$N_2O$ -reduction on free Pt-sites. This reaction is also written in Fig. 10 although this remains somewhat speculative.

At the end of this paper we would like to emphasize that the main reaction path is based on the evidence obtained with our MSCV-experiments. All the intermediates NOH, NO and  $NO_2^-$  were identified in the potential range where they are formed. Therefore the mechanism given in Fig. 10 has a high degree of probability. MSCV clearly demonstrates its ability to deliver more insight into a complicated process such as  $NH_2OH$ -oxidation, than any other method used to study this reaction up to now.

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# Sonolysis of Chloroform

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# Radiation Chemistry / Radicals / Sonolysis

Chloroform is decomposed by irradiation with ultrasonic waves to yield a large number of products. The major products are various unsaturated compounds. Decomposition occurs only in the presence of a monoatomic- or diatomic gas. Free radicals and carbenes are postulated as intermediates of sonolysis which can only be scavenged by volatile additives such as O<sub>2</sub> or c-hexene. In the presence of 10% c-hexene, the rate of sonolysis of chloroform is increased and various additional products are formed. Pure c-hexene is decomposed at a much lower rate than chloroform. The sonolysis of chloroform proceeds at a rate comparable to that of water.

#### Introduction

Most of the observations of sonochemical reactions, in which chemical bonds in a liquid are ruptured, have been made for aqueous solutions [1, 2]. The redox reactions occurring there, such as the oxidation of iodide, were ascribed to the decomposition of the solvent into H + OH, and the subsequent action of these radicals upon the dissolved substance. In fact, the H and OH radicals have recently been traced using ESR spin-trapping techniques [3]. The chemical effects are often accompanied by luminescence of the sonicated solution [4].

The first example of sonolysis in a non-aqueous solvent was the decoloration of the stable radical diphenylpicrylhydracyl and the polymerization of acrylamide in methanol solutions [5]. These experiments proved that free radicals are formed in the sonication of organic liquids. The decomposition of chloroform was also observed, the product detected being hydrogen chloride [6]. Later on, a weak decomposition of acetonitrile (observed products: N<sub>2</sub>, H<sub>2</sub>, and CH<sub>4</sub>) and of carbon tetrachloride (observed product: Cl<sub>2</sub>) was found [7]. In more recent times, the sonolysis of nitrobenzene [8, 9], metal carbonyls [10], and decane [11] have been reported. All these effects are believed to arise due to the high temperatures and pressures which exist in the compression phase of oscillating or collapsing gas bubbles [12 - 14]. In fact, the chemical effects are only observed when a gas is present in the solution. It should finally be mentioned that numerous reports have recently appeared in which the acceleration of heterogeneous organic reactions have been described [15]. These effects, which might be of preparative interest, are caused by the emulsifying action of the ultrasound, by its cleaning action on the surfaces of metal catalysts in the system, and by the local heat development at such surfaces.

The purpose of the present investigation was to make a complete analysis of the products formed in the sonolysis of an organic liquid, since only when this is achieved one can discuss the mechanism of sonolysis and compare it to other decomposition modes of the liquid, such as radiolysis. It seems that, with the exception of the work on decane [11], no efforts have yet been made to obtain a complete mass balance of the products of sonolysis. Combined gas chromatography and mass spectrometry were used to detect the various reaction products of chloroform. Furthermore, mixtures of chloroform with c-hexene here investigated in a more provisional manner.

Table 1		
Product yield and material balance in the sonication of chloroform irradiated under helium	for	1.5 ł

Product		Concentration [10 <sup>-4</sup> M]	Sum	Material balance and fragmentation abundances
inorganic	H <sub>2</sub> HCl	0 46	46	total conversion: $6.7 \cdot 10^{-3}$ M CHCl <sub>3</sub> summary formula of all products: $C_1H_{1.09}Cl_{3.12}$
saturated organic	CH <sub>2</sub> Cl <sub>2</sub> CCl <sub>4</sub>	5 10	15	ratio CCl <sub>3</sub> group/CHCl <sub>2</sub> group in the saturated products: 1.6
	C₂H₂Cl₄ C₂HCl₅ C₃Cl₄	2 7 4	13	
unsaturated organic	trans- $C_2H_2Cl_2$ $C_2HCl_3$	< 1 4	13	ratio CCl <sub>2</sub> group/CHCl group in the unsaturated products: 4.0
	C <sub>2</sub> Cl <sub>4</sub>	8		

### Experimental

The frequency of the ultrasound was 300 kHz, the high frequency power delivered to the quartz oscillator was 3.5 Watt/cm<sup>2</sup>. 50 cm<sup>3</sup> of liquid were irradiated in a thin wall glass vessel. The temperature in the bulk solution was not higher than 22°C. Chloroform was first distilled and then purified over Al<sub>2</sub>O<sub>3</sub> shortly before use, and c-hexene was freshly distilled after treatment with aqueous NaOH. Before sonication, through the liquid the desired gas was bubbled for 20 minutes.  $\gamma$ -irradiation was carried out under an argon atmosphere.

## Results

Chloroform acquires a yellow color upon sonication, which indicates the formation of highly unsaturated products. The absorption spectrum contains a band with  $\lambda_{max} = 232$  nm. The absorbance (1 cm optical path) was 1.5 after one hour of irradiation under an atmosphere of helium. As the absorption coefficient of unsaturated compounds is about 10<sup>4</sup> M<sup>-1</sup> cm<sup>-1</sup> at the maximum, it can be estimated that these products had been formed in rather low concentration, i.e. about  $1 \cdot 10^{-4}$  M. The main products are listed in Table 1. Their summary formula shows that they contain little more H and Cl than CHCl<sub>3</sub> itself, which is also an indication for the formation of strongly unsaturated products in low yield (which cannot be detected by gas chromatography). The total conversion rate was  $4.5 \cdot 10^{-3}$  M  $\cdot$  h<sup>-1</sup> of consumed CHCl<sub>3</sub>; under the same irradiation conditions H<sub>2</sub>O<sub>2</sub> was formed in aerated water at a rate of  $3.3 \cdot 10^{-3}$  M  $\cdot$  h<sup>-1</sup>. This shows that sonolytical reactions occur with comparable yields in chloroform and water.

Chloroform was also  $\gamma$ -irradiated with a dose which produces the same amount of HCl as in the sonolysis experiment of table 1 (dose rate:  $8 \cdot 10^4$  rad/h; time: 15 h). No coloration was observed. While the ratio of saturated to unsaturated C<sub>2</sub>-products was 1 for sonolysis, it amounted to 6 for the  $\gamma$ -radiolysis. CCl<sub>4</sub> and CH<sub>2</sub>Cl<sub>2</sub> were also found as reaction products.

The sonolysis was also carried out with other gases. The largest HCl yield was observed for oxygen. Putting the yield equal to one for  $O_2$ , the following relative yields were observed: helium: 0.7; argon: 0.6; hydrogen: 0.5; nitrous oxide: 0; carbon dioxide: 0. Note that sonolysis takes place only in the presence of a monoatomic or diatomic gas. Helium is more effective than argon, quite in contrast to the observations of chemical effects in aqueous solutions, where helium promotes the chemical reactions very little. In the case of  $O_2$  the yields of all the organic products were smaller than under helium by a factor of about 8 and mainly  $CO_2$  was formed.

Experiments were also carried out with mixtures of chloroform and c-hexene and with pure c-hexene. In the presence of small amounts of c-hexene, the coloration is stronger than in pure chloroform, as can be recognized from Fig. 1. The yield of HCl showed a similar dependence. The gas chromatogram of a mixture with 10 vol.-% c-hexene contained the peaks of all the products from the sonolysis of pure chloroform. In addition, a number of new peaks were present. No effort was made in the present work to analyse all of them, however, it should be noted that one of the products was 7,7-dichloro-bicyclo[4.1.0]heptane. We regard its formation as proof for intermediate dichloro-carbene. Furthermore, c-hexyl chloride, dichloromethyl-cyclohexane, dichloromethyl-cyclohexene, di-c-hexenyl and chloromethyl-c-hexane were identified. In sonicated pure c-hexene, a few new peaks could be detected, although the intensity was smaller than in the mixtures containing mainly chloroform by a factor of at least ten. It is concluded that c-hexene undergoes sonolysis at a substantially lower rate than chloroform.



260 nm absorbance and HCl concentration of various chloroformcyclohexene mixtures after 30' irradiation under helium

#### Discussion

As already mentioned, the overall decomposition of chloroform proceeds with a rate similar to that of water sonolysis. The rate of decomposition of c-hexene was found to be lower by a factor of about ten. Unfortunately, our results cannot be compared to those of the studies on the sonolysis of other liquids [7-11], as different sonication techniques were applied. It would be desirable, if the experimentalists would always compare their results with respect to a simple standard system such as water itself (H<sub>2</sub>O<sub>2</sub> production) or 0.1 M KI (I<sub>2</sub> production). We have repeated the experiments on the sonolysis of carbon tetrachloride [7] and have found a rate of decomposition smaller, by more than a factor of ten, than for chloroform.

A great number of products were observed in Table 1, i.e. the sonolysis of chloroform is not specific. It therefore seems that the preparative use of ultrasound is not promising. However, it should be mentioned in this respect that H. Möckel in this laboratory has recently observed the formation of only one product in the sonolysis of carbon disulfide, which according to its HPLC behaviour must be some kind of dimer. It therefore cannot be excluded that ultrasonic waves may be used as a preparative tool in special cases. In Table 1 all the saturated compounds are presented which can possibly be formed by the various combinations of the radicals  $\text{CCl}_3$ ,  $\text{CHCl}_2$  and the atoms H and Cl. One mode of decomposition of chloroform must consist of breaking of single bonds

$$CHCl_{2} + Cl$$
(1)

$$\dot{c}Cl_3 + \dot{H}$$
 (2)

However, all the products also appear which could be formed from combinations of the carbenes CHCl and  $CCl_2$ . A second mode of decomposition by molecular elimination is therefore postulated

$$CHCl_{2} + HCl$$
(3)

$$CHCl + Cl_2.$$
(4)

From the abundances of CHCl<sub>2</sub>, CCl<sub>3</sub>, CCl<sub>2</sub>, and CHCl groups in the products one derives that reaction 3 is roughly three times more frequent than reaction 4, and that the "molecular" processes 3 and 4 occur about twice as frequently as the "radical" processes 1 plus 2. While the ratio of saturated to unsaturated C<sub>2</sub>-products was 1 for sonolysis, it amounted to 6 for the  $\gamma$ -radiolysis. The molecular eliminations in the decomposition of CHCl<sub>3</sub> are much less important in the radiolysis.

Our experiments cannot distinguish between the formation of carbenes via true first order elimination (as it is expressed by Eqs. (3) and (4)) and second order processes in which two radicals are involved, such as the disproportionation reactions

$$2CHCl_2 \longrightarrow CH_2Cl_2 + CCl_2$$
(5)

and

$$\operatorname{CCl}_3 + \operatorname{CHCl}_2 \longrightarrow \operatorname{CCl}_4 + \operatorname{CHCl}.$$
(6)

The formation of CCl<sub>4</sub> and CH<sub>2</sub>Cl<sub>2</sub> (Table 1) which also occurs in the  $\gamma$ -radiolysis would best be explained by these reactions. In order to understand why carbenes are formed more frequently in the sonolysis of chloroform, one must either assume an additive carbene formation via true molecular elimination or a different type of behavior of the radicals. Such a different kind of behavior could indeed be expected, as reactions 5 and 6 probably do not occur in the liquid, but in the gas bubbles. It is known from free radical chemistry that the ratio of disproportionation to combination of radicals is strongly dependent on the phase. Furthermore, the high temperatures of several thousand K which are believed to exist in the gas bubbles [12-14] may considerably change the ratio of disproportionation to combination. The thermal decomposition of chloroform has been studied by Shilov and Sabirova [16]. They also came to the conclusion that carbenes occur as the most important intermediates of decomposition.

In the earlier studies, it was shown that  $I_2$  is consumed in sonicated chloroform solutions, and this was explained by a reaction of radicals with  $I_2$  [6]. However, the rate of  $I_2$  consumption was far smaller than the overall rate of decomposition of chloroform. This means that the radicals rarely escape the hot spots where they are formed. In order to interfere more efficiently with the reactions occurring in the sonolysis of chloroform, a scavenger of intermediates has to be used, which is present in the gas bubbles themselves. The decreased yield of all products and the formation of  $CO_2$  in the presence of oxygen are understood in this way. It might be recalled in this respect that a peroxide which oxidizes I<sup>-</sup> (added after sonication) has previously been found in the sonolysis of chloroform under oxygen [6].

c-Hexene was also an additive which strongly influenced the sonolysis of chloroform. In fact, it can be expected that c-hexene also penetrates the gas bubbles to act there as a scavenger for certain intermediates. The enhanced decomposition of chloroform in the presence of small amounts of c-hexene (Fig. 1) is explained by the scavenging of Cl-atoms, which in the absence of c-hexene undergo back reactions to re-form CHCl<sub>3</sub> molecules. The formation of c-hexylchloride and di-c-hexenyl is understood in terms of an initial Cl-addition to the double bond or H-abstraction by Cl from the  $\beta$ -position in c-hexene. The formation of 7,7-dichloro-bicyclo[4.1.0]heptane is explained by the addition of CCl<sub>2</sub> to the double bond of c-hexene. However, there are other products such as chloromethyl-c-hexane in which groups are present that did not exist in the reacting materials. The formation of these products must have occurred in a more complex manner, and this shows that unusual reaction conditions do exist in the ultrasonic field in a liquid.

In order to obtain high temperatures in the adiabatic compression phase of gas bubbles, gases with a high value of y (ratio of the specific heats) are especially effective. This explains why sonolysis occurred only in the presence of a monoatomic or diatomic gas. It has often been argued that the vapor of volatile organic compounds decreases y and that this is the reason why chemical effects in organic liquids are hardly to be found. However, one must also consider the stability of the liquid to be decomposed. In water very high temperatures in the gas bubbles are required to rupture the strong H-OH bond, and volatile solutes, therefore, quench the sonolysis of water. Chloroform is less stable and does not require such extreme conditions; its vapor therefore does not strongly suppress the chemical reactions. In c-hexene, which also has a rather high vapor pressure, the stability of the bonds is too high to allow chemical reactions to occur with significant yields.

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## Chemical Kinetics / Cis-Trans Isomerization / Laser Flash Photolysis / Photochemistry / Triplet State

Quantum yields for the direct trans  $\rightarrow$  cis ( $\Phi_{t \rightarrow c}$ ) and cis  $\rightarrow$  trans ( $\Phi_{c \rightarrow 1}$ ) photoisomerization of 4-nitro-, 4,4'-dinitro-, and 4-nitro-4'-methoxystilbene (NS, DNS, and NMS, respectively) were measured in solution at room temperature as a function of the concentration of quenchers (ferrocene, azulene, and oxygen). The results are in full agreement with a previously proposed reaction scheme for NMS, involving a triplet state as an intermediate in the trans  $\rightarrow$  cis photoisomerization and both triplet and excited singlet states in the cis  $\rightarrow$  trans photoisomerization. The branching ratios for decay of twisted configurations of the first excited singlet ( $^{1}p^{*}$ ) and the lowest triplet ( $^{3}p^{*}$ ) into the ground states and the yields for intersystem crossing from the first excited trans and cis singlet configurations to the lowest triplet state ( $\Phi_{isc}^{t}$  and  $\Phi_{isc}^{c}$ , respectively) were determined.  $\Phi_{isc}^{t}$  and  $\Phi_{isc}^{c}$  are large (0.45 - 0.86) for NS and DNS and significantly smaller for NMS in polar solvents. Since the trans triplet state ( $^{3}t^{*}$ ) is in thermal equilibrium with  $^{3}p^{*}$  it is this  $^{3}t^{*} \neq ^{3}p^{*}$  equilibrium which is accessible for the influence of triplet quenchers and solvent properties in the cis  $\Rightarrow$  trans photoisomerization. At room temperature oxygen quenches mainly  $^{3}p^{*}$  while at lower temperatures (between 0 and  $-140^{\circ}$ C) also  $^{3}t^{*}$  is quenched. The yields for the conversion  $^{1}t^{*} \rightarrow ^{1}p^{*}$  and for formation of 4a,4b-dihydrophenanthrene (DHP) are small. From the kinetic analysis no indication was found for involvement of excited states of DHP in the cis  $\rightarrow$  trans photoisomerization of 4-nitrostilbenes.

# 1. Introduction

In previous work a model has been suggested which describes the various pathways involved in the cis ≠ trans photoisomerization of 4-nitro-4'-methoxystilbene (NMS) in solution [2-9]. The main features for trans  $\rightarrow$  cis photoisomerization are the following: Excitation of the trans ground state (1t) leads to the first excited trans singlet state (1t\*) which is deactivated by fluorescence (to <sup>1</sup>t) and by intersystem crossing to the lowest (planar) trans triplet state  $({}^{3}t^{*})$ . At ambient temperature  ${}^{3}t^{*}$  is in thermal equilibrium with the perpendicular triplet configuration (<sup>3</sup>p\*) and possibly with the corresponding cis triplet configuration  $({}^{3}c^{*})$  which is non-planar. The rate of establishment of the  ${}^{3}t^{*} \neq {}^{3}p^{*}$  equilibrium is much faster than that of decay. The lowest triplet decays by intersystem crossing from <sup>3</sup>p\* to the perpendicular ground state (<sup>1</sup>p) which converts into the trans and cis ground states (<sup>1</sup>t and <sup>1</sup>c) with almost equal probabilities ( $\alpha$  and 1- $\alpha$ , respectively).

Answers to two open questions have been attempted in this paper. The first question is whether or not twisting in the first excited singlet state plays a role in trans  $\rightarrow$  cis photoisomerization of nitrostilbenes. The second question concerns a possible involvement of a triplet state of 4a,4b-dihydrophenanthrene (DHP). According to the proposed model for cis  $\rightarrow$  trans photoisomerization, excitation of the cis form leads to the excited cis singlet state (<sup>1</sup>c\*) which converts almost exclusively into the perpendicular excited singlet state (<sup>1</sup>p\*). The <sup>1</sup>p\* state deactivates to <sup>3</sup>p\* and to <sup>1</sup>p' with the yields  $\Phi_{isc}^{p}$  and  $1-\Phi_{isc}^{p}$ , respectively. The <sup>1</sup>p' state, which shows a behaviour similar to <sup>1</sup>p, converts into <sup>1</sup>t and <sup>1</sup>c. In this model formation of DHP plays no role in the cis  $\rightarrow$  trans photoisomerization pathway. However, Saltiel et al. have recently raised the question as to whether or not an alternative route exists for nitrostilbenes, namely population of the cis triplet state  $({}^{3}c^{*})$  from  ${}^{1}c^{*}$  via the triplet state of DHP, similar to the case of bromostilbenes [10, 11].

In order to gain further insight into the mechanism of in a non-polar and a polar solvent. The present work contains and 4-nitro- and 4,4'-dinitrostilbene (NS and DNS, respectively). In the absence of the methoxy group some features are easier to analyze. For example, due to the exceedingly small fluorescence quantum yield ( $\Phi_f$ ) of the trans isomer [12, 13] the fluorescence lifetime  $(\tau_{e})$  is very small and fluorescence quenching by ferrocene or azulene can be neglected for NS and DNS in contrast to NMS. A further simplification results from the photoisomerization. Particularly, the variation of  $\Phi_{t \rightarrow c}$  is considerably smaller for NS and DNS than for NMS. The results presented in this work are in full agreement with the mechanism outlined above.

#### 2. Experimental

For irradiation at 366 nm either a 1000-W high-pressure xenonmercury lamp and a monochromator [9] or a 200-W high-pressure mercury lamp and an interference filter [3 – 5] were used. The quantum yields of cis  $\rightleftharpoons$  trans photoisomerization, the photostationary trans/cis ratio, and the relative fluorescence intensity of the trans isomer were determined as described in previous papers [4, 5, 7]. For determination of  $\phi_{t\to c}$  and  $\phi_{c\to t}$  the ferrioxalate actinometer was applied, cf. [4, 7]. Unless indicated otherwise the samples were deoxygenated by purging with argon. Temperature dependent  $\phi_{t\to c}$  measurements were carried out as described elsewhere [7 – 9]. For measurements with oxygen concentra-

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