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Kinetics of the reactions oxygen ($O(3P)$ and $O(1D)$) with chlorine

ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY · AUGUST 1985

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however, generally much less reactive toward undissociated thiols owing to the internal stabilization of the three-electron-bonded species. The $R_2S^+ + R_2S \rightleftharpoons (R_2S \cdots SR_2)^+$ equilibrium therefore constitutes a system in which the sulfide concentration essentially controls the overall reactivity. A parameter which seems to affect the actual rate constant of the reaction of $(R_2S \cdots SR_2)^+$ with thiols is the stability of the resulting thiyl radical. This is apparent from the relatively fast oxidations of thiophenol compared to aliphatic

thiols.

Acknowledgment. These investigations were in part conducted pursuant to a contract with the National Foundation of Cancer Research.

Registry No. EtSH, 75-08-1; PhSH, 108-98-5; CySH, 52-90-4; *t*-BuSH, 75-66-1; CyS^- , 56-89-3; $(t-Bu)_2S^+$, 60991-58-4; Me_2S^+ , 34480-65-4; $(Me_2S \cdots SMe_2)^+$, 51137-15-6.

Kinetics of the Reactions of $O(^3P)$ and $O(^1D)$ with Cl_2

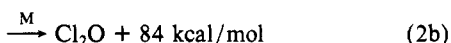
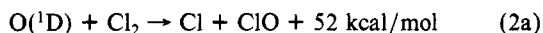
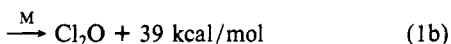
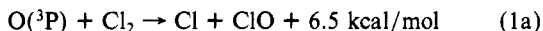
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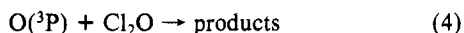
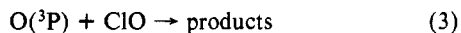
$O(^3P)$ has been monitored by using time-resolved resonance fluorescence spectroscopy following 248-nm pulsed laser photolysis of $O_3/Cl_2/N_2$ and $O_3/Cl_2/He$ mixtures. Rate coefficients for the reaction $O(^3P) + Cl_2 \xrightarrow{k_1}$ products have been measured over the temperature range 245–371 K under conditions where the $O(^3P)$ temporal behavior was unaffected by fast secondary reactions of $O(^3P)$ with products. The data are well described by the following Arrhenius expression: $k_1(T) = (7.4 \pm 2.4) \times 10^{-12} \exp[(-1650 \pm 100)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. By monitoring the appearance of $O(^3P)$, the rate coefficient for total removal of $O(^1D)$ by Cl_2 has been determined to be $(2.81 \pm 0.42) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K. $25 \pm 10\%$ of the $O(^1D) + Cl_2$ quenching interactions result in formation of $O(^3P)$.

Introduction

The reactions of ground-state and electronically excited oxygen atoms with molecular chlorine



are of interest to kineticists both for furthering our understanding of the rates and mechanisms of small molecule reactions and also as potential photolytic laboratory sources of the important stratospheric radical ClO. While kinetic data for both reaction 1¹⁻⁶ and reaction 2^{7,8} are reported in the literature, neither k_1 nor k_2 is firmly established. Kinetics investigations of reaction 1 are subject to interferences from the fast secondary reactions



None of the studies carried out to date employed sufficiently large Cl_2 to $O(^3P)$ concentration ratios to avoid this complication. The only direct measurement of k_2 reported to date⁷ employed an experimental approach which, based on comparison with results from several laboratories for a number of $O(^1D)$ reactions, seems to systematically overestimate $O(^1D)$ reaction rates by more than a factor of 2.

In this paper we report the results of a temperature-dependent kinetics study of reaction 1. Also, we report a 298 K study of reaction 2 where both the overall rate coefficient and the branching ratio for reactive vs. nonreactive quenching were determined. Both reactions were studied under experimental conditions where secondary removal or formation of $O(^3P)$, the monitored species, was unimportant.

Experimental Section

The experimental approach is described elsewhere.⁹⁻¹¹ It involves time-resolved resonance fluorescence detection of $O(^3P)$ following 248-nm pulsed laser photolysis of O_3 . All experiments were carried out under slow flow conditions with the concentration of each component in the reaction mixture determined from measurements of the appropriate mass flow rates and the total pressure. In studies of reaction 1, where Cl_2 levels were relatively high, the Cl_2 concentration was measured directly by UV photometry at 326.1 nm; the Cl_2 absorption cross section at the monitoring wavelength was taken to be $2.58 \times 10^{-19} \text{ cm}^2$.¹² The light source for the absorption measurement was a cadmium pen ray lamp and the absorption cell, plumbed in series with the reaction cell, was 60 cm in length. Experiments were carried out with the reaction mixture traversing the absorption cell both before and after flowing through the reactor. The observed kinetics were independent of the relative positions of the absorption cell and reactor.

The gases used in this study had the following stated minimum purities: He 99.999%, N_2 99.995%, O_2 99.99%, Cl_2 99.96%. He,

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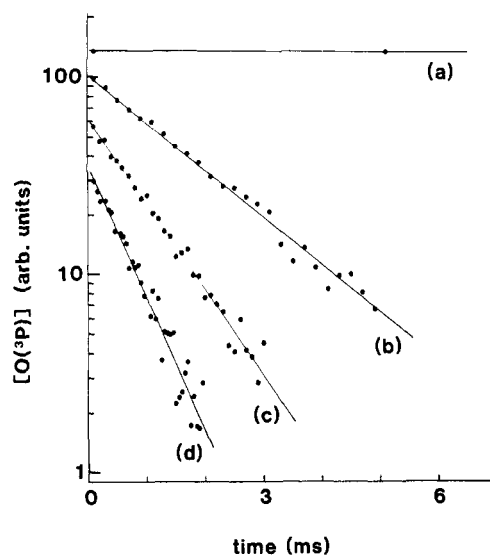
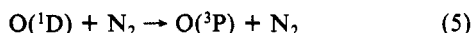


Figure 1. Typical O(³P) temporal profiles observed in studies of the reaction O(³P) + Cl₂ → products. Experimental conditions: $T = 279$ K; $P = 150$ torr; buffer gas = N₂; [O₃] in units of 10¹² cm⁻³ = (a) 2.2, (b) 1.6, (c) 3.1, (d) 2.6; [Cl₂] in units of 10¹⁶ cm⁻³ = (a) 0, (b) 2.41, (c) 4.52, (d) 7.13; [Cl₂]/[O(³P)]₀ = (b) 2.8 × 10⁵, (c) 4.5 × 10⁵, (d) 4.5 × 10⁵. Number of laser shots averaged = (a) 18, (b) 350, (c) 700, (d) 1235. Pseudo-first-order rate coefficients derived from the data = (a) 6.5 s⁻¹, (b) 495 s⁻¹, (c) 1000 s⁻¹, (d) 1560 s⁻¹.

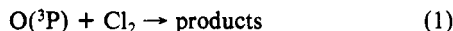
N₂ and O₂ were used as supplied while Cl₂ was subjected to repeated freeze(77 K)–pump–thaw cycles before use. O₃ was prepared by passing UHP O₂ through a commercial ozonator and stored on silica gel at 197 K. Before use it was degassed at 77 K to remove O₂.

Results and Discussion

1. O(³P) + Cl₂. In studies of reaction 1, nitrogen was used as the buffer gas at a pressure of 150 torr. In all experiments the N₂ concentration exceeded the Cl₂ concentration by more than a factor of 50. Since $k_2 \sim 10k_5$, more than 80% of the photochemically produced O(¹D) was deactivated by N₂.



$k_5 = 2.6 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹,¹² so conversion of O(¹D) to O(³P) was complete in 50 ns, which is instantaneous on the time scale for O(³P) decay. All experiments were carried out under pseudo-first-order conditions with [Cl₂] ≫ [O(³P)]₀. Reaction of O(³P) with O₃ was negligibly slow under our experimental conditions. Therefore, in the absence of complicating secondary reactions, the O(³P) temporal profile should be controlled by



O(³P) → loss by diffusion from the detector field of view and reaction with background impurities (6)

and simple first-order kinetics should be obeyed:

$$\ln \{[\text{O}(\text{}^3\text{P})]_0/[\text{O}(\text{}^3\text{P})]_t\} = (k_1[\text{Cl}_2] + k_6)t \equiv k't \quad (I)$$

As predicted by eq I, exponential O(³P) decays and linear dependencies of k' on [Cl₂] were observed under nearly all experimental conditions investigated. The only exceptions were a few preliminary experiments where the ratio [Cl₂]/[O(³P)]₀ was intentionally made low. Under these conditions the O(³P) decay rate increased with increasing time after the photolysis flash due to reaction of O(³P) with ClO and/or Cl₂O generated as products of reaction 1. Only experiments where [Cl₂]/[O(³P)]₀ > 2.5 × 10⁴ were used to obtain values for $k_1(T)$. Under such conditions, large variations in [O(³P)]₀ and [O₃] had no effect on measured rate coefficients.

Typical O(³P) temporal profiles observed under conditions of high [Cl₂]/[O(³P)]₀ are shown in Figure 1 and typical k' vs. [Cl₂] plots are shown in Figure 2. The rate data for reaction 1 are

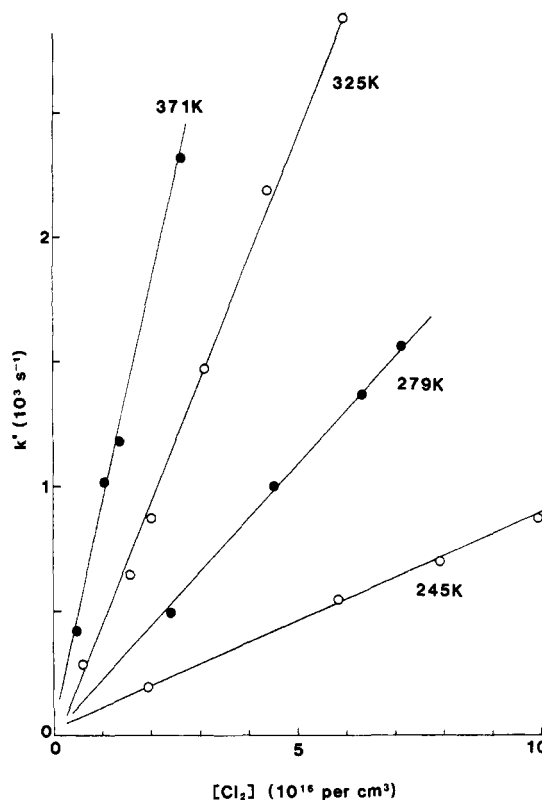


Figure 2. k' vs. [Cl₂] plots at four temperatures for the reaction O(³P) + Cl₂ → products. Solid lines are obtained from linear least-squares analyses and give the bimolecular rate coefficients tabulated in Table I.

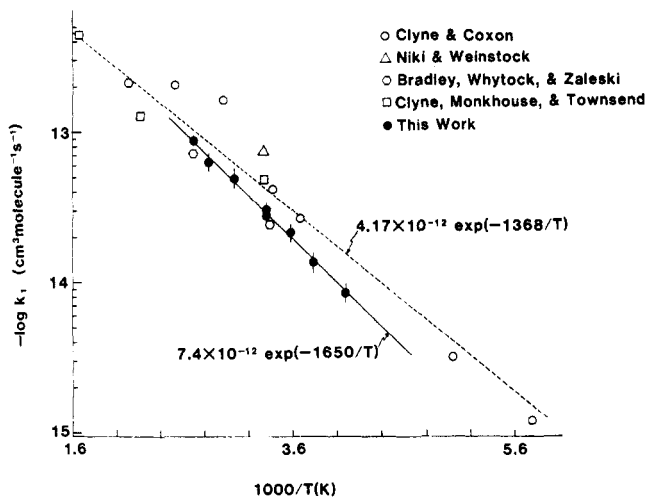


Figure 3. Arrhenius plot for the reaction O(³P) + Cl₂ → products. Dashed line is the recommendation of Baulch et al. (ref 13) which is based on all previous studies. Solid line is obtained from a linear least-squares analysis of our data.

summarized in Table I. Errors quoted in Table I are 2σ and represent the precision of the slope of the k' vs. [Cl₂] plots. The absolute accuracy of each $k_1(T)$ is affected by uncertainties in the Cl₂ concentration measurement as well as the precision of the data and is estimated to be ±12%. An Arrhenius plot of the results for reaction 1 is shown in Figure 3. An unweighted linear least-squares analysis of the $\ln k_1$ vs. 1/T data gives the following Arrhenius expression:

$$k_1(T) = (7.4 \pm 2.4) \times 10^{-12} \exp[(-1650 \pm 100)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

Errors in the Arrhenius parameters are 2σ and refer to precision only ($\sigma_A \equiv A\sigma_{\ln A}$).

Our results for reaction 1 are compared with those obtained in other laboratories in Figure 3. We obtain a somewhat larger

TABLE I: Kinetic Data for the Reaction of O(³P) with Cl₂^a

T, K	[O ₃], 10 ¹² cm ⁻³	[Cl ₂], 10 ¹⁶ cm ⁻³	10 ⁻⁵ ([Cl ₂]/ [O(³ P)] ₀)	k', s ⁻¹	10 ¹⁴ (k ₁ ± 2σ), ^b cm ³ molecule ⁻¹ s ⁻¹
245	4.0	0		11.0	
	2.3	1.94	1.3	196	
	5.7	5.83	1.4	546	
	5.4	7.91	3.3	700	
264	5.4	9.93	3.3	873	0.865 ± 0.036
	2.3	0		6.0	
	1.0	1.20	1.3	169	
	1.2	3.24	4.1	506	
279	2.0	4.47	4.5	644	
	1.9	7.09	2.4	1020	
	2.5	9.33	4.7	1260	1.36 ± 0.09
	2.2	0		6.5	
298	1.6	2.41	2.8	495	
	3.1	4.52	4.5	1000	
	2.6	6.33	4.0	1370	
	3.2	7.13	4.5	1560	2.18 ± 0.08
298	470	0		9.9	
	440	1.29	1.3	433	
	450	3.21	5.3	911	
	440	4.56	5.2	1420	
298	520	7.80	8.7	2140	2.75 ± 0.27
	300	0		10.4	
	280	0.686	5.4	186	
	340	2.18	4.8	685	
298	300	4.90	7.7	1500	
	260	6.67	11	2010	3.03 ± 0.08
	0.36	0		7.2	
	2.0	1.48	4.0	417	
325	0.39	3.37	18	892	
	3.0	5.81	11	1780	3.02 ± 0.38
	1.6	0		6.6	
	0.92	0		7.9	
352	2.0	0.587	0.69	287	
	2.4	1.56	4.3	647	
	0.78	2.01	4.6	875	
	1.6	3.10	5.3	1470	
371	0.64	4.40	7.7	2190	
	0.92	5.95	9.8	2890	4.93 ± 0.24
	1.8	0		8.1	
	0.73	0		8.9	
371	1.2	0.415	0.35	314	
	1.8	1.09	0.57	679	
	1.8	1.93	0.97	1300	
	2.1	2.32	1.9	1630	
371	0.97	3.25	6.3	2130	
	1.8	3.71	1.7	2310	6.37 ± 0.43
	3.1	0		15.0	
	1.6	0.487	0.37	420	
371	1.9	1.05	0.66	1020	
	3.1	1.36	1.4	1180	
	1.8	2.64	0.91	2320	8.72 ± 0.54

^a All experiments were carried out in N₂ buffer gas at a total pressure of 150 torr. ^b Errors are 2σ and represent precision only.

activation energy and larger *A* factor than currently recommended.¹³ At 298 K and below, our data suggest that *k*₁ is significantly slower than previously believed. All previous investigations of reaction 1 employed discharge flow systems and most used relatively insensitive detection schemes. Consequently, in all previous studies it was necessary to correct the raw kinetic data for contributions from the rapid secondary reactions of O(³P) with ClO and/or Cl₂O. Our experiments employed such large Cl₂:O(³P) concentration ratios that the contribution of secondary removal to the observed O(³P) kinetics was negligible.

Our results provide little information concerning the relative importance of channels 1a and 1b. In experiments where the [Cl₂]/[O(³P)]₀ ratio was intentionally made low, the O(³P) decay rate was found to be time dependent, increasing with increasing time after the photolysis flash. However, since both ClO and Cl₂O react rapidly and at nearly the same rate with O(³P), the above

observation does not allow one to distinguish between the two reaction channels. A few preliminary experiments were carried out at a total N₂ pressure of 50 torr—a factor of 3 lower than the pressure used in a vast majority of the experiments. Within experimental error, *k*₁(298 K) was found to be the same at 50 torr as at 150 torr. *k*_{1b} would probably be pressure dependent at N₂ pressures below 150 torr, so this observation can be considered weak evidence that Cl + ClO are the major products of reaction 1. However, a significant addition channel should not be ruled out, particularly since Parrish and Herschbach,¹⁴ in a molecular beam study of reaction 1, found evidence for a short-lived Cl₂O intermediate.

2. O(¹D) + Cl₂. In studies of reaction 2, helium was used as the buffer gas at a pressure of 25 torr. The concentration of O₃ photolyte was typically 7 × 10¹² per cm³ and the photolysis laser power was kept low enough that less than 10% of the O₃ in the beam was photolyzed. Photolytically produced O(¹D) interacted with O₃, He, background impurities, and Cl₂ to produce some O(³P). In the absence of rapid secondary O(³P) production or removal processes, measurement of the O(³P) appearance rate constitutes a measurement of the total O(¹D) removal rate. Since the primary photolysis yield of O(³P) is accurately known,¹⁰ measurement of the ratio of instantaneously produced O(³P) to that produced as a result of O(¹D) deactivation provides information concerning the branching ratio for nonreactive vs. reactive quenching. More precise information about the branching ratio can often be obtained from comparison of fluorescence signals obtained in excess Cl₂ with those obtained in excess N₂ [N₂ deactivates O(¹D) to O(³P) with unit yield].

Over the range of experimental conditions employed to measure *k*₂, O(³P) formed directly from O₃ photolysis appeared as an instantaneous signal synchronous with the laser firing while O(³P) formed from collisional deactivation of O(¹D) appeared as an exponentially rising signal with a time constant of 36–260 μs. Since secondary production of O(³P) should be negligible on the time scale for reaction 2, the O(³P) temporal profile is described by the following relationship

$$[\text{O}(\text{}^3\text{P})]_t = \frac{k_a[\text{O}(\text{}^1\text{D})]_0\theta}{k_d - k_a} [\exp(-k_a t) - \exp(-k_d t)] + [\text{O}(\text{}^3\text{P})]_0 \exp(-k_d t) \quad (\text{II})$$

where *k*_a and *k*_d are pseudo-first-order rate coefficients for the appearance and decay of O(³P), [O(¹D)]₀ and [O(³P)]₀ are the initial concentrations of photolytically produced atoms, and θ is the number of O(³P) formed for each O(¹D) removed. *k*_d was directly measured by monitoring the O(³P) decay after O(¹D) deactivation was complete, and was found to be ~50 s⁻¹ in all experiments. *k*_a was significantly faster than in the O(³P) + Cl₂ experiments (Table I) because the experiments were carried out at lower pressure in helium buffer gas and because much faster flow rates were employed in order to minimize reactions of O(¹D) with background impurities.

Typical O(³P) temporal profiles are shown in Figure 4. To obtain *k*_a from the data, it is necessary to determine *S*_{max}^{corr}, the maximum signal which would have been obtained if no O(³P) loss occurred before O(¹D) removal was complete. The iterative procedure used to obtain *S*_{max}^{corr} from the measured *S*_{max} has been described previously.⁹ Because *k*_a was more than 70 times *k*_d in all experiments, the required corrections were small and *S*_{max}^{corr} was determined quite accurately. Values for *k*_a were obtained from linear least-squares analyses of ln (*S*_{max}^{corr} - *S*_i) vs. *t* plots. The results are plotted as a function of [Cl₂] in Figure 5. A linear least-squares analysis vs. [Cl₂] data gives the rate coefficient *k*₂ = (2.81 ± 0.13) × 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹, where the uncertainty is 2σ and represents precision only. On the basis of estimates of possible systematic errors and uncertainties in the determination of the Cl₂ concentration, we feel that the absolute accuracy of

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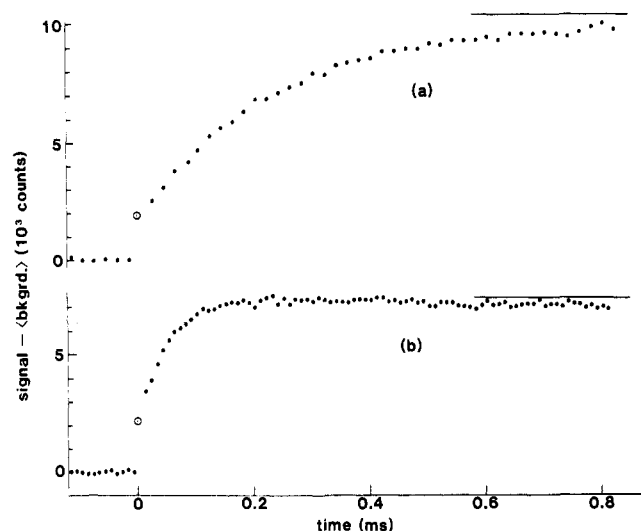


Figure 4. Typical O(³P) temporal profiles observed in studies of the reaction O(¹D) + Cl₂ → products. Experimental conditions: *T* = 298 K; *P* = 25 torr; buffer gas = He; [O₃] = 7 × 10¹² cm⁻³; [Cl₂] in units of 10¹³ cm⁻³ = (a) 0, (b) 5.57; laser photon fluence = 10 mJ/cm². Number of laser shots averaged = (a) 700, (b) 2065. Solid lines represent the corrected maxima, i.e., the maximum signal level which would have been attained if O(³P) did not decay during the time required for O(¹D) removal to go to completion. The photolysis laser fired at *t* = 0. The circled point is the extrapolated signal at *t* = 0. Results derived from the data are (a) *k_a* = 3890 s⁻¹, β = 0.222 and (b) *k_a* = 19 000 s⁻¹, β = 0.405.

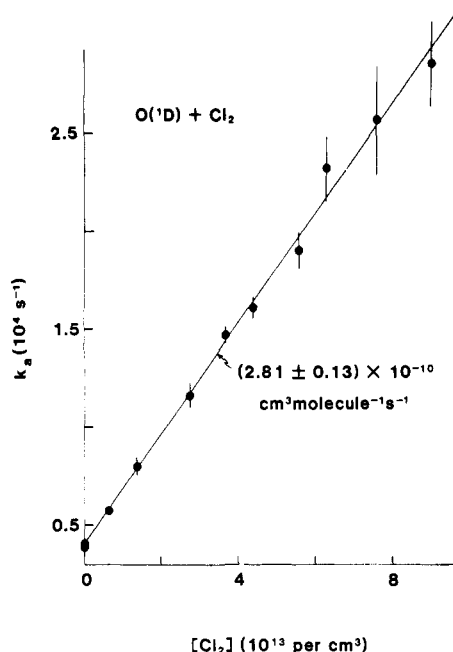


Figure 5. *k_a* vs. [Cl₂] plot. The solid line is obtained from a linear least-squares analysis, and its slope represents the bimolecular rate coefficient for the reaction O(¹D) + Cl₂ → products.

our determination of *k₂* is ±15%.

The kinetic data used to determine *k₂* were also used to estimate the fraction of O(¹D) deactivation which proceeds via nonreactive quenching, i.e., *k_{2c}/k₂*. First, β, the ratio of O(³P) produced by photolysis to that produced by O(¹D) deactivation, was determined for each temporal profile measured:

$$\beta \equiv \frac{[\text{O}(\text{}^3\text{P})]_0}{[\text{O}(\text{}^1\text{D})]_0\theta} = \frac{S_0}{S_{\text{max}}^{\text{cor}} - S_0} \quad (\text{III})$$

In the above equation *S*₀ represents the fluorescence signal immediately after the laser fires. The β vs. *f*_{Cl₂} data were then simulated for different choices of *k_{2c}/k₂* (*f*_{Cl₂} ≡ the fraction of

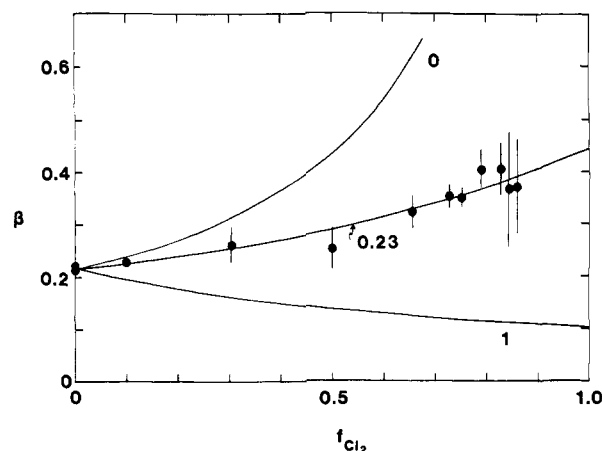


Figure 6. β vs. *f*_{Cl₂} plot. Solid lines represent simulations carried out using a procedure described in the text. Values for *k_{2c}/k₂* used in the simulations are shown in the figure.

O(¹D) removed by Cl₂). The following equations govern the *f*_{Cl₂} vs. β dependence:

$$f_{\text{Cl}_2} = k_2[\text{Cl}_2]/k_a = (k_a - k_a^0)/k_a \quad (\text{IV})$$

$$\beta^* = \beta\theta \quad (\text{V})$$

$$\theta = (k_Q + k_{2c}[\text{Cl}_2])/k_a \quad (\text{VI})$$

$$k_Q + k_R = k_a^0 \quad (\text{VII})$$

$$k_Q/k_a^0 = \beta^*/\beta^0 \quad (\text{VIII})$$

In the above equations, β* represents β under conditions where O(¹D) is deactivated to O(³P) with unit yield (β* = 0.103 ± 0.031¹⁰) while *k_a*⁰ and β⁰ represent *k_a* and β when [Cl₂] = 0. The rate coefficients *k_Q* and *k_R* cannot be associated with a particular physical process, but serve to operationally separate O(¹D) deactivation in the absence of Cl₂ into a component which results in O(³P) production (*k_Q*) and a component which results in no O(³P) production (*k_R*). According to eq IV–VIII, β and *f*_{Cl₂} are related as follows:

$$\beta = \beta^*k_a^0\{k_Q + [(k_{2c}/k_2)k_a^0 - k_Q]f_{\text{Cl}_2}\}^{-1} \quad (\text{IX})$$

The β vs. *f*_{Cl₂} data are shown in Figure 6 along with simulations calculated from eq IX. The best reproduction of the data was obtained in the simulation which assumed *k_{2c}/k₂* = 0.23. For comparison, simulations which assume *k_{2c}/k₂* = 0 and 1 are also shown in Figure 6. It is worth noting that the value of *k_{2c}/k₂* obtained by the above method is quite sensitive to the value of β*, i.e., the O(³P) photolysis yield. In addition to our measurement of β*,¹⁰ Greenblatt and Wiesenfeld have reported β* = 0.064.¹⁵ β vs. *f*_{Cl₂} simulations which employ Greenblatt and Wiesenfeld's result give the best reproduction of our data when *k_{2c}/k₂* is taken to be 0.15. Considering the sensitivity of the result to the assumed value for β* and potential systematic errors in the determination of β, we estimate that the accuracy of this branching ratio determination is about ±60%, i.e., *k_{2c}/k₂* = 0.23 ± 0.14.

A potentially more accurate, though slightly less direct, determination of *k_{2c}/k₂* was performed by using reaction mixtures where Cl₂ was added in sufficient quantity (>10¹⁶ per cm³) to completely dominate O(¹D) removal. Experiments were carried out on a time scale (50 μs per channel) where the O(³P) appearance was essentially instantaneous but the O(³P) decay was temporally resolved. The signal at time *t'* (= a time shortly after the laser fired when O(³P) formation had gone to completion but no appreciable decay had occurred) could be determined very accurately and represented O(³P) produced both by direct photolysis and by O(¹D) deactivation. A single determination of an O(³P) yield involved back-to-back experiments where the signal at *t* = *t'* was determined with N₂ as the dominant O(¹D) quencher (signal = *S*_{N₂}), then with Cl₂ as the dominant quencher (signal

$\equiv S_{\text{Cl}_2}$), then again with N_2 as the dominant quencher. Signals were normalized for $[\text{O}_3]$ and laser power. In addition, it was necessary to correct S_{Cl_2} for absorption of resonance lamp radiation by Cl_2 . The procedure for making this correction is described elsewhere.¹⁰ At the highest Cl_2 concentration employed, absorption of resonance lamp radiation resulted in a 25% drop in signal count rate. Since it is known that $\text{O}(^1\text{D})$ deactivation by N_2 produces $\text{O}(^3\text{P})$ with unit yield, k_{2c}/k_2 could be determined from the relationship

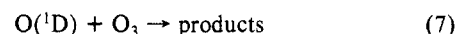
$$k_{2c}/k_2 = \{(S_{\text{Cl}_2}/S_{\text{N}_2}) - \Phi\}(1 - \Phi)^{-1} \quad (\text{X})$$

where Φ is the quantum yield for producing $\text{O}(^3\text{P})$ from O_3 photolysis at 248 nm, a quantity which we have previously measured to be $0.093 \pm 0.028[\beta^*/(1 + \beta^*) = \Phi]$.¹⁰ Fourteen determinations of $S_{\text{Cl}_2}/S_{\text{N}_2}$ gave an average value of 0.323 with $2\sigma = 0.060$. According to eq X, we obtain for k_{2c}/k_2 the value 0.254 ± 0.097 where the quoted error is 2σ and includes uncertainties in both $S_{\text{Cl}_2}/S_{\text{N}_2}$ and Φ . Two points are worth noting regarding this result. First, it is unlikely that secondary chemistry involving Cl , ClO , or photolytically produced $\text{O}_2(^1\Delta)$ could have influenced the measurement of k_{2c}/k_2 ; in order to be important, secondary chemistry would have had to occur on a time scale of a few hundred microseconds. Also, in addition to our measurement of Φ , Greenblatt and Wiesenfeld¹⁵ have determined Φ to be 0.06 ± 0.01 . Using their value in eq X would have only a minor effect on the result, changing k_{2c}/k_2 from 0.254 to 0.280.

Weighting the more precise of the two independent determinations more strongly, we report $k_{2c}/k_2 = 0.25 \pm 0.10$. Reaction 2 has generally been assumed to proceed exclusively via the reactive channel 2a.^{7,16} Our results, however, indicate that the

physical quenching channel is significant.

There is one absolute determination of k_2 reported in the literature. Fletcher and Husain,⁷ employing flash photolysis in conjunction with time-resolved resonance absorption detection of $\text{O}(^1\text{D})$, obtained the value $k_2 = (2.2 \pm 0.2) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Husain and co-workers have studied a large number of $\text{O}(^1\text{D})$ reactions and, in nearly all cases, report rate coefficients which are about a factor of 2.2 larger than those measured by other experimental techniques; this systematic difference is presumably due to incorrect determination of γ , a parameter which relates the absorbance to the $\text{O}(^1\text{D})$ concentration. Interestingly, our value for k_2 is about 25% faster than the value reported by Fletcher and Husain. The reason for this deviation from the trend observed for other reactions is unclear at this time. In addition to Fletcher and Husain's measurement, Freudenstein and Biedenkapp⁸ have employed flash photolysis in conjunction with kinetic absorption spectroscopic detection of ClO to obtain a measurement of k_{2a} , the rate coefficient for the reactive channel which produces ClO , relative to the rate coefficient for the process



Their result was $k_{2a}/k_7 = 0.75 \pm 0.25$. Using our value for $k_{2a} + k_{2b}$, $(2.11 \pm 0.34) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, in conjunction with the recommended value¹² for k_7 , gives $(k_{2a} + k_{2b})/k_7 = 0.88$. Our results are consistent with those of Freudenstein and Biedenkapp. Although it appears that $k_{2a} \gg k_{2b}$, the combined uncertainties of the two studies are large enough that a significant rate for a channel 2b cannot be completely ruled out.

Acknowledgment. This work was supported by the Fluorocarbon Program Panel of the Chemical Manufacturers Association.

Registry No. O_2 , 7782-44-7; Cl_2 , 7782-50-5.

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One-Electron Redox Reactions in Aqueous Solutions of Sulfite with Hydroquinone and Other Hydroxyphenols

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The one-electron oxidation of hydroquinone and other hydroxyphenols by the sulfite radical, SO_3^- , and the peroxysulfate radical, SO_5^- , has been investigated along with the oxidation of sulfite by several phenoxyl radicals. Rate constants for the oxidation of hydroxyphenols by SO_3^- are small in neutral solution but increase dramatically in basic solution, in correspondence to the deprotonation of the hydroxyphenol. SO_5^- reacts with most hydroxyphenols at moderate rates ($k \sim 1-5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$) in neutral solution. The phenoxyl radicals with higher redox potentials, from phenol, resorcinol, and phloroglucinol, were found to oxidize sulfite in neutral solutions.

In 1882, Berkely discussed the use of sulfite as a preservative in hydroquinone-based developer solutions,¹ where it inhibits hydroquinone autoxidation.² The use of hydroquinone and other phenolic compounds to inhibit sulfite autoxidation was demonstrated more recently.³⁻⁶ It was shown that in the hydroquinone-sulfite system, mono- and disulfonates were formed in

the early stages of the reaction.⁷ Since phenolic substances and many other organic compounds also inhibit the photoinduced oxidation of sulfite,⁸⁻¹⁰ it was suggested that the inhibition was due to their scavenging free radicals and therefore breaking the chain reaction.¹⁰ Studies on the comparative effect of phenolic inhibitors show a rough correlation between their effectiveness and their two-electron redox potentials.^{11,12}

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