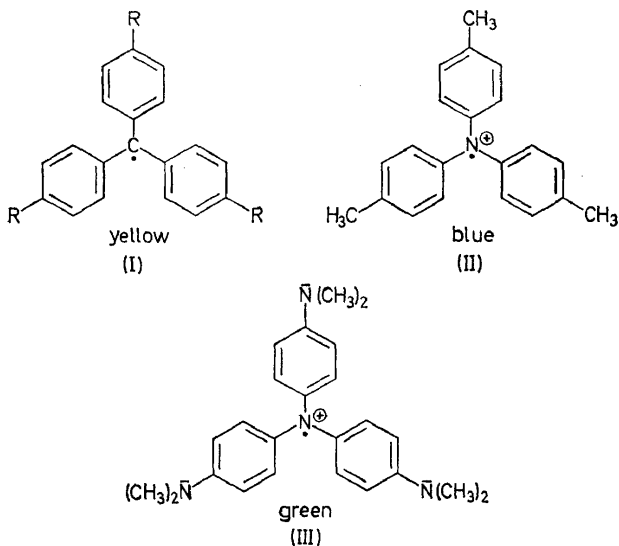# STABLE RADICAL IONS

Siegfried Hünig

(Based on contributions of H. Balli, H. Conrad, H. Friedrich, J. Groß, G. Kiesslich, G. Ruider, G. Sauer and D. Scheutzow)

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INTRODUCTION

Up to 1900 the overwhelming success of Kekule's structural theory convinced organic chemists that carbon compounds with "free valencies" would not exist. The ingenious discovery of the first stable free radical by Moses Gomberg[1] therefore placed a new landmark in preparative chemistry and stimulated our understanding of chemical valency enormously.
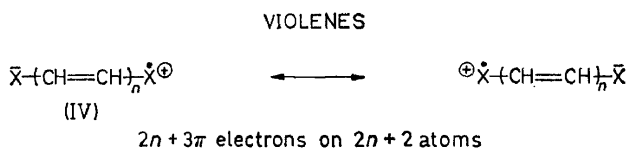
Gomberg's triarylmethyl radicals (I) can formally be envisaged as products of hydrogen (atom) abstraction from triarylmethanes. Following these lines the homomorphic triarylamines are expected to loose *one* electron, thereby forming radicals which are cations at the same time. Actually, as early as 1926 Ernst Weitz[2] was able to isolate the deep blue radical ion (II).
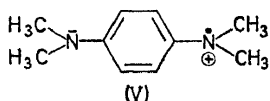
yellow
(I)

blue
(II)

green
(III)

Introduction of three *p*-dimethylamino groups produces the intense green radical ion (III) which due to its stability and light absorption can be mistaken for a triphenylmethane dye[3].
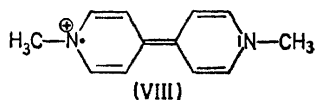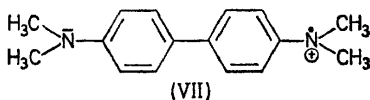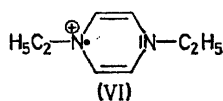
THE VIOLENES

The radical ion (III) owes its unusual stability not only to its relationship to triphenylmethyl but also to a discrete class of compounds which can be derived from the general formula (IV). The special feature of (IV) consists in the distribution of an odd number of π-electrons over an even number of atoms, arranged in a chain. This arrangement involves a strong delocalization of the single electron into the π-cloud, symbolized by the two symmetrical resonance structures, thus causing a high stability and a long wavelength absorption. It is the main object of this lecture to show that

VIOLENES

$\bar{X}+CH=CH)_{\overline{n}}\overset{\bullet}{X}^{\oplus}$ ⟷ $^{\oplus}\overset{\bullet}{X}+CH=CH)_{\overline{n}}\bar{X}$

(IV)

$2n + 3\pi$ electrons on $2n + 2$ atoms

Wurster's radicals

(V)

Weitz' radicals

(VI)

(VII)

(VIII)
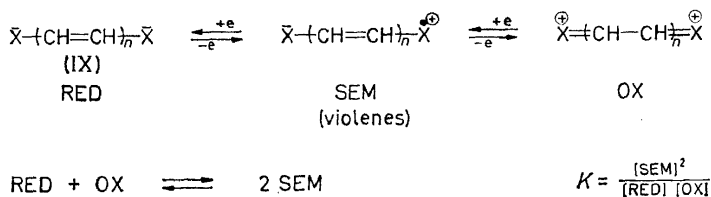
seemingly different radical ions can be related to the general system (IV). Therefore we suggest the name "violenes" for all radical ions of this type. It should be mentioned here that the term "viologenes" is used for the dipyridylium ion derived from type (VIII). When the methine groups are incorporated into aromatic rings leaving the end groups outside, the well known Wurster's radicals (V) and (VII) arise. Contrary to the common opinion E. Weitz established first the radical character of the Wurster's salts by molecular weight determination[2]. The same is true for the dipyridyl derivative (VIII)[2], which may be compared with (VII) and the pyridazine derivative (VI), which corresponds to (V) in a certain way. Here again the methine groups of (IV) are incorporated into a nearly aromatic ring but now including the end groups also. We shall call this seldom acknowledged type "Weitz' radicals".

The violenes are part of a two-step redox system, namely (IX). According to the fundamental work of Michaelis started in 1931 the three oxidation levels will be called reduced form (RED), semiquinone (SEM) and oxidized

$$\bar{X}+CH=CH\}_{\overline{n}}\bar{X} \quad \underset{-e}{\overset{+e}{\rightleftharpoons}} \quad \bar{X}+CH=CH\}_{\overline{n}}\overset{\oplus}{X} \quad \underset{-e}{\overset{+e}{\rightleftharpoons}} \quad \overset{\oplus}{X}+CH-CH\}_{\overline{n}}\overset{\oplus}{X}$$

$$\begin{array}{ccc} \text{(IX)} & & \\ \text{RED} & \text{SEM} & \text{OX} \\ & \text{(violenes)} & \end{array}$$

$$\text{RED + OX} \quad \rightleftharpoons \quad \text{2 SEM} \qquad K = \frac{[\text{SEM}]^2}{[\text{RED}]\,[\text{OX}]}$$

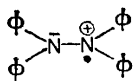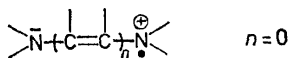form $(\text{OX})^4$. In principle the redox system is a reversible one so that the stability of the radical ion is given by K, the semiquinone formation constant. One should keep in mind that even a high value of this thermodynamic constant does not guarantee that the radical ions can be isolated unless all three members are reasonably stable in the reaction medium.

I may point out here that all conclusions drawn so far are valid too for radical anions corresponding to the general formula (IV). However, I shall concentrate now on violenes of the open chain and the Weitz type, excluding the thoroughly investigated Wurster's type. All radical ions I am dealing with have been identified by some of the following methods:

1. Electron paramagnetic resonance spectra. Since most of the examples show no or insufficient hyperfine structure the spectra indicate paramagnetism only.
2. Shifting of the n.m.r. signal of an indicator substance. This method allows determination of the radical content in dilute solution[5].
3. Ultraviolet and visible spectra which normally differ completely from that of the reduced and the oxidized form[6].
4. Polarographic determination of the redox potentials and assuring one electron transfer by the same approach.

We shall come back to some of these methods later after having dealt with the scope of the aforementioned general principle of violenes.
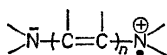
Let us start with X equal to amino nitrogen which may or may not be incorporated into an heterocyclic ring. For $n = 0$ we find the prototype of the whole family, namely a hydrazinylium ion, substituted by four phenyl

$$\overset{\ominus}{>}\overset{|}{N}+\overset{|}{C}=\overset{|}{C}\}_{\overline{n}}\overset{\oplus}{N}< \qquad n = 0$$

$$\begin{array}{c} \phi \diagdown \quad \diagup \phi \\ >\overset{\ominus}{N}-\overset{\oplus}{N}< \\ \phi \diagup \quad \diagdown \phi \end{array}$$

violet

$(\text{X})_{\text{SEM}}$

groups. The proposed general name "violenes" is due to the intense violet colour of that stable radical ion. E. Weitz[2] obtained $(\text{X})_{\text{SEM}}$ easily by oxidizing tetraphenyl hydrazine with the Gomberg reagent: silver perchlorate plus iodine. Going on to $n = 1$, several rather different radical cations can be cited:
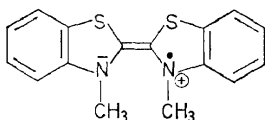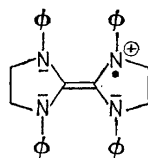
$$\underset{}{>}\overset{-}{N}+\overset{|}{C}=\overset{|}{C}\overset{}{+_n}\overset{\oplus}{\underset{\bullet}{N}}<$$

$n=1$

$$H_5C_2-\overset{-}{N}\overset{}{\underset{\bullet}{}}\overset{\oplus}{N}-C_2H_5$$

(VI)$_{SEM}$

$$\begin{array}{cc} (CH_3)_2\overset{-}{N} & \overset{\oplus}{\underset{\bullet}{N}}(CH_3)_2 \\ (CH_3)_2\overset{-}{N} & \overset{}{N}(CH_3)_2 \end{array}$$

(XI)$_{SEM}$
orange $K=2\times10^2$

(XII)$_{SEM}$
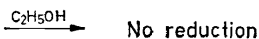orange red $K=1\times10^3$

(XIII)$_{SEM}$
violet

All these radicals form stable solutions over hours to months. Again, (XI)[7]$_{SEM}$, (XII)[8]$_{SEM}$, (XIII)[9]$_{SEM}$ can be produced by abstraction of one electron from the corresponding reduced form using chemical or anodic oxidation. The dication (VI)$_{OX}$ resulting from dialkylation of pyridazine, possesses such a high electron affinity that even alcohol as a solvent acts as a reducing agent producing the aforementioned (VI)[10]$_{SEM}$. The dialkylated pyrimidine (XIV) is not reduced under these conditions[10] probably because the expected radical ion is not related to the violene type.

$$H_5C_2-\overset{\oplus}{N}\overset{}{}\overset{\oplus}{N}-C_2H_5 \xrightarrow{C_2H_5OH} H_5C_2-\overset{-}{N}\overset{}{\underset{\bullet}{}}\overset{\oplus}{N}-C_2H_5$$

(VI)$_{OX}$ (VI)$_{SEM}$

$$\underset{}{\overset{H_5C_2}{\underset{}{}}}\overset{\oplus}{N}\overset{}{}\overset{\oplus}{N}-C_2H_5 \xrightarrow{C_2H_5OH} \text{No reduction}$$
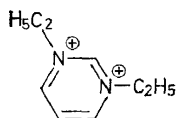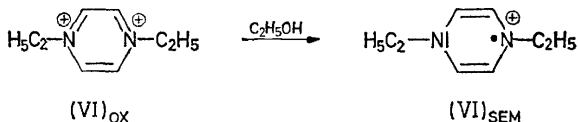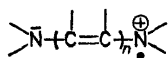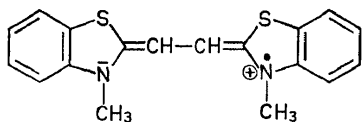
(XIV)

In the case of the next vinylogous hydrazinylium ion with $n = 2$ two examples are known up to now, namely the benzothiazole- and quinoline derivatives (XV)$_{SEM}$ and (XVI)$_{SEM}$.
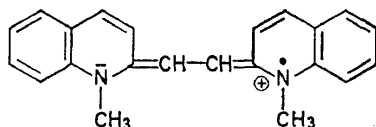
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$$\Large\text{>N}\!\!+\!\!\text{C}\!\!=\!\!\text{C}\!\!+\!\!\overset{\oplus}{\underset{\bullet}{\text{N}}}\!\!<$$

n = 2

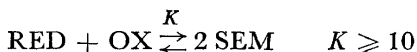red $K = 7 \times 10^4$

(XV)$_{\text{SEM}}$

red violet $K = 1 \times 10^3$

(XVI)$_{\text{SEM}}$

In cases like these where the reduced and the oxidized forms are easily accessible another method of radical formation is extremely useful. Since we are dealing with reversible redox systems according to the equation

$$\text{RED} + \text{OX} \overset{K}{\rightleftarrows} 2\,\text{SEM} \qquad K \geqslant 10$$

the reduced and the oxidized forms tend to reach the thermodynamically favoured level of the radical ion stage. This very often observed behaviour is called comproportionation[11]. Thus, for instance, the colourless solutions of (XV)$_{\text{RED}}$ and (XV)$_{\text{OX}}$ on mixing exhibit immediately the red colour of the radical ion (XV)$_{\text{SEM}}$. This behaviour was not unexpected since Kiprianov and Kornilov during the synthesis of (XV)$_{\text{OX}}$ from (XV)$_{\text{RED}}$ (by treating with bromine) had mentioned an intermediate red colour during oxidation[12].

(XV)$_{\text{RED}}$

$\Big| \text{Br}_2$

OX

2 Br$^{\ominus}$

(XV)$_{\text{OX}}$
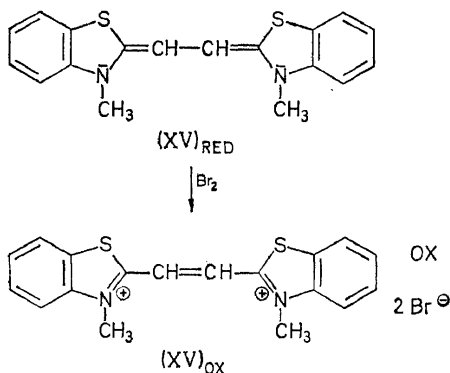
In the series of vinylogous violenes with nitrogen end groups the Weitz radical ion (VIII)$_{\text{SEM}}$ itself can be envisaged as an example for $n = 3$.
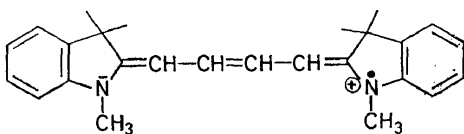
For the blue radical ion (XVII)$_{\text{SEM}}$ there exists no model in the literature. Following the structural principle of violenes it can be easily produced by reduction of the dication (XVII)$_{\text{OX}}$. The latter results from the condensation of 1,3,3-trimethyleneindolenine-2 (XVIII) with glyoxal in the

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$$\text{>N}-(\text{CH}=\text{CH})_n-\overset{\oplus}{\underset{\bullet}{\text{N}}}<$$
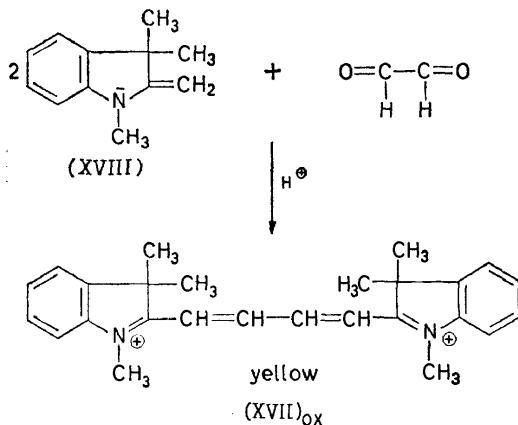$$n=3$$
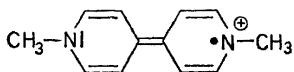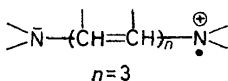
blue $K=1\times10^6$

(VIII)$_{SEM}$

blue $K=1\times10^3$

(XVII)$_{SEM}$

presence of acids. These examples would have proved that the violene principle is valid for vinylogous hydrazinylium ions.

(XVIII)

$$\text{O}=\overset{\underset{|}{H}}{\text{C}}-\overset{\underset{|}{H}}{\text{C}}=\text{O}$$
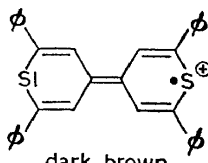
$H^{\oplus}$

yellow

(XVII)$_{OX}$

Instead of amino nitrogen at the end of the polymethine chain other electron donors may be used, especially oxygen and sulphur. The two pyrone derivates (XIX)[13]$_{SEM}$ and (XX)[14]$_{SEM}$ are hidden in the literature. As early as 1907 A. v. Bayer[15] gave careful instructions for the preparation of a yellow "bipyrane", which is the reduced form (XIX)$_{RED}$, according to

$$\bar{X}-(\overset{\underset{|}{C}}{}=\overset{\underset{|}{C}}{})_n-\overset{\oplus}{\underset{\bullet}{X}} \qquad X=O, S$$

blue violet
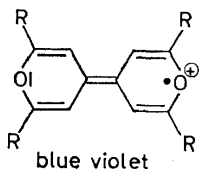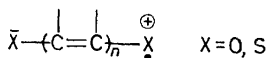
(XIX)$_{SEM}$ R=CH$_3$ $K=6\times10^4$

(XX)$_{SEM}$ R=ϕ $K=1\times10^4$

dark brown $K=4\times10^2$

(XXI)$_{SEM}$

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our nomenclature, and a related blue salt. While he ascribed quinhydrone character to it, E. Weitz in 1954 pointed out[2] that the blue compound might be a radical ion, a supposition which turned out to be correct.
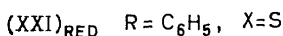
Arndt and Lorenz[16], who were interested in the oxidation of the tetra-phenylbipyrane $(XX)_{RED}$ and -thiobipyrane $(XXI)_{RED}$ narrowly missed the stable radical ions. Using an excess of chlorine or bromine as oxidizing agents they obtained orange precipitates which turned nearly black during isolation. Since the compounds still analyzed nearly for two halogens per one bipyrane molecule the deeply coloured products were thought to be addition
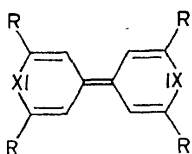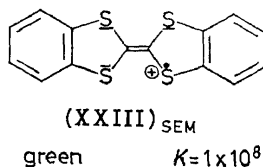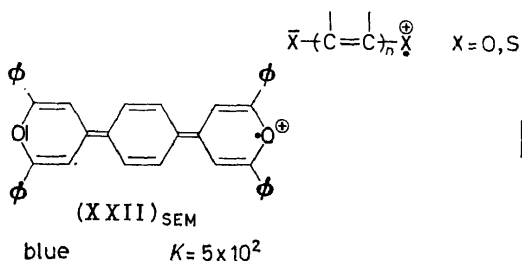

$(XIX)_{RED}$ R = CH$_3$, X=O

$(XX)_{RED}$ R = C$_6$H$_5$, X=O

$(XXI)_{RED}$ R = C$_6$H$_5$, X=S

$(XX)_{OX}$ X=O

$(XXI)_{OX}$ X=S
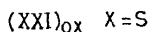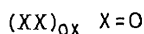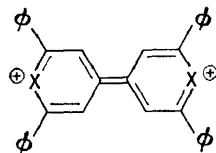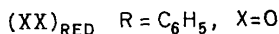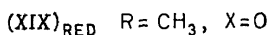
products of the halogen to the central double bond of $(XX)_{RED}$ and $(XXI)_{RED}$ respectively. Actually, due to their high electron affinity $(XX)_{OX}$ and $(XXI)_{OX}$ had oxidized some chloride or bromide at the surface of the crystals and thereby produced some of the intensely coloured radical ions. The example is very instructive since it illustrates that unequivocal results will only be obtained if the charged species are combined with anions of low polarizability and oxidizability, e.g. tetrafluoroborate or perchlorate. Another example of violenes having X = O is the phenylogue $(XXII)_{SEM}$ produced by reduction of the corresponding dipyrylium dication $(XX)^{17}_{OX}$.

Parallel to the aforementioned radical ions derived from tetraamino-ethylene the green tetrathio compound $(XXIII)_{SEM}$ shows a remarkably high semiquinone formation constant[18]. Here again the nature of the anion is of decisive importance, since the redox potential for $(XXIII)_{SEM} \overset{E_1}{\rightleftharpoons} (XXIII)_{RED}$ is quite high, namely +896 mV (acetonitrile, standard calomel electrode).

$$\bar{X}\!-\!(C\!=\!C)_{\overline{n}}\!\overset{\oplus}{X}\!\cdot \quad X=O,S$$

$(XXII)_{SEM}$

blue $K= 5 \times 10^2$

$(XXIII)_{SEM}$

green $K = 1 \times 10^8$

What is true with regard to anions also holds true for solvents, which should exhibit neither nucleophilic nor reducing power, especially towards the oxidized forms of the reviewed redox systems. Without

considering this possibility an experimental observation easily can be mis-interpreted as the result of a simple acid-base reaction. This happened to D. H. Reid and M. Fraser[19]. They presented an elegant synthesis for the red diperchlorate (XXIV)$_{OX}$ from 1,2-dimethylindolizine and glyoxal with excess perchloric acid in the aprotic (!) acetonitrile. On dissolving (XXIV)$_{OX}$ in alcohol the solution turned blue and a monoperchlorate separated, which was believed to be a result of a deprotonation. Though not very pleased by the idea, the authors finally ascribed the allenic struc-ture (XXV) to the blue monoperchlorate. Since they were able to obtain the orange base (XXIV)$_{RED}$ by reduction of the blue salt the latter was

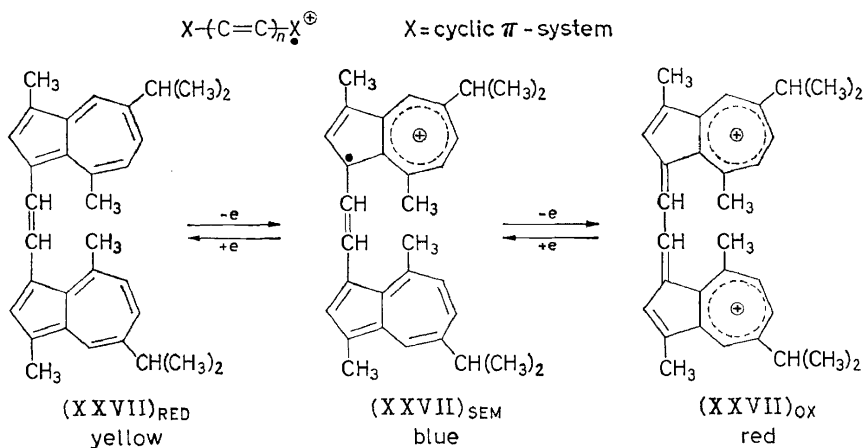orange   blue   red

(XXIV)$_{RED}$ (XXV)   (XXIV)$_{OX}$
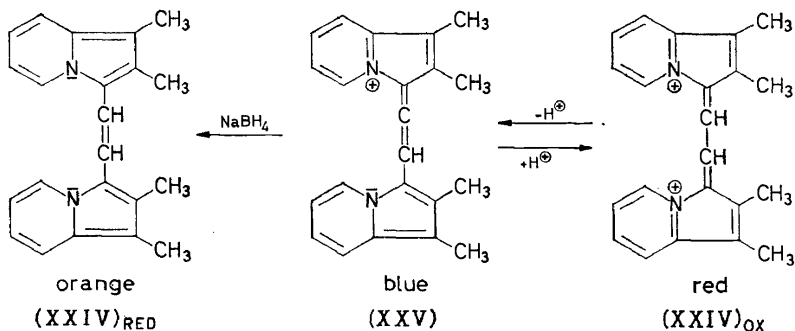
suspected of being a violene. Indeed, as disclosed by the n.m.r. method the blue perchlorate proved to be quantitatively the violene (XXIV)[20]$_{SEM}$. The same is true of the isomeric salt (XXVI)$_{SEM}$. Since the British chemists

(XXIV)$_{SEM}$ (XXVI)$_{SEM}$

blue $K = 8 \times 10^2$ blue $K = 5 \times 10^2$
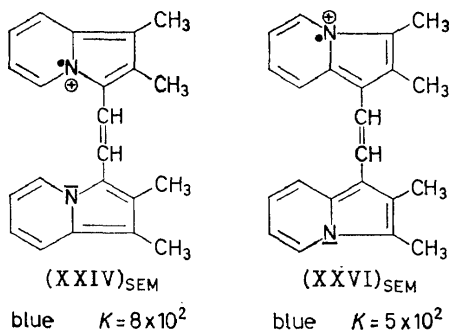
used the indolizine system just for its known similarity to the azulene system, they synthesized the red dication (XXVII)$_{OX}$ analogous to (XXIV)[21]$_{OX}$. This again is transformed into a blue monoperchlorate by methanol which instead of being allenic exhibits paramagnetism [(XXVII)$_{SEM}$]. Judging from its radical content of at least 95 per cent it seems to be the first stable hydrocarbon radical cation[22] besides the inde-pendently obtained radical cation derived from tetraphenyl-p-xylylene[23]. As may be expected equivalent amounts of (XXVII)$_{OX}$ and the newly syn-thesized reduced form (XXVII)$_{RED}$ produce immediately nearly two equivalents of (XXVII)$_{SEM}$ by comproportionation. This demonstrates that in the general formula of the violenes X can even be a suitable cyclic π-system without any hetero atom.
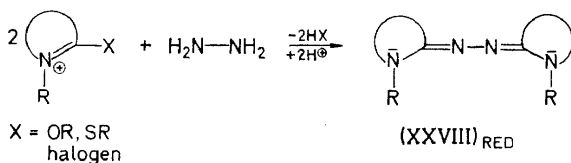
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$$X\text{-}(C=C)_n\text{-}X^{\oplus}_{\bullet} \qquad X = \text{cyclic } \pi\text{ - system}$$

(XXVII)$_{RED}$ (XXVII)$_{SEM}$ (XXVII)$_{OX}$
yellow   blue   red

THE AZAVIOLENES

A further simple variation of the general violene structure arises by from substitution of methine groups by nitrogen thus forming azaviolenes[24]. A very simple route to diazaviolenes consists in the reaction of hydrazine with a heterocyclic quaternary salt possessing a good leaving group in

$$2 \underset{R}{\overset{}{\bigcirc}}\text{-}X \; + \; H_2N\text{---}NH_2 \; \xrightarrow[+2H^{\oplus}]{-2HX} \; \underset{R}{\overset{}{\bigcirc}}\text{=N---N=}\underset{R}{\overset{}{\bigcirc}}$$

X = OR, SR   (XXVIII)$_{RED}$
halogen

position two or four. The resulting azines (XXVIII)$_{RED}$ are the reduced form of a reversible redox system containing a red azodication (XXVIII)$_{OX}$ at the other end and an intensely coloured radical cation (XXVIII)$_{SEM}$

(XXVIII)$_{RED}$ (XXVIII)$_{SEM}$ (XXVIII)$_{OX}$

$$E_1 \sim \frac{SEM}{RED} \qquad\qquad E_2 \sim \frac{OX}{SEM}$$
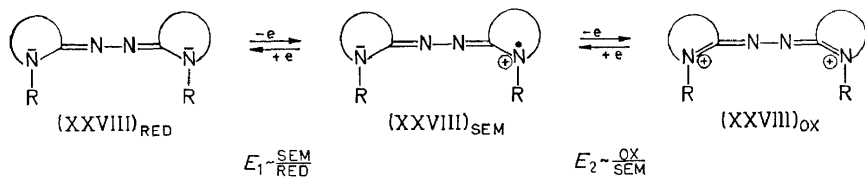
in between. In nearly every case, so far investigated, all three oxidation levels could be isolated because of the remarkably high semiquinone formation constants of $K = 10^5\text{--}10^{10}$.

Typical violenes of this type are given by the formulae (XXIX)$_{SEM}$ to (XXXV)$_{SEM}$. Here and in the aforementioned examples the semiquinone formation constants have been determined via d.c. or a.c. polarography. Provided that one electron transfer and reversible electrode processes have been established the two potentials E_1 and E_2 can be ascribed to the two
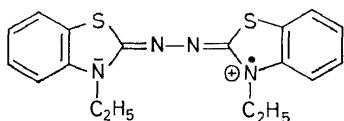
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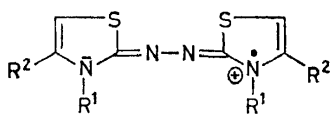
(XXIX)$_{SEM}$
blue or green $K=4\times10^8-2\times10^{10}$
$R^1=CH_3$, aryl $R^2=CH_3$, H
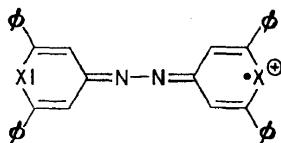
(XXX)$_{SEM}$ $X=\rangle N-CH_3$ violet $K=1\times10^4$
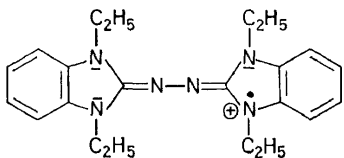(XXXI)$_{SEM}$ $X=\rangle S$ violet $K\sim7\times10^2$

(XXXII)$_{SEM}$
blue $K=9\times10^6$
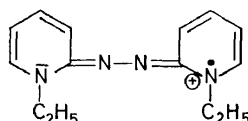
(XXXIII)$_{SEM}$
blue $K=7\times10^6$

(XXXIV)$_{SEM}$
violet $K=2\times10^9$
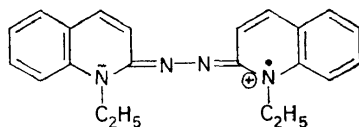
(XXXV)$_{SEM}$
violet $K=2\times10^5$

connected redox systems (cf. *Figure 1*). Values of K of at least 100 (83 per cent radical ion in equilibrium) can be obtained directly from the redox potentials E_1 and E_2 according to Michaelis[4]. If only electron transfer is involved the potentials E_1 and E_2 should be independent of the acidity of the solution.

$$\log K = \frac{E_2-E_1}{0\cdot06}\,(V, 25°C)$$
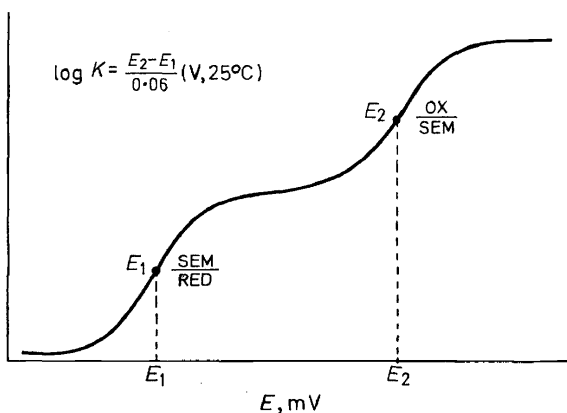
Figure 1. Redox potentials E_1 and E_2 from two connected redox systems and determination of the value of K

However, sometimes E_1, and only E_1, is shifted to higher voltage when the acidity of the solution is raised. This means that at least one member of the redox system becomes increasingly protonated. Since the semiquinone form is also part of the pH independent redox system OX/SEM (E_2) it must be the reduced form (XXVIII)$_\text{RED}$, the azine, which acts as a base. This behaviour can easily be understood, because only the reduced form bears no positive charge. In the case of the azines (XXVIII)$_\text{RED}$ which include an amidine system the acid–base equilibria may be written as in the following scheme.
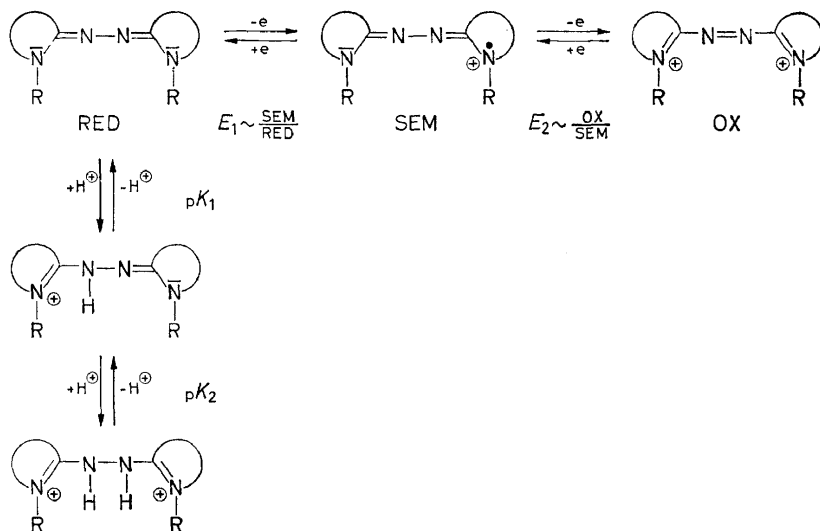
Typical examples[24] for the pH dependence of E_1 are seen in *Figure 2*. Only the benzothiazolone azine is so weakly basic that it resists protonation from pH 11 down to pH 2·3. The other three azines all show pH dependence at lower pH's changing to a pH independent curve at higher basicity. The intersection of the two curves marks the pK_1 of the azines. These pK's correspond well to those determined optically. According to Clark and Cohen a given redox potential depends on the pH of the medium in the following way:

$$\frac{\mathrm{d}E}{\mathrm{dpH}} = 60\,\frac{a}{n}\ (\mathrm{mV},\ 25\,^\circ\mathrm{C})$$

where a = difference in number of protons, and n = difference in number of electrons referred to the stoichiometry of the electrode process.

Since we are dealing with one-electron transfers the expected slopes are

$$\left.\begin{array}{l} a = 0 \\ n = 1 \end{array}\right\} = 0 \qquad \left.\begin{array}{l} a = 1 \\ n = 1 \end{array}\right\} = 60\,\frac{\mathrm{mV}}{\mathrm{pH}}$$
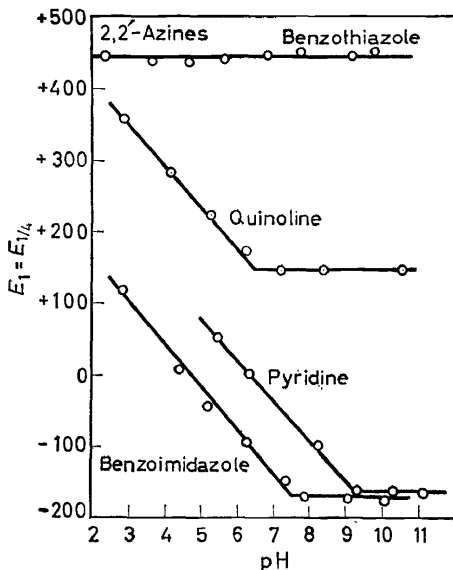
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Figure 2. Dependence of potential E_1 on pH

These are exactly the data from *Figure 2* since the experimental slopes are zero and 58–60 mV/pH respectively.

The possible protonation of one component of the redox system has some important consequences.

1. Because the protonated reduced form is no longer a member of the redox system, the redox equilibrium becomes disturbed and is shifted to the left side.

$$RED + OX \rightleftarrows 2\ SEM$$
$$H^{\oplus}\downarrow\uparrow$$
$$RED \cdot H^{\oplus}$$
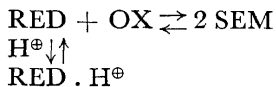
If one starts with a system containing, say, 99·9 per cent radical ion, the radical ion will vanish completely if the reduced form becomes fully protonated. The result is a *disproportionation* of the semiquinone. The spectra given in *Figure 3* demonstrate this behaviour taking the quinoline system (XXXV) as an example[25]. The absorption band of the *protonated* azine (XXXV)$_{RED}$ ends at about 300 mμ. The oxidized form (XXXV)$_{OX}$, being an azo dication exhibits a strong transition at about 500 mμ. The radical cation shows two characteristic absorption bands only, slightly overlapped by the RED 2H$^{\oplus}$ and OX bands. Addition of some perchloric acid to the solution of the radical ion detroys the blue colour immediately and generates the red colour of the azo dication. The new absorption curve DIS discloses clearly that by disproportionation equivalent amounts of the protonated reduced form and the oxidized form are produced. By adding base the process is completely reversed, comproportionation taking place. The whole cycle may easily be taken as a simple acid–base reaction if the semiquinone
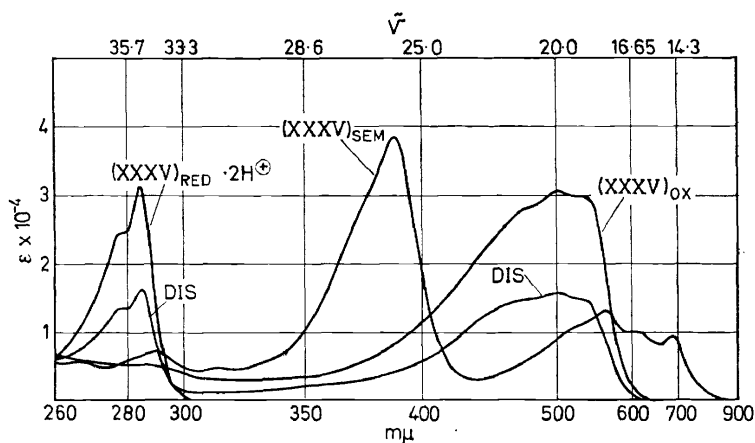
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Figure 3. Spectra of the quinoline system (XXXV) demonstrating the *disproportionation* of the semiquinone

character of the investigated substance is not known. From this point of view the aforementioned misinterpretation of the discussed indolizine and azulene examples can be well understood. The authors not only observed the transformation of the dication $(XXIV)_{OX}$ to the blue monocation supposed to be (XXV) but also the reverse process. Addition of perchloric acid to the blue compound in acetonitrile brought back the red dication $(XXIV)^{19}_{OX}$. It is not surprising now that the yield remained below 50 per cent.

2. A further direct consequence of protonation on the redox equilibrium consists in the apparent pH dependence of the semiquinone formation constant as shown in *Figure 4*.

The intersection of the sloping and the horizontal lines corresponds again to the pK values, of course. The diagram demonstrates that a comparison of uncorrected semiquinone formation constants only is valid above the pK's
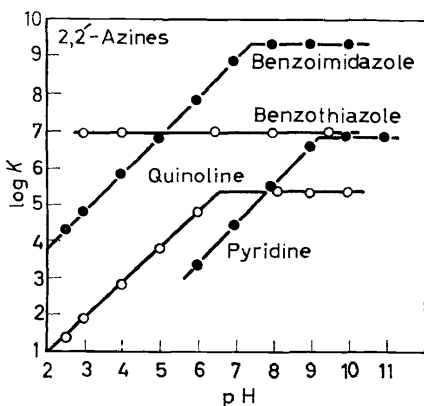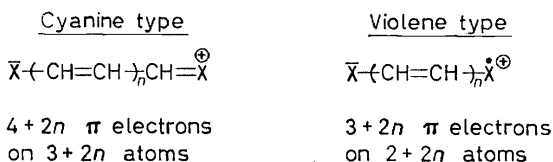

Figure 4. Protonation on the redox equilibrium. Apparent pH dependence of the semi-quinone formation constant.

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of the reduced forms. Besides one can see that the actual stability of two violenes may be reversed by increasing the acidity of the solution[23].

It is obvious from the preceding discussion that the high variability of the violene type enables us to design very different redox systems with two consecutive one-electron transfer steps. In these systems, besides different semiquinone formation constants, dramatic changes of the redox potentials are also observed. Because of their high reversibility these systems may be of some value for the study of electron transfer reactions, including biological ones. However, the violene type itself deserves our interest because of a possible relationship to the cyanine type. As mentioned at the beginning the stability of violenes is due to the special arrangement of an uneven number of π-electrons on an even number of atoms. The cyanine type owes its existence to a comparable phenomenon. An even number of π-electrons

Cyanine type	Violene type
$\bar{X}\text{--}(CH=CH)_n\text{--}CH=\overset{\oplus}{X}$	$\bar{X}\text{--}(CH=CH)_n\text{--}\overset{\bullet\oplus}{X}$
$4 + 2n$ π electrons on $3 + 2n$ atoms	$3 + 2n$ π electrons on $2 + 2n$ atoms

are distributed over an uneven number of atoms. Consequently all discussed examples of violenes can easily be supplemented by the corresponding cyanines. It can be expected therefore that the thoroughly explored chemistry of cyanines can be transferred to the violene type[24]. Work under progress in our laboratory is intended to shed some light on these two aspects of violene chemistry.

References

[1] M. Gomberg and W. E. Bachman. *J. Am. Chem. Soc.* **49**, 236 (1927).
[2] cf. E. Weitz. *Angew. Chem.* **66**, 658 (1954).
[3] O. Neunhoeffer and P. Heitmann. *Chem. Ber.* **92**, 245 (1959).
[4] cf. L. Michaelis. *Chem. Rev.* **16**, 243 (1935).
[5] H. J. Friedrich. *Z. Naturforsch.* **196**, 280 (1964); *Angew. Chem.* **76**, 946 (1964).
[6] The data below the formulae read as absorption maximum at longest wavelength, log E and solvent.
[7] K. Kuwata and D. H. Geske. *J. Am. Chem. Soc.* **86**, 2101 (1964).
[8] H. D. Scheutzow. Dissertation, Universität Würzburg (1966).
[9] D. M. Lemal and K. I. Kawano. *J. Am. Chem. Soc.* **84**, 1761 (1962).
[10] T. J. Curphey. *J. Am. Chem. Soc.* **87**, 2064 (1965).
[11] This expression was introduced by L. Anschütz, K. Broeker, and A. Ohneiser. *Ber. dtsch. chem. Ges.* **77**, 443 (1944)).
[12] A. I. Kiprianov and M. J. Kornilov. *Zhur. Obshchei. Khim.* **31**, 1699 (1961).
[13] S. Hünig and B. G. Garner, unpublished results.
[14] G. Ruider. Diplomarbeit, Universität Würzburg (1965).
[15] A. v. Bayer and J. Piccard. *Liebigs. Ann. Chem.* **354**, 163 (1907).
[16] F. Arndt and L. Lorenz. *Ber. dtsch. chem. Ges.* **63**, 3121 (1930).
[17] S. Hünig and G. Ruider, unpublished results.
[18] S. Hünig and G. Kiesslich, unpublished results.
[19] M. Fraser and H. D. Reid. *J. Chem. Soc.* 1421 (1963).
[20] S. Hünig, H. J. Friedrich, D. Scheutzow, and W. Brenninger. *Tetrahedron Lett.* 181 (1964).
[21] E. C. Kirby and D. H. Reid. *J. Chem. Soc.* 3580 (1961), 1 c [19]
[22] S Hünig, D Scheutzow, and H. J. Friedrich. *Angew. Chem.* **76**, 818 (1964).
[23] H. Hart, J. S. Fleming, and J. L. Dye. *J. Am. chem. Soc.* **86**, 2079 (1964).
[24] S. Hünig, H. Balli, H. Conrad, and A. Schott. *Liebigs. Ann. Chem.* **676**, 36, 52 (1964).
[25] S. Hünig. *Liebigs Ann. Chem.* **676**, 32 (1964).