Stability of Quinone and Reduced Forms in Hydrogen Fluoride and Hydrogen Fluoride–Antimony Pentafluoride Superacid Systems: an Electrochemical and Proton Nuclear Magnetic Resonance Study

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Two techniques, electrochemistry and ^{1}H n.m.r., are shown to be complementary in the study of the stability limits of benzoquinone, semiquinone, and hydroquinone and their conjugated acids at various protonation stages in the HF derived superacid system. Acidity constants are determined and conditions for the disproportionation of the semiquinone form are established. The complete potential–pH diagram in HF could be defined.

GILLESPIE [1] has shown more than a decade ago that extremely high acidities may be reached by the combination of fluorinated Lewis and Brönsted acids. The so-called superacids have found numerous applications both in fundamental and in applied chemistry and this subject has been recently reviewed.[2] The main field of application, the isomerisation and cracking of alkanes, in which various superacids are involved, has emphasized the importance of acidity. Two aspects are involved, first, the necessity for the control of the acidity level in a given superacid medium and secondly, the necessity for a comparison between the acidity levels of various classes of superacids.

Various methods have been used to estimate the acidity of superacid media.[3–6] We have recently suggested the use of electrochemical pH indicators.[7–10] The use of chloranil, for example, has permitted the establishment of an accurate acidity scale with HF as solvent. One major question however which cannot be answered directly by electrochemical techniques is the state of protonation of the electroactive species: variations of equilibrium potential *versus* pH give information about the number of H^{+} ions involved in the electrochemical process, but not about the initial state of protonation.

Since the work of Olah,[11] it has been known that the protonation of very weak bases in superacid media may be demonstrated by n.m.r. spectroscopy; for this reason, we have investigated electrochemical pH indicators by both electrochemical redox potential measurements and by ^{1}H n.m.r., and show that these techniques are complementary for the determination of the stability of *p*-benzoquinone and its reduced forms, semiquinone and hydroquinone, in their various protonation stages.

EXPERIMENTAL

The apparatus used for handling of HF and superacid mixtures has been described previously.[12] Hydrogen fluoride (Matheson) was purified by two successive condensations. Antimony pentafluoride (Allied Chemical) was twice distilled before experiment in all-glass distil-

lation apparatus. Other fluorides, TaF$_5$, NbF$_5$ (Fluorochem), PF$_5$ (Pfaltz and Bauer), and BF$_3$ (Matheson), were used for making other buffers without further purification.

Electrochemical Study.—The reference electrode was made from Ag–AgI system (Ag electrode in saturated AgF + 1M KF; potential E +0.230 V *versus* Cu–CuF$_2$, 0.2M KF system). The working electrode was a bright platinum electrode, S 3.14 mm^2.

N.m.r.—N.m.r. spectra were recorded on a Perkin-Elmer R32 spectrometer equipped with a variable temperature probe.

RESULTS

(I) *Voltammetry of Quinone and Hydroquinone.*—(1) *Reduction of* p-*benzoquinone in strongly basic media.** The
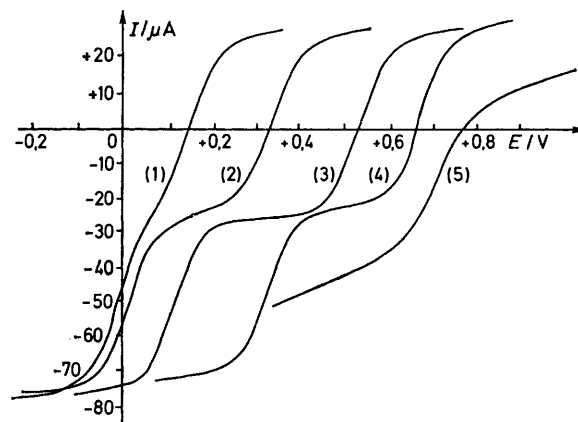

FIGURE 1   Voltammograms of a 2mM mixture of *p*-benzoquinone and semiquinone at a vitreous carbon (diameter 2.5 mm) rotating electrode (*w* 500 r.p.m.), as a function of the acidity level: (1) 0.15M-KF; (2) 0.15M-PF$_6$$^{-}$ + PF$_5$ (saturated); (3) 0.15M-BF$_4$$^{-}$ + BF$_3$ (saturated); (4) 0.15M-TaF$_6$$^{-}$ + 0.1M-TaF$_5$; (5) 0.15M-SbF$_6$$^{-}$ + 0.1M-SbF$_5$

voltammogram of *p*-benzoquinone (Q) in 0.1M-KF (strongly basic media) exhibits two mono-electronic reduction waves at a glassy carbon electrode (Figure 1, Table 1), corresponding to the Q(0)–Q(−I) and Q(−I)–Q(−II) steps. The

* pH Values refer to the acidity scale recently published for anhydrous HF,[8] pH 0 corresponds to a 1M-SbF$_6$ solution in HF. A 1M strongly basic solution (KF) fixes the pH at 13.7 (or pF 0).

TABLE 1

Characteristics of the voltammograms of p-benzoquinone in various buffers in anhydrous HF

Buffer	1.8M-KF	0.15M-KF	0.1M-BF$_4^-$ + sat BF$_3$	0.1M-TaF$_6^-$ + 0.1M-TaF$_5$	0.1M-SbF$_6^-$ + 0.15M-SbF$_5$	0.6M-SbF$_5$
pH$_{HF}$	14	12.8	6.8	4.6	0.84	0.20
$E_{1/2}$/V	−0.015 [a]	0.105 −0.020	0.530 0.120	0.630 0.412	0.751 [a,c]	0.765 [a,b]

[a] Single dielectronic wave [b] Q unstable.

variation of the half-wave potential of a platinum electrode in a Q–Q(−I) mixture with KF concentration has a slope (54 mV) which indicates the exchange of one H$^+$ per electron (Figure 2).
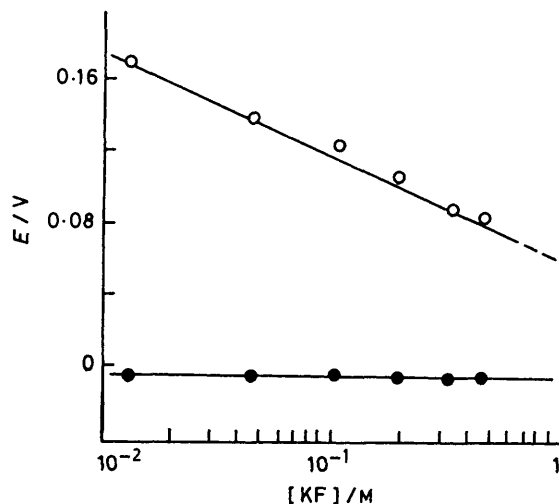

FIGURE 2 Variation of the half-wave potential of a rotating platinum electrode (w 500 r.p.m.) in a solution of 1.6mM-p-benzoquinone as a function of KF concentration in HF: ○, Q(0)–Q(−I) system; ●, Q(−I)–Q(−II) system

If we consider that such a quinone is already mono-protonated in less acidic media (such as water–HF mixtures or concentrated solutions of KF [13-15]), we can write the first reduction step as equation (1). Figure 2 shows that the

$$QH^+ + H^+ + e^- \rightleftharpoons QH_2^+ \qquad (1)$$

half-way potential of the second reduction wave is inde-pendent of KF concentration. Then, the electrochemical reaction is (2).

$$QH_2^{\cdot+} + e^- \rightleftharpoons QH_2 \qquad (2)$$
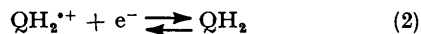
Disproportionation of the Semiquinone.—When the acidity of the media decreases (by increase in the KF concentration), the first reduction wave of the quinone shifts towards negative values as is predicted from equilibrium (1). For KF concentration, >1.5M, a one-step two-electron wave is observed. This implies a disproportionation of the semi-quinone form, according to equation (3). This dispro-

$$2QH_2^{\cdot+} \rightleftharpoons QH^+ + QH_2 + H^+ \qquad (3)$$
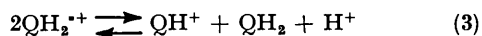
portionation equilibrium is characterized by a constant K_D. This behaviour has already been observed in water–HF mixtures at the same acidity level.

Buffered media. In PF$_5$PF$_6^-$ buffered solution (10 < pH < 12) p-benzoquinone behaves as in strongly basic media. When the acidity increases (for example in BF$_3$–BF$_4^-$ buffer), the half-wave potential of the Q(0)–Q(−I) pair shifts according to equilibrium (1), but the potential of

the Q(−I)–Q(−II) pair which is independent of the acidity level in basic or slightly acidic media, shifts towards positive values, then there must exist a small region in which a monoprotonated hydroquinone form is present, according to the redox equilibrium (4) (pH > 6).

$$QH_2^{\cdot+} + H^+ + e^- \rightleftharpoons QH_3^+ \qquad (4)$$
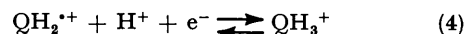
At lower values, the exchange of 2H$^+$ for 1e$^-$ implies the redox equilibrium (5).

$$QH_2^{\cdot+} + 2H^+ + e^- \rightleftharpoons QH_4^{2+} \qquad (5)$$
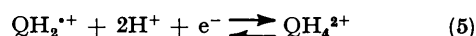
In TaF$_5$–TaF$_6^-$ media (4 < pH < 6), voltammograms are always formed of two monoelectronic waves (Figure 1, Table 1) and the half-wave potential variations of both Q(0)–Q(−1) and Q(−I)–Q(−II) pairs are in accord with equilibria (1) and (4).

Strongly acidic media–SbF$_5$ ($pH < 2$). The quinone form turns from yellow to orange, showing a change in the degree of protonation (QH$^+$ ⟶ QH$_2^{2+}$). The voltammogram shows only one dielectronic wave. The electrochemical reaction is (6). Taking into account the various species in

$$QH_2^{2+} + 2H^+ + 2e^- \rightleftharpoons QH_4^{2-} \qquad (6)$$
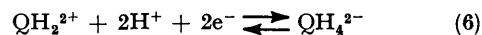
acidic media, a second disproportionation must be con-sidered. The reaction is (7). The equilibrium is character-

$$2QH_2^{\cdot+} + 2H^+ \rightleftharpoons QH_2^{2+} + QH_4^{2+} \qquad (7)$$

ized by a disproportionation constant K_D'.

(2) *Oxidation of* p-*hydroquinone.* The electrochemical oxidation of p-benzoquinone differs from that expected when we consider the electrochemical behaviour of the cor-responding phenol: the height of the oxidation waves seems to depend on the value of the pH (Figure 3), but the
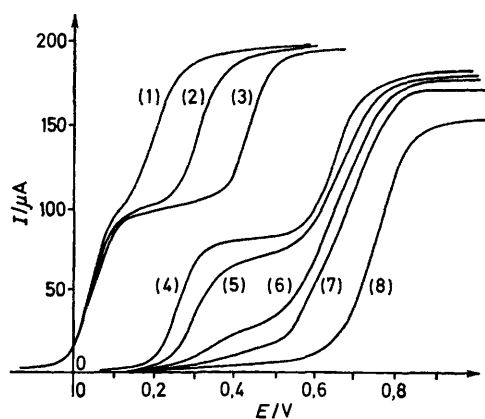

FIGURE 3 Voltammograms of 2.1mM-hydroquinone at a vitreous carbon (diameter 2.5 mm) rotating electrode (w 500 r.p.m.) as a function of the acidity level: (1) 0.1M-KF; (2) and (3) during the neutralization of KF by BF$_3$ (gas); (4) 0.1M-BF$_4^-$ + BF$_3$ (saturated); (5) and (6) after addition of TaF$_5$; (7) 0.1M-TaF$_6^-$ + 0.15M-TaF$_5$; (8) 0.15M-SbF$_5$

half-wave potential shift of both redox couples is in good accord with that of the oxidized forms.

In basic or slightly acidic media (pH > 8) both oxidation waves are of the same magnitude; in more acidic media (4 < pH < 8) the anodic wave of the $Q(-I)-Q(0)$ couple increases while that of $Q(-I)-Q(-II)$ diminishes. For pH < 2, only a double wave is observed corresponding to the $Q(-II)-Q(0)$ couple (Figure 3).

This behaviour of the quinone form, still observed for other non-superacid media,[16-18] shows that kinetic factors should be taken into account in a pH range where we observe at the same time the exchange of H$^+$ and e$^-$, but the half-wave potential shifts are in good accordance with the proposed redox schemes.*

(II) *The N.m.r. Spectra of Protonated Species.*—The electrochemical techniques used so far allow the observation of a change in the protonation stage of the indicator during the electron transfer step. They do not, however, allow us to know precisely the protonation stage of the indicator. For this reason it is necessary to investigate solutions of quinone and hydroquinone in the superacid by n.m.r.
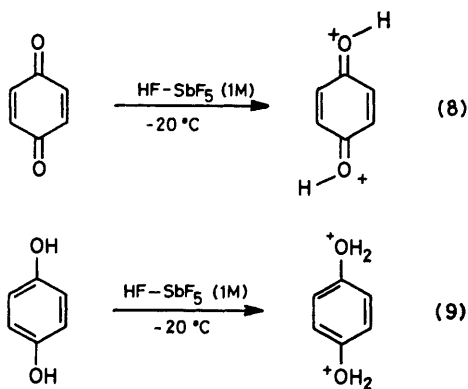
TABLE 2

^{1}H N.m.r. chemical shifts and peak intensities of protonated quinone and hydroquinone in HF–SbF$_5$ (1M)

	H$_a$		H$_b$	
	δ ^{a}	p ^{b}	δ ^{a}	p ^{b}
	8.0	4	14.2	2
	7.5	4	13.1	4

^{a} Chemical shifts measured from external Me$_4$Si. ^{b} p = Relative peak areas.

spectroscopy which has been widely used for structural studies of protonated weak bases.[11,19] When benzoquinone or hydroquinone is dissolved in the HF–SbF$_5$ (1M) medium, at −40 °C, the n.m.r. spectra display a pattern consistent

HF–SbF$_5$ (1M) $\xrightarrow{-20\ °C}$ (8)

HF–SbF$_5$ (1M) $\xrightarrow{-20\ °C}$ (9)

* *p*-Benzoquinone is stable in strongly acidic media at low temperature (< −20 °C). At 0° a slow spontaneous reduction is observed and the hydroquinone form is also slowly decomposed. The stability is sufficient for the scale-time of the hydrodynamic voltammetry.

only with diprotonation of these bases at this acidity. As the proton exchange is very slow at −40 °C the observed spectra correspond to reactions (8) and (9). The structure of the diprotonated base and the chemical shifts are in accord with the band areas (Table 2).

DISCUSSION

E–pH Diagram.—The evolution of the electrochemical properties of benzoquinone and reduced forms can be summarized by a potential–pH diagram (or potential–pF slot where pF = −log [F$^-$], pF and pH being linked by the autoprotolysis constant of the solvent: pF + pH = pK_i = 13.7). The acid–base constants to be considered are, for the quinone, K_1[QH$^+$]/[QH$_2{}^{2+}$], and for the hydroquinone, K_2'[QH$_2$]/[QH$_3{}^+$] and K_3'[QH$_4{}^{2+}$]. The pH stability range of the semiquinone is limited by the disproportionation which appears for pH > pH$_D$ towards basic media and pH < pH$_D'$ towards acidic media. The variations of the half-wave potentials of the pairs $Q(0)-Q(-I)$ and $Q(-I)-Q(-II)$ can be written as a function of the acidity constants according to equations (10) and (11), $E_1°$ and $E_2°$ being the standard

$$E_{1/2}[Q(0)-Q-(I)] = E_1° + \frac{2.3RT}{F}$$
$$\log \{[H^+]/(1 + [H^+]K_1\} \quad (10)$$

$$E_{1/2}[Q(-1)-Q(-II)] = E_2° + \frac{2.3RT}{F}$$
$$\log \{[H^+]^2 + K_3'[H^+] + K_2'K_3'\} \quad (11)$$

potentials of the corresponding pairs at pH 0.

In acidic media (pH < pH$_D$) the variation of E with pH for $Q(0)-Q(-II)$ is given by equation (12). $E_0' =$

$$E_{1/2}[Q(0)-Q(-II)] = E_0' - \frac{2.3RT}{F}\,pH \quad (12)$$

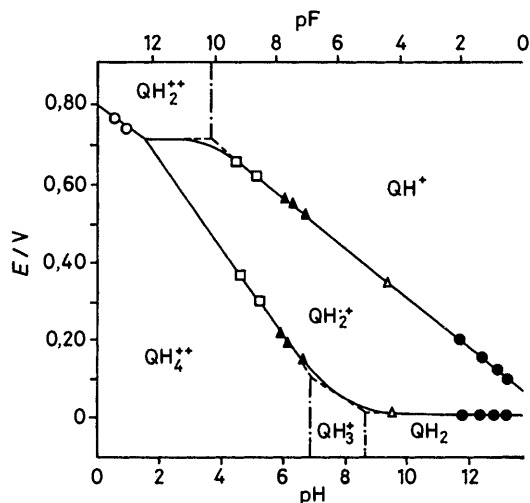0.790 V [standard potential of $Q(0)-Q(-II)$ at pH 0]. A plot of δ versus pH is in Figure 4. Extrapolation of

FIGURE 4 Potential $(E_{1/2})$–pH (or pF) diagrams of *p*-benzo-quinone in HF. Buffers ●, KF; △, PF$_6{}^-$–PF$_5$; ▲, BF$_4{}^-$–BF$_3$; □, TaF$_6{}^-$–TaF$_5$; ○, SbF$_5$

the straight-line sections gives the acidity constants reported in Table 3.

<div align="center">TABLE 3</div>

Acidity constants of p-benzoquinone $Q(0)$ and p-hydroquinone $Q(-II)$, and disproportionation constants of the semiquinone form $Q(-I)$

$pK_1[QH^+]/[QH_2^{2+}]$	3.7
$pK'_2[QH_2]/[QH_3^+]$	8.6
$pK'_3[QH^+]/[QH_4^+]$	6.9
pK_D	16.6
pK_D	−2.6

The disproportionation constants in basic media (K_D) and in acidic media (K_D') have been calculated from the relations (13) and (14) with E_1° 0.949 and E_2° 0.887 V.

$$pK_D' = -\log K_D' = (E_1^\circ - E_2^\circ)\frac{2.3RT}{F} - pK_1 \quad (13)$$

$$pK_D = -\log K_D'/K_1K_2'K_3' \quad (14)$$

The calculated values of the constants are reported in Table 3.

Our results show that p-benzoquinone, monoprotonated in basic media, is diprotonated in acidic media. These results have to be compared with those recently obtained for chloranil,[8] a less basic quinone which is monoprotonated at high acidity (neutral medium in HF) and not diprotonated over the whole acidity range of HF. The results are in good accord with the different acid–base properties of both quinones.

We have observed a stabilization of the semiquinone form $QH_2^{\cdot+}$ which implies new possibilities of disproportionation of the quinone in this intermediate oxidation state. The acidity range of stability of the semiquinone is then $1.8 < pH < 15$. This value corresponds approximately, on the H_0 scale to $-7.1 < H_0 < -10.3$, and on the R_0 (H) scale to $-12.9 < R_0 < -26.1$.

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