Role of Triplet Biradical Intermediates

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Hg(6^3P_1) photosensitization of cyclohexanone results in the formation of pent-1-ene, cyclopentane and hex-5-enal, just as observed in the direct photolysis. As the pressure of added SF₆ or Ar bath gas is increased, both the total product quantum yield and that of the hydrocarbon products decrease, while that of hex-5-enal increases. A comprehensive mechanism, differing in detail from those previously proposed, is now formulated to account quantitatively for the experimental observations. Two sequentially formed, energy randomized, vibrationally excited triplet biradicals are believed to be the important intermediates that lead to product formation. Thus α -C—C bond cleavage of triplet cyclohexanone yields an acyl-alkyl biradical, ⁸B*, that can give rise to both hex-5-enal and also, by loss of CO, to the penta-1,5-diyl biradical, ⁸PD*, the precursor of the hydrocarbon products. Rate constants for intersystem crossing of the two biradicals are deduced along with that for the fragmentation of ⁹B*. An RRKM treatment of this decomposition suggests that the observed rate constant is best fitted using a biradical excitation energy calculated by assuming a heat of formation for ³B greater than the value computed by conventional methods, which neglect electronic interaction. In addition, relative rate constants are obtained for the intramolecular disproportionation and cyclisation of ¹B and ¹PD when both vibrationally excited and thermalized. It is concluded that the critical energy for ring closure of ¹PD is greater than that for isomerization to pent-1-ene.

Photodecomposition of medium-ring-size cycloalkanones is thought to proceed principally via the triplet state.¹⁻⁵ While the general features of the overall mechanisms are fairly well understood, the exact nature of the triplet intermediates involved and their precise roles are still somewhat uncertain. In particular, for cyclohexanone the type of triplet state intramolecular isomerisation process leading to hex-5-enal, and the behaviour of excited pentamethylene biradicals require further investigation. In addressing ourselves to these problems we have prepared triplet cyclohexanone by energy transfer from excited $Hg(6^3P_1)$ atoms and now report results that not only require the previously accepted mechanism¹ for photodecomposition to be modified, but also enable it to be developed in greater detail.

EXPERIMENTAL

Cyclohexanone, obtained from both the Aldrich Chemical Co and Fluka, was purified before use by vapour-phase chromatography on a Carbowax 200 M column. It was subsequently stored *in vacuo* at 77 K. Argon (B.O.C.) and sulphur hexafluoride (Air Products Ltd, stated purity $\ge 99.9\%$) were used without further purification. Two conventional Pyrex glass, grease-free vacuum lines constructed with Teflon stopcocks (J. Young & Co Ltd) were used to make up gas mixtures for photolysis. The lamps used were flat-spiral, low pressure, mercury resonance lamps (Hanovia Detectolite). The incident radiation was filtered through 2 cm

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path-length aqueous solutions of nickel sulphate (2.5 mol dm⁻³) and 2,6-dimethyl-3,7-diaza-1,6-cycloheptadiene perchlorate (0.002 mol dm⁻³), to prevent light of wavelengths other than 253.7 nm from reaching the cell. The cylindrical Pyrex reaction cells, volume *ca*. 30 cm³, were each fitted with a 5 cm diameter Spectrosil window. Mercury vapour was provided by a small mercury droplet.

Reaction mixtures were analysed both on a 2 m \times 3 mm squalane/alumina column operated at 100 °C, fitted to a modified Pye 104 gas chromatograph equipped with a home-made rotary gas-sampling valve, and on a 2 m \times 3 mm Porapak Q-S column fitted to a Perkin-Elmer F11 gas chromatograph. Each instrument was equipped with a flame-ionization detector. Peak areas on the chart recorder traces, estimated by planimetry, were converted to relative product yields by multiplying them with the following measured detector calibration factors: pent-1-ene 1.0, cyclopentane 1.0, hex-5-enal 1.633.

pressure ^b /Torr	$\Phi_{ m hex}$	$\Phi_{ ext{CP}}$	Φ_{PE}
9.0		0.269	0.622
12.0	0.019	0.269	0.606
13.5		0.267	0.687
19.0	0.020	0.255	0.640
25.0	_	0.248	0.689
25.0	_	0.247	0.635
27.0		0.244	0.655
35.0	_	0.227	0.656
40.0	0.025	0.207	0.582
50.0	_	0.227	0.648
69.5	_	0.212	0.640
80.0	0.031	0.177	0.514
142.0	0.046	0.161	0.500
252.0	0.060	0.130	0.417
282.0	0.049	0.120	0.388
282.0	0.054	0.116	0.369
328.0	0.046	0.102	0.321
372.0	0.063	0.108	0.353
441.0	0.063	0.097	0.301
496.0	0.067	0.086	0.278
578.0	0.071	0.080	0.254
683.0	0.072	0.072	0.232
745.0	0.076	0.066	0.209

TABLE 1.—PRODUCT QUANTUM YIELDS^a USING SF₆ bath Gas

^{*a*} See text for explanation of symbols; ^{*b*} Total pressure of 3.0 Torr cyclohexanone plus that of SF_6 .

Actinometry was carried out as described previously using the $Hg(6^{3}P_{1})$ photosensitized isomerization of *cis*-but-2-ene.⁶ At pressures above 30 Torr* the mercury photosensitization quantum yield for this process is 0.5 for low conversion levels.⁷ The quenching cross-sections for $Hg(6^{3}P_{1})$ of Ar and SF₆, used as bath gases in this work, are very much smaller than that of cyclohexanone,⁸ and consequently their inclusion in the reaction mixture did not significantly affect the rate of quenching of the excited Hg atoms by the ketone, even when present in large excess.

* 1 Torr = 133.3 Pa.

RESULTS

As in both the direct and benzene-sensitized photodecomposition,¹ the sole hydrocarbon products at low extents of conversion (< 0.5%) from the Hg($6^{3}P_{1}$) photosensitization of cyclohexanone at 295 K are pent-1-ene and cyclopentane. No lower molecular-weight products are observed, but in contrast to an earlier study,⁹ the present work shows that hex-5-enal is formed, particularly at high pressures,



FIG. 1.—Variation of the product ratio pent-1-ene to cyclopentane with total pressure (3 Torr cyclohexanone plus SF₆). Inset: Expansion of low pressure data. (\bigcirc , data points for which product quantum yields were measured, *cf.* table 1; \triangle , additional points for which Φ values were not obtained). Solid line is computed as described in the text.

although only in small yields. Photolyses were carried out using a constant pressure of cyclohexanone, 3.0 Torr, in the presence of either argon (0-544.0 Torr), or sulphur hexafluoride (0-742.0 Torr). At the lowest pressure used, the product quantum yields resemble those obtained in the direct photolysis at wavelengths < 280 nm. Table 1 shows the observed mercury photosensitization quantum yields as a function of pressure of added SF_6 . The data show that as the pressure increases, the yields of both pent-1-ene and cyclopentane decrease, as does the total product quantum yield, from a value that is close to unity at 3 Torr, whereas the yield of hex-5-enal increases. Furthermore, the ratio of pent-1-ene to cyclopentane $(\Phi_{\rm PE}/\Phi_{\rm CP})$ goes up as the pressure increases and appears to approach a limiting value as the pressure tends to infinity, as shown in fig. 1. Similar but less pronounced trends are observed using argon as bath gas. Fig. 2 and 3 display the variation of the inverse of the total C_5 hydrocarbon quantum yield, Φ_{C_s} , and the ratio of the yield of hex-5-enal, Φ_{hex} , to that of C_5 hydrocarbon, with total pressure, respectively, using SF₆ as the bath gas. Both plots are linear, in contrast to graphs of the variation of the hex-5-enal yield or inverse yield, against either pressure or inverse pressure, all of which show noticeable curvature.



FIG. 3.—Variation of the product ratio of hex-5-enal to C₅ hydrocarbon yield with total pressure.

DISCUSSION

In the direct photolysis of medium-ring-size cyclic ketones, product formation proceeds *via* a vibrationally excited triplet state of the parent ketone.^{1.5} For cyclohexanone, the products observed in the present work from the $Hg(6^{3}P_{1})$ sensitized decomposition are the same as in the direct photolysis and their yields are similar,

particularly at low pressures and short wavelengths, indicating that both photodecompositions probably proceed largely through common intermediates.

In the direct photolysis of 2,6-dimethylcyclohexanone there is also strong evidence for the formation of a long-lived biradical,¹⁰ and similar biradicals are thought to be important intermediates as precursors to both hydrocarbon and aldehyde products in the photolysis of cyclopentanones^{2, 3} and cycloheptanone.^{4, 5} A third type of intermediate, a cyclic oxycarbene, has also been postulated,¹¹ most recently by Shortridge and Lee for the photolysis of cyclohexanone,¹ as that leading to aldehyde products. They postulated this intermediate to account for an observed apparent invariance of hex-5-enal yield with pressure over the small range of their study. In the present work a much wider pressure range has been used and it is evident that Φ_{hex} increases as the pressure increases, indicating that the hex-5-enal is formed from an intermediate which has suffered collisional deactivation. Direct photolysis experiments over a wider pressure range with careful monitoring of the hex-5-enal quantum yields would help to resolve the ambiguity between the two sets of data.

Our results do not in themselves allow the pressure quenchable intermediate to be identified with certainty. However, in view of the earlier compelling evidence, we propose that it is a biradical and that it is also the precursor to the C₅ hydrocarbon products. If the hex-5-enal and C₅ products are formed from different pressurequenchable intermediates they cannot be formed sequentially *en route* to the hydrocarbons, or otherwise the plot of $\Phi_{C_s}^{-1}$ against pressure would be curved. The simplest interpretation is therefore that these intermediates are the same species and that the major features of the mechanism are represented by the following skeleton scheme, where T* and ³B* represent the triplet ketone and the vibrationally excited ring-opened acyl-alkyl triplet biradical

$$CH \xrightarrow{Hg(6^3P_1)} T^* \xrightarrow{3} B^* \xrightarrow{M} hex-5-enal$$

This mechanism is analogous to that proposed by Hamer and Huber for the short wavelength ($\lambda < 300$ nm) photolysis of cycloheptanone,⁵ in which they propose that the biradical precursor is a non-pressure-quenchable, possibly non-energy-randomized short-lived triplet species, T_1^+ .

To account for the variation of product yields with pressure, the fate of ${}^{3}B^{*}$ must be considered in more detail. In common with others^{1, 5} we accept that the C₅ products are produced by an excited 1,5-pentadiyl biradical (PD) formed by CO loss from ${}^{3}B^{*}$. The lifetime of the excited singlet pentadiyl biradical (${}^{1}PD^{*}$) is so short as to preclude collisional interception. Thus the observed pressure dependences of the C₅ product yields must arise from effects occurring before ${}^{3}PD^{*}$ is lost by intersystem crossing to ${}^{1}PD^{*}$. The simplest interpretation is that the essential competition is between intersystem crossing and collisional deactivation. Since the relative yields of pent-1-ene and cyclopentane will depend upon the degree of excitation of the ${}^{1}PD$, such a mechanism leads to pressure dependent yields of these products and, as shown later, conforms quantitatively to the observed pressure dependences.

Whilst ring closure of PD to form cyclopentane can only occur after intersystem crossing, it is conceivable that pent-1-ene could be formed *via* its triplet state, directly from ³PD*. A simple RRK calculation based on estimated Arrhenius parameters for the necessary 5*sp* hydrogen transfer¹² and the relevant estimated heats of formation¹³ shows that this pathway is negligibly slow however, even if *all* the excess vibrational energy of ³B* were to be acquired by ³PD*.

The re-formation of cyclohexanone, implied by the lower total product quantum yield at higher pressures, and the formation of hex-5-enal from ${}^{3}B^{*}$, are also pressure dependent channels. The pressure dependence is analogous to the behaviour of that

for the hydrocarbon products, and similar arguments can be used to construct a parallel reaction scheme with competition between collisional quenching of ³B*, intersystem crossing to ¹B* and loss of CO to form ³PD*. These channels have been incorporated in the overall reaction mechanism shown in fig. 4. The inclusion of the route to hex-5-enal via ¹PD* satisfactorily accounts for the small yield of this compound at zero pressure, illustrated by the non-zero intercept of fig. 3. Reactions (4) and (6) are depicted as yielding only cyclohexanone. It is conceivable that other



FIG. 4.—Proposed mechanism for the reaction of vibrationally excited triplet cyclohexanone.

undetected products, e.g. n-butylketene, might be formed in these reactions, but this seems unlikely as the total product quantum yield extrapolates to unity, within experimental error, at zero Torr. For the same reason, intersystem crossing of T* to ground-state cyclohexanone can also be omitted.

Whilst alternative mechanisms could be devised, that proposed seems to be the simplest scheme capable of accounting for (i) the decrease in total product quantum yield with pressure, (ii) the linear dependences of both $\Phi_{C_5}^{-1}$ and Φ_{hex}/Φ_{C_5} on pressure and (iii) the increase in pent-1-ene yield with respect to the cyclopentane yield with increasing pressure. A steady-state treatment of the mechanism demonstrates these points and allows a limited analysis of the data, sufficient to show that it leads to plausible values for the rate parameters, as follows.

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Eqn (1)-(3) are those derived by the kinetic analysis.

$$\Phi_{\rm PE}/\Phi_{\rm CP} = \frac{\{\alpha\delta(1+\gamma) + \gamma(1+\alpha)[M]\}}{\{\delta(1+\gamma) + (1\alpha)[M]\}}$$
(1)

$$\Phi_{C_5}^{-1} = 1 + \rho \mu + \mu[M] \tag{2}$$

$$\Phi_{\rm hex}/\Phi_{\rm C_s} = \rho\mu\xi + \tau\mu[M] \tag{3}$$

The rate constant ratios are defined as $\alpha = k_7/k_8$, $\gamma = k_9/k_{10}$, $\delta = k_{13}/\omega$, $\rho = k_{12}/\omega$, $\xi = k_5/(l_5 + k_6)$, $\mu = \omega/k_2$, $\tau = k_3/(k_3 + k_4)$, [M] is the total pressure and ω is the collision rate. The data obtained using SF₆ bath gas, shown in fig. 2 and 3 can be analysed by eqn (2) and (3). In this way the slope of fig. 2 gives the half-quenching pressure for ³B* decomposition, μ^{-1} , equal to 290 ± 30 Torr, and that of fig. 3 gives, when combined with the value for μ , $\tau = (9.65 \pm 1.7) \times 10^{-2}$, leading to $k_3/k_4 = (0.107 \pm 0.021)$. The intercept of fig. 2, 1.017, is too close to unity for a meaningful value of ρ to be derived directly, but an upper limit of 40 Torr can be calculated from the estimated error limits in $(1 + \rho\mu)$ and μ . The intercept of fig. 3, $(1.6 \pm 1.0) \times 10^{-2}$ enables $\rho \xi = (4.6 \pm 3.4)$ Torr to be calculated. ξ reflects the branching ratio k_5/k_6 and must lie between zero and unity. Therefore the minimum value for ρ , identified as the half-quenching pressure for ³B* intersystem crossing, is (4.6 ± 3.4) Torr. Using the estimated maximum value for ρ , 40 Torr, gives $\xi = (0.115 \pm 0.085)$, corresponding to a minimum value for k_5/k_6 of (0.13 ± 0.1) . Thus, despite the well characterised value for τ , the large range of possible values for ξ rules out conclusions concerning the effect of excess vibrational energy on the importance of the aldehydeforming isomerization reaction of ¹B relative to cyclisation.

The hydrocarbon yield data obtained using argon as bath gas in the pressure range 100-500 Torr, can also be plotted as a function of pressure in a manner analogous to fig. 2. The slope of this plot is considerably lower than that for SF₆ bath gas, reflecting the lower relative collisional deactivation efficiency, β_p , of Ar compared with SF₆. It can be increased to the same value, however, by constructing the graph against the effective pressure, calculated from a β_p value of 0.13 ± 0.02 . This value for β_p can be compared with those measured previously, *e.g.* 0.16 for the collisional deactivation of vibrationally excited ground-state 2,3-dimethylcyclobutanone.¹⁴

The form of eqn (1) rules out the use of any simple method for the evaluation of α , γ and δ from the variation of $\Phi_{\rm PE}/\Phi_{\rm CP}$ with pressure. It was therefore necessary to adopt a computer-modelling approach of the kind successfully employed previously to analyse data from the $Hg(6^{3}P_{i})$ photosensitizations of 3-methylbut-1-ene¹² and 3,3-dimethylbut-1-ene.⁶ The method fits a curve to the data by using an iterative procedure to refine initial estimates of the unknown parameters, ultimately giving optimum values as defined by a least-squares criterion. In this way it was found that eqn (1) could best be fitted to the data obtained using SF₆ as bath gas when $\alpha = 1.52$, $\gamma = 3.26$ and $\delta = 7.29$ Torr. Fig. 1 shows the curve computed from these values. γ is the limiting value of $\Phi_{\rm PE}/\Phi_{\rm CP}$ at infinite pressure. Above 250 Torr the measured ratio of $\Phi_{\rm PE}/\Phi_{\rm CP}$ is essentially constant. γ is therefore defined fairly precisely, the estimated error being $\pm 2\%$. Error estimates for α and δ are best obtained by constructing the linear plot of $(\gamma - \Phi_{\rm PE}/\Phi_{\rm CP})[M]/(1+\gamma)$ against $\Phi_{\rm PE}/\Phi_{\rm CP}$, using the known γ value. By rearranging eqn (1) it can be shown that the intercept/slope ratio of this plot is $-\alpha$ and the slope $\delta/(1+\alpha)$. In this way error limits of ± 0.2 and ± 2.5 Torr were obtained for α and δ , respectively.

Ratios of pent-1-ene to cyclopentane show a smaller pressure dependence using Ar as bath gas, reflecting the lower relative collisional deactivation efficiency, β_{p} , of Ar,

so that a similar analysis of the data yields less precise α , γ and δ values. Equally good fits to the data could be obtained for β_p values in the range 0.1-0.28, corresponding to limiting optimum values for α and δ of 0.8-1.8 and 1.3-9.2 Torr, respectively, and an optimum γ value of 3.47.

The rate constant ratio γ is the intramolecular disporportionation/combination ratio for *thermalised* singlet pentamethylene biradicals, whereas α is the same ratio for the *excited* singlet biradical. As $\alpha < \gamma$, the 5sp isomerization reaction must have a lower activation energy than does the cyclisation reaction, *i.e.* $E_{g} < E_{10}$. This conclusion complements previous reports that the activation energies for the selfdisproportionations of ethyl,¹⁵ iso-propyl^{16,17} and sec-butyl radicals¹⁷ are all less than those for self-combination.

The half quenching pressure for ³PD* intersystem crossing, δ , must correspond to an averaged rate-constant value, due to the presumably fairly wide spread in internal energies of ³PD*. However, as rate constants for similarly excited biradicals appear not to be particularly energy dependent,18 the range of averaged rate-constant values

$k_2/10^9 { m s}^{+1}$	$k_{12}/10^7 \text{ s}^{-1}$	$k_{13}/10^7 \text{ s}^{-1}$	k ₃ /k ₄	k_{5}/k_{6}	k ₇ /k ₈	k_{9}/k_{10}
(3.1±0.3)	(1.28-42.8)	(7.8 ± 2.7)	(0.107±0.021)	> 0.031	1.52 ± 0.2	3.26 ± 0.06

TABLE 2.—BIRADICAL REACTION RATE CONSTANTS

is probably not very large. It is also possible that the value of δ is overestimated as a result of the strong collision assumption incorporated in our mechanism, which postulates that all ³PD* species that undergo a deactivating collision ultimately react to give the two hydrocarbon products only in the ratio γ . A similar overestimate of the intersystem crossing half-quencing pressure was noted for 2-methylbuta-1,3-diyl biradicals.18

The collision rate for ³B* and ³PD* with SF₆, ω , can be calculated as $1.07 \times 10^7 \text{ Torr}^{-1} \text{ s}^{-1}$ (1.97 × 10¹⁴ cm³ mol⁻¹ s⁻¹) at 295 K by assigning a collision diameter of 501 pm to SF_6 and estimating collision diameters of 630 pm and 570 pm for ${}^{3}B^{*}$ and ${}^{3}PD^{*}$, respectively, by analogy to those for other molecules of similar size and carbon skeleton.¹⁹ Using this collision rate the half-quenching pressures μ , δ and ρ can be converted to the rate constant values, shown in table 2, if the collisional deactivation efficiency of SF₆ is assumed to be unity.

The rate constants k_{12} and k_{13} apply to the interstystem crossing of ³B* and ³PD*. Their magnitudes are comparable with those obtained for the analogous intersystem crossing of triplet 2,2-dimethylbuta-1,3-diyl⁶ and 2-methylbuta-1,3-diyl¹² biradicals $(3.33 \times 10^8 \text{ s}^{-1} \text{ and } 4.56 \times 10^8 \text{ s}^{-1}$, respectively), vibrationally excited by ca. 200 kJ mol⁻¹. The maximum excitation levels of ³B* and ³PD* can be calculated as 164 and 122 kJ mol⁻¹, respectively, by the usual thermochemical methods¹³ from known bond strengths, the standard heats of formation^{1, 20} of cyclohexanone $(-221.9 \text{ kJ mol}^{-1}),$ $(-110.5 \text{ kJ mol}^{-1})$ carbon monoxide and n-pentane $(-146.4 \text{ kJ mol}^{-1})$, and the known excitation energy of the Hg (6^3P_1) atom. In calculating these excitation energies no allowance has been made for the possible destabilising effect of biradical electronic interaction,²¹ currently thought to be non-zero, and in consequence the values are upper limits. In addition, for ³PD* the partitioning of energy accompanying its formation as ³B* dissociates will certainly result in reduced levels of excitation.

Computed values for the critical energy, E_0 , of reaction (2), ³B* decomposition, can be obtained from the value of k_2 using RRKM theory. Calculations were carried out using the same procedures as employed previously.^{6,12} Log₁₀(A/s^{-1}) for the reaction was set equal to 13.5 by analogy with A-factor values for other acyl radical decompositions,²²⁻²⁷ and appropriate reactant and activated complex molecule frequencies assigned accordingly, as detailed in the Appendix. Calculations were performed using various values for the excitation energy E^* up to the maximum computed value, 164 kJ mol⁻¹, over a range of E_0 values. In this way the values of E_0 for each E^* value were found that gave equivalent computed and experimental k_2 values. Thus for $E^* = 164$ kJ mol⁻¹, $E_0 = 85$ kJ mol⁻¹; $E^* = 140$ kJ mol⁻¹, $E_0 = 72$ kJ mol⁻¹; and for $E^* = 120$ kJ mol⁻¹, $E_0 = 66.5$ kJ mol⁻¹. The uncertainty in each E_0 value resulting from the experimental error limits for k_2 is ± 1 kJ mol⁻¹. Wider limits of ± 10 kJ mol⁻¹ result, however, if $\log_{10}(A/s^{-1})$ is allowed to increase or decrease by 0.5.

Activation energies reported for acetyl radical decomposition are 62.8,²² 91.0^{23} and 72.0^{24} kJ mol⁻¹, and for propionyl decomposition values of 61.5,²⁵ 46.4^{26} and 60.2^{27} kJ mol⁻¹ have been measured. The value of E_0 (= 85 kJ mol⁻¹) required by an excitation energy of 164 kJ mol⁻¹ is towards the upper end of this range of measured values and in our opinion is likely to be too high. A lower value implies a higher value for the heat of formation of ³B than that calculated neglecting electronic interaction between the two radical centres, but the magnitude of the discrepancy cannot be determined acurately from our results. However, the calculated by the commonly used thermochemical approach.¹³

In conclusion we find that our data can be adequately explained in a quantitative manner by a mechanism involving two, sequentially formed, vibrationally excited, energy-randomised triplet biradicals, both of which can yield products either before or after collisional deactivation. The precursor, T^* , of the first of these intermediates, ³B^{*}, is best interpreted in terms of an initially formed non-collision-interceptable triplet. Our data give no information on the internal energy distribution of T^* and therefore we are unable to identify it with certainty as either the non-energy-randomised triplet species, T_1^+ , or the quenchable, energy-randomised species, T_1^* , proposed by Hamer and Huber⁵ in their generalised partial mechanism for the deomposition of C_5 - C_7 ring cycloalkanones by direct photolysis.

APPENDIX

RRKM CALCULATION FOR THE DECOMPOSITION OF ${}^{3}B^{*}$

In the absence of published vibrational frequency assignments for molecules such as hexanal that could serve as suitable models for the frequency assignment of ³B, frequencies were chosen with values typical for each of the relevant vibrational modes. The model for the activated complex was constructed to correspond to $\log(A/s^{-1}) = 13.5$, by considering the frequency changes taking place as the C—CO bond was extended. The reaction coordinate was taken as the stretching frequency of this bond. The statistical parameter, L^{\ddagger} , is unity, and the value used for the ratio of partition functions for the adiabatic modes of the complex and reactant molecules, Q_1^+/Q_1 , was 1.5.

The following frequencies (wavenumber/ cm^{-1}) were common to both reactant and complex (degeneracies in parenthesis):

3020 (2)	2926 (4)	2853 (4)	1460 (5)	1300 (9)	850 (4)	780 (5)
400 (2)	300	85	27	22	17	

additional reactant frequencies:

1740 430 300 235 27

additional complex frequencies:

2000 225 180 23

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