Reactions of Atomic Carbon $C(2^3P_J)$ by Kinetic Absorption Spectroscopy in the Vacuum Ultra-Violet

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Time-resolved attenuation of the atomic emission transition $C(3^3P_J^\circ \rightarrow 2^3P_J)$ at 166 nm has been used to study the reactions of $C(2^3P_J)$. The decay of this atom, following its generation by the vacuum ultra-violet flash photolysis of carbon suboxide, has been monitored directly in the presence of a number of gases. The following rate data for 300 K have been obtained:

$$C(2^3P_J)+NO \rightarrow CN+O,\ k = 7.3\pm2.2\times10^{-11}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

$$C(2^3P_J)+O_2 \rightarrow CO+O,\ k = 3.3\pm1.5\times10^{-11}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

$$C(2^3P_J)+N_2O \rightarrow CO+N_2,\ k = 2.5\pm1.6\times10^{-11}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$
$$\text{or } CN+NO$$

$$C(2^3P_J)+H_2O \rightarrow CO+H_2\ k \leqslant 3.6\times10^{-13}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$
$$\text{or } CH_2O$$

$$C(2^3P_J)+CO_2 \rightarrow 2CO,\ k < 10^{-14}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

$$C(2^3P_J)+CH_4 \rightarrow C_2H_4,\ k < 2\times10^{-15}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

$$C(2^3P_J)+N_2+M \rightarrow CN_2+M,\ k = 3.1\pm1.5\times10^{-33}\ \text{cm}^6\ \text{molecule}^{-2}\ \text{s}^{-1}\ (M = Ar)$$

$$C(2^3P_J)+H_2+M \rightarrow CH_2+M,\ k = 7.1\pm2.5\times10^{-32}\ \text{cm}^6\ \text{molecule}^{-2}\ \text{s}^{-1}\ (M = He)$$

$$C(2^3P_J)+CO+M \rightarrow C_2O+M,\ k = 6.3\pm2.7\times10^{-32}\ \text{cm}^6\ \text{molecule}^{-2}\ \text{s}^{-1}\ (M = He)$$

The kinetic study of free atomic carbon, though of fundamental interest, presents considerable experimental difficulties. The free energy of this atom is very high, and only one case of its formation by chemical reaction at thermal energies has recently been proposed.[1] Moreover, the number of exothermic reaction pathways available for this atomic species is generally high, and the life time in most chemical environments is consequently very short. Despite these difficulties, many studies of the reactions of atomic carbon have been carried out. Problems inherent in the generation of the free atom have been overcome in a number of ways, including the use of arcs, photolyses and recoil techniques, and a summary of the methods employed has been given by Shevlin and Wolf.[1] The chemistry of atomic carbon has been reviewed by Wolf,[2] Wolfgang,[3,4] Mackay and Wolfgang,[5] and recently by Braun *et al.*[6] Most of this work has, however, been either qualitative or purely mechanistic in nature, not involving direct observation of the atoms, and often it has not been possible to distinguish directly between the reactions of atomic carbon in its three lower lying electronic energy levels $C(2^3P_J)$, $C(2^1D_2)$ and $C(2^1S_0)$. Skell and co-workers [7-9] have studied reaction mechanisms for atomic carbon by trapping carbon vapour from an arc in inert, low-temperature solid matrices and have postulated processes for the atoms in defined electronic quantum states. Martinotti, Welch and Wolf [10] have obtained limited kinetic data for carbon atoms, probably in the $C(2^3P_J)$ state, following their production by the action of a microwave discharge on carbon suboxide in a flow system. Kinetic studies employing direct spectrographic observations of atomic carbon have been employed by Meaburn and Perner,[11] who have studied $C(2^1S_0)$, following its generation by pulse radiolysis of carbon compounds, and by Braun *et al.*[6] who have monitored $C(2^3P_J)$, $C(2^1D_2)$ and $C(2^1S_0)$ at a fixed time delay (10 μs) following the vacuum ultra-violet flash photolysis of carbon suboxide. Thus, the extent of quantitative kinetic data is limited, and further studies of atomic carbon in defined electronic quantum states particularly by direct observations are of value. The authors have recently reported a method for kinetic measurements of $C(2^3P_J)$ for the complete decay curve employing photoelectric detection of the attenuation of the atomic carbon transitions at $\lambda = 166$ nm $(C(3^3P_J^\circ)\rightarrow(2^3P_J))$, following the flash photolysis of carbon suboxide in the Schumann region.[12] We now describe the first extensive set of kinetic data for the reaction of $C(2^3P_J)$, with a wide range of simple molecules, obtained by this technique.

EXPERIMENTAL

The general experimental arrangement for the direct study of atomic reactions by time-resolved monitoring of resonance radiation in the vacuum ultra-violet attenuated by transient atoms has been described previously.[13, 14] The specific configuration of the apparatus employed in the present experiments has also been described.[12] Carbon atoms were generated by the flash photolysis of carbon suboxide at low wavelength ($\lambda \sim 160$ nm) in a coaxial lamp and vessel assembly, and were detected in their ground electronic state $C(2^3P_J)$ by monitoring the attenuation of the resonance multiplet $(3^3P_J\rightarrow 2^3P_J)$ at 166 nm. This radiation was produced by subjecting a 1 % mixture of acetylene in helium at 270 N m^{-2} total pressure to a microwave discharge in a flow system. A limitation on the time resolution of the apparatus was the effect of the scattered light pulse from the photolysis flash. This was minimized by blackening the inner surface of the Pyrex reaction vessel before attaching the lithium fluoride windows employed for the low wavelength transmission ($\lambda > 105$ nm) of both spectroscopic and photolytic radiation. The duration of the initiating flash could be reduced by employing nitrogen rather than argon in the photolysis lamp. The photomultiplier was gated for the first 50 μs following the triggering of the photolysis lamp by shorting together the fifth and seventh dynodes of the chain using a high-voltage video transistor triggered by a Schmidt pulse generator. A photolysis energy of 1125 J (10 μF at 15 kV) was employed throughout this work, and the microwave lamp was operated at an indicent power of 125 W. The time constant of the photomultiplier anode circuit was *ca.* 5 μs. Under these conditions, measurements of the $C(2^3P_J)$ concentrations could be made after 90-100 μs, and the pressures employed were such that transient absorption could be monitored for up to 500 μs. To minimize any photolysis of the sample by the spectroscopic source before triggering of the photoflash lamp, the gaseous mixtures were not admitted to the reaction vessel until after the high-voltage capacitor was charged. The residence time in the reaction vessel before firing of the lamp was always less than 5 s.

MATERIALS

CARBON SUBOXIDE was prepared by the method described by Miller and Fately.[15] The product was stored at liquid-nitrogen temperature (−196°C), and periodically redistilled from CO_2+ethanol temperature (−78°C) to liquid-nitrogen temperature to remove polymerization products. Uniform samples diluted in inert gas were used for each series of kinetic experiments.

NITRIC OXIDE.—Cylinder NO (Matheson Co.) was degassed at −196°C and distilled twice from liquid-oxygen temperature (−183°C) to −196°C.

WATER.—Distilled water was degassed before use.

NITROUS OXIDE.—Cylinder N_2O (Air Products Ltd) was degassed at −196°C and twice distilled from −95°C (toluene slush) to −196°C.

HELIUM.—Cylinder helium (Grade A, British Oxygen Company) was passed through a molecular sieve at liquid-nitrogen temperature then over freshly prepared heated copper with a quantity of copper oxide to remove any hydrogen or oxygen present, followed by passage through a series of traps containing activated molecular sieve at −196°C.

NITROGEN.—Research-grade cylinder nitrogen (Air Products Ltd.) was stored in a bulb fitted with a cold finger maintained at −196°C before use.

Ar, CO, O_2, H_2, CH_4 AND CO_2.—Grade X gases (B.O.C. Ltd.) were used directly. Gases employed in reaction mixtures were manipulated in a mercury-free vacuum system.

PHOTOLYSIS LAMP

Cylinder nitrogen (White Spot, O_2-free, B.O.C. Ltd) was passed through a trap containing activated molecular sieve at −196°C before use in the photolysis lamp.

FLOW LAMP

HELIUM.—Cylinder helium (Grade A, B.O.C. Ltd) was passed through a trap containing activated molecular sieve at −196°C before use in the microwave atomic flow lamp.

ACETYLENE.—Cylinder acetylene (B.O.C. Ltd) was degassed at −196°C and distilled from −78 to −196°C.

RESULTS

Carbon suboxide exhibits strong absorption continua in the vacuum ultraviolet of which the transition at $\lambda = 159$ nm is the most intense ($\varepsilon = 7000\ \text{cm}^{-1}$).[16] Under comparable experimental conditions to those reported here, photolytic dissociation in this wavelength region occurs by the process [6]

$$C_3O_2 + h\nu \rightarrow 2CO + C. \tag{1}$$

Carbon atoms are generated in the three low-lying electronic states, $C(2^3P_J$, 2^1D_2 and $2^1S_0)$. Braun *et al.*[6] have observed that $C(2^1S_0)$ and $C(2^1D_2)$ are relatively minor products with most atoms (~80 %) being formed in the ground state. Further, Braun [6] has deduced that $C(2^1S_0)$ is derived from secondary photolytic processes. In all cases with added gases in this investigation, the results of Braun [6] show that the small yields of $C(2^1D_2)$ will be completely deactivated to the electronic ground state before the first kinetic observations are carried out (100 μs) where quenching of this state is the dominant removal processes; where chemical reaction of $C(2^1D_2)$ takes place, this will not significantly affect the data derived from spectroscopic observations on $C(2^3P_J)$ itself. Further, $C(2^1D_2)$ could not be positively identified in these experiments via the transition at 193.1 nm ($C(3^1P_1^\circ) \rightarrow C(2^1D_2)$). The f value for this transition is comparable to those of the lines at 165.7 nm [17] and thus we conclude the atom in the 2^1D_2 state was not present in any appreciable concentration during the course of these kinetic measurements. With the optical resolution employed, transitions corresponding to the three J states of $C(2^3P_J)$ are not separated, and we may confindently assume that a Boltzmann distribution is maintained between these close lying levels ($J = 1$: 16 cm^{-1}; $J = 2$: 43 cm^{-1}) throughout the course of the rate measurements.

The degree of photolytic dissociation in this investigation has been estimated as *ca.* 25-30 %.[12] Removal of $C(2^3P_J)$ following photolysis in the absence of added gas is probably due to reaction with the parent molecule C_3O_2. We therefore assume the simplified kinetic scheme for the removal of $C(2^3P_J)$ of pseudo first-order kinetics, and of the pseudo first-order rate coefficient k' of the form

$$k' = K + k_R[R], \tag{i}$$

where k_R is the second-order rate coefficient due to an added reactant R, and the constant K represents an empirical rate coefficient in the absence of added reactant. We further employ an absorption law of the Beer-Lambert form[12]

$$I_{tr} = I_0 \exp -(\varepsilon lc) \qquad \text{(ii)}$$

to describe the attenuation of radiation at $\lambda = 166$ nm by $C(2^3P_J)$. Thus a plot of ln(ln (I_0/I_{tr})) against time yields a straight line of slope k', the first-order rate coefficient. In general, slight curvature in the first-order plots was apparent and this may indicate a more complex form of the absorption law, which could not be determined in the present investigation. For the kinetic analysis, the best straight line

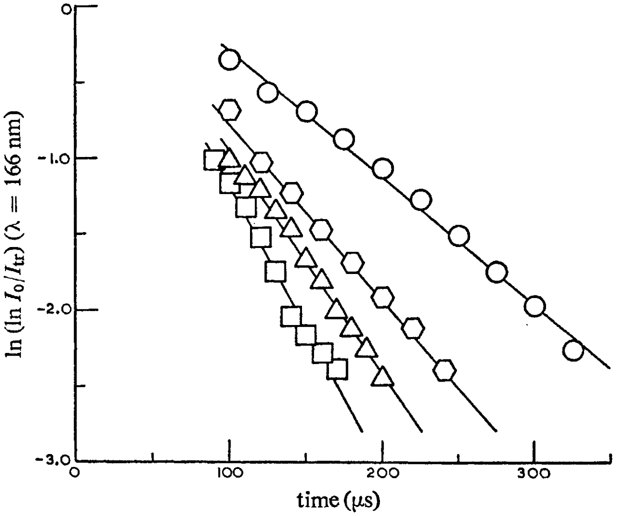

FIG. 2.—Typical pseudo first-order plots for the decay of $C(2^3P_J)$ in the presence of hydrogen. $p_{C_3O_2} = 0.27$ N m^{-2}; p_{total} with He = 20.0 kN m^{-2}; E = 1125 J. p_{H_2} (N m^{-2}): ○, 0.0; ⬡, 60.8; △, 104; □, 113.

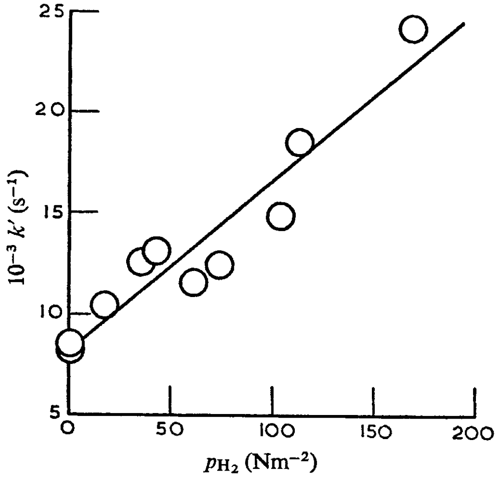

FIG. 3.—Plot of pseudo first-order rate coefficient k' for the removal of $C(2^3P_J)$ against pressure of hydrogen. $p_{C_3O_2} = 0.27$ N m^{-2}; p_{total} with He = 20.0 kN m^{-2}; E = 1125 J.

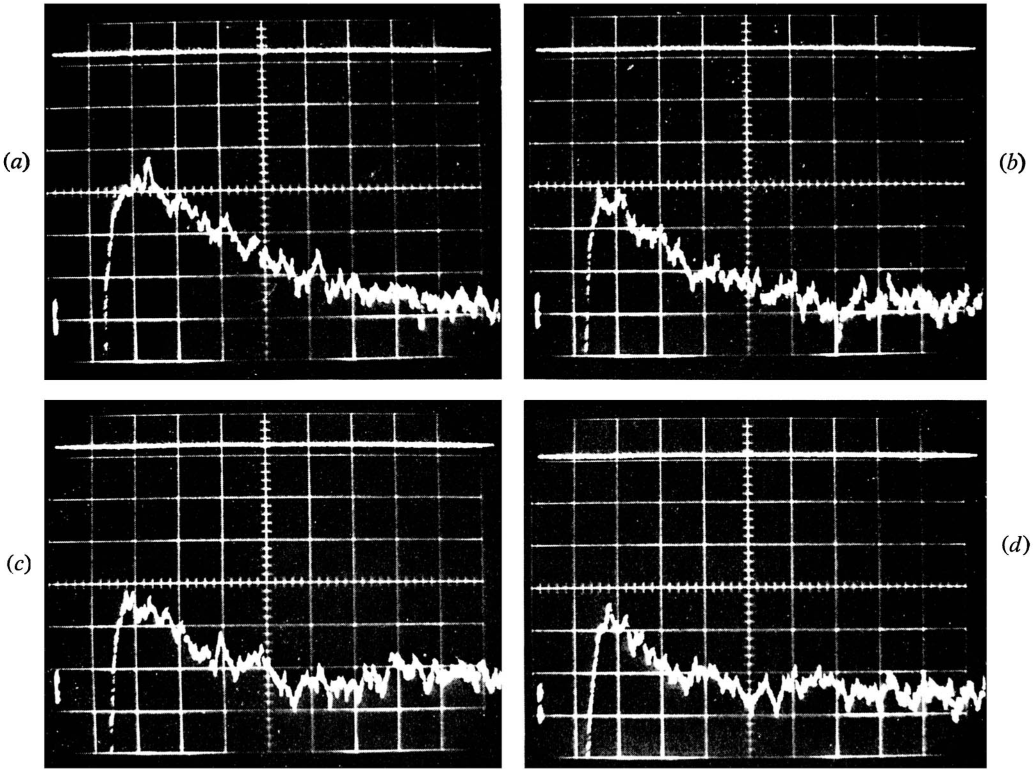

FIG. 1.—Typical oscilloscopic traces for the decay of $C(2^3P_J)$, obtained by monitoring the light absorption at $\lambda = 166$ nm, in the presence of hydrogen. $p_{C_3O_2} = 0.27$ N m^{-2} ; p_{total} with He = 20.0 kN m^{-2} ; $E = 1125$ J ; time scale = 50 μs/division. p_{H_2} (N m^{-2}) : (*a*) 0.0 ; (*b*) 60.8 ; (*c*) 104 ; (*d*) 113.

through each set of kinetic data was computed. This kinetic technique has been applied previously to the reaction of $C(2^3P_J)+NO$ [12] and given good agreement with the existing data reported by Braun.[6] This method is further substantiated by the excellent agreement with the data of $C(2^3P_J)$ with O_2 (see discussion).

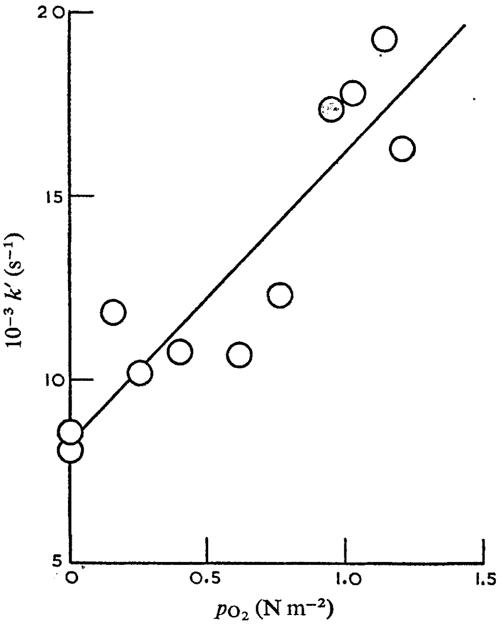

FIG. 4.—Plot of pseudo first-order rate coefficient k' for the removal of $C(2^3P_J)$ against pressure of oxygen. $p_{C_3O_2} = 0.27$ N m^{-2} ; p_{total} with He $= 20.0$ kN m^{-2} ; E = 1125 J.

Fig. 1 illustrates typical oscilloscope traces obtained for the decay of $C(2^3P_J)$ in the presence of increasing pressures of hydrogen, and fig. 2, the first-order plots derived from these traces. Plots of k' against pressure for H_2 and O_2 are given in fig. 3 and 4, respectively. The scatter in these plots arises from the relatively low signal-to-noise ratio resulting from the application of this type of experimental system to such rapid decay processes, particularly in the presence of high pressures of reactant gas. The slopes of these plots thus yield the second-order removal rate rate constants k_R of $C(2^3P_J)$ by these species (see eqn (i)). The kinetic data obtained for O_2, NO,[12] N_2O and H_2O are listed in table 1(*a*). A number of reactions of $C(2^3P_J)$ were found to exhibit third-order kinetics and thus the values of k_R obtained from such plots as fig. 3 depended on the pressure of inert gas employed to maintain isothermal conditions (300 K). The kinetic data for the third-order reactions of $C(2^3P_J)$ with H_2, N_2 and CO are presented in table 1(*b*). Writing

$$k'' = k' - K, \qquad \text{(iii)}$$

where k' is the rate coefficient for the decay of $C(2^3P_J)$ in the presence of a fixed pressure of H_2 and given total pressure, and K is the rate coefficient measured from a blank experiment in the absence of H_2 at the same total pressure, a plot of k'' against total pressure is expected to yield a straight line passing through the origin. This plot is shown in fig. 5 for $C(2^3P_J)+H_2$. Whilst there is considerable scatter in this plot, the reaction is clearly pressure dependent. Table 1(*c*) lists the values of k'' obtained for the reactions of $C(2^3P_J)$ with H_2, N_2 and CO over a range of total pressures, and the third-order rate coefficients derived from these values.

TABLE 1.—KINETIC DATA FOR THE DECAY OF $C(2^3P_J)$, FOLLOWING THE FLASH PHOTOLYSIS OF C_3O_2, IN THE PRESENCE OF DIFFERENT GASES.
$p_{C_3O_2} = 0.27$ N m^{-2} ; $E = 1125$ J.

A. SECOND-ORDER REACTIONS

Pseudo first-order rate coefficients (k') for the decay of $C(2^3P_J)$ in the presence of NO, O_2, N_2O, and H_2O.

p_{total} with He = 20.0 kN m^{-2}

NO		O_2	
NO (N m^{-2})	10^{-3} k (s^{-1})	p_{O_2} (N m^{-2})	10^{-3} k (s^{-1})
0	5.5	0	8.1
0	6.6	0	8.5
0.106	8.5	0.154	11.8
0.136	8.8	0.247	10.2
0.198	10.1	0.398	10.8
0.208	11.7	0.605	10.7
0.259	11.3	0.757	12.3
0.260	10.4	0.938	17.4
0.346	13.2	1.015	17.8
0.408	12.5	1.129	19.4
0.408	12.7	1.194	16.3
0.468	15.5		

N_2O		H_2O	
p_{N_2O} (N m^{-2})	10^{-3} k (s^{-1})	p_{H_2O} (N m^{-2})	10^{-3} k' (s^{-1})
0	6.4	0	9.1
0	8.6	1.33	10.0
0.309	9.2	4.495	10.0
0.529	10.7	5.027	9.9
0.734	13.0	57.2	7.8
0.962	10.2	76.9	12.6
1.149	9.6	83.0	13.5
1.237	20.6	128	14.6
1.478	14.5	131	12.9
1.639	16.7	200	20.1
1.724	18.2	216	17.6
1.772	19.0	221	18.8

B. THIRD-ORDER REACTIONS

Pseudo first-order rate coefficients k' for the decay of $C(2^3P_J)$ in the presence of N_2, H_2 and CO at a fixed total pressure.

N_2(p_{total} with Ar = 39.9 kN m^{-2})		H_2(p_{total} with He = 20.0 kN m^{-2})		CO(p_{total} with He = 20.0 kN m^{-2})	
p_{N_2} (kN m^{-2})	10^{-3} k' (s^{-1})	p_{H_2} (N m^{-2})	10^{-3} k' (s^{-1})	p_{CO}(N m^{-2})	10^{-3} k' (s^{-1})
0	8.2	0	8.3	0	7.2
0	6.8	0	8.4	0	8.8
0.39	10.8	16.6	10.3	0	8.8
0.605	10.9	35.8	12.5	37.2	13.1
0.78	9.7	42.4	13.1	62.5	15.9
0.83	14.9	60.8	11.5	84.3	19.1
1.10	13.4	73.8	12.3	110	14.6
1.29	13.6	104	14.7	124	18.8
1.60	13.2	113	18.4	161	18.8
1.98	26.4	169	24.2	179	23.5
2.46	25.5				

C. THIRD-ORDER REACTIONS

Dependence of the pseudo first-order rate coefficient (k'') for the decay of $C(2^3P_J)$ in the presence of fixed pressures of N_2, H_2 and CO with total pressure.

N_2, $p_{N_2} = 1.07$ kN m^{-2}

p_{total} with Ar (kN m^{-2})	$10^{-3}\,k''$ (s^{-1})	third-order rate constant $10^{33}\,k_{N_2}$ (cm^6 molecule^{-2} s^{-1}) (300 K)
20.0	1.9	1.5
26.6	4.7	2.8
39.9	7.8	3.1
53.2	12.1	3.6
66.5	10.4	2.5

H_2, $p_{H_2} = 62.6$ N m^{-2}

p_{total} with He (kN m^{-2})	$10^{-3}\,k''$ (s^{-1})	$10^{32}\,k_{H_2}$ (cm^6 molecule^{-2} s^{-1}) (300 K)
13.3	2.0	4.0
20.0	5.3	7.1
26.6	9.0	9.1
39.9	10.8	6.9
53.2	11.0	5.9

CO, $p_{CO} = 66.5$ N m^{-2}

p_{total} with He (kN m^{-2})	$10^{-3}\,k''$ (s^{-1})	$10^{32}\,k_{CO}$ (cm^6 molecule^{-2} s^{-1}) (300 K)
13.3	6.1	11.7
20.0	4.9	6.3
26.6	7.1	6.7
39.9	8.4	5.4
53.2	13.9	6.6

For methane and carbon dioxide, no significant reaction of $C(2^3P_J)$ could be detected over the pressure range of added gas studied. Some increase in the value of k' was observed when relatively low pressures of CH_4 ($\sim$2 kN m^{-2}) were employed; however, on further addition of this molecule up to a pressure of 30 kN m^{-2} no further increase in k' resulted. It would therefore appear that the increase in rate arises from the photolysis products of methane itself at the lower pressures employed, the yield of these products decreasing upon further addition of methane due to strong absorption of photolyzing radiation by this gas ($\lambda < 144$ nm)[18] close to the windows of the reaction vessel. No increase in k' was observed when CO_2 was added up to a pressure of 1.3 kN m^{-2}, and although a slight increase in k' was significant at double this pressure, this is consistent with reaction of $C(2^3P_J)$ with CO produced by the photolysis of CO_2 ($\lambda \sim 140$ nm).[19] Upper limits have therefore been placed on the reaction rate constants of $C(2^3P_J)$ with CH_4 and CO_2 of 2×10^{-15}, and 10^{-14} cm^3 molecule^{-1} s^{-1} (300 K), measured at a total pressure of 20.0 kN m^{-2} (M = He). These estimates are based on the minimum increase in k' which would be significant under the present experimental conditions.

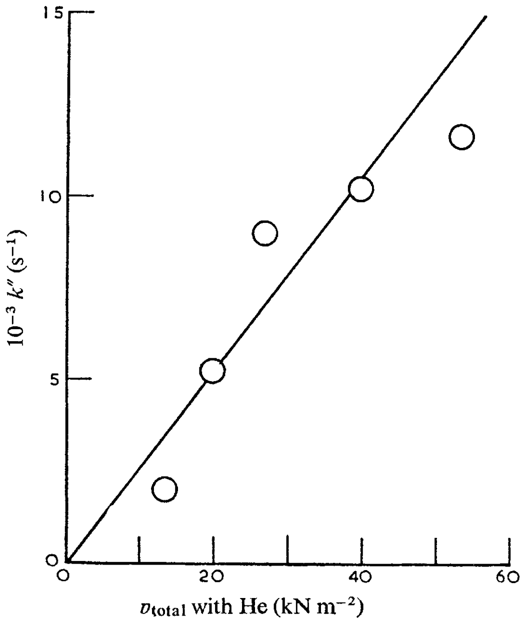

FIG 5.—Variation of the pseudo first-order rate coefficient k'' for the removal of $C(2^3P_J)$ by H_2 with total pressure. $p_{C_3O_2} = 0.27\ N\ m^{-2}$; $p_{H_2} = 62.6\ N\ m^{-2}$; $E = 1125$ J.

The rate constants derived from least-squares analyses of the data presented in tables 1(*a*) and (*b*) are given in table 2, and compared with existing data in the literature. The reactions are discussed individually below.

TABLE 2.—RATE CONSTANTS FOR THE REACTIONS OF $C(2^3P_J)$

SECOND-ORDER REACTIONS

reagent	k (cm^3 molecule^{-1} s^{-1}) (300 K)	Braun *et al.*	Wolf *et al.*
NO	$7.3 \pm 2.2 \times 10^{-11}$	1.1×10^{-10}	
O_2	$3.3 \pm 1.5 \times 10^{-11}$	3.3×10^{-11}	2.5×10^{-12}
N_2O	$2.5 \pm 1.6 \times 10^{-11}$		
H_2O	$\leqslant 3.6 \times 10^{-13}$		
CO_2	$< 10^{-14}$		
CH_4	$< 2 \times 10^{-15}$	$< 5 \times 10^{-15}$	$< 6 \times 10^{-17}$

THIRD-ORDER REACTIONS

reaction	M	k (cm^6 molecule^{-2} s^{-1}) (300 K)
$C + N_2 + M \rightarrow CN_2 + M$	Ar	$3.1 \pm 1.5 \times 10^{-33}$
$C + CO + M \rightarrow C_2O + M$	He	$6.3 \pm 2.7 \times 10^{-32}$
$C + H_2 + M \rightarrow CH_2 + M$	He	$7.1 \pm 2.5 \times 10^{-32}$

(errors = 3 standard deviations)

DISCUSSION

$C(2^3P_J) + NO$

The rate constant derived for the reaction of $C(2^3P_J)$ with NO of $7.3 \pm 2.2 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} (300 K) has been reported previously.[12] This value is in good agreement with that obtained by Braun *et al.*[6] of 1.1×10^{-10} cm^3 molecule^{-1} s^{-1} (300 K). The pressure dependence of this reaction was not investigated although Braun *et al.*[6] have reported traces of NCO as a product at high total pressures, and Milligan and Jacox [20] report the formation of this radical by the reaction of these species in low-temperature matrices. It may be inferred, however, from the very high collisional efficiency for this reaction ($Z \approx 4$) that the contribution from any kinetically third-order process may only constitute a small proportion of the overall rate. Thus, we conclude that the reaction is most probably due to the exothermic process:

$$C(2^3P_J)+NO(X^2\Pi)\rightarrow CN(X^2\Sigma^+)+O(2^3P_J), \quad \Delta H = -1.05 \text{ eV}, \tag{2}$$

occurring via the pathways $(^2A'+2^2A''+^4A'+2^4A'')$ although some decay via the close to thermoneutral reaction

$$C(2^3P_J)+NO(X^2\Pi)\rightarrow CN(A^2\Pi_i)+O(2^3P_J), \quad \Delta H = +0.09 \text{ eV}, \tag{3}$$

may also take place by means of the surfaces $(2^2A'+^2A''+2^4A'+^4A'')$.[21]

$C(2^3P_J)+O_2$

The second-order rate constant obtained for the reaction of $C(2^3P_J)+O_2$ ($3.3 \pm 1.5 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} (300 K), table 2) supports the values reported by Braun *et al.*[6] rather than that of Martinotti *et al.*[10] Dissociation of molecular oxygen by light from both the photolytic and microwave lamps may generate a small error in this value, however, the relative integrated absorption coefficients [16, 19] indicate that fission due to the former effect should be considerably less than the degree of dissociation estimated for C_3O_2. The latter effect was minimized as previously described. The reaction is clearly very efficient, in accordance with the correlation diagram connecting the states of $C+O_2$ and $CO+O$ given by Donovan and Husain,[21] which shows highly exothermic reaction pathways correlating with the products $CO(X^1\Sigma^+)+O(2^3P_J)$ ($\Delta H = -6.0$ eV, $^3A'+^3A''$), or $CO(X^1\Sigma^+)+O(2^1D_2)$ ($\Delta H = -4.03$ eV, $2^1A'+^1A''$).

$C(2^3P_J)+N_2O$

Consideration of the correlation diagrams connecting the states of $C+N_2O$ with $CN+NO$ or N_2+CO indicates the availability of exothermic reaction pathways for the following processes:

$$C(2^3P_J)+N_2O(X^1\Sigma^+)\rightarrow CO(a^3\Pi_i)+N_2(X^1\Sigma_g^+)\Delta H = -3.39\text{eV} \quad (^3A'+^3A'') \tag{4}$$

$$C(2^3P_J)+N_2O(X^1\Sigma^+)\rightarrow CO(X^1\Sigma^+)+N_2(B^3\Pi_g), \quad \Delta H = -2.03 \text{ eV} \quad (^3A'') \tag{5}$$

$$C(2^3P_J)+N_2O(X^1\Sigma^+)\rightarrow CN(X^2\Sigma^+)+NO(X^2\Pi), \quad \Delta H = -2.61 \text{ eV} \quad (^3A'+^3A'') \tag{6}$$

$$C(2^3P_J)+N_2O(X^1\Sigma^+)\rightarrow CN(A^2\Pi_i)+NO(X^2\Pi), \quad \Delta H = -1.47 \text{ eV} \quad (^3A'') \tag{7}$$

The rapid rate observed (table 2) is consistent with reaction by fully-allowed pathways and time-resolved measurement of the reaction products in specific states would thus be of interest for a detailed consideration of this decay process.

$C(2^3P_J)+H_2O$

Quantitative removal of $C(2^3P_J)$ with the addition of H_2O was observed (table 1(*a*)) and the apparent rate constant was invariant with total pressure over the range 6.7-53.2 kN m^{-2}(He). Strong absorption of the atomic radiation at 166 nm by

H_2O and appreciable photolysis of this molecule by radiation from the photolytic and spectroscopic lamps limited the accuracy of the measurement. Nevertheless, it is clear that rapid reaction analogous to that of $C(2^3P_J)$ with O_2 or NO does not occur. The close to thermoneutral reaction,

$$C(2^3P_J)+H_2O(X^1A_1)\rightarrow H_2(X^1\Sigma_g^+)+CO(a^3\Pi_i),\ \Delta H = -0.03\ \text{eV}, \qquad (8)$$

may account for these observations as may the spin-forbidden reaction to form both products in their ground electronic states. Maddock and co-workers[22] have observed formaldehyde as a product of the reaction of carbon atoms directed onto an ice surface. The second-order kinetics observed in these gas-phase studies require that the lifetime of any state of CH_2O formed on the collision between $C(2^3P_J)+H_2O$ be long, or that stabilization occurs by means of radiation. A further possibility arising from the photolytic dissociation of H_2O is the reaction

$$C(2^3P_J)+OH(X^2\Pi_i)\rightarrow CO(X^1\Sigma^+)+H(1^2S_{\frac{1}{2}}),\quad \Delta H = -6.72\ \text{eV}. \qquad (9)$$

We therefore express our result for $C+H_2O$ as an upper limit of $k_{H_2O}\leqslant 3.6\times 10^{-13}$ cm^3 molecule^{-1} s^{-1} (300 K) which is double the apparent rate from the data in table 1.

$C(2^3P_J)+CO_2$

No spin-allowed exothermic pathways are available for the process :

$$C(2^3P_J)+CO_2\rightarrow 2CO. \qquad (10)$$

For reaction the spin-forbidden process :

$$C(2^3P_J)+CO_2(X^1\Sigma_g^+)\rightarrow 2CO(X^1\Sigma^+),\ \Delta H = -5.64\ \text{eV}, \qquad (11)$$

or the endothermic reaction ($^3A''+{}^3A'$) :

$$C(2^3P_J)+CO_2(X^1\Sigma_g^+)\rightarrow CO(X^1\Sigma^+)+CO(a^3\Pi_i),\ \Delta\text{H} = 0.39\ \text{eV}, \qquad (12)$$

will take place. These considerations are consistent with the experimental observations, which indicate an upper limit for the reaction of 10^{-14} cm^3 molecule^{-1} s^{-1} (300 K) (table 2).

$C(2^3P_J)+CH_4$

An upper limit is placed on the rate of this reaction in accord with the results of Braun *et al.*[6] and Martinotti *el al.*,[10] and also with those of Skell and Engel,[23] who observed no products from the reaction of $C(2^3P_J)$ with saturated hydrocarbons.

$C(2^3P_J)+N_2$, H_2 AND CO

The third-order kinetics observed for these reactions is consistent with the results of Braun *et al.*[6] who report a pressure-dependent process but present only semi-quantitative rate data. Exothermic metathetical pathways are not available for these reactants, and thus recombination is the only mechanism available at thermal energies. Braun *et al.*[6] have shown that the most likely products are the radicals CN_2, CH_2 and C_2O for $C(2^3P_J)+N_2$, and H_2 and CO respectively. An order-of-magnitude calculation assuming unit collision efficiencies for both formation and deactivation leads to estimates of 5×10^{-14}, 10^{-12} and 10^{-12} s for the lifetime of the energised intermediates derived from $C(2^3P_J)+N_2$, H_2 and CO, respectively, employing the third-order rates presented in table 2.

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