# **38. BUNSEN-KOLLOQUIUM**

## Deutsche Bunsen-Gesellschaft für Physikalische Chemie

Thema: Höchstreine Lösungsmittel – Herstellung, Handhabung und Anwendung –

Organisation: Professor H. Baumgärtel, Berlin; Professor K. G. Weil, Darmstadt unter Mitwirkung der MERCK AG

Bis jetzt sind folgende Vorträge vorgesehen:

- 1. Dr. V. Koppe, Leiter des Analytischen Zentrallaboratoriums der Merck AG: "Reinheitskriterien aus der Sicht des Herstellers"
- 2. Professor H. Baumgärtel, Institut für Physikalische Chemie der Freien Universität Berlin: "Elektrochemie in höchstreinem Acetonitril"

Interessenten werden gebeten, Themen für Kurzvorträge bis zum 1. Dezember 1987 an Prof. Dr. K. G. Weil, Institut für Physikalische Chemie-Elektrochemie, Technische Hochschule Darmstadt, Petersenstraße 20, D-6100 Darmstadt, zu melden. Besonderer Wert wird auf die Präsentation neuer chemischer Erkenntnisse gelegt, zu deren Gewinnung der Einsatz höchstreiner Lösungsmittel erforderlich ist.

Das Kolloquium soll im Chemie-Quartier der Technischen Hochschule Darmstadt auf der Lichtwiese stattfinden. Vorgesehener Termin: 29. Januar 1988.

> Der Erste Vorsitzende Prof. Al. Weiss

# On the Removal of Metallic Mirrors by Free Radicals

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Methods and Systems / Radicals

Large Radicals can be formed by passing chlorinated organic compounds at pressures of a few mm., through a furnace containing a pellet of sodium and heated to 350-400 °C. It seems to us that the only radicals that will remove metallic mirrors (of tellurium or antimony, etc., previously deposited beyond the furnace) are those that can decompose into methyl or ethyl radicals plus an unsaturated molecule, without undergoing any transmigration of atoms.

## Introduction

Among the sciences, Chemistry made a late start. While the sister sciences, Mathematics, Physics and Biology had attained a reasonable degree of maturity, most chemists at the end of the seventeen hundreds still believed that chemical reactivity was determined by a mythical substance called phlogiston, which had been proposed by Becher and Stahl (1703). The Atomic Theory, proposed by John Dalton (1807), at last put Chemistry on the right track, resulting in a marvellous development up to the present time. The idea of valency was one of the cornerstones of the new theory: thus carbon had a valency of 4 and hydrogen a valency of l, so that the simplest combination of carbon and hydrogen was the gas methane,  $CH_4$ . Groups such as  $CH_3$ ,  $CH_2$ , and CH were supposed not to exist in the free state, although they could form parts of complete molecules. An example of how strongly this view was held may be illustrated by the following sentence taken from Richter's Organic Chemistry (1915), p. 24, "the assumption of the existence of radicals, capable of existing alone and playing a special role in molecules has long been abandoned." The discovery of methyl by Paneth and Hofeditz (1929) who produced it by heating the vapor of tetramethyl lead at low pressures in a flowing system, and the further work of Rice and his co-workers, summared in the book "Free Radicals" by F. O. Rice (1958), showed that free radicals not only exist, but that, in spite of having an extremely short life, they probably play a major role in the mechanism of many organic transformations. In the course of exploring the stability of larger free radicals formed by the decomposition of a series of monochlorinated hydrocarbons, we studied their effect on cold metallic mirrors, and found some unexpected results.

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#### **Experimental**

The apparatus (Fig. 1) was constructed entirely of Pyrex glass, and a small piece of metallic sodium was placed in the furnace. which could be heated to 300-450°C. When the vapor of a monochlorinated hydrocarbon was passed through the furnace at pressures of 2.7 - 4.0 mbar, the sodium would tear off the chlorine atom to form sodium chloride, and the resulting free radicals (and undecomposed hydrocarbon) emerged from the furnace and were then free to react with a standard metallic mirror of tellurium or antimony previously deposited on the wall of the Pyrex tube several centimeters beyond the furnace. The resulting disappearance of the mirror is quite striking. A metal mirror can easily become covered with a unimolecular layer of oxide which prevents removal of the mirror by a free radical: hence the non-removal of a standard mirror might be due to faulty technique. In our apparatus we are quite sure that the non-removal of a standard mirror was not due to the mirror being covered by a layer of oxide.



Fig. 1 A: Reservoir; B: Sliding furnace; C: Tellurium mirror; D: Vacuum Pump

### Results

In our experiments we used a series of hydrocarbons of increasing complexity, in each case one hydrogen atom had been replaced by a chlorine atom. We found that methyl chloride, ethyl chloride, and 1-chloropropane all readily removed a cold standard metallic mirror of tellurium or antimony. But to our surprise, under our conditions, 2-chloropropane when passed through the furnace, did not remove a standard mirror. We conclude from this experiment that the isopropyl radical, although almost certainly produced and stable under the conditions of our experiment, does not remove a standard metallic mirror. At this point we began to wonder whether only methyl and ethyl radicals could remove metallic mirrors.

We next continued our research by decomposing larger and larger monochlorinated hydrocarbons and determining whether or not the vapor issuing from the furnace removed standard metallic mirrors. We obtained the mixed, and originally perplexing results shown in Table 1.

	Τa	able 1		ee radicals	
Removal	of metallic	mirrors by	free	radicals	

#### Discussion

We used metallic sodium in the furnace on the assumption that the removal of chlorine by the sodium would be by far the predominant reaction, so that we knew the exact structure of the radical first formed. However we found, especially in the case of larger monochlorinated molecules, that there was some decomposition, approximately half, even in the absence of metallic sodium. We hope that this complicating side reaction which is always present does not invalidate our conclusions. There is still some controversy as to whether organic transformations proceed through a molecular decomposition or through a free radical chain. For example, acetone might decompose in a single elementary act into ketene and methane by a direct migration of a hydrogen atom according to the following equation:

$$CH_3COCH_3 \rightarrow CH_2 = CO + CH_4$$

or by a free radical chain:

 $CH_3COCH_3 \rightarrow 2CH_3 - + CO$  $CH_3 - + CH_3COCH_3 \rightarrow CH_4 + CH_2COCH_3 CH_2COCH_3 - \rightarrow CH_2 = CO + CH_3 - .$ 

How do we explain the fact that some large radicals remove standard mirrors and some do not? A reasonable explanation becomes apparent when we consider the probable method of decomposition of large radicals. For example, the normal octyl radical obtained from 1-chlorooctane would be expected to decompose by the successive dropping off of ethylene molecules, finally leaving an ethyl radical, which of course would remove a metallic mirror. It would seem that all radicals that decompose into one or more unsaturated molecules and either methyl or ethyl radicals without involving any transmigration of hydrogen (or any other) atoms will remove a standard metallic mirror (Rice and Teller,

Removal of metallic mirror	s by free radicals	Table 2   Assumed method of decomposition of large free radicals		
Mirror removed	Mirror not removed	$CH_{3}CH_{2}CH_{2} - \rightarrow CH_{2} = CH_{2} + CH_{3} -$		
1-chlorobutane CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Cl	2-chlorobutane CH <sub>3</sub> CHClCH <sub>2</sub> CH <sub>3</sub> isobutyl chloride (CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> Cl tert. butyl chloride (CH <sub>3</sub> ) <sub>3</sub> CCl	n-propyl radical $\rightarrow$ ethylene + methyl radical $CH_3CH_2CH_2CH_2- \rightarrow CH_2=CH_2 + CH_3CH_2 -$ n-butyl radical $\rightarrow$ ethylene + ethyl radical $(CH_3)_2CHCH_2 \rightarrow CH_3CH=CH_2 + CH_3 -$ isobutyl radical $\rightarrow$ propylene + methyl radical $(CH_3)_2CHCH_2 - CH_3 -$		
1-chloropentane1-chloro 3-methyl butaneCH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Cl(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> CH <sub>2</sub> Cl		Tert. butyl radical, stable $CH_2CH_2CH_3CH_3CH_4 \rightarrow 2CH_3 = CH_3 + CH_3 - CH_3 + CH_3 + CH_3 - CH_3 + CH_$		
1-chlorohexane CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> Cl 3(chloromethyl) pentane CH <sub>3</sub> CH <sub>2</sub> CH(CH <sub>2</sub> Cl)CH <sub>2</sub> CH <sub>3</sub>	2-chloro 4-methyl pentane (CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> CHClCH <sub>3</sub>	n-amyl radical $\rightarrow$ ethylene + methyl radical (CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> CH <sub>2</sub> - $\rightarrow$ CH <sub>2</sub> =CH <sub>2</sub> + (CH <sub>3</sub> ) <sub>2</sub> CH- iso-amyl radical $\rightarrow$ ethylene + isopropyl radical (CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> CHCH <sub>3</sub> $\rightarrow$ CH <sub>3</sub> CH = CH <sub>2</sub> + (CH <sub>3</sub> ) <sub>2</sub> CH -		
1-chloroheptane CH <sub>3</sub> CH <sub>2</sub> Cl		1,3-methyl butyl $\rightarrow$ propylene + isopropyl radical CH <sub>3</sub> CH <sub>2</sub> CH(CH <sub>2</sub> )CH <sub>2</sub> CH <sub>3</sub> $\rightarrow$ CH <sub>3</sub> CH <sub>2</sub> CH=CH <sub>2</sub> + CH <sub>3</sub> CH <sub>2</sub> $-$		
1-chlorooctane CH <sub>3</sub> CH <sub>2</sub>		2-ethyl butyl $\rightarrow$ butylene + ethyl radical		

1938). Consider, for example, the decomposition of the radical,

$$CH_3 - CH_2 - CH_2 - CH_2 - CH_3$$
  
 $CH_2$ 

This moiety could be expected to decompose into butene and an ethyl radical which would remove a metallic mirror. On the other hand, occasionally we may find a large radical that will not remove a mirror. As an example, the radical,

$$(CH_3)_2 - CH - CH_2 - CH - CH_3$$

obtained by passing 2-chloro 4-methylpentane through the furnace, would be expected to decompose into propylene

and the isopropyl radical, and would thus not be expected to remove a mirror. Another radical that would not be expected to remove a mirror is tert. butyl,

$$(CH_3)_3 - C -$$

which could not decompose further under our conditions without transmigration of atoms occurring. The assumed method of decomposition of these and other larger free radicals is given in Table 2.

#### Summary

We have concluded, therefore, that so far as we now know, only methyl and ethyl radicals will remove metallic mirrors, under the experimental conditions described.

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# Kinetics and Mechanism of the Oxidation of N,N-Diethyl-p-phenylenediamine by 12-Tungstocobaltate(III)

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## Chemical Kinetics / Complex Compounds / Redox Reactions / Solutions / Spectroscopy, Visible

The almost irreversible oxidation of N,N-diethyl-p-phenylenediamine by 12-tungstocobaltate(III) was studied by means of a multi-mixing, stopped-flow apparatus with optical detection. Both unprotonated and simple protonated p-phenylenediamine are oxidized rapidly to form p-semiquinonedimine. The reaction rate is dependent on the concentration of all ions present in the solution, as well as on the choice and concentration of the buffer. The rate constant varies from  $3 \cdot 10^4 \text{ M}^{-1} \text{ s}^{-1}$  to  $1.4 \cdot 10^6 \text{ M}^{-1} \text{ s}^{-1}$  at 25°C. The activation energy in all cases is very small.

### Introduction

N-substituted p-phenylenediamines  $\overline{R}$  are ideal model substances for the investigation of redox mechanisms both in homogeneous solution [1] and at the surface of electrodes



------ spectra of unprotonated N,N-diethyl-p-phenylenediamine R, its semiquinonediimine S<sup>+</sup> and its quinonediimine T<sup>+</sup> (left hand scale); ----- spectra of 12-tungstocobaltate(III) and its reduced form, 12-tungstocobaltate(II) (right hand scale)

[2] or metal-colloids [3], because the first oxidation product, p-semiquinonediimine S<sup>+</sup>, is intensely coloured [4] and the totally oxidized form, p-quinonediimeT<sup>+(+)</sup>, exhibits strong absorbance near 300 nm [5]. Fig. 1 shows the UVvis spectra of N,N-diethyl-p-phenylenediamine and its oxidized forms [5]. Reactions with oxidants ( $\overline{Ox}$ ) or reducing agents (Red) can therefore easily be followed optically [6-8]. Furthermore, most p-phenylenediamines are electrochemically active [9] and their chemical behaviour can be changed immensely by varying the substituents at the nitrogen atoms or at the ring [10].

In addition to the reversible two-step oxidation according to the Eqs. (1) and (2), a symproportionation reaction takes place between the reduced and the totally oxidized form [4]. The value of the equilibrium constant  $K_3 = k_3/k_{-3}$  strongly depends on the substituents of the p-phenylenediamine [5,11].

$$\overline{\mathbf{R}} + \overline{\mathbf{Ox}} \qquad \xrightarrow{k_1} S^+ + \overline{\mathrm{Red}} \tag{1}$$

$$S^+ + \overline{Ox} \qquad \xrightarrow{k_2} T^+ + \overline{Red} + H^+$$
 (2)