

Atmospheric Fate of Unsubstituted Alkoxy and Carbonyl Radicals

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Introduction

Alkoxy ($R_1C(R_2)(R_3)O\bullet$) and Carbonyl ($RC(\bullet)O$) radicals are important intermediates in the degradation chain of hydrocarbons. Both classes of radicals are subject to competing reaction channels leading to different products which exhibit different ozone formation potentials:

Alkoxy radicals -

- (1) Reaction with O_2 (k_{O_2} , \Rightarrow aldehyde/ketone + HO_2);
- (2) thermal decomposition (k_{dis} , \Rightarrow aldehyde/ketone + alkyl/H);
- (3) isomerization (k_{iso} , \Rightarrow hydroxyaldehyde/hydroxyketone).

Carbonyl Radicals -

- (4) Reaction with O_2 (k_{O_2} , $\Rightarrow RO_2$, + $NO_2 \Rightarrow$ peroxyxynitrate (alkyl substituted PAN));
- (5) thermal decomposition (k_{dis} , $\Rightarrow CO$ + alkyl).

In the present work, the ratios k_{dis}/k_{O_2} were determined for a number of unsubstituted C_4 and C_5 alkoxy and carbonyl radicals, linear and branched, with the main aim of measuring the effect of branching at the α -C atom and of the chain length of R on the ratio k_{dis}/k_{O_2} .

Experimental

Experiments are performed in a 12 L temperature controlled photoreactor from stainless steel (Figure 1).

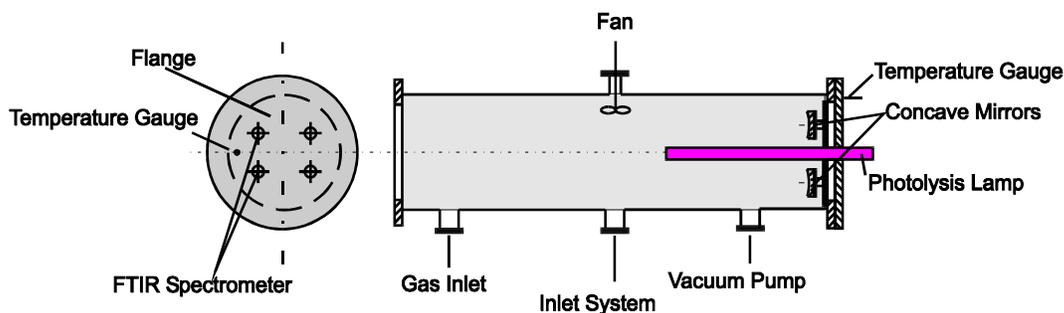
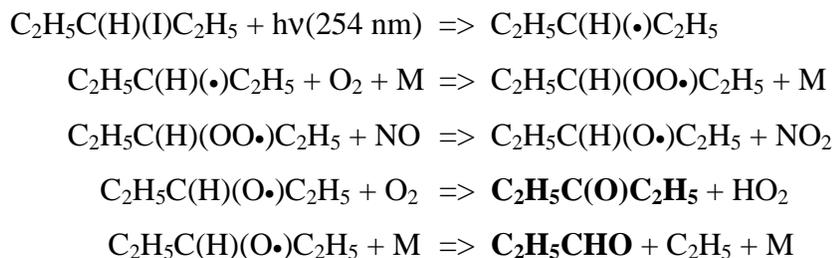


Figure 1. Temperature controlled photoreactor (v = 12 L) from stainless steel

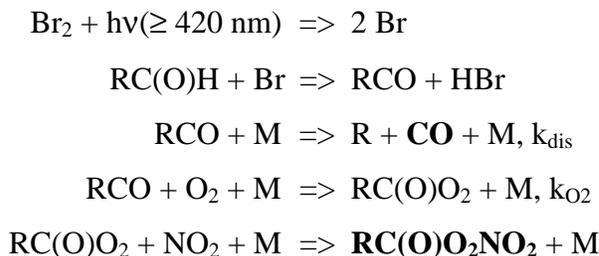
Alkoxy radicals are produced by photolyzing the appropriate iodides in the presence of O₂, NO, and N₂ as a buffer gas. For example, in the photolysis of 3-iodopentane the following mechanism is effective:



The products in bold letters are analyzed by FT-IR absorption (optical pathlength = 2 m), and the rate constant ratios $k_{\text{dis}}/k_{\text{O}_2}$ are determined using the equation

$$\text{(I)} \quad \frac{k_{\text{dis}}}{k_{\text{O}_2}} = \frac{\Delta[\text{C}_2\text{H}_5\text{CHO}] \times [\text{O}_2]}{\Delta[\text{C}_2\text{H}_5\text{C}(\text{O})\text{C}_2\text{H}_5]}$$

Carbonyl radicals are formed by stationary photolysis of Br₂ in the presence of the corresponding aldehyde, O₂, NO₂, and N₂ as a buffer gas. The important reactions taking place are:



The products in bold letters are analyzed by FT-IR absorption, and the rate constant ratios $k_{\text{dis}}/k_{\text{O}_2}$ are determined using the equation

$$\text{(II)} \quad \frac{k_{\text{dis}}}{k_{\text{O}_2}} = \frac{\Delta[\text{CO}] \times [\text{O}_2]}{\Delta[\text{RC}(\text{O})\text{O}_2\text{NO}_2]}$$

Results and Discussion

1. Alkoxy Radicals

In Figures 2 and 3, the experimental data points are shown for 3-pentoxy. For large O₂ partial pressures, the rate constant ratios $k_{O_2}/k_{dis} = \Delta[C_2H_5C(O)C_2H_5]/(\Delta[C_2H_5CHO]x[O_2])$ (inverse of eq. (I)) approach $k_{O_2}/k_{dis} = (1.32 \pm 0.33) \times 10^{-19} \text{ cm}^3$ or $k_{dis}/k_{O_2} = (7.6 \pm 1.9) \times 10^{18} \text{ cm}^{-3}$. This value corresponds to the following product distribution at 298 K in synthetic air:

Reaction with O₂ (40 %): 3-pentanone + HO₂

Thermal decomposition (60 %): propanal + C₂H₅

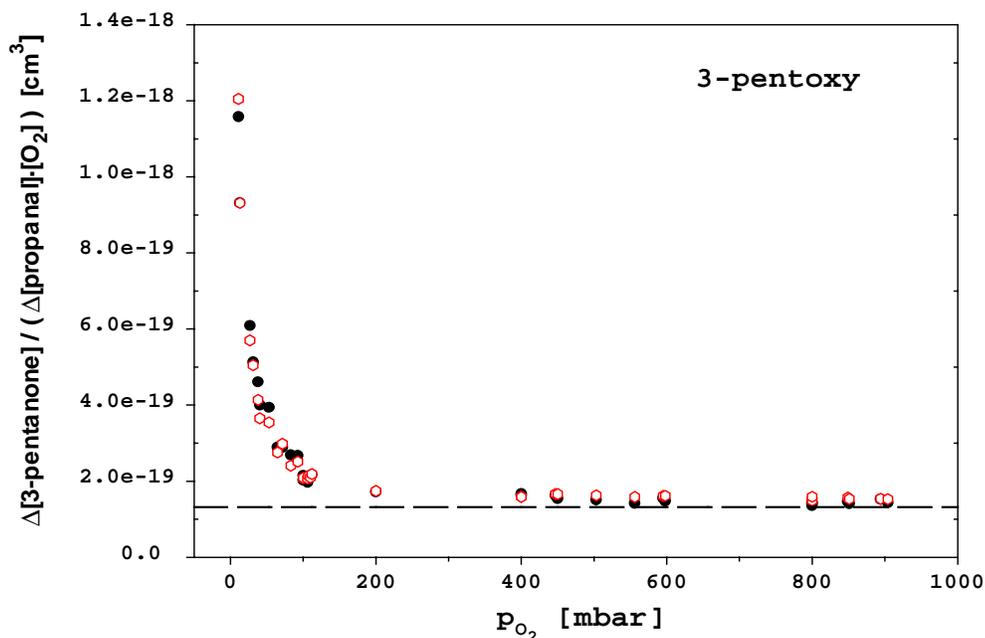


Figure 2. Determination of k_{O_2}/k_{dis} for 3-pentoxy radicals at 298 K, 1 bar ($M = N_2 + O_2$) (open points: experimental; full points and broken line: calculated with a simple mechanism)

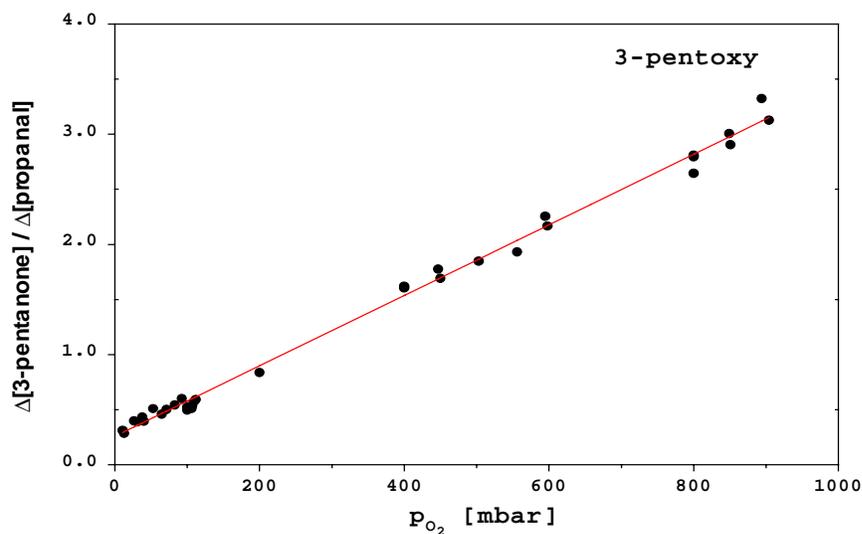
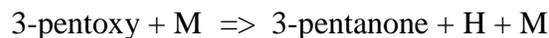
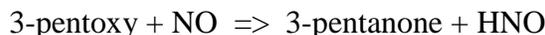


Figure 3. Determination of k_{O_2}/k_{dis} for 3-pentoxy at 298 K, 1 bar ($M = N_2 + O_2$)

The increase of k_{O_2}/k_{dis} at low O_2 partial pressures originates in an additional, O_2 independent source of 3-pentanone the nature of which is still unknown. Possible reactions which can explain this additional formation of 3-pentanone are:



Depending on the nature of the additional 3-pentanone source, the O_2 channel can be larger by 20 % under atmospheric conditions (corresponding to the intercept on the vertical axis in fig. 3). A behaviour similar to that shown in figures 2 and 3 was also observed for the other investigated alkoxy radicals. Further studies on these and other alkoxy radicals are under way.

In table 1, data which have been determined in the present work for 3-pentoxy, 2-butoxy, *i*-butoxy, and 3-methyl-2-butoxy at 298 K are summarized and compared with experimental, semi-empirical and ab-initio values from the literature.

Table 1. Data on $k_{\text{dis}}/k_{\text{O}_2}$ at 298 K for selected alkoxy radicals**2-Butoxy**

$k_{\text{dis}}/k_{\text{O}_2}$ (298 K) [cm^{-3}]	Reference	Remarks
2.1×10^{18} ¹⁾	Carter et al. ²⁾	complex reaction system
$(2.2 \pm 0.4) \times 10^{18}$ ¹⁾	Cox et al. ³⁾	Mixture of isomers
1.9×10^{18}	Blitz et al. ⁴⁾	2-butoxy from 2-butyl nitrite + hv
$(3.6 \pm 2.1) \times 10^{18}$	Hein et al. ⁵⁾	pure 2-butoxy isomer
3.7×10^{18}	Somnitz, Zellner ⁶⁾	<i>ab-initio</i> calculation
2.5×10^{18}	Atkinson ⁷⁾	semi-empirical
$(2.9 \pm 0.6) \times 10^{18}$	this work	pure 2-butoxy isomer

***i*-Butoxy**

$k_{\text{dis}}/k_{\text{O}_2}$ (298 K) [cm^{-3}]	Reference	Remarks
1.3×10^{18}	Atkinson ⁷⁾	semi-empirical, with IUPAC value ⁸⁾ for the heat of formation of <i>i</i> -C ₃ H ₇
6.2×10^{18}	Atkinson ⁷⁾	semi-empirical, with JPL value ⁹⁾ for the heat of formation of <i>i</i> -C ₃ H ₇
$(5.9 \pm 1.7) \times 10^{18}$	this work	pure <i>i</i> -butoxy isomer

3-Methyl-2-butoxy

$k_{\text{dis}}/k_{\text{O}_2}$ (298 K) [cm^{-3}]	Reference	Remarks
8.6×10^{19}	Atkinson ⁷⁾	semi-empirical
$(6.7 \pm 1.8) \times 10^{19}$	this work	pure 3-pentoxy isomer

3-Pentoxy

$k_{\text{dis}}/k_{\text{O}_2}$ (298 K) [cm^{-3}]	Reference	Remarks
$(3.8^{+3.8}_{-1.9}) \times 10^{18}$	Atkinson et al. ¹⁰⁾	Mixture of isomers
8.0×10^{18}	Somnitz, Zellner ⁶⁾	<i>ab-initio</i> calculation
5.3×10^{18}	Atkinson et al. ⁷⁾	semi-empirical
$(7.6 \pm 1.9) \times 10^{18}$	this work	pure 3-pentoxy isomer

References and notes: ¹⁾ original value extrapolated to 298 K; ²⁾ W.P.L. Carter, A.C. Lloyd, J.L. Sprung, J.N. Pitts, Jr., Int. J. Chem. Kinet. 11(1979)45; ³⁾ R.A. Cox, K.F. Patrick, S.A. Chant, Environ. Sci. Technol. 15(1981) 587; ⁴⁾ M.A. Blitz, M.J. Pilling and P.W. Seakins, 15th Int. Symp. on Gas Kinetics, 1998, Bilbao; ⁵⁾ H. Hein, H. Somnitz, A. Hoffmann, R. Zellner, CMD- Konferenz, Karlsruhe, 1998; ⁶⁾ H. Somnitz, R. Zellner, 15th Int. Symp. on Gas Kinetics, 1998, Bilbao; ⁷⁾ R. Atkinson, J. Phys. Chem. Ref. Data 26(1997)215; ⁸⁾ R. Atkinson et al., J. Phys. Chem. Ref. Data 26(1997)521; ⁹⁾ W.B. DeMore et al., JPL Publication 97-4, Pasadena, 1997; ¹⁰⁾ R. Atkinson, E.S.C. Kwok, J. Arey, S.M. Aschmann, Faraday Discuss. 100(1995)23

In table 2, all the alkoxy radicals $\text{HC}(\text{R}_1)(\text{R}_2)\text{O}$ are listed for which isomerization via a six-membered transition state is impossible and thus intramolecular H atom migration is unlikely (see e.g. [1,2]). During thermal decomposition, the larger (or equally large) fragment (here: R_2) generally leaves the alkoxy radical as an alkyl radical whereas the smaller (or equally large) fragment (here: R_1) ends up as the carbonyl compound $\text{R}_1\text{C}(\text{O})\text{H}$. Table 2 supports the assumption underlying the semi-empirical method to estimate k_{dis} of Atkinson [1] that it is the size of the alkyl radical R_2 being released during thermal decomposition which predominantly determines the thermal lifetime of the alkoxy radical rather than the size of the aldehydic product $\text{R}_1\text{C}(\text{O})\text{H}$. Moreover, however, table 2 shows that the atmospheric fates of alkoxy radicals with identical R_2 also may depend on the nature of R_1 even if $\text{R}_1 \neq \text{H}$ (see 2-butoxy vs. 3-pentoxy).

Table 2. Alkoxy radicals $\text{HC}(\text{R}_1)(\text{R}_2)\text{O}$ for which isomerization is unimportant because the formation of a 6-center transition state is impossible

$\text{HC}(\text{R}_1)(\text{R}_2)\text{O}$	R_1	R_2	$k_{\text{dis}}/(k_{\text{O}_2}\text{x}[\text{O}_2])$ for 1 bar of synth. air, 298 K
Ethoxy	H	CH_3	0.000053 ¹⁾⁺²⁾
Propoxy	H	C_2H_5	0.0075 ¹⁾⁺²⁾
<i>i</i> -Butoxy	H	<i>i</i> - C_3H_7	1.19 (this work)
2,2-Dimethylpropoxy	H	<i>t</i> -butyl	
<i>i</i> -Propoxy	CH_3	CH_3	0.024 ³⁾⁺²⁾
2-Butoxy	CH_3	C_2H_5	0.44 (this work)
3-Methyl-2-butoxy	CH_3	<i>i</i> - C_3H_7	13.3 (this work)
3,3-Dimethyl-2-butoxy	CH_3	<i>t</i> -butyl	
3-Pentoxy	C_2H_5	C_2H_5	1.47 (this work)
2-Methyl-3-pentoxy	C_2H_5	<i>i</i> - C_3H_7	
2,2-Dimethyl-3-pentoxy	C_2H_5	<i>t</i> -butyl	
2,4-Dimethyl-3-pentoxy	<i>i</i> - C_3H_7	<i>i</i> - C_3H_7	
2,2,4-Trimethyl-3-pentoxy	<i>i</i> - C_3H_7	<i>t</i> -butyl	
2,2,4,4-Tetramethyl-3-pentoxy	<i>t</i> -butyl	<i>t</i> -butyl	

References:

¹⁾ H. Somnitz, R. Zellner, 15th Int. Symp. on Gas Kinetics, 1998, Bilbao; ²⁾ R. Atkinson, J. Phys. Chem. Ref. Data 26(1997)215; ³⁾ P. Devolder et al., PCCP1(1999)675.

For atmospheric applications, $k_{\text{dis}}/(k_{\text{O}_2}x[\text{O}_2])$ values between ≈ 0.1 and ≈ 10 (last column in table 2) are most interesting since here the competition between channels (1) and (2) is most effective.

2. Carbonyl Radicals

Experimental results on $k_{\text{dis}}/k_{\text{O}_2}$ at 1 bar, $M = \text{O}_2 + \text{N}_2$ are summarized in table 3. Since experimental data on the recombination of acetyl radicals with O_2 [2] suggest that there is no notable barrier for reaction (4), the temperature dependence of $k_{\text{dis}}/k_{\text{O}_2}$ is considered to be strongly dominated by the temperature dependence of k_{dis} . Adopting the k_{O_2} value for CH_3CO radicals at 298 K and high pressures, $k_{\text{O}_2} = 3.2 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ [3], for the larger carbonyl radicals, k_{dis} can be calculated from the measured ratios $k_{\text{dis}}/k_{\text{O}_2}$. The resulting thermal decomposition rate constants k_{dis} are collected in table 4. The data at 298 K for all radicals except pivaloyl (where the 298 K value has been measured) were obtained by extrapolation from the values measured at 317 K, using the experimental activation energy for *i*-butyryl from Tomas et al. [4].

Table 3. Experimental data on $k_{\text{dis}}/k_{\text{O}_2}$

RCO	$k_{\text{dis}}/k_{\text{O}_2}$ [10^{15} cm^{-3}]		
	317 K	307 K	298 K
<i>n</i> -C ₃ H ₇ -CO	< 0.7		
<i>n</i> -C ₄ H ₉ -CO	< 0.7		
CH ₃ C(H)(CH ₃)CH ₂ -CO	1.0 ± 0.5		
CH ₃ C(H)(CH ₃)-CO	12.6 ± 1.8		
C ₂ H ₅ C(H)(CH ₃)-CO	16.4 ^{+4.1} _{-3.1}		
(CH ₃) ₃ C-CO	275 ⁺⁵⁵ ₋₃₈	154 ± 21	92 ⁺²⁴ ₋₁₇

Table 4. Estimated data on k_{dis} , total pressure 1 bar, $M = \text{O}_2 + \text{N}_2$

RCO	$k_{\text{dis}} [\text{s}^{-1}]$, this work ¹⁾	
	317 K	298 K
<i>n</i> -butyryl	< 2,300	< 700 ²⁾
<i>n</i> -pentanoyl	< 2,300	< 700 ²⁾
3-methylbutyryl	3,200	1,000 ²⁾
2-methylpropionyl (= <i>i</i> -butyryl)	40,300	12,100 ²⁾
2-methylbutyryl	52,500	15,800 ²⁾
pivaloyl	880,000	295,000

Notes: ¹⁾ with $k_{\text{O}_2} = 3.2 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ [3];

²⁾ extrapolated from higher temperatures with $E_a = 49.6 \text{ kJ mol}^{-1}$ from Tomas et al. [4].

The present data at 298 K are higher for pivaloyl and *i*-butyryl than recent data of Tomas et al. [4] and much lower than early values by Cadman et al. [5,6]. The major part of these discrepancies may be due to the long range of extrapolation necessary to convert the rate constants of refs. 4-6 from the high temperatures of the experiments to 298 K.

The data in tables 3 and 4 show that

- (i) k_{dis} increases by about a factor of 15 for each H atom connected to the α -C-atom in CH_3CO which is replaced by a methyl group (corresponding to increasing branching of R);
- (ii) even for the thermally most unstable radicals of table 4, i.e. pivaloyl, only 1.8 % decompose rather than add O_2 at 298 K in dry air.

Future Work

Work on alkoxy and carbonyl radicals will be continued, using both the photoreactor shown in fig. 1 and a new reaction chamber from quartz (figure 4) which is under construction and close to being finished. It consists of two concentric quartz tubes with teflon-coated end flanges from stainless steel. The space between the quartz tubes is filled with the cooling agent (silicon oil); photolysis lamps are placed around the outer quartz tube. The quartz tube ($v = 190 \text{ L}$) has several advantages as compared to the cell from stainless steel:

- (i) More homogeneous distribution of temperature and photolysis light intensity;
- (ii) larger sensitivity due to longer light paths (by a factor of 20 both in the IR and UV/VIS);
- (iii) much better volume:surface ratio;
- (iv) less reactive wall materials.

The final experimental set-up is shown in figure 5.

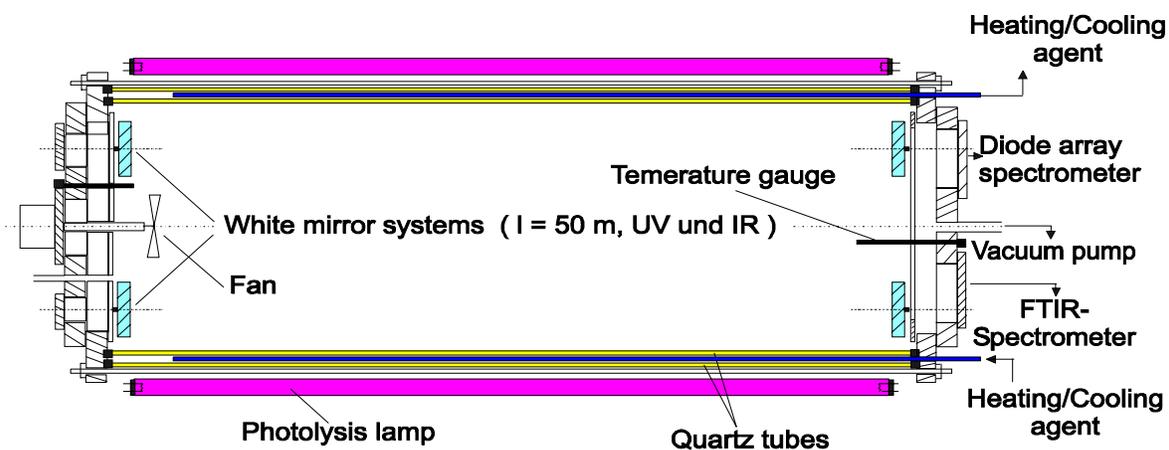


Figure 4. Sketch of the 190 L photoreactor from quartz

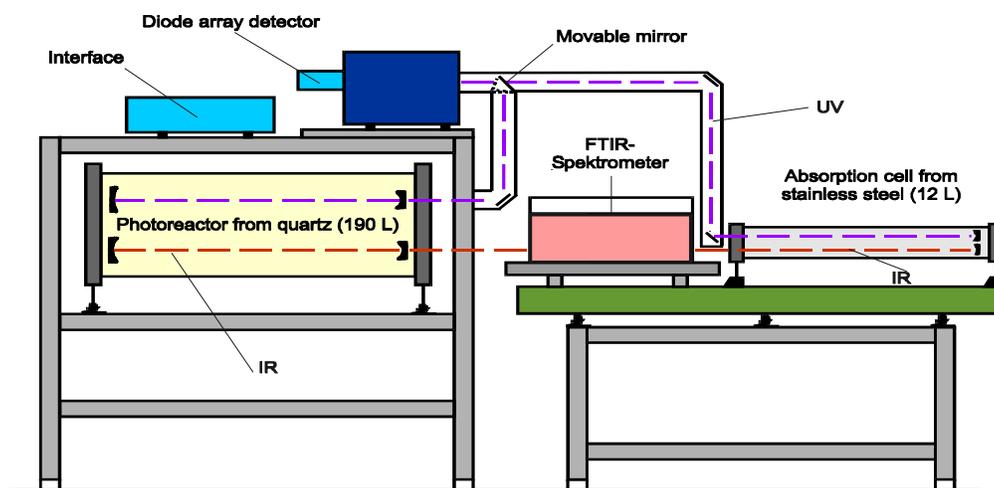


Figure 5. Experimental set-up for the investigation of UV spectra of gaseous compounds and of the kinetics of chemical reactions in the gaseous phase, using a diode array spectrometer and an FT-IR spectrometer

References

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