Experimental and Computer Studies of the Kinetics and Distribution of Vibrational Energy in both Products of the Reaction: $O(^3P) + CS_2 \rightarrow SO + CS$

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The reaction, $O(^3P)+CS_2 \rightarrow SO+CS$ (2), was initiated by flashing NO_2+CS_2 mixtures with radiation of wavelengths >3000 Å. Its progress was monitored by kinetic absorption spectroscopy of the CS $A^1\Pi - X^1\Sigma^+$ (0,0) band and these measurements yielded

$$\log_{10} k_2 = 9 \cdot 8(\pm 0 \cdot 2) - 600(\pm 300) \text{ cal/mole}/2 \cdot 303RT.$$

At higher NO_2 and CS_2 concentrations, other absorption bands, from both this system and the SO $B^3\Sigma^- - X^3\Sigma^-$ system, were observed. By comparing the relative intensities of bands from different ground state vibrational levels, the relative rates into individual quantum states were determined and the total vibrational energy yields were estimated to be 8 % of $-\Delta H$ in CS and about 18 % in SO. A preliminary investigation of the kinematics by computer simulation of collinear reactions over various energy hypersurfaces showed that excitation of the CS vibration results from release of energy as repulsion between the products. The yield is sharply dependent on the steepness of the interaction potential between the separating products and seems likely to vary with the impact parameters of the reactive collision.

The absorption spectra of vibrationally excited molecules produced by chemical reaction were first observed by Norrish and his co-workers.[1] They generated oxygen atoms by flash photolysis of a triatomic molecule XO_2 (X = N, O or Cl) and showed that at least part of the O_2 formed in the subsequent reaction,

$$O + XO_2 \rightarrow O_2 + XO,$$
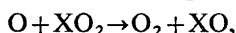
was in highly excited vibrational levels. The early, largely qualitative experiments on reactions of the type,

$$A + BCD \rightarrow AB + CD,$$
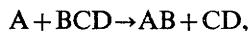
were reviewed in 1960 by Basco and Norrish,[2] who concluded that in simple metathetical reactions, the newly formed molecule (AB) was probably formed in a range of quantum states up to a limit set by the exothermicity of the reaction.

Two main problems must be solved if the rate constants (k_v) for reaction into single vibrational levels are to be determined. First, the observed line or band intensities have to be converted to vibrational state populations (N_v) and then, to obtain a set of k_v it may be necessary to allow for rapid vibrational relaxation, particularly by vibrational-vibrational energy exchange. If absolute integrated absorption coefficients have been measured, absolute N_v can be obtained directly. Alternatively, the relative intensities of several bands can be determined and relative N_v calculated using the Franck-Condon factors. The second method may yield absolute results if the total concentration of product is known and bands from sufficient vibrational levels can be observed.

This paper reports the application of this method to a four-atom metathetical reaction in which the spectra of both products have been observed and the vibrational

energy yield in the " old bond " (CD) quantitatively determined for the first time. The measurement of the overall rate constant is briefly described but emphasis is laid on the determination of the relative rates of reaction into individual vibrational levels of both products. Various simple kinematic models which might give rise to the observed energy distribution are discussed and then a description is given of the results from a preliminary computer study in which the classical equations for collinear motion were solved for the four atoms on modified London-Eyring-Polanyi-Sato (L.E.P.S) energy hypersurfaces.

EXPERIMENTAL

The flash photolysis apparatus was of conventional design. The reaction vessel was 80 cm long and constructed from Pyrex tubing, with quartz end-windows, in order to restrict the radiation entering it to wavelengths >3000 Å. The lamp and vessel were enclosed in aluminium reflectors which were replaced later by magnesium oxide. Charging two 25 μF condensers to 10 kV provided a photolytic flash of 2500 J with a half-life of 55 μsec. Spectra were recorded on Ilford HP3 plates using a Hilger medium quartz spectrograph with a slit width of 0·03 mm. Plates were photometered on a Joyce-Leobl (El2, mark III) double-beam recording microdensitometer.

Carbon disulphide was supplied " spectroscopically pure " (B.D.H. Ltd.) and thoroughly degassed. Nitrogen dioxide from a cylinder (Matheson Co.) was purified by low-temperature distillation and thorough degassing at $-196°$C. Argon from a cylinder (British Oxygen Co.) was passed through a glass wool packed trap at $-196°$C and stored over P_2O_5 and granulated copper at about 300°C before use.

RESULTS AND DISCUSSION

REACTION KINETICS OF $O(^3P) + CS_2 \rightarrow SO + CS$

With the limitation of the incident radiation to wavelengths >3000 Å, the only significant primary photochemical process in $NO_2 + CS_2$ mixtures was the production of $O(2^3P)$ atoms by

$$NO_2 + h\nu(> 3000 \text{ Å}) \rightarrow NO + O(2^3P). \tag{1}$$
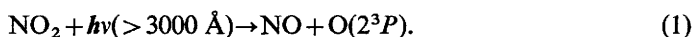
Absorption in the weak CS_2 bands at about 3250 Å only led to significant amounts of CS, at CS_2 partial pressures above 1 torr. Oxygen atoms could then react either with CS_2 or with NO_2 which remained undissociated.

$$O(^3P) + CS_2 \rightarrow SO + CS \tag{2}$$

$$O(^3P) + NO_2 \rightarrow O_2 + NO \tag{3a}$$

$$O(^3P) + NO_2 + M \rightarrow NO_3 + M \tag{3b}$$

The occurrence of (2) was proved by the observation of the CS $A^1\Pi - X^1\Sigma^+$ band system in absorption. Lowering the flash energy and hence the extent of NO_2 photodissociation, made it possible to determine the relative rates of reaction of $O(^3P)$ with CS_2 and NO_2 by observing the variation of the CS yield with reactant concentration.[3] These experiments showed that at 298°K and 100 torr total pressure, $k_2/(k_{3a} + k_{3b}) \simeq 1/1·8$.

To determine k_2 absolutely, the progress of reaction (2) was monitored by kinetic absorption spectroscopy of the CS $A—X$ (0,0) band. The initial concentrations of NO_2 and CS_2 were from 0·005 to 0·012 torr and from 0·060 to 0·130 torr respectively, so that the atoms produced by (1) reacted almost exclusively by reaction (2), thereby producing CS in a pseudo-first-order reaction with a half-life of about 100 μsec. Part of a typical plate is shown in fig. 1. The details of the kinetic analysis, which

requires an expression for the rate of (1), will be published elsewhere.[3] Determinations of the rate constant k_2 at 305°K and 410°K, yield

$$\log_{10} k_2 = 9.8(\pm 0.2) - 600(\pm 300) \text{ cal/mole}/2.303 \, RT.$$

RELATIVE REACTION RATES INTO PRODUCT QUANTUM STATES

When mixtures containing greater NO_2 and CS_2 concentrations were flashed, a number of bands from the CS $A^1\Pi - X^1\Sigma^+$ system could be detected and it became clear that CS was not produced exclusively in $v = 0$ by reaction (2). For example, with $[NO_2] = 0.25$ torr and $[CS_2] = 1.25$ torr, CS bands from levels up to and including $v = 2$ became strong enough for plate photometry. SO was more difficult to observe. However, replacement of the aluminium reflectors by magnesium oxide led to greater photolysis of NO_2, which was shown by an increased yield of CS, including the observation of bands from $v = 3$, and the distinct appearance of SO $B^3\Sigma^- - X^3\Sigma^-$ bands. Fig. 2 shows that SO with up to 4 vibrational quanta was produced but that chemical removal caused its rapid disappearance from the system. The considerable increase in the maximum SO concentration which was achieved by greater NO_2 photodissociation was consistent with its removal by

$$SO + NO_2 \rightarrow SO_2 + NO, \tag{4}$$

for which Clyne, Halstead and Thrush [4] have reported the rate constant, $k_4 = 5 \times 10^9$ l. mole^{-1} sec^{-1}. The spectrum of SO_2 did appear as that of SO disappeared but it was weak and other reactions might contribute to removing SO.

The intensities of the SO bands relative to one another remained constant during the short period they could be observed. It appeared, therefore, that any reactions contributing significantly to the consumption of SO occurred at rates which were independent of the vibrational state of SO and that the short lifetime with respect to chemical removal rendered the effects of vibrational relaxation unimportant. CS, on the other hand, is chemically extremely stable. The populations in the lowest three vibrational levels remained approximately constant relative to one another throughout the flash which suggested that $v = 2$ was both depopulated, and populated from higher levels, by collisional relaxation. This conclusion was later confirmed by the observation of bands from $v = 3$.

The integrated absorption coefficient of a band is related to the vibrational state concentration, by

$$\int k_\nu \mathrm{d}\nu = N_{v''} h\nu (8\pi^3/3h^2c) \left| R_{n'v'n''v''} \right|^2.$$

Here, relative band intensities were compared by measuring the plate density change at the band heads. This method gives an absorption averaged over a large number of lines and since spectrographic dispersion increases to shorter wavelengths, the frequency factor was ignored. Any error introduced will be small because all the bands which were measured fall into a narrow range of wavelengths.

The small difference (0.039 Å) between the equilibrium internuclear distances in the $A^1\Pi$ and $X^1\Sigma^+$ states of CS [5] results in the strongest bands being those with small or zero changes in the vibrational quantum number. There are two other likely consequences of importance. First, the Morse Franck-Condon factors calculated by Felenbok [6] will probably be close to any calculated with more realistic potential data and, indeed, to the actual values. Secondly, $\bar{R}_e^2$, the square of the electronic transition moment, will be approximately equal for the strongest transitions between low-lying levels with the result that the relative absorption intensities should be quite
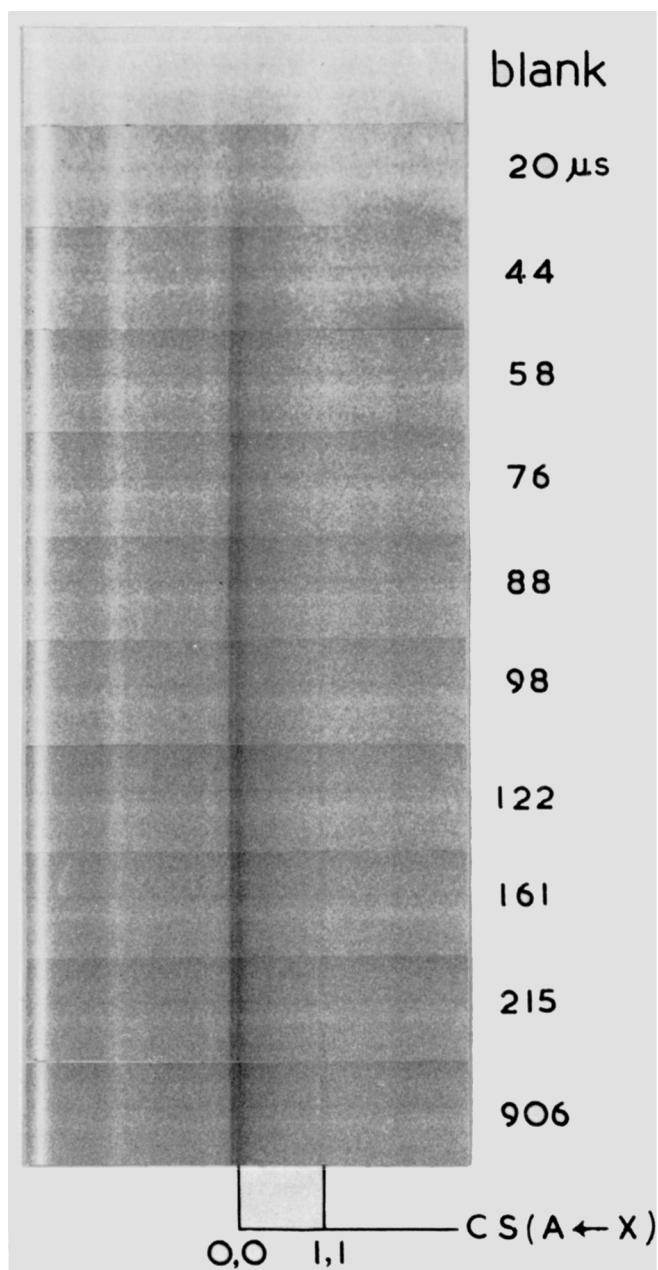
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20 μs

44

58

76

88

98

122

161

215

906

$CS(A \leftarrow X)$

0,0   1,1

FIG. 1.—Formation of CS.   0·01 torr NO_2, 0·13 torr CS_2, 80 torr Ar; 2500J.
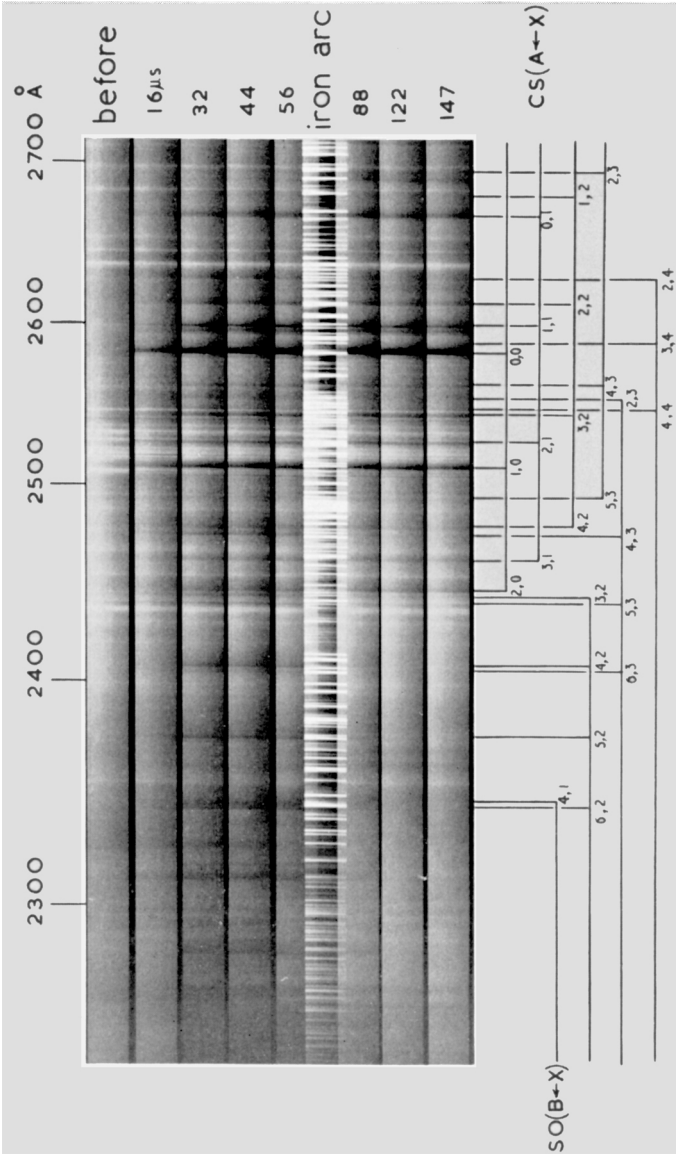
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FIG. 2.—Formation of vibrationally excited CS and SO. 0·25 torr NO_2, 1·25 torr CS_2, 80 torr Ar; 2500J.

accurately converted to N_v by dividing by the Franck-Condon factors. Relative concentrations of CS in $v = 3, 2, 1$ and 0 were determined from measurements on the (0,0), (0,1), (2,2), (3,2) and (4,3) bands. Fig. 3 shows that $N_{v=0}$, $N_{v=1}$ and $N_{v=2}$ correspond to a Boltzmann temperature of 1775°K but that the concentration in $v = 3$ demonstrated that CS concentrations in higher levels might fall away from this distribution. Limits on the total energy yield may be set by assuming (a) a Boltzmann distribution of vibrators at 1775°K, (b) that the complete range of populations was observed and that rates into levels with $v > 3$ were negligible. These limits put the CS vibrational energy yield between 2·0 and 1·65 kcal/mole.
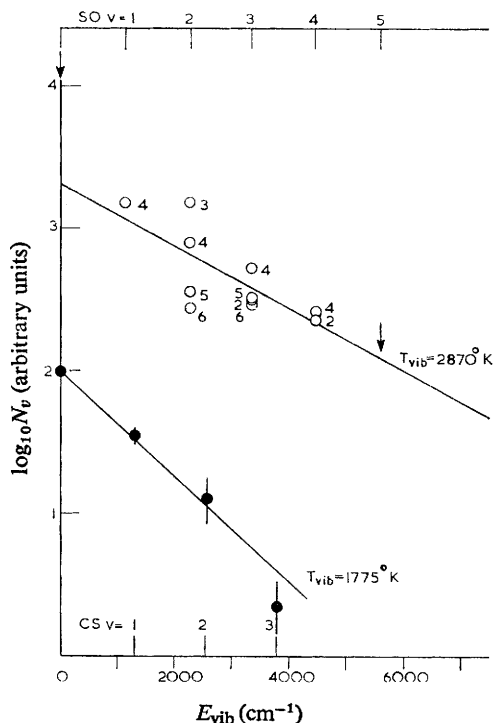

FIG. 3.—Vibrational state distributions of CS (●) and SO ($\bigcirc_{v'}$). For SO, points for individual bands are given.
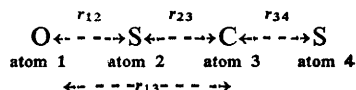
To determine the SO relative vibrational state populations was more difficult. The observed bands were much weaker, partly as a result of the rapid chemical removal of SO and also because the intensity of the electronic transition is dispersed over a great number of individual bands because of the large change in equilibrium inter-nuclear separation. Furthermore, the strongest bands from $v'' = 0$ and $v'' = 1$ are below 2200 Å where accurate plate photometry was impossible due to interference by CS_2 absorption. Finally, the vibrational frequencies in the $B^3\Sigma^-$ and $X^3\Sigma^-$ states differ by approximately two so that there is considerable overlapping of bands.

Relative SO concentrations in the levels $v = 1$-4 were determined from bands above 2300 Å and are presented in fig. 3, together with maximum limits for $N_{v=0}$ and $N_{v=5}$. Franck-Condon factors have not been published for this system, so these were calculated using Morse potentials constructed from the spectroscopic constants compiled by Norrish and Oldershaw [7] and will be published separately.[8] Perturbations of certain levels in the upper $B^3\Sigma^-$ state are known to occur, because the

vibrational levels are spaced irregularly.[7] An erratic variation in $\bar{R}_e^2$ could result and for this reason individual points are presented for each band on which measurements were made. The best line equivalent to a Boltzmann distribution corresponds to $T_{vib} = 2870°K$ and a total vibrational energy yield of 4·2 kcal/mole.

REACTION KINEMATICS OF $O(^3P) + CS_2 \rightarrow SO + CS$

The molecular dynamics of the reaction are now considered in the light of the experimentally determined kinetics and product energy distributions. To simplify the ensuing discussion, the individual atoms and internuclear distances are identified by the following symbols:

$$O \overset{r_{12}}{\leftarrow - - - \rightarrow} S \overset{r_{23}}{\leftarrow - - - - \rightarrow} C \overset{r_{34}}{\leftarrow - - - \rightarrow} S$$

atom 1　　atom 2　　atom 3　　atom 4

$$\leftarrow - - - r_{13} - - - \rightarrow$$

First, however, mention is made of the thermochemistry of the reaction, so that the vibrational energy yields may be expressed as percentages of the total energy released.

The thermochemistry of sulphur-containing molecules has been reviewed by Mackle and O'Hare [9] and the dissociation energies of the group 6A diatomic molecules by Drowart and Goldfinger.[10] They both concluded that $D_0(S_2) = 101$ kcal/mole, a value which now appears to be established and which yields,

$$C_g + 2S_g = CS_{2g} + 275·5 \text{ kcal/mole}.$$
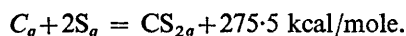
Unfortunately, the dissociation energies of CS and SO are not accurately known. Lagerqvist et al.[11] report 175 (± 7) kcal/mole for $D_0(CS)$. For SO, Norrish and Oldershaw combined their renumbering of the ground-state vibrational levels with Martin's [12] earlier observations on the onset of predissociation, to obtain 123·5 kcal/mole for D_0, compared to 127·1 kcal/mole determined by McGarvey and McGrath [13, 14] by extrapolation of the vibrational levels of SO $B^3\Sigma^-$. Drowart and Goldfinger prefer the former value which leads to 23 kcal/mole for the heat of reaction (2), and yields of 8 % and about 18 % in the CS and SO vibrations.

This is believed to constitute the first quantitative determination of the vibrational energy yield in the "old bond" of a metathetical reaction. There are three mechanisms which might lead to this degree of vibrational excitation; (i) release of energy as the $CS_{(4)}$ bond contracts, possibly after it has been extended earlier in the reaction; (ii) formation of a weakly bound CS_2O intermediate which subsequently decomposes to CS and SO; (iii) release of energy as repulsion between the products.

The CS bond length in CS is only 0·0196 Å shorter than in CS_2 and an upper limit to the vibrational energy resulting from this shortening is easily estimated, classically by a Hooke's law calculation or by determining the energy on the CS Morse potential at $(r - r_e) = 0·0196$ Å, which equals 228 cal/mole. Alternatively, instantaneous energy release can be equated to a Franck-Condon transition and approximate overlap integrals calculated by the method of Bates,[15] which gives $k_{v=0} = 0·94$, $k_{v=1} = 0·058$, $k_{v=2} = 0·00048$ and a total vibrational energy $= 215$ cal/mole. A bond contraction of at least 0·05 Å would be needed to produce the observed excitation and clearly this could only take place if attraction between the reactants early in the reaction caused some overall extension of the CS_2 configuration. Strong evidence against this possibility is provided by the experimental observation that the bond lengths in CS_2^+ and CS_2 differ by less than 0·001 Å.[16]

Excitation of the CS vibration would occur if the reaction proceeded via a weakly bound intermediate capable of surviving several vibrations, since, before the complex

decomposed to SO and CS, the energy of its formation could have undergone considerable internal redistribution. This process is not amenable to computer simulation since considerable computer time would be used during the lifetime of the intermediate. Nevertheless, the mechanism can probably be rejected since it is not consistent with a positive activation energy or with a pre-exponential factor which is " normal " for reaction between an atom and a linear, symmetrical molecule proceeding through a linear transition state. The formation of a bound CS_2O intermediate would correspond to a recombination taking place on a markedly attractive energy hypersurface and would probably have a zero or negative activation energy and a large pre-exponential factor because of the possibility of reaction for collisions with large impact parameters.

A detailed, quantitative investigation of the molecular dynamics has been carried out by computer simulation. Wall, Hiller and Mazur [17, 18] first used a computer to study reaction kinematics and the method for three atoms restricted to coplanar motion has been developed by Blais and Bunker [19-21] and Polanyi and his co-workers.[22, 23] The product energy distribution appears to be controlled largely by the nature of the hypersurface but to be insensitive to either the relative kinetic energy or the impact parameters of the reactive collision. This conclusion apparently remains unaltered when the calculations are extended from two to three dimensions.[21, 24] Raff has applied a Monte Carlo analysis to the reaction $K + C_2H_5I \rightarrow KI + C_2H_5$ considered as a four-body problem.[27] In the preliminary study described here, the four atoms taking part have been confined to collinear motion.

Potential hypersurfaces were constructed by a method similar to the modified L.E.P.S. treatment described by Kuntz et al.[23] The valence-bond potential energy function was reduced to a three-body expression by evaluating Coulomb and exchange integrals for the pair of atoms S and O (Q_{12} and J_{12}) and for the " pseudo-pairs " SC and S (Q_{234} and J_{234}) and SC and O(Q_{134} and J_{134}). The function was then completed by the addition of a modified Morse expression for the $CS_{(4)}$ interaction, so that

$$V(r_{12}, r_{23}, r_{34}) = \frac{Q_{12}}{(1+a)} + \frac{Q_{234}}{(1+b)} + \frac{Q_{134}}{(1+c)} - \left\{ \frac{J_{12}^2}{(1+a)^2} + \frac{J_{234}^2}{(1+b)^2} + \right.$$
$$\left. \frac{J_{134}^2}{(1+c)^2} - \frac{J_{12}J_{234}}{(1+a)(1+b)} - \frac{J_{234}J_{134}}{(1+b)(1+c)} - \frac{J_{12}J_{134}}{(1+a)(1+c)} \right\}^{\frac{1}{2}} +$$
$$D_{34}\{\exp[-2\beta_{34}(r_{34}-r_{34}^\circ)] - 2\exp[-\beta_{34}(r_{34}-r_{34}^\circ)]\},$$

where a, b and c are formally the squares of the overlap integrals and can be adjusted to change the nature of the hypersurface.

To determine the Coulomb and exchange integrals by Sato's method,[25] Morse and anti-Morse potentials were needed for each pair or " pseudo-pair ". The bond energy for SC—S was given the form $D_{23} = D_{23}' (1\cdot0 + p \exp[-q(r_{23}-r_{23}^\circ)])$ and the final term in the potential expression was correspondingly modified by setting $D_{34} = D_{34}' (1\cdot0 + 2p - p \exp[-q(r_{23}-r_{23}^\circ)])$. This refinement took account of the attenuation of the $CS_{(2)}$ bond and the strengthening of the $CS_{(4)}$ bond as the reaction proceeded and clearly, $D_{23}' = D_{34}'$, and $D_{23}' (1\cdot0 + p)$ and $D_{34}' (1\cdot0 + 2p)$ are the CS bonding energies in CS_2 and CS respectively. q was estimated by considering the increase in bond strength in carbon-carbon bonds as the bond length decreases and the orbital overlap is improved. The constants used in the Morse-like potentials were $D_{23}' = D_{34}' = 100\cdot4$ kcal/mole, $p = 0\cdot38$, $q = 5\cdot6$ Å^{-1}, $\beta_{23} = 1\cdot99$ Å^{-1}, $\beta_{34} = 1\cdot86$ Å^{-1}; $D_{12} = 127\cdot0$ kcal/mole, $\beta_{12} = 2\cdot12$ Å^{-1}; $D_{13} = 140\cdot5$ kcal/mole, $\beta_{13} = 2\cdot30$ Å^{-1}; hence, $\Delta H = -26\cdot6$ kcal/mole. Some collinear surfaces with $r_{34} = r_{34}^\circ$ are shown in fig. 4.

Collinear trajectories were computed by numerical integration of the 6 classical equations of motion by the Runge-Kutta-Gill routine with time increments of 5×10^{-16} sec. Reaction was initiated with $r_{12} = r^o_{12} + 3 \text{ Å}$ and was considered complete when $r_{23} > r^o_{23} + 3 \text{ Å}$.

Kuntz *et al.* have demonstrated that the vibrational excitation in the newly formed product of a three-atom reaction is approximately equal to the energy released before significant product repulsion sets in. This was classified as the sum of the attractive (A) and mixed (M) energy release and definitions were put forward for these terms. In fig. 5, the computed energy yield in the SO vibration, expressed as a percentage of the total available energy, is plotted against $\%(A+M)$. The
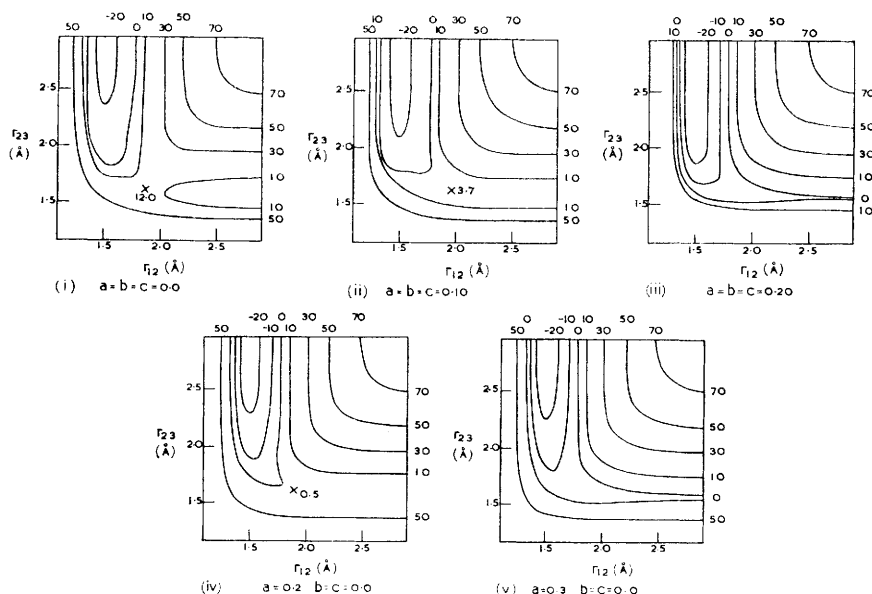

FIG. 4.—Energy surfaces for collinear reaction with $r_{34} = r^o_{34}$. These represent sections through the 4-dimensional hypersurfaces $(r_{34} \neq r^o_{34})$ used in the calculations.

correlation between these two quantities was confirmed but only modified hyper-surfaces, with a, b and c not all equal, were sufficiently repulsive in character to match the experimentally observed SO vibrational yield.

The vibrational excitations in CS following reaction on various hypersurfaces are shown in table 1. The computed vibrational energy was much less than that found experimentally but on a close examination of the trajectories some important conclusions could be reached.

The effect of the contraction of the $CS_{(4)}$ bond length was investigated by comparing the results from two sets of calculations on hypersurfaces (ii) and (iii). In the first set, it was assumed that r^o_{34} remained constant and in the second that $r_{34} = r_e(CS) + 0.0196 \exp[-q(r_{23} - r^o_{23})]$. Allowing for bond contraction in this way, increased the energy in the CS vibration by only 25-50 cal/mole or 0.1-0.2 % of the total energy, much less than that calculated by assuming an instantaneous shortening of the bond. Furthermore, even with a as large as 0.3, corresponding to considerable long-range attraction between the reactants, r_{34} was extended by only 0.002 Å during the early part of the reaction. It can be concluded that the attractive energy release

(mechanism (i) above) in the CS vibration must form an insignificant part of the observed excitation.

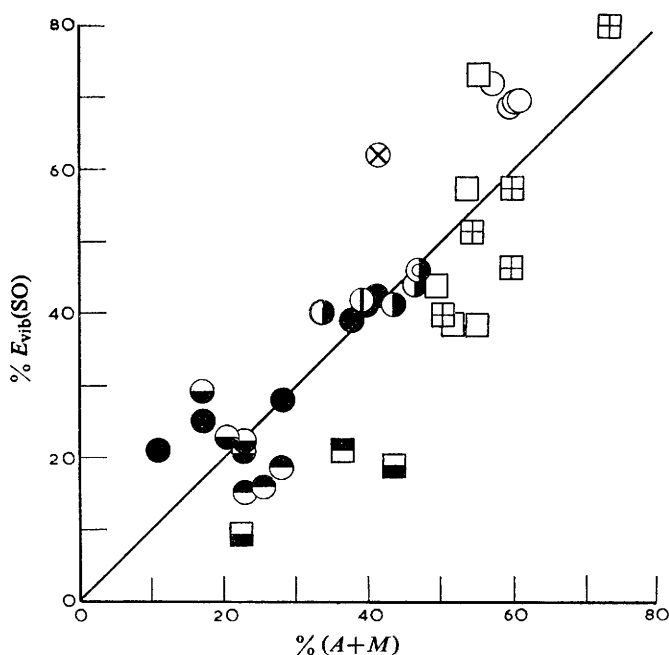The strongest repulsive force between C and $S_{(2)}$ causing compression of $CS_{(4)}$

FIG. 5.—Percentage yield in the SO vibration plotted against the % attractive plus mixed energy release. Circles refer to reactions on hypersurfaces for which a, b and c were constant but the initial kinetic energy was varied. ●, $a = b = c = 0\cdot0$; ◐, $a = b = c = 0\cdot1$; ○, $a = b = c = 0\cdot2$; ◓, $a = 0\cdot2$, $b = c = 0\cdot0$; ◒, $a = 0\cdot3$, $b = c = 0\cdot0$; ⊗, $a = 0\cdot3$, $b = 0\cdot1$, $c = 0\cdot0$; ◑, $a = 0\cdot2$, $b = 0\cdot1$, $c = 0\cdot0$. % $(A+M)$ was calculated as % of the total exothermicity released when $r_{34} = r_{34}^o$ and r_{23} was that when the calculated trajectory first crossed $r_{12} = r_{12}^o$. Squares refer to reactions on hypersurfaces where a, b and c were functions of $(r_{12}+r_{23})$ with initial kinetic energy = 2·3 kcal/mole. ⊞, $a^o = b^o = c^o = 0\cdot3$, $\gamma = 1\cdot0$-$8\cdot0$ Å^{-1}; □, $a^o = b^o = c^o = 0\cdot2$, $\gamma = 2\cdot0$-$16\cdot0$ Å^{-1}; ⊟, $a^o = 0\cdot3$, $b^o = c^o = 0\cdot0$, $\gamma = 2\cdot0$, $4\cdot0$ Å^{-1}; ▱, $a^o = 0\cdot2$, $b^o = c^o = 0\cdot0$, $\gamma = 4\cdot0$ Å^{-1}. % $(A+M)$ was calculated from where the computed trajectory first crossed $r_{12} = r_{12}^o$. The solid line corresponds to % $E_{vib} = $ % $(A+M)$.

TABLE 1.—PERCENTAGE OF TOTAL ENERGY CONVERTED TO VIBRATIONAL ENERGY IN CS

			$E_{initial}$-$E_{activation}$ (kcal/mole)	% CS vibrational energy	
a	b	c		r_{34}^o contraction	r_{34}^o constant
0·0	0·0	0·0	0·5-5·0	—	0·37-0·40
0·1	0·1	0·1	0·3-2·8	0·42-0·47	0·32-0·36
0·2	0·2	0·2	0·034-1·9	0·38-0·42	0·17-0·18
0·2	0·0	0·0	0·5-2·3	0·39-0·46	—
0·3	0·0	0·0	0·034-2·3	0·73-1·10	—
0·2	0·1	0·0	2·3	0·68	—
0·3	0·1	0·0	2·3	0·85	—

operated at a point close to that where the computed trajectory crossed $r_{12} = r_{12}^o$. The amount of repulsive energy which was released at this stage into the $CS_{(4)}$ vibration was generally close to that observed in this product, but as the atoms recoiled

the oscillation was damped and the eventual yield was greatly diminished. Fig. 6(i) shows details of a typical trajectory. This behaviour is similar to that reported by Sharp and Rapp [26] during the high-energy, collinear collision of a diatomic molecule with an atom.

It was concluded that the excitation in the CS vibration would depend critically on the steepness of the repulsive potential between the separating products and to test this, the potential expression was adjusted so as to increase V near $r_{12} = r_{12}^\circ$, $r_{23} = r_{23}^\circ$. This was achieved by decreasing, a, b and c in this region by making $a = a^\circ f(r_{12} + r_{23})$, $b = b^\circ f(r_{12} + r_{23})$ and $c = c^\circ f(r_{12} + r_{23})$, where $f(r_{12} + r_{23}) = \tanh[\gamma(r_{12} + r_{23} + \delta)]$. This might be identified with the onset of " chemical saturation " when the atoms are all close together.
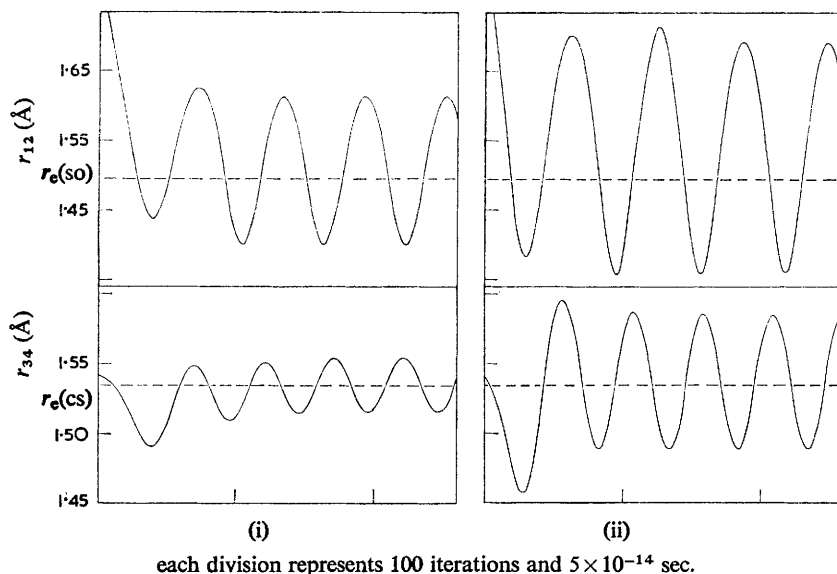
each division represents 100 iterations and 5×10^{-14} sec.

FIG. 6.—Variation of r_{12} and r_{34} during part of reactive collisions. (i) $a = 0.3$, $b = c = 0.0$, $E_{\text{initial}} = 560$ cal/mole; % $(A+M) = 20.3$, % $E_{\text{vib}}(SO) = 23.0$, % $E_{\text{vib}}(CS) = 0.88$. (ii) $a^\circ = b^\circ = c^\circ = 0.3$, $\gamma = 4.0$ Å^{-1}, $E_{\text{initial}} = 140$ cal/mole; % $(A+M) = 61.8$, % $E_{\text{vib}}(SO) = 54.5$, % $E_{\text{vib}}(CS) = 5.2$.

The results of calculations on these adjusted hypersurfaces are summarized in fig. 5. and table 2. Again, %$E_{\text{vib}} \sim$ %$(A+M)$, unless $(\delta + r_{12}^\circ + r_{23}^\circ)$ is given a negative value when there is an increasing tendency for the trajectory to " cut the corner " on the hypersurface lowering the vibrational energy relative to the $(A+M)$ energy release.

The marked increase in the CS vibrational energy on certain of these hypersurfaces resulted from the steeper potential operating between the products. It demonstrated that the vibrational energy yield in CS is determined not so much by the proportion of energy released as repulsion but rather by the suddenness with which this energy is dissipated. Details of a reactive trajectory leading to considerable CS excitation are shown in fig. 6(ii). The contrast with the behaviour shown in fig. 6(i) is striking. The rapid release of repulsive energy resulted in greater initial compression of r_{34} and considerably less damping on recoil, since, by this time, little interaction between the products remained. These hypersurfaces, however, are not entirely satisfactory since the SO vibrational energy yields are at least twice that which is found experimentally.

Finally, a more complete understanding of the reaction kinematics must await the extension of these calculations to two dimensions. In a non-linear configuration, the repulsive force between the products will not be directed along the $CS_{(4)}$ bond and only the component in this direction will operate to change the vibrational energy. Removal of the collinear restriction could result in increased CS vibrational excitation if the initial, steep repulsion acted whilst the S—C—S atoms were still

TABLE 2.—PERCENTAGE OF TOTAL ENERGY CONVERTED TO VIBRATIONAL
ENERGY IN CS

γ (Å^{-1})	$(\delta + \overset{\circ}{r}_{12} + \overset{\circ}{r}_{23})$ (Å)	$E_{initial} - E_{activation}$ (kcal/mole)	% E_{vib} (CS)
		$\overset{\circ}{a} = \overset{\circ}{b} = \overset{\circ}{c} = 0.3$	
1.0	0	1.0	0.36
2.0	0	2.3	1.26
3.0	0	2.3	3.7
4.0	0	0.14, 2.3	5.2, 6.2
4.0	−0.3	2.3	0.19
8.0	0	2.3	9.8
16.0	0	2.3	10.6
∞	0	0.6	0.19
		$\overset{\circ}{a} = \overset{\circ}{b} = \overset{\circ}{c} = 0.2$	
2.0	0	1.9	0.60
3.0	0	2.3	1.30
4.0	0	0.14, 2.3	1.52, 2.20
8.0	0	2.3	2.5
16.0	0	2.3	0.63
∞	0	1.9	0.42
		$\overset{\circ}{a} = 0.3, \overset{\circ}{b} = \overset{\circ}{c} = 0.0$	
2.0	0	0.01	0.26
4.0	0	2.3	0.51
∞	0	2.3	1.10
		$\overset{\circ}{a} = 0.2, \overset{\circ}{b} = \overset{\circ}{c} = 0.0$	
4.0	0	0.024	0.37
∞	0	2.3	0.46

nearly collinear but the configuration had become twisted by the time the C and $S_{(4)}$ atoms recoiled so that damping of the vibration was reduced. If this was so, the choice of collinear reaction would be particularly unfortunate since it would lead to the minimum CS excitation. In similar reactions where the triatomic reactant (BCD) is bent, the yield in the CD vibration will be much reduced because only a fraction of the early repulsive force will operate to compress the CD bond.

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