

## RATE CONSTANTS FOR THE GASEOUS INTERACTIONS OF O( $2^1D_2$ ) AND O( $2^1S_0$ ) — A CRITICAL EVALUATION

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### Summary

An extensive critical evaluation has been completed of all the available rate coefficients and their temperature dependences that describe the interactions of gaseous O( $2^1D_2$ ) and O( $2^1S_0$ ) with numerous species. An examination of the nature of the processes involved, namely physical quenching or chemical reaction, is included. The recommended set of data comprises a much improved tabulation of values for use in modelling kinetic processes and includes all data published before 1978.

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### 1. Introduction

At present, an extensive effort is in progress to evaluate critically the chemical kinetic constants for interactions involving electronically excited states of atoms and diatomics. Most recently completed are the important and extensively studied O( $2^1D_2$ ) and O( $2^1S_0$ ) metastable species. Owing to their significant roles in atmospheric chemistry and chemical laser developments a preview of the recommended values is summarized and includes all data published prior to 1978.

Current values used by kinetic modelers are based on Cvetanovic's 1974 evaluation [1] and on the 1975 U.S. National Bureau of Standards compilation and evaluation of rate data for the Climatic Impact Assessment Program [2]. As will be noted, significant modifications to these are now recommended. Owing to the extensive experimental studies since that time, absolute values, particularly for O( $1D_2$ ), are much improved.

The chemistries of O( $1D$ ) and O( $1S$ ) are markedly different and it is quite intriguing that the longevity of the more energy-rich O( $1S$ ) state is much greater in a number of environments. Where possible, a direct comparison illustrates the unpredictable nature of excited state chemistry. For example, of 20 species where data for each are available O( $1D$ ) shows enhanced reactivity with 12 (CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, CO<sub>2</sub>, CO, N<sub>2</sub>O, O<sub>2</sub>, H<sub>2</sub>, N<sub>2</sub>, Ne, Ar, Kr, Xe), less with six (C<sub>2</sub>H<sub>4</sub>, NH<sub>3</sub>, NO<sub>2</sub>, O<sub>3</sub>, SF<sub>6</sub>, NO) and about the same for C<sub>3</sub>H<sub>6</sub> and H<sub>2</sub>O. There is no satisfactory general theory to encompass this behavior.

TABLE 1

Recommended rate constant values for  $O(2^1D_2)$  at 298 K ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )

| Interactant                         | Rate constant                           | Nature      | Interactant                    | Rate constant                           | Nature  |
|-------------------------------------|---|-------------|--------------------------------|---|---------|
| $\text{CBrF}_3$                     | fast                                    | $R^a$       | neo- $\text{C}_5\text{H}_{12}$ | $5.2 (\pm 1.0) \times 10^{-10}$         | R       |
| $\text{CCl}_4$                      | $4.7 (\pm 0.9) \times 10^{-10}$         | R           | c- $\text{C}_6\text{H}_{12}$   | $6.3 (\pm 0.6) \times 10^{-10}$         | R       |
| $\text{CCl}_3\text{F}$              | $3.0 (\pm 0.6) \times 10^{-10}$         | R           | $\text{C}_8\text{H}_{18}^e$    | $7.4 (\pm 0.7) \times 10^{-10}$         | R       |
| $\text{CCl}_2\text{F}_2$            | $2.6 (\pm 0.5) \times 10^{-10}$         | R           | $\text{CH}_3\text{OH}$         | $6.6 (\pm 3.4) \times 10^{-10}$         | R       |
| $\text{CClF}_3$                     | $1.3 (\pm 0.3) \times 10^{-10}$         | R           | $\text{C}_2\text{N}_2$         | no data                                 | R       |
| $\text{CCl}_2\text{FH}$             | $2.6 (\pm 0.5) \times 10^{-10}$         | R           | $\text{CO}_2$                  | $1.0 (\pm 0.2) \times 10^{-10}$         | Q       |
| $\text{CClF}_2\text{H}$             | $1.3 (\pm 0.3) \times 10^{-10}$         | R           | $\text{C}_3\text{O}_2$         | $2.1 (\pm 0.6) \times 10^{-10}$         | R       |
| $\text{CClF}_2\text{CClF}_2$        | $2.0 (\pm 0.4) \times 10^{-10}$         | R           | $\text{COS}$                   | $1.5 (\pm 0.3) \times 10^{-10}$         | R       |
| $\text{CClF}_2\text{CCl}_2\text{F}$ | $2.9 (\pm 0.6) \times 10^{-10}$         | R           | $\text{CS}_2$                  | no data                                 | R       |
| $\text{CClF}_2\text{CCH}_2$         | $2.5 (\pm 0.5) \times 10^{-10}$         | R           | $\text{H}_2\text{O}$           | $2.0 (\pm 0.3) \times 10^{-10}$         | R       |
| $\text{CClF}_2\text{CH}_3$          | $2.2 (\pm 0.4) \times 10^{-10}$         | R           | $\text{H}_2\text{O}_2$         | $2.8 (\pm 1.0) \times 10^{-10}$         | R       |
| $\text{CCH}_2\text{CF}_3$           | $2.3 (\pm 0.5) \times 10^{-10}$         | R           | $\text{NH}_3$                  | $2.7 (\pm 0.4) \times 10^{-10}$         | R       |
| $\text{CCl}_2\text{HCF}_3$          | $3.4 (\pm 0.7) \times 10^{-10}$         | R           | $\text{NO}_2$                  | $1.4 (\pm 0.3) \times 10^{-10}$         | R       |
| $\text{CCl}_2\text{O}$              | $5.5 (\pm 2.2) \times 10^{-10}$         | R           | $\text{N}_2\text{O}$           | $1.2 (\pm 0.15) \times 10^{-10}$        | $R^f$   |
| $\text{CClFO}$                      | $3.4 (\pm 0.7) \times 10^{-10}$         | R           | $\text{O}_3$                   | $2.3 (\pm 0.3) \times 10^{-10}$         | R       |
| $\text{CF}_4$                       | $1.7 (\pm 0.3) \times 10^{-11}$         | $Q^b$       | $\text{SF}_6$                  | 0                                       | $\xi$   |
| $\text{CF}_3\text{H}$               | $5.4 (\pm 1.1) \times 10^{-11}$         | R and $Q^c$ | $\text{SO}_2$                  | $\approx 1.3 (\pm 0.7) \times 10^{-10}$ | R       |
| $\text{CF}_2\text{H}_2$             | $7.2 (\pm 1.4) \times 10^{-11}$         | $R^d$       | $\text{CN}$                    | no data                                 | ?       |
| $\text{CF}_3\text{CF}_2\text{H}$    | $7.2 (\pm 1.4) \times 10^{-11}$         | $R^d$       | $\text{CO}$                    | $3.6 (\pm 0.5) \times 10^{-11}$         | Q       |
| $\text{CF}_3\text{CH}_3$            | $9.0 (\pm 1.8) \times 10^{-11}$         | $R^d$       | $\text{Cl}_2$                  | $1.8 (\pm 1.0) \times 10^{-10}$         | R       |
| $\text{CF}_2\text{O}$               | $3.5 (\pm 0.7) \times 10^{-11}$         | R           | $\text{D}_2$                   | $(0.67 - 1.0) k_{H_2}$                  | R       |
|                                     | $\approx 1.0 (\pm 0.4) \times 10^{-10}$ | Q           | $\text{H}_2$                   | $1.2_6 (\pm 0.25) \times 10^{-10}$      | R       |
| $\text{C}_2\text{F}_4$              | $\approx 2(-1) \times 10^{-10}$         | $R^d$       | $\text{HCl}$                   | $1.3 (\pm 0.3) \times 10^{-10}$         | R       |
| $\text{C}_2\text{F}_6$              | $< 5 \times 10^{-12}$                   | $Q^b$       | $\text{N}_2$                   | $2.8 (\pm 0.3) \times 10^{-11}$         | Q       |
| $\text{CH}_4$                       | $1.5 (\pm 0.3) \times 10^{-10}$         | R           | $\text{NO}$                    | $4.0 (\pm 1.0) \times 10^{-11}$         | R or Q? |

|                                  |                                    |   |                |                                 |         |
|----------------------------------|------------------------------------|---|----------------|---------------------------------|---------|
| C <sub>2</sub> H <sub>4</sub>    | $\approx 4(\pm 2) \times 10^{-10}$ | R | O <sub>2</sub> | $3.7 (\pm 0.3) \times 10^{-11}$ | Q       |
| C <sub>2</sub> H <sub>6</sub>    | $3.2 (\pm 0.5) \times 10^{-10}$    | R | OH             | no data                         | R or Q? |
| C <sub>3</sub> H <sub>8</sub>    | $10 (\pm 1) \times 10^{-10}$       | R | H              | no data                         | Q       |
| c-C <sub>3</sub> H <sub>6</sub>  | $3.2 (\pm 0.3) \times 10^{-10}$    | R | N              | no data                         | R or Q? |
| C <sub>3</sub> H <sub>8</sub>    | $4.0 (\pm 0.8) \times 10^{-10}$    | R | O              | no data                         | R or Q? |
| 1-C <sub>4</sub> H <sub>8</sub>  | $\approx 4(\pm 2) \times 10^{-10}$ | R | He             | $< 3 \times 10^{-16}$           | Q       |
| c-C <sub>4</sub> H <sub>8</sub>  | $4.5 (\pm 0.5) \times 10^{-10}$    | R | Ne             | $5 (\pm 2) \times 10^{-15}$     | Q       |
| n-C <sub>4</sub> H <sub>10</sub> | $5.1 (\pm 0.5) \times 10^{-10}$    | R | Ar             | $3 (\pm 2) \times 10^{-13}$     | Q       |
| i-C <sub>4</sub> H <sub>10</sub> | $4.9 (\pm 0.5) \times 10^{-10}$    | R | Kr             | $6.6 (\pm 1) \times 10^{-12}$   | Q       |
| c-C <sub>5</sub> H <sub>10</sub> | $5.4 (\pm 0.5) \times 10^{-10}$    | R | Xe             | $7.2 (\pm 1.4) \times 10^{-11}$ | Q       |
| n-C <sub>5</sub> H <sub>12</sub> | $5.8 (\pm 0.6) \times 10^{-10}$    | R |                |                                 |         |

<sup>a</sup>R, chemical reaction; Q, physical quenching.

<sup>b</sup>Negligible reaction.

<sup>c</sup>Quenching may not be significant.

<sup>d</sup>Quenching not significant.

<sup>e</sup>2,2,4-trimethylpentane.

<sup>f</sup>Proceeds via two reaction channels of equal probability.

<sup>g</sup>No reaction, negligible quenching at  $10 \text{ MN m}^{-2}$ .

## 2. Interactions of O( $2^1D_2$ )

Of all the electronically excited species, the chemistry of O( $^1D$ ) has undoubtedly been studied in greatest detail and a considerable literature is available spanning the past 15 years. However, many of the quantitative data are more recent in origin and the number of pertinent references has doubled since Cvetanovic's evaluation [1] which constituted the first attempt to organize the large amount of relative values for the various interactions. As seen from Table 1, quantitative data are now available for those rate constants that describe the interactions of O( $^1D$ ) with 62 different species.

Studies have encompassed an extremely broad diversity of methods for producing and detecting O( $^1D$ ). It is invariably produced by direct photolysis. The gases and wavelengths most used include O<sub>3</sub> (228.8, 253.7, 266, 280, 313 nm and broadband), N<sub>2</sub>O (184.9 and 213.9 nm), NO<sub>2</sub> (228.8 nm and broadband), O<sub>2</sub> (147 nm and broadband) and CO<sub>2</sub> (147, 163.3 nm). Because these produce initially the O( $^1D$ ) with varying degrees of translational energy, from almost thermoneutrality (NO<sub>2</sub>, 228.8 nm) to close to 150 kJ mol<sup>-1</sup> (N<sub>2</sub>O, 184.9 nm, assuming half the available energy channels into the O( $^1D$ )), many of the early discrepancies were incorrectly considered in that context. An analysis of data currently available indicates that no effects can be positively identified as being due to "hot" O( $^1D$ ). However, more detailed studies are necessary which spectrum analyze the translational energy of the photolytic products [3] and monitor O( $^1D$ ) directly to resolve this question finally.

Two direct methods (630 nm "forbidden" emission and 115.2 nm absorption) and numerous indirect detection techniques have been used to monitor the O( $^1D$ ) concentration. The latter have nearly always provided relative measures and it is only with the advent of signal-averaging techniques that the direct measures have provided the necessary absolute values to help clarify the situation. Nevertheless, even these have not been without their problems and inconsistencies. One such major issue stems from the absorption law expression used by Husain and coworkers, principal advocates of the 115.2 nm absorption technique. They noted that the absorption appears to be best described by the modified Beer-Lambert law expression

$$I_{tr} = I_0 \exp\{-\epsilon(cl)^\gamma\}$$

with the empirical constant  $\gamma$  taking a value of 0.41. However, Phillips [4] calculated that for such a source and absorption parameters the deviations from Beer's law should be slight, if any, and suggested that a value for  $\gamma$  of 0.9 would be more appropriate. Since the rate constant  $k$  is proportional to  $\gamma^{-1}$  this change introduces a factor of 2.2 discrepancy which has posed somewhat of a dilemma. However, a re-examination of the whole data base lends substantial support to Phillips' conclusion. For example, considering one such case, the rate coefficients for O( $^1D$ ) with CCl<sub>4</sub> and neo-C<sub>5</sub>H<sub>12</sub> correspond to a unit gas kinetic collision efficiency for  $\gamma = 0.9$  and are consistent

TABLE 2  
Measured temperature dependences of O( $2^1D_2$ )

| Interactant      | $k$ ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) | Temperature range (K) |
|------------------|--|-----------------------|
| CH <sub>4</sub>  | $1.5 (\pm 0.3) \times 10^{-10}$                            | 198 - 357             |
| CO <sub>2</sub>  | $6.8 \times 10^{-11} \exp(+120(\pm 25)/T)$                 | 200 - 354             |
| H <sub>2</sub> O | $2.0 (\pm 0.3) \times 10^{-10}$                            | 253 - 353             |
| NH <sub>3</sub>  | $2.7 (\pm 0.4) \times 10^{-10}$                            | 204 - 354             |
| N <sub>2</sub> O | $1.2 (\pm 0.15) \times 10^{-10}$                           | 204 - 359             |
| O <sub>3</sub>   | $2.3 (\pm 0.3) \times 10^{-10}$                            | 103 - 393             |
| H <sub>2</sub>   | $1.25 (\pm 0.25) \times 10^{-10}$                          | 204 - 352             |
| HCl              | $1.3 (\pm 0.3) \times 10^{-10}$                            | 199 - 379             |
| N <sub>2</sub>   | $1.9 \times 10^{-11} \exp(+110(\pm 10)/T)$                 | 104 - 354             |
| O <sub>2</sub>   | $2.9 \times 10^{-11} \exp(+70(\pm 10)/T)$                  | 104 - 354             |

with other data; otherwise the indication would be that their cross sections were twice the normal gas kinetic value.

The evaluation of a recommended set of rate constants is difficult owing to the volume of data, a large fraction of which is expressed only in relative terms and not always with respect to the same molecule. Consequently, an iterative technique has been used to work gradually toward a consistent set of values and to sift out unreliable data. In this respect, Cvetanovic's (1974) recommended values were useful as an initial input. However, it soon became apparent that many of these required significant modification. The data for each species in turn were assessed, starting with those most extensively studied, coupling in the reported relative measures against all those species whose rates are known within a reasonable error range. Extreme values could then be eliminated and a more refined estimate of the rate constant determined to be fed back into the continuing analysis. This was repeated through the whole list of reactants many times until the data converged to an invariant set. Published relative values included in this analysis were taken from refs. 5 - 50 and absolute measures from refs. 51 - 60.

In absolute terms,  $k(\text{CO}_2)$  appears to be one of the best defined values which helped the analysis initially to fix rates in absolute terms. However, several other absolute measures now appear to be extremely close to their recommended values. Consequently, the recommended set in Table 1 can now be considered to be largely independent of each other and modifications to some will only have slight bearing on the values of others.

Various temperature dependences have been measured and are listed in Table 2 [59, 60]. Their general insensitivity to temperature may account for the absence of "hot" O( $^1D$ ) effects. Theoretical treatments which predict slight temperature dependences [61 - 63], not experimentally apparent, indicate a need for some refinement of these models.

TABLE 3

Electronic-vibration and electronic-electronic energy transfer efficiencies of  $O(2^1D_2)$

| Reaction  | Efficiency (%)  |
|---|---|
| $O(^1D_2) + CO \rightarrow O(^3P) + CO(v < 7)$                    | $30 \pm 10$   |
| $O(^1D_2) + N_2 \rightarrow O(^3P) + N_2(v < 7)$                  | $33 \pm 10$   |
| $O(^1D_2) + O_2 \rightarrow O(^3P) + O_2(b^1\Sigma_g^+, v = 0,1)$ | $80 \begin{smallmatrix} +30 \\ -20 \end{smallmatrix}$ |

The products of the interactions have been monitored in various cases and the nature of the process, chemical or physical, is indicated in Table 1. Such an understanding of the chemistry of  $O(^1D)$  derives from the large body of qualitative experimental data [64 - 125] and theoretical treatments that are available [61 - 63, 126 - 136].

For the cases of CO,  $N_2$  and  $O_2$ , relaxation is via E-V or E-E energy transfer. An evaluation of the measured efficiencies of such processes leads to those values listed in Table 3 [26, 29, 37, 52, 88, 96, 98, 107, 111, 113, 114, 116].

### 3. Interactions of $O(2^1S_0)$

Although not as extensively studied as  $O(^1D)$  a reasonable amount of data is now beginning to accumulate for  $O(^1S)$ . This has been facilitated almost entirely by monitoring the 557.7 nm  $O(^1S_0-^1D_2)$  emission which is less rigorously forbidden ( $\tau \approx 0.8$  s) than its 630 nm  $O(^1D_2-^3P_2)$  counterpart ( $\tau \approx 148$  s). Experimental difficulties have hinged rather on the ability to produce  $O(^1S)$  in systems free of other kinetic complications. Generally this has involved the use of 105 - 147 nm photolysis of O-bearing molecules such as  $N_2O$ ,  $CO_2$  or  $O_2$ . Although studies are limited, as with  $O(^1D)$ , no observed effects can be ascribed to the fact that the  $O(^1S)$  produced initially is translationally "hot" from  $CO_2$  or  $N_2O$ . This may partly arise from the presence of excess carrier gas that is generally used to facilitate thermalization of the  $O(^1S)$  particularly in the less efficient interactions, or from temperature-independent rate coefficients. Detailed studies have not yet been made in full concerning this aspect.

Published measurements are illustrated in Fig. 1 for the 25 interactions of  $O(^1S)$  that have been reported and show the spread of the data. The recommended set of values is listed in Table 4. In this case the evaluation followed more conventional lines and consisted in establishing the more reliable data sets by analyzing the systems and data reduction techniques used, correcting for any parameters since improved upon, and intercomparing the data obtained for all species in all the reported studies. In several

TABLE 4

Recommended rate constant values for  $O(2^1S_0)$  at 298 K ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )

| Interactant                   | Rate constant  | Nature <sup>a</sup>  | Interactant    | Rate constant                       | Nature         |
|-------------------------------|--|----------------------|----------------|-------------------------------------|----------------|
| CH <sub>4</sub>               | $2.7 \times 10^{-14}$ , $\pm 100\%$                      | R or Q?              | H <sub>2</sub> | $2.6 \times 10^{-16}$ , $\pm 100\%$ | R or Q?        |
| C <sub>2</sub> H <sub>2</sub> | $9 \times 10^{-10}$ , $\pm 100\%$                        | R?                   | HC             | no data, fast?                      | R?             |
| C <sub>2</sub> H <sub>4</sub> | $1.0 \times 10^{-9}$ , $\pm 50\%$                        | R?                   | N <sub>2</sub> | $< 5 \times 10^{-17}$               | Q <sup>b</sup> |
| C <sub>2</sub> H <sub>6</sub> | $1.0 \times 10^{-12}$ , $\pm 100\%$                      | R or Q?              | NO             | $5.7 (\pm 0.6) \times 10^{-10}$     | Q <sup>d</sup> |
| C <sub>3</sub> H <sub>6</sub> | $8 \times 10^{-10}$ , $\pm 100\%$                        | R?                   | O <sub>2</sub> | $2.8 (\pm 0.8) \times 10^{-13}$     | Q <sup>d</sup> |
| C <sub>2</sub> N <sub>2</sub> | $2 \times 10^{-10}$ , $\pm 100\%$                        | R?                   | OH             | no data                             | R or Q?        |
| CO <sub>2</sub>               | $3.6 (\pm 0.4) \times 10^{-13}$                          | Q <sup>d</sup>       | H              | no data                             | R or Q?        |
| H <sub>2</sub> O              | $5.0 \times 10^{-10}$ , $\pm 100\%$                      | R and Q <sup>d</sup> | N              | $< 1 \times 10^{-12}$               | R or Q?        |
| NH <sub>3</sub>               | $5.0 \times 10^{-10}$ , $\pm 50\%$                       | R?                   | O              | $1.8 \times 10^{-11}$ , $\pm 50\%$  | Q              |
| NO <sub>2</sub>               | $5.0 \times 10^{-10}$ , $\pm 50\%$                       | R?                   | He             | $\approx 7 \times 10^{-20}$         | Q <sup>c</sup> |
| N <sub>2</sub> O              | $9.4 (\pm 1.9) \times 10^{-12}$                          | Q <sup>d</sup>       | Ne             | $3.6 (\pm 1.0) \times 10^{-19}$     | Q <sup>c</sup> |
| O <sub>3</sub>                | $5.8 (\pm 1.2) \times 10^{-10}$                          | R?                   | Ar             | $4.8 (\pm 1.0) \times 10^{-18}$     | Q <sup>c</sup> |
| SF <sub>6</sub>               | $4.9 \times 10^{-14}$ , $\pm 50\%$                       | Q                    | Kr             | $2.0 (\pm 0.5) \times 10^{-17}$     | Q <sup>c</sup> |
| CO                            | $9.4 \times 10^{-14}$ , $\pm 1.9$<br>$-(\times 10^{-1})$ | Q                    | Xe             | $2.5 (\pm 1.0) \times 10^{-16}$     | Q <sup>c</sup> |

<sup>a</sup>R, chemical reaction; Q, physical quenching.<sup>b</sup>Quenched partially via collision induced emission.<sup>c</sup>Quenched predominantly via collision induced emission.<sup>d</sup>Product channels identified [161].

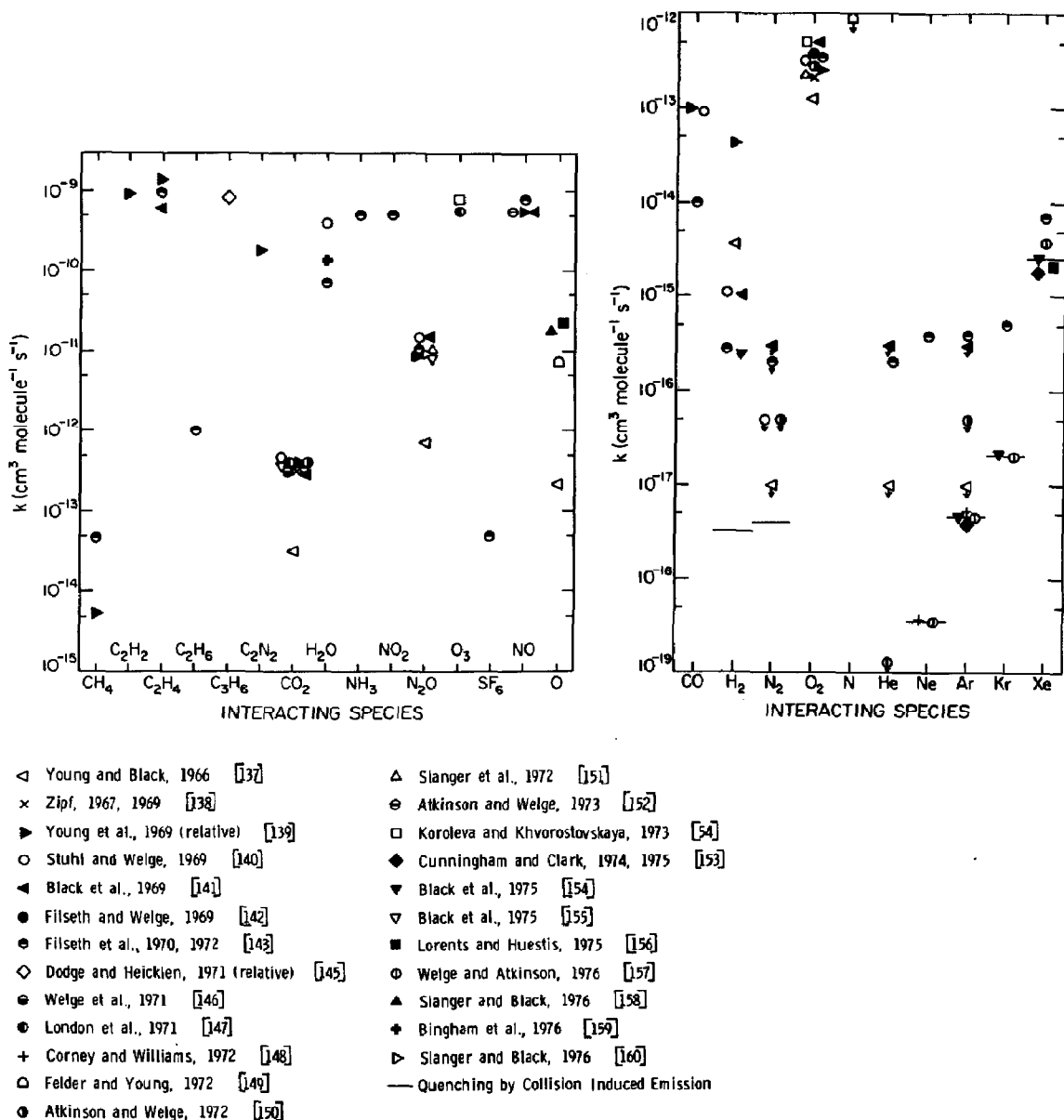


Fig. 1. Measured rate constants for the interactions of  $\text{O}(2^1\text{S}_0)$  at 298 K with various species.

cases, for example with  $\text{CO}_2$ ,  $\text{N}_2\text{O}$ ,  $\text{O}_3$ ,  $\text{NO}$ ,  $\text{O}_2$ ,  $\text{Ne}$ ,  $\text{Ar}$ ,  $\text{Kr}$  and  $\text{Xe}$ , sufficient data exist that a narrow error limit range can be confidently quoted. Otherwise, with species where possibly only a single measure is available ( $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_6$ ,  $\text{C}_2\text{N}_2$ ,  $\text{NH}_3$ ,  $\text{NO}_2$ ,  $\text{SF}_6$  and  $\text{N}$ ) the confidence levels have to be based on the reliability of other measurements made in the same study and are consequently subject to a greater uncertainty. Table 4 is based



TABLE 5

Measured temperature dependences of O( $2^1S_0$ )

| Interactant      | $k$ ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )                    | Temperature range (K) |
|------------------|---|-----------------------|
| CO <sub>2</sub>  | $3.0 \times 10^{-11} \exp(-1320/T), \pm 30\%$                                 | 150 - 500             |
| N <sub>2</sub> O | $3.8 \times 10^{-11} \exp(-420/T), \pm 20\%$                                  | 200 - 370             |
| N <sub>2</sub>   | $< 5 \times 10^{-17}$ ( $4.0 \times 10^{-18}$ temp. independent) <sup>a</sup> | 200 - 380             |
| NO               | $3.3 \times 10^{-11} T^{1/2}, \pm 10\%$                                       | 200 - 300             |
| O <sub>2</sub>   | $4.8 \times 10^{-12} \exp(-850/T), \pm 40\%$                                  | 200 - 450             |
| O                | $5.0 \times 10^{-11} \exp(-300/T), \pm 50\%$                                  | 200 - 370             |
| Ne               | $3.6 (\pm 1.0) \times 10^{-19}$   | 200 - 300             |
| Ar               | $4.8 (\pm 1.0) \times 10^{-18}$   | 200 - 380             |
| Kr               | $2.0 (\pm 0.5) \times 10^{-17}$   | 200 - 300             |
| Xe               | $7 \times 10^{-16} \exp(+380/T), \pm 40\%$                                    | 200 - 300             |

<sup>a</sup>Temperature independent if collision-induced emission is dominant.

on data taken from refs. 54, 122 and 137 - 161 and the various theoretical analyses for several of these interactions [127, 133, 162 - 165].

Quantitative identification of product channels and the relative importance of chemical reactions to physical quenching has been reported only recently for several species [161], and remains uncertain for about half of the interactions studied.

Known temperature dependences for these rate coefficients are listed in Table 5 [146, 150 - 152, 157 - 158, 160]. Although small, they are more pronounced in many cases than for O( $^1D$ ).

#### 4. Discussion

It is apparent that with the exception of several physical quenching processes (CF<sub>4</sub>, C<sub>2</sub>F<sub>6</sub>, He, Ne, Ar and Kr) the gas phase chemistry of O( $^1D$ ) is characterized by very fast efficient collision processes, the majority of which are chemical in nature. No such generalized statement is possible for O( $^1S$ ), the interactions of which encompass a wide range of collision efficiencies, rate constants ranging from  $10^{-9}$  to  $10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Both states are particularly noteworthy in exhibiting surprisingly efficient non-adiabatic relaxation processes which are difficult to explain theoretically.

It is well known that energy and spin considerations alone are insufficient to predict the reactive behavior of electronically excited states. At present, only the linear correlation diagrams as exemplified by the work of Donovan and Husain [127] have been of general value in qualitatively explaining, for example, the fact that whereas the interaction of H<sub>2</sub> with O( $^1D$ ) is very fast that with the more energetic O( $^1S$ ) is slow. However, their

predictive power for *a priori* assessments of preferred reaction pathways is very limited. On analyzing those cases considered here, it does give a satisfactory qualitative insight into the nature of the interactions of  $O(^1D)$  with  $H_2O$ ,  $N_2O$ ,  $O_3$ ,  $CO$ ,  $Cl_2$ ,  $HCl$ ,  $H_2$ ,  $N_2$  and  $NO$ . They do not explain or predict the fast physical quenching by  $CO_2$ . Likewise with  $O(^1S)$  such correlations are of less value, often because of the larger energies involved which introduces a more complex manifold of possible excited states. However, they prove satisfactory for  $O(^1S)$  with  $CO_2$ ,  $CO$ ,  $N_2O$ ,  $N_2$  and  $H_2$  but fail in describing the behavior with  $H_2O$  and  $NO$ . Of the few areas of substantial theoretical understanding, only that involving the excimer chemistry of  $O(^1D)$  and  $O(^1S)$  with the inert gases appears to be well founded [133, 164, 165].

The present evaluation shows a significant improvement in the accuracy of values, particularly for  $O(^1D)$ , over those previously published [1, 2]. The absolute magnitudes for the rate coefficients of  $O(^1D)$  reactions are all decreased by factors ranging from about 1.6 to 2.7. That for  $NO$  decreases by a factor of 4. The changes for  $O(^1S)$  are not as dramatic, mainly because of the smaller number of quantitative studies that have been reported in the last few years. Nevertheless, values for  $O(^1S)$  with  $CH_4$ ,  $H_2O$ ,  $N_2O$ ,  $O$  and the inert gases all have been significantly improved upon.

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