

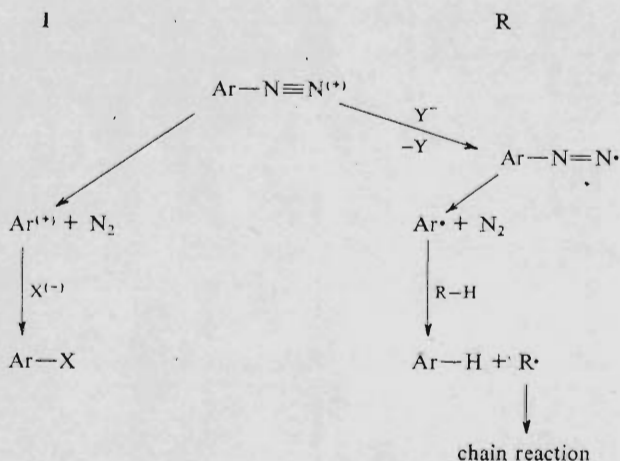
## PHOTOINDUCED DECOMPOSITION OF ARYLDIAZONIUM SALTS

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Flash photolysis of 1,4-benzoquinone ( $10^{-3}$  mol l<sup>-1</sup>) in an acetonitrile/water mixture (16 : 9 v/v) leads in the presence of 2,4,6-tri-*tert*-butylphenol ( $5 \cdot 10^{-2}$  mol l<sup>-1</sup>) to semiquinone- and phenoxy radicals. In this paper the reactivity of semiquinone with benzenediazonium tetrafluoroborate and six of its *para* substituted derivatives was studied. A significant effect of the substituents on the reaction rate was observed and the direct electron transfer from semiquinone to the diazonium salt was found to be the rate determining step. Different reactivity of the acid-base forms of semiquinone leads, depending on the pH, to rate constant changes within a range of five orders of magnitude.

The aryldiazonium salts decompose with heat or by interaction with light. Their sensitivity to heat is used with advantage in organic synthesis and the photochemical decomposition is of fundamental importance in the reprographic technique of diazography. The decomposition of aryldiazonium salts<sup>1</sup> is assumed to proceed by the ionic or radical mechanism (Scheme 1). The decomposition is started by a charge



SCHEME 1

transfer to the diazonium group. With the ionic mechanism (I) the electron is transferred from the aryl part of molecule while in case of the radical mechanism (R) it is supplied by another donating molecule. The main interest in the spectral sensitization studies and in attempts to increase the sensitivity of the diazoprocess is concentrated on the photoinduced chain decomposition of aryldiazonium salts. This process is based on a photochemical electron transfer from the spectral sensitizer to the diazonium salt. The formed free radicals can react with further diazonium ions and induce in this way a chain reaction, leading to multiple quantum yields. The properties of the electron donor are decisive for efficient initiation of the radical decomposition. Suitable sensitizers are found to be *e.g.* the semiquinone radicals, which appear as short living intermediates in the photoreduction of quinoid dyes<sup>2</sup>.

### EXPERIMENTAL

The photolysis was carried out either using the second harmonic generated from the fundamental frequency of a laboratory built pulsed ruby laser (pulse half-width  $\sim 15$  ns, pulse energy at the fundamental and second harmonic frequency  $\sim 1$  J and  $\sim 100$  mJ resp.) or by means of a xenon flash tube of our own construction (pulse half-width  $5 \mu\text{s}$ ,  $2 \cdot 10^{18}$  photons in the 250–350 nm region), equipped with a WG 5 filter (Saale-Glas, GmbH). The kinetic data were recorded by a storage oscilloscope Tektronix 7633 and by a Transient Recorder DL 920 (Datalab, Ltd) instrument. By flash photolysis, the photoreduction of *p*-benzoquinone ( $10^{-3} \text{ mol l}^{-1}$ ) by 2,4,6-tri-*tert*-butylphenol ( $5 \cdot 10^{-2} \text{ mol l}^{-1}$ ) was studied in the presence of a series of *p*-substituted benzenediazonium tetrafluoroborates. The measurements were carried out in the acetonitrile/water medium (16 : 9 v/v) to which phosphate buffers and sulfuric acid were added. Quinone<sup>3</sup>, phenol<sup>4</sup> and diazonium salts<sup>5</sup> were prepared by described procedures. Oxygen was removed by passing nitrogen through the solution. By means of the fast spectroscopy absorption measurements the following short lived intermediates were studied: the triplet state of quinone (410 nm), semiquinone radical (410 nm,  $4600 \text{ l mol}^{-1} \text{ cm}^{-1}$ ) (ref.<sup>6</sup>), semiquinone radical anion (430 nm,  $\in 7300 \text{ l mol}^{-1} \text{ cm}^{-1}$ ) (ref.<sup>6</sup>), phenoxy radical (400 nm,  $\in 1800 \text{ l mol}^{-1} \text{ cm}^{-1}$ ) (ref.<sup>7</sup>) and phenoxy radical cation (430 nm,  $\in 1700 \text{ l mol}^{-1} \text{ cm}^{-1}$ ) (ref.<sup>7</sup>).

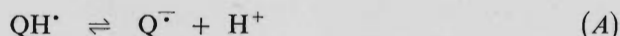
TABLE I

Rate constants (*k*) of the *p*-benzosemiquinone reaction with *p*-X-substituted benzenediazonium tetrafluoroborates in acetonitrile/water (16 : 9 v/v) at the pH = 7 and the polarographic reduction potentials of the diazonium salts<sup>10</sup>( $E_{\text{red}}$ )

X	OCH <sub>3</sub>	CH <sub>3</sub>	H	Cl	Br	COOC <sub>2</sub> H <sub>5</sub>
<i>k</i> ( $\text{l mol}^{-1} \text{ s}^{-1}$ )	$1.2 \cdot 10^6$	$5.2 \cdot 10^6$	$8.0 \cdot 10^6$	$3.2 \cdot 10^7$	$4.0 \cdot 10^7$	$1.1 \cdot 10^8$
$E_{\text{red}}$ (V)	0.14	0.25	0.30	0.35	0.38	0.40

## RESULTS AND DISCUSSION

Formation of the triplet state of quinone was observed after the light absorption. In the presence of phenol, the semiquinone- and phenoxy radicals are formed by a fast reaction ( $k \doteq 10^{10} \text{ l mol}^{-1} \text{ s}^{-1}$ ). Formation of an acid-base equilibrium between the semiquinone radical ( $\text{QH}^\cdot$ ) and the radical anion ( $\text{Q}^{\cdot-}$ ) was observed in the protic medium:



For reaction (A) the following equilibrium constant  $(4 \pm 1) \cdot 10^{-5} \text{ mol l}^{-1}$  was determined (for 293 K).

At the pH = 3, two bimolecular reactions with very different reaction rates were observed (Fig. 1). The fast process, with the rate constant  $8.5 \cdot 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$  ( $\epsilon_{400} 4500 \text{ l mol}^{-1} \text{ cm}^{-1}$ ) corresponds to the decay of the semiquinone radical. The slow process, with the reaction constant  $2.2 \cdot 10^4 \text{ l mol}^{-1} \text{ s}^{-1}$  ( $\epsilon_{400} 1800 \text{ l} \cdot \text{mol}^{-1} \text{ cm}^{-1}$ ) was assigned to the reaction of the phenoxy radical cation. The observed processes correspond both to the described disproportionation of semiquinone to quinone and hydroquinone<sup>8</sup> and to the dimerization of phenoxy to quinol ether<sup>4</sup>. At the pH 7, only one bimolecular process (Fig. 1), with the reaction rate constant  $1.5 \cdot 10^7 \text{ l mol}^{-1} \text{ s}^{-1}$  ( $\epsilon_{430} 9000 \text{ l mol}^{-1} \text{ cm}^{-1}$ ) was found. Under the latter conditions, the reaction between the semiquinone radical anions and phenoxy

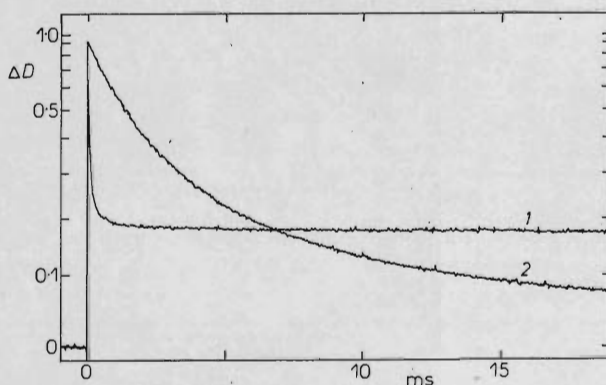
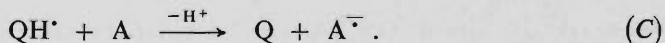
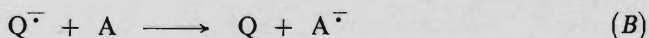


FIG. 1

Time dependence of the absorbance change ( $\Delta D$ ) of the semiquinone- and phenoxy radicals obtained by flash photolysis of *p*-benzoquinone ( $10^{-3} \text{ mol l}^{-1}$ ) and 2,4,6-tri-*tert*-butylphenol ( $5 \cdot 10^{-2} \text{ mol l}^{-1}$ ) in acetonitrile/water (16 : 9 v/v): 1 400 nm, pH 3; 2 430 nm, pH 7

radicals leads to the formation of quinone and phenol. In a presence of easily reducible compounds A (in our case of the aryldiazonium salts) the following reactions can take place:



Quinone in the ground state is formed as a product and it acts therefore as a photo-catalyst.

*Effect of substitution:* The rate constants of the *p*-benzosemiquinone radical anion reaction with individual *para*-substituted benzenediazonium tetrafluoroborates are shown in (Table I); the dependence of the logarithmic values of the rate constants on the reduction potentials of diazonium salts is given in Fig. 2. A straight line was fitted with the experimental points, giving the following parameters:  $\log k = 4.97 + 7.16E_{\text{red}}$ ,  $r = 0.978$ . The slope value ( $7.16 \text{ V}^{-1}$ ) speaks for a strong substituent effect and suggests that direct electron transfer plays an important role in the reaction of the semiquinone radical anion with the aryldiazonium salt<sup>9</sup>.

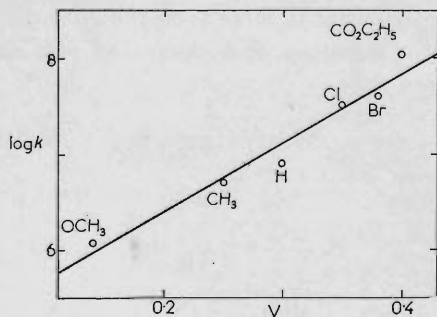


FIG. 2

Dependence of the logarithms of the rate constants ( $\log k$ ) of the *p*-benzosemiquinone radical-anion reaction with *para*-substituted benzenediazonium tetrafluoroborates on the reduction potentials of the diazonium salts ( $E_{\text{red}}$ )

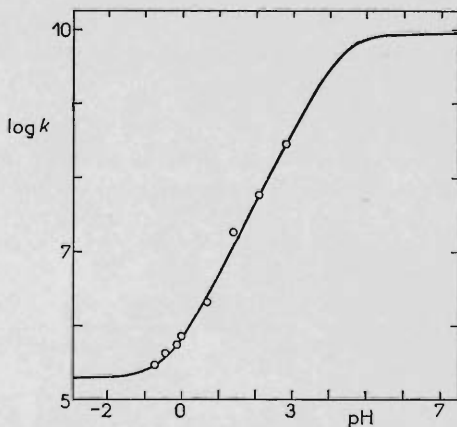


FIG. 3

Dependence of the logarithms of the rate constants ( $\log k$ ) of the *p*-benzosemiquinone reaction with *p*-nitrobenzenediazonium tetrafluoroborate on the pH values and the corresponding theoretical curve

*Effect of the pH:* In excess of the diazonium salt, semiquinone is removed mostly by reactions (B) and (C). For the reaction rate then follows:

$$v = k_{Q^-}[A][Q^{\cdot-}] + k_{QH^{\cdot}}[A][QH^{\cdot}], \quad (1)$$

where  $[A]$ ,  $[Q^{\cdot-}]$  and  $[QH^{\cdot}]$  denote the molar concentrations of the diazonium salt, the anion- and the neutral form of semiquinone and  $k_{Q^-}$ ,  $k_{QH^{\cdot}}$  are the corresponding rate constants. Applying the relations for the dissociation constant of semiquinone  $K = [H^+][Q^{\cdot-}]/[QH^{\cdot}]$  and for its total concentration  $[SQ^{\cdot}] = [Q^{\cdot-}] + [QH^{\cdot}]$  to equation (1) we get:

$$v = k[A][SQ^{\cdot}], \quad (2)$$

where  $k = (k_{Q^-}K + k_{QH^{\cdot}}[H^+])/(K + [H^+])$ .

Relation (2) holds as long as formation of the equilibrium proceeds much faster than reactions (B) and (C), as it is in our case. The dependence of the reaction rate on acidity of the medium was studied for the reaction of *p*-benzosemiquinone with *p*-nitrobenzenediazonium tetrafluoroborate. The results are given in Table II and shown in Fig. 3. The experimental points are best fitted by the theoretical curve (2) for parameters  $K = 5.1 \cdot 10^{-5} \text{ mol l}^{-1}$ ,  $k_{QH^{\cdot}} = 2.0 \cdot 10^5 \text{ l mol}^{-1} \text{ s}^{-1}$  and  $k_{Q^-} = 9.4 \cdot 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$  (The last value was obtained by extrapolation of the dependence of the above given logarithmic values of the rate constants on the substitution constants<sup>11</sup>  $\sigma_p$ ). Validity of the relation (2) is verified by agreement between the calculated dissociation constant value and the value obtained spectroscopically ( $K = (4 \pm 1) \cdot 10^{-5} \text{ mol l}^{-1}$ ). The  $k_{QH^{\cdot}}$  value is several orders of magnitude lower than  $k_{Q^-}$ . This proves that the protonization of semiquinone is connected with an increase of the oxidation potential.

TABLE II

Rate constants ( $k$ ) of the *p*-benzosemiquinone reaction with *p*-nitrobenzenediazonium tetrafluoroborate in acetonitrile/water (16 : 9 v/v) for various concentrations of sulfuric acid

pH	-0.7	-0.4	-0.1	0	0.7	1.4	2.1	2.8
$k (\text{l mol}^{-1} \text{ s}^{-1})$	$2.9 \cdot 10^5$	$4.1 \cdot 10^5$	$5.6 \cdot 10^5$	$6.9 \cdot 10^5$	$2.1 \cdot 10^6$	$1.8 \cdot 10^7$	$6.0 \cdot 10^7$	$2.8 \cdot 10^8$

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