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Collisional removal of atomic carbon, $C[2p^2(^3P_J)]$, by aldehydes and ketones, investigated by time-resolved atomic resonance absorption spectroscopy in the vacuum ultra-violet

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Abstract

A kinetic study is presented of the collisional removal of ground state atomic carbon, $C[2p^2(^3P_J)]$, with various aldehydes and ketones in the gas phase following pulsed irradiation. The atomic carbon was generated by the photolysis of C_3O_2 ($\lambda >$ ca. 160 nm) in the presence of excess helium buffer gas and the added reactant gases in a slow flow system, kinetically equivalent to a static system, and monitored photoelectrically by time-resolved atomic resonance absorption spectroscopy in the vacuum ultra-violet at $\lambda = 166$ nm ($3^3P_J \leftarrow 2^3P_J$) using signal averaging techniques. Absolute second-order rate constants (k_R/cm^3 molecule^{-1} s^{-1}, 300 K) for the removal of $C(2^3P_J)$ with these reactants were found to be as follows: formaldehyde $6.2 \pm 0.3 \times 10^{-10}$; acetaldehyde $5.4 \pm 0.3 \times 10^{-10}$; propionaldehyde $4.1 \pm 0.3 \times 10^{-10}$; *n*-butyraldehyde $6.6 \pm 0.3 \times 10^{-10}$; pentanal $4.6 \pm 0.2 \times 10^{-10}$; hexanal $5.3 \pm 0.4 \times 10^{-10}$; acetone $5.9 \pm 0.3 \times 10^{-10}$; butanone $5.1 \pm 0.2 \times 10^{-10}$; 2-pentanone $3.8 \pm 0.2 \times 10^{-10}$; and 3-pentanone $4.6 \pm 0.1 \times 10^{-10}$. No significant monotonic variation is thus observed in the rate data within these series of collisional processes where, from the similarity in the observed results, it is concluded that reaction is dominated by attack on the carbonyl group. The large values of these rate constants indicate that reactions of $C(2^3P_J)$ with aldehydes and ketones, some of which have been observed by radio frequency spectroscopy in interstellar clouds and considered to be generated initially by hot atom reactions, are sufficiently rapid to be included in modelling of the interstellar medium. ©1999 Elsevier Science S.A. All rights reserved.

Keywords: Atomic carbon, $C(2^3P_J)$); Collisional removal; Gas phase reactions; Time-resolved atomic resonance absorption spectroscopy; Vacuum ultra-violet; Reaction rates with aldehydes and ketones

1. Introduction

Laboratory investigation of the collisional behaviour of atomic carbon in its $C[2p^2(^3P_J)]$ electronic ground state with organic molecules has been stimulated in recent years by the inclusion of its reactions with hydrocarbons, in particular, in interstellar modelling [1–4]. Absolute rate constants for many reactions of $C(2^3P_J)$ with unsaturated organic molecules, determined primarily by time-resolved atomic resonance absorption spectroscopy in the vacuum ultra-violet [5–11], have been found to be characterised by cross sections comparable with those of the Langevin cross sections for ion-molecule reactions and thus are sufficiently rapid at the low densities and temperatures of interstellar clouds. Clary et al. [11] have described a classical capture theory for the reactions of $C(2^3P_J)$ with olefins and acetylenes where the dominant term in the potential energy surface is governed by the isotropic dispersion term described using the standard C_6 coefficients [12]. An extensive range of observations on $C[2p^2(^3P_J)]$ in the interstellar medium have been reported using the magnetic dipole-allowed transitions between the closely spaced spin orbit components ($J = 0$, 0; $J = 1$, 16.4 cm^{-1}; $J = 2$, 43.4 cm^{-1}) [13]. The spin orbit splittings have been characterised at high resolution by laser magnetic resonance [14,15] and the Einstein A_m coefficients calculated by Nussbaumer [16] and Garstang [17]. Thus, radio frequency observations have been made at 809.3435 GHz ($^3P_2$–$^3P_1$) and 492.1611 GHz ($^3P_1$–$^3P_0$) [18–23] and have been employed to map atomic carbon in the interstellar medium. More recently, the $^3P_2$–$^3P_1$ transition for carbon-12 has been characterised even more precisely in absorption using a terahertz spectrometer yielding a frequency of 809.34197 GHz [24] and which was combined with

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astronomical observations [25]. Analogous measurements have also been reported for the transitions in carbon-13, including nuclear hyperfine structure [24]. Such accuracy is significant as astronomically observed line shapes are combined with dynamical models of interstellar clouds.

The very detailed paper by Smith and co-workers on the temperature dependence of the reactions of $C(2^3P_J)$ with O_2, C_2H_2, C_2H_4 and C_3H_6 using the 'CRESU' method, where low temperatures are achieved in a flow system by isentropic expansion [26], may be taken as a modern review on the range of experimental methods that have now been developed in the laboratory for the study of the collisional behaviour of atomic carbon in its electronic ground state. That paper, where $C(2^3P_J)$ was monitored using the molecular chemiluminescence from $NO(B^2\Pi–X^2\Pi)$ resulting from the reaction of $C + NO_2$, together with accounts given in earlier papers from this laboratory [9–11,27], will thus be taken as the experimental background to the present manuscript. In the present paper, we describe the measurement of absolute rate data for the reactions of $C(2^3P_J)$ with a range of aldehydes and ketones. Interstellar observations have been observed for a number of molecular microwave transitions for molecules such as formaldehyde, acetaldehyde and acetone [28–30]. Roessler has reviewed a range of laboratory measurements for reactions of translationally energised ^{11}C, derived from nuclear recoil, with H_2O in the solid, liquid and gaseous phases, including the production of CH_2O, in order to simulate cometary conditions [31]. Formaldehyde was observed directly on the reactions of $C + H_2O$ for the solid and liquid phases and where, from the vapour phases, its production was concluded on a mechanistic basis and considered to be metastable under the prevailing experimental conditions [31]. $C(2^3P_J)$ was generated in the present measurements by pulsed irradiation of C_3O_2 and monitored by time-resolved atomic resonance absorption spectroscopy in the vacuum ultra-violet. A new body of absolute rate data are presented for the collisional removal of atomic carbon with aldehydic and ketonic organic targets. Reaction rates are all found to be very rapid, clearly of magnitudes comparable to those of the collision numbers. No monotonic variation of the absolute second-order rate constants with molecular size was observed from which it is concluded that reaction is dominated by attack on the carbonyl group.

2. Experimental

The experimental method for generating $C(2^3P_J)$ from the pulsed irradiation of C_3O_2 and monitoring this ground state atom in the vacuum ultra-violet by time-resolved atomic resonance absorption spectroscopy has been described previously [5,6,27]. Photolysis of C_3O_2 in the presence of excess helium buffer gas was thus carried out using a coaxial lamp and vessel with the common high purity quartz 'Spectrosil' wall ($\lambda > 160$ nm). Smith et al. [26] have presented a range of photodissociation channels thermodynamically accessible on photolysis at $\lambda = 193$ nm following Anderson and Rosenfeld [32]. The vacuum ultra-violet absorption spectrum of C_3O_2 which exhibits a strong absorption system whose maximum lies at $\lambda = 158.7$ nm, of particular relevance to the present investigation, has been extensively characterised by Roebber and co-workers [33–35]. Thus, various photolytic investigations in the vacuum ultra-violet have been reported [36–38] of which that by Strauss et al. [39], who have presented a detailed study of the photodissociation dynamics of C_3O_2 at $\lambda = 157.6$ nm using an F_2 excimer laser, is especially relevant here in terms of the low wavelength cut-off by Spectrosil quartz ($\lambda > 160$ nm) used in the present coaxial lamp and vessel reactor assembly. It was thus demonstrated that the relative yields of $C(2^3P)$ and $C(2^1D_2)$ were 97 and 3%, respectively, using laser-induced fluorescence on the atomic carbon and thus the present system will be essentially free from collisional relaxation into $C(2^3P_J)$ from the higher lying ^1D state. Repetitive photolytic pulsing in the Schumann region was employed (0.2 Hz, $E = 88$ J) for the purpose of signal averaging [5,6,27] using the present slow flow system, kinetically equivalent to a static system.

$C(2^3P_J)$ was monitored in absorption by means of a microwave-powered atomic emission resonance source at $\lambda = 166$ nm $(3^3P_J–2^3P_J)$ [40,41] optically isolated using a 1 m concave grating vacuum monochromator and monitored by means of a 'solar-blind' photomultiplier. The photoelectric output from the current-to-voltage converter used for photoelectric amplification of the time-resolved resonance absorption signals for $C(2^3P_J)$ was captured with a transient digitiser ('Digital Storage Adaptor, Thurlby DSA 524) interfaced to a computer [27]. After the capture of 16 individual decay profiles for $C(2^3P_J)$, this number being limited principally by the reproducibility by the pulsed irradiation source, the data were averaged and transferred to a computer by a commercial programme. As hitherto [27], the resonance absorption signals were analysed using the standard Beer–Lambert law of $I_{tr}(\lambda = 166\,\text{nm}) = I_0 \exp(-\epsilon cl)$. I_0 and I_{tr} are the unattenuated and attenuated photoelectric signals for $\lambda = 166$ nm, $c = [C(2^3P_J)]_t$, varying with time, and where the other symbols have their usual meaning. The value of I_0 is automatically recorded on the digital storage adapter and the first-order decay of the ground state atom is given by $[C(2^3P)]_t = [C(2^3P)]_{t=0} \exp(-k't)$. The transmitted light signals may thus be written as $I_{tr} = I_0 \exp(-A \exp(-k't))$ and subjected to a computerised fit of this form to avoid the use of logarithms at the low degrees of light absorption by $C(2^3P_J)$ necessarily involved in this type of measurement. k', the overall first-order decay coefficient of the atom, 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 programme (Golden Software, Colorado, USA) as previously [27]. The He buffer gas, Kr for the repetitively pulsed coaxial lamp and C_3O_2 were prepared as described previously [5,6,27]. Low pressures of formaldehyde were prepared by heating paraformaldehyde (Sigma, 95%) under vacuum in the standard manner. The remaining aldehydic and ketonic reactants were obtained commercially and degassed by freeze–pump–thaw cycles before use (Aldrich): acetaldehyde (99%), propionaldehyde (97%), *n*-butyraldehyde (99%), pentanal (valeraldehyde, 97%), hexanal (98%), acetone (99%), butanone (99%), 2-pentanone (97%) and 3-pentanone (97%). It may be stressed, as hitherto [27], that neither excessively high levels of purity nor consideration of low levels of photolytic fragments are critical in this investigation where reaction rates of $C(2^3P_J)$ are found to proceed at the order of the respective collision numbers.

3. Results and discussion

Decay profiles for $C(2^3P_J)$ 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) as described previously [5,6,27]. Thus, the kinetic loss term for the diffusional removal of $C(2^3P_J)$ at the walls of the reactor and whose functional form is clear, namely, inversely proportional to the total pressure, is permitted to vary. In fact, it will be seen that the collisional removal of $C(2^3P_J)$ by the aldehydic and ketonic reagents here dominates the overall kinetic removal so that diffusional removal in the excess helium buffer gas is small and barely detectable. It must be stressed, as hitherto [5,6,27], that, with this procedure, the photochemical yields of $C(2^3P_J)$ resulting from the varying initial concentration 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 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 $C(2^3P_J)$ with a given reactant such as formaldehyde, for example, a mixture of fixed composition of the form $f_1 = [C_3O_2]/([C_3O_2] + [\text{formaldehyde}] + [\text{He}])$ and $f_2 = [\text{formaldehyde}]/([\text{formaldehyde}] + [C_3O_2] + [\text{He}])$ is prepared where He is in excess.

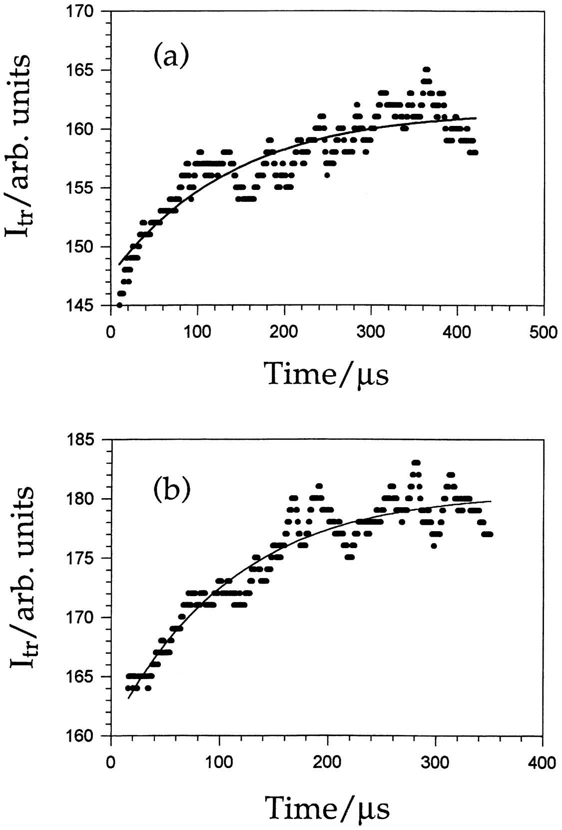

Fig. 1. Examples of the computerised fitting of the kinetic decay profiles of $C(2^3P_J)$ obtained by time-resolved atomic resonance absorption spectroscopy in the vacuum ultra-violet $\{\lambda = 166\,\text{nm}, C[(3s(^3P^0)] \leftarrow C[2p^2(^3P)]\}$ following the repetitively pulsed irradiation of C_3O_2 ($\lambda > 160$ nm) in the presence of formaldehyde and hexanal reactants (R) and excess helium buffer gas. $f_1 = [C_3O_2]/([C_3O_2] + [R] + [He]) = f_2 = [R]/([R] + [C_3O_2] + [He]) = 4.0 \times 10^{-5}$; $E = 88$ J, Repetition rate = 0.2 Hz. No. of experiments for averaging = 16. Full curve: $I_{tr} = I_0 \exp(-A(\exp - k't))$. (a) R = Formaldehyde, p(Total)/Torr = 9.0, (b) R = Hexanal, p(Total)/Torr = 12.0.

Fig. 1 (a) and (b) gives examples of the raw data (I_{tr} vs. time) and the computerised fitting of the kinetic decay profiles for $C(2^3P_J)$ to the above form obtained by time-resolved atomic resonance absorption spectroscopy in the vacuum ultra-violet $\{\lambda = 166\,\text{nm}, C[(3s(^3P^0)] \leftarrow C[2p^2(^3P)]\}$ following the repetitively pulsed irradiation of C_3O_2 ($\lambda > 160$ nm) in the presence of formaldehyde and hexanal, the lightest and heaviest aldehydic reactants, and excess helium buffer gas. The principal source of signal noise arises from the microwave-powered atomic emission source [27]. A series of such profiles were thus recorded using different total pressures of these mixture of defined fractional compositions. The first-order rate coefficients, k', for $C(2^3P_J)$ in Fig. 1(a) and (b) are thus obtained from computerised analysis of the form $I_{tr}(\lambda = 166\,\text{nm}) = I_0 \exp(-A \exp(-k't))$ and can be written as

$$k' = \beta/p_T + k_1 f_1 p_T + k_2 f_2 p_T \qquad (1)$$

where the rate constants k_1 and k_2 are now in units of $\text{Torr}^{-1}\,\text{s}^{-1}$. In the case of Fig. 1(a), 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 formaldehyde in this instance, and the term β/p_T, diffusional loss. The present analysis involves the use of k_1 which has been determined previously essentially by the present method using the combination of a transient recorder with transfer of data to a computer [5,7] yielding $k_1(C_3O_2, 300\,\text{K}) = (1.8 \pm 0.10) \times 10^{-10}\,\text{cm}^3\,\text{molecule}^{-1}\,\text{s}^{-1}$. Husain and Young [42] reported $k_1(C_3O_2, 300\,\text{K}) = (1.8 \pm 0.20) \times 10^{-10}\,\text{cm}^3\,\text{molecule}^{-1}\,\text{s}^{-1}$ employing a totally different technique for analysis of the photoelectric signals representing the resonance absorption decay profiles, namely

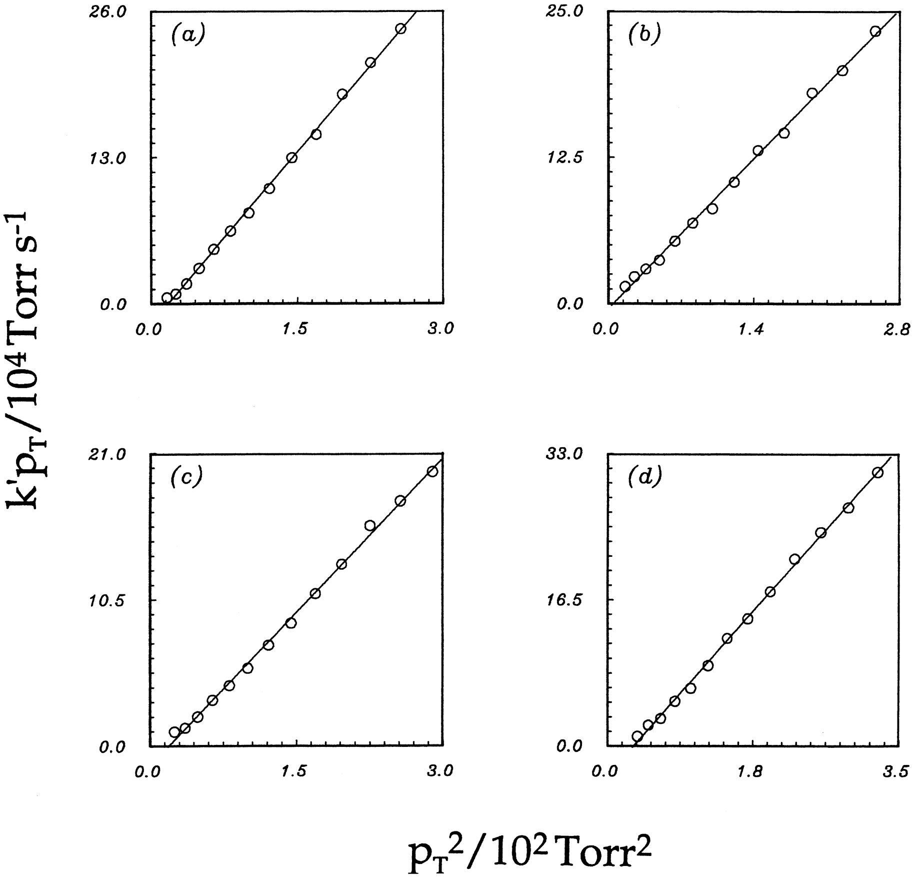

Fig. 2. Variation of the pseudo-first-order rate coefficient (k') for the decay of C(2^3P_J) obtained by time-resolved atomic resonance absorption spectroscopy in the vacuum ultra-violet {$\lambda = 166$ nm, C[(3s($^3P^0$)] $\leftarrow$ C[2p^2(^{3}P)]} following the repetitively pulsed irradiation of C_3O_2 in the presence of the reactants (R): (a) Formaldehyde, (b) Acetaldehyde, (c) Propionaldehyde and (d), *n*-Butyraldehyde and excess helium buffer gas. $f_1 = [C_3O_2]/([C_3O_2] + [R] + [He]) = f_2 = [R]/([R] + [C_3O_2] + [He]) = 4.0 \times 10^{-5}$; $k'p_T$ versus $p_T{}^2$. $T = 300$ K.

using a rapid response precision logarithmic amplifier with output to a signal averager and yielding a result in excellent agreement with the later variation of the present method [5,7]. k_2 in general is thus determined by difference using a variant of Eq. (1).

It can thus be seen that two practical criteria of concentrations need to be satisfied in the present type of measurement. The concentrations of C_3O_2, controlled via the value of f_1 at a given total pressure, p_T, need to be sufficiently high to yield concentrations of C(2^3P_J) which can be monitored by resonance absorption but sufficiently low to ensure that the decay profiles are accessible to the time-scales convenient with the present electronic systems. Further, the values of f_1 and f_2, the latter, in turn, reflecting the concentrations of the added reactant, formaldehyde in the present initial example, are chosen so that k_1f_1 and k_2f_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 each reactant here. Thus, Eq. (1) can thus be recast in the form

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

For the special case of $f_1 = f_2 = f$ (=4.0 × 10^{-5} here) Eq. (2) becomes

$$k'p_T = \beta + (k_1 + k_2) f p_T^2 \qquad (3)$$

and hence a plot of $k'p_T$ versus $p_T{}^2$ thus yields a straight line of slope $(k_1 + k_2)f$.

Fig. 2 shows the plots for C_3O_2 + formaldehyde, acetaldehyde, propionaldehyde and *n*-butyraldehyde of $k'p_T$ versus $p_T{}^2$ based on Eq. (3). From the above value of k_1 for C_3O_2 [5,7,42] coupled with the chosen value of $f = 4.0 \times 10^{-5}$, these slopes (Fig. 2(a)–(c)) yield the values of k_2, namely, k_2(formaldehyde, 300 K) = $(6.2 \pm 0.3) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, k_2(acetaldehyde, 300 K) = $(5.4 \pm 0.3) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, k_2(propionaldehyde, 300 K) = $(4.1 \pm 0.3) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} and k_2(*n*-butyraldehyde, 300 K) = $(6.6 \pm 0.3) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. Fig. 3 shows analogous plots to those in Fig. 2 with the aldehydic reactants pentanal and hexanal where it is found that k_2(pentanal, 300 K) = $(4.6 \pm 0.2) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} and k_2(hexanal, 300 K) = $(5.3 \pm 0.3) \times 10^{-10}$ cm^3

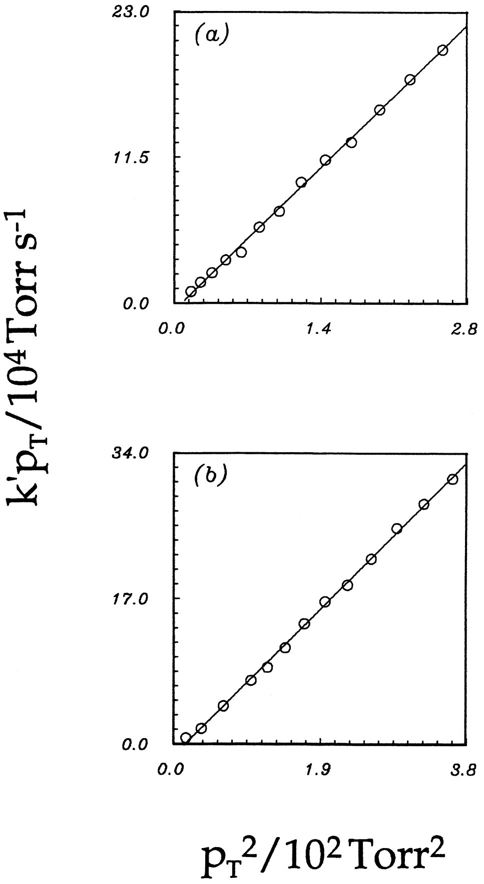

Fig. 3. Variation of the pseudo-first-order rate coefficient (k') for the decay of $C(2^3P_J)$ obtained by time-resolved atomic resonance absorption spectroscopy in the vacuum ultra-violet $\{\lambda = 166\,nm, C[(3s(^3P^0)] \leftarrow C[2p^2(^3P)]\}$ following the repetitively pulsed irradiation of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

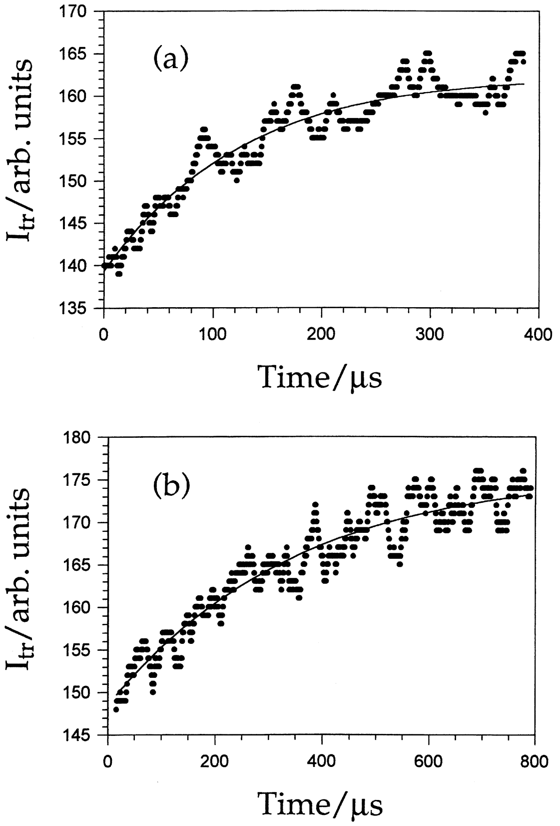

Fig. 4. Examples of the computerised fitting of the kinetic decay profiles of $C(2^3P_J)$ obtained by time-resolved atomic resonance absorption spectroscopy in the vacuum ultra-violet $\{\lambda = 166\,nm, C[(3s(^3P^0)] \leftarrow C[2p^2(^3P)]\}$ following the repetitively pulsed irradiation of C_3O_2 ($\lambda > 160\,nm$) in the presence of the reactants (R) acetone and 3-pentanone reactants and excess helium buffer gas. $f_1 = [C_3O_2]/([C_3O_2] + [R] + [He]) = f_2 = [R]/([R] + [C_3O_2] + [He]) = 4.0 \times 10^{-5}$; $E = 88\,J$, Repetition rate = 0.2 Hz, No. of experiments for averaging = 16. Full curve: $I_{tr} = I_0 \exp(-A(\exp -k't))$. (a) R = Acetone, p(Total)/Torr = 9.0, (b) R = 3-Pentanone, p(Total)/Torr = 6.0.

molecule^{-1} s^{-1}. 2σ errors are quoted from the slopes of the plots. The true errors are difficult to assess though the linearity in the plots such as those in Fig. 2 based on Eq. (3) indicate that the values of k_2 are reliable to better than 10%. Further, the errors in the intercepts, representing diffusional loss are greater. In principle, the values of the intercepts, β, could be used to estimate the diffusion coefficient, D_{12}, of carbon atoms in helium, the principle gas present, using the ‘long-time solution’ of the diffusion equation for a cylinder [43,44]. Unfortunately, $D_{12}\{C(2^3P_J)/He\}$ cannot be determined quantitatively with any reliability from the intercepts of plots such as those in Fig. 2 or in time-resolved kinetic measurements on $C(2^3P_J)$ of the present type in general where collisional removal is dominant, if only by the C_3O_2 precursor. As with previous time-resolved kinetic measurements on $C(2^3P_J)$ using resonance absorption [5–11], a value of $D_{12}(C(2^3P_J)–He)$ can be approximated using the value of $D_{12}(Si(3^3P_J)–He)) = 0.48 \pm 0.04\,cm^2\,s^{-1}$ at 1 atm. (300 K) reported by Basu and Husain [45]. This, coupled with the geometry of the cylindrical reactor [43,44] ($r = 1\,cm$, $l = 30\,cm$) can be used to yield an estimate β, namely, 2×10^3 Torr s^{-1}. This estimated intercept based on Eq. (3) can be compared with the magnitudes of the ordinates of plots of the type given in Figs. 2 and 3 which reach values 3×10^5 Torr s^{-1}, demonstrating the dominance of collisional removal of $C(2^3P_J)$ in the present investigation.

Fig. 4(a) and (b) show analogous examples to those in Fig. 1 of the raw data and the computerised fitting of the kinetic decay profiles for $C(2^3P_J)$ following the repetitively pulsed irradiation of C_3O_2 ($\lambda > 160\,nm$) in the presence of acetone and 3-pentanone, the lightest and heaviest ketonic reactants, and excess helium buffer gas. Analogous plots to those given in Figs. 2 and 3 are presented in Fig. 5 of $k'p_T$ versus $p_T{}^2$ for the removal of $C(2^3P_J)$ by acetone, butanone, 2-pentanone and 3-pentanone. Using the procedure described above, the slopes of these plots yield the absolute second-order rate constants, k_2/cm^3 molecule^{-1} s^{-1} (300 K), for the removal of $C(2^3P_J)$

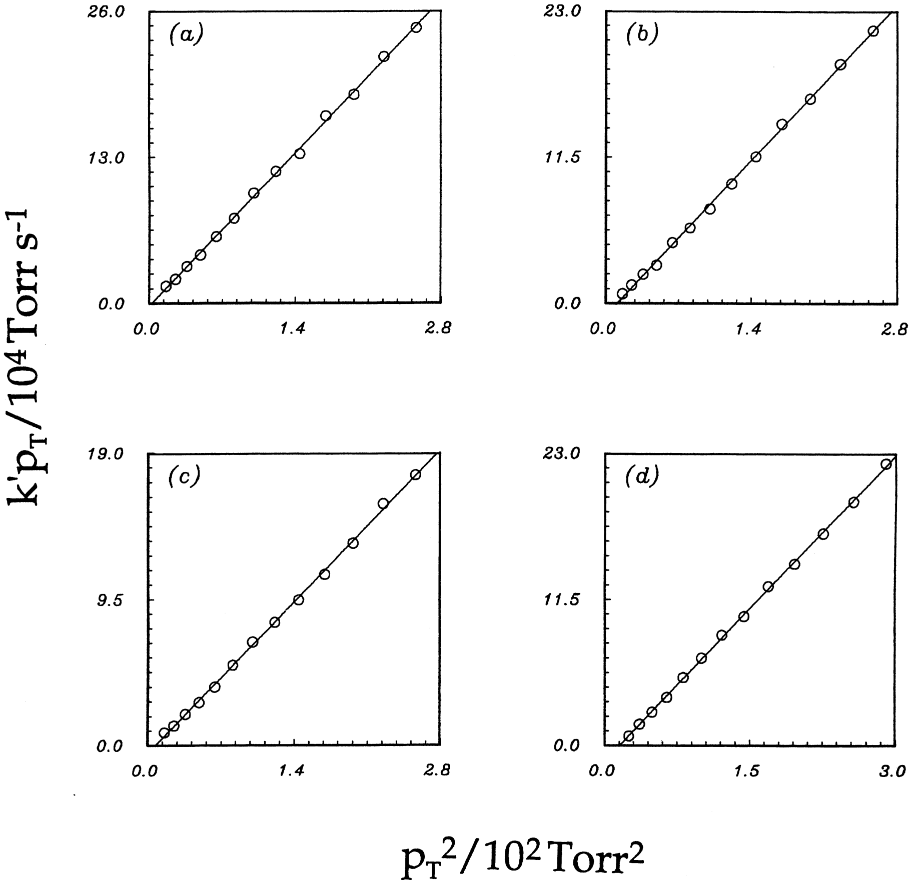

Fig. 5. Variation of the pseudo-first-order rate coefficient (k') for the decay of C(2^3P_J) obtained by time-resolved atomic resonance absorption spectroscopy in the vacuum ultra-violet $\{\lambda = 166\,\text{nm}, \text{C}[(3s(^3P^0)] \leftarrow \text{C}[2p^2(^3P)]\}$ following the repetitively pulsed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

Table 1
Absolute second-order rate constants, k_R/cm^3 molecule^{-1} s^{-1} (300 K), for the collisional removal of C(2^3P_J) by various aldehydes and ketones (R) determined by time-resolved atomic resonance absorption spectroscopy in the vacuum ultra-violet following pulsed irradiation

Reactant (R)	k_R/cm^3 molecule^{-1} s^{-1} (300 K)
Formaldehyde	$6.2 \pm 0.3 \times 10^{-10}$
Acetaldehyde	$5.4 \pm 0.3 \times 10^{-10}$
Propionaldehyde	$4.1 \pm 0.3 \times 10^{-10}$
n-Butyraldehyde	$6.6 \pm 0.3 \times 10^{-10}$
Pentanal	$4.6 \pm 0.2 \times 10^{-10}$
Hexanal	$5.3 \pm 0.4 \times 10^{-10}$
Acetone	$5.9 \pm 0.3 \times 10^{-10}$
Butanone	$5.1 \pm 0.2 \times 10^{-10}$
2-Pentanone	$3.8 \pm 0.2 \times 10^{-10}$
3-Pentanone	$4.6 \pm 0.1 \times 10^{-10}$

by these reactants, namely, acetone $5.9 \pm 0.3 \times 10^{-10}$, butanone $5.1 \pm 0.2 \times 10^{-10}$, 2-pentanone $3.8 \pm 0.2 \times 10^{-10}$ and 3-pentanone $4.6 \pm 0.1 \times 10^{-10}$. All the rate data obtained in this investigation are presented in Table 1. To the best of our knowledge, there are no analogous rate data for the reactions of atomic carbon with which the present results can be compared. No monotonic variation of the absolute second-order rate constants with molecular size was observed from which it is concluded that reaction is dominated by attack on the carbonyl group. This is a fundamental conclusion in itself. It is also hoped that such measurements can be included in modelling of the interstellar medium where some of these aldehydic and ketonic species have been detected [28–30] and in models designed to simulate cometary conditions where laboratory measurements, at least, have demonstrated the role of the reaction of translationally energised carbon atoms with water in different phases in the production of CH_2O [31].

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References

[1] R.P.A. Bettens, E. Herbst, Astrophys. J. 478 (1997) 585.
[2] E. Herbst, H-H. Lee, D.A. Howe, T.J. Millar, Mon. Not. Roy. Astronom. Soc. 268 (1994) 335.
[3] D.R. Flower, Int. Rev. Phys. Chem. 14 (1995) 421.
[4] J.R. Heath, R.J. Saykally, Sci. 274 (1996) 1480.
[5] N. Haider, D. Husain, J. Chem. Soc. Faraday Trans. 89 (1993) 7.
[6] N. Haider, D. Husain, J. Photochem. Photobiol. 70 (1993) 119.
[7] N. Haider, D. Husain, Z. Phys. Chem. Bd. 176 (1992) 133.
[8] N. Haider, D. Husain, Int. J. Chem. Kinetics. 25 (1993) 423.
[9] N. Haider, D. Husain, Ber. Bunsen. Ges. Phys. Chem. 97 (1993) 571.
[10] N. Haider, D. Husain, Comb. Flame 93 (1993) 327.
[11] D.C. Clary, N. Haider, D. Husain, M. Kabir, Astrophys. J. 422 (1994) 416.
[12] J.O. Hirschfelder, C.F. Curtiss, R.B. Bird, Molecular Theory of Gases and Liquids, Wiley, New York, 1954.
[13] Nat. Bur. Stand. Circular 467, in: C.E. Moore (Ed.), vol. 1–III, Atomic Energy Levels, US Government Printing Office, Washington, DC, 1958.
[14] A.L. Cooksy, R.J. Saykally, J.M. Brown, K.M. Evenson, Astrophys. J. 309 (1986) 828.
[15] R.J. Saykally, K.M. Evenson, Astrophys. J. 238 (1980) L107 –L111.
[16] H. Nussbaumer, Astrophys. J. 166 (1971) 411.
[17] R.J. Garstang, Mon. Not. Roy. Astronom. Soc. 111 (1951) 115.
[18] M.A. Frerking, K. Keene, G.E. Black, T.G. Phillips, Astrophys. J. 344 (1989) 311.
[19] R. Genzel, A.I. Harris, T.J. Jaffe, J. Stutki, Astrophys. J. 332 (1988) 1049.
[20] J. Keene, G.A. Blake, T.G. Phillips, P.J. Huggins, C.A. Beichman, Astrophys. J. 299 (1985) 967.
[21] G.J. White, R. Padman, Nature 354 (1991) 511.
[22] J. Zmuidzinas, A.L. Betz, R.T. Boreika, D.M. Goldhaber, Astrophys. J. 355 (1988) 774.
[23] J. Zmuidzinas, A.L. Betz, D.M. Goldhaber, Astrophys. J. 307 (1986) L75–L79.
[24] H. Klein, F. Lewen, F.Schieder.J. Stutzki, G. Winnewisser, Astrophys. J. 494 (1998) L125–L128.
[25] J. Stutzki, U.U. Graf, S. Haas, C.E. Honingh, D. Hottgenroth, K. Jacobs, F. Schieder, R. Simon, J. Staghun, G. Winnewisser, R.N. Martin, W.L. Peters, J.P. McMullin, Astrophys. J. 477 (1997) L33–L36.
[26] D. Chaistang, P.L. James, I.R. Sims, I.W.M. Smith, Phys. Chem. Chem. Phys. 1 (1999) 2247.
[27] D. Husain, A.X. Ioannou, J. Chem. Soc. Faraday Trans. 93 (1997) 3625.
[28] W.W. Duley, D.A. Williams, Interstellar Chemistry, Academic Press, New York, 1984.
[29] S. Taylor, D. Williams, Chem. Britain, 1993, 680 pp.
[30] F.J. Lovas, J. Phys. Chem. Ref. Data 21 (1992) 181.
[31] K. Roessler, Handbook of Hot Atom Chemistry, in: J-P. Adloff, P.P. Gaspar, M. Imamura, A.G. Maddock, T. Matsuura, H. Sano, K. Yoshihara (Eds.), Kodansha, Tokyo V.C.H. Publishers, New York, 1992, p. 601 (Chapter 7.6).
[32] D.J. Anderson, R.N. Rosenfeld, J. Chem. Phys. 94 (1991) 7857.
[33] H.H. Kim, J.L. Roebber, J. Chem. Phys. 44 (1966) 1709.
[34] J.L. Roebber, J.C. Larrabee, R.E. Huffman, J. Chem. Phys. 46 (1967) 4594.
[35] J.L. Roebber, J. Chem. Phys. 54 (1971) 4001.
[36] M. Umemoto, H. Shinohara, N. Nishi, R. Shimada, J. Photochem. 20 (1982) 277.
[37] J. McFarlane, J.C. Polanyi, J.G. Shapter, J.M. Williamson, J. Photochem. Photobiol. A 46 (1989) 139.
[38] K.H. Becker, R. König, R. Meuser, P. Wiesen, K.D. Bayes, J. Photochem. Photobiol. A 64 (1992) 1.
[39] C.E.M. Strauss, S.H. Kable, G.K. Chawla, P.L. Houston, I.R. Burak, J. Chem. Phys. 94 (1991) 1837.
[40] D.D. Davis, W. Braun, Appl. Optics 7 (1968) 2071.
[41] F.C. Fehsenfeld, K.M. Evenson, H.P. Broida, Rev. Sci. Instrum. 36 (1965) 294.
[42] D. Husain, A.N. Young, J. Chem. Soc. Faraday Trans. II 71 (1975) 525.
[43] A.C.G. Mitchell, M.W. Zemansky, Resonance Radiation and Excited Atoms, Cambridge University Press, London, 1961.
[44] M.W. Zemansky, Phys. Rev. 34 (1929) 313.
[45] S.C. Basu, D. Husain, J. Photochem. Photobiol. A 42 (1988) 1.