absolute rate constants for the collisional removal of $C(2^3P_J)$ by the precursor, C_3O_2 and the added reactant gas, f_1 and f_2 the respective fractional compositions and p_T is the total pressure. The term β/p_T represents the diffusional loss. Eq. (4) can thus be recast in the form:

$$k' p_T = (k_1 f_1 + k_2 f_2) p_T^2 + \beta \quad (5)$$

and hence a plot of $k' p_T$ versus p_T^2 yields a straight line of slope $k_1 f_1 + k_2 f_2$. For the special case of $f_1 = f_2 = f = 4.0 \times 10^{-5}$, purely for convenience here where the values of k_1 and k_2 are of similar magnitude, Eq. (5) becomes

$$k' p_T = (k_1 + k_2) f p_T^2 + \beta \quad (6)$$

and hence the plot of $k' p_T$ versus p_T^2 thus yields in that case a straight line of slope $(k_1 + k_2)f$. The choice of the value f is constrained by both the overall rate of removal of $C(2^3P_J)$ within the accessible time scale of measurement and also by the attenuation of the atomic resonance transition at $\lambda = 166$ nm by the absorption continuum of the added reactant.

Fig. 1 shows examples of the raw data and the computerised fitting using Eq. (3) for the decay of $C(2^3P_J)$ following the repetitive pulsed irradiation of C_3O_2 ($\lambda > 160$ nm) in the presence of reactants (R), H_2S and OCS, in the presence of excess helium buffer gas with similar chosen values of f_1 and f_2 for C_3O_2 and R. Analogous profiles are shown in Fig. 2 for the decay of $C(2^3P_J)$ in the presence of SO_2 and CS_2, respectively. Figs. 3 and 4 of $k' p_T$ versus p_T^2 are shown for the removal of $C(2^3P_J)$ in the presence of the different reactants based on Eqs. (5) and (6) yielding $k_1 f_1 + k_2 f_2$. The values of k_2 require the value of k_1 for C_3O_2 derived from the slope of an analogous plot for a C_3O_2/He mixture shown in Fig. 5. The absolute second-order rate constant determined for the removal of $C(2^3P_J)$ by C_3O_2 was thus subsequently found to be $k_1(C_3O_2, 300\,K) = 1.8 \pm 0.3 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} and employed throughout this work. This is in full agreement with previous measurements (Table 1).

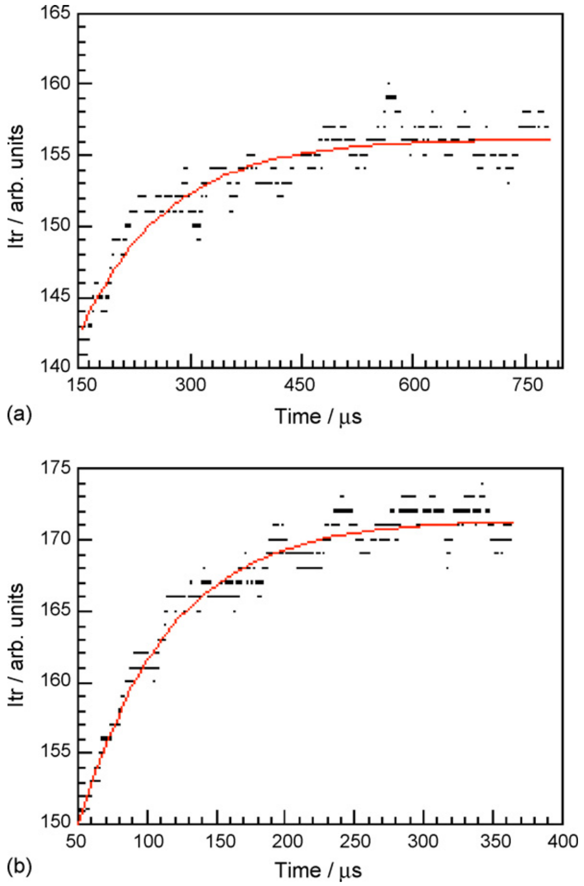

Fig. 1. Examples of computerised fitting indicating the first-order kinetic decays of $C(2^3P_J)$ obtained by time-resolved atomic resonance absorption spectroscopy in the vacuum ultra-violet $\{\lambda = 166\,\text{nm}, C[3s(^3P^0) \leftarrow 2p^2(^3P)]\}$ following the repetitive pulsed irradiation of C_3O_2 in the presence of (a) H_2S and (b) OCS (R) and excess helium buffer gas. $f_1 = [C_3O_2]/([C_3O_2] + [R] + [He])$, $f_2 = [R]/([R] + [C_3O_2] + [He])$; $E = 88$ J; repetition rate = 0.2 Hz; no. of experiments for averaging = 16; full curve given by Eq. (3).

R	f_1	f_2	p_T (Torr)
(a) H_2S	4.0×10^{-5}	4.0×10^{-5}	14.0
(b) OCS	4.0×10^{-4}	4.0×10^{-5}	17.0

In principle, the diffusion loss term β/p_T could be expressed in terms of the ‘long-time solution’ of the diffusion equation for a cylinder [56] (length l, radius r, where $l \gg r = 1$ cm). The diffusion coefficient D_{12}, for $C(2^3P_J)$ in He, which is excess, cannot be determined quantitatively with any reliability from the intercepts of the plots of the type shown in Figs. 3–5. On the basis of the “long-time solution” of the diffusion equation for a cylinder [55,56] ($k_{diff} = \beta/p_T = 5.81 D_{12}/r^2$ and $D_{12} = D^0_{12}/p_T$, where $r = 1$ cm) and using the reported estimate for $D_{12}[Si(3^3P_J)–He)] = 0.48 \pm 0.04$ cm^2 s^{-1} at 1 atm (300 K) of Basu and Husain [57] as that for $D_{12}[C(2^3P_J)–He)]$, the intercept β of plots of the kind shown in Figs. 3–5 should be of the order of 2×10^3 Torr s^{-1}. This can be compared with a range in the ordinates of *ca.* 2–3 $\times 10^5$ Torr s^{-1}.

All the rate data obtained in this part of the investigation are presented in Table 1. The value of the rate constant for the reaction between $C(^3P_J) + H_2S$ obtained in this study from the direct detection of the carbon atoms is found to be close to that reported in Dorthe’s later kinetic measurements [44] where the decay of the carbon atom resonance fluorescence signal was monitored. The earlier measurement employed chemiluminescence from electronically excited $CS(a^3\Pi–^1\Sigma^+)$ which is relatively long-lived (16 ± 3 ms [58]) and was comparable to those of the decay profiles for atomic carbon reported by Dorthe *et al.* [45] from the reaction of C + OCS. Removal by H_2S is seen to proceed at the order of the collision number. This appears to be surprising

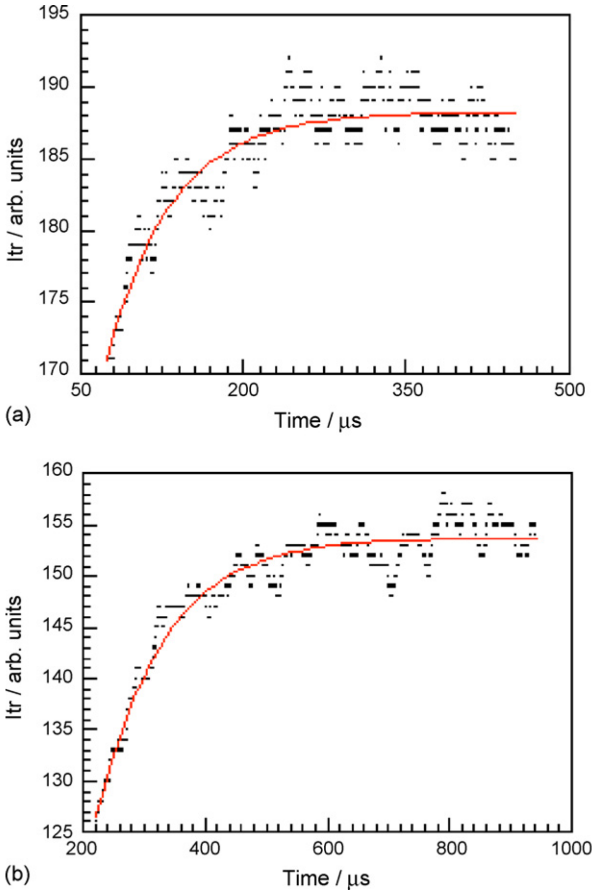

Fig. 2. Examples of computerised fitting indicating the first-order kinetic decays of $C(2^3P_J)$ obtained by time-resolved atomic resonance absorption spectroscopy in the vacuum ultra-violet {$\lambda = 166$ nm, $C[3s(^3P^0) \leftarrow 2p^2(^3P)]$} following the repetitive pulsed irradiation of C_3O_2 in the presence of (a) SO_2 and (b) CS_2 (R) and excess helium buffer gas. $f_1 = [C_3O_2]/([C_3O_2] + [R] + [He])$, $f_2 = [R]/([R] + [C_3O_2] + [He])$; $E = 88$ J; repetition rate = 0.2 Hz; no. of experiments for averaging = 16; full curve given by Eq. (3).

R	f_1	f_2	p_T (Torr)
(a) SO_2	4.0×10^{-5}	2.0×10^{-5}	20.0
(b) CS_2	4.0×10^{-5}	4.0×10^{-5}	21.0

at first sight as H-atom abstraction is endothermic:

$$C(^3P_J) + H_2S(X^1A_1) \rightarrow CH(X^2\Pi) + SH(X^2\Pi),$$
$$\Delta H = +43.2\ \text{kJ mol}^{-1} \qquad (7)$$

This strongly suggested the formation of the hitherto unobserved $HSC(X^2A')$ radical in the interstellar medium. One important conclusion, consistent with above measurements and calculations on $C + H_2S$, is the role of the effective overall insertion into the S–H bond following C atom addition,

$$C(^3P_J) + H_2S(X^1A_1) \rightarrow H_2SC$$
$$\rightarrow HCS(X^1A') + H(^2S_{1/2}), \quad \Delta H = -181\ \text{kJ mol}^{-1} \qquad (8)$$

The present result and that of Dorthe *et al.* [46] clearly support such effective insertion as calculated by Kaiser and coworkers [34,42,43] together with the observation of $HCS(X^2A')$ in molecular beams.

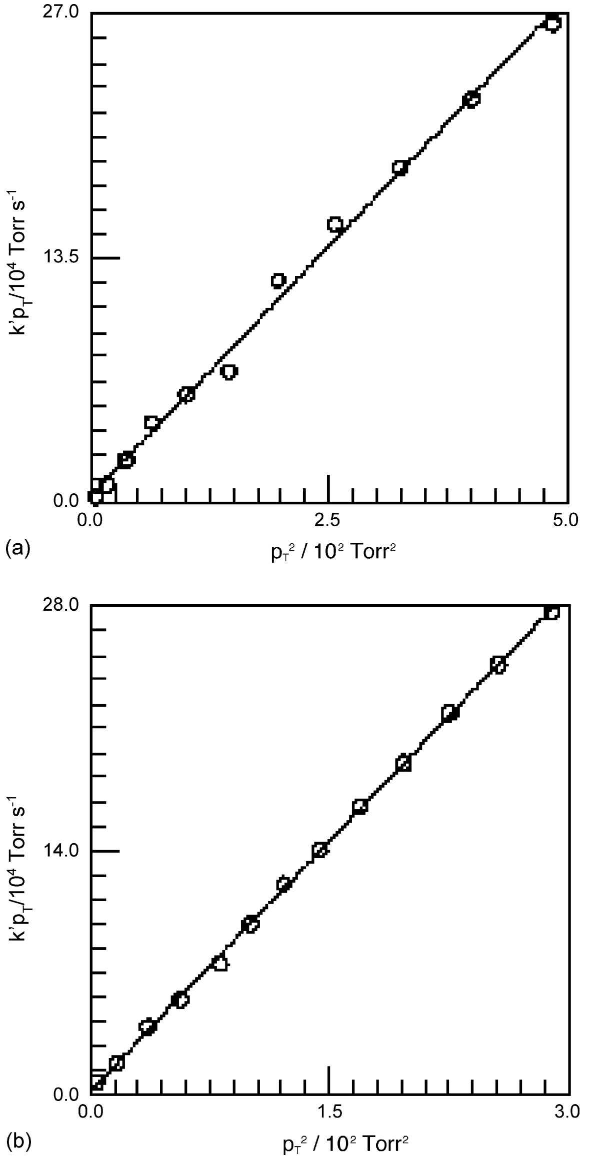

Fig. 3. Variation of the pseudo-first-order rate constant (k') for the decay of $C(2^3P_J)$ obtained by time-resolved atomic resonance absorption spectroscopy in the vacuum ultra-violet {$\lambda = 166$ nm, $C[3s(^3P^0) \leftarrow 2p^2(^3P)]$} following the repetitive pulsed irradiation of C_3O_2 in the presence of (a) H_2S and (b) OCS (R) and excess helium buffer gas. $k'p_T$ vs. p_T^2; $T = 300$ K; $f_1 = [C_3O_2]/([C_3O_2] + [R] + [He]) = 4.0 \times 10^{-5}$, $f_2 = [R]/([R] + [C_3O_2] + [He]) = 4.0 \times 10^{-5}$ for (a) and 4.0×10^{-4} for (b).

Neither beam studies on dynamics nor theoretical calculations have so far been performed on the reactions of atomic carbon with carbonyl sulfide or sulfur dioxide. As far as thermochemistry is concerned [59,60], the reaction channel,

$$C(^3P_J) + OCS(X^1\Sigma) \rightarrow CS(X^1\Sigma^+) + CO(X^1\Sigma^+),$$
$$\Delta H = -351.7\ \text{kJ mol}^{-1} \qquad (9)$$

is clearly favourable. The other possible reaction channel leading to $CS(a^3\Pi)$,

$$C(2^3P_J) + OCS(X^1\Sigma) \rightarrow CS(a^3\Pi) + CO(X^1\Sigma^+),$$
$$\Delta H = -20.3\ \text{kJ mol}^{-1} \qquad (10)$$

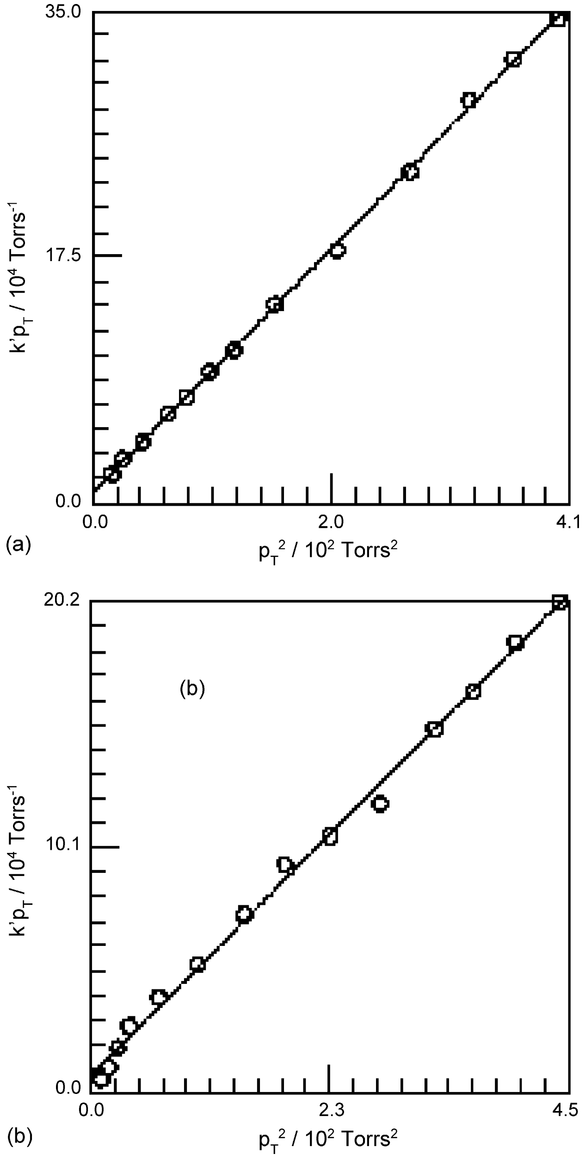

Fig. 4. Variation of the pseudo-first-order rate constant (k') for the decay of $C(2^3P_J)$ obtained by time-resolved atomic resonance absorption spectroscopy in the vacuum ultra-violet $\{\lambda = 166\,nm,\ C[3s(^3P^0) \leftarrow 2p^2(^3P)]\}$ following the repetitive pulsed irradiation of C_3O_2 in the presence of (a) SO_S and (b) CS_2 (R) and excess helium buffer gas. $k'p_T$ vs. p_T^2; $T = 300\,K$; $f_1 = [C_3O_2]/([C_3O_2] + [R] + [He]) = 4.0 \times 10^{-5}$, $f_2 = [R]/([R] + [C_3O_2] + [He]) = 2.0 \times 10^{-4}$ for (a) and 4.0×10^{-5} for (b).

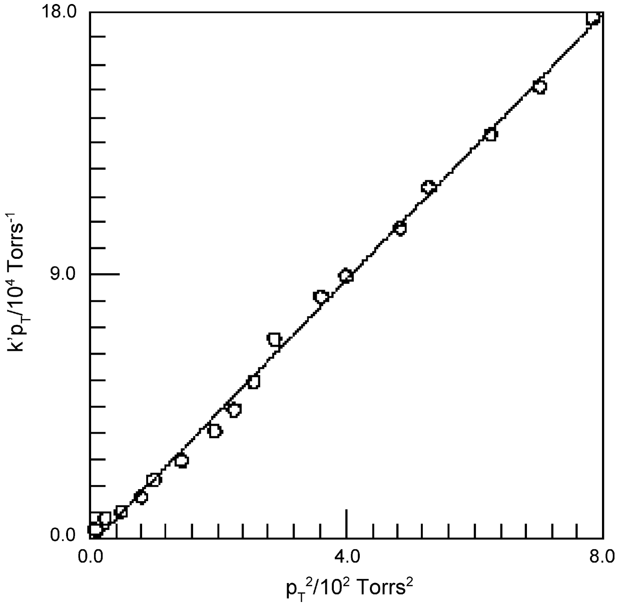

Fig. 5. Variation of the pseudo-first-order rate constant (k') for the decay of $C(2^3P_J)$ obtained by time-resolved atomic resonance absorption spectroscopy in the vacuum ultra-violet $\{\lambda = 166\,nm,\ C[3s(^3P^0) \leftarrow 2p^2(^3P)]\}$ following the repetitive pulsed irradiation of C_3O_2 in the presence of excess helium buffer gas. $k'p_T$ vs. p_T^2; $T = 300\,K$; $f = [C_3O_2]/([C_3O_2] + [He]) = 4.0 \times 10^{-5}$.

is thermodynamically less favourable in accord with the chemiluminescence measurements (Dorthe *et al.* [45]) where either none or a very small amount of $CS(a^3\Pi)$ was produced in the reaction.

The process,

$$C(2^3P_J) + SO_2(X^1A_1) \rightarrow CO(X^1\Sigma^+) + SO(X^3\Sigma^-),$$
$$\Delta H = -528.6\,kJ\,mol^{-1} \tag{11}$$

is highly favourable energetically and reaction is rapid as observed here (Table 1) and by Dorthe *et al.* [45]. Further, the reaction channel,

$$C(^3P_J) + CS_2(X^1\Sigma) \rightarrow CS(X^1\Sigma^+) + CS(X^1\Sigma^+),$$
$$\Delta H = -283.0\,kJ\,mol^{-1} \tag{12}$$

is also exothermic, whereas,

$$C(^3P_J) + CS_2(X^1\Sigma) \rightarrow CS(a^3\Pi) + CS(X^1\Sigma^+),$$
$$\Delta H = +54.6\,kJ\,mol^{-1} \tag{13}$$

Table 1
Absolute second-order rate constants, k_R ($cm^3\,molecule^{-1}\,s^{-1}$, 300 K), for the reactions of $C(2^3P_J)$ with sulfur containing and reference compounds by time-resolved atomic resonance absorption spectroscopy in the vacuum ultra-violet

	k_R ($cm^3\,molecule^{-1}\,s^{-1}$, 300 K)[a]
Sulfur compounds	
H_2S	$2.5 \pm 0.6 \times 10^{-10}$[b]
	$2.1 \pm 0.5 \times 10^{-10}$ [44]
	$8.3 \pm 1.8 \times 10^{-11}$ [45]
OCS	$5.6 \pm 0.2 \times 10^{-11}$[b]
	$1.0 \pm 0.7 \times 10^{-10}$ [45]
SO_2	$9.7 \pm 0.3 \times 10^{-11}$[b]
	$6.9 \pm 1.7 \times 10^{-11}$ [45]
CS_2	$1.6 \pm 0.4 \times 10^{-10}$[b]
Reference compound	
C_3O_2	$1.8 \pm 0.3 \times 10^{-10}$[b]
	$1.8 \pm 0.1 \times 10^{-10}$ [13]
	$1.8 \pm 0.2 \times 10^{-10}$ [19]

[a] Errors calculated at 95% confidence limits.

[b] This work.

is thermodynamically unfavourable (thermodynamic data [59,60]).

The only available kinetic data for the reaction of $C(^3P_J)$ with OCS and SO_2 with which the present results may be directly compared are those of Dorthe *et al.* [45] fast flow studies where indirect investigation was carried out by monitoring CS chemiluminescence ($a^3\Pi$–$X^1\Sigma^+$) with its limitations arising from the long life-time of $CS(a^3\Pi)$ described earlier. Those results for the rate data for C + OCS and C + SO_2 (Table 1) appear comparable with the results obtained here though the present result for k_R(C + OCS) is approximately two-fold slower in the case with carbonyl sulfide. To the best of our knowledge, there are no analogous rate data for the reaction of atomic carbon with CS_2 with which the present results may be compared. Overall, the rate data for the removal of atomic carbon with all the small sulfur-bearing molecules studied here at room temperature ($k = 5.6 \times 10^{-11}$ to 2.5×10^{-10} cm^3 molecule^{-1} s^{-1}; Table 1) are seen to be rapid. For such reactions there seem to be no significant energy barriers as already mentioned earlier and therefore, this, in fact, clearly suggests that these reactions should be temperature independent or very weakly dependent and hence should be rapid at the low interstellar temperatures. One can conclude, therefore, that the present rate measurements can be included in modelling of the interstellar medium where these sulfur bearing species have already been detected. However, it must be stressed here that further complementary investigations are clearly necessary, such as the determination of rate data at the low temperatures of the interstellar medium together with the detection of primary reaction products by molecular beam methods to include those of astrochemical importance, coupled with computational calculations of the energies of the appropriate intermediate sulfur-bearing species.

4. Conclusions

Absolute rate data for the collisional removal of atomic carbon in its $C(2^3P_J)$ electronic ground state with H_2S, OCS, SO_2 and CS_2 have been determined by time-resolved atomic spectroscopy in the vacuum ultra-violet following the generation of $C(2^3P_J)$ by the pulsed photolysis of C_3O_2 as has that of the reaction rate with the photochemical precursor, itself, used as a kinetic standard. The results were mainly compared, where possible, with those derived from fast flow techniques and showing sensible agreement. For the particular case of H_2S, where H atom abstraction would be endothermic, the observed rapid reaction supports overall effective insertion following C atom addition as has been demonstrated with the detection of HCS in molecular beam measurements.

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