Scavenging of Radicals from the Gas Phase by Freezing with Dimethyl Disulfide

2. Radicals from Discharges and a Flame of Acetylene

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Elementary Reactions / Flames / Radicals

The method of detecting radicals from low-pressure gas-phase systems by scavenging with dimethyl disulfide (DMD) has been applied to microwave discharges in C_2H_2/He mixtures and to a C_2H_2/O_2 flame. It was accomplished by condensing a supersonic nozzle beam from the reaction system together with a beam of DMD on a liquid-N₂ cooled surface. The scavenging products were measured by GC/MS after warming-up. Radicals measured in the discharge were C_2H , C_4H , C_6H , C_3H_2 , C_2 besides H atoms. Preliminary measurements on the flame showed that C_6H_5 (phenyl), CH_2 , C_3H_2 , besides H and O atoms were prominent radicals at the end of the oxidation zone. The concentration of phenyl is of the same order as that of e.g. naphthalene. The method provides a means to distinguish condensible flame products from those that are formed during the sampling process when no scavenger is added.

1. Introduction

The identification and quantitative analysis of hydrocarbon radicals in gas phase reaction systems such as flames, where they exist together with many other stable hydrocarbon molecules, is still a difficult problem [1-3]. The difficulties become more severe when larger radicals are concerned. In a recent paper a scavenging method using dimethyl disulfide was introduced and tested for light radicals [4]. This report deals with the application of the method in particular to hydrocarbon- and other radicals that are present in low-pressure discharges of C_2H_2/H_2 and in fuel-rich premixed low-pressure flames of C_2H_2/O_2 . These reaction systems have been chosen since they are relatively wellknown what concerns their composition with respect to non-radicalic products [5-9]. There are also papers that report on radical concentrations in these systems [5, 7-9].

The aims of this work are to identify and measure sulphurcontaining scavenging products, to correlate them with hydrocarbon radicals in the reaction systems, and to follow the radical concentrations during gas-phase reaction by measuring the respective concentrations of scavenger products. The method of condensing flame products together with a radical scavenger can be compared to collecting methods without simultaneous scavenging. This should help to distinguish between products that are present in the flame and those that are formed by radical reactions during the sampling process when no radical scavenger is added.

2. Experimental

2.1. Preparation of Samples

Samples were taken from behind a continuous microwave discharge in a flow of C_2H_2/He and from a premixed, flat, standard low-pressure C_2H_2/O_2 flame using a supersonic nozzle and dimethyl disulfide (DMD) as a radical scavenger. The experimental set-up and the general procedure has been described earlier [4,10]. In short: The nozzle beam from the orifice in a quartz probe was directed to a liquid-nitrogen-cooled plate of quartz or steel placed in the vacuum chamber. Condensible components and radicals were captured in a matrix of frozen dimethyl disulfide from a second beam containing DMD only. After collecting an appropriate amount of sample the frozen substances were warmed up to room temperature. The products were analyzed by GC/MS.

The 2.45 GHz microwave discharge was stabilized in an 8 mm i.d. quartz tube at a total pressure, p_0 (He), of 250 Pa. The molar ratio He/C₂H₂ was approximately 1000:1. A total volume flow of 15 cm³ s⁻¹ at STP conditions gave a flow velocity of 130 m s⁻¹. The total number flow through the sampling nozzle of 0.8 mm diameter was $1.1 \cdot 10^{19}$ s⁻¹ under these conditions.

The flame was stabilized at a pressure of 2670 Pa (20 Torr) on a water-cooled flat flame burner of sintered metal as used in earlier investigations [7]. The C/O ratio was 1.0 (slightly sooting) and the cold gas velocity 45 cm s⁻¹. The number flow through a 0.5 mmdiameter sampling nozzle was $6.4 \cdot 10^{18}$ s⁻¹ at a flame temperature of 1800 K.

2.2. Conditions for Analysis

General

Analyses were performed by means of a combination of (capillary) gas chromatography (GC) and mass spectrometry (MS). In addition to the instruments mentioned in [4] a Dani 6500 GC connected to a Finnigan ITD 700 MS was used. After warming up the frozen sample a fraction of it was admitted to the capillary column by (i) split-injection, (ii) split-/splitless-injection, and (iii) a pre-column. The techniques (ii) and (iii) allowed only the analysis of substances eluted after the main component, DMD, which served as a solvent. Technique (i), however, was less sensitive than (ii) and (iii) [4].

Qualitative Analysis

The samples from the discharged C_2H_2/He were normally analyzed applying temperature programmed GC with injection methods (i) or (ii) in combination with the ITD 700 MS detection. The more complex mixtures sampled from the fuel-rich flame were, in addition, subjected to isothermal GC with technique (iii) which gave additional qualitative information on account of the (isothermal) retention indices of the substances. This was complementary to the information obtained by the mass spectra. Basic features are given in [11] and examples are discussed in sections 3.2 and 4.

Quantitative Analysis

The number per time, $\dot{N}_r(j)$, of sulfur-containing molecules j being formed on the plate by reaction is calculated from the concentration of the respective compound in the sample, from the total mass of the sample and from the collecting time. In an analogous way the number rate of molecules j condensing, $\dot{N}_c(j)$, is determined. This

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Table 1 Products and scavenging products from an C_2H_2 /He mw discharge in the order of elution from an OV1701 GC column

			Ň _r resp.			
No.	Compound	Comment	(a)	$\dot{N}_{\rm c}/10^{10} {\rm \ s}^{-1}$ (b)	(c)	
I	CH ₃ SH	SC: H	590			
11	C_4H_2	НС	6600			
111	$C_2H - SCH_3$	SC: C ₂ H	56			
IV	C ₆ H ₂	нс	260			
v	CH ₃ SSCH ₃	scavenger	$\leftarrow 2 \cdot 10^7 \rightarrow$			
VI	C ₈ H ₆	HC (ethynyl benzene)	traces (≈ 1)			
VII	C ₄ H-SCH ₃	SC: C ₄ H	18	9	_	
VIII	CH ₃ SSSCH ₃	I, SC: H	not quant.	(≈10)		
IX	C ₈ H ₂	HC	4.8	3.8	29	
х	$C_2(SCH_3)_2$	SC: C ₂	11	3.7		
XI	CH ₃ SSCH ₂ SCH ₃	PH, SC: H	10	10	15	
XII	$C_3H_2(SCH_3)_2$	SC: C ₃ H ₂	46	37	15	
XIII	$C_3H_2(SCH_3)_2$	isomer of XII	7	5	_	
XIV	C ₆ H-SCH ₃	SC: C ₆ H	3	_	_	
XV	C ₆ H ₃ -SCH ₃	DE	trace	_	-	
SC:	scavenged radical		(a) residence time: 0.16 ms			
HC:	hydrocarbon			mw-power, $P =$	= 20 W	
I:	impurity		(b) $P = 40 \text{ W}$			
PH:	photolysis product		(c) residence time: 0.2 ms			
DE:	decomposition product					

rate has to be calibrated for the number per time of radicals/condensibles entering through the sampling orifice (cf. [4]). External alkane standards rather than the pure sulfur-containing substances were used to calibrate the GC/MS system. This procedure seemed to be adequate since we were mainly interested in the order of magnitude of the $\dot{N}_{r/e}(j)$ and in the observation of trends in the radical concentrations of the gas phase systems. The data of Table 1 are based on uncorrected peak areas from the analysis by the ITD 700 MS.

The data of Table 2 were obtained using a flame ionization detector (FID) and comparing the signals with internal and external standards. For compounds containing sulfur each C atom in the molecule was assumed to make the same contribution to the FID signal as a C atom in an alkane molecule. It was checked by comparing the calculated and measured response factors of the compounds V, XVI, XVIII and XXII (of Tables 1 and 2) that this assumption is justified and works better than in case of the analogous oxygen compounds.

3. Results

3.1. Acetylene-Helium Discharge

The results are comprised in Table 1 which shows the analyzed compounds in the order of their elution from an OV1701 GC column. The first column of the table gives the number of the compound by which it is also referred to in the text. The molecular or structural formula (if known) is entered next. The third column comments on the nature of the product and on its origin. The number rate of formation or condensation, respectively, is given for different experimental conditions.

The compounds collected from the plate were mainly poly-ynes, C_4H_2 to C_8H_2 , and scavenging products containing one or two characteristic SCH₃ groups. The sulfur-containing products without carbon-carbon triple bonds, namely I, VIII and XI, are the scavenging products of H atoms known from previous investigations [4]. A contribution by other radicals to the formation of VIII and XI was possible but could not be clearly separated from that by H atoms. Several compounds containing two SCH₃ groups have been detected, among which were four isomers with the formula $C_5H_8S_2$. One of it was the scavenging product formed in the highest con-

centration. Two of the isomers were present only in trace concentrations and are not included in the table. While the structures of these isomers are not known with certainty (see Discussion) X was identified as 1,2-bis(methylthio)acetylene originating from the C_2 radical.

When the residence time of the gas between the discharge and the sampling nozzle increased the amounts of III, VII, X, XII, XIII and XIV, i.e. the scavenging products of hydrocarbon radicals or C_2 , respectively, decreased (cf. experiments a and c in Table 1). An increase of the nominal mw power caused a decrease in the concentrations of hydrocarbon radicals while that of H atoms was not affected.

XV is probably an artifact. Its concentration increased with the storage time of the sample at room temperature.

The main hydrocarbon products were poly-ynes the concentrations of which decreased strongly with increasing even number of C atoms in the molecule. The only aromatic compound detected in traces was ethynyl benzene but aromatic radicals could not be found. With progressive deposition of a brownish-black polymer on the walls of the discharge tube and on the sampling probe other hydrocarbons, namely C_7H_4 , C_8H_4 and C_9H_4 , appeared in the chromatogram of products. Simultaneously the amount of scavenged radicals decreased. The mass spectra of these hydrocarbons were identical to those reported by Wenz who analyzed premixed, sooting, low-pressure flames by condensing the samples without a scavenger [6].

3.2. Premixed Low-Pressure Acetylene-Oxygen Flame

The results from sampling at a height of 8 mm above the burner, which is near the end of the oxidation zone, are given in Table 2. In addition to the name or the formula of the compound, respectively, the Kovats index and its temperature dependence is given for identification purposes. The entries in the table are not a complete set of analytical data for that flame height. Instead the analysis was concentrated on substances eluted after the DMD within a range of Kovats indices from 830 to 1200 referenced to a SE30 GC column. This was done since it could be expected that the scavenging products of monoradicals containing six C atoms would fall into this range, as judged from the index increments of a thiyl group and the hydrocarbon rest. (Details are given in [10]). Radicals with

Table 2Products and scavenging products of an C_2H_2/O_2 flame in the order of elutionfrom a SE30 GC column (chemically bonded phase) at 100°C; C/O = 1.0,p = 2760 Pa, h = 8 mm

No.	Compound	Kovats- Index, I	$\frac{\mathrm{d}I/\mathrm{d}T}{\mathrm{K}^{-1}}$	$\frac{N_{\rm r}, N_{\rm c}}{10^{10}{\rm s}^{-1}}$
v	CH ₃ SSCH ₃	743.3±0.7	0.23 ± 0.04	2 · 10 ⁷
XVI	CH ₃ SSC ₂ H ₅	835.9 ± 0.1	0.30 ± 0.01	8
XVII	C ₈ H ₁₀ , not id.	see text	-	50
VI	$C_6H_5-C_2H$	872.2±0.4	0.19 ± 0.02	330
XVIII	CH ₃ SCH ₂ SCH ₃	886.2±0.4	0.32 ± 0.02	0.8
XIX	$C_6H_5-C_2H_3$	889.1 ± 0.4	0.24 ± 0.06	20
VIII	CH ₃ SSSCH ₃	966.7±0.4	0.46 ± 0.02	not quant.
XX	CH ₃ S(O)SCH ₃	968.8±1.3	0.15 ± 0.02	980
IX	C_8H_2	987.0±0.5	-0.28 ± 0.03	400
XXI	C ₆ H ₅ OH (phenol)	-	_	150
XXII	CH ₃ S(O) ₂ SCH ₃	1037.8±1.2	0.33 ± 0.06	400
XXIII	C ₉ H ₈ (indene)	1040.9 ± 0.5	0.46 ± 0.02	55
XXIV	C ₆ H ₅ -SCH ₃	1072.9 ± 0.4	0.39 ± 0.02	100
XI	CH ₃ SCH ₂ SSCH ₃	1112.2±0.4	0.51 ± 0.02	110
XXV	C ₁₀ H ₈ (naphth.)	1172.5 ± 0.2	0.63 ± 0.01	320
XXVI	$C_{10}H_7 - CH_3$	1274.8±1.1	0.68 ± 0.08	29
	(2-methyl naphthale	ene)		
XXVII	not identified	1277.8±1.2	0.35 ± 0.08	25
XXVIII	$C_{10}H_7 - CH_3$	1288.5±1.3	0.73 ± 0.08	26
	(1-methyl-naphthale	ene)		

six C atoms are of particular interest for the formation of aromatic compounds in fuel-rich flames. The index range investigated corresponded roughly to the range of elution of the compounds V - XV of Table 1.

The range analyzed covered C_{8^-} to C_{11} -hydrocarbons, mainly aromatic in nature. The scavenging products are due to reactions with H and O atoms, CH₂, C₃H₂, and the phenyl radical (see Discussion). No scavenging products from C_{2n} H radicals could be found. Since the Kovats index of XII is $I = 1172.1 \pm 0.4$ and its temperature coefficient $dI/dT = 0.50 \pm 0.04 \text{ K}^{-1}$ it was not separated from naphthalene on SE30 at any normally used temperature. Using an OV1701 column which separates the two we made sure that its concentration in the sample was small compared to that of naphthalene or of methyl-phenyl-sulfide.





Dependence of the number of molecules condensing (c) or being formed (r) on the condensing rate of the scavenger, N_c(DMD)
(◇) Octatetrayne ×0.2 (c), (●) 1-Methyl naphthalene (c), (+) Naphthalene ×0.2 (c), (●) unknown (see text) (r), (○) Methyl phenyl sulfide (r), (◆) Ethyl methyl disulfide ×2 (r), (□) 2,3,5-Trithiahexane (r), (●) 2,4-Dithiapentane ×10 (r), (×) 2-Methyl naphthalene (c)

In addition to the overview at a height of 8 mm two more experiments were performed:

- (i) using different flow rates of dimethyl disulfide (DMD) while sampling from the same flame height and
- (ii) scavenging at different heights above the burner.

The amounts of hydrocarbons in the sample are in general only weakly influenced by the scavenger flow rate as shown for some examples in Fig. 1. This was also found for the scavenging products 2,3,5-trithiahexane(XI), methyl ethyl disulfide(XVI) and 2,4-



Fig. 2 Condensing rates, \dot{N}_{e} , of non-radicalic flame products when sampling from different heights above the burner



Rate of formation, \dot{N}_r , of sulfur compounds when sampling from different heights above the burner

dithiapentane(XVIII). However, the number formation rate of methyl phenyl sulfide and that of an unidentified sulfur-containing compound depended markedly on the condensation rate of DMD, \dot{N}_c (DMD).

Fig. 2 gives the variation of the concentration of some aromatic hydrocarbons and of the poly-yne C_8H_2 along the flame height as reflected in the number condensation rate, N_c , of the respective molecules on the plate. It shows the typical decrease of intermediate aromatic compounds towards the end of the oxidation zone while the concentration of C_8H_2 (like that of the other polyynes present in the flame) still increases [6, 8, 9].

Fig. 3 shows the analogous profiles of $\dot{N}_r(j)$ for the scavenging products j (see Discussion).

4. Discussion

4.1. Scavenging of Radicals from the Discharge

The main scavenging reaction scheme of monoradicals with dimethyl disulfide is

$$(S) \qquad \mathbf{R}^{\bullet} + \mathbf{C}\mathbf{H}_{3}\mathbf{SSCH}_{3} \rightarrow \mathbf{R} - \mathbf{SCH}_{3} + \mathbf{SCH}_{3}.$$

According to this mechanism CH_3SH is due to H atoms as shown previously by scavenging H from a discharge in $H_2/$ He [4]. A mechanism how compounds VIII and XI are formed from H atoms is also proposed in [4].

The presence of the radicals C_2H , C_4H and C_6H can be concluded in a similar way on account of the structure of the respective products $HC_2 - SCH_3$ (III), $HC_4 - SCH_3$ (VII) and $HC_6 - SCH_3$ (XIV). These radicals are formed by dissociation of acetylene and poly-ynes in the discharge while the latter hydrocarbons in turn are produced by reaction of the $C_{2n}H$ radicals with acetylene [5, 12]:

$$C_{2n}H_2 \xrightarrow{\text{mwdischarge}} C_{2n}H + H$$

$$C_{2n}H + C_2H_2 \xrightarrow{\text{mwdischarge}} C_{2n+2}H_2 + H$$

It is known that molecular hydrogen and unreacted acetylene which both cannot be analyzed by the present trapping method are also products of the discharge [5].

Scavenging products containing two SCH₃ groups per molecule may be formed from diradicals or reactants in a triplet state. In this work the detection of $C_2(SCH_3)_2$ and $C_3H_2(SCH_3)_2$ indicates the presence of C_2 and C_3H_2 , respectively. The direct mass spectrometric analysis of C_2 in C_2H_2 discharges has been reported by Lange et al. [5]. However, products to be expected from scavenging of C atoms, also reported by Lange et al., could not be detected in the DMD matrix. Of the several isomeric species, $C_3H_8S_2$, the most abundant seems to have the structure

$$SCH_{3}$$

$$|$$

$$HC \equiv C - CH$$

$$|$$

$$SCH_{3}$$

as judged from the mass spectra of other thioacetals. No products of CH-scavenging could be detected although $CH(A^2\Delta)$ and $CH(X^2\Pi)$ are reported intermediates in acetylene discharges [13,14]. Studies of the reaction system $C_2H_2 + O(^{3}P)$ have shown that addition of CH to C_2H_2 is

a very fast reaction leading to C_3H_3 and C_3H_2 (+H) [15]. C_3H_2 in turn reacts much slower with acetylene and butadiyne [15, 16] so that a relatively high concentration of C_3H_2 may build up during microwave dissociation of acetylene. This would explain the formation of C_3H_2 while the steadystate concentration of CH was too low to be detected.

 $C_3H_3 - SCH_3$ was not detected. On the OV1701 column it would have been eluted before or together with the scavenger which always was present as the solvent. This might be the reason why it escaped detection. $C_4H_3 - SCH_3$ was expected to be eluted close to $C_4H - SCH_3$ as $C_6H_3 - SCH_3$ was eluted close to $C_6H - SCH_3$. However, the hypothetical scavenging product of C_4H_3 was absent. This is in line with the observation that neither could C_4H_3 be found in the direct reaction $C_2H + C_2H_2$. If it is formed as a chemically activated intermediate it has a very short life time and dissociates into C_4H_2 and H [12]. The gas-phase chemistry in the acetylene discharge is controlled by hydrogen-poor radicals.

The hydrocarbons C_7H_4 , C_8H_4 and C_9H_4 detected during progressive contamination of the flow tube are probably formed under the influence of heterogeneous reactions. This may be of importance when flame gases are condensed without a radical scavenger, since these compounds are obviously identical to those found in condensate from fuel-rich flames [6].

4.2. Flame Analysis

4.2.1. Hydrocarbon Products

The aromatic hydrocarbons and phenol listed in Table 2 and partly shown in Fig. 2 have also been found and analyzed in fuel-rich acetylene flames using other methods (beam sampling with direct MS analysis, mere condensation of gas samples followed by GC-MS analysis) [6-9]. The present experiments confirm that they are products of flame reactions.

Their profiles and relative concentrations are also comparable to those obtained by the other methods. Particularly the appearance of phenol in a narrow flame zone with a distinctly steeper flank in its concentration profile, as compared to the profiles of the aromatic hydrocarbons, was also found by the present sampling method.

Butadiynyl benzene, ($C_{10}H_6$), which was reported by Wenz [6], Heddrich [17] in a slightly richer flame and also by Westmoreland [9] in an even leaner flame was, however, not found in our samples. Its concentration was reported as being about 20% of that of naphthalene. The GC columns used were in all cases identical or of very similar polarity to the SE30 column used in this work. Butadiynyl benzene should have been eluted shortly before naphthalene but there was no unidentified compound in the chromatogram between indene and naphthalene with more than 5% of the naphthalene concentration.

Another unresolved question concerns the hydrocarbon C_8H_{10} (XVII). There were two isomers with this molecular formula which were co-eluted from the GC column SE30 (Table 2) but could be separated on OV1701. This behaviour is like that of m- and p-xylene which also have mass spectra similar to that of XVII. Accordingly, compounds with a

mass of 106 u have been associated with xylenes and also with ethylbenzene in the Refs. [6,9,17]. Our results throw some doubts on this identification. It turned out that the retention index of compound XVII is almost identical to that of ethylbenzene on SE30 but that ethylbenzene is eluted separately from the xylenes on all GC columns in question. This excludes the xylenes but leaves the question of the two isomers since ethylbenzene has no other aromatic isomers. The determination of the identity of the compound(s) XVII needs further work.



Fig. 4

Ratio of naphthalene (condensing) and methyl phenyl sulfide (being formed) when sampling from different heights above the burner

4.4.2. Scavenging Products

All sulfur compounds except DMD resulted from reactions of molecular beam particles with the scavenger.

Radicals reacting according to the scavenging scheme (S) for monoradicals are phenyl radicals giving methyl-phenylsulfide(XXIV) [18]. The profile of XXIV in Fig. 3 shows that phenyl radicals are a comparatively late intermediate in the reaction zone of the flame, being formed simultaneously with the oxidation of one- and two-ring aromatic hydrocarbons but not with their formation. The concentration of C_6H_5 -SCH₃ in the samples is of the same order as that of naphthalene which is one of the prominent polycyclic aromatic hydrocarbons in sooting flames. Fig. 4 shows that within the accuracy of the method there is no influence of the diameter of the sampling nozzle on the concentration ratio of a stable product to a radical condensing or being scavenged on the plate. This demonstrates that the phenyl radicals are not affected by any cooling or stabilization process inside the sampling probe.

No other C_6H_n -(SCH₃) compounds could be detected in this flame by scavenging with DMD. If there were such respective radicals their concentration would be smaller than that of phenyl by at least a factor of 10, assuming similar scavenging efficiency. On the other hand, this result shows that phenyl radicals, when condensed with sampled flame gas without a scavenger, can generate an amount of non-flame products of the order of that of naphthalene during the sampling process. This must be kept in mind when interpreting the results of such analyses.

A scavenging product arising from a substituted phenyl radical could not be identified with certainty. A product such as $C_2H_n - C_6H_4 - SCH_3$ would have a retention index of about 1275 since substitution of H by a C_2H_n group in compound XXIV would raise the index by about 200 units. Up to I = 1320 there is only one unidentified peak, XXVII, in the chromatogram at I = 1277.8. This peak is absent when flame gases are condensed without a scavenger [6,9,17]. The only hydrocarbons eluted close to XXVII are the methylnaphthalenes, but the low temperature dependence of the index of XXVII rules out another two-ring compound [10, 19]. A mono-ring hydrocarbon substituted with a short side chain is not possible because of the high value of I(XXVII). It is therefore probable that XXVII is a scavenging product of a substituted phenyl radical but the question must be left open. At any rate is the concentration of the phenyl radical higher than that of any possible substituted phenyl.

The compounds XVI and XVIII are by-products when scavenging radicals from a discharge in methane where they result from an insertion of CH₂ into the C-S- or S-S bond, respectively [4]. XVI was usually formed in larger concentration than XVIII but the two products did not always show a parallel behaviour. In the flame profiles (Fig. 3) their maximum concentrations are not found at the same height. The reason for this is not clear but may be due to different yields of the scavenging products from singlet and triplet methylene. If the scavenging efficiency for the methylene is of the same order as that of O or CH₃ [4] the amount of scavenging product would indicate a mole fraction, $x(CH_2)$ = O(10⁻⁶), which is lower than the values reported using direct molecular beam MS [8,9].

XI is an unspecific scavenging product to which many monovalent radicals besides H atoms contribute. Moreover, it is a known photolysis product of DMD which might have been formed by UV radiation from the flame.

The scavenging product with the largest concentration is CH₃S(O)SCH₃, (XX), which is formed by the reaction O + DMD [4]. Assuming a scavenging efficiency for O of 0.05, as obtained from the experiments with O_2 /He discharges, the formation rate of XX when sampling from 11 mm above the burner corresponds to a mole fraction $x(O) \approx 6 \cdot 10^{-5}$ in the flame.

The compound XXII, a thiosulfonic acid ester, accompanies the formation of XX when scavenging O atoms from an O_2 /He discharge. It turned out that the presence of O_2 promotes its rate of formation. Therefore, we assume that the decrease of O_2 towards the end of the oxidation zone in the flame is reflected in the decrease of the otherwise unspecific product XXII. Up to now it is not known whether OH radicals also contribute to the formation of XX and/or XXII.

5. Further Aspects and Conclusions

In a previous work it was shown that the scavenging efficiency of DMD for radicals depends on the excess of DMD over the radicals [4]. This is still more critical when scavenging flame radicals. The curves of Fig. 1 show that for certain radicals, e.g. phenyl, an excess of about 10⁶ is necessary to suppress the loss of radicals by other reactions. In these cases it is not so much the excess over the radical concentration that is important, but that over other reactants, for example unsaturated hydrocarbons, with which the radicals can also react when they condense together.

The use of a cooled plane plate having only a low rim is not yet satisfactory with respect to the scavenging and condensation efficiency. If one compares the number of aromatic molecules (e.g. naphthalene, ethynyl benzene, etc.) condensing per time on the plate with their inflow through the nozzle, calculated on account of their mole fraction in the flame as determined by other methods, one obtains a condensing efficiency of only about 2%. The reason for this is probably the relatively high velocity of the molecules in the beam and a comparatively broad beam when sampling from a high temperature source. The collecting device is therefore reconstructed with the aim to reach a scavenging or condensing efficiency, respectively, much nearer to one. If this could be accomplished the method would be nearly independent of calibration methods for radicals.

These experiments which must still be regarded as preliminary have shown that it is possible to scavenge large radicals from flames and other low-pressure reaction systems by reaction with DMD in the condensed phase. On the other hand can the analysis of stable trace components (e.g. polycyclic aromatic hydrocarbons) be put on more solid grounds by comparing the composition of samples drawn with and without a radical scavenger. The method inevitably needs sampling and suffers therefore from the notorious disadvantages connected with it. It is not suitable for every radical, for example not for H atoms and radicals that give unspecific scavenging products. Different radicals, in particular carbenes, react in a different way with the scavenger and it is necessary to study different types of reactions with

DMD in separate experiments. The example of phenyl has shown that it can be usefully applied to medium sized monoradicals which react with DMD in a simple and unequivocal manner. An improvement of the method by changing some constructional details is being undertaken.

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Hydrogen Abstraction Reactions by $NH_2(\tilde{X}^2B_1)$ -Radicals from Hydrocarbons in the Gas Phase

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Elementary Reactions / Radicals

Rate constants for the reactions of the $NH_2(\tilde{X}^2B_1)$ radical with ethane, propane and cyclohexane were measured in an isothermal flow system. Kinetic data were obtained at 4 mbar helium pressure in the high temperature range given below. [NH₂](t)-profiles were mapped at pseudo-first order conditions $[NH_2]_0 \ll [RH]_0$ with the laser induced fluorescence technique. The temperature dependance of the rate constants is represented by the following Arrhenius-expressions: A in [cm³/mol s] and E_A in [kJ/mol]:

> $NH_2 + C_2H_6$ (1) $k_1(T) = 9.7 \cdot 10^{12} \exp(-44.4 \pm 3/RT)$ 598 $\leq T/K \leq 973$ $NH_2 + C_3H_8$ (2) $k_2(T) = 8.5 \cdot 10^{12} \exp(-39.3 \pm 4/RT)$ $550 \le T/K \le 1073$ $NH_2 + C_6H_{12}$ (3) $k_3(T) = 2.7 \cdot 10^{13} \exp(-37.3 \pm 5/RT)$ $544 \le T/K \le 973$.

A correlation of the activation energy with the energy of the broken C-H bond of various hydrocarbons is discussed.

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