High-Temperature Dissociation of Oxygen Diluted in Argon or Nitrogen

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The dissociation of O_2 diluted in Ar or N_2 has been measured in the temperature range $2400\ K \leq T \leq 4100\ K$ at pressures between 0.9–2 bar using the shock-tube technique. Mixtures of O_2/Ar and O_2/N_2 were shock heated and the time-dependent concentrations of oxygen atoms were monitored in the postshock reaction zone by using atomic resonance absorption spectroscopy (ARAS). From the slope of the oxygen concentration profiles, rate coefficients for the dissociation reaction $O_2 + M \rightarrow O + O + M$ of $k = 1.6 \times 10^{18}\ T^{-1} \exp(-59{,}380\ K/T)\ cm^3mol^{-1}s^{-1}$ (M = Ar) and $k = 3.4 \times 10^{18}\ T^{-1} \exp(-59{,}380\ K/T)\ cm^3mol^{-1}s^{-1}$ ($M = N_2$) could be directly determined. These were confirmed by detailed computer simulations.

Introduction

INCREASING interest in hypersonic flight has again enhanced the discussion of the kinetics of high-temperature air. Reaction systems with several neutral species, and with additional electronically or vibrationally excited species or ionic species, were considered in the description of the kinetic behavior of air that had been heated by a bow shock near the solid surface of hypersonic vehicles. It seems clear that the entire mechanism starts with the generation of oxygen atoms resulting from the high-temperature dissociation of O_2. By reaction with N_2, the oxygen atoms break the strong $N \equiv N$ bond and open the paths to nitrogen chemistry.

The literature values of the rate coefficient of the O_2 dissociation were all obtained from shock-tube experiments. Either the time-dependent density or the concentration of O_2 were measured behind incident or reflected shock waves by applying interferometry or uv absorption spectroscopy. Only Watt and Myerson[1] determined the dissociation rate coefficient in O_2/Ar mixtures by oxygen-atom absorption measurements at $\lambda = 130.4$ nm. Baulch et al.[2], who critically reviewed all experimental data up to 1976, recommended a rate coefficient for the dissociation of O_2 in the temperature range $3000\ K \leq T \leq 18{,}000\ K$

$$O_2 + M \rightarrow O + O + M$$

to be $k = 1.81 \times 10^{18}\ T^{-1} \exp(-59{,}380\ K/T)\ cm^3mol^{-1}s^{-1}$ (M = Ar).

The suggested error in this temperature range is about a factor of two. Relative collision efficiencies with respect to argon for $M = O_2$, N_2, O, and other collision partners were only summarized but no values were recommended by Baulch et al.[2]

From the practical point of view of high-temperature air dissociation, the collision partner $M = N_2$ is very important. In the review articles of Bascombe[3] and Bortner and Golden,[4] the collison efficiency of N_2 in O_2 dissociation was assumed equal to that of Ar. The only direct experiment on O_2 dissociation in O_2/N_2 mixtures is known from Generalov and Losev.[5] They followed the uv absorption of O_2 at $\lambda = 224.5$ nm and determined a rate coefficient in the temperature range $3700\ K \leq T \leq 7000\ K$ to be $k = 3.63 \times 10^{18}\ T^{-1} \exp(-59{,}380\ K/T)\ cm^3mol^{-1}s^{-1}$ ($M = N_2$), which is a factor of two higher than the recommended value of Baulch et al.[2] for M = Ar.

In the present study, the dissociation of O_2 was measured in O_2/Ar as well as O_2/N_2 mixtures. The time-dependent increase of oxygen atoms in the postshock reaction zone was monitored by using atomic resonance absorption spectroscopy (ARAS). The aims are to measure the dissociation rate coefficient of O_2 and to determine the relative collison efficiency of Ar and N_2.

Experimental

The experiments were conducted in a 50-mm internal diameter ultra-high vacuum (UHV) shock tube, consisting of 5-m-long running section of borosilicate glass and a 3-m-long driver section made of stainless steel. The tube can be pumped down to a pressure of about 10^{-8} mbar by using a turbomolecular pump. The typical leak-plus-outgassing rate is of the order of 4×10^{-8} mbar s^{-1}. A detailed description of the apparatus and experimental method is given in Ref. 6. The test gases were supplied by Messer-Greisheim, Germany. They were certificated to be of the following purities: Ar = 99.9999%, O_2 = 99.998%, and N_2 = 99.9995%, impurities not specified. Mixtures of 10,000 ppm to 187.5 ppm O_2 in N_2 or Ar were prepared by the partial pressure method and stored in a stainless steel UHV vessel. The oxygen atom concentration measurements were made behind reflected shock waves, 15 mm from the end flange of the shock tube. Under these conditions, cooling of the reaction volume by heat transfer in the temperature boundary layer can be assumed to be small. The mean temperature and pressure were computed from the incident shock speed by using one-dimensional gasdynamic equations. The shock speed was measured by laser schlieren technique. It is known that shock/boundary-layer effects can cause changes in the steadiness conditions behind the reflected shock. This was ignored in the data evaluation. The rate coefficients were determined from the oxygen atom increase measured at short dissociation times. Therefore, any changes in the postshock conditions were assumed to have negligible effects on the results reported here.

The measurement technique used in this investigation is atomic resonance absorption spectroscopy (ARAS) of oxygen atoms at the OI-triplet ($\lambda = 130.5$ nm). It is a line-emission line-absorption method for measuring oxygen atoms in the range of 10^{12}–10^{14} atoms cm^{-3}. The spectral shape of the emitter line is not known precisely. It is influenced by self-absorption and self-reversal. Precise shock-wave calibration measurements have been done to obtain the relation between the measured resonance absorption and the oxygen-atom concentration. In those measurements, the partial equilibrium of oxygen atoms which can be realized in shock-heated Ar/N_2O

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mixtures has been used. More details on the calibration procedure are given in Refs. 6–8.

Results

The dissociation of oxygen was studied both in O_2/Ar as well as O_2/N_2 mixtures. The experiments with argon being the diluent were conducted in the temperature range $2369 \text{ K} \leq T \leq 4158 \text{ K}$ at pressures of 1.31–1.87 bar. In 12 shock-tube experiments, the relative initial concentrations of O_2 were between 1000 ppm and 10,000 ppm. The experiments in O_2/N_2 mixtures were conducted in the temperature range $2463 \text{ K} \leq T \leq 3999 \text{ K}$ at pressures of 0.96–1.96 bar. In 16 shock-tube experiments, the relative initial concentrations of O_2 were between 187 ppm and 10,000 ppm. The conditions of all experiments are listed in Tables 1 and 2.

In each experiment, the measured incident shock speed served to calculate the temperature and pressure behind the reflected shocks. The oxygen-atom resonance absorption signals were monitored from the reacting gas mixture. A representative absorption profile is shown in Fig. 1. Using the calibration curve given in Ref. 8, each absorption signal can be easily transformed to the oxygen-atom concentration profile. One example is shown in Fig. 2. All O_2/Ar experiments show a nearly linear oxygen-atom increase during the measurement time. In O_2/N_2 experiments, as in Fig. 2, linearity occurs in the first 500 μs. Short-induction periods of about 10–15 μs were observed in some experiments. This is caused by the vibrational relaxation or reaction incubation processes. Deviations from linearity at later times are due to secondary reactions. They are ignored in this study.

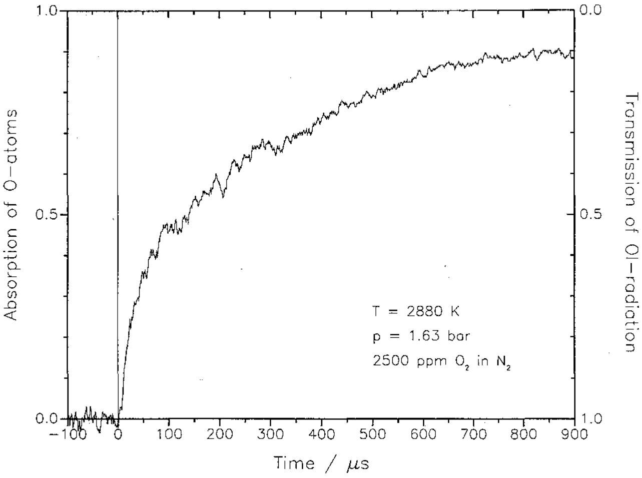

Fig. 1 Typical absorption profiles of oxygen atoms measured at λ = 130.5 nm.

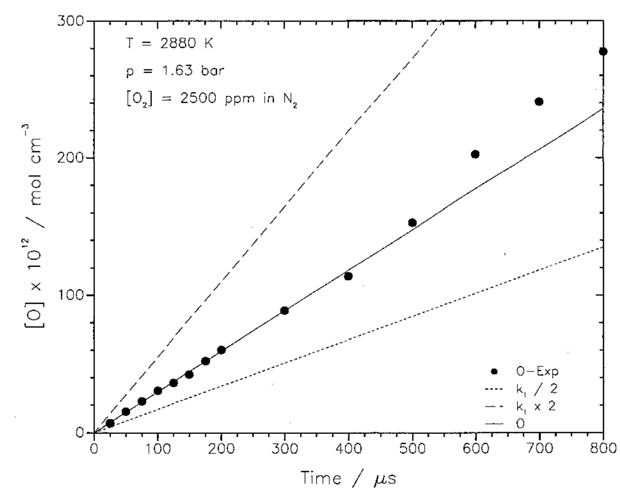

Fig. 2 Example of measured and computed oxygen-atom concentration profiles in shock-heated O_2/N_2 mixture.

Table 1 Experimental conditions and inferred rate coefficients for the dissociation of O_2 (M = Ar)

T,K	p, bar	$[O_2]$, ppm	$k_{O_2,M}$,cm^3 $mol^{-1}s^{-1}$
2743	1.82	10,000	1.89×10^5
2570	1.71	10,000	5.06×10^4
2437	1.76	10,000	1.67×10^4
2369	1.87	10,000	4.64×10^3
2942	1.71	2500	9.64×10^5
2747	1.71	2500	2.89×10^5
4158	1.31	1000	2.93×10^8
3526	1.41	1000	3.52×10^7
3451	1.58	1000	1.93×10^7
3268	1.60	1000	4.94×10^6
2995	1.64	1000	1.47×10^6
2963	1.53	1000	1.35×10^6

Table 2 Experimental conditions and inferred rate coefficients for the dissociation of O_2 (M = N_2)

T/K	p, bar	$[O_2]$, ppm	$K_{O_2,M}$,cm^3 $mol^{-1}s^{-1}$
2599	1.34	10,000	2.00×10^5
2555	1.63	10,000	1.05×10^5
2463	1.96	10,000	4.97×10^4
2880	1.63	2500	1.12×10^6
3314	1.47	1250	1.54×10^7
3003	1.60	1250	2.02×10^6
2709	1.82	1250	3.83×10^5
3519	1.23	1100	4.82×10^7
3144	1.59	1100	5.06×10^6
3011	1.66	1100	1.97×10^6
3182	1.16	1000	1.07×10^7
2797	1.43	1000	1.13×10^6
2753	1.86	1000	4.25×10^5
3496	1.06	750	4.34×10^7
3862	1.04	375	1.93×10^8
3999	0.96	187	2.63×10^8

Discussion

Experiments with O_2/Ar mixtures

The first step in data interpretation was made by considering a reaction with an unspecified collision partner:

$$O_2 + M \rightarrow O + O + M$$

and evaluating the quantity

$$k_{O_2,M} = \frac{d[O]/dt}{2[O_2]\ [M]}$$

as a function of the reciprocal temperature. The above equation represents the rate coefficient of the O_2 dissociation if Ar and O_2 are assumed to have the same collision efficiency. If the values of $k_{O_2,M}$ were plotted in an Arrhenius diagram, a slight deviation from the linear behavior was observed, particularly under conditions of low temperatures and relatively high O_2 concentrations. This can be explained by the fact that O_2 is a more effective collision partner than Ar.

A more detailed kinetic interpretation of the dissociation experiments was done by considering the reactions

$$O_2 + Ar \rightarrow O + O + Ar$$

and

$$O_2 + O_2 \rightarrow O + O + O_2$$

The rate coefficient $k_{O_2,Ar}$ can therefore be described as

$$k_{O_2,Ar} = \frac{d\ [O]/dt}{2[O_2]([Ar] + \eta\ [O_2])}$$

Table 3 Simplified high-temperature O_2/N_2 reaction system

	Reaction			Rate coefficient, $cm^3mol^{-1}s^{-1}$	Ref.
R1	O_2+N_2	$\rightleftharpoons$	$O+O+N_2$	$3.40\times10^{18}\ T^{-1}\exp(-59{,}380\ K/T)$	see text
R2	O_2+O_2	$\rightleftharpoons$	$O+O+O_2$	$3.40\times10^{18}\ T^{-1}\exp(-59{,}380\ K/T)$	see text
R3	N_2+N_2	$\rightleftharpoons$	$N+N+N_2$	$2.58\times10^{28}\ T^{-3.3}\exp(-113{,}220\ K/T)$	10
R4	N_2+O	$\rightleftharpoons$	$NO+N$	$1.80\times10^{14}\exp(-38{,}300\ K/T)$	7
R5	$N+O_2$	$\rightleftharpoons$	$O+NO$	$6.40\times10^{9}\ T^{-1}\exp(-3150\ K/T)$	2
R6	N_2+O_2	$\rightleftharpoons$	$NO+NO$	$4.60\times10^{24}\ T^{-2.5}\exp(-64{,}700\ K/T)$	12
R7	N_2+O_2	$\rightleftharpoons$	$O+N_2O$	$6.30\times10^{13}\exp(-55{,}200\ K/T)$	2
R8	$NO+NO$	$\rightleftharpoons$	$O+N_2O$	$9.03\times10^{12}\exp(-35{,}000\ K/T)$	7
R9	N_2O+M	$\rightleftharpoons$	$O+N_2+M$	$9.3\times10^{14}\exp(-29{,}826\ K/T)$	13
R10	$NO+M$	$\rightleftharpoons$	$N+O+M$	$9.64\times10^{14}\exp(-74{,}700\ K/T)$	7

where η is the collision efficiency of O_2 relative to Ar. Normally, the collision efficiency can be assumed to be independent of temperature. In the present case, the influence of η on the dissociation rate coefficient $k_{O_2,Ar}$ is very weak because of the relative high dilution in Ar. With the assumption of $\eta=3$, the rate coefficient was determined as given in the last column of Table 1, and in the Arrhenius diagram of Fig. 3. An analytical rate-coefficient expression was obtained by assuming the activation energy equal to the dissociation energy of O_2. Converted to temperature, this results in a value of 59,380 K, see Ref. 2. Best fit to the experimental data was obtained by assuming the temperature exponent in the pre-exponential factor to be $n=-1$. This lead to the expression:

$$k_{O_2,Ar}=1.6\times10^{18}\ T^{-1}\exp(-59{,}380\ K/T)\ cm^3mol^{-1}s^{-1}$$

with a percentage standard deviation due to the experimental scatter of about ± 25%.

For the temperature range of this experimental study, the presented value of $k_{O_2,Ar}$ is in good agreement with estimates obtained from the weak collision unimolecular reaction rate theory of Troe,[9] even though it is known that this theory is normally valid only for molecules with more than one vibrational degree of freedom. According to this theory, the dissociation rate coefficient in the low-pressure region can be expressed as

$$k_{O_2,Ar}=k^{sc}_{O_2,Ar}\beta_c$$

where $k^{sc}_{O_2,Ar}$ is the strong collision rate coefficient and β_c is the weak collision factor. The strong collision rate coefficient depends on several molecular quantities and can be calculated for the temperature range of the present study. The weak collision factor includes all of the uncertainities in the theory and experiments and will, in general, be fitted to the experimentally determined rate. In the present case, a mean value of $\beta_c=0.03$ was obtained. This result seems to be in reasonable agreement with experimental values determined from dissociation experiments of similar molecules.[10]

Experiments with O_2/N_2 mixtures

Because of the relatively low O_2 concentrations in the high-temperature O_2/N_2 decomposition system, it seems reasonable to assume in a first interpretation step that the measured oxygen-atom formation is mainly the result of the dissociation reaction

$$O_2+M\rightarrow O+O+M$$

with $M=N_2$ or $M=O_2$, respectively. According to this reaction, the initial slope of the measured oxygen-atom concentrations can be used to determine the rate coefficient of the O_2 dissociation:

$$k_{O_2,N_2}=\frac{d\,[O]/dt}{2[O_2]\,([N_2]+\xi\,[O_2])}$$

The factor ξ is the dissociation efficiency of O_2 relative to N_2. In the present case, ξ is assumed to be equal to 1. It should be noted that this is not a critical assumption because of the low concentration of O_2 with respect to N_2. From the measured oxygen-atom slope at early reaction time, the rate coefficient k_{O_2,N_2} can be determined for each shock-tube experiment. Results are shown in the last column of Table 2 as well as in the Arrhenius plot of Fig 4. A fit of the measured data leads to the expression:

$$k_{O_2,N_2}=3.4\times10^{18}\ T^{-1}\exp(-59{,}380\ K/T)\ cm^3mol^{-1}s^{-1}$$

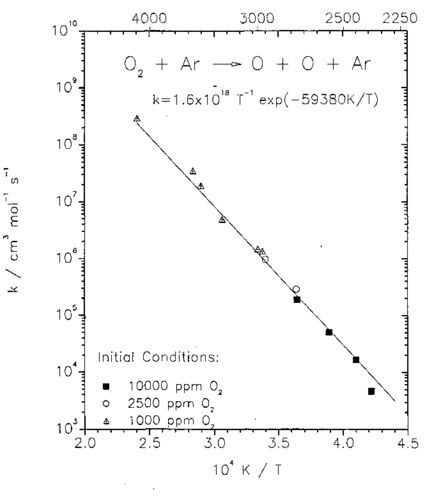

Fig. 3 Arrhenius diagram of the measured rate coefficient of the reation O_2 + Ar → O + O + Ar.

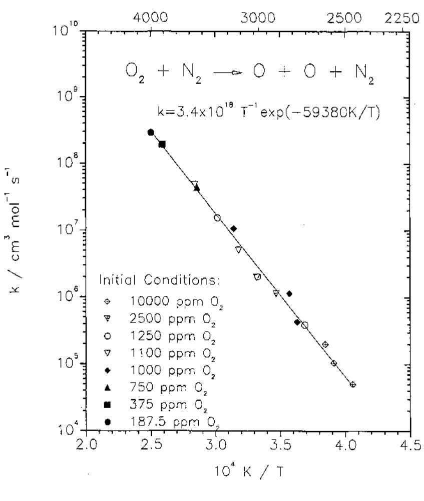

Fig. 4 Arrhenius diagram of the measured rate coefficient of the reaction O_2 + N_2 → O + O + N_2.

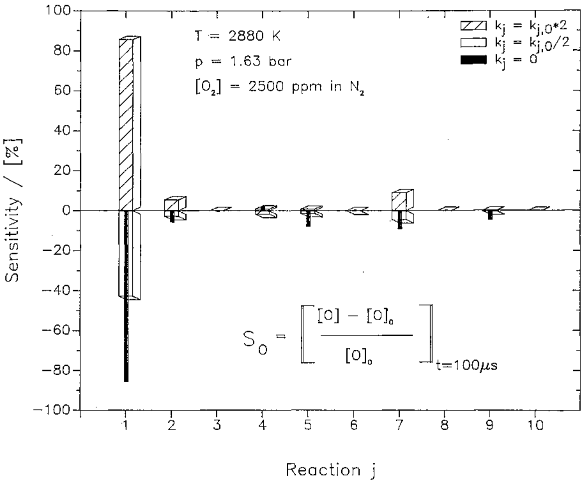

Fig. 5 Sensitivity analysis of the reaction scheme of Table 3.

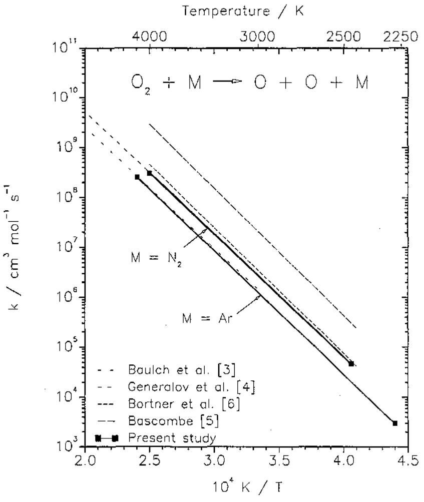

Fig. 6 Comparison of various shock-tube measurements of the rate coefficients for the thermal decomposition of O_2.

with a percentage standard deviation due to the experimental scatter of about 25%.

For a more detailed kinetic description of the high-temperature O_2/N_2 system, reactions other than the first decomposition step of O_2 have to be considered. These are mainly due to the decomposition of N_2 and secondary reactions of oxygen and nitrogen atoms with N_2 and O_2. The reaction mechanism of Table 3, together with corresponding rate coefficients, was used for a more extended computer simulation of the O_2 dissociation. The reverse rate coefficients were obtained from the equilibrium constants as calculated from the JANAF thermochemical data.[11] In all cases, nearly completed agreement was obtained between measured and calculated oxygen-atom profiles during the first 500 μs. This is shown in Fig. 2, for example. This indicates that the oxygen-atom formation is mainly determined by reactions (R1) and (R2). A sensitivity analysis of the reaction system of Table 3 with respect to the oxygen-atom concentrations confirms this observation. An individual example is given in Fig. 5. It shows the percentage changes in the computed atom concentrations with respect to the correct values at the reaction time $t = 100$ μs, when the rate coefficients of Table 3 were successively varied by factors 2, 0.5, and 0. From this analysis, it is clear that primary significance goes to the rate coefficients of reaction (R1), which is directly responsible for the formation of oxygen atoms in the early reaction times. The same relationship was found for all other experiments. The rate coefficient k_{O_2,N_2} obtained with the above simple data analysis is completely confirmed by the computer analysis. When compared to the weak collision unimolecular theory of Troe,[9] the weak collision factor results in a mean value of $\beta_c = 0.058$, and this value seems to be reasonable for the present dissociation process.

Comparison with Other Results

The measured rate coefficients for the dissociation of O_2 by collisions with Ar or N_2 show the same temperature dependence within experimental error. The ratio of both the values

$$\frac{k_{O_2,N_2}}{k_{O_2,Ar}} \approx 2.1$$

gives a measure of the relative collision efficiency of N_2 with respect to Ar. The present result is in sufficiently good agreement with the only available result; namely, that of Generalov and Losev,[5] who obtained a value of 1.5 in their experiments.

A comparison of the rate coefficients of the present study with literature values is shown in Fig. 6. Again, the absolute values are in good agreement with the results of Generalov and Losev,[5] as well as with the recommendation of Baulch et al.[2] for $M = Ar$. The rate coefficient of Bortner and Golden[4] for $M = Ar$ is slightly above the present value for $M = N_2$ and is therefore higher than the present value by about a factor of two; the rate coefficient reported by Bascombe[3] seems to be much too high.

Acknowledgment

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