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High-Temperature Oxidation of Fullerene C_{60} by Oxygen Atoms

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The reaction of O atoms with fullerene C_{60} was studied behind reflected shock waves by time dependent atomic and molecular resonance absorption spectroscopy. Mixtures of C_{60}/N_2O highly diluted in argon were shock heated, and the absorption of O atoms at $\lambda = 130.5$ nm and of $CO[X^1\Sigma^+(\nu' = 0) \rightarrow A^1\Pi(\nu'' = 1)]$ at 151.0 nm was monitored. Simultaneously, the time behavior of spectrally resolved light emitted by the shock-heated mixtures was recorded by an intensified CCD camera in the wavelenghth range 315 nm $\leq \lambda \leq$ 570 nm. The experiments were performed in the temperature range 1870K $\leq T \leq$ 2625 K at pressures around 1.30 bar. A kinetic model for the reaction system was developed. The evaluation of O atom concentration measurements resulted in the following rate coefficient for the reaction $C_{60} + O \rightarrow CO +$ products: $k_2 = 3.0 \times 10^{15} \exp(-11\,450\ \mathrm{K}/T)$ cm^3 mol^{-1} s^{-1}. The uncertainty in k_2 is expected to be ±50%.

Introduction

The existence of fullerenes as a new carbon modification has been established during the last few years.[1] The C_{60} molecule discovered to be stable by Kroto et al. in 1985 was proposed to be a soccer-ball-shaped cage, where the carbon atoms are placed at the edges of 12 pentagons and 20 hexagons. The proposed structure was confirmed in an immense number of experimental studies. In contrast to many investigations concerning the thermal stability of fullerene molecules, the chemical stability at high temperatures has not been studied in detail, although this may give insights into modern aspects of combustion chemistry and other scientific areas. In spite of the great interest concerning the chemical stability of fullerenes, reliable kinetic data for fullerene reactions with atomic species at high temperatures are still limited. The chemical stability of fullerenes with respect to molecular species like NO, SO_2, H_2, CO, NH_3, and O_2 has been investigated by Zhang et al.[2] at room temperature. Furthermore, the conversion of C_{60} to amorphous carbon was studied in a pure O_2 atmosphere at 500 K, and, at higher temperatures, the oxidation products CO and CO_2 were observed. The high-temperature oxidation of C_{60} by O_2 was investigated in a previous shock tube study of our group by both following the emission of C_2 and infrared diode laser absorption measurements of CO and CO_2.[3] A shock tube study on the thermal stability of C_{60} was performed earlier[4] by time dependent absorption measurments of C_2, which is the primary product during fullerene decomposition. From this study, a temperature limit for the thermal stability of C_{60} of $T \leq 2650$ K was determined to be relevant for shock tube conditions.

The aim of the present work is to study the reaction of C_{60} with O atoms by monitoring the concentrations of both O atoms and CO in high-temperature experiments. For this purpose the well-known dissociation of N_2O, which has recently been verified by Ross et al.,[5] was used as a source for O atoms. Mixtures of C_{60}/N_2O highly diluted in argon were shock heated to temperatures below 2650 K to ensure a direct reaction of C_{60} with O. Two different diagnostic tools were used to follow the shock-induced oxidation. The sensitive ARAS/MRAS technique was applied to monitor time dependent O atom and CO concentration. Simultaneously, emission spectroscopy with an intensified CCD camera was employed to obtain further information about possible additional species such as C_2 and CN.

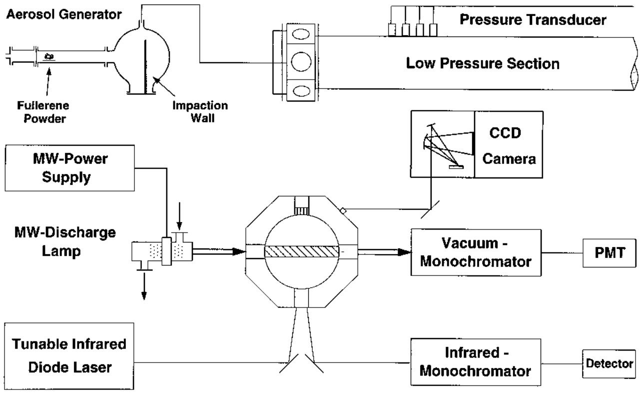

Figure 1. Schematic of the experimental setup including shock tube, aerosol generator, and different optical diagnostics.

Experimental Section

The experimental setup used during the present study is shown schematically in Figure 1. It consists of an aerosol generator for dispersing the fullerene powder, the main shock tube for heating the $C_{60}/N_2O/Ar$ mixtures to high temperatures, an ARAS/MRAS spectrometer for measuring O and CO absorption, a spectrograph with an intensified CCD camera for the detection of spectral and time-resolved emission, and an IR diode laser system.

The C_{60} powder was dispersed in argon by an expansion wave driven aerosol generator.[6] It consists of a glass vessel of $V = 3 \times 10^4$ cm^3 volume connected to a glass tube of 5 cm inner diameter, which was separated by a thin diaphragm from a high-pressure tube of the same diameter. A thin dispersion plate was positioned near the diaphragm, which carried for every experiment about 100 mg of the fullerene powder. Before the powder dispersion was started, the low-pressure section of the aerosol generator was evacuated to a pressure of about 5×10^{-5} mbar. Subsequently, argon was filled into the high-pressure tube. After the bursting of the diaphragm, the high-pressure gas argon expanded in the form of a supersonic expansion wave into the evacuated vessel, thus dispersing the fullerene powder

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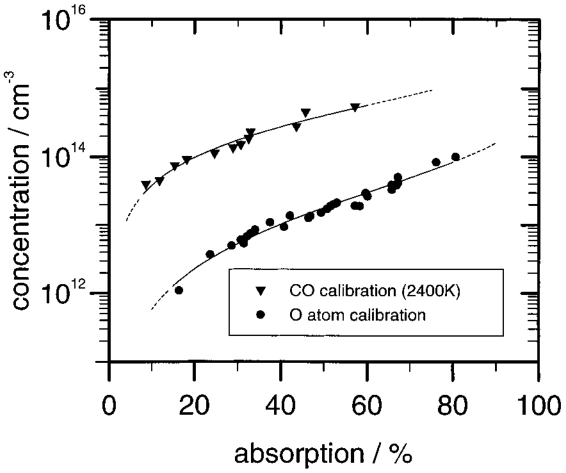

Figure 2. ARAS/MRAS calibration curves for O atoms and CO at 2400 K.

and bringing it into aerosol form. The fullerene C_{60} powder used during the present experiments was supplied by Hoechst AG, Germany, with a purity better than 99.7%. The generated aerosol was mixed with N_2O/Ar mixtures and subsequently transferred into the running section of the main shock tube.

The stainless steel shock tube, which was used as an isothermal−isobaric wave reactor, has an inner diameter of 8 cm, a total length of 11 m, and a running section of 7.2 m in length. The initial pressure of the aerosol, measured by calibrated diaphragm type pressure transducers, was in the range of 19−30 mbar. The shock velocity was measured by four piezoelectric pressure transducers positioned at known distances along the shock tube axis. The postshock temperature and pressure were calculated from the incident shock speed by applying one-dimensional conservation equations. The shock wave running into the fullerene-containing aerosol caused a sudden temperature and pressure increase initiating first the evaporation of the solid fullerene particles in less than 5 μs. Subsequently, the fullerene vapor started to react by a homogeneous gas phase reaction.[4,7]

The optical setup for measuring time dependent O and CO absorption consists of a microwave discharge lamp, the optical absorption path, a vacuum UV monochromator and a solar blind photomultiplier. The OI and $CO[X^1\Sigma^+(\nu' = 0) \rightarrow A^1\Pi(\nu'' = 1)]$ transitions were excited in gas mixtures of He containing 1% of O_2 or 1% of CO_2, respectively, passing through the lamp at a pressure of 5 mbar. The spectral lines were selected by a $^1/_5$ m vacuum UV monochromator. To obtain the relation between measured absorption and the corresponding O and CO concentration, the ARAS/MRAS diagnostic was calibrated. For this purpose, gas mixtures of N_2O or CO, both highly diluted in argon, were shock heated and the absorption of O and CO was measured and related to the known species concentration. Calibration curves for O atoms and CO are shown in Figure 2. The calibration for O atoms, which is temperature independent, can be expressed by a modified Lambert−Beer law

$$A(\mathrm{OI}) = 1 - \exp\{-L \times 1.0 \times 10^{-9}\ \mathrm{cm}^{0.8}[\mathrm{O}]^{0.6}\} \qquad (1)$$

In the temperature range of the present study, the relation between absorption and concentration in the case of CO slightly depends on temperature. Lower temperatures are related to a higher sensitivity for CO absorption. As an example, the calibration curve for $T = 2400$ K is also illustrated in Figure 2. It is obvious that absorption of CO is more than 1 order of magnitude less sensitive compared to the absorption of O atoms. The CO calibration can be expressed by the following equation:

$$A(\mathrm{CO})_{2400\ \mathrm{K}} = 1 - \exp\{-L \times 1.8 \times 10^{-13}\ \mathrm{cm}^{1.4}[\mathrm{CO}]^{0.8}\} \qquad (2)$$

The light emitted from the shock-heated reactive gas mixture was focused via a light fiber at the entrance slit of a $^1/_8$ m spectrograph, which has a spectral range of $\Delta\lambda = 255$ nm and a resolution of 1.3 nm. The spectrally resolved light was detected by an intensified CCD camera allowing a fast time shift of the optical information. For this purpose only a few lines at the top of the CCD sensor chip were illuminated for a certain time interval. The stored spectral emission was transferred stepwise line by line into the dark zone of the CCD chip, which served as memory. Accordingly, the spectral as well as the temporal behavior of the emitted light was recorded. Spectral characteristics of the quantum efficiency of the intensifier and of the diffraction grid were taken into account. The intensified CCD camera system (Streak Star) with spectograph was supplied by L.A. Vision.

For a quantitative data interpretation in terms of kinetic parameters, the initial concentration of C_{60} was required. For this purpose, fullerene C_{60} powder was dispersed in Ar containing about 6% of O_2. The aerosol mixtures were heated by the shock wave to conditions similar to the experiments of the present study and resulted in a complete oxidation of C_{60} by O_2. The gas phase oxidation products CO and CO_2 were quantitatively measured by tunable infrared diode laser spectroscopy, from which an initial C_{60} gas phase concentration of about 40 ppm could be deduced, see ref 8.

Results

The experiments on high-temperature C_{60}/N_2O/Ar mixtures were performed behind reflected shock waves at temperatures between 1870 and 2625 K and at pressures around 1.3 bar. In 13 individual experiments with N_2O concentrations ranging between 5 and 20 ppm, the absorption by O atoms at $\lambda = 130.5$ nm was monitored. To quantify the formation of CO, a few experiments were performed under similar conditions, while molecular resonance absorption of CO at $\lambda = 151.0$ nm was measured. Due to the relatively nonsensitive absorption of CO compared to O atoms, CO measurements could only be done with relatively high initial N_2O concentrations above 25 ppm. Furthermore, CO absorption was recorded at temperatures above 2300 K to ensure a high degree of conversion of O atoms to CO. Simultaneous to the ARAS/MRAS absorption measurements, the spectral and time-resolved emission of the reacting gas mixture was recorded.

Typical examples of O atom absorption profiles obtained from shock-heated N_2O/Ar mixtures without and with addition of C_{60} are shown in Figure 3. The absorption profile measured in the experiment without C_{60} shows a fast increase after shock arrival followed by a steady state behavior for the remaining observation time. The addition of C_{60} to the reaction system results in a strong decrease of the measured O atom absorption after rapid formation. This principal behavior was observed in all experiments. Each individual O atom absorption profile obtained from shock-heated C_{60}/N_2O/Ar mixtures was converted to absolute O atom concentration via the modified Lambert−Beer law of eq 1. Examples are shown in Figure 4; the noisy experimental lines are apparent. The experimental conditions and characteristics of all measured O atom concentration profiles are summarized in Table 1.

The CO absorption profiles were measured at temperatures above 2300 K with initial N_2O concentrations between 25 and 40 ppm. After a short induction period, the absorption increases to approximately 20−30% at the end of the reaction time,

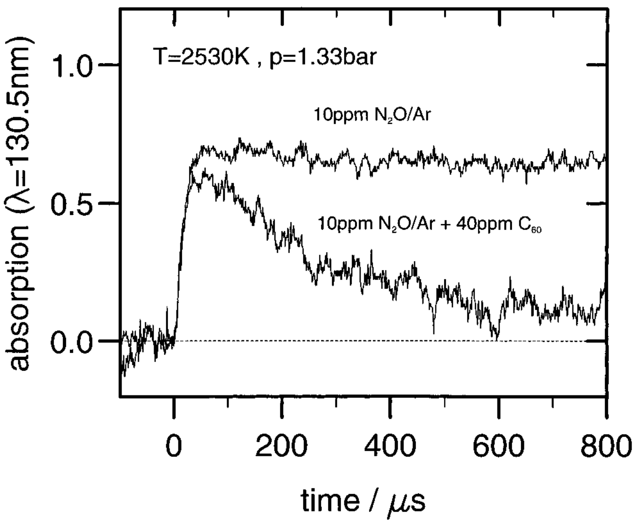

Figure 3. Examples of time dependent O atom absorption measured in N_2O/Ar and C_{60}/N_2O/Ar mixtures.

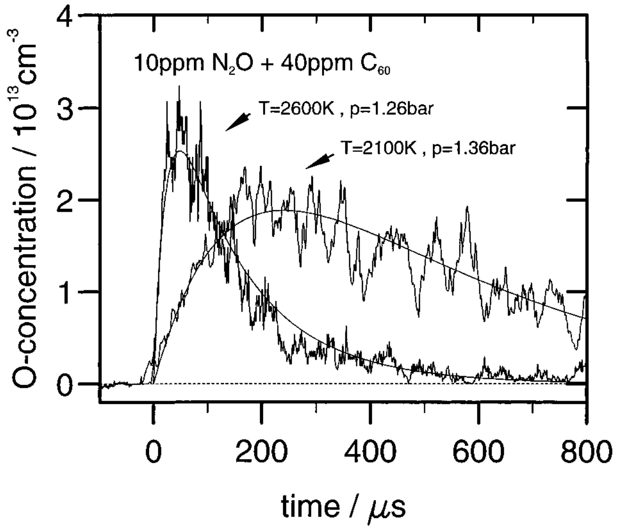

Figure 4. Comparison between measured (noisy lines) and calculated (solid lines) O atom concentration profiles for two different temperatures.

TABLE 1: Experimental Conditions and O Atom Concentration Characteristics Obtained from High-Temperature C_{60}/N_2O/Ar Reaction Systems[a]

T/K	p/ bar	ppm N_2O	$t([O]_{max})$/ μs	$[O]_{max}$	$[O]_{200\mu s}$	$[O]_{400\mu s}$	$[O]_{600\mu s}$	$[O]_{800\mu s}$
1870	1.39	20	800	3.21	1.58	2.56	2.99	3.21
1990	1.26	5	400	0.69	0.56	0.69	0.63	0.53
2030	1.34	10	285	1.40	1.32	1.30	0.98	0.69
2040	1.44	10	250	1.50	1.47	1.31	0.93	0.57
2100	1.36	10	240	1.88	1.83	1.63	1.14	0.71
2215	1.32	10	165	2.28	2.25	1.49	0.82	0.46
2250	1.35	5	118	1.09	0.97	0.44	0.30	0.18
2280	1.26	5	115	1.04	0.90	0.41	0.23	0.19
2300	1.38	5	88	1.20	0.98	0.40	0.24	0.21
2320	1.30	10	100	2.25	1.72	0.56	0.25	0.22
2530	1.33	10	51	2.70	1.33	0.47	0.14	0.11
2600	1.26	10	40	2.58	0.96	0.30	0.15	0.10
2625	1.28	5	37	1.30	0.42	0.11	0.10	0.10

[a] All concentrations in 10^{13} cm^{-3}.

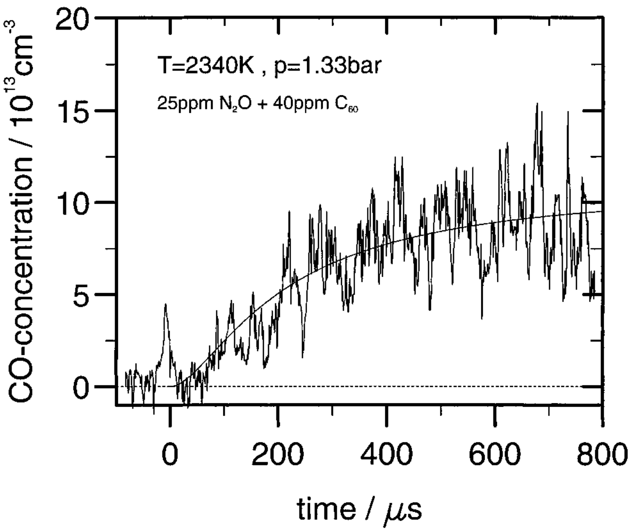

Figure 5. Comparison between measured (noisy line) and calculated (solid line) CO concentration profiles.

corresponding to CO concentrations of around 1 × 10^{14} cm^{-3}. A typical example of a measured absorption profile converted to CO concentration with its noisy signal is shown in Figure 5. Because of the relatively nonsensitive detection technique, the signal to noise ratio is low. We therefore have not further evaluated the signals in terms of kinetic parameters. The spectrally and time-resolved emission measurements using the intensified CCD camera in the wavelength range 315 nm $\leq \lambda \leq$ 570 nm showed no characteristic radiation for all shock tube experiments of the present study. Especially C_2 and CN, which have strong spectroscopic bands within this region, could not be observed during the present experiments.

Discussion

It can be assumed that several subsequent processes occur in the shock-heated gases containing C_{60} in highly dispersed particle form. Due to the relatively high vapor pressure of C_{60}, the solid agglomerated carbonaceous particles evaporate rapidly at high temperatures. This process starts behind the incident shock wave, where temperatures are in the range 1000 K $\leq T \leq$ 1300 K, and continues behind the reflected wave much more rapidly because of higher temperatures. The particle size after powder dispersion was determined by scanning electron microscopy resulting in particle diameters of less than 900 nm. An upper limit for a fullerene particle evaporation time of about 5 μs can be calculated[8,9] for conditions of the present study. The given upper limit for the evaporation time was experimentally confirmed by laser light scattering experiments behind shock waves.[7] We therefore can assume for our experimental conditions that the initial reactant C_{60} is in the vapor phase for nearly the total observation time and that reactions described in this study are dominated by homogeneous gas phase kinetics.

The dissociation of N_2O at high temperatures is well-known and has frequently been used as a pyrolytic source for O atoms. Recently, Ross et al.[5] verified the decomposition of N_2O by measurements of O atom concentration and evaluated a rate coefficient within the uncertainty limit of previous work. In gas mixtures of relatively low initial reactant concentration, the decomposition of N_2O proceeds via direct O atom abstraction without any significant secondary reactions:[10]

$$N_2O + Ar \rightleftharpoons N_2 + O + Ar \qquad (R1)$$

$$k_1 = 9.28 \times 10^{14} \exp(-29\,920\ K/T)\ cm^3\ mol^{-1}\ s^{-1}$$

It seems reasonable to interpret the observed consumption of O atoms caused by the addition of C_{60} as a direct reaction between these species to form the oxidation product CO:

$$C_{60} + O \rightarrow CO + products \qquad (R2)$$

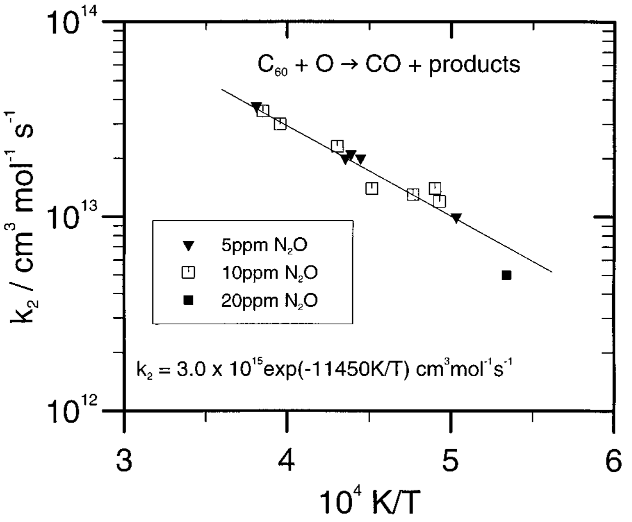

Figure 6. Arrhenius diagram for the rate coefficient k_2 determined in the present study.

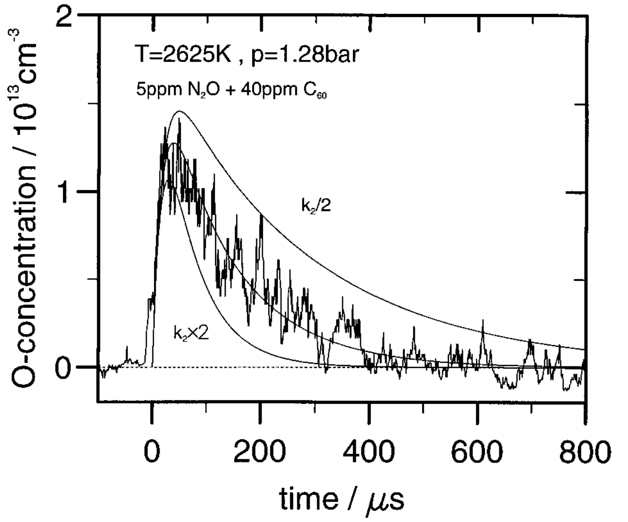

Figure 7. Sensitivity of the evaluated rate coefficient demonstrated by variations of k_2.

Reaction R2 includes a sufficient description of both experimental facts, the decrease in O atom concentration and also the formation of CO. The remaining question, what kind of species are the further products of R2 cannot be answered satisfactorily from the present experiments. Nevertheless, the fact that C_2 radicals were not observed in the reaction system clearly indicates that a breakdown of C_{60} induced by O atoms would not proceed via C_2 abstraction as observed in pyrolysis experiments of C_{60}.[4] Due to the relatively insensitive detection technique for CO, the consumption of O and the formation of CO could not be measured under the same experimental conditions. The initial N_2O concentration was significantly higher in the CO formation experiments compared to the O consumption experiments. Nevertheless we regard the observed CO concentration as a confirmation of CO being the main but probably not the only oxidation product. The addition reaction of O to the π double bonds in C_{60}

$$C_{60} + O \rightarrow C_{60}O$$

to form an epoxide structure has been observed earlier[11,12] and could at least be considered as a second channel for fullerene oxidation.

The strategy for evaluating the measured O atom profiles in terms of a rate coefficient k_2 seems to be clear from the above analysis. For each individual shock tube experiment, the measured absorption was converted to absolute species concentration and compared to computer simulations based on reactions R1 and R2. The rate coefficient k_2 was a variable parameter used to achieve a good fitting of the measured profiles. Examples obtained from different shock tube experiments are illustrated by th smooth lines in Figure 4 for O atoms and in Figure 5 for CO. Nearly complete agreement between calculated and measured concentration profiles for the two examples as well as for all other experiments was obtained. It seems that the rather simple mechanism with one O atom forming and one O atom consuming reaction is sufficient to describe the O atom perturbation experiments. The results indicate that further reactions of expected fullerene fragments and other intermediate species must have only a minor influence on the measured properties. All individual rate coefficients k_2 obtained as best fit parameters are shown in the Arrhenius diagram of Figure 6. A least-squares fit to the data points represented by the solid line is expressed by:

$$k_2 = 3.0 \times 10^{15} \exp(-11\,450 \text{ K}/T) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

The scattering of the data points around the given mean value is comparatively low. The influence of variations of k_2 on the calculated O atom concentration profile is demonstrated for one experiment in Figure 7. The example demonstrates that the rate coefficient k_2 determined in this study is very sensitive to the measured property and that the uncertainty in k_2 can be expected to be ±50%.

Compared to bimolecular reactions of O atoms with small molecules, the preexponential factor of 3.0×10^{15} cm^3 mol^{-1} s^{-1} in the Arrhenius expression for k_2 seems to be unusually high. With respect to the size of C_{60}, this should at least be discussed in terms of the gas kinetic collision frequency together with the steric factor. For this purpose we estimated the frequency $Z_{C_{60}-O}$ for collisions of O atoms with C_{60}, which is given by

$$Z_{C_{60}-O} = N_A d^2_{C_{60}-O} \sqrt{8\pi kT \frac{m_{C_{60}} + m_O}{m_{C_{60}}\, m_O}} \qquad (3)$$

where $d_{C_{60}-O} = (d_{C_{60}} + d_O)/2$ is the mean atomic or molecular diameter and $m_{C_{60}}$ and m_O are the masses of the reacting species. Values of $d_{C_{60}} = 0.75$ nm and $d_O = 0.15$ nm lead to the collision frequency of approximately $Z_{C_{60}-O} = 1 \times 10^{15}$ cm^3 mol^{-1} s^{-1} at 2500 K, which is very close to the evaluated preexponential factor and can be regarded as a hint for the correctness of the magnitude. Furthermore, due to the high symmetry of fullerenes, the probability for reactive collisions between C_{60} and atomic species should not significantly depend on the geometry, and therefore the deviation of the steric factor from 1 is assumed to be small.

Conclusion

Mixtures of N_2O highly diluted in argon were shock heated and used as well-characterized thermal O atom sources. The reaction system was perturbed by the addition of C_{60}, resulting in changes of the O atom concentration and in the formation of CO. O atoms and CO were measured by atomic and molecular resonance absorption spectroscopy. A kinetic model was developed to describe the time behavior of the measured species and a rate coefficient for the reaction $C_{60} + O \rightarrow CO +$ products was determined.

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