

Kinetic investigation of reactions of atomic carbon, C[2p²(³P_J)], with simple nitrogen-containing molecules and aromatic heterocyclic compounds

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Abstract

The reactions of atomic carbon in its electronic ground state, C[2p²(³P_J)], with some simple nitrogen-containing molecules and aromatic heterocyclic compounds have been investigated by time-resolved atomic resonance absorption spectroscopy in the vacuum ultra-violet following the generation of C(2³P_J) by the pulsed photolysis of C₃O₂. Decay profiles for atomic carbon were derived from resonance absorption measurements at $\lambda = 166$ nm (3³P_J–2³P_J) using repetitive pulsing techniques coupled with signal averaging. Absolute rate data for the collisional removal of C(2³P_J) by these gases were obtained as follows: k_R (cm³ molecule⁻¹ s⁻¹, 300 K): NH₃ < 1.1 × 10⁻¹, 1-propanamine < 8.2 × 10⁻¹², 2-methylpyridine = 5.3 ± 0.6 × 10⁻¹⁰, 4-methylpyridine = 5.5 ± 0.2 × 10⁻¹⁰, 1-methylpyrrole = 2.3 ± 0.5 × 10⁻¹⁰, thiazole = 2.9 ± 0.2 × 10⁻¹⁰, oxazole = 2.4 ± 0.2 × 10⁻¹⁰ and isoxazole = 2.2 ± 0.3 × 10⁻¹⁰. The rate data were compared, where possible, with absolute rate data for analogous collision targets reported hitherto and considered within the context of the role of atomic carbon in the interstellar medium.

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1. Introduction

Many neutral–neutral reactions of atomic carbon in its C[2p²(³P_J)] ground state have been shown to be sufficiently rapid at low temperatures to contribute to the chemistry of the interstellar medium (ISM). For both fundamental and such applied reasons, kinetic methods for characterising absolute rate data of atomic carbon have been developed. These include time-resolved atomic resonance absorption spectroscopy [1–11], the ‘CRESU’ method for extending investigations to low temperatures [12–20], molecular beams [21–24] and also spectroscopic observations on fast flow systems [25–27]. Chemical models of dark interstellar clouds indicate that N₂ should be present in these regions and predict a ratio of N₂ to H₂ of about 10⁻⁵ [28–30]. Recently, interstellar N₂ has been detected in the far-ultraviolet of the star HD 124314 in the constellation of Centaurus yielding fractional abundances of N₂/H₂ = 3.3 × 10⁻⁷

[31], similar to those estimated from N₂H⁺ observations of dark molecular clouds [29]. This, in fact provides some support for the hypothesis that the most nitrogen-containing compounds observed in the interstellar medium (ISM) were synthesised from N⁺ ion produced by direct cosmic ray ionisation of N₂ [32].

Ammonia (NH₃) was the first polyatomic molecule detected in the ISM and, since its initial discovery by Cheung et al. [33], NH₃ has proved to be an invaluable spectroscopic tool in the study of the ISM [34]. Among the many problems in this context is the variability of the HNC/HCN abundance ratio in interstellar clouds [35–38]. The reaction channels from C + NH₃ are considered to participate in the formation and destruction of both HCN and HNC in interstellar models [39–41]. Though no detailed investigations of the reaction of C(2³P_J) with NH₃ at 300 K have been performed, attempts at studying the reaction at different temperatures have been reported [42–45]. Shevlin and co-workers [43,44] used thermal C atoms extracted from an arc discharge as the source of carbon and the carbon vapour, assumed to include C(¹D) atoms on energetic grounds, was co-condensed with NH₃ on a cold (77 K) surface and products analysed by classical methods. It was reported that methyleneimine

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and HCN were initial products. In other studies, chemiluminescent reactions of $C(^3P)$ atoms and $C^+(^2P)$ ions with NH_3 at hyperthermal energies were investigated in the 12–1000 eV energy range, the typical range of the so-called “hot-atom reactions”, using a beam/gas arrangement [42]. The fast carbon atoms were generated from $C^+(^2P)$ ions by near-resonant charge transfer with CCl_4 . The reaction products $NH(A^3\Pi)$, $CN(B^2\Delta)$, and $CH(A^2\Delta)$ were studied mainly by means of the $NH(A-X)$, $CN(B-X)$, and $CH(A-X)$ emission spectra. From the foregoing, the need for a direct kinetic investigation of $C(^3P_J)$ with NH_3 , which is, indeed, one of the objectives of the present investigation, is apparent.

Recent compilations of species detected in interstellar clouds and circumstellar envelopes include large organic species with molecules containing up to 13 atoms [46,47]. Earlier kinetic measurements on the reactions of ground state carbon atoms with aromatic ring compounds containing N, O and S atoms have been reported using atomic resonance absorption in the vacuum ultra-violet [1,2]. This is developed further in the present investigations yielding absolute rate data for reaction of $C(^3P_J)$ with these targets and with all processes taking place at the order of the collision number, and essentially independent of small substituents on the rings. Comparison of the present results is made with those from analogous investigations of carbon atom reactions with simpler aromatic target reagents. Comparison is further made with absolute rate data reported previously for the reactions of $C(^3P_J)$ with sulphur-containing targets of the type RSH [11,48]. Those rapid processes support the initial addition of $C(^3P_J)$ to the S atom followed by H atom migration to yield overall insertion. This is in contrast with the present investigations using small nitrogen-containing molecules where reactions with atomic carbon are relatively slow.

2. Experimental

The experimental arrangement for studying time-resolved atomic resonance absorption spectroscopy of $C(^3P_J)$ in the vacuum ultra-violet has been described hitherto [1,4,7,8,10,11,48]. $C(^3P_J)$ was generated from the repetitive, pulsed photolysis ($\lambda > 160$ nm) of C_3O_2 in the presence of excess helium buffer gas in a coaxial lamp and vessel assembly constituting part of a slow flow system, kinetically equivalent to a static system. The spectrum of C_3O_2 includes a strong absorption system whose maximum lies at $\lambda = 158.7$ nm and extending to ca. $\lambda = 172$ nm [49–51]. Photodissociation of C_3O_2 at $\lambda = 157.6$ nm using an F_2 excimer laser has been shown to generate relative yields of $C(^3P_J)$ and $C(^1D_2)$ of 97 and 3%, respectively [52]. Thus, the present system will essentially be free from collisional relaxation into $C(^3P_J)$ from the higher lying 1D state. The $C(^3P_J)$ ground state can be considered as a single entity from the collisional viewpoint on account of the small spin-orbit splittings involved [53]. $C(^3P_J)$ was monitored in absorption at $\lambda = 166$ nm ($3^3P_J-2^3P_J$) using the microwave-powered emission source [54,55]. The resulting photoelectric signals were then amplified without distortion [56] and transferred to the data handling and analysis systems.

The resonance absorption signals were analysed using the standard Beer–Lambert law

$$I_{tr}(\lambda = 166 \text{ nm}) = I_0 \exp(-\epsilon cl) \quad (1)$$

coupled with the first-order decay of the ground state atom

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

to yield the transmitted light signals in the form:

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

The resulting profiles were then subject to a computerised fit (“Origin” OriginLab Corporation, Northampton, USA) from which the overall first-order decay coefficient of the atom, k' , is extracted 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 described hitherto [1,4,7,10,11,48]. He (BOC, 99.999%) and Kr (BOC, 99.995%) (for the repetitively pulsed coaxial lamp) were used directly from cylinders. C_2H_2 (cylinder BOC) was degassed at -196°C and distilled from -78 to -196°C . Ammonia (BOC, 99%) was degassed at -196°C before use. The liquid chemicals were obtained commercially (Aldrich Chemical Company) and degassed by freeze-pump-thaw cycles before use: 1-propanamine (98% GC), 2-methylpyridine (98%), 4-methylpyridine (98% GC), 1-methylpyrrole (99% GC), thiazole (99%), oxazole (98%), and isoxazole (99%). As indicated earlier [11,48], with liquid reactants whose vapours were required, these were also initially pumped at room temperature, sacrificing a fraction of the liquid in order to achieve improved degassing. It may be stressed again, that neither excessively high levels of purity nor consideration of low levels of photolytic fragments are normally critical in this investigation where rates of $C(^3P_J)$ are mostly found to proceed at the order of the respective collision numbers.

3. Results and discussion

The kinetic procedure and analysis have been described hitherto [10,11,48]. Decay profiles for $C(^3P_J)$ were recorded by monitoring the atomic resonance signals at $\lambda = 166$ nm following the pulsed irradiation of a single flow of a mixture of fixed composition of C_3O_2 + reactant + He at varying total pressures (p_T). Thus, the kinetic loss term for the diffusional removal of $C(^3P_J)$ at the walls of the reactor, which is inversely proportional to the total pressure, is permitted to vary. In fact, it will be seen that the collisional removal of $C(^3P_J)$ by the nitrogen containing reagents here and the precursor, C_3O_2 itself dominate the overall kinetic removal. With this procedure, the initial photochemical yields of $C(^3P_J)$ resulting from the varying initial concentrations of C_3O_2 are also permitted to vary. The first-order kinetic decays only require relative atomic densities as a function of time, and the low initial atomic concentrations

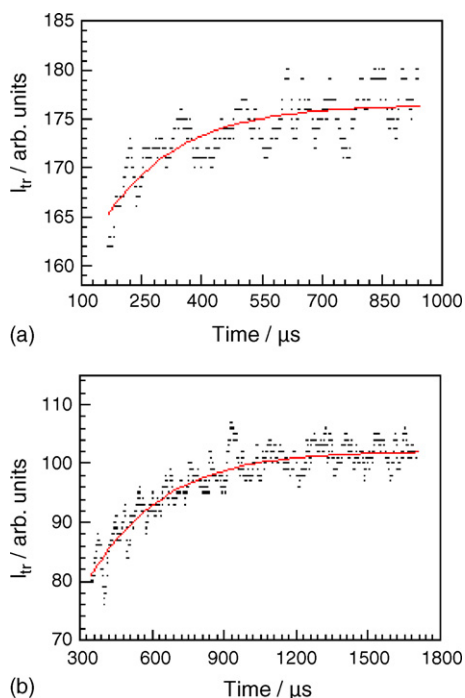


Fig. 1. Examples of computerized fitting indicating the first-order kinetic decays of $C(2^3P_1)$ obtained by time-resolved atomic resonance absorption spectroscopy in the vacuum ultra-violet ($\lambda = 166$ nm, $C[3s(3^3P^0) \leftarrow 2p^2(3^3P)]$) following the repetitive pulsed irradiation of C_3O_2 in the presence of ammonia, 1-propanamine (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; number of experiments for averaging = 16; full curve given by Eq. (3).

R	f_1	f_2	p_T (Torr)
(a) Ammonia	4.0×10^{-5}	2.0×10^{-4}	30.0
(b) 1-Propanamine	4.0×10^{-5}	2.0×10^{-4}	12.0

can still be monitored across a useful concentration range with the present data handling system. For characterisation of the absolute rate constant for the reaction of $C(2^3P_1)$ with a given reactant such as ammonia, for a example, a mixture of fixed composition of the form $f_1 = [C_3O_2]/([C_3O_2] + [NH_3] + [He])$ and $f_2 = [NH_3]/([NH_3] + [C_3O_2] + [He])$ was prepared where He is in excess.

Fig. 1(a) and (b) give examples of the raw data (I_{tr} versus time) and the computerised fitting of the kinetic decay profiles for $C(2^3P_1)$ to the form of Eq. (3) following the pulsed irradiation of C_3O_2 ($\lambda > 160$ nm) in the presence of ammonia and 1-propanamine, respectively, and excess helium buffer gas. The principal source of signal noise arises from the standard variation in the intensity of the microwave-powered atomic emission source [10]. A series of such profiles was thus recorded using different total pressures of this mixture of defined fractional compositions. The first-order rate coefficients, k' , for $C(2^3P_1)$ in Fig. 1 are hence obtained from computerised non-linear least squares analysis of the form of Eq. (3) and can be written as,

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

k_1 and k_2 represent absolute rate constants for the collisional removal of $C(2^3P_1)$ by the precursor, C_3O_2 , and ammonia in this instance, and the term (β/p_T) , diffusional loss. The present analysis involves the use of the value of k_1 determined by this method, i.e., $k_1(C_3O_2, 300\text{ K}) = 1.8 \pm 0.3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [10,11,48] which is in excellent agreement with the value reported earlier by Husain and co-workers [4,9] and which will be used for further analyses. The values of f_1 and f_2 , the latter, in turn, reflecting the concentrations of the added reactant, ammonia in the present initial example, are preferably chosen so that $k_1 f_1$ and $k_2 f_2$ are of comparable magnitudes. When the rate constants k_1 and k_2 are similar, and of the order of the collision numbers as seen in terms of the above value of k_1 , these two conditions are conveniently satisfied by preparing mixtures where $f_1 = f_2 = f$ which is the case with some reactants here. Thus, Eq. (4) can be recast in the form,

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

For the special case of $f_1 = f_2 = f$ ($= 4.0 \times 10^{-5}$ later here) Eq. (5) becomes,

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

and hence a plot of $k' p_T$ versus p_T^2 thus yields a straight line of slope $(k_1 + k_2)f$ according to the Eq. (6) or $(k_1 f_1 + k_2 f_2)$ according to Eq. (5) when $f_1 \neq f_2$ as with the case of ammonia and 1-propanamine.

Fig. 2(a) and (b) show the plots for C_3O_2 + ammonia and 1-propanamine of $k' p_T$ versus p_T^2 based on Eq. (5). From the above value of k_1 for C_3O_2 coupled with the values of f_1 and f_2 where $f_1 = 4.0 \times 10^{-5}$ and $f_2 = 2.0 \times 10^{-4}$, these slopes yield the values of k_2 , in these cases, upper limits. As will be subsequently seen in a more quantitative manner, the values of k_2 for ammonia and 1-propanamine can only be reported as upper limits as the reaction rates of $C(2^3P_1)$ with these molecules are slow. Clearly, in such cases, the values of $k_1 f_1$ and $k_2 f_2$ are not of comparable magnitudes. Ideally, one would like to increase the values of f_2 for these reactants to improve the quality of the limits. In practice, this is not feasible as increasing the pressures of ammonia and 1-propanamine causes attenuation of the resonance source at $\lambda = 166$ nm by significant light absorption at this wavelength by the reactants, themselves. Normally, the study of the rates of reactions of $C(2^3P_1)$ is restricted to processes that are relatively rapid with this type of system.

Profiles of raw data of $I_{tr}(\lambda = 166 \text{ nm})$ analogous to those in Fig. 1 together with the computerised fittings of the decay profiles for $C(2^3P_1)$ following the repetitive pulsed irradiation of C_3O_2 ($\lambda > 160$ nm) in the presence of 2-methylpyridine, 4-methylpyridine, 1-methylpyrrole, thiazole, oxazole, isoxazole and excess helium buffer gas were recorded. Analogous plots to those in Fig. 2 are presented in Figs. 3–5 for these added gases where the values of k_2 were obtained from resulting slopes $(k_1 + k_2)f$. All values of second order rate constants for reaction of $C(2^3P_1)$ with the gases studied here are listed in Table 1. Notwithstanding the variation in the emission intensity of the microwave-powered atomic source (Fig. 1), the plots of $k' p_T$ versus p_T^2 are constructed on the basis of weighted least squares

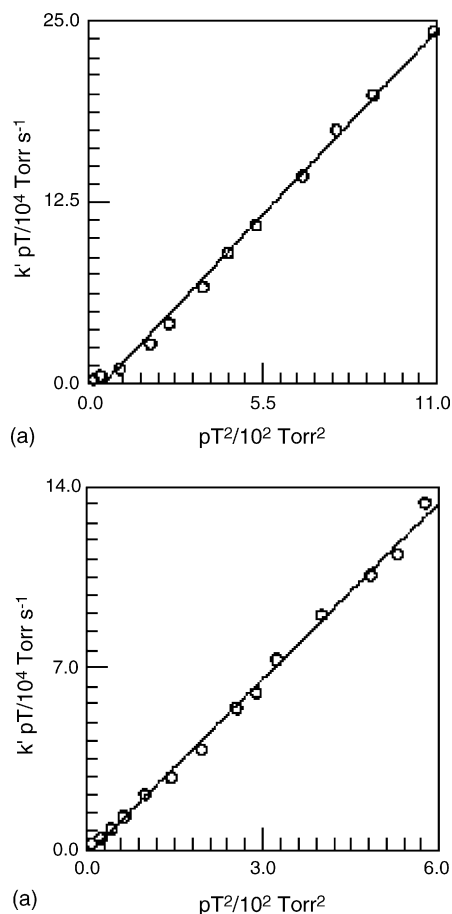


Fig. 2. Variation of the pseudo-first-order rate constant (k') for the decay of $C(2^3P_1)$ obtained by time-resolved atomic resonance absorption spectroscopy in the vacuum ultra-violet ($\lambda = 166$ nm, $C[3s(3^3P^0) \leftarrow 2p^2(3^3P)]$) following the repetitive pulsed irradiation of C_3O_2 in the presence of ammonia, 1-propanamine (R) and excess helium buffer gas. $k'p_T$ versus p_T^2 ; $T = 300$ K; $f_1 = [C_3O_2]/([C_3O_2] + [R] + [He]) = 4.0 \times 10^{-5}$, $f_2 = [R]/([R] + [C_3O_2] + [He]) = 2.0 \times 10^{-4}$; (a) ammonia; (b) 1-propanamine.

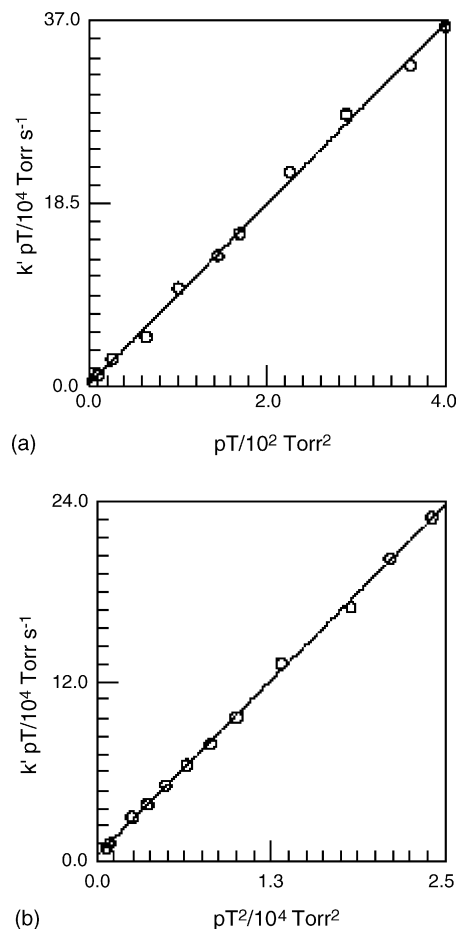


Fig. 3. Variation of the pseudo-first-order rate constant (k') for the decay of $C(2^3P_1)$ obtained by time-resolved atomic resonance absorption spectroscopy in the vacuum ultra-violet ($\lambda = 166$ nm, $C[3s(3^3P^0) \leftarrow 2p^2(3^3P)]$) following the repetitive pulsed irradiation of C_3O_2 in the presence of 2-methylpyridine, 4-methylpyridine (R) and excess helium buffer gas ($T = 300$ K); $f_1 = f_2 = f = 4.0 \times 10^{-5}$; $k'p_T$ vs. p_T^2 . (a) 2-Methylpyridine; (b) 4-methylpyridine.

Table 1

Absolute second-order rate constants, for the reactions of $C(2^3P_1)$ with nitrogen containing and analogous compounds by time-resolved atomic resonance absorption spectroscopy in the vacuum ultra-violet

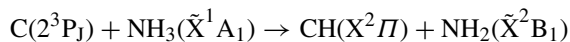
Reactant	k_R ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, 300 K) ^{a,b}
NH ₃	$<1.1 \times 10^{-11a}$
1-Propanamine	$<8.2 \times 10^{-12a}$
Benzene	$4.8 \pm 0.3 \times 10^{-10}$ [2] $2.8 \pm 0.8 \times 10^{-10}$ [64]
Pyridine	$4.8 \pm 0.3 \times 10^{-10}$ [1]
Toluene	$5.5 \pm 0.3 \times 10^{-10}$ [2]
2-Methylpyridine	$5.3 \pm 0.6 \times 10^{-10a}$
4-Methylpyridine	$5.5 \pm 0.2 \times 10^{-10a}$
Pyrrole	$2.0 \pm 0.1 \times 10^{-10}$ [1]
1-Methylpyrrole	$2.3 \pm 0.5 \times 10^{-10a}$
Thiophene	$3.0 \pm 0.2 \times 10^{-10}$ [1]
Thiazole	$2.9 \pm 0.2 \times 10^{-10a}$
Furan	$2.3 \pm 0.2 \times 10^{-10}$ [47]
Oxazole	$2.4 \pm 0.2 \times 10^{-10a}$
Isoxazole	$2.2 \pm 0.3 \times 10^{-10a}$

^a This work.

^b Errors calculated at 95% confidence limits.

analyses (experimental) and the quoted errors represent confidence limits of 95% for the rapid reactions but not, of course, for the upper limits. On the other hand, the contribution to diffusional loss by the term β/p_T cannot be determined quantitatively with any reliability from the intercepts of plots of the type shown in Figs. 2–5. The magnitude of β can be estimated using the long-time solution of the diffusion equation for a cylinder [57,58]. Using the reported estimate for $D_{12}[\text{Si}(3^3P_1)\text{-He}] = 0.48 \pm 0.04 \text{ cm}^2 \text{ s}^{-1}$ at 1 atm (300 K) of Basu and Husain [59] as that for $D_{12}[C(2^3P_1)\text{-He}]$, β should be the order of $2 \times 10^3 \text{ Torr s}^{-1}$ [11]. This can be compared with a range in the ordinates in Figs. 2–5 of ca. $2 \times 10^5 \text{ Torr s}^{-1}$.

To the best of our knowledge there are no rate data available for the reactions of $C(2^3P_1)$ with NH₃ and alkyl amines at room temperature. The hydrogen atom abstraction processes with NH₃



$$\Delta_R H = +114.3 \text{ kJ mol}^{-1}$$

and all the alkyl amines are highly endothermic and therefore hydrogen abstraction is very unlikely to take place with

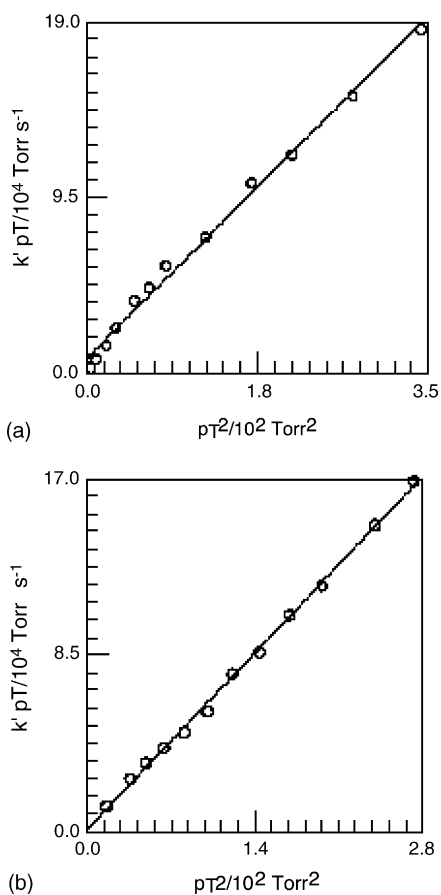


Fig. 4. Variation of the pseudo-first-order rate constant (k') for the decay of $C(2^3P_J)$ obtained by time-resolved atomic resonance absorption spectroscopy in the vacuum ultra-violet ($\lambda = 166 \text{ nm}$, $C[3s(3P^0) \leftarrow 2p^2(3P)]$) following the repetitive pulsed irradiation of C_3O_2 in the presence of 1-methylpyrrole, thiazole (R) and excess helium buffer gas ($T = 300 \text{ K}$); $f_1 = f_2 = f = 4.0 \times 10^{-5}$; k'_{pT} vs. pT^2 . (a) 1-Methylpyrrole; (b) thiazole.

ground state carbon atoms with such molecules [60]. In this study, for NH_3 and 1-propanamine, no significant reaction of $C(2^3P_J)$ could be detected over the pressure range of the added gas studied. Upper limits have therefore been placed on the reaction rate constants of $C(2^3P_J)$ with NH_3 and 1-propanamine of 1.1×10^{-11} and $8.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively. These estimates are based on the minimum increase in k' which could be detected under the present experimental conditions. Nevertheless, the upper limit of k_2 for $C(2^3P_J) + NH_3$ is considered a particularly important result within the context of astrochemistry for reasons described above. It clearly constrains the nature of interstellar models of $C(2^3P_J)$ with nitrogen-containing species as it places a limit on the reaction rate of this simple molecule, which would necessarily occur, early in an overall mechanism. The upper limit of the reaction rate of $C(2^3P_J) + 1$ -propanamine is also of use as it appears to eliminate rapid overall insertion of atomic carbon into the NH bond following initial addition in contrast to analogous reactions with H_2S and thiols [11,48].

The reaction of $C(2^3P_J)$ with benzene has been studied extensively both in terms of experiment and theory. Room temperature kinetic measurements by Haider and Husain [2] showed

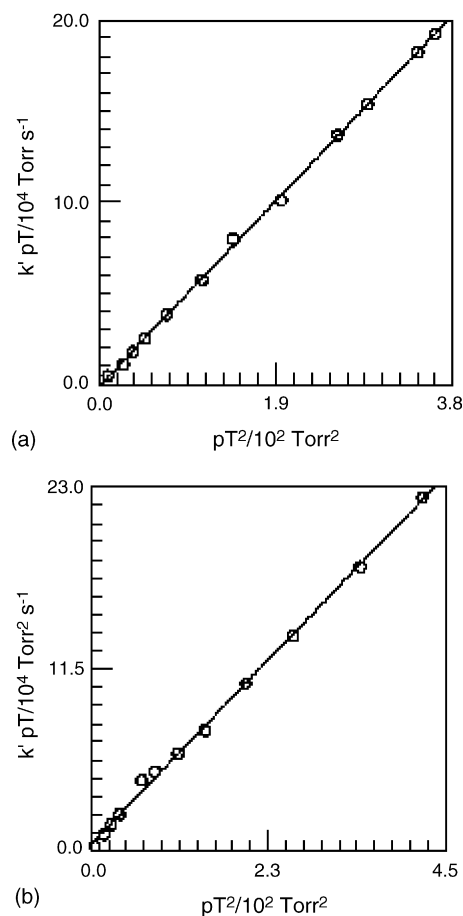


Fig. 5. Variation of the pseudo-first-order rate constant (k') for the decay of $C(2^3P_J)$ obtained by time-resolved atomic resonance absorption spectroscopy in the vacuum ultra-violet ($\lambda = 166 \text{ nm}$, $C[3s(3P^0) \leftarrow 2p^2(3P)]$) following the repetitive pulsed irradiation of C_3O_2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

that the reaction of benzene with carbon was very fast (i.e., $k_R(C_6H_6, 300 \text{ K}) = 4.8 \pm 0.3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) and obtained the same value for the reaction of $C(2^3P_J)$ with pyridine demonstrating highly attractive potentials with no subsequent barriers to reaction in both cases. The same authors investigated the reaction of carbon with toluene where the reaction rate found to be higher than with benzene. The reaction of atomic carbon with benzene (C_6H_6 ; $1A_{1g}$) has been studied extensively, under single-collision conditions in crossed beam experiments [61,62], theoretically [62,63] and via flow studies at room temperature [64]. The dynamics were investigated at collision energies between 8.8 and 52.5 kJ mol^{-1} showing that atomic carbon adds barrier-less to the π -system to form a weakly stabilized intermediate [65]. The benzene ring opens via a small barrier of about only 4 kJ mol^{-1} to a seven-membered ring intermediate followed by an H atom ejection to give a 1,2-didehydro-drocycloheptatrienyl radical C_7H_5 (X^2B_1) in a reaction without an exit barrier.

In this study, the same trend was observed when investigating the reaction of $C(2^3P_J)$ with 2-methylpyridine and 4-methylpyridine though no effect was observed for isomerism (Table 1). The rate of atomic carbon with 1-methylpyrrole was

found to be similar to that of pyrrole indicating that the attack of $C(2^3P_J)$ would be into the π electron system as observed with benzene under molecular beam conditions and from theoretical studies. This general effect is further observed in this study when the reaction rate of $C(2^3P_J)$ with thiazole is found to be comparable with that of thiophene. Similarly, the reaction rates of $C(2^3P_J)$ with oxazole and isoxazole are comparable with that of furan. This suggests that the heteroatoms in these cyclic aromatic compounds do not play a prominent role in the initial part of the mechanism.

All the rate data obtained in this study and analogous data available are listed in Table 1 for comparison. Overall, a new body of kinetic data are presented for the reactions of $C(2^3P_J)$ with simple nitrogen-containing molecules and aromatic heterocyclic compounds, further extending the already well-established carbon atom insertion into unsaturated and aromatic systems. These results, in fact, may provide important information to formulate basic mechanisms of atomic addition to complex unsaturated ring systems and to generalise concepts on how complex molecules can be synthesised in the interstellar medium.

4. Conclusions

Absolute rate data for the collisional removal of atomic carbon in its $C(2^3P_J)$ electronic ground state are reported for ammonia, 1-propanamine and some aromatic heterocyclic nitrogen-containing compounds by time-resolved atomic resonance absorption spectroscopy. The results for ammonia and 1-propanamine only yielded upper limits, constrained by the experimental method itself, of less than ca. one in ten collisions in each case, H-atom abstraction being endothermic. These results are contrasted with reactions of $C(2^3P_J)$ with thiols, investigated previously, where H-atom abstraction is also endothermic but where reactivity proceeds rapidly in every case, close to those of the collision numbers, and consistent with overall C atom insertion into the S–H bond which is energetically favourable. Reaction $C(2^3P_J)$ of with 2-methylpyridine, 4-methylpyridine, 1-methylpyrrole, thiazole, oxazole and isoxazole proceeds essentially at every collision in each case, consistent with analogous measurements on unsubstituted aromatic rings, especially benzene, itself, where ring insertion has been demonstrated. The results are considered in the context of the chemistry of the interstellar medium, particularly the upper limit for the reaction rate of $C(2^3P_J) + NH_3$.

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