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FORMATION OF AROMATIC RADICAL-CATIONS BY OXIDATION WITH ELECTRONEGATIVELY SUBSTITUTED QUINONES IN ACID MEDIA; KINETICS AND MECHANISM

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Abstract—Electronegatively substituted quinones are shown to oxidize electron-rich aromatic molecules to the corresponding radical-cations in acid medium via a reversible two step mechanism. The influence of acid strength on the rate of the reaction suggests that a protonated quinone molecule acts as the primary electron acceptor. The rate of formation of the radical cations depends on the one electron oxidation potential of the parent aromatic molecules in a way typical for endothermic outer-sphere electron-transfer.

Aromatic radical cations are obtained from one-electron oxidation of the parent aromatic molecules ($\mathrm{ArH} \rightarrow \mathrm{ArH}^{+\cdot} + e$). This oxidation can be accomplished by many methods including electron impact,[1] radiolysis,[2] photo-ionization,[3,4] anodic oxidation[5] and chemical oxidation.[6,7]

Efficient chemical oxidants invariably contain strong Brönstedt or Lewis acids which either have oxidizing properties (e.g. H_2SO_4, $AlCl_3$, $SbCl_5$) or derive these from added oxidants. The efficiency of such oxidizing mixtures has generally been measured from their ability to produce radical-cation solutions suitable for spectroscopic (ESR, UV) investigation. In most cases the oxidation mechanism and even the products—besides the radical cation—formed are unknown.[6]

In the course of a study[8,9] on the (photo) chemical reactivity of charge-transfer complexes between aromatic molecules and electronegatively substituted quinones we observed the formation of radical cations upon addition of small amounts of trifluoroacetic acid (TFA) to several such complexes in organic solvent systems.

Earlier[10] the formation of aromatic radical cations by the combined action of quinones and strong acids (e.g. H_2SO_4, HSO_3F/SbF_5) on aromatic hydrocarbons had been observed. Furthermore radical cations have been postulated[11] as intermediates in HCl or HBr induced reactions of complexes between *o*-chloranil and several polynuclear aromatic hydrocarbons. The present paper describes a study on the scope and the mechanism of this radical cation formation.

RESULTS AND DISCUSSION

Electronegatively substituted quinones such as 2,3,5,6-tetra-chloro-1,4-benzoquinone (chloranil) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) form complexes of the charge-transfer type[12] with electron rich aromatic molecules. Addition of a strong acid such as TFA to solutions of these complexes leads in a number of cases to the formation of the corresponding aromatic radical cations. In Fig. 1 and Fig. 2 the ESR and UV/VIS spectra of the 9,10-diphenylanthracene (DPA) and perylene radical cations, thus prepared in CH_2Cl_2/TFA solution, are shown.

These spectra correspond very well with those reported in literature[13-15] for these radical cations.

Other radical cations identified include those derived from: 3,4-benzpyrene,[16] 9,10-di(α-naphthyl)-anthracene (DNA);[17] anthracene;[16] 1,2,4-trimethoxybenzene and 1,2,4,5-tetramethoxybenzene.[18]

The ease of formation of the radical cations in CH_2Cl_2/TFA quinone medium decreases rapidly for less easily oxidizable aromatic molecules.

However for many aromatic molecules which do not give detectable amounts of radical cations (such as anisole and methylated benzenes), reactions occur[8,9] which can be formulated as proceeding through radical cation intermediates. These reactions will be the subject of future publications.

Redox equilibrium between DPA and DDQ in acid solution. Because of the high stability of its radical cation the oxidation of 9,10-diphenylanthracene (DPA) by DDQ in acid medium was studied more quantitatively.

Figure 3 shows the effect of TFA concentration on the conversion of DPA into its radical cation as monitored spectrophotometrically (595 nm; ϵ = 10,000) at constant DPA and DDQ concentrations.

Figure 4 shows the effect of the DDQ concentration at constant DPA (10^{-4} M) and TFA (10%) concentrations on the conversion of DPA into its radical cation.

From these data it can be concluded that an equilibrium exists in which one molecule of the quinone (Q) oxidizes two molecules of the aromatic species (ArH) and that at "high" acid concentration (e.g. at 10% TFA for the DPA/DDQ system) this equilibrium lies almost completely to the right. (At 10% TFA the protonation of DPA is still negligible and conversion to $DPA^{+\cdot}$ by atmospheric oxygen[19] amounts to no more than 2.0%.)

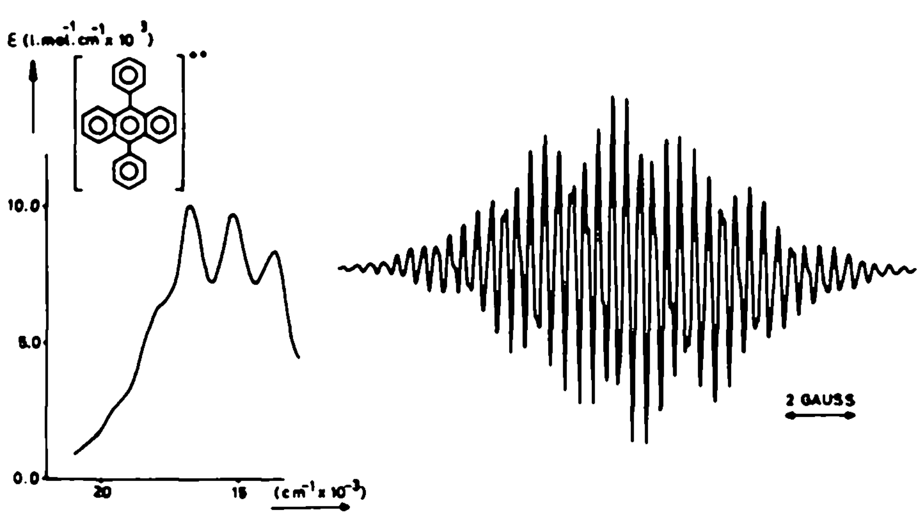

Fig. 1. Electron spin resonance spectrum and electronic absorption spectrum of the DPA radical cation obtained by oxidation of DPA with excess DDQ in respectively 9:1 and 20:1 CH_2Cl_2/TFA media.

From these findings and from the fact that no other paramagnetic species than $ArH^{+\cdot}$ can be detected by ESR spectroscopy the equilibrium (1) is proposed:

$$2ArH + Q + 2H^{+} \rightleftharpoons 2ArH^{+\cdot} + QH_2 \qquad (1)$$

In (1) conversion of the quinone (Q) to the corresponding hydroquinone (QH_2) is assumed to be involved.

The stoichiometry of (1) is equivalent to that (1a) suggested by Buck c.s.[10] for the oxidation of aromatic molecules by diphenoquinone or 3,3,',5,5'-tetrabromodiphenoquinone in strong acids (e.g. H_2SO_4, HSO_3F, HSO_3F/SbF_5).

$$2ArH_2^{+} + Q \rightleftharpoons 2ArH^{+\cdot} + QH_2 \qquad (1a)$$

In (1a) however the protonated form of the aromatic molecule was assumed to be reactive, losing (formally) a hydrogen atom to the quinone during formation of the radical cation. An apparent equilibrium constant for (1) at a given acidity is defined by (2):

$$K = \frac{[ArH^{+\cdot}]^2[QH_2]}{[ArH]^2[Q]} \qquad (2)$$

In Fig. 3 the dependence of K on the TFA concentration has been plotted.

The equilibrium was studied in more detail in a mixture of TFA, acetic acid and benzene (3:3:2 v/v) which constitutes a reproducible medium of intermediate acidity.

From (2) relation (3) can be derived for $2[Q]_0 > [ArH]_0$:

$$\frac{[ArH^{+\cdot}]^3}{([ArH]_0 - [ArH^{+\cdot}])^2} = 2K[Q]_0 \qquad (3)$$

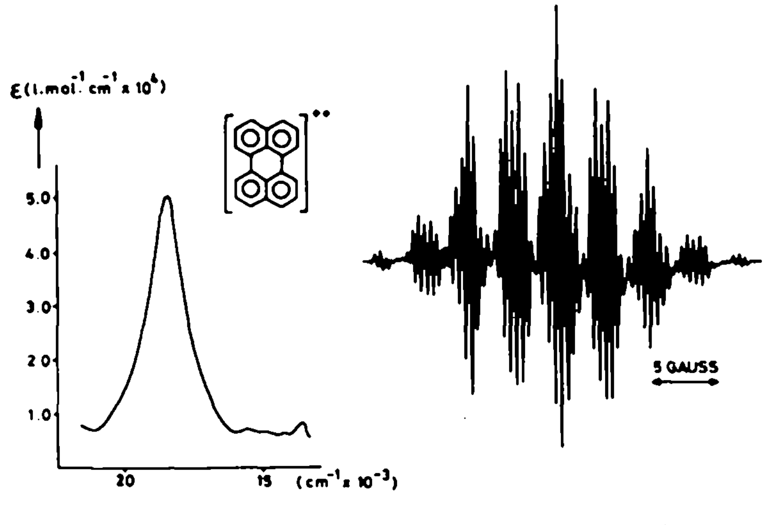

Fig. 2. Electron spin resonance spectrum and electronic absorption spectrum of the perylene radical cation obtained by oxidation of perylene with excess DDQ in respectively 9:1 and 20:1 CH_2Cl_2/TFA media.

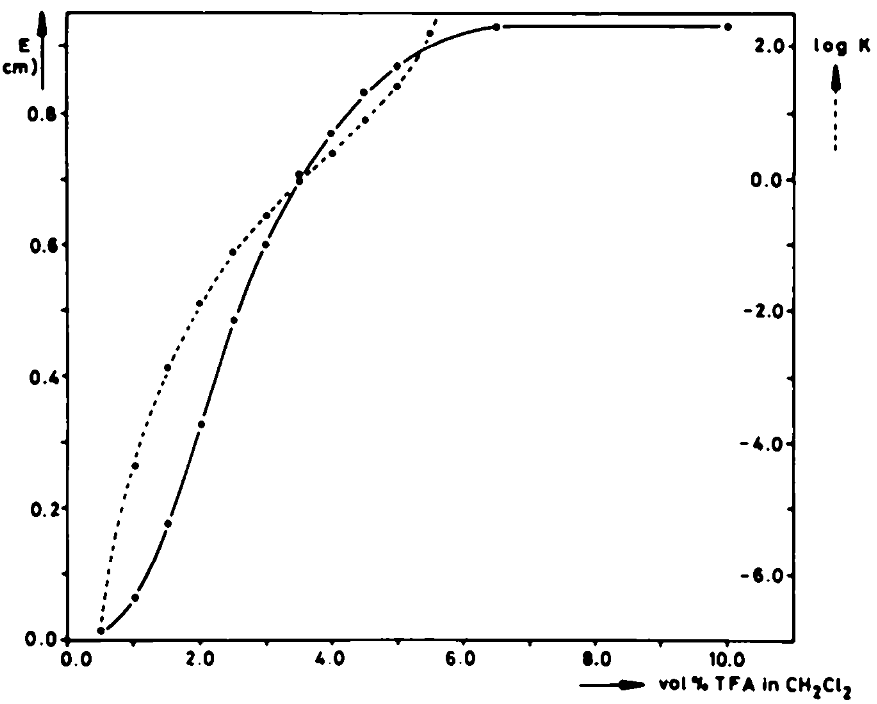

Fig. 3. Conversion of DPA ($[ArH]_0 = 0.93 \times 10^{-4}$ M) into $DPA^{+\cdot}$ by DDQ ($[Q]_0 = 4.02 \times 10^{-4}$ M) in various CH_2Cl_2/TFA mixtures (drawn curve) at 20°C. The value of the apparent equilibrium constant for the process $2ArH + Q \rightleftharpoons 2ArH^{+\cdot} + Q^{2-}$ has been indicated by the dashed curve.

In Fig. 5 it is shown that under these conditions a plot of $2[Q]_0$ against $[ArH^{+\cdot}]^3/([ArH]_0 - [ArH^{+\cdot}])^2$ yields a perfectly straight line with $K = 1.27 \times 10^{-2}$. This corresponds with the values found in TFA/CH_2Cl_2 at a TFA concentration of about 2% (cf. Fig. 3).

For other aromatic species evaluation of K was hampered by the rather rapid decay of their radical cations through subsequent chemical reactions.

Kinetics of the oxidation of DPA by DDQ and chloranil in acid media. During the measurement of the redox equilibrium between DDQ and DPA (*vide supra*) it was observed that at low acid concentrations the establishment of this equilibrium requires considerable time (cf. Fig. 6).

With chloranil as an electron acceptor the equilibration takes even longer.

It was found that the initial rate of appearance of

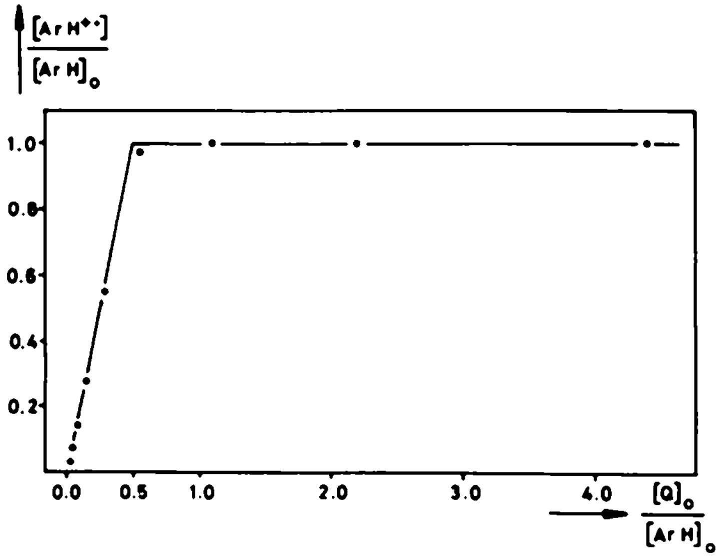

Fig. 4. Conversion of DPA ($[ArH]_0 = 1.0 \times 10^{-4}$ M) into $DPA^{+\cdot}$ upon addition of increasing amounts of DDQ ($1.69 \times 10^{-6} - 4.32 \times 10^{-4}$ M) in a 10% TFA in CH_2Cl_2 (v/v) solvent system at 20°C.

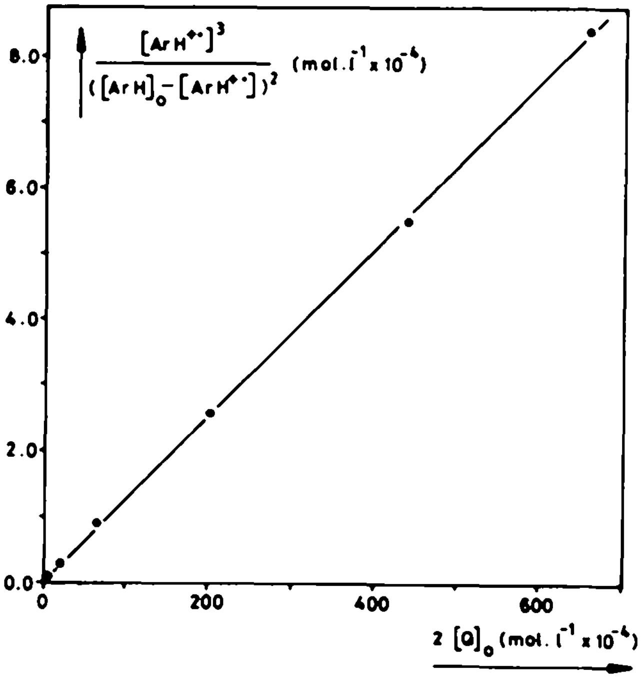

Fig. 5. Dependence of DPA$^{+\cdot}$ concentration ($[ArH^{+\cdot}]$) upon DDQ concentration ($[Q]_0$) in a TFA/AcOH/C_6H_6 (3:3:2 v/v) solvent system at 20°C. $[ArH]_0 = 1.78 \times 10^{-4}$ M, $[Q]_0$ varied from 2–330 × 10^{-4} M.

DPA$^{+\cdot}$ obeys first order kinetics both in DPA and in the quinone (4):

$$\left(\frac{[ArH^{+\cdot}]}{dt}\right)_{t=0} = k_{obs}[ArH]_0[Q]_0 \qquad (4)$$

These results clearly indicate that the process described by (1) must involve a rate limiting bimolecular step, which can be accounted for by (5) and (6) with $k_1 \ll k_2$.

$$ArH + Q + H^{\oplus} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ArH^{+\cdot} + QH^{\cdot} \qquad (5)$$

$$ArH + QH^{\cdot} + H^{\oplus} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} ArH^{+\cdot} + QH_2 \qquad (6)$$

$$2ArH + Q + 2H^{\oplus} \rightleftharpoons 2ArH^{+\cdot} + QH_2 \qquad (1)$$

When $k_1 \ll k_2$ (which explains why the semiquinone radical QH$^{\cdot}$ is not observed) the initial rate of radical cation formation is given by (7):

$$\left(\frac{d[ArH^{+\cdot}]}{dt}\right)_{t=0} = k_{obs}[ArH]_0[Q]_0 = 2k_1[ArH]_0[Q]_0 \qquad (7)$$

The assumption $k_1 \ll k_2$ implies that QH$^{\cdot}$ is consi-

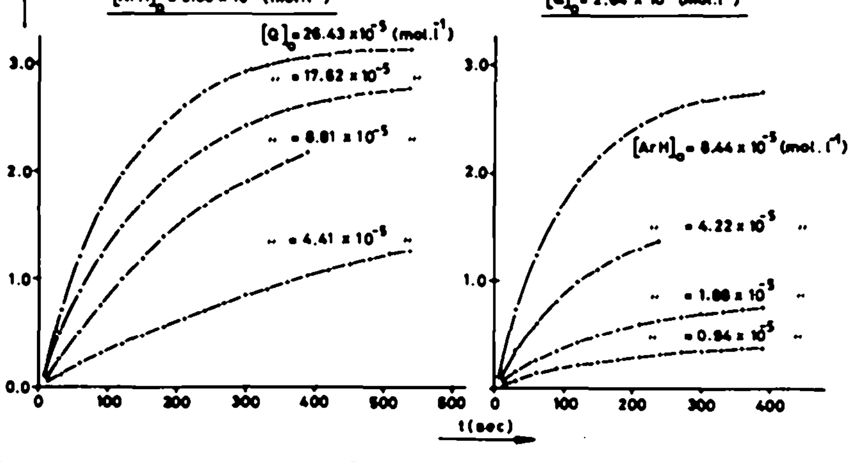

Fig. 6. Increase of DPA$^{+\cdot}$ concentration ($[ArH^{+\cdot}]$) as monitored spectrophotometrically after mixing of separate DPA and DDQ solutions in a TFA/AcOH/C_6H_6 (3:3:2 v/v) solvent system at 20°C.

dered to be a much better electron acceptor than Q, which corresponds with the explanation given for the electrochemical behaviour of quinones in acid media by Peover[20] and recently discussed by Murray c.s.[21]

In order to reveal more explicitly the role of the acid, tentative H_0 values[22] for the CH_2Cl_2/TFA medium were derived by measuring the degree of protonation of the indicator bases (B) 2-nitro aniline ($pK_a = -0.29$)[23] and 2-nitro-4-chloro aniline ($pK_a = -1.03$)[23] in various CH_2Cl_2/TFA mixtures. Rather surprisingly the difference in the pK_a values ($\Delta pK_a = 0.74$) reported[23] for these bases in aqueous solution was reproduced by the difference in their $\log[BH^+]/[B]$ values measured spectrophotometrically in CH_2Cl_2/TFA mixtures (cf. exp.) thus allowing the construction of a tentative H_0 scale between 0.25 and ~40 vol. % TFA.

As shown in Fig. 7 linear plots are obtained for the dependence of $\log k_{obs}$ upon these H_0 values in the oxidation of DPA by DDQ as well as in its oxidation by chloranil. It is generally agreed[24] that such linear plots indicate a protonated species to be involved in the rate limiting step of the reaction. The non-unity slope of the plots in Fig. 7 testifies once again the statement[24] that "each individual base defines its own acidity function" although these different acidity functions are generally linearly related[24] over quite a wide range of acidity.

The different slopes observed (cf. Fig. 7) for DDQ and chloranil oxidation of DPA exclude DPA as being the species protonated. This then leads to the logical conclusion that the protonated quinone ($QH^{\oplus}$) acts as the primary electron acceptor in (5), this in spite of the low basicity[23,25] of electronegatively substituted quinones such as DDQ and chloranil. It should be realized however that the linearity of plots like those shown in Fig. 7 is certainly no absolute proof for the intermediacy of a protonated species. Because of their double

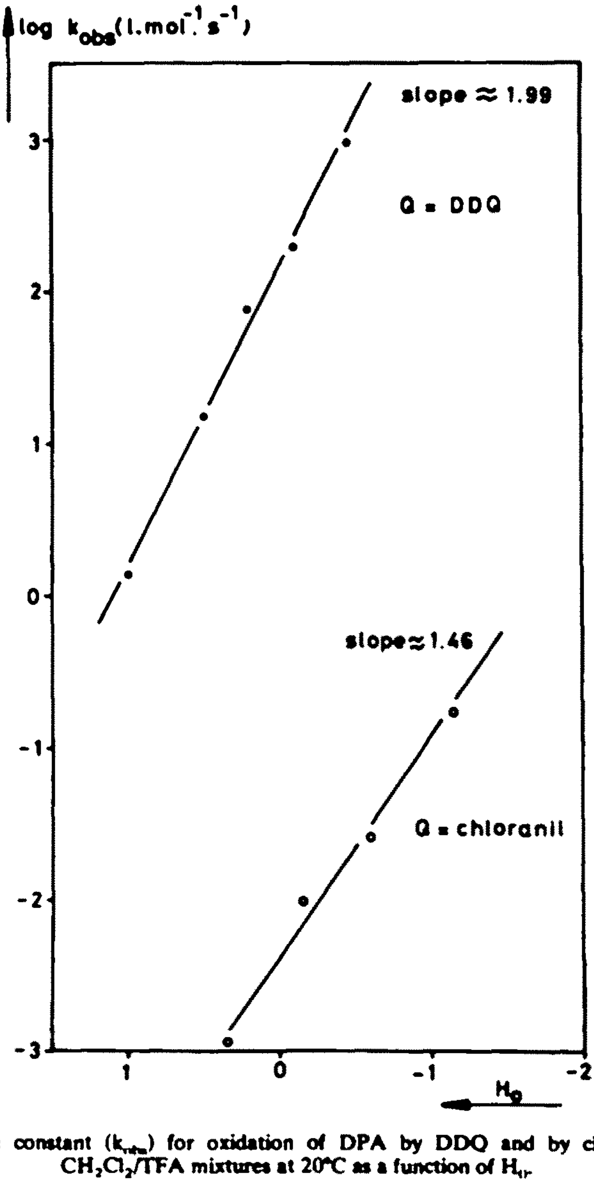

Fig. 7. Initial rate constant (k_{obs}) for oxidation of DPA by DDQ and by chloranil in various CH_2Cl_2/TFA mixtures at 20°C as a function of H_0.

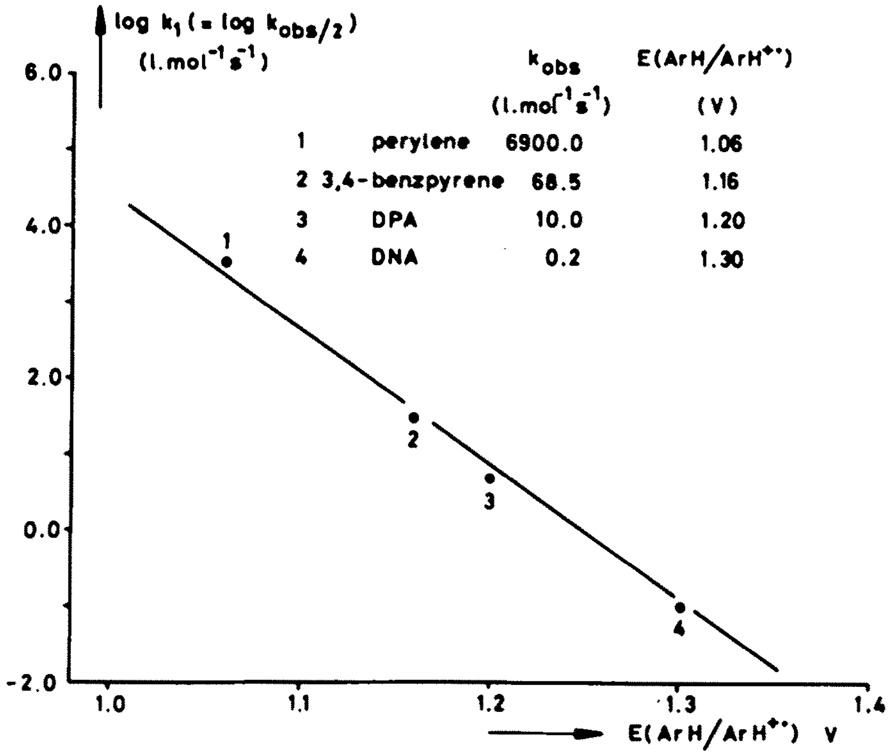

Fig. 8. Dependence of initial oxidation rate by DDQ in TFA/AcOH/C_6H_6 (3:3:2 v/v) at 20°C upon the oxidation potential for several aromatic molecules.

logarithmic nature such plots tend to be rather insensitive as a diagnostic tool. Thus a concerted acid catalysis in which proton and electron transfer occur simultaneous—as also proposed in the electrochemical reduction of quinones in acid media—cannot be excluded completely.

Influence of electron donor strength on oxidation kinetics. The initial rate of radical cation formation by oxidation with DDQ was found to be measurable for a few other aromatic molecules than DPA.

The log k_1 values ($k_1 = k_{obs}/2$ cf. eqn (7) measured in TFA/AcOH/C_6H_6 (3:3:2 v/v) at 20°C for perylene; 3,4-benzpyrene; DPA and 9,10-di-(α-naphthyl)anthracene are plotted in Fig. 8 against the one-electron oxidation potentials of these molecules measured[17,26] under *reversible* conditions in acetonitrile† relative to the saturated calomel electrode.

A linear correlation (8) is found:

$$\log k_1 = -17.39E(\mathrm{ArH}/\mathrm{ArH}^{+}) + 21.74 \qquad (8)$$

The free enthalpy change (ΔG) involved in outer-sphere one-electron transfer between an electron donor molecule (D) and electron acceptor molecule (A) in a polar medium can be expressed[27] by (9) in terms of the oxidation potential of D,

$$\Delta G(\mathrm{kcal/mol}) = 23.06[E(D/D^{+}) - E(A^{-}/A)] - C \qquad (9)$$

the reduction potential of A and a (small) coulomb stabilisation (C) of the resulting ion-pair.

Furthermore the expressions (10) and (11) have been found[27] to describe the kinetics of outer-sphere one-electron transfer (rate constant k_e) over a wide range of positive and negative ΔG values.

$$k_e = 10^{11}e^{-\Delta G^{\neq}/RT} \quad (\mathrm{l \cdot mol^{-1} \cdot s^{-1}}) \qquad (10)$$

$$\Delta G^{\neq} = \Delta G/2 + [(\Delta G/2)^2 + (\Delta G^{\neq}(o))^2]^{1/2} \qquad (11)$$

In (11) $\Delta G^{\neq}(o)$ represents the free enthalpy of activation for a process with ΔG = 0 e.g. for degenerate electron exchange. For endothermic electron transfer (i.e. $\Delta G > \Delta G^{\neq}(o)$) (11) simplifies to $\Delta G^{\neq} = \Delta G$, from which through relations (9) and (10) the expression (12) is derived for the relation between the rate of one-electron transfer from various donors (D) to a single electron acceptor at 20°C:

$$\log k_e = -17.06\,E(D/D^{+}) + \mathrm{constant} \qquad (12)$$

The slope of this relation corresponds remarkably well with that (8) observed in Fig. 8. In our opinion this observation proves that the oxidation mechanism involves an endothermic one electron transfer from the aromatic molecule to the (protonated) quinone as the rate limiting step. Thus complete protonation of the aromatic molecules is expected to inhibit their oxidation. This explains the retardation of quinone mediated radical cation formation in very strong acids as observed by Buck c.s.[10]

In conclusion, it seems that the mechanism proposed above for oxidation of aromatic molecules by

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† For 9,10-di-(α-naphthyl)antracene the reversible potential reported in dichloromethane[17] (1.32 V) was reduced by the difference between the reversible potentials measured for DPA in dichloromethane[26a] and in acetonitrile[26b] respectively.

quinones in acid media explains both the catalytic role of the acid and the virtual absence of the semiquinone radical. This mechanism seems closely related to that proposed earlier[19] for oxidations involving molecular oxygen when $Q^{-\cdot}$ and QH_2 are regarded as vinylogues of $O_2^{-\cdot}$ and H_2O_2 respectively. We feel that a mechanism in which protonation of the radical anion formed by one electron transfer to the oxidant leads to a molecule capable to accept a second electron may play a role in many of the acid catalyzed oxidations commonly used to produce radical cations.

It should be noted that for many such oxidations as well as for our systems photoenhancement[8,9] of the rate of oxidation is observed. In our opinion this photoenhancement must occur during the first (strongly endothermic) electron transfer step.

EXPERIMENTAL

Purification of reagents. The aromatic compounds were obtained commercially and were purified by recrystallization. DDQ was obtained from Fluka and purified by recrystallization from chloroform (m.p. 217–219°). Chloranil was obtained from Fluka and purified by recrystallization from benzene (m.p. 294°). TFA (Aldrich) was purified by fractional distillation (b.p. 71–72°C), after addition of about 3% of trifluoroacetic anhydride, and was stored at 5°C. CH_2Cl_2 was obtained from Merck ("für Fluoreszenz-Spektroskopie"). It is essential to use dry CH_2Cl_2 which is free from ethanol (a common stabilizer) since DDQ (and to a lesser degree chloranil) react with ethanol and water.

Spectra. ESR spectra were recorded on a Varian E-3 ESR spectrometer in solutions deoxygenated by purging with nitrogen. UV/VIS spectra were recorded on Cary-14 and Cary-17D recording spectrophotometers in teflon stoppered silica cells at 20°.

Absorption spectra of perylene, DPA and DNA radical cations were recorded by addition of solid DDQ to a solution of the parent aromatic molecule ($\sim 10^{-4}$ M) in CH_2Cl_2/TFA (9 : 1 v/v for perylene and DPA; 7 : 3 v/v for DNA) in a 1 cm pathlength cell, until complete conversion into the radical cation had occurred ([DDQ]$\sim 0.5 \times 10^{-4}$ M).

The visible absorption of the radical cations (which does not overlap with the DDQ absorption) was then measured. This gave the following data λ_{max} nm(ϵ):

Perylene$^{+\cdot}$: 540 (50,000)
DPA$^{+\cdot}$: 546 sh (6,300); 596 (10,000); 653 (9,700); 724 (8,400)
9,10-di-(α-napthyl)anthracene$^{+\cdot}$: 651 (8,750); 596 (6,300); 555 sh (3,000).

The DPA$^{+\cdot}$ shows the highest stability (a decline of 2.5% over 24 hrs period), while 9,10-di-(α-naphthyl)-anthracene$^{+\cdot}$ and especially perylene$^{+\cdot}$ are definitely less stable. It should be noticed, that the stability of the radical cations strongly depends on the concentration DDQ and TFA present. Increasing these concentrations leads to a decreased stability of the radical-cations.

Kinetic and equilibrium measurements. In these measurements the formation of ArH$^{+\cdot}$ was monitored spectrophotometrically at the following wavelengths. Perylene: 540 nm ($\epsilon = 50,000$); DPA 596 nm ($\epsilon = 10,000$); 9,10-di-(α-naphthyl)anthracene: 651 nm ($\epsilon = 8,750$); 3,4-benzpyrene: 521 nm ($\epsilon = 21,600$). The influence of $[Q]_0$ and $[ArH]_0$ on the rate of oxidation of DPA by DDQ in TFA/AcOH/C_6H_6 (3 : 3 : 2 v/v) (Fig. 6) was measured by rapid mixing of known volumes of separate DDQ and DPA solutions in this solvent and monitoring the increase of the DPA$^{+\cdot}$ concentration. Table 1 contains some of the data obtained as well as data on the oxidation of perylene; 3,4-benzpyrene and 9,10-di-(α-naphthyl)anthracene in this medium.

The initial rate of DPA oxidation by chloranil and by DDQ in various CH_2Cl_2/TFA mixtures (cf. Fig. 7) was measured after addition of TFA with a microliter syringe to a solution of DPA and the quinone in 2 ml of CH_2Cl_2 in a cuvet of 1 cm pathlength. Quantitative data are compiled in Table 2.

Determination of H_0*-values for* TFA/CH_2Cl_2 *mixtures.* For the indicator bases (B) 2-nitroaniline and 2-nitro-4-chloroaniline the ratio of protonated (BH^+) to free base was determined spectrophotometrically in various TFA/CH_2Cl_2 mixtures from the extinction measured for the base in pure CH_2Cl_2 (E_0) and that in a TFA/CH_2Cl_2 mixture (E') at the same stoichiometric concentrations through:

$$[BH^+]/[B] = (E_0 - E')/E'$$

The extinctions were read at the band maximum of the free base (which shifts slightly to longer wavelength upon increasing TFA concentration) where the absorption of BH^+ is negligible. Over the range of TFA concentrations (i.e. between 2 and 15%) in which the ratio $[BH^+]/[B]$ is measurable for *both* bases a constant difference of 0.74 ± 0.03 between their $\log[BH^+]/[B]$ values was observed which agrees with the difference between their pK_a values[23] in aqueous medium (−0.29 and −1.03 respectively).

Table 3 compiles the H_0 values[22] thus determined for TFA/CH_2Cl_2 mixtures between 0.25 and 40 vol.%. In

Table 1. Initial rates of ArH$^{+\cdot}$ formation by oxidation with DDQ in TFA/AcOH/C_6H_6 (3 : 3 : 2 v/v) as monitored spectrophotometrically at 20°C.

ArH	$[ArH]_0$ ($M \times 10^{-5}$)	$[Q]_0$ ($M \times 10^{-5}$)	$(d[ArH^{+\cdot}]/dt)_{t=0}$ ($M \cdot s^{-1} \times 10^{-8}$)	k_{obs} ($M^{-1} \cdot s^{-1}$)
DPA	9.38	4.41	3.67	8.9
DPA	9.38	8.81	8.33	10.1
DPA	9.38	17.62	16.67	10.1
DPA	9.38	26.43	23.33	9.4
DPA	0.94	26.40	2.33	9.4
DPA	1.88	26.40	5.33	10.7
DPA	4.22	26.40	11.60	10.4
DPA	8.44	26.40	24.60	10.8
Perylene	0.66	0.22	10.00	6900.0
3,4-Benzpyrene	15.30	2.20	23.10	68.5
9,10-di-(α-naphthyl)-anthracene	1.70	1050.0	3.42	0.2

Table 2. Initial rate of DPA oxidation by DDQ and chloranil in TFA/CH_2Cl_2 mixtures at 20°C (cf. Fig. 7).

Q	TFA in CH_2Cl_2 (vol %)	$[Q]_0$ ($M\times10^{-4}$)	$[ArH]_0$ ($M\times10^{-4}$)	k_{obs} ($M^{-1}\cdot s^{-1}$)
DDQ	1.0	1.16	1.13	1.4
	2.0	1.16	1.13	15.2
	3.0	1.16	1.13	76.0
	4.5	0.23	0.22	197.0
	7.5	0.23	0.22	985.0
chloranil	2.5	28.0	12.2	1.17×10^{-3}
	5.0	28.0	12.2	8.78×10^{-3}
	9.0	26.7	11.6	25.82×10^{-3}
	20.0	22.4	9.8	173.0×10^{-3}

Table 3. H_0 values for various TFA/CH_2Cl_2 mixtures.

[TFA] (vol %)	[TFA] ($mol\cdot l^{-1}$)	H_0	[TFA] (vol %)	[TFA] ($mol\cdot l^{-1}$)	H_0
0.25	0.02	2.00	10	0.88	−0.65
0.5	0.04	1.54	12	1.05	−0.80
1	0.09	0.96	16	1.40	−1.00
2	0.18	0.49	20	1.75	−1.15
3	0.26	0.20	25	2.19	−1.27
4	0.35	0	30	2.63	−1.35
6	0.53	−0.30	35	3.07	−1.41
8	0.70	−0.50	40	3.51	−1.45

this range volume additivity was found to be obeyed which allows simple conversion from vol.% to molar concentration (cf. Table 3).

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