tative value of $k_{el} = k_q$. The lower value of 1.24×10^9 M^{-1} s^{-1} obtained in this work which compares with a diffusion-corrected Marcus rate of 2.9×10^9 M^{-1} s^{-1} is more in keeping with the trend of lower experimental values. Since this work indicates that this value of k_{el} may be measuring, in part, an energy-transfer pathway, meaningful comparison of k_{el} with the Marcus theory results must await evaluation of and correction for energy transfer.

Conclusion

An actinometric technique has been devised for flash photolytic excitation of the $Ru(bpy)_3^{2+}$ MLCT transition. The technique, which is applicable to systems where sensitizer bleaching and quencher absorption may occur, has been applied to the reversible photoredox reaction between $Ru(bpy)_3^{2+}$ and $Co(phen)_3^{3+}$ to determine the fraction of quenching events which result in separated photoredox products. In reactions for which the detailed model of Hoselton et al.[7] applies, if model diffusion rate constants are known and the oxidation step subsequent to energy transfer, k_4, can be neglected, k_{el}/k_q leads to the detailed efficiency parameters of the reaction including the excited-state electron- and energy-transfer rate constants and the degree of excited-state redox product cage recombination. This and other techniques[2-4] which measure k_{el}/k_q should aid in contributing to the model for photoinduced electron transfer in solution and in optimizing homogeneous solutions for energy conversion.

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Rate Constant for the Reaction between OH and CS_2 at 298 and 520 K

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In an attempt to resolve discrepancies between published values of the rate constant for the reaction between the hydroxyl radical and carbon disulfide, the reaction has been studied in a discharge flow system by using resonance fluorescence for kinetic measurements and mass spectrometry for product analysis. On the basis of the measured rate constant for disappearance of OH and measurements of the amount of carbonyl sulfide formed, it was estimated that for the reaction $HO + CS_2 \rightarrow HS + OCS$, $k \leq 3 \times 10^{-15}$ cm^3 s^{-1} at 520 K and $\leq 7 \times 10^{-15}$ cm^3 s^{-1} at 298 K, upper limits being specified because of the inability to isolate exclusively this reaction channel, and because of possible involvement of wall reactions. These results confirm the low values found for this rate constant in two very recent studies.

Introduction

The discovery that both CS_2 and OCS are present in the earth's atmosphere[1-4] has generated considerable interest in their sources and sinks.[5-9] Computations based upon Kurylo's value[10] for the rate constant for the reaction

$$OH + CS_2 \rightarrow \text{products} \qquad (1)$$

with the products presumed to be HS and OCS have indicated that this reaction is both a major sink for CS_2 and a major source of OCS in the atmosphere.

However, reported values of the rate constant k_1[10-14] differ markedly as shown in Table I. Although Wine et al.[14] demonstrated that the two previous flash photolysis studies[10,12] were probably in error because of interference from reactions of photofragments of CS_2 (which has a strong UV absorption in the wavelength range of the photolyzing flash) and while they went to considerable lengths to minimize this problem (by filtering the flash and using SF_6 as carrier gas), their value of the rate constant is so different from that of the previous direct studies that confirmation by a different technique seemed desirable. The huge difference between the two relative rate studies, one based upon $-d[CS_2]/dt$,[11] the other upon $d[OCS]/dt$,[13] raises doubts about the widely held assumption that the products of reaction 1 are OCS and HS.

TABLE I: Rate Constants for the Reaction of OH with CS_2

exptl technique[a]	$10^{15}(k_1$ or $k_2)/(cm^3\ s^{-1})$	T/K	ref
FPRF	<70	300	12
FPRF	185 ± 34	296	10
FPRF	≤1.5	297	14
	≤1.6	363	
	≤9.9	251	
SPC, $-d[CS_2]/dt$	430 ± 160	298	11
SPC, $d[OCS]/dt$	≤3	298	13
DFRFMS, $-d[OH]/dt$	29 ± 5	298	this study
	4.1 ± 0.5	520	
$d[OCS]/dt$	≤7	298	
	≤3	520	

[a] FPRF, flash photolysis resonance fluorescence, k based upon $-d[OH]/dt$. SPC, static photolysis, competitive method. DFRFMS, discharge flow, resonance fluorescence, mass spectrometry.

In an attempt to resolve these discrepancies we have studied the reaction using discharge flow, resonance

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fluorescence, and mass spectrometry. Discharge flow provided a source of OH free of any possible photofragments from CS_2 while the molecular beam type of mass spectrometry used allowed us to study reaction stoichiometry. Although this study provides confirmation of the main findings of the two most recent papers,[13,14] it is unable to resolve all problems because of possible interference by wall reactions, a common disadvantage with flow methods.

Experimental Section

The 2.5-cm i.d. thermostatted Pyrex flow tube had a fixed radical source (H + excess NO_2), fixed detectors (resonance fluorescence cell just upstream of a pinhole leak to a molecular beam mass spectrometer), and a movable inlet for CS_2. Full details were reported previously.[15-18]

Carbon disulfide (Baker Analyzed Reagent) was purified by first removing volatiles at 196 K and then by collecting the middle 50% of a distillation from approximately 273 to 196 K. Based on vapor pressure data, this procedure reduced H_2S concentration to less than 0.01%. CS_2 vapor at a constant pressure flowed from a darkened Pyrex reservoir (of liquid plus vapor) maintained at 293 K then through a mass flow meter and needle valve to the movable inlet.

Results

Since quenching of OH fluorescence by CS_2 places constraints upon the range of conditions which can be used for kinetics studies, we have measured the quenching constant k_q in order to provide some quantitative estimate of the extent of quenching although values for k_q are not needed for kinetic analysis. A Stern–Volmer type experiment was performed as described previously for OCS[17] and it lead to the value 6.5×10^{-10} cm^3 s^{-1} at 298 K. While this value is high enough to cast doubt upon the adequacy of the Stern–Volmer mechanism upon which the analysis is based, it suffices for giving some indication of the efficiency of CS_2 in quenching OH fluorescence.

Kinetics. Kinetic measurements were performed by measuring the OH fluorescence as a function of CS_2 injector distance from the fluorescence cell with $[CS_2] >> [OH]_0$ where $[OH]_0$ is the "initial" concentration of OH, that is, the concentration of OH at the most distant upstream point to which the CS_2 inlet was withdrawn. It was calculated from $[OH]^0_{cell}$ the measured concentration at the fluorescence cell with zero added CS_2 by means of $[OH]_0 = [OH]^0_{cell} \exp\{k_w x/v\}$ where k_w is the first-order rate constant for wall loss of OH, x the distance from fluorescence cell, and v the linear flow velocity. The rate constant k_w was measured regularly throughout the investigation by adding NO_2 through the movable inlet to an excess of hydrogen atoms and by measuring fluorescence as a function of inlet distance from fluorescence cell. Values for k_w were in the ranges 5–15 s^{-1} at 520 K and 10–20 s^{-1} at 298 K. In the presence of CS_2, OH decay followed a first-order rate law for about two half-lives.

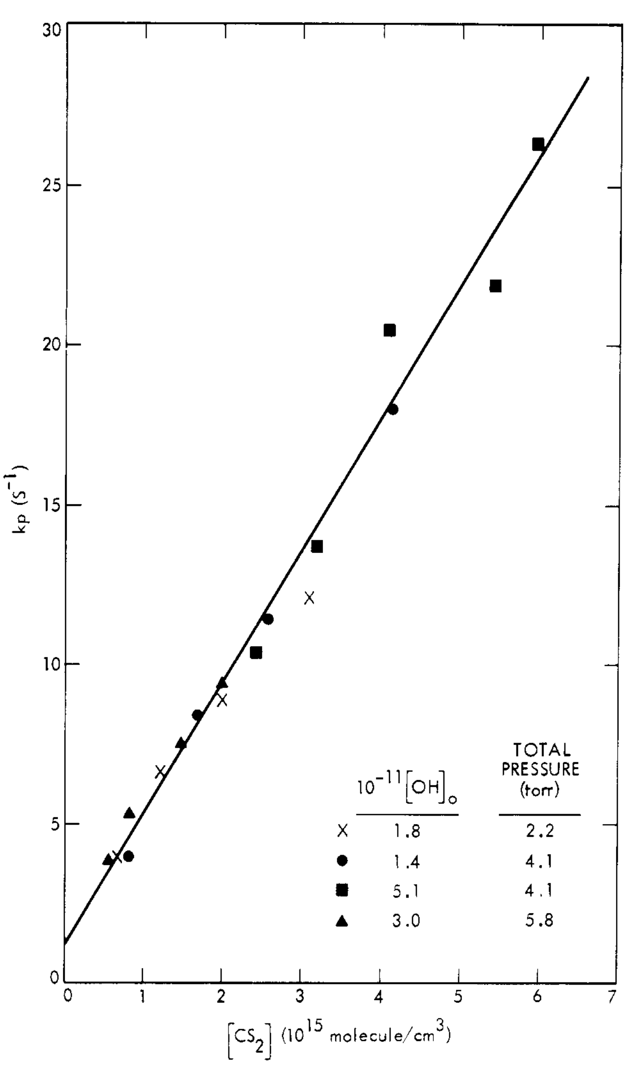

Figure 1. Dependence of the first-order rate constant k_p upon $[CS_2]$ at 520 K.

The pseudo-first-order rate constant k_p showed a linear dependence upon $[CS_2]$ as would be expected if reaction 1 were second order. All results at 520 K are shown in Figure 1. The fact that all points fall on the one straight line establishes (a) that the second-order rate constant k_1 is independent of $[OH]_0$ at least in the range 1.4×10^{11}–5.0×10^{11} molecule cm^{-3}, and (b) that k_1 is independent of pressure in the range 2.2–5.8 torr. A least-squares analysis yields $k_1 = (4.1 \pm 0.16) \times 10^{-15}$ cm^3 s^{-1} with an intercept of (1.1 ± 0.5) s^{-1} where in each case the error is one standard deviation.

Figure 2 summarizes the results of 27 experiments at 298 K. Again it is shown that k_1 is independent of pressure in the range 1.1–7.7 torr and of $[OH]_0$ in the range 1.0×10^{11}–2.7×10^{11} cm^{-3}. By least squares, $k_1 = (2.9 \pm 0.3) \times 10^{-14}$ cm^3 s^{-1} with an intercept of 15 ± 3 s^{-1} where again in each case the error is one standard deviation.

While the intercept at 520 K is probably insignificant (in that it is only just over two standard deviations from zero and represents only 4% of the highest value of k_p measured), at 298 K the intercept seems quite significant (representing 22% of the highest k_p value). This large intercept at 298 K combined with the fact that at this temperature the scatter of points about the line is much worse than at 520 K and is also worse than that observed

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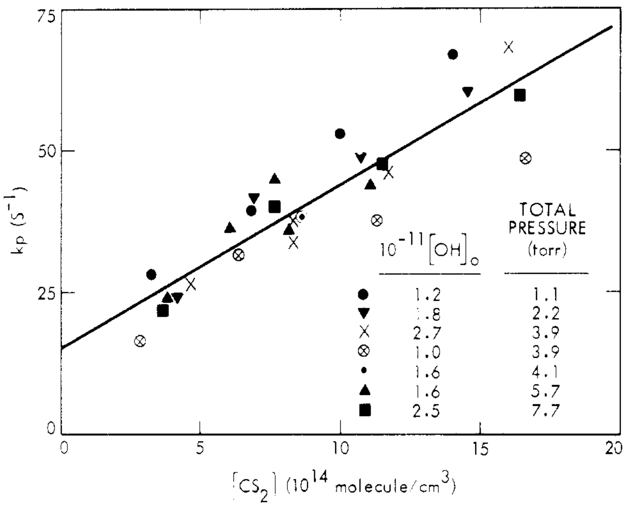

Figure 2. Dependence of the first-order rate constant k_p upon [CS$_2$] at 298 K.

by us in studies of OH with OCS[17] and H_2S[18] where the same equipment and techniques were used leads to the suspicion that significant surface reactions (other than that accounted for by k_w) may be involved.

When a systematic error of 7% (as explained previously[17]) is added to the statistical error quoted above, we obtain as our final estimates for the rate constant of reaction 1, based upon the rate of disappearance of OH: $k_1 = (4.1 \pm 0.5) \times 10^{-15}$ cm^3 s^{-1} at 520 K and $(2.9 \pm 0.5) \times 10^{-14}$ cm^3 s^{-1} at 298 K.

Product Analysis. Reaction products were detected with the mass spectrometer by injecting CS_2 well upstream of the mass spectrometer inlet (to allow sufficient time for OH and CS_2 to react) and by performing discharge on (OH present), discharge off (zero OH) experiments while monitoring suspected product peaks one at a time. Such experiments were performed at both 298 and 520 K. In this way products were seen at m/e values of 60 (presumably OCS) and 48 (a fragment from SO_2 as explained below).

The ratio, $f = \Delta[\mathrm{OCS}]/\Delta[\mathrm{OH}]_{\mathrm{CS}_2}$, where Δ[OCS] is the increase in concentration of OCS due to reaction of OH with CS_2 and $\Delta[\mathrm{OH}]_{\mathrm{CS}_2}$ is the decrease in OH concentration caused by reaction with CS_2, was calculated by measuring Δ[OCS] at m/e 60 in a discharge on/off experiment and simultaneously measuring by fluorescence $\Delta[\mathrm{OH}]_{\mathrm{total}}$ defined by

$$\Delta[\mathrm{OH}]_{\mathrm{total}} = [\mathrm{OH}]_0 - [\mathrm{OH}]_{\mathrm{cell(CS_2\ present)}}$$

Since

$$\Delta[\mathrm{OH}]_{\mathrm{total}} = \Delta[\mathrm{OH}]_{\mathrm{wall}} + \Delta[\mathrm{OH}]_{\mathrm{CS}_2}$$

$$\Delta[\mathrm{OH}]_{\mathrm{CS}_2} = \left(\frac{k_p}{k_+ + k_w}\right)\Delta[\mathrm{OH}]_{\mathrm{total}}$$

f could be calculated provided k_p, k_w, and $[\mathrm{OH}]_0$, all defined above, were also measured. k_w was measured as explained above and had the values 10 and 15 s^{-1} at 520 and 298 K, respectively. Fluorescence signals were converted to absolute OH concentrations by performing a calibration experiment in which fluorescence was measured as a function of [NO$_2$] when small flows of NO$_2$ were added through the movable inlet to much larger concentrations of H atoms with the inlet positioned to allow sufficient time for $H + NO_2 \rightarrow OH + NO$ to go to virtual completion without any significant loss of OH by wall reaction so that [OH] = [NO$_2$]. Such calibration plots were linear up to at least 2×10^{12} or 3×10^{12} cm^{-3}. The mass spectrometer was calibrated for OCS by adding known flows of a known OCS/helium mixture to the gas stream immediately after such stoichiometric measurements. Values obtained for f in four experiments at 520 K and two at 300 K are shown in Table II.

TABLE II: Measurements of $f = \Delta[\mathrm{OCS}]/\Delta[\mathrm{OH}]_{\mathrm{CS}_2}$

T/K	$10^{-11} \times [\mathrm{OH}]_0$/cm^3	$10^{-14} \times [\mathrm{CS}_2]$/cm^3		f
520	8.0	23.6		0.60
520	7.9	35.1		0.47
520	8.2	29.0		0.42
520	7.0	29.0		0.59
			av	0.52
298	26	5.1		0.14
298	37	4.4		0.16
			av	0.15

In addition to these measurements with the OCS inlet well upstream of the pinhole to the mass spectrometer, the OCS peak could be seen to grow as the CS_2 injector was progressively moved from near the mass spectrometer leak to positions further upstream though with insufficient precision to be able to calculate a rate constant from its rate of growth.

The product at m/e 48 could be seen with an electron accelerating voltage of 30 V but could not be seen at 15 V. This suggests that it is SO_2 rather than SO because the radical would be expected to have a relatively low ionization potential. Calibration of the mass spectrometer with SO_2 implied that, if this peak were SO_2, then the amount produced would be of the order of 50% of the amount of OH consumed by CS_2 in experiments where the precision of such a measurement would be ±50%. SO_2 could not be seen (in the required concentration range of 0.5×10^{11} to 3×10^{11} cm^{-3}) at m/e 64 because of the large fragmentation peak (S_2^+) from CS_2.

Attempts to detect HS at m/e 33 were unsuccessful, though based upon measurements of HS in $H + H_2S$ under very similar conditions (as explained elsewhere[18]), we had a detection limit as low as 5×10^{10} cm^{-3}. Since HS reacts very rapidly with NO_2[18] and since [NO$_2$] was in the ranges $(5\text{–}15) \times 10^{12}$ cm^{-3} at 520 K and $(2\text{–}5) \times 10^{12}$ cm^{-3} at 298 K, we would not expect to see HS in this system; it would be quickly converted to SO and SO_2. Attempts to see HOS at m/e 49 under a variety of conditions were also unsuccessful, although in view of the small background at m/e 49 we had good instrumental sensitivity.

Exhaustive attempts under a variety of conditions to detect an adduct at m/e 93 were unsuccessful.

Because OCS was not the predominant product at 298 K, consideration was given to the possibility that OCS had been formed in some secondary or side reaction such as $O + CS_2$ or $CS + NO_2$. Careful examination of conditions used allowed such possibilities to be eliminated.

The detection of OCS and SO_2 as the only stable products suggests that the reaction

$$\mathrm{OH} + \mathrm{CS_2} \rightarrow \mathrm{HS} + \mathrm{OCS} \qquad (2)$$

followed by

$$\mathrm{HS} + x\mathrm{NO_2} \longrightarrow \mathrm{SO_2} + ...$$

represents one but perhaps not the only pathway for the overall reaction 1.

The product fk_1 is therefore k_2, the rate constant for formation of OCS and this is $(2.1 \pm 0.7) \times 10^{-15}$ cm^3 s^{-1} at 520 K and $(4 \pm 3) \times 10^{-15}$ cm^3 s^{-1} at 298 K, where the error assigned to f is 20 and 50% at 520 and 298 K, respectively. Because as discussed below the complete chemistry of this system has not been elucidated so that there is the possibility that some OCS is being formed heterogeneously, we prefer to regard these values as upper limits for the homogeneous rate constant.

Discussion

As stated in the Introduction, our main purpose had been to try to confirm whether Wine et al.[14] were correct in attributing the high rate constants reported by Atkinson et al.[12] and by Kurylo[10] to interfering reactions of photofragments of CS_2 and in claiming that the true rate constant at 297 K was $\leq 1.5 \times 10^{-15}$ cm^3 s^{-1}. Such confirmation seemed desirable because of some unresolved problems with their study:

(1) Although they went to considerable lengths to minimize interference from photolysis of CS_2, their rate constants were measured under conditions in which about as many CS_2 molecules were photolyzed as water molecules (based on their quoted figures) so that the validity of their measurements rested upon the hypothesis that products from photolysis of CS_2 after vibrational quenching by SF_6 did not contribute to the rate of removal of OH.

(2) The actual contribution of the reaction between OH and CS_2 to the total rate of removal of OH in their experiments at 297 and 363 K (as shown in their Figure 6) was only 2–24% of the removal rate in the absence of CS_2; such a small contribution from the reaction under study combined with the necessary assumption that the first order OH removal rate (normally considered as diffusional loss) remained constant in the presence of varying amounts of added CS_2 means that there could be significant error in the value obtained for the rate constant.

(3) Virtually the same value was obtained for the rate constant at 363 and 297 K but there was a sevenfold increase in going to 251 K; this temperature dependence is unusual and warrants confirmation.

In addition we wished to determine whether the discrepancy between Iyer and Rowland's value[13] for the rate constant based upon d[OCS]/dt and Cox and Sheppard's value[11] based upon $-$d[CS_2]/dt occurred because reaction 2 was only a minor pathway for reaction between OH and CS_2 or because interference by CS_2 photofragments in Cox and Sheppard's work had been inadequately allowed for.

Our value of $10^{15}k_2 = (4 \pm 3)$ cm^3 s^{-1} at 298 K is in reasonable agreement with Iyer and Rowland's upper limit of ≤ 3; and a failure to find any reaction product other than OCS, despite exhaustive searching with equipment which had adequate sensitivity and which had successfully found a range of products in other studies,[17,18] seems to support the view that reaction 2 is the only effective path for OH + CS_2. Cox and Sheppard's result is thus probably erroneous.

Our results can be interpreted in terms of the sequence

$$HO + CS_2 \rightleftarrows HOCS_2^* \qquad (a)$$

$$HOCS_2^* \rightarrow HS + OCS \qquad (b)$$

$$HOCS_2^* \rightarrow Z \qquad (c)$$

This scheme is consistent with the small negative temperature dependence observed for k_2 ($= fk_1$), and if reaction c is a predominantly heterogeneous process which effectively removes OH as either H_2O or H_2O_2 while regenerating CS_2, it is also consistent with our failure to detect other products (because of high background peaks at m/e 17 and 18 and of a sulfur isotope peak from CS_2 at 34) and with the fact that $(1 - f)k_1$ decreases by a factor of 12 as temperature increases from 298 to 520 K.

Since there is evidence to suggest that reaction c is a wall reaction, the question arises as to whether there is any heterogeneous component in the measured second-order rate constant k_2 for OCS formation. Unfortunately, the compromises made in the design of our apparatus in order to have both mass spectrometric and resonance fluorescence detection prevented us from being able to vary the surface-to-volume ratio of the flow tube or to alter the surface coating on the flow tube walls without a major disruption of the whole apparatus. Hence we were unable to collect further evidence for or against heterogeneous involvement in k_2. In view of this we prefer to consider our measured k_2 values as upper limits for the homogeneous rate constants. The measured values for k_2 were (4 $\pm$ 3) $\times 10^{-15}$ cm^3 s^{-1} at 298 K and (2.1 $\pm$ 0.7) $\times 10^{-15}$ at 520 K. Hence we suggest that

$$k_2 \leq 7 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1} \quad \text{at} \quad 298 \text{ K}$$

$$\leq 3 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1} \quad \text{at} \quad 520 \text{ K}$$

each value being the sum of the mean and the estimated error.

Possibilities for reaction c are that it may be a wall reaction in which the excited adduct becomes stabilized to a long-lived one or in which $HOCS_2^*$ reacts with adsorbed OH (leading to recombination or disproportionation), or it may be a reaction of adduct with some other reagent such as NO_2 leading to removal of OH and regeneration of CS_2. However, no one explanation seems entirely satisfactory. The endothermicity

$$OH + CS_2 \rightarrow HOS + CS$$

seems to preclude the possibility of $HOCS_2^*$ falling apart to HOS and CS.

If reaction c is a surface reaction, then we would not expect it to be involved in the flash photolysis study of Wine et al. because in their apparatus the reaction and observation zone is remote from the walls so that it is k_2 which should be comparable to their rate constant. Our upper limit for $10^{15}k_2$ at 298 K, 7 cm^3 s^{-1}, is somewhat higher than their upper limit of 1.5 although, because of the large uncertainty associated with our measurement of f at this temperature, the actual values obtained, 4 $\pm$ 3 in our case, 1 $\pm$ 0.5 in theirs, do not differ very significantly. Unfortunately, at 520 K where our measurements were much more precise (because of the improved accuracy in measurement of both k_1 and f) and much less likely to involve a heterogeneous component, no comparisons are possible except to note that the slight negative temperature dependence is qualitatively consistent with the observations of Wine et al.

Despite discrepancies, the three most recent studies (ref 13 and 14 and this study) are in agreement that the rate constant for reaction 2 is very much less than the Kurylo value which had been used for atmospheric modeling computations[5-9] and that it probably lies in the range 1 $\times 10^{-15}$ to 5 $\times 10^{-15}$ cm^3 s^{-1} at 298 K so that reaction 2 is not a major source of OCS in the atmosphere nor is reaction with OH a major sink for CS_2.

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