

Kinetic Study of Reactions of Ground State Silicon Atoms, $\text{Si}[3p^2(^3P_J)]$, by Atomic Absorption Spectroscopy

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We present a kinetic study of ground state silicon atoms, $\text{Si}[3p^2(^3P_J)]$. The silicon atoms were generated by the repetitive pulsed irradiation of SiCl_4 and monitored photoelectrically in absorption by time-resolved attenuation of resonance radiation of the group of lines at $\lambda = 251.6 \text{ nm}$ ($4^3P_J \leftarrow 3^3P_{0,1,2}$), coupled with signal averaging. Absolute rate constants, including those obtained in the previous study concerned with the development of the method itself, are reported for the molecules H_2 , N_2 , O_2 , Cl_2 , CO , NO , CO_2 , N_2O , CH_4 , CF_4 , C_2H_2 , C_2H_4 and SiCl_4 . The results are compared and discussed, where appropriate, with analogous data for the other adjacent group IV atoms, $\text{C}(2^3P_J)$ and $\text{Ge}(4^3P_J)$. The nature of the potential surfaces involved in reactions of $\text{Si}(3^3P_J)$ are assumed to be described following symmetry arguments based on the weak spin orbit coupling approximation.

We have recently described a method for the direct detailed kinetic study of ground state silicon atoms, $\text{Si}[3p^2(^3P_J)]$.¹ The atoms were generated by repetitive pulsed irradiation and monitored photoelectrically by resonance line absorption coupled with signal averaging using the system designed initially for investigating the collisional behaviour of $\text{P}(3^4S_3)$.^{2, 3} The initial work on $\text{Si}(3^3P_J)$ was primarily concerned with the development of the technique. Particular attention was paid to the collisional behaviour of the individual spin orbit levels in the $3p^2$ state $\{\text{Si}[3p^2(^3P_J)]: J = 0, 0; J = 1, 77 \text{ cm}^{-1}; J = 2, 233 \text{ cm}^{-1}\}$,⁴ including the relationship between atomic concentration and the extent of absorption of resonance radiation for transitions associated with both individual spin orbit levels and groups of levels. It was shown that the spin orbit levels maintained a Boltzmann equilibrium during the kinetic decays and that absolute rate constants could be determined by monitoring any of the individual spin orbit levels or groups of levels in $\text{Si}(3^3P_J)$ using the appropriate light absorption law.¹

In this paper, we describe kinetic studies of $\text{Si}(3^3P_J)$ with various molecules and report second-order absolute rate constants for chemical reaction. We have stressed hitherto what we regard as the principal context of the present study, namely, to characterise the collisional behaviour of the $np^2(^3P_J)$ ground states of $\text{C} \rightarrow \text{Pb}$ with various molecules in order to investigate the rôle of spin orbit coupling on chemical reactivity.⁵ The fundamental framework for discussion is to employ correlations based on the weak spin orbit coupling approximation for light atom-molecule collisions^{6, 7} and (J, Ω) coupling for heavy atom-molecule collisions.⁵ The rate constants obtained here for $\text{Si}(3^3P_J)$ are compared with the analogous data for $\text{C}(2^3P_J)$ ^{8, 9} where the weak spin orbit coupling approximation can clearly be applied,⁸ and with those for $\text{Ge}(4^3P_J)$ ^{10, 11} where both this approximation and that of the extreme coupling case for heavy atom-molecule collisions are of limited use,¹⁰⁻¹² and where, ideally, one should employ an intermediate coupling case.

EXPERIMENTAL

The experimental arrangement has been given previously¹ and here we summarise the technique. $\text{Si}(3^3P_J)$ was generated by the repetitive (0.2 Hz) pulsed irradiation ($E = 45 \text{ J}$) at $\lambda > \sim 165 \text{ nm}$ of SiCl_4 in a coaxial lamp and vessel assembly.^{13, 14} The atoms were monitored in absorption using the unresolved group of lines at $\lambda = 251.6 \text{ nm}$.¹ The resonance radiation for the spectroscopic source was derived from a microwave discharge¹ using an Evenson cavity.¹⁵ The photoelectric pulses, representing resonance line absorption, were analysed by a data handling system comprising essentially a fast transient recorder used in the "A/B" mode, interfaced to a signal averager.¹ The A/B mode permits averaging of the unattenuated signal, I_0 , for each individual decay, on a separate time base to that employed for the attenuated signal, I_{tr} . The unattenuated signals are not directly shown here but are implicitly included in the computerised output of data that are derived from the ratio, I_0/I_{tr} . Resonance absorption for the unresolved group of lines at $\lambda = 251.6 \text{ nm}$ has been shown to be described by a modified Beer-Lambert law:¹⁶

$$I_{\text{tr}} = I_0 \exp[-\varepsilon(cl)^\gamma] \quad (\text{i})$$

or

$$I_{\text{tr}} = I_0 \exp[-(\varepsilon cl)^\gamma] \quad (\text{ii})$$

where $\gamma = 0.51 \pm 0.04$ ¹ for the optical conditions employed here. All the results are subjected to the numerical data smoothing procedure of Savitsky and Golay.¹⁷

MATERIALS

All materials were prepared essentially as described in previous papers [He, Kr (for the photoflash lamp), SiCl_4 , H_2 , N_2 , Cl_2 , CO , NO , CO_2 , CF_4 , C_2H_2 and C_2H_4].^{1, 3, 8, 11, 18}

RESULTS AND DISCUSSION

Fig. 1(a) shows the computerised output of the digitised time-variation of the transmitted light intensity at $\lambda = 251.6 \text{ nm}$ indicating the decay of resonance absorption by $\text{Si}(3^3P_J)$. Fig. 1(b) and 1(c) show the effect on the lifetime of $\text{Si}(3^3P_J)$ by the addition of nitric oxide. Fig. 2 shows the computerised form of the first-order kinetic plots derived from the data of fig. 1. The slopes of these plots, following eqn (i) or (ii), are given by $-\gamma k'$ where k' is the overall first-order decay coefficient for $\text{Si}(3^3P_J)$ in a given experiment. $\gamma = 0.51 \pm 0.04$ as indicated above.¹ We have shown hitherto that we may neglect any complication to the kinetics of $\text{Si}(3^3P_J)$ resulting from physical quenching of the low yields of $\text{Si}[3p^2(^1D_2)]$ and $\text{Si}[3p^2(^1S_0)]$ which were detected in this system.¹

In general, k' may be expressed in the form :

$$k' = K + k_{\text{R}}[\text{R}] \quad (\text{iii})$$

where k_{R} is the second-order reaction rate constant for the removal of the ground state silicon atom in the presence of the reactant gas, R. For third-order kinetic removal, as presumed for reaction with some gases, k_{R} becomes, of course, the second-order decay coefficient equal to $k_3^{\text{R}}[\text{M}]$ where k_3^{R} is the third-order reaction rate constant, characteristic of the third body M, principally He in this system. K is a constant in a series of kinetic experiments in which $[\text{R}]$ is varied and arises mainly from first-order contributions to the decay of $\text{Si}(3^3P_J)$ due to reaction with the parent molecule, SiCl_4 ($K \simeq k_{\text{SiCl}_4}[\text{SiCl}_4]$ where $k_{\text{SiCl}_4} = 7.2 \pm 1.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, 300 K).¹ Fig. 3 shows the variation of $k'(\gamma k')$ with $[\text{NO}]$ and $[\text{C}_2\text{H}_4]$. Similar plots were obtained with the other gases for which absolute second-order reaction rate constants are reported. The slopes of such plots together with the above value of γ yield the absolute values of k_{R} . Table 1 lists the values of k_{R} obtained from the present type of investigation together with the analogous data for

GROUND STATE SILICON ATOMS

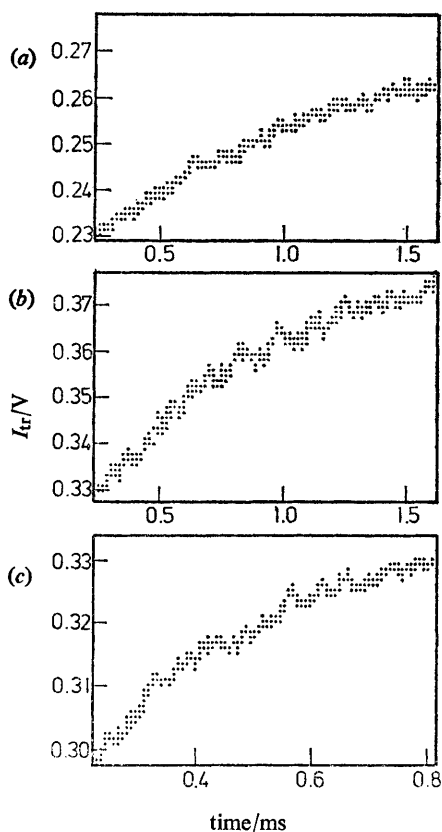
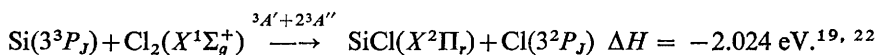


FIG. 1.—Digitised time-variation of the transmitted light intensity at $\lambda = 251.6$ nm ($4^3P_J \leftarrow 3^3P_J$) indicating the decay of resonance absorption by $\text{Si}(3^3P_J)$ in the presence of NO. $p_{\text{SiCl}_4} = 0.02$ N m $^{-2}$; $p_{\text{total with He}} = 2.8$ kN m $^{-2}$; $E = 45$ J; repetition rate = 0.2 Hz; no. of experiments for averaging = 32. $p_{\text{N}_2\text{O}}/\text{N m}^{-2}$: (a) 0.0; (b) 0.06; (c) 0.17.

$\text{C}(2^3P_J)$ and $\text{Ge}(4^3P_0)$. Some differences in kinetic behaviour have been observed for the three spin orbit states of $\text{Ge}[4p^2(^3P_J)]$ ^{10, 11} ($J = 0, 0$; $J = 1, 557$; $J = 2, 1410$ cm $^{-1}$; 1 cm $^{-1} = 1.239\,81 \times 10^{-4}$ eV).¹⁹ We restrict our comparison of rate data here to the 3P_0 ground state of atomic germanium.

DIATOMIC MOLECULES

Rapid removal of $\text{Si}(3^3P_J)$ with Cl_2 , which proceeds at a rate approaching that of the collision number (table 1), is in accord with correlations based on the weak spin orbit coupling approximation. Chemical reaction to yield ground state products is highly exothermic and there are three potential surfaces available for this overall process:



There are no analogous data for $\text{C}(2^3P_J)$ and $\text{Ge}(4^3P_J)$ with which this result can be compared.

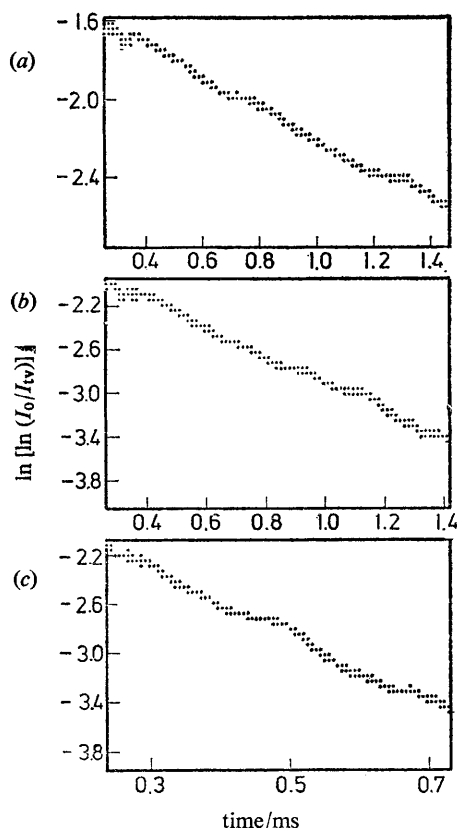
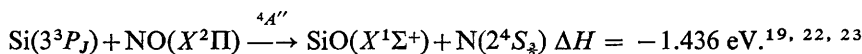


FIG. 2.—Pseudo first-order plots obtained by monitoring the absorption of resonance radiation at $\lambda = 251.6$ nm ($4^3P_J \leftarrow 3^3P_J$) indicating the decay of $\text{Si}(3^3P_J)$ in the presence of NO. $p_{\text{SiCl}_4} = 0.02$ N m $^{-2}$; $p_{\text{total with He}} = 2.8$ kN m $^{-2}$; $E = 45$ J; repetition rate = 0.2 Hz; no. of experiments for averaging = 32. $p_{\text{N}_2\text{O}}/\text{N m}^{-2}$: (a) 0.0; (b) 0.06; (c) 0.17.

Chemical reaction of $\text{Si}(3^3P_J)$ with NO is exothermic, ground state reactants and products correlating *via* a $^4A''$ surface:



Removal of $\text{Si}(3^3P_J)$ by NO is very rapid (table 1), more rapid indeed than $\text{C}(2^3P_J)$ (table 1), and we would presume that $\text{SiO}(X^1\Sigma^+)$ is the product. Reaction to yield SiN is highly endothermic, even on the basis of the higher estimated bond dissociation energy for this molecule reported by Vedeneyev *et al.*²⁴ [$D(\text{NO}) = 6.493$ eV,^{19, 23} $D(\text{SiN}) = 4.5 \pm 0.4$ eV,¹⁹ $D(\text{SiN}) = 5.2 \pm 0.4$ eV²⁴]. This conclusion may be contrasted with the removal of $\text{C}(2^3P_J)$ by NO. The plate photometric measurements of Braun *et al.*²⁰ clearly demonstrated the production of CN, observed *via* its intense ultraviolet absorption system, and also weak absorption by NCO at higher pressures resulting from three-body recombination. Husain and Kirsch⁸ have given the correlations leading to $\text{CN}(X^2\Sigma^+) + \text{O}(2^3P_J) (^2A' + 2^2A'' + ^4A' + 2^4A'')$ for which reaction is exothermic ($\Delta H = -1.05$ eV^{19, 23}). The analogous process to that proposed above for $\text{Si}(3^3P_J)$, leading to $\text{CO}(X^1\Sigma^+) + \text{N}(2^4S_{3/2})$, is highly exothermic ($\Delta H = -4.60$ eV^{19, 23}) and for which there is also a $^4A''$ surface. The absence of

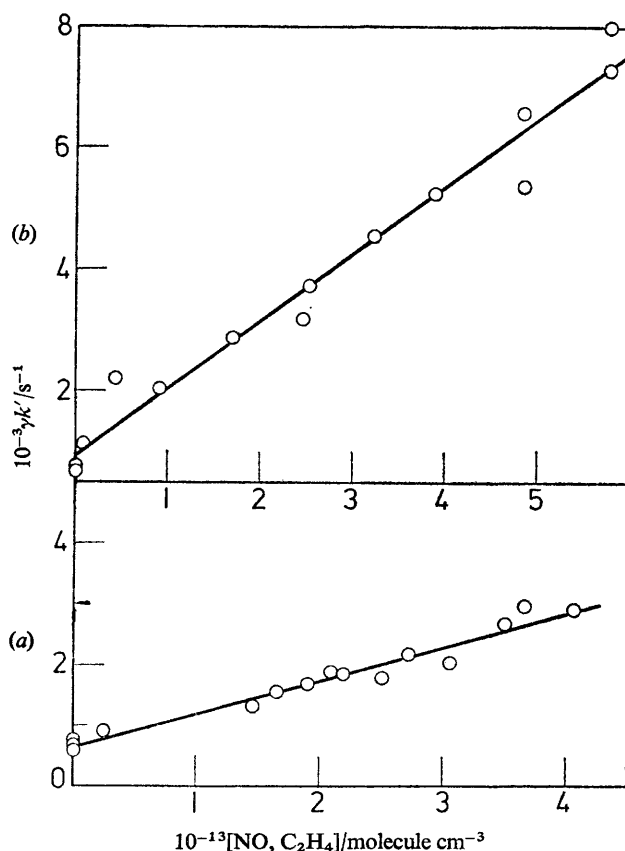


FIG. 3.—Plots of pseudo first-order rate coefficients ($\gamma k'$) for the decay of $\text{Si}(3^3P_J)$ in the presence of (a) NO and (b) C_2H_4 .

this pathway is surprising and the slower rate for $\text{C}(2^3P_J) + \text{NO}$ compared with that for $\text{Si}(3^3P_J) + \text{NO}$ (table 1) may reflect the two different types of routes for the two atoms. In further contrast to both $\text{C}(2^3P_J)$ and $\text{Si}(3^3P_J)$, chemical reaction of $\text{Ge}(4^3P_0)$ with NO is endothermic. The rate of removal of $\text{Ge}(4^3P_0)$ by NO (table 1) is sufficiently different to those for the other low lying spin orbit states $\{10^{12}k[\text{Ge}(4^3P_J) + \text{NO}](\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, 300 \text{ K})$:

$$J = 0, 3.8 \pm 0.6; J = 1, 2.5 \pm 0.2; J = 2, 2.1 \pm 0.2\}^{10}$$

to conclude that the apparent second-order rate constant for $\text{Ge}(4^3P_0) + \text{NO}$ does *not* arise from a Boltzmann equilibrium between the three spin orbit levels. Any third order kinetic dependence of $\text{Ge}(4^3P_0) + \text{NO}$ was not investigated.¹⁰ From the total pressures employed,¹⁰ one may calculate a third order rate constant of $k[\text{Ge}(4^3P_0) + \text{NO} + \text{He}] \approx 4.7 \times 10^{-30} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ (300 K), indicating a mean lifetime for an initially produced energised GeNO^* molecule of $\approx 10^{-10} \text{ s}$, a sensible value for a species of this atomicity.

A detailed discussion of the chemical reaction of all the $np^2(3P_0)$ group IV atoms, $\text{C} \rightarrow \text{Pb}$, with molecular oxygen has been given hitherto¹ in terms, where appropriate, of symmetry arguments on the nature of the potential surfaces involved. Briefly, symmetry-allowed, exothermic routes to both $\text{SiO}(X^1\Sigma^+) + \text{O}(2^3P_J)$ and $\text{SiO}(X^1\Sigma^+) +$

TABLE 1.—COMPARISON OF RATE DATA FOR THE COLLISIONAL REMOVAL OF $C(2^3P_J)$, $Si(3^3P_J)$ AND $Ge(4^3P_0)$ BY VARIOUS GASES.

$(k_R/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, \text{ at } 300 \text{ K})$			
R	$C(2^3P_J)$	$Si(3^3P_J)^*$	$Ge(4^3P_0)$
H_2	<i>a, b</i>	<i>f</i>	—
N_2	<i>c</i>	<i>g</i>	$2.5 \pm 0.2 \times 10^{-13}$ (11)
O_2	$2.6 \pm 0.3 \times 10^{-11}$ (9)	$2.7 \pm 0.3 \times 10^{-10}$ (1)	$1.2 \pm 0.1 \times 10^{-10}$ (10)
	$3.3 \pm 1.5 \times 10^{-11}$ (8)		
	3.3×10^{-11} (20)		
	2.5×10^{-12} (21)		
Cl_2	—	$3.3 \pm 0.3 \times 10^{-10}$	—
CO	<i>d</i>	<i>h</i>	$3.6 \pm 0.4 \times 10^{-13}$ (10)
NO	$4.8 \pm 0.8 \times 10^{-11}$ (9)	$1.1 \pm 0.1 \times 10^{-10}$	$3.8 \pm 0.6 \times 10^{-12}$ (10)
	$7.3 \pm 2.2 \times 10^{-11}$ (8)		
	1.1×10^{-10} (20)		
CO_2	$< 10^{-15}$ (9)	$1.1 \pm 0.1 \times 10^{-11}$	$6.0 \pm 0.5 \times 10^{-12}$ (11)
	$< 10^{-14}$ (8)		
N_2O	$1.3 \pm 0.3 \times 10^{-11}$ (9)	$1.9 \pm 0.2 \times 10^{-10}$ (1)	$5.8 \pm 0.8 \times 10^{-12}$ (11)
	$2.5 \pm 1.6 \times 10^{-11}$ (8)		
CH_4	$< 2 \times 10^{-15}$ (8)	$< 10^{-14}$	—
	$< 5 \times 10^{-15}$ (20)		
	$< 6 \times 10^{-17}$ (21)		
CF_4	—	$2.4 \pm 0.3 \times 10^{-12}$	$1.5 \pm 0.1 \times 10^{-13}$ (11)
C_2H_2	$< 6.3 \times 10^{-17}$ (21)	$4.9 \pm 0.3 \times 10^{-10}$	$2.7 \pm 0.4 \times 10^{-10}$ (11)
C_2H_4	$< 6.3 \times 10^{-17}$ (21)	$2.2 \pm 0.2 \times 10^{-10}$	$8.3 \pm 0.4 \times 10^{-12}$ (11)
$SiCl_4$	—	$7.2 \pm 1.2 \times 10^{-11}$ (1)	—

* This work. References are in brackets.

a, b—third order ($k/\text{cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$, 300 K, $M = \text{He}$), $6.9 \pm 1.2 \times 10^{-32}$ (9), $7.2 \pm 2.5 \times 10^{-32}$ (8); *c*—third order ($M = \text{Ar}$), $3.1 \pm 1.5 \times 10^{-33}$ (8); *d*—third order ($M = \text{He}$), $6.3 \pm 2.7 \times 10^{-32}$ (8); *f, g, h*—expressed as third-order rate constants ($M = \text{He}$): $f < 10^{-33}$; $g < 4 \times 10^{-32}$; $h < 3 \times 10^{-33}$.

$O(2^1D_2)$ are available, and the high reactivity between $Si(3^3P_J)$ with O_2 (table 1) reflects this. Identical arguments apply to $C(2^3P_J) + O_2$.^{1, 7, 8} Ogryzlo *et al.*²⁵ concluded from infrared emission measurements on the vibrational distribution in $CO(X^1\Sigma^+)$ from the reaction of $C + O_2$ in a flow system, that the channel leading to $O(2^1D_2)$ was preferred. The correlation diagram connecting the states of $Ge + O_2$ and $GeO + O$ in (J, Ω) coupling has been given by Brown and Husain¹⁰ and employed to discuss the reactivity of atomic germanium in the three low lying individual spin orbit levels.^{1, 10} The kinetically second-order rapid reaction of $Sn(5^3P_0) + O_2$ ²⁶ has been briefly considered in terms of both weak spin orbit coupling and (J, Ω) coupling. Reaction between $Pb(6^3P_0) + O_2$ is endothermic and exhibits kinetics which are overall third-order.²⁷

Reactions with H_2 , N_2 and CO to yield SiH , SiN and SiO are endothermic ($\Delta H = +1.42$,¹⁹ $+4.56$ to 5.26 ^{19, 24} and $+3.161$ eV,^{19, 24} respectively) and the observed rates are expressed as limits for third-order rate constants, calculated from the total pressures with helium that were employed. The present flow system permits only a limited variation in total pressure at constant p_{SiCl_4} . Whilst we would, therefore, not wish to press strongly a general comparison of the calculated third-order limits for $Si(3^3P_J)$ with measured third-order rate constants for $C(2^3P_J)$ (table 1), the difference between the data for $C(2^3P_J) + H_2$ and $Si(3^3P_J) + H_2$, in particular (table 1), is noticeably large $\{k[C(2^3P_J) + H_2 + He]/k[Si(3^3P_J) + H_2 + He] > \sim 70$

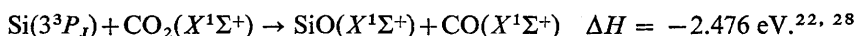
(table 1)}. Both CH_2 and SiH_2 are species whose electronic spectra have been reported.²⁸ In the case of CH_2 , $\text{C}(2^3P_J) + \text{H}_2(X^1\Sigma_g^+)$ correlates *via* a $^3A''$ surface with the $\text{CH}_2(X^3\Sigma_g^-)$ ground state.^{7, 28} Herzberg²⁸ designates the ground state of SiH_2 as (\tilde{X}^1A_1) but indicates that the assignment of the observed spectrum to the ground state is uncertain. If the ground state were indeed $\text{SiH}_2(\tilde{X}^1A_1)$, $\text{Si}(3^3P_J) + \text{H}_2(X^1\Sigma_g^+)$ would not correlate with this species on the basis of spin alone, and the explanation of the significantly slower rate for $\text{Si}(3^3P_J) + \text{H}_2 + \text{He}$ (table 1) would arise from the effect of either a non-adiabatic transition (N.A.T.) involving a spin change or a thermochemically favoured pathway to a triplet state of SiH_2 .

TRIATOMIC MOLECULES

There are two general aspects of the chemistry of atoms in specific electronic states with the molecules N_2O and CO_2 which invariably present themselves in the discussion of the collisional processes. First, both favourable thermochemistry and direct pathways are limited guides in considering reaction rates at a fixed temperature. There are many atomic reactions with these molecules where these two criteria are favourable but which exhibit slow rates.^{5, 29, 30} This is usually attributed to the closed shell, 18-electron structure of these molecules, leading to energy barriers for reaction, a point which emphasises one important difference between a correlation diagram and a potential energy surface. Recent experiments by Wiesenfeld and Yuen²⁶ on the temperature dependence of the reaction of $\text{Sn}(5^3P_0) + \text{N}_2\text{O}$ further emphasises this difference by indicating the favoured role of processes involving N.A.T.s compared to symmetry-allowed processes characterised by significant energy barriers. It must further be emphasised that correlations for atomic reactions with these molecules employ C_s symmetry in the collision, which is not, of course, the 'least symmetrical complex'.⁶ Secondly, the low bond energy of N_2O [$D(\text{N}_2 - \text{O}) = 1.677 \text{ eV}$]²⁸ yields reaction exothermicities which are so high as to prevent the construction of correlation diagrams to the point of thermoneutrality on account of ignorance of the complete manifold of diatomic oxide states to these energies.

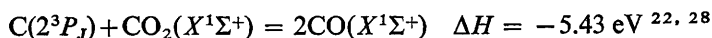
The above considerations comprised the essential basis of our recent discussion of the reactions of group IV atoms in the $np^2(^3P_J)$ state with N_2O .¹ Whilst, at least on the basis of the weak spin orbit coupling approximation, reaction to yield ground state CO , SiO and $\text{GeO} + \text{N}_2$ is simply spin-forbidden, favourable channels to excited states may be expected, quite apart from the contribution to the overall rate from exothermic processes involving N.A.T.s of relatively high probability. The very high reaction rate for $\text{Si}(3^3P_J)$, close to that for the collision number (table 1), would indicate reaction by direct pathways as opposed to N.A.T.s. For $\text{C}(2^3P_J)$, there are also exothermic, symmetry-allowed pathways to states of $\text{CN} + \text{NO}$;⁸ for $\text{Si}(3^3P_J)$, reaction to yield SiN is a matter of conjecture in view of the uncertainty in the thermochemistry of SiN .^{19, 24}

The reaction rate for $\text{Si}(3^3P_J)$ with CO_2 is relatively high, (table 1), despite the spin-forbidden nature of the process:



This is far from a unique observation. Donovan and Husain⁷ have emphasised in their survey of atomic reactions, which included many spin forbidden processes, that the N.A.T.s resulting from a spin change with a light atom yield probabilities of the order of 10^{-2} , once surface crossing has taken place. The very low rates observed for many spin forbidden processes arise principally from the effect of spin on the correlation, *i.e.*, the region where the surface crossing actually takes place, and ob-

served *via* the energy barrier. The temperature dependence of the rate of the highly exothermic reaction:



has not been reported, but the slow rate observed at room temperature (table 1) presumably arises from an energy barrier, at least, in part. A similar rate to that observed for $\text{Si}(3^3P_J)$ has been obtained for the spin-forbidden exothermic reaction of $\text{Ge}(4^3P_0) + \text{CO}_2$ ($\Delta H = -1.33 \text{ eV}$)^{19, 28} (table 1).

POLYATOMIC MOLECULES

The upper limit for the rate of $\text{Si}(3^3P_J)$ with CH_4 (table 1) is commensurate with the endothermicity of reaction to yield SiH ($\Delta H = +1.35 \text{ eV}$)^{19, 28} and similar to the result for $\text{C}(2^3P_J) + \text{CH}_4$ (table 1). Reaction with CF_4 to yield SiF is exothermic ($\Delta H = -1.01 \text{ eV}$)^{19, 24} and the observed removal of $\text{Si}(3^3P_J)$ by this molecule is in accord with this. The rapid removal of $\text{Si}(3^3P_J)$ by the unsaturated molecules C_2H_2 and C_2H_4 (table 1) is presumed to result from efficient addition with ring insertion. This can be contrasted with the slow rates for the removal of $\text{C}(2^3P_J)$ by these molecules, reported by Martinotti *et al.*²¹ (table 1), which may partly reflect the regeneration of carbon atoms under the complex chemical conditions pertaining during plasmolysis. Following the use of nuclear recoil techniques, Wolfgang *et al.*^{31, 32} attributed the insertion of ^{11}C into the C—C bond of C_2H_4 to the reaction of singlet atomic carbon. Skell and Engel³³ also postulated the reaction of singlet carbon with C_2H_4 from the analysis of the reaction of the products of the species derived from a carbon arc with this molecule. However, CNDO calculations³⁴ have

demonstrated the high stability of an intermediate of the type $\text{CH}_2-\overset{\text{C}}{\text{CH}_2}$ with respect to $\text{C}(2^3P_J) + \text{C}_2\text{H}_4$. In our opinion, a further *direct* measurement on the addition of $\text{C}(2^3P_J)$ with both C_2H_4 and C_2H_2 would be justified in view of the uncertainty of the rates of these fundamental processes.

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