Electron Transfer and Agglomeration in the Systems Phenanthrenequinone, Acenaphthenequinone, Their Dianions, Radical Ions, and Dimers

T. L. Staples and M. Szwarc

Contribution from the Department of Chemistry,
State University College of Forestry at Syracuse University,
Syracuse, New York 13210. *Received January 10, 1970*

Abstract: The kinetics of the electron transfer from phenanthrenequinone dianion (PQ^{2-},$2Na^+$) to the parent quinone (PQ) was investigated. The reaction produces a paramagnetic "red" species ($PQ\cdot^-$,Na^+) which dimerizes in a subsequent slower step into a diamagnetic "green" species (D^{2-},$2Na^+$). The results are described by the equations $(PQ^{2-},2Na^+) + (PQ) \rightleftharpoons 2(PQ\cdot^-,Na^+)$ ("red"), $k = 2\text{–}3 \times 10^6\ M^{-1}\ sec^{-1}$; and $2(PQ\cdot^-,Na^+)$ ("red)" $\rightleftharpoons$ $(D^{2-},2Na^+)$ ("green"), $k \sim 10^4\ M^{-1}\ sec^{-1}$. However, the free $PQ\cdot^-$ ions do not dimerize. The spectra of all the pertinent species were examined and fully recorded. The green species further agglomerate forming $(D^{2-},2Na^+)_2$, etc., which are spectrally indistinguishable from (D^{2-},$2Na^+$). The thermodynamics of the reversible dimerization and tetramerization was studied quantitatively. The nature of the dimer was discussed and a tentative structure for it was proposed. The acenaphthenequinone system behaves similarly, its comprehensive study being prevented by technical reasons. The "blue" species, described recently by some investigators and believed to be the acenaphthenequinone dianion (ACQ^{2-}), probably is the diamagnetic dimer of $ACQ\cdot^-$,Na^+. The genuine spectrum of ACQ^{2-},$2Na^+$ was recorded and shown to be unmistakably different from that of the blue species.

Dimerization of ion pairs, or their association into still larger aggregates, is a well-known phenomenon caused by the Coulombic attractions.[1] Such forces, we believe, may facilitate the formation of π–π bonds between suitable partners and yield associates having properties fundamentally different from those of the electrostatically bonded dimers of ion pairs. The salts of radical ions derived from phenanthrenequinone (PQ) and acenaphthenequinone (ACQ) seem to form such π–π bonded dimers.

Experimental Section

9,10-Phenanthrenequinone and 9,10-acenaphthenequinone were acquired commercially and purified by crystallization and vacuum sublimation. The solutions of quinones were prepared on a high-vacuum line, and their concentrations were determined spectrophotometrically. Solutions of phenanthrenequinone were found to be light sensitive, their yellow color rapidly disappearing on exposure to daylight. Therefore, they had to be stored and handled in darkness.

Results

On contact with sodium mirror the quinones are reduced, the reaction being completed after a day or two. Titration with HCl of samples withdrawn after completion of the reduction demonstrated that 2 equiv of sodium reacted with each mole of quinone, *i.e.*, dianions of the quinones were produced. The reduction of phenanthrenequinone by magnesium mirror in THP led to a product possessing only 1 equiv of base/mol of quinone. Apparently, no dianion of quinone is formed with Mg. The dianions are diamagnetic, but paramagnetic species are formed on the addition of the respective quinones.

Reactions Involving Phenanthrenequinone (PQ). The optical spectra of PQ and of its dianion (PQ^{2-},$2Na^+$) are shown in Figure 1. Their shape is not affected either by dilution or by variation of temperature. Addition of a slight excess of PQ to PQ^{2-},$2Na^+$ drastically changes the spectrum; the characteristic 381-nm peak disappears. However, as was first shown by Maruyama,[2] the shape of the resulting spectrum depends on temperature and on the concentration of the product. These spectral variations were investigated by recording the absorption of the relevant solution, kept in an evacuated optical cell which was immersed in a dewar equipped with optical windows and maintained at the desired temperatures. The concentration was then varied by pouring a fraction of the investigated solution into a calibrated side arm attached to the main container and then back-distilling the solvent.

The spectrum indicated that only one species ("red") is present in 10^{-5} *M* solution at 25°, while in 10^{-3} *M* solution below −30° another species ("green") is the only component. Their spectra are displayed in Figure 2. λ_{max} of the red species is at 499 nm (ϵ 0.46 × 10^4), and this species does not absorb light of $\lambda > 600$ nm, while the green species exhibits λ_{max} at 670 (ϵ 0.49 × 10^4) and 440 nm (ϵ 0.46 × 10^4). Accordingly, the OD at 499 nm is a linear function of the OD at 670 nm and of the total concentration, *C*, of the investigated species; *i.e.*

$$\mathrm{OD}(499) = [(\epsilon_{499,G} - \epsilon_{499,R})/\epsilon_{670,G}]\mathrm{OD}(670) + \epsilon_{499,R}C$$

Such a linear relation is fulfilled in THP over the whole accessible range of concentrations and temperatures; however, in THF some curvature was noted at the lowest temperatures and for the highest concentrations. Examination of the spectra revealed that in THF, but not in THP, the absorption maximum of the green species shifts to 660 nm as the temperature is lowered to −80°. This may account for the observed deviations.

On dilution, the equilibrium is displaced toward the red (R) species, as illustrated in Table I. In THP the plots of log [G] (G = the green species) *vs.* log [R] are linear and mutually parallel at each temperature, their slopes being equal to 4 (see, *e.g.*, Figure 3). Ap-

---

[1] R. M. Fuoss and C. A. Kraus, *J. Amer. Chem. Soc.*, **55**, 2387 (1933).

[2] K. Maruyama, *Bull. Chem. Soc. Jap.*, 37, 553 (1964).

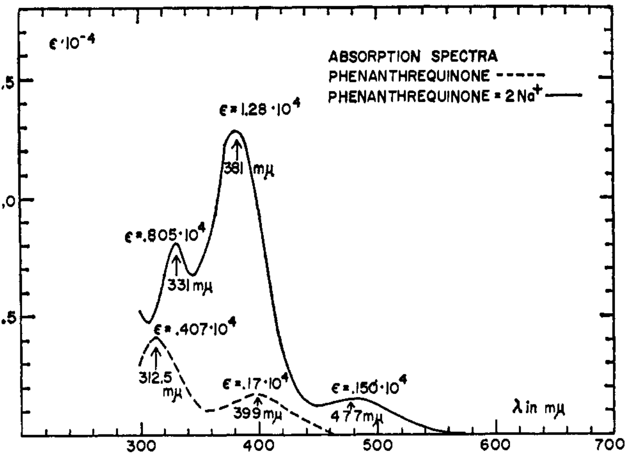


Figure 1. Absorption spectrum of phenanthrenequinone (— — —) and of its dianion, $PQ^{2-},2Na^+$ (——) in THP.

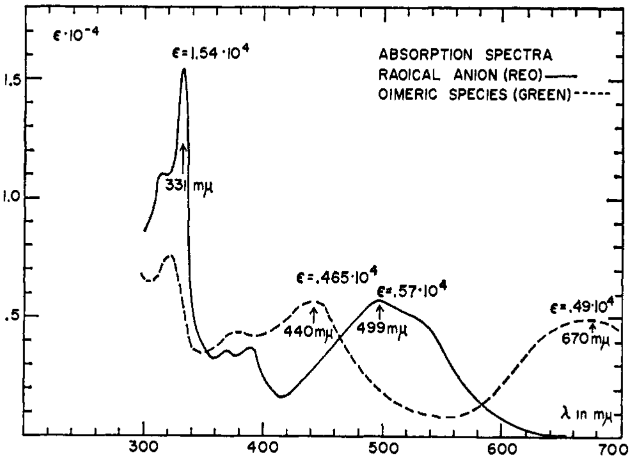


Figure 2. Absorption spectrum of phenanthrenequinone radical anion, $PQ\cdot^-,Na^+$ (the "red" species) and of its diamagnetic dimer (or tetramer), $D^{2-},2Na^+$ (the "green" species) in THP.

parently, in this solvent G is a tetramer. In view of Maruyama's results,[2] R is identified with the paramagnetic radical ion ($PQ\cdot^-,Na^+$) and G with its diamagnetic aggregate, denoted, for reasons which will be obvious later, by $(D^{2-},2Na^+)_2$.

Table I. $4(PQ\cdot^-,Na^+) \rightleftarrows (D^{2-},2Na^+)_2$[a]

Expt	OD_{500}	OD_{670}	$[PQ\cdot^-,Na^+] \times 10^4$, N	$[D^{2+},2Na^+]_2 \times 10^4$, N
A1	2.78	3.43	2.38	6.96
A2	1.58	1.42	1.74	2.88
A3	1.02	0.600	1.35	1.22
A4	0.601	0.120	0.966	0.244
A5	0.375	0.025	0.640	0.0507
B1	3.06	3.84	2.56	7.79
B2	1.85	1.77	1.95	3.59
B3	1.22	0.750	1.60	1.52

Solvent, tetrahydropyrane; temperature, 25°.

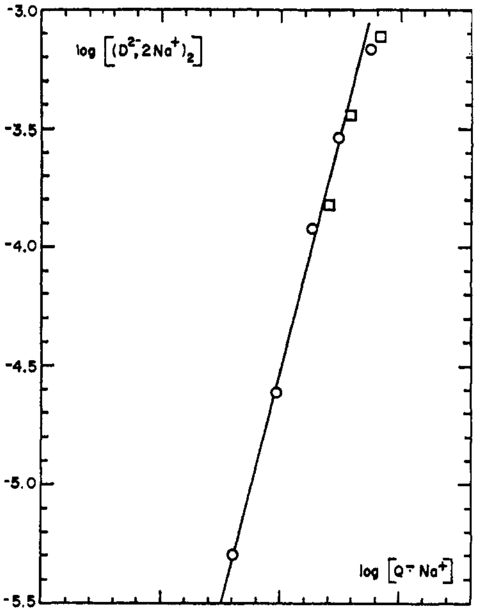


Figure 3. Log $[(D^{2-},2Na^+)_2]$ = log [G] (the "green" species) *vs.* log $[PQ\cdot^-,Na^+]$ = log [R] (the "red" species) in THP at 25°. The concentrations are given in normalities.

A more complex situation is encountered in the THF system. The plots of log [G] *vs.* log [R] become steeper as the temperature decreases and curve upward at higher concentrations. Apparently, several spectrally undistinguishable green species are present in THF, and the equilibrium is governed then by the equations

$$\underset{\text{red}}{2[PQ\cdot^-,Na^+]} \rightleftharpoons \underset{\text{green}}{[D^{2-},2Na^+]}$$

$$\underset{\text{green}}{2[D^{2-},2Na^+]} \rightleftharpoons \underset{\text{green}}{[D^{2-},2Na^+)_2]} \qquad \text{etc.}$$

Denoting by K_1, K_2, etc., the successive equilibrium constants, and by [G] the sum $2[D^{2-},2Na^+] + 4[(D^{2-}2Na^+)_2] + \ldots$, we find

$$[G] = 2K_1[PQ\cdot^-,Na^+]^2 + 4K_2K_1^2[PQ\cdot^-,Na^+]^4 \ldots$$

Higher terms are assumed to be insignificant. In the THP system, $2K_2K_1[PQ\cdot^-,Na^+]^2 \gg 1$ and therefore the first term is not significant, whereas both terms are important in the THF system. Hence, the plots of $[G]/[PQ\cdot^-,Na^+]^4$ *vs.* $1/[PQ\cdot^-,Na^+]^2$ or $[G]/[PQ\cdot^-,Na^+]^2$ *vs.* $[PQ\cdot^-,Na^+]^2$ should be linear for each temperature. Such plots are shown in Figures 4a and 4b, and their slopes and intercepts provide the data needed for the calculation of K_1 and K_2.

The $K_2K_1^2$ values obtained in the THP system are listed in Table II, and the plot of log $K_2K_1^2$ *vs.* $1/T$ is

Table II. Temperature Dependence of the Equilibrium Constant, $K_2K_1^2$, for $4(PQ\cdot^-,Na^+) \rightleftarrows (D^{2-},2Na^+)_2$ in Tetrahydropyrane

Temp, °C	$[PQ\cdot^-,Na^+] \times 10^4$, M	$[(D^{2-},2Na^+)_2] \times 10^4$, M	$K_2K_1^2 \times 10^{-10}$, M^{-3}
9.8	0.74	0.24	21
7.1	0.72	0.27	26
0.3	0.67	0.32	42
−5.6	0.62	0.38	66
−9.6	0.58	0.44	94
−14.9	0.52	0.50	171
−19.2	0.48	0.55	250
−22.8	0.45	0.59	345
−25.1	0.425	0.62	470
−30.5	0.385	0.69	775
−39.6	0.300	0.79	2510
−43.3	0.270	0.83	4030

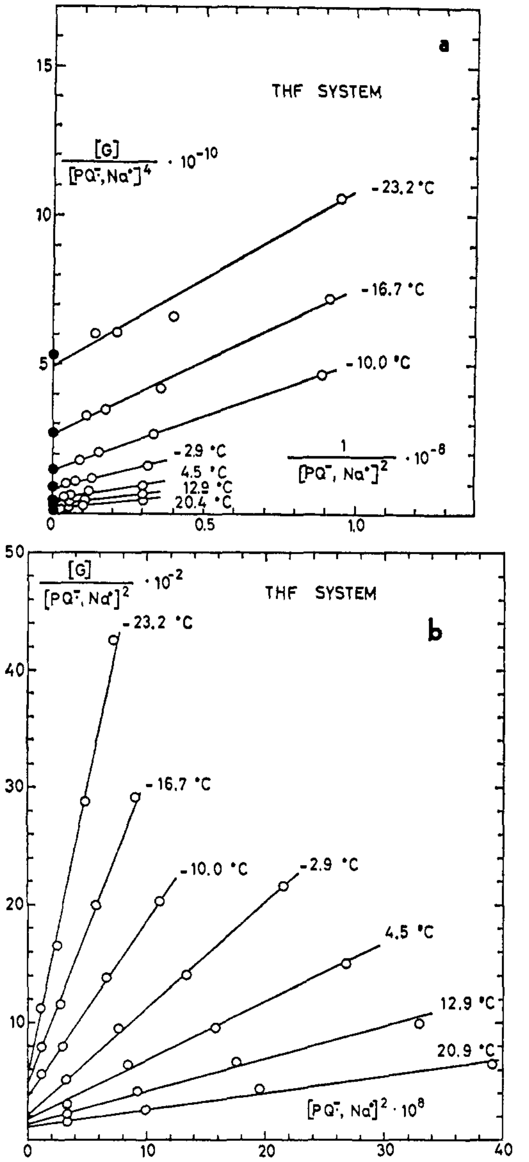


Figure 4. (a) Plot of $[G]/(PQ\cdot^{-},Na^{+}]^4$ *vs.* $1/[PQ\cdot^{-},Na^{+}]^2$. (b) Plot of $[G]/[PQ\cdot^{-},Na^{2+}]^2$ *vs.* $[PQ\cdot^{-},Na^{+}]^2$. Both for the THF system. Temperatures are marked on the respective lines.

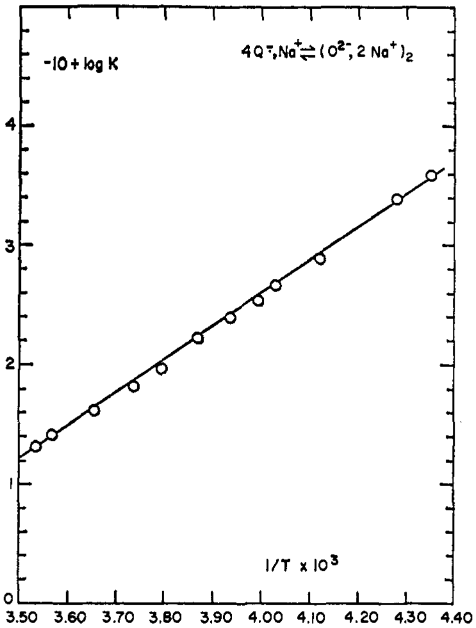


Figure 5. Plot of log $K_1{}^2K_2$ *vs.* $1/T$ for the THP system.

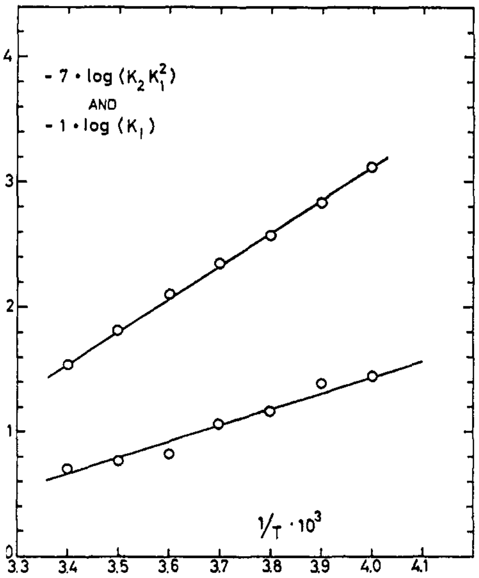


Figure 6. Plot of log $K_1{}^2K_2$ and log K_1 *vs.* $1/T$ for the THF system.

shown in Figure 5. The results lead to $\Delta H = 2\Delta H_1 + \Delta H_2 = 6.5$ kcal/mol and $\Delta S = 2\Delta S_1 + \Delta S_2 = 5.8$ eu. The data obtained in the THF system are collected in Table III, and the respective van't Hoff plots for $K_2K_1{}^2$ and K_1 are shown in Figure 6. The values of ΔH_1, ΔH_2, and $2\Delta H_1 + \Delta H_2$ are listed at the bottom of Table III. It seems that in the THF systems K_2 is temperature independent, its value being about $(16 \pm 5) \times 10^4\ M^{-1}$.

Table III. Temperature Dependence of the Equilibrium Constants Established in the THF System: $2(PQ\cdot^{-},Na^{+}) \rightleftarrows (D^{2-},2Na^{+})$, K_1; $2(D^{2-},2Na^{+}) \rightleftarrows (D^{2-},2Na^{+})_2$, K_2

Temp, °C	$K_2K_1{}^2 \times 10^{-10}$, M^{-3}	$K_1 \times 10^{-2}$, M^{-1}	$K_2 \times 10^{-4}$, M^{-1}
20.9	0.0345	0.51	13
12.5	0.0655	0.58	19
4.5	0.125	0.66	28
−2.9	0.22	1.1	18
−10.0	0.37	2.0	9
−16.7	0.68	2.5	11
−23.2	1.3	2.8	17
$2\Delta H_1 + \Delta H_2 = -11.7$ kcal/mol		$2\Delta S_1 + \Delta S_2 = \sim 0$ eu	
$\Delta H_1 = -6$ kcal/mol		$\Delta S_1 = -13$ eu	
$\Delta H_2 = +0.3$ kcal/mol		$\Delta S_2 = +26$ eu	

The associations discussed above involve ion pairs only. The free $PQ\cdot^{-}$ anions do not agglomerate; only the red species are present in hexamethylphosphoramide (HMPA), a solvent in which virtually all ion pairs are dissociated.[3] A solution of $PQ\cdot^{-}$ in HMPA was prepared by adding a small excess of PQ to sodium biphenylide $(B\cdot^{-},Na^{+})$ in that solvent.

The red HMPA solution is paramagnetic, and its esr spectrum matches that reported by Maruyama[2] for $PQ\cdot^{-}$ free radical anions in liquid ammonia. Interestingly, on freezing the solvent, the resulting mass becomes green, but turns red again on melting. Ap-

---

(3) A. Cserhegyi, J. Jagur-Grodzinski, and M. Szwarc, *J. Amer. Chem. Soc.*, **91**, 1892 (1969).

parently, separation of phases, caused by freezing, brings the $PQ\cdot^-$ species close together and leads to their dimerization.

Magnesium Salt of $PQ\cdot^-$. The spectrum of the magnesium salt of $PQ\cdot^-$ in THP shows peaks at 480–500 and 655 nm, indicating that both the red and the green species are present in this system. The shape of this spectrum is not affected by dilution (from 3×10^{-3} to $3 \times 10^{-4}\,N$), implying that the equilibrium is represented by the equation

$$\underset{\text{red}}{Mg^{2+}(PQ\cdot^-)_2} \rightleftharpoons \underset{\text{green}}{(D^{2-},Mg^{2+})}$$

in which the green species dominates. This observation is important. It indicates that the electrostatically bonded paramagnetic pair is different from the diamagnetic pair denoted by D^{2-}.

Kinetic Studies of the Electron-Transfer Reaction $PQ^{2-},2Na^+ + PQ \rightarrow$ Products. Kinetics of the electron-transfer process $PQ^{2-},2Na^+ + PQ$ was investigated in THP at room temperature using the Durrum stop-flow spectrophotometer adapted for handling air- and moisture-sensitive solutions. The reaction was followed by monitoring the OD at 380–390, 500, and 670 nm about 6 msec after mixing the reagents. The $PQ^{2-},2Na^+$ dianions strongly absorb at 381 nm, while the absorption of the red and green species is weak in this region. Moreover, at this wavelength the latter two species have similar extinction coefficients (see Figures 1 and 2), and therefore, any conversion of R to G, or *vice versa*, does not affect the OD_{381} which measures the rate of the electron-transfer process.

Table IV. Kinetic Results for the Electron Transfer $PQ^{2-},2Na^+ + PQ \rightarrow 2(PQ\cdot^-,Na^+)$ in THP at 25°

$[PQ^{2-},2Na^+]_0 \times 10^4$, M	$[PQ]_0 \times 10^4$, M	$10^{-6}k$(electron transfer), M^{-1} sec^{-1}
2.6	2.3	1.6
2.9	2.5	1.6
2.9	3.7	3.5
2.9	4.0	2.8
2.9	7.6	2.9
4.0	21	Too fast to measure

The oscilloscope tracings obtained at 381 nm led to the second-order rate constants listed in Table IV. The rate of the electron transfer is about $2\text{–}3 \times 10^6\ M^{-1}$ sec^{-1}, although there is some scatter of the data.

At high concentration of the reagents the electron transfer is completed in a time too short to be measured. However, these experiments show that the first product formed in the transfer reaction is the radical ion, $PQ\cdot^-$,Na^+, and give the rate of its dimerization into $D^{2-},2Na^+$. After completion of the electron transfer, the OD_{500} decreases with time, whereas the absorption at 670 nm increases, *i.e.*

$$PQ^{2-},2Na^+ + PQ \longrightarrow 2(PQ\cdot^-,Na^+)$$

and the latter subsequently dimerizes into the green, diamagnetic $D^{2-},2Na^+$

$$2(PQ\cdot^-,Na^+) \longrightarrow D^{2-},2Na^+$$

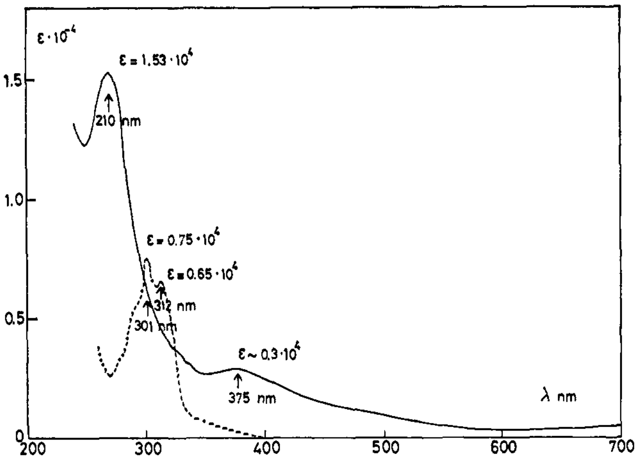


Figure 7. Spectra of acenaphthenequinone (— — —) and the sodium salt of its dianion, $ACQ^{2-},2Na^+$ in THP (———).

The bimolecular rate constant of the dimerization was calculated from the oscilloscope tracers, the pertinent data being given in Table V. The dimerization is much slower than the electron transfer; its rate constant is only $\sim 10^4\ M^{-1}$ sec^{-1}. The reaction $2(D^{2-},2Na^+) \rightarrow (D^{2-},2Na^+)_2$ is not revealed by our kinetic studies because its progress does not affect the spectrum of the reacting solution.[3a]

Table V. Kinetic Results for the Dimerization $2(PQ\cdot^-,Na^+) \rightarrow DPQ^{2-},2Na^+$ in THP at 25°

$[PQ^{2-},2Na^+]_0 \times 10^4$, M	$[PQ]_0 \times 10^4$, M	$[PQ\cdot^-,Na^+]_0 \times 10^4$	$10^{-4}k$(dimerization), M^{-1} sec^{-1}
5.3	2.4	4.8	1.1
7.6	2.4	4.8	1.2
6	3.1	6.2	0.7
6	2.2	4.4	0.7

The Acenaphthenequinone (ACQ) System. The spectra of acenaphthenequinone and of its diamagnetic dianion ($ACQ^{2-},2Na^+$) in THF and THP are shown in Figure 7. The titration of the latter gives the anticipated 1:2 ratio for ACQ to alkali.

Addition of the quinone to the solution of the dianions in THF or THP leads to a blue coloration with a pronounced absorption at 560 nm. In HMPA, electron transfer from sodium biphenylide to an excess of the quinone produces a nearly colorless, paramagnetic solution giving an esr signal comparable to that reported for the $ACQ\cdot^-$ radical ion.[4,5] At high concentrations, or on cooling, a reversible process converts the radical ions into some diamagnetic species; the esr signal diminishes and the solution becomes blue. Similar reversible changes were observed in THF and in dimethoxyethane (DME) by two groups of workers,[5,6] and were interpreted in terms of disproportionation of radical ions into dianions, $2PQ\cdot^- \rightleftharpoons PQ^{2-} + PQ$.

(3a) The limited range of conditions within which this reaction was studied does not permit us to exclude definitely the mechanism $2(PQ\cdot^-,Na^+) \rightleftharpoons D^{2-},2Na^+$ establishing rapidly a minute equilibrium concentration of the dimer, followed by the rate-determining step $2D^{2-},2Na^+ \rightarrow (D^{2-},2Na^+)_2$. However, this kinetically fourth order reaction seems to be unlikely.

(4) E. Warhurst and A. M. Wilde, *Trans. Faraday Soc.*, **65**, 1413 (1969).

(5) R. Dehl and G. K. Fraenkel, *J. Chem. Phys.*, **39**, 1793 (1963).

(6) A. G. Evans, J. C. Evans, and E. H. Godden, *J. Chem. Soc. B*, 546 (1969).

Thus, the equilibrium constant of the presumed disproportionation was calculated[6] by assuming that the spectrum of the dianions ($PQ^{2-},2Na^+$) has an absorption maximum at 560 nm. In view of our results, this assumption is erroneous.

The nature of the blue species was not established by our studies. Analogy with the PQ system suggests that this might be a diamagnetic, $\pi-\pi$-bonded dimer of the radical ion. It is significant that its proportion *increases* as the solution becomes more concentrated, while a *simple* disproportionation, *e.g.*

$$2(ACQ\cdot^-,Na^+) \rightleftharpoons (ACQ^{2-},2Na^+) + ACQ$$

should be concentration independent.

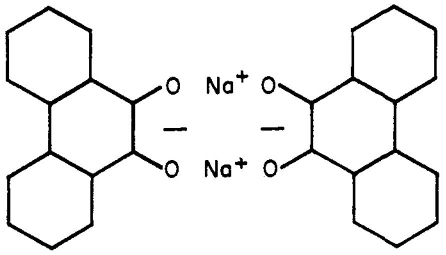
No blue band appears in the spectrum of $ACQ\cdot^-$ formed in HMPA. This spectrum is structureless: the absorption rapidly increases below 340 nm, but falls virtually to zero at $\lambda > 370$ nm.

Systematic studies of the ACQ system were prevented by the precipitation of the blue species, a phenomenon reported also by Evans, *et al.*,[6] and consequently these investigations were not pursued further.

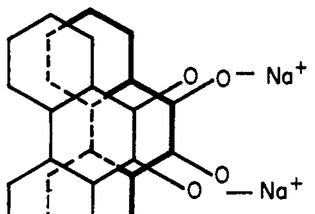
Discussion

Two distinct problems will be considered: (1) the mechanism of the electron transfer, $PQ^{2-},2Na^+ + PQ \rightarrow 2(PQ\cdot^-,Na^+)$, and (2) the phenomenon of association leading to the formation of the diamagnetic dimer ($D^{2-},2Na^+$) and of its agglomerate.

The electron transfer from $PQ^{2-},2Na^+$ to PQ proceeds simultaneously with Na^+ ion transfer. This imposes limitations on the conceivable structures of the transition state of the process, namely, the two Na^+ ions and the four oxygens have to be grouped together. Examples of such structures are shown by A and B.

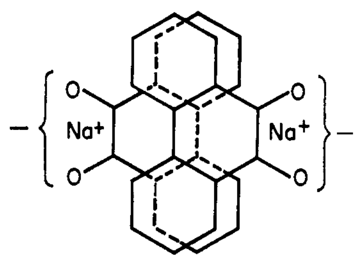


A



B

These structures cannot be attributed to the diamagnetic dimer ($D^{2-},2Na^+$) because in such a case the dimer, and not the monomeric radical ions ($PQ\cdot^-,Na^+$), would be the first product of the electron transfer. Since the reverse sequence of events was demonstrated by our studies, the tentative structure C is proposed for the diamagnetic dimer.



C

The two aromatic moieties are assumed to be placed one upon the other and bound by the transannular $\pi-\pi$ interaction. The proposed location of the oxygen atoms minimizes the electrostatic repulsion, while the presence of the counterions, which probably are partially squeezed into the sandwich, stabilizes the structure. Although this proposal need not be the unique solution of our problem, it accounts, nevertheless, for all our observations.

The transannular $\pi-\pi$-bonded structure of the dimer is indicated by its optical spectrum. The dimer absorbs at *longer wavelength* than the monomeric radical ion; such behavior is also observed in other transannular compounds, *e.g.*, in paracyclophane[7-11a] or its analogs.[11b] However, the $\pi-\pi$ bonding does not suffice to assure the stability of the dimer, and the supporting attractive interaction is provided by the binding caused by the counterions. Its importance is indicated by the lack of dimerization of the free $PQ\cdot^-$ ions (as shown by their behavior in the HMPA solution) and by the relation between the degree of agglomeration and the size of the bonding cation—the smaller the cation the more extensive the association.[2]

Studies of the magnesium salt provide valuable information about the structure of the dimer. The optical spectrum of this salt, as well as its paramagnetic behavior, indicates again the presence of two species, *i.e.*, the red and green ones. Their proportions depend on temperature, but not on their concentrations. It is plausible to represent the red species by A or B and the green one by C. In the latter the Mg^{2+} cation is visualized as squeezed in the middle of the sandwich or rapidly oscillating between the two binding sites. The conversion of A or B into C requires the surmounting of a potential energy barrier, a condition necessary for the existence of two thermodynamically different species, whereas it is difficult to visualize such a barrier preventing, *e.g.*, the conversion of A into B.

Covalently bonded dimers of radical ions are well known, ketyl of benzophenone being a classic example.[12] Radical ions of quinoline and of other heteroaromatics apparently are also covalently bonded.[13] Such a dimerization leads, however, to a hypsochromic shift in the light absorption; *e.g.*, the

---

(7) M. T. Vala, J. Hoebig, and S. A. Rice, *J. Chem. Phys.*, **43**, 886 (1965).

(8) M. T. Vala, I. H. Hillier, S. A. Rice, and J. Jortner, *ibid.*, **44**, 23 (1966).

(9) I. H. Hillier, L. Glass, and S. A. Rice, *ibid.*, **45**, 3015 (1966).

(10) J. W. Longworth and F. A. Bovey, *Biopolymers*, **4**, 1115 (1966).

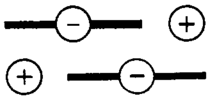
(11) (a) A. Ishatami and S. Nagakura, *Mol. Phys.*, **12**, 1 (1967); (b) J. R. Froines and P. J. Hagerman, *Chem. Phys. Lett.*, **4**, 135 (1969).

(12) N. Hirota and S. I. Weissman, *J. Amer. Chem. Soc.*, **86**, 2537, 2538 (1964).

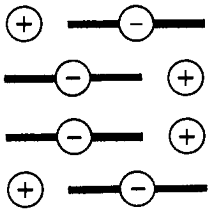
(13) J. Chaudhuri, S. Kume, J. Jagur-Grodzinski, and M. Szwarc, *ibid.*, **90**, 6421 (1968).

free quinoline·⁻ radical anion (in HMPA) has absorption maxima at 715 and 750 nm, whereas its dimer (formed in THF) absorbs at λ_{max} 360 nm. Therefore, the bathochromic shift observed in the dimerization of $PQ\cdot^-,Na^+$ is incompatible with covalent bonding.

The dimerization of the dimers (tetramerization) is an interesting phenomenon. The available thermodynamic data obtained in the THF system show that the reaction $2(PQ\cdot^-,Na^+) \rightleftharpoons (D^{2-},2Na^+)$ is exothermic and decreases the entropy of the system. This decrease may be accounted for by the loss of translational freedom of one particle. Apparently the degree of solvation (physical and chemical) of the dimer is comparable to that of the two monomers, a reasonable conclusion if the dimer is represented schematically by



and its agglomerate by



This implies a substantial desolvation of the reagents when dimers are converted into tetramers. This indeed is shown by our data.

The magnesium salts cannot tetramerize if Mg^{2+} is deeply squeezed into the sandwich of the dimer. This again seems to be the case.

Acknowledgment. The financial support of this study by the National Science Foundation and by the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

Vibration–Vibration Coupling in the Dissociation of a Diatomic Gas[1]

D. L. S. McElwain and H. O. Pritchard

Contribution from the Centre for Research in Experimental Space Science, York University, Downsview, Ontario, Canada. *Received December 31, 1969*

Abstract: Our previous formulation of the master equation for the dissociation of a dilute diatomic gas is extended to the nondilute case by the inclusion of V–V transitions. Using existing experimental and theoretical data for other molecules, estimates are made for the V–V transition probabilities in H_2. The master equation is solved for the dissociation of a series of $M-H_2$ mixtures at 2000°K, and the results are compared with those previously obtained for the same reaction at infinite dilution. The present solution is achieved by brute-force integration, continued through the transient period and out into the pseudosteady regime. Under weak V–V coupling conditions, the system is relatively well behaved, and it is possible to define (almost) unique values for the dissociation rate constants $k_{d.M}$ and k_{d,H_2}. However, when V–V transitions are very efficient, nonintegral rate laws of the form rate $= k_d{}^*[M]^x[H_2]^y$ with $x < 1 < y$ are obtained; the reaction orders x and y are constant only over limited concentration ranges, and the total order $m = (x + y)$ is always less than two.

We have shown recently, that it is possible, assuming a set of T–V transition probabilities, to solve the coupled vibration–dissociation relaxation problem for a gas resembling H_2 at infinite dilution[2,3] (equations and tables in these two papers will be designated hereinafter by prefixes I and II, respectively). This calculation neglected processes of the type

$$H_2(v_1J_1) + H_2(v_2J_2) \rightleftharpoons H_2(v_3J_3) + H_2(v_4J_4) \qquad (1)$$

$$H_2(v_1J_1) + H_2(v_2J_2) \rightleftharpoons H_2(v_3J_3) + H + H \qquad (2)$$

which are known to be important in any dissociation or recombination reaction, even at the highest experimentally feasible dilutions.[4] We have already alluded to the mathematical difficulties introduced by considering such V–V processes,[2] but a recapitulation of our earlier results[3] shows that it is possible to deduce the effect of including (1) and (2) in the relaxation process without being able to solve the complete problem.

We found[3] that, if H_2 was heated instantaneously from 0 to 2000°K, there were very rapid changes in the vibrational populations for a period lasting a little over 10^{-8} sec. At the end of this transient period,[5] a pseudosteady state was achieved, and this was maintained throughout the remainder of the dissociation process

---

(1) Research supported by the Defence Research Board of Canada (Grant No. 9550-35) and by the National Research Council of Canada.

(2) V. A. LoDato, D. L. S. McElwain, and H. O. Pritchard, *J. Amer. Chem. Soc.*, **91**, 7688 (1969). (We reproduce here for the reader's convenience a brief outline of the notation used in our previous work. n_i represents the population of state i in molecules/cc, $n_{(n+1)}$ the number per cc of dissociated molecules and n_n the concentration of transient pairs through which all *chemical* events proceed. P_{ji} is the probability per collision of a transition from state i to state j, $\bar{P}_{in}$ is the mean probability per collision that a transient pair will be deactivated to state i, and $\bar{P}_{(n+1)n}$ is the mean probability per collision that it will be dissociated into two atoms; the assumption that pairs are always in equilibrium with atoms implies that $\bar{P}_{(n+1)n}$ and $\bar{P}_{n(n+1)} \rightarrow \infty$ while still maintaining a ratio required by detailed balancing. $\bar{n}_i$, etc., represent equilibrium populations at the temperature of the experiment.)

(3) D. L. S. McElwain and H. O. Pritchard, *ibid.*, **91**, 7693 (1969).

(4) H. O. Pritchard in "Transfer and Storage of Energy by Molecules," Vol. 2, Wiley, London, 1969, pp 368–389.

(5) B. Widom, *Science*, **148**, 1555 (1965).