Relative Rate Data for the Reactions of \( S(3^1D_2) \) using the \( \text{NS} \) Radical as a Spectroscopic Marker

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Received 21st January, 1972

The reactions of \( S(3^1D_2) \), produced in the ultra-violet photolysis of OCS, have been studied with the gases, \( \text{C}_2\text{H}_6, \text{C}_2\text{H}_4, \text{CH}_4, \text{SF}_6, \text{CO}_2, \text{OCS}, \text{N}_2\text{O}, \text{NO}, \text{CO}, \text{N}_2, \text{H}_2, \text{He}, \text{Ne}, \text{Ar}, \text{Kr} \) and \( \text{Xe} \). Relative rate data have been determined using the \( \text{NS} \) radical, formed in the reaction \( S(3^1D_2) + \text{N}_2\text{O} \rightarrow \text{NS} + \text{NO} \) as a spectroscopic marker.

The reactions of \( S(3^1D_2) \) with the lower alkanes and alkenes have been studied extensively by Strausz and Gunning et al.,\(^1\)\(^2\) and provided one of the earliest demonstrations that the chemistry of electronically excited states may differ significantly from that of the ground state.\(^3\) Quenching of \( S(3^1D_2) \) by the noble gases,\(^4\) \( \text{CO}, \text{CO}_2, \text{SF}_6 \) and reaction with \( \text{N}_2\text{O} \)\(^5\)\(^6\) and \( \text{CS}_2 \)\(^5\) have also been reported. Unfortunately no single study has been made to bring together rate data for \( S(3^1D_2) \) with a wide range of gases; any comparison based on separate studies leads to large uncertainties in the relative data.\(^3\)

The reaction of \( S(3^1D_2) \) with \( \text{N}_2\text{O} \) yields \( \text{NS} \) radicals which may be readily observed via the intense \( \text{C} \leftarrow \text{X} \) transition at 230 nm.\(^6\) The intensity of this transition is approximately one order of magnitude greater than the nitric oxide bands lying in the same region; the \( \text{NS} \) radical was thus used in the present work as a convenient "spectroscopic marker"\(^7\) to study the relative reaction rates of electronically excited sulphur atoms with a range of atoms and molecules.

**Experimental**

The flash photolysis apparatus was of conventional design with the flash lamp and reaction vessel, both 1 m in length and constructed of Vitreosil quartz (Thermal Syndicate), lying parallel and optically coupled with a highly polished aluminium reflector. The spectroscopic lamp was positioned with the capillary directed along the axis of the reaction vessel and gave rise to sufficient intensity that only one flash was required for quantitative plate photometry above 210 nm \((E = 170 \text{ J}; \tau_e = 10 \mu s)\). The main photolysis flash was connected to a single 10 \( \mu \)F rapid discharge capacitor which was charged to 14 kV for all experiments \((\tau_e = 20 \mu s)\). Spectra were recorded with a Hilger medium quartz spectrograph, using Kodak Pancho Royal film sensitized for short wavelengths by immersion in a saturated solution of sodium salicylate in ethanol. The film was developed for 5 min in Ilford Contrast FF developer, diluted 1 + 3 at 294 K. A Joyce-Loebl double-beam recording microdensitometer (Mark 3) was used for all plate photometry.

Gases were handled using a conventional glass high vacuum line and mixtures made up prior to use with a magnetically driven stirrer. \( \text{SF}_6 \) was used as diluent gas in all experiments and mixtures were made up to a total pressure of 50 Torr \(^*\) to reduce effects due to pressure broadening of the \( \text{NS} \) spectrum, and to maintain isothermal conditions. Rate data are quoted for 300 K.

\* 1 Torr = 133.3 N m\(^{-2}\)
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MATERIALS

He, Ne, Kr, Xe and CO_2: "grade X" (B.O.C. Ltd) were used directly from glass break-
seal containers. Purities given as He (99.9995 %); Ne (99.95 %, main impurity He); 
Kr and Xe (99.99 %); CO_2 (99.995 %). CH_4, C_2H_6, C_2H_4, Ar and CO: "research grade" 
(Matheson Co. Inc.) gases were used directly. Purity given as CH_4 (99.99 %); 
C_2H_6 (99.9 %); C_2H_4 (99.9 %); Ar (99.9995 %); CO (99.9 %). H_2: cylinder grade 
(B.O.C. Ltd.) hydrogen was purified by passage through a palladium thimble. N_2: 
B.O.C. "white spot" grade (99.9 %) was passed through traps at liquid nitrogen temperature (77 K). 
NO: cylinder grade (Matheson Co. Inc.) nitric oxide was trapped at 77 K and then fraction-
ally distilled from 90 K to a trap held at 77 K. OCS and SF_6: cylinder grade (Matheson 
Co. Inc) gases were thoroughly degassed by repeatedly trapping at 77 K and pumping on 
the samples. N_2O: B.O.C. "medical" grade (>99 %) was thoroughly degassed and 
used directly.

RESULTS

It has been shown that the NS radical is formed in the reaction,
\[
S(3^1 D_2) + N_2O \rightarrow NS + NO
\] (1)

and that the analogous reaction for ground state sulphur atoms does not occur to any 
significant extent at 300 K. With the present apparatus, the optimum conditions for 
producing the NS radical were \(P_{OCS} = 0.49 \text{Torr} \); \(P_{N_2O} = 4.6 \text{Torr} \); \(P_{SF_6} = 50 \text{Torr} \); 
flash energy \(= 1000 \text{ J} \). The radical was monitored via the \((0,0)\) band of the 
\(C^-X^\) system at 230 nm, and found to reach its maximum concentration by 
c.a 200 ps. The concentration remained essentially constant during the first 
500 ps and had a 
half life of ca 5 ms.

In the presence of an added gas (M) which reacts with, or relaxes \(S(3^1 D_2)\) to the 
ground state, the yield of NS (measured between 200-500 \(\mu\)s) is reduced:
\[
S(3^1 D_2) + M \rightarrow MS \text{ (or } S(3^3 P_2) + M \).
\] (2)

The fraction of \(S(3^1 D_2)\) yielding NS in the presence of an added gas is given by 
\(k_1[N_2O]/(k_1[N_2O] + k_2[M] + T)\), which is proportional to the yield of NS \([NS]_0\); 
\(T\) is the rate for removal of \(S(3^1 D_2)\) by all other reaction channels.

Thus provided \(T\) and \([N_2O]\) are kept constant, a plot of the reciprocal of \([NS]_0\) 
against \([M]\) should yield a straight line, the slope of which is proportional to \(k_2/ 
k_1[N_2O]\).

These plots may be normalized by plotting \([NS]_0/[NS]_\infty\), where \([NS]_\infty\) is the NS 
yield in the absence of added gas (M), and the slope is now equal to \(k_2/[k_1[N_2O] + T]\).

The Beer-Lambert exponent, relating the observed optical density change (\(\Delta \text{ O.D.}\)) 
at 230 nm to the concentration of NS, was determined by comparing the change in 
optical density for the fully illuminated vessel with that for the vessel only half illumin-
ated by the flash. The relationship established was \(\Delta \text{ O.D.} \propto [NS]^{0.67 \pm 0.07}\). Thus 
relative NS concentrations could be determined by raising the observed optical 
density changes to the power of 1.5.

Typical data are shown in fig. 1 and 2. The slopes of such plots are given in table 
1, together with the derived rate data. In those cases where both quenching and 
reaction are possible, the reported rate data refer to the sum of the rate constants for 
these processes. The slopes of the plots for the gases He, Ne and SF_6 were all zero 
within the experimental error; quenching by these gases is thus at least one order of 
magnitude less efficient than quenching by argon. The data obtained for OCS and 
N_2O are less precise than for the other molecules studied, due to the experimental 
limitations imposed by the range of partial pressure which could be employed. Thus 
for high partial pressures, both OCS and N_2O obscure the NS(C\^-X) system; at
low partial pressures the spectrum of NS is too weak to allow the determination of quantitative data. Despite these limitations on the present technique we have determined $k_{\text{OCS}} / k_{C_2H_4} = 1.5 \pm 0.5$ and $k_{\text{N}_2O} / k_{C_2H_4} \approx 0.1$.

![Plot of [NS]_o/[NS]_o against the pressure of added gas (M). M = N_2 (△), Kr (□), Ar (○).](image)

The spectroscopic marker technique is valid provided the marker does not undergo rapid reaction with the added gases (or their reaction products). We have therefore looked for such reactions but have only found one case. Thus, in the presence of added O_2, the NS radical decayed significantly faster than usual; this is due to the reaction

$$O + \text{NS} \rightarrow \text{N} + \text{SO}. \quad (3)$$

Oxygen atoms are produced by the rapid reaction between S(3^3P_2) and O_2. The ground state sulphur atoms are produced both in the primary photochemical process, and from quenching by N_2O and possibly OCS. Under the conditions of our experiment, [NS] \ll [O] and the NS radical is thus expected to undergo a pseudo first order decay, as we have in fact observed. Furthermore, the rate of decay was first order with respect to the relative concentration of atomic oxygen. Unfortunately we have been unable to determine the absolute concentration of ground state oxygen atoms precisely, and have thus only obtained an approximate value for $k_3 (\sim 2 \times 10^{-11}$
The SO radical was observed in absorption via the $B \leftrightarrow X$ system, but the bands were too weak for quantitative measurements.

**Fig. 2.**—Plot of $\left[\text{NS}_{2}\right]/\left[\text{NS}_{0}\right]$ against the pressure of added gas (M). $M = \text{C}_2\text{H}_4$ ($\triangle$), $\text{C}_2\text{H}_6$ ($\square$), $\text{CH}_4$ ($\bigcirc$).

**Table 1.**—Slopes of plots of $\left[\text{NS}_{2}\right]/\left[\text{NS}_{0}\right]$ against [M], and relative rate data

<table>
<thead>
<tr>
<th>added gas (M)</th>
<th>slope/Torr$^{-1}$</th>
<th>$k_M/k_{\text{C}_2\text{H}_4}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{C}_2\text{H}_6$</td>
<td>0.28 ± 0.04</td>
<td>$1.7 \times 10^{-1}$</td>
</tr>
<tr>
<td>$\text{C}_2\text{H}_4$</td>
<td>1.6 ± 0.20</td>
<td>1.0</td>
</tr>
<tr>
<td>$\text{CH}_4$</td>
<td>0.12 ± 0.02</td>
<td>$7.6 \times 10^{-2}$</td>
</tr>
<tr>
<td>$\text{CO}_2$</td>
<td>0.38 ± 0.07</td>
<td>$2.4 \times 10^{-1}$</td>
</tr>
<tr>
<td>NO</td>
<td>1.1 ± 0.15</td>
<td>$6.8 \times 10^{-1}$</td>
</tr>
<tr>
<td>CO</td>
<td>0.31 ± 0.04</td>
<td>$1.9 \times 10^{-1}$</td>
</tr>
<tr>
<td>$\text{N}_2$</td>
<td>0.10 ± 0.01</td>
<td>$6.2 \times 10^{-2}$</td>
</tr>
<tr>
<td>$\text{H}_2$</td>
<td>0.36 ± 0.04</td>
<td>$2.2 \times 10^{-1}$</td>
</tr>
<tr>
<td>Ar</td>
<td>0.016 ± 0.002</td>
<td>$9.7 \times 10^{-3}$</td>
</tr>
<tr>
<td>Kr</td>
<td>0.046 ± 0.008</td>
<td>$2.8 \times 10^{-2}$</td>
</tr>
<tr>
<td>Xe</td>
<td>0.27 ± 0.04</td>
<td>$1.6 \times 10^{-1}$</td>
</tr>
</tbody>
</table>

**Discussion**

Approximate values for quenching of $S(3^{1}D_2)$ by the noble gases He, Ar and Xe have been given previously. The present results are in reasonable agreement with those results and give a considerable improvement in precision. The mechanism for quenching has been discussed previously and the spin orbit coupling induced by the
heavier noble gases in the region of crossing of the potential surfaces has been considered. The present results clearly show that Xe is the most efficient quencher, as with O(21D2), and thus spin orbit coupling is again at an optimum for xenon.

Quenching by the diatomic species N2, CO and NO is very efficient as observed with O(21D2). The higher efficiency for CO relative to N2, with which it is iso-electronic, is unlikely to be due to any difference in the strength of spin orbit coupling. More probably, the bond strength for the lowest singlet state of SCO (i.e., the ground state) will be greater than that for SNN, and thus the collision complex will survive a larger number of vibrations before re-dissociating. The SCO collision complex will therefore have a greater probability of undergoing a non-adiabatic transition in the region where the singlet and triplet surfaces cross. It should be noted however, that the lifetime of the SCO collision complex is too short for significant stabilization to occur under the conditions of our experiment, as Breckenridge and Taube5 were unable to detect O18CS when S(31D2) atoms were produced in the presence of O18C, under similar conditions. The high efficiency for relaxation of S(31D2) by NO, parallels the efficiency for relaxation of O(21D2) and has been discussed in terms of the high probability of crossing between the numerous doublet surfaces on which collisions between 3P and 1D atoms with NO(X21Π) occur. (See fig. 11, ref. (3)).

Relaxation of S(31D2) by CO2 is not significantly more efficient than relaxation by CO, which is contrary to the generally reported situation for O(21D2). A significantly weaker bond for SCO2 relative to CO3 would be in accord with the failure to observe SCO2 using matrix isolation techniques and might account for the lower efficiency for quenching S(31D2).

Sulphur atoms in the 31D2 state are known to react rapidly with alkanes, yielding mercaptans by direct insertion into the C—H bonds. Strausz and Gunning et al.,1 2 have shown that indiscriminate attack on C—H bonds occurs in the gas phase, and that 60-70% of S(31D2) is quenched to S(33P2) by ethane and the higher paraffins9; methane, however, is reported to be less efficient in quenching S(31D2), with insertion being the dominant channel for removal. Our data would therefore suggest that the rates for insertion are similar for CH4 and C2H6, and that the faster rate for overall removal of S(31D2) by C2H6 is due to the presence of the channel leading to quenching. In the liquid phase, Gollnick et al.9 have shown that reaction of S(31D2) with alkanes is sensitive to bond order.

Ethylene was found to be the most efficient species for removing S(31D2) in this study. The dominant process is reported to be reaction yielding vinyl mercaptans and the episulphide.1 2 If the present relative data are considered together with the lower limit for the absolute rate of reaction with OCS, then it can be seen4 that S(31D2) reacts with ethylene at almost every gas kinetic collision (<4 collisions).

The data obtained for quenching and reaction with OCS and N2O are rather imprecise using the present technique, due to the problems associated with varying their partial pressures over a significant range. However, reaction with these molecules has been examined using kinetic spectroscopy in the vacuum ultra-violet, where it has been possible to examine the relative rates into the various possible reaction channels.4 6 Further work in the vacuum ultra-violet is now required to determine the relative rates into the various possible channels for S(31D2) with H2, the alkanes and alkenes.

We thank Prof. C. Kemball, for encouragement and laboratory facilities and the S.R.C., for the award of a maintenance grant to D. J. L. We also thank the S.R.C., for an equipment grant.
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