An extension of the present investigation of XY(g)-type interchalcogen molecules to TeO(g), TeS(g), SO(g) and SeO(g) is in progress.

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Temperature Dependence of the Rate Constants of the Reaction $O + NO + M \rightarrow NO_2 + M$ (M = He, NO, N_2, CH_4)

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Freie Radikale / Gase / Photochemie / Reaktionskinetik

Values of absolute rate constants of the termolecular reaction $O + NO + M \rightarrow NO_2 + M$ were determined for different third bodies (M = He, NO, N_2, and CH_4) at temperatures ranging from 200 to 370 K. Small amounts of O atoms were generated in the H_2-laser photolysis of NO and were monitored by NO_2^* chemiluminescent emission. The temperature dependence of the rate constants can be expressed by $k_{1,M} = B \times (T/K)^{-n}$ with $n = (1.10 \pm 0.06)$ and $B = 3.3\,(+1.4; -1.0) \cdot 10^{-29}\,cm^6\,s^{-1}$ for M = He; $n = (1.38 \pm 0.06)$ and $B = 3.3\,(+1.2; -0.9) \cdot 10^{-28}\,cm^6\,s^{-1}$ for M = NO; $n = (1.44 \pm 0.10)$ and $B = 3.2\,(+2.5; -1.4) \cdot 10^{-28}\,cm^6\,s^{-1}$ for M = N_2; and $n = (1.55 \pm 0.15)$ and $B = 7.9\,(+10.7; -4.6) \cdot 10^{-28}\,cm^6\,s^{-1}$ for M = CH_4. These results are discussed and compared with previous experimental and theoretical work.

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Introduction

The reaction of oxygen atoms with nitric oxide

$$O + NO + M \rightarrow NO_2 + M \quad (1)$$

belongs to the most studied termolecular combination reactions [1 – 3]. Both the dependence of the rate constant on temperature and on the nature of the third body has been investigated extensively using different experimental methods such as discharge flow coupled with mass spectrometric or chemiluminescent emission detection and pulsed VUV photolysis combined with resonance fluorescence or chemiluminescence for the detection of O atoms.

An earlier review [1] resulted for M = O_2 and Ar in a value of $k_1 = 3.0 \cdot 10^{-33} \exp(+940/T)$ cm^6 s^{-1} ($\pm 20\%$) for temperatures ranging from 200 to 500 K. This result is mainly based on measurements of Klein and Herron [4] and of Clyne and Thrush [5]. A table of values of relative efficiencies of third bodies such as M = He, N_2, CH_4 is also given in this review [1]. In a recent evaluation [3], a value of $k_1 = 1.2 \cdot 10^{-31} (T/300\ \text{K})^{-1.82}$ cm^6 s^{-1} at 200 – 300 K has been recommended for M = N_2. The reliability of this value is given to be $\pm 26\%$. The corresponding negative activation energy, E_a, is given by $E_a/R = -585$ K. This recommendation is based primarily on the data reported by Whytock, Michael, and Payne [6] and Michael, Payne, and Whytock [7]. Their value for k_1 (M = Ar) has been recently confirmed by Anderson and Stephens [8].

Evidently, the more recent work [6 – 8] implies a much weaker temperature dependence of k_1 than previous work [1]. We have reinvestigated the kinetics of Reaction (1) for four different third bodies (M = He, NO, N_2, CH_4) and find an even less pronounced temperature dependence of k_1 than previously observed [6 – 8]. Methane was included as a third body in this study since it represents a polyatomic molecule which barely absorbs H_2 laser light.

Experimental

The experimental setup consists of an H_2-VUV-laser, a reaction chamber, and a detection system for light emission. This setup has been previously used for the investigation of the kinetics of the quenching of $O_2(b^1\Sigma_g^+)$ and has been described in detail [9].

Briefly, an H_2-laser which emits light at around 160 nm was operated at a repetition frequency of 1 to 2 Hz. The energy of a single light pulse is about 5 μJ ($\approx 4 \cdot 10^{12}$ quanta per flash). This light pulse was used to photodissociate NO in the reaction chamber made of stainless steel which is surrounded by a temperature bath. The temperature was varied from 200 to 370 K. Care was taken to determine the temperature in the reaction chamber precisely. Therefore, the temperature of the reactor was measured at three positions using one platinum resistance thermometer and two Cu-constantan thermocouples. The temperatures at the inlet and at the outlet of the bath were observed to differ at most by 2.5 K at the lowest and by no more than 1 K at the highest temperature. In the reactor, the temperature was constantly monitored at a position close to the illuminated reaction region. Here, the temperature was found to be between those measured at the inlet and outlet. The accuracy of the measurements of the temperature is therefore estimated to be within ±1 K.

In a number of preliminary experiments with M = He and Ar the reactants were mixed in the reactor under static conditions. In the experiments presented in this work, the reactants were premixed in a flow system at about atmospheric pressure. Then a part of the mixture was introduced into the reactor under slow flow conditions exchanging the gas in the reactor (4.5 l) every 5 to 10 s. The mixing ratio of the reactants was determined using separate flow meters (Rotameter) for NO and for M. Ratios of [NO]:[M] ranging from 1:5 to 1:10^3 could thus be adjusted. The total pressure was measured (within ±2%) with capacitance manometers (MKS, type 222 AHS-D-B-10 for up to 27 mbar and type 222 AHS-D-B-100 for up to 133 mbar). The NO, He, N_2 and CH_4 samples (Messer-Griesheim) had the following stated minimum purities: 99.85; 99.996; 99.999; and 99.9995%, respectively. NO was carefully purified, since unpurified NO resulted in unusually short decay times of the O atoms. Therefore, NO was first fed through Oxisorb (Messer-Griesheim) and then through a trap cooled by a slush of n-pentane and liquid N_2 (143 K). N_2 and CH_4 were also purified by Oxisorb. Helium was fed through a trap at liquid N_2 temperature. Shortly before the gas mixture entered the reactor, it passed an additional trap at low pressure at the temperature of liquid O_2.

The decay of the O atoms generated in the photolysis of NO was monitored using the chemiluminescent emission in their reaction with NO [10]. The intensity of this chemiluminescence is directly proportional to the concentrations of the O atoms and of NO [5].

Time resolved emissions were monitored by a cooled red sensitive photomultiplier (EMI, type 9658 R) in the wavelength range 320 to 870 nm. Stray light from the laser was weak and did not interfere in this wide wavelength region of detection. In one experiment this wavelength range was limited to 610 nm $< \lambda <$ 870 nm without affecting the decay rate. The signal from the photomultiplier was fed to a multichannel analyzer (Tracor Northern, type NS 575) where the signals from 32 to 2048 decays were accumulated. The dwell times of the channels were varied from 0.02 to 5 ms and decay times between 0.06 and 14 ms were measured.

The time base of the multichannel analyzer used was compared with that of another multichannel analyzer. Furthermore, the time base was checked using a frequency generator. From each of the decay curves stored, the background signal (< 1 to 90 counts/channel) caused by the dark current was subtracted. With the present detection system the sensitivity for O atoms is two orders of magnitude higher than that used when this method was applied the first time [10]. In the present experiments concentrations of O atoms down to about 10^8 atoms cm^{-3} were routinely monitored.

Results

The intensity of the chemiluminescence was observed to be independent of the concentration of the third body M. This result was obtained at 205 ± 5 K for pressures of M ranging from 6.7 to 73.3 mbar while the pressure of NO stayed constant at 0.27 mbar. It was however observed in these experiments that the intensity depends on the nature of the third body. For M = He, N_2, and CH_4, the nature of the third body appears to influence the relative intensities stronger at low temperatures than at room temperature [11].

The dependence of the intensity of the chemiluminescence on the concentration of NO was studied for a constant pressure of M = He, N_2, and CH_4 (13.3 mbar) at a temperature of 250 K. NO pressures up to 1.33 mbar were used in these experiments. The intensity was observed to depend on the square of the pressure of NO for pressures below 0.13 mbar and to depend linearly on the pressure of NO for pressures above 0.13 mbar. At low concentrations of NO, the O atom concentration generated in the photolysis of NO most likely depends linearly on the concentration of NO. Since the intensity of the chemiluminescence, $I_{Cl} \sim [O] \cdot [NO] \sim [NO]^2$ [5], the square dependence appears to be reasonable. At higher pressures of NO, the quenching of the chemiluminescence by NO might become dominant, thus, resulting in a linear dependence of the intensity on the pressure of NO.

The decays of the O atoms were always found to be exponential. Fig. 1 shows an example of the decay on both a linear and a logarithmic scale. For this decay curve, 3.39 mbar NO in the absence of other reactants was photolysed and 128 single decays were accumulated in the multichannel analyzer. The decays of O atoms were usually registered for as long as four to five decay times, τ.

Besides being first order in the concentration of O atoms, the reaction was found to be first order in both reactants, NO and M. This is demonstrated in Fig. 2 by the dependence of the decay rate, τ_{cor}^{-1}, on the square of the concentration of NO (M = NO). In Fig. 2, the decay rates are plotted for different temperatures ranging from 200 to 370 K. In this figure, the intercepts are displaced by different amounts for the

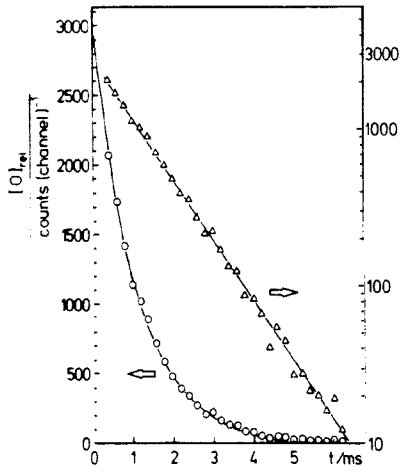

Fig. 1
Decay of O atoms in the presence of 3.39 mbar NO at 295 K. The relative concentration of the O atoms is given both on a linear scale (left) and on a logarithmic scale (right). 128 single decays were averaged for this data

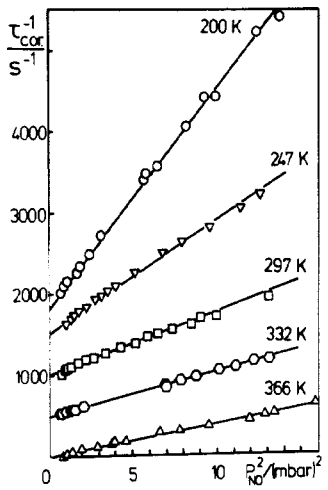

Fig. 2
Corrected decay rates, τ_{cor}^{-1}, (see text) for O atoms as a function of the square of the pressure of NO (M = NO). For clarity, the decay rates are displaced by 1800 s^{-1} for runs at 200 K, by 1500 s^{-1} for 247 K, by 1000 s^{-1} for 297 K and by 500 s^{-1} for 332 K

sake of clarity. The slopes of these plots determine the rate constants, $k_{1,NO}$, of Reaction (1) (M = NO) at the temperatures given.

The observed exponential O atom decays, such as that displayed in Fig. 1, determine the experimental decay rates, τ^{-1}, which are assumed to be given by

$$\tau^{-1} = k_{1,M}[NO]\cdot[M] + k_{1,NO}[NO]^2 + k_i[imp] + \frac{k_d}{[M]}. \quad (I)$$

In this equation, the first term represents the termolecular decay by the third body M. This term is zero for M = NO. Since NO is always present in this system the termolecular combination with NO as a third body is considered by the second term in Eq. (I). This term is dominant for M = NO. Reactions of O atoms with possible impurities are taken into account by the third term. Because of the low leak rate of the vacuum system, these impurities would have to be contained in the samples of the reactants. The concentrations of the impurities, [imp], would then be given by $a\cdot[M]$ or $b\cdot[NO]$, where a and b are the respective mixing ratios of the impurities in the samples of M and NO. The last term in Eq. (I) takes into account diffusion from the illuminated reaction zone. This term is assumed to be inversely proportional to the total pressure which is dominantly given by the concentration of M.

Based on Eq. (I), for M = NO, we obtain

$$\tau^{-1}[NO] = \left(k_{1,NO} + \frac{k_i'}{[NO]}\right)\cdot[NO]^3 + k_d \quad (II)$$

were $k_i' = b\cdot k_i$. By plotting $\tau^{-1}[NO]$ vs. $[NO]^3$, we obtained straight lines with intercepts k_d. Thus, within the precision of these experiments, $k_i' = 0$, i.e. there are no significant amounts of impurities in the NO sample. Finally, we obtain $k_{1,NO}$ by the slopes of plots $\tau^{-1} - \frac{k_d}{[NO]}$ vs. $[NO]^2$ according to

$$\tau_{cor}^{-1} = \tau^{-1} - \frac{k_d}{[NO]} = k_{1,NO}\cdot[NO]^2. \quad (III)$$

Note in Fig. 2 that τ_{cor}^{-1} is plotted and not the experimental decay rate, τ^{-1}.

For M ≠ NO, Eq. (I) is rearranged to give

$$(\tau^{-1} - k_{1,NO}[NO]^2)\cdot[M] = k_{1,M}[NO]\cdot[M]^2 + k_i''\cdot[M]^2 + k_d \quad (IV)$$

where $k_i'' = a\cdot k_i$. By plotting $(\tau^{-1} - k_{1,NO}\cdot[NO]^2)\cdot[M]$ vs. $[M]^2$, we obtained values for k_d by the intercepts; by plotting the same

Table I
Summary of the experimental data

T/K	Rate constant[a] $k_{1,M}^{exp}$	$k_{1,M}$	P_{NO}/mbar	P_M/mbar	Z
M = NO					
200	20.4	21.0±1.0	0.87–3.69		16
201	20.1	21.1±1.6	1.15–4.68		8
202	22.0	22.4±1.6	1.21–4.56		12
204	19.8	20.4±1.8	1.36–4.89		13
205	20.7	20.9±0.5	1.32–4.51		17
241	15.9	17.0±2.3	1.15–3.99		7
247	15.2	16.4±0.8	1.03–3.55		16
259	13.7	15.0±1.0	1.11–4.59		14
295	11.5	12.6±1.4	0.64–3.39		10
297	13.1	13.4±1.3	0.76–4.76		14
297	12.1	13.1±0.9	0.92–3.61		17
298	11.3	12.0±0.5	1.11–4.92		10
298	12.3	13.1±0.8	0.71–3.37		15
298	11.5	11.7±0.2	0.40–6.40		23
298	11.3	12.5±0.6	1.15–5.65		12
332	10.4	11.3±0.4	0.85–3.63		16
363	8.7	10.2±1.3	0.81–3.72		12
366	9.2	10.1±1.2	0.94–3.99		15
369	8.9	10.0±0.7	0.86–4.47		16
M = He					
196	8.7	9.7±1.3	0.27	6.67–73.4	7
199	9.4	9.1±1.4	0.20–1.34	44.0	6
200	8.4	8.7±1.7	0.20	22.0–70.5	3
200	8.9	9.6±0.8	0.27	6.65–73.4	10
200	9.2	8.9±0.6	0.12–1.43	66.7	11
201	12.2	10.2±0.9	0.11–1.24	13.3	6
202	10.0	9.5±0.5	0.05–1.23	40.0	10
204	8.6	8.8±0.9	0.27	6.70–73.3	7
205	11.4	9.7±0.5	0.08–1.21	13.3	13
205	9.3	9.0±0.9	0.09–0.97	66.7	10
221	7.7	8.3±0.8	0.27	6.67–73.3	11
239	7.9	7.4±0.8	0.10–1.21	33.8	12
247	7.8	7.6±0.6	0.12–1.48	66.7	10
247	9.8	8.3±0.6	0.12–1.43	13.3	10
298	5.6	5.9±1.2	0.27	6.64–73.4	4
298	7.2	6.1±0.6	0.08–1.20	13.3	14
298	6.1	5.9±0.5	0.13–1.36	66.7	15
333	5.5	5.3±0.4	0.14–1.47	66.7	10
333	7.0	5.6±0.5	0.13–1.49	13.3	11
364	5.4	5.0±0.3	0.06–1.44	40.0	10
365	7.2	5.9±0.7	0.09–1.26	13.3	12
365	4.9	4.9±0.4	0.10–1.38	66.7	12
365	4.0	4.6±0.8	0.27	6.68–73.4	8
370	3.7	4.4±0.6	0.27	6.65–73.4	10
371	6.3	4.9±0.5	0.09–1.34	13.3	9
371	5.0	4.8±0.3	0.27	66.6	11

Table I (continued)

T/K	Rate constant[a] $k_{1,M}^{exp}$	$k_{1,M}$	P_{NO}/mbar	P_M/mbar	Z
M = N_2					
196	15.4	14.8±2.4	0.48–1.33	39.5	4
199	13.7	14.0±2.8	0.28	15.7–58.7	4
206	18.2	16.2±0.9	0.09–1.43	13.3	11
207	13.7	13.1±1.4	0.18–1.48	66.6	9
207	12.6	13.7±1.5	0.27	6.68–73.5	6
248	13.1	11.5±0.9	0.09–1.36	13.3	9
248	10.8	10.6±1.9	0.17–1.44	66.7	10
297	8.1	7.0±0.7	0.28–1.35	20.0	9
299	7.5	7.9±1.2	0.27	6.68–73.3	7
299	10.5	9.2±1.4	0.11–1.46	13.3	10
299	8.8	8.6±0.8	0.10–1.47	66.7	11
332	7.8	7.5±0.4	0.11–1.42	66.6	10
332	9.0	7.8±0.6	0.11–1.37	13.3	12
370	6.4	6.3±0.5	0.12–1.37	66.7	11
370	8.4	7.3±0.6	0.10–1.32	13.3	10
370	5.7	6.3±1.0	0.27	6.70–73.2	8
M = CH_4					
208	23.2	21.2±2.0	0.09–1.33	13.3	8
209	18.0	17.7±3.4	0.15–1.34	66.7	8
209	19.6	19.9±1.4	0.26	6.69–73.4	7
247	17.2	15.9±2.1	0.12–1.36	13.3	10
247	15.1	14.9±1.9	0.18–1.33	66.6	8
295	12.1	12.4±1.7	0.27	6.68–73.2	7
295	13.6	12.1±1.2	0.12–1.33	13.3	9
295	12.2	11.7±1.5	0.17–1.44	66.7	8
332	11.3	10.0±1.5	0.10–1.45	13.3	7
368	10.4	8.8±0.8	0.11–1.27	13.3	8
368	9.1	8.2±1.6	0.15–1.45	66.7	7
369	9.4	7.2±1.1	0.27	6.67–73.2	7

[a] Rate constants are given in units 10^{-32} cm^6 s^{-1}.
Z = Number of runs performed.

expression vs. [NO], the intercept gives $k_i'' \cdot [M]^2 + k_d$. Within the precision of the experiments we found $k_i'' = 0$, i.e. there are no impurities in the samples of M significantly removing O from the present system. Hence, we gain values for $k_{1,M}$ from plots of $\tau_{cor}^{-1} = \tau^{-1} - k_{1,NO} \cdot [NO]^2 - \frac{k_d}{[M]}$ vs. [NO] and vs. [M]. For M = CH_4, the additional reaction of O atoms with CH_4 [12] has to be taken into account for the determination of τ_{cor}^{-1}. Because of the large activation energy of this reaction its contribution to the O atom decays is significant only at high temperatures ($T > 300$ K).

Table I summarizes the results obtained for M = NO, He, N_2, and CH_4. The values of the rate constants $k_{1,M}$ were obtained by using the corrected O atom decay rates τ_{cor}^{-1}. The error limits which range from 1.7 to 20% represent three times the standard deviation. To demonstrate the correction applied to obtain τ_{cor}^{-1}, also the values of the experimental rate constants $k_{1,M}^{exp}$ are displayed. No error limits were calculated for these values which were directly taken from the observed O atom decay rates τ^{-1}.

Discussion

Light of the H_2 laser emission lines excites NO into states 7.7 to 8.0 eV above the ground state. It is very likely that some of these excited states are predissociated. In fact, the existence of the chemiluminescent emission immediately after the laser shot strongly indicates the formation of O atoms in the H_2 laser photolysis of NO:

$$NO + h\nu(H_2\text{-laser}) \rightarrow N(^4S) + O(^3P), \quad (2)$$

$$N(^4S) + NO \rightarrow N_2 + O(^3P). \quad (3)$$

Reaction (3) occurs very efficiently [3] with a time constant faster than 10 μs at the pressures of NO ($P > 0.13$ mbar) used in these experiments.

Recently Slanger [13] has irradiated NO in the presence and in the absence of He, N_2, and O_2. He observed emissions in the wavelength range 190 to 440 nm. In the presence of He at 13.3 mbar, the near UV bands disappeared and the NO γ-bands became dominant. Decay rate measurements were performed by Slanger. They indicate for the present experimental conditions that the total uv emission [13] has a lifetime of much shorter than 5 μs. Hence, these emissions are not expected to interfere with the much slower decays of the chemiluminescence observed in the present work.

The excited NO_2 formed in the chemiluminescent reaction of O atoms with NO has a relatively long radiative lifetime of several 10^{-5} s [4]. The emissions from excited NO_2 however are efficiently quenched by He and N_2 [14, 15] (and most likely by NO and CH_4 also). Hence, in the present system, the excited molecules decay several orders of magnitude faster than the chemiluminescence observed. Their decay is therefore not expected to influence that of the chemiluminescence.

Table (I) shows that the rate constants measured in the present work depend on temperature for all third bodies M. Such combination rate constants are often presented in the form $k_{1,M} = B \cdot T^{-n}$ [3, 16], therefore we have plotted log $k_{1,M}$ vs. log T in Fig. 3 for M = NO, He, N_2, and CH_4. The data of Whytock et al. [6] and Michael et al. [7] are included in this figure. The slopes of these plots represent n and the intercepts represent log B. Values for B and n are given in Table (II) together with the values obtained by Whytock et al. [6] and Michael et al. [7]. The error limits given in Table (II) represent three times the standard deviation. No error limits are reported by Whytock et al. [6] and Michael et al. [7] for B and n. We have attempted to apply the same statistical procedure for

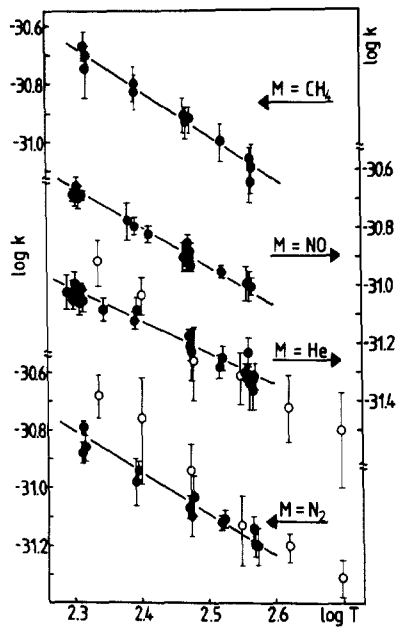

Fig. 3
Temperature dependence of the rate constants for M = CH_4, NO, He, and N_2 displayed on a double logarithmic scale. The rate constants for M = NO and He are given on the right side of this figure and those for M = CH_4 and N_2 on the left side. The data of Ref. [6] and [7] is included by open circles

Table II
Parameters B and n for the rate constants $k_{1,M} = B \cdot T^{-n}$

M	n	B / cm^6 s^{-1}	$k_{1,M}$(300 K) / cm^6 s^{-1}	Ref.
	1.10 ± 0.06	$\left(3.3\ {}^{+1.4}_{-1.0}\right) \cdot 10^{-29}$	$6.2 \cdot 10^{-32}$	this work
He	1.63	$7.22 \cdot 10^{-28}$	$6.6 \cdot 10^{-32}$	Ref. [7]
	1.75 ± 0.35	$\left(15\ {}^{+90}_{-13}\right) \cdot 10^{-28}$	$6.8 \cdot 10^{-32}$	Ref. [7]a)
	1.44 ± 0.10	$\left(3.2\ {}^{+2.5}_{-1.4}\right) \cdot 10^{-28}$	$8.8 \cdot 10^{-32}$	this work
N_2	1.82	$3.80 \cdot 10^{-27}$	$11.8 \cdot 10^{-32}$	Ref. [6]
	1.77 ± 0.25	$\left(23\ {}^{+77}_{-18}\right) \cdot 10^{-28}$	$9.5 \cdot 10^{-32}$	Ref. [6]a)
	1.38 ± 0.06	$\left(3.3\ {}^{+1.2}_{-0.9}\right) \cdot 10^{-28}$	$12.6 \cdot 10^{-32}$	this work
NO	–	–	$15 \cdot 10^{-32}$	Ref. [10]
	1.55 ± 0.15	$\left(7.9\ {}^{+10.7}_{-4.6}\right) \cdot 10^{-28}$	$11.5 \cdot 10^{-32}$	this work
CH_4	–	–	$14 \cdot 10^{-32}$	Ref. [12]

The error limits represent three times the standard deviation.

a) To obtain error limits, the data of Refs. [6] and [7] were treated by the same statistical procedure used for the present data.

calculating error limits to the data presented in these author's publications and have obtained the data displayed in Table II. On the basis of empirical correlations, Benson et al. [16] have suggested the temperature variation of the rate constant for the combination to NO_2 to be nearly $T^{-1.5}$. These authors also estimated B to be $4 \cdot 10^{-28}$ cm^6 s^{-1}.

We have also calculated the parameters A and E_a for the Arrhenius presentation, $k_{1,M} = A \times \exp(-E_a/RT)$, and obtain the following values [the values reported by Michael et al. [7] are given in parentheses] for E_a/kJ mol^{-1} and A/cm^6 s^{-1}: -2.41 ± 0.14 [-4.35 ± 0.75] and $(2.28 \pm 0.16) \cdot 10^{-32}$ [$(1.08 \pm 0.36) \cdot 10^{-32}$] for M = He; -3.16 ± 0.21 [-4.85 ± 0.88] and $(2.44 \pm 0.23) \cdot 10^{-32}$ [$(1.55 \pm 0.6) \cdot 10^{-32}$] for M = N_2; -2.95 ± 0.09 and $(3.75 \pm 0.15) \cdot 10^{-32}$ for M = NO; and -3.44 ± 0.33 and $(2.81 \pm 0.49) \cdot 10^{-32}$ for M = CH_4. The error limits represent three times the standard deviation.

A comparison of the data in Table II reveals that the present values of $k_{1,M}$ for M = He and N_2 are different from those reported previously [6, 7]. While, at 300 K, the present values of $k_{1,M}$ agree with those obtained previously [6, 7], the temperature dependence represented by n shows significant differences for M = He and N_2. The reason for this discrepancy is not evident.

In view of these differences we have carefully checked the measurements of reaction time, concentration of reactants, and temperature and the purity of the reactants. Moreover, the value of the rate constant for the quenching of $O_2(b^1\Sigma_g^+)$ by H_2 obtained with the same experimental setup [9] is in excellent agreement with the literature value over a wide range of temperature. For M = NO and CH_4, no temperature studies of $k_{1,M}$ have been reported. Previously reported values for $k_{1,CH_4} = 1.4 \cdot 10^{-31}$ cm^6 s^{-1} [11] and for $k_{1,NO} = 1.5 \cdot 10^{-31}$ cm^6 s^{-1} [10] at 300 K are slightly larger than the values from the present work. Most likely the previously stated error range of $\pm 10\%$ [10] is too small for single shot experiments.

Finally, the present results are to be compared with calculations of rate constants for recombination reactions by Troe [17]. These calculations were performed for strong collisions of M = Ar and yield values, $k_{1,Ar}^{sc}$ at 200, 300, and 400 K. These values are displayed in Table III together with the values obtained in the present work for M = He, $k_{1,He}$. It was namely observed during the present experiments that $k_{1,Ar}$ is only slightly ($\sim 5\%$) larger than $k_{1,He}$. From a comparison of $k_{1,Ar}^{sc}$ and $k_{1,He}$ one obtains experimental values of the collision efficiency, β_c^{exp}, which is equal to one for strong collisions [17]. These experimental values are also shown in Table III for the data measured in this work and for those determined previously [7, 17]. In agreement with theory [17], the present experimental values of β_c^{exp} do not exceed one and decrease with temperature. Previously, Michael and Lee [18] have modified Troe's theory with the result that their values of β_c^{exp} are well below one but constant with temperature. The present rate constants would yield even lower values for β_c^{exp} which however increase with temperature when using this modification [18].

Table III
Comparison of the present rate constants, $k_{1,He}$, with $k_{1,Ar}^{sc}$ calculated by theory [17]

T/K	$k_{1,He}$ / cm^6 s^{-1}	$k_{1,Ar}^{sc}$ / cm^6 s^{-1}	β_c^{exp} this work	β_c^{exp} Ref. [7]
200	$9.7 \cdot 10^{-32}$	$9.9 \cdot 10^{-32}$	0.98	1.47
300	$6.2 \cdot 10^{-32}$	$7.9 \cdot 10^{-32}$	0.78	0.87
400	$4.5 \cdot 10^{-32}$	$6.8 \cdot 10^{-32}$	0.66	0.60

β_c^{exp} are the experimentally determined collision efficiencies.
The experimental values of $k_{1,He}$ were found to be very similar to those of $k_{1,Ar}$.

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Anomalies in the Magnetic Circular Dichroism of Benzene in Cyclohexane?

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Flüssigkeiten / Magnetischer Circulardichroismus / Magnetismus / Optische Aktivität

A magneto-optical anomaly in the MORD of benzene dissolved in cyclohexane was reported by von Loewis in 1976; a similar "asymmetry" of MCD spectrum upon reversal of the magnetic field had been published by Komiyama and Miwa in 1979. Introducing a 20 mm thick iron plate to shield the CD stress modulator from stray magnetic field apparently eliminates this anomaly. Therefore the observed phenomenon seems to be an apparative artefact.

1. Introduction

In 1976 M. von Loewis reported a hitherto unknown magneto-optical effect [1]: A pronounced inversion asymmetry of the magnetic optical rotatory dispersion (MORD) was observed upon inversion of the magnetic field. The MORD spectrum of benzene dissolved in cyclohexane apparently shows a contribution, which did *not* depend on the direction of the magnetic field; if this effect could be confirmed independently the consequences of this observation would be rather fundamental, – the Verdet law would no longer be valid in the classical form

$$\alpha(\lambda) = V(\lambda) \int_0^l B \, \mathrm{d}l \tag{1}$$

but should be re-formulated as

$$\alpha(\lambda) = a(\lambda) \int_0^l |B \, \mathrm{d}l| \tag{2}$$

a being a constant analogous to the Verdet constant V.

Three years later a similar inversion of symmetry was independently reported by Komiyama and Miwa [2]. Aqueous solutions of D-, L-, and DL-phenylalanine were subjected to parallel and antiparallel magnetic fields and the magnetic circular dichroism (MCD) – after correction for the intrinsic CD – was not found to be symmetric upon inversion of the applied field. In this paper we describe MCD measurements for the case of benzene in solution, which aimed at a possible confirmation of the MORD results of M. von Loewis through application of different instrumentation, careful elimination of possible systematic artefacts, and variations of independent parameters not investigated before.

2. Experimental

Benzene and cyclohexane were obtained in UVASOL grade quality (suitable for spectroscopic work) from Merck, Darmstadt. Samples were prepared by weighing corresponding quantities into the solvent cyclohexane, aliquots of the final solutions (ranging from $7 \cdot 10^{-5}$ to $4.5 \cdot 10^{-3}$ M) were transferred to cylindrical quartz cells of 10 mm pathlength. We used a "Jasco 41 A", equipped with data processing facilities to measure circular dichroism from 190 to 700 nm; signal to noise ratio is such that we detected absolute ellipticities exceeding 0.2 millidegrees in the near UV spectral region from 230 to 300 nm. An electromagnet obtained from Bruker, Karlsruhe, produced homogeneous magnetic fields according to our specifications: maximum magnetic field strength between poles is 1.25 T, variable between 0.003 and ± 1.25 T, homogeneity and constancy better than 10^{-4} relative, the magnetic field lines are parallel to the light beam, the diameter of the opening is 6 mm. The magnet was fitted into the cell compartment and is water-cooled. After some heating-up period a constant temperature of 20 °C was maintained. The field could be inverted by changing the direction of the electric current.

For maximum shielding from magnetic stray fields of the stress modulator and/or the photomultiplier detector system two spherical plates made of pure iron could be fitted to each side side of the electromagnet within the cell compartment.

3. Results and Discussion

The whole instrumental device was tested using various reference samples and comparison with literature data:

a) We found excellent agreement with standard MCD spectra of inorganic complex salts such as $K_3Fe(CN)_6$, which supported our confidence in the reliability of the device used.
b) Good agreement was found between our spectra and those described by Komiyama and Miwa [2] for L-phenylalanine. In the case of the corresponding enantiomer D-phenylalanine the agreement was less satisfactory.

*) The first author, who had initiated this study, had deceased in summer 1982; W. T. and U. J., who are greatly indebted to W. Haberditzl, hope to have finished that part of the work, in which he had not participated anymore, according to his academic standard and intention.
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