ylene at 5 position), 2.17 (m, 0.24 H, allylic, corresponding to 94% deuterium incorporation at positions 2 and 6), and 4.58 (s, 2 H, exo methylene); the mass spectrum had a main parent peak at 119 mass units. Anal. Calcd for C_8H_{14}: C, 87.19; H, 12.81. Found: C, 87.15; H, 12.94.

References and Notes

(1) (a) This work was supported by the National Science Foundation (Grant No. MPS-72-05006) and by the donors of the Petroleum Research Fund, administered by the American Chemical Society; (b) National Science Foundation Trainee, 1969–1970.

(2) (a) The conformational preference of the lone pair in piperidines has recently been reviewed: J. B. Lambert and S. I. Featherman, *Chem. Rev.*, **75**, 611 (1975). (b) For leading references on the π electron steric effect, see J. P. Idoux, V. S. Cantwell, J. Hinton, S. O. Nelson, P. Hollier, and R. Zarillo, *J. Org. Chem.*, **39**, 3946 (1974).

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Effect of Solvents and Counterions on the Equilibrium and Kinetics of Disproportionation of Tetracenide Radical Ions

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Abstract: We studied the disproportionation of the salts of tetracenide radical anions, $2Te\cdot^-,Cat^+ \rightleftarrows Te + Te^{2-},2Cat^+$, involving Li^+, Na^+, K^+, and Cs^+ cations. The reaction was investigated in the following solvents: tetrahydrofuran, dioxane, and diethyl ether. The disproportionation constant varies within ten orders of magnitude, being as low as 6×10^{-9} for the lithium salt in tetrahydrofuran and as high as 16.4 in diethyl ether. The kinetics of disproportionation was investigated by flash photolysis. The rate constant of disproportionation is very low for the lithium salt in tetrahydrofuran ($\sim 36\ M^{-1}\ s^{-1}$), higher for the other salts in that solvent (10^4–$10^5\ M^{-1}\ s^{-1}$), and very high for the Li^+ and Na^+ salts in dioxane and diethyl ether (10^6–$10^8\ M^{-1}\ s^{-1}$). The rate constants of reapportionation, $Te + Te^{2-},2Cat^+ \rightarrow 2Te\cdot^-,Cat^+$, are in the range of 10^9–$10^{10}\ M^{-1}\ s^{-1}$ for most of the investigated systems; however, for the Li salt in DOX its value is as low as $1.1 \times 10^8\ M^{-1}\ s^{-1}$ and still lower in diethyl ether, namely $3.6 \times 10^6\ M^{-1}\ s^{-1}$. The significance of these results is discussed.

The thermodynamics of the disproportionation of radical anions

$$2A\cdot^- \rightleftarrows A + A^{2-} \qquad K_{\text{dispr}}$$

was extensively studied by polarographic[1] and potentiometric[2] techniques. These methods provide us with the first and the second reduction potentials of the parent compounds (ϵ_1 and ϵ_2), and therefore allow us to calculate K_{dispr} from the relation $0.06 \log K_{\text{dispr}} = \epsilon_2 - \epsilon_1$. Planar aromatic hydrocarbons were the main objects of these studies. The results showed that K_{dispr}'s are very small, 10^{-5} or less, implying that these disproportionations are highly unfavorable.

Exceptions were known. For example, the disproportionation equilibria of radical anions of tetraphenylethylene,[3] stilbene,[4] or cyclooctatetraene[5] are shifted far to the right, the respective equilibrium constants exceeding 1000 for some of those systems. However, these findings were rationalized by invoking the operation of special factors, e.g., those caused by changes of geometry of the reduced species. Since the reduction of planar aromatic hydrocarbons is not associated with any drastic changes of their geometry, the smallness of the respective K_{dispr}'s remained undisputed.

Subsequent studies, which utilized spectrophotometric and ESR techniques, showed that the disproportionation of radical anions is more complex than has been believed.[6] The radical anions may exist as free ions or be paired with counterions, while three distinct ionic species involve the dianions, namely A^{2-}, A^{2-},Cat^+, and $A^{2-},2Cat^+$. Hence, three elementary equilibria participate in a disproportionation:

$$2A\cdot^-,Cat^+ \rightleftarrows A + A^{2-},2Cat^+ \qquad K_1$$

$$A\cdot^- + A\cdot^-,Cat^+ \rightleftarrows A + A^{2-},Cat^+ \qquad K_2$$

$$2A\cdot^- \rightleftarrows A + A^{2-} \qquad K_3$$

These elementary equilibrium constants, referred to the same system, may greatly differ in their values, e.g., for the system sodium salt of tetraphenylethylene radical anion in THF at 25 °C $K_1 = 400$, $K_2 = 3.6$, and K_3 is probably as low as 10^{-10}.

Table I. Heat and Entropy of the Disproportionation of Radical Anions

System	Temp range, °C	ΔH°, kcal/mol	ΔS°, cal/(deg mol)
$\mathrm{Te}\cdot^-,\mathrm{Na}^+$; DOX	20–60	4.0	8.0
$\mathrm{Te}\cdot^-,\mathrm{Na}^+$; DEE	−60–20	9.5	27.0
$\mathrm{Te}\cdot^-,\mathrm{Li}^+$; DEE	Becomes endothermic below −30 °C		

The nature of solvent and counterion may affect these values, e.g., $K_1 = 9$ for the lithium salt of tetraphenylethylene in THF,[7] i.e., it is ~40 times lower than for its sodium salt.

The effect of counterions and solvents upon the disproportionation constants of the planar anthracenide and perylenide salts was revealed by the recent potentiometric studies of Rainis and Szwarc[8] and by Parker and his coworkers. Although the respective K_1's varied by a factor greater than 1000 when Li^+ was substituted by Cs^+ and THF by DME, their values were still small ranging from 10^{-5} to 10^{-8} for anthracenide ion pairs and from 10^{-6} to 10^{-10} for those of perylenides. It was surprising, therefore, to find in the present studies that the disproportionation constant of the planar lithium tetracenide is as large as 0.06 in dioxane (DOX) and even larger for the lithium pair in diethyl ether (DEE), namely 16.4 at ambient temperature. These findings are significant because they demonstrate that factors other than steric ones may make the dianion salts more stable than those of the radical anions. We decided therefore to fully investigate the thermodynamics and kinetics of these disproportionations in a variety of solvents, for different counterions, and over a wide temperature range.

Our knowledge of the kinetics of the disproportionation of radical anions is scanty. Studies of only two systems have been reported: tetraphenylethylene[7,9] and cyclooctatetraene.[10] Flash photolysis of an equilibrated solution of radical anions ($\mathrm{A}\cdot^-$), dianions (A^{2-}), and their parent compound A, leads to ejection of electrons. In systems containing a high proportion of $\mathrm{A}\cdot^-$, an electron ejected from one radical anion may be captured by another and thus an excess of A and A^{2-} is produced by the flash. When dianions and the parent compound form a high proportion of the equilibrated mixture, an electron ejected from A^{2-} may be captured by A, and then the concentration of radical anions increases after the flash and becomes higher than their equilibrium value. In either case the equilibrium is disturbed and the system relaxes to its equilibrium state in the dark period following the flash. The return to equilibrium is monitored by spectrophotometric or ESR techniques and the results are combined with the equilibrium studies, allowing one to determine the rate constants of the forward and backward reactions. This approach, described in detail elsewhere,[7,9] was utilized in the present studies of the kinetics of the disproportionation of tetracenide radical anions.

Results

Disproportionation constants of the tetracenide salts in tetrahydrofuran (THF) are very small, 10^{-5} or less. They were determined by the potentiometric technique described elsewhere.[2b] However, in dioxane (DOX) and diethyl ether (DEE) the proportion of tetracene dianions in equilibrated mixtures of the parent compound and its radical anions is sufficiently high to permit spectrophotometric determination of their concentration. The relevant extinction coefficients were determined for each salt and solvent system and the disproportionation constants were calculated from the relation

$$[\mathrm{Te}][\mathrm{Te}^{2-},2\mathrm{Cat}^+]/[\mathrm{Te}\cdot^-,\mathrm{Cat}^+]^2 = K_{\mathrm{dispr}}$$

[the dissociation of the ionic aggregates being negligible in those solvents (DOX and DEE)]. The disproportionation constants of the sodium salt in dioxane were determined for temperatures ranging from 19 to 65 °C and of the lithium and sodium salts in diethyl ether in the range −60 °C to ambient temperature. The details of these studies will be reported later, but the relevant values of ΔH° and ΔS° are listed here in Table I. The investigated disproportionations are endothermic and are associated with an increase in the entropy of the system.

The flash-photolytic technique described previously[7,9] led to bleaching of the absorption of radical anions when the salts are dissolved in THF. In this solvent system either the initial concentration of the dianions is vanishingly small (in $\mathrm{Te} + \mathrm{Te}\cdot^-$ mixtures) or the initial concentration of the hydrocarbon is too low for detection (in $\mathrm{Te}\cdot^- + \mathrm{Te}^{2-}$ mixtures). In either case, the concentration of the dianions increases after the flash and it decays to its original value in the dark period of the reaction. At any time of that period ($t > 30\ \mu\mathrm{s}$) the $-\Delta[\mathrm{Te}\cdot^-] = 2\Delta[\mathrm{Te}^{2-}]$ and no other transient is seen in the course of the process (triplets, if formed, are rapidly quenched by $\mathrm{Te}\cdot^-$ radical anions[11]).

The general treatment of the kinetics of disproportionation leads to the relation

$$\begin{aligned}\ln \{[\mathrm{Te}]_e + [\mathrm{Te}^{2-},2\mathrm{Cat}^+]_e + 4K_{\mathrm{dispr}}[\mathrm{Te}\cdot^-,\mathrm{Cat}^+]_e \\ - (1 - 4K_{\mathrm{dispr}})X\}/X = k_{-1}([\mathrm{Te}]_e + [\mathrm{Te}^{2-},2\mathrm{Cat}^+]_e \\ + 4K_{\mathrm{dispr}}[\mathrm{Te}\cdot^-,\mathrm{Cat}^+]_e)t + \text{constant}\end{aligned}$$

For the THF system this relation is reduced to

$$\ln (a + X)/X = k_{-1}at + \text{constant}$$

where X denotes the excess concentration of $\mathrm{Te}^{2-},2\mathrm{Cat}^+$ and a the initial concentration of Te (in $\mathrm{Te} + \mathrm{Te}\cdot^-$ system) or of $\mathrm{Te}^{2-},2\mathrm{Cat}^+$ (in the $\mathrm{Te}\cdot^- + \mathrm{Te}^{2-}$ system). The plots of $\ln (a + X)/X$ vs. time are linear and their slopes yield $k_{\mathrm{obsd}} = k_{-1}a$. Thus, $k_{-1} = k_{\mathrm{obsd}}/a$ and the value of k_1 is then calculated from the potentiometrically determined K_{dispr}. All the results are listed in Table II and its last column shows that in spite of substantial variation of $[\mathrm{Te}\cdot^-,\mathrm{Cat}^+]_0$, $[\mathrm{Te}]_0$, and $[\mathrm{Te}^{2-},\mathrm{Cat}^+]_0$ the values of k_{-1} are reproducible. To avoid any complications arising from ionic dissociation of $\mathrm{Te}\cdot^-,\mathrm{Cat}^+$ or $\mathrm{Te}^{2-},2\mathrm{Cat}^+$, the appropriate salt of tetraphenylboride was added to the investigated solutions. (The concentration of the added salt is 10^{-4} M, sufficient to prevent the dissociation of the investigated ion pairs, but insignificant otherwise.)

Kinetic results obtained in the dioxane or diethyl ether system had to be worked out with the aid of the general equation. Thus, k_{-1} is obtained from the slopes of the linear plots of $\ln (r \mp SX)/X$ vs. time, where $r = [\mathrm{Te}]_0 + [\mathrm{Te}^{2-},2\mathrm{Cat}^+]_0 + 4K_{\mathrm{dispr}}[\mathrm{Te}\cdot^-,\mathrm{Cat}^+]_0$ and $S = (1 - 4K_{\mathrm{dispr}})$. The slopes of the resulting lines give the $k_{\mathrm{obsd}} = k_{-1}r$. Flash photolysis may lead to bleaching of the absorption of the dianion and increasing the concentration of the radical ions. Such a result requires a change of the minus sign in the ln expression into the plus sign. For each run and for each cation-solvent system the plots of $\ln (r + SX)/X$ vs. time were linear and the points determined by k_{obsd} and r conformed to a straight line passing through the origin. The k_{-1} values determined from their slopes are listed in Table III.

Interestingly, no bleaching was observed in the photolysis of the K^+ or Cs^+ salts in dioxane. These results are reminiscent of the findings reported in the study of the kinetics of disproportionation of the sodium salt of tetraphenylethylene dianions in dioxane[7] (see also ref 12). The lack of bleaching is probably caused by a very fast return of the photoejected electron which could not escape from the Coulombic field of the counterions.

Discussion

The variation of K_{dispr} values collected in Table IV, covering

Table II. Disproportionation of $Te\cdot^-,Cat^+$ in THF at 20 °C

Cation	$[Te]_0 \times 10^7/M$	$[Te^{2-},2Cat^+]_0 \times 10^7/M$	$[Te\cdot^-,Cat^+]_0 \times 10^7/M$	$k_{obsd} \times 10^3$ s	$k_{-1} = k_{obsd}/a^a \times 10^{-9}$ M s
Li^+	5.15	0.0	17.4	4.0	7.8
Li^+	5.8	0.0	11.7	4.4	7.6
Li^+	7.5	0.0	23.4	4.2	5.6
Li^+	8.3	0.0	43.	4.5	5.4
Li^+	12.8	0.0	72.	7.2	5.6
Li^+	16.6	0.0	117.	8.3	5.0
Li^+	0.0	1.46	1.6	0.77	5.3
Li^+	0.0	2.2	2.2	1.8	8.3
					Av 6.3 ± 1.3
Na^+	33.0	0.0	9.7	18.6	5.6
Na^+	16.2	0.0	9.7	8.9	5.5
Na^+	7.5	0.0	4.3	4.3	5.7
Na^+	4.5	0.0	2.8	2.7	6.0
Na^+	13.3	0.0	7.3	7.4	5.7
Na^+	28.2	0.0	15.2	14.3	5.1
Na^+	27.4	0.0	15.4	14.3	5.2
Na^+	13.6	0.0	7.0	6.3	4.6
Na^+	11.6	0.0	10.3	6.4	5.7
Na^+	4.6	0.0	4.0	2.4	5.3
Na^+	21.0	0.0	24.0	11.4	5.4
Na^+	4.4	0.0	5.6	2.4	5.5
Na^+	1.9	0.0	2.0	0.94	4.9
Na^+	2.3	0.0	8.4	1.56	6.8
Na^+	6.0	0.0	24.1	3.6	6.0
Na^+	0.0	3.75	5.4	1.70	4.5
Na^+	0.0	7.2	5.7	3.7	5.2
Na^+	0.0	6.2	3.5	3.1	5.0
Na^+	0.0	18.0	9.2	11.0	6.1
					Av 5.5 ± 0.06
K^+	24.9	0.0	6.8	17.0	6.8
K^+	38.0	0.0	69.	22.0	5.8
K^+	0.0	3.3	34.	2.1	6.4
K^+	0.0	7.6	55.	5.5	7.2
					Av 6.55 ± 0.6
Cs^+	22.9	0.0	60.	17.9	7.8

[a] Denotes the concentration of Te in the Te–$Te\cdot^-$ system, or of Te^{2-} in the $Te\cdot^-$–Te^{2-} system.

a range of ten orders of magnitude, is surprising. Therefore, the factors that affect this equilibrium should be examined.

(1) The Coulombic repulsion between the two electrons originally located on separated $A\cdot^-$ radical anions and subsequently forced to move in the same orbital of a dianion hinders the disproportionation and substantially contributes to its endothermicity. Quantitative treatment of this problem was reported by Hush[13a] and others.[13b]

(2) The Coulombic energy resulting from the attraction between a dianion and its two cations is at least four times greater than the attraction energy released in the formation of an $A\cdot^-,Cat^+$ pair. (The aggregates like $A^{2-},2Cat^+$ are tighter than the respective ion pairs $A\cdot^-,Cat^+$.) This favors the disproportionation. On the whole, the gain is larger the tighter the aggregates and the smaller the ions.

(3) In THF the small cations, Li^+ and Na^+, are surrounded by a tight solvation shell that increases their effective radius. Apparently the Li^+ ions remain solvated in both the $Te\cdot^-,Li^+$ pairs and in the $Te^{2-},2Li^+$ aggregates. Hence, the cation–anion interactions do not contribute much to the disproportionation of $Te\cdot^-,Li^+$ and this accounts for the exceedingly low K_{dispr} value of this system. In contrast, although the sodium salt, $Te\cdot^-,Na^+$, forms also loose, solvent separated ion pairs, the $Te^{2-},2Na^+$ aggregate seems to be tighter. The partial desolvation of Na^+ cations in $Te^{2-},2Na^+$ favors the disproportionation because it greatly increases the Te^{2-}–Na^+ interaction, although the loss of some solvation energy substantially reduces the net gain in energy.

(4) The reduction in the degree of cation solvation, if it occurs in the disproportionation, has another important effect; it considerably favors the disproportionation by increasing the entropy of that reaction. This might be a decisive factor, greatly contributing to the free energy of disproportionation and accounting for the large increase in K_{dispr} when $Te\cdot^-,Na^+$ is compared with $Te\cdot^-,Li^+$.

(5) The degree of solvation of K^+ and Cs^+ ions in THF is low.[14] Hence, the previously mentioned gain in entropy may be small in the disproportionation of $Te\cdot^-,K^+$ and $Te\cdot^-,Cs^+$ in THF. This might rationalize the lower values of K_{dispr} of these salts when compared with that of $Te\cdot^-,Na^+$. Nevertheless, the smaller size of the poorly solvated K^+ or Cs^+ as compared with the well-solvated Li^+ (see ref 14) makes K_{dispr} of $Te\cdot^-,K^+$ and $Te\cdot^-,Cs^+$ greater than that of $Te\cdot^-,Li^+$. This nonconventional gradation of K_{dispr} reported here for the alkali salts in THF was also noted in the disproportionation of other radical ions.[8]

(6) The change of solvent has perhaps the greatest effect on the disproportionation equilibrium. It affects the solvation of the cations and the Coulombic forces acting between the oppositely charged ions. As may be seen from the data collected in Table IV, the disproportionation is appreciably favored in DOX and even more so in DEE. In these solvents the gradation of K_{dispr} is monotonic, decreasing along the series $Li^+ > Na^+ > K^+ > Cs^+$. In these media the cations are poorly solvated and hence their sizes, which determine the gain in Coulombic energy arising from the cation–anion interaction, are related

Table III. Kinetics of Disproportionation of Tetracenide Salts in DOX and DEE at ~20 °C

Cation	$[\text{Te}]_0$ $\times 10^6/\text{M}$	$[\text{Te}\cdot^-,\text{Cat}^+]_0$ $\times 10^6/\text{M}$	$[\text{Te}^{2-},2\text{Cat}^+]_0$ $\times 10^6/\text{M}$	K_{dispr}	k_{obsd} $\times 10^{-3}$ s	r $\times 10^6$	k_{-1} $\times 10^{-8}$ M s
				Dioxane			
Li^+	4.2	2.8	10.14	7.5×10^{-2}	6.4	5.18	1.2
Li^+	11.2	7.5	0.38	7.6×10^{-2}	12.0	13.9	0.87
Li^+	3.4	6.8	0.93	6.8×10^{-2}	7.3	6.18	1.2
Li^+	3.3	8.2	1.48	7.2×10^{-2}	7.7	7.14	1.1
Li^+	0.73	2.3	0.42	5.8×10^{-2}	1.8	1.68	1.1
Li^+	0.58	2.7	0.66	5.2×10^{-2}	2.5	1.80	1.4
Li^+	1.3	5.7	1.58	6.3×10^{-2}	4.2	4.32	0.97
				Av $(6.6 \pm 0.9) \times 10^{-2}$			Av 1.1 ± 0.2
Na^+	20.	57.	9.4	5.7×10^{-2}			
Na^+	7.2	55.	27.	6.4×10^{-2}			
Na^+	1.2	1.1	0.062	6.1×10^{-2}			
Na^+	5.0	5.4	0.35	6.0×10^{-2}	2.0	6.60	3.0
Na^+	3.8	3.17	0.25	9.5×10^{-2}	1.27	4.73	2.7
Na^+	2.4	2.14	0.12	6.3×10^{-2}	0.83	3.06	2.8
Na^+	2.2	3.45	0.31	5.7×10^{-2}	0.87	3.30	2.6
Na^+	1.2	3.1	0.052	6.4×10^{-2}	0.92	2.04	4.5
Na^+	0.27	1.7	0.72	6.7×10^{-2}	0.45	1.44	3.1
				Av $(6.5 \pm 1) \times 10^{-2}$			Av 3.1 ± 0.7
				Diethyl Ether			
Li^+	330.	30.0	87.0	18.7			
Li^+	236.	20.0	51.7	13.1			
Li^+	5.6	0.51	0.85	18.8	0.13	39.9	0.033
Li^+	7.2	0.51	1.6	18.0	0.22	61.2	0.036
Li^+	11.9	1.64	3.0	13.2	0.49	122.0	0.041
				Av 16.4 ± 2.6			Av 0.036 ± 0.004
Na^+	124.	241.	59.6	1.27×10^{-1}			
Na^+	145.	236.	51.8	1.35×10^{-1}			
Na^+	232.	165.	18.0	1.51×10^{-1}			
Na^+	3.50	7.0	1.51	1.1×10^{-1}	16.3	8.09	20.0
Na^+	1.98	3.65	0.83	1.2×10^{-1}	8.4	4.56	18.4
Na^+	4.32	8.3	1.92	1.2×10^{-1}	19.0	4.84	39.2(?)
Na^+	0.56	1.25	0.30	1.1×10^{-1}	3.4	1.40	24.4
Na^+	2.16	1.50	0.12	1.2×10^{-1}	5.1	2.97	17.2
Na^+	5.30	3.08	0.21	1.2×10^{-1}	12.5	6.95	18.0
				Av $(1.23 \pm 0.13) \times 10^{-1}$			Av 19.6 ± 2.8

to the usual crystal radii. The large increase in the disproportionation constant reflects the decrease in the *local* dielectric constant of the medium, which benefits the Coulombic cation–anion interaction in the $\text{Te}^{2-},2\text{Cat}^+$ aggregate more than in the $\text{Te}\cdot^-,\text{Cat}^+$ ion pair.

(7) It is tacitly assumed that the salts of radical ions and dianions are not aggregated beyond the stage of ion pairs and ion triplets. In a future publication we shall discuss the problem of a possible further aggregation of these reagents. It should be stressed, however, that the solutions investigated here are highly dilute (~10^{-6} M) and this reduces the degree of any aggregation.

(8) All the disproportionations studied during our present work seem to be endothermic. The Li^+,DEE system seems to be exceptional in this respect and will be considered later. A similar observation was reported for the azobenzene system.[15] There the disproportionation of the lithium salt was found to be exothermic. The repulsion between the electrons, mentioned in point (1), is responsible for the endothermic character of these reactions.

Kinetics of Disproportionation. The disproportionation of tetracenide ion pairs is relatively slow when the reaction takes place in THF. Its sluggishness is attributed mainly to its high endothermicity which we hope to measure in the future. The disproportionation of $\text{Te}\cdot^-,\text{Li}^+$ is believed to be the most endothermic and the 1000-fold increase in the rate of reaction as Li^+ is substituted by Na^+, K^+, or Cs^+ is presumably due to the decrease in its endothermicity. The reverse reaction, governed by k_{-1}, is slightly slower than a diffusion controlled process, implying that the simultaneous electron and cation transfer from $\text{Te}^{2-},2\text{Cat}^+$ to Te proceeds with little, if any, activation energy when the reaction takes place in THF. Thus, $\Delta G^{\ddagger}$ of the forward reaction is approximately equal to ΔG.

Although the attraction of cation to radical anion is stronger in dioxane and diethyl ether, disproportionation proceeds much faster in those solvents, presumably due to the substantial decrease of their endothermicity. Even the ion pairs of Li^+ or Na^+ may be classified as tight in these media, although they are probably "solvated" externally, e.g., $\text{Te}\cdot^-,\text{Cat}^+,(\text{S})_n$. This organized shell of solvent molecules has to be removed or rearranged in the transition state of disproportionation, which may be depicted as

$$\text{A}\cdot^-,\text{Cat}^+,\text{A}\cdot^-,\text{Cat}^+(\text{S})_n$$

The smaller lithium ion holds the solvent molecules stronger than the larger sodium ion, and this accounts for the higher k_1 values found for the disproportionation of $\text{Te}\cdot^-,\text{Na}^+$ in DOX or DEE when compared with those found for the lithium pairs. The strong attachment of the cations to Te^{2-} hinders the reverse reaction, which becomes especially low for $\text{Te}^{2-},2\text{Li}^+$ in dioxane. The increasing "tightness" of this aggregate is reflected in a large hypsochromic shift in its absorption band (see Table IV).

Are the aggregates $\text{Te}^{2-},2\text{Li}^+$ and $\text{Te}^{2-},2\text{Na}^+$ "tighter" in

Table IV. Equilibria and Kinetics of Disproportionation of Tetracene Radical Anions at 20 °C

$$2\mathrm{Te}{\cdot}^{-},\mathrm{Cat}^{+} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{Te} + \mathrm{Te}^{2-},2\mathrm{Cat}^{+} \qquad K_1$$

Solvent	Cation	$\lambda_{\max}$, nm $\mathrm{Te}{\cdot}^{-},\mathrm{Cat}^{+}$	$\lambda_{\max}$, nm $\mathrm{Te}^{2-},2\mathrm{Cat}^{+}$	K_1	k_1, M s	k_{-1}, M s
THF	Li^+	719	620	5.8×10^{-9}	3.6×10	6.3×10^{9}
THF	Na^+	719	620	1.0×10^{-5}	5.5×10^{4}	5.5×10^{9}
THF	K^+	717	635	4.6×10^{-6}	3.0×10^{4}	6.5×10^{9}
THF	Cs^+	710	~630	3.2×10^{-6}	2.5×10^{4}	7.8×10^{9}
DOX	Li^+	702	598	6.6×10^{-2}	6.0×10^{6}	1.1×10^{8}
DOX	Na^+	700	613	6.5×10^{-2}	2.0×10^{7}	3.1×10^{8}
DOX	K^+	698	628	1.1×10^{-2}	*a*	*a*
DOX	Cs^+	705	640	6.5×10^{-3}	*a*	*a*
DEE	Li^+	700	580	1.64×10	5.9×10^{7}	3.6×10^{6}
DEE	Na^+	698	603	1.2×10^{-1}	2.4×10^{8}	2.0×10^{9}

[a] Flash of visible light (λ <400 nm) does not lead to bleaching. Our observation starts 25 μs after flash.

THF than those involving K^+ or Cs^+ ions? The position of $\lambda_{\max}$ (see again Table IV) might lead to this conclusion, which is not plausible. We will try to resolve this problem later.

Which Species Is Bleached in the Photolysis? It has been remarked earlier that the radical anion is bleached and the dianion formed on photolysis of solutions of tetracenide salts mixed with the respective dianions or their parent hydrocarbons, provided that the pertinent K_{dispr} is very low. Such phenomenon was observed in the photolysis of the THF solutions; however, this result is trivial and does not deserve any comments. The question of which species is bleached becomes not trivial when K_{dispr} is not too small and the concentrations of the parent hydrocarbon, its radical anion, and dianion in the equilibrated solutions are of comparable magnitude. Such solutions are formed in DOX and in DEE.

Consider photolysis leading to a small fraction of ejected electrons. Let us denote by ϕ_{-} and ϕ_{2-} the quantum yields of electron ejection from $\mathrm{Te}{\cdot}^{-}$ and Te^{2-}, respectively, and by k^0 and k^-, the bimolecular rate constants of electron capture by Te and $\mathrm{Te}{\cdot}^{-},\mathrm{Cat}^{+}$, respectively. It is assumed that $\mathrm{Te}^{2-},2\mathrm{Cat}^{+}$ does not capture any electrons.

The total amount of photoejected electrons per unit volume and for unit energy of absorbed radiation is

$$[e] = \phi_{-}[\mathrm{Te}{\cdot}^{-},\mathrm{Cat}^{+}]_0 + \phi_{2-}[\mathrm{Te}^{2-},2\mathrm{Cat}^{+}]_0$$

When all the ejected electrons have been captured by Te or $\mathrm{Te}{\cdot}^{-},\mathrm{Cat}^{+}$, then for each unit of absorbed radiation the concentration of the latter increases by Δ^-, viz.,

$$\begin{aligned}\Delta^- = \{(k^0[\mathrm{Te}]_0 - k^-[\mathrm{Te}{\cdot}^{-},\mathrm{Cat}^{+}]_0)/(k^0[\mathrm{Te}]_0 \\ + k^-[\mathrm{Te}{\cdot}^{-},\mathrm{Cat}^{+}]_0)\}[e] \\ + \phi_{2-}[\mathrm{Te}^{2-},2\mathrm{Cat}^{+}]_0 - \phi_{-}[\mathrm{Te}{\cdot}^{-},\mathrm{Cat}^{+}]_0\end{aligned}$$

whereas the concentration of the dianions increases by Δ^{2-}

$$\begin{aligned}\Delta^{2-} = \{k^-[\mathrm{Te}{\cdot}^{-},\mathrm{Cat}^{+}]_0/(k^0[\mathrm{Te}]_0 + k^-[\mathrm{Te}{\cdot}^{-},\mathrm{Cat}^{+}]_0)\}[e] \\ - \phi_{2-}[\mathrm{Te}^{2-},2\mathrm{Cat}^{+}]_0\end{aligned}$$

It is easy to verify that $\Delta^- + 2\Delta^{2-} = 0$, and this equality permits us to cast Δ^{2-} into the form

$$\begin{aligned}-\Delta^{2-} = \{k^0\phi_{2-}[\mathrm{Te}]_0[\mathrm{Te}^{2-},2\mathrm{Cat}^{+}]_0 \\ - k^-\phi_{-}[\mathrm{Te}{\cdot}^{-},\mathrm{Cat}^{+}]_0{}^2\}/(k^0[\mathrm{Te}]_0 + k^-[\mathrm{Te}{\cdot}^{-},\mathrm{Cat}^{+}]_0)\end{aligned}$$

Since $[\mathrm{Te}]_0[\mathrm{Te}^{2-},2\mathrm{Cat}^{+}]_0/[\mathrm{Te}{\cdot}^{-},\mathrm{Cat}^{+}]_0{}^2 = K_{\mathrm{dispr}}$, we find

$$\begin{aligned}\Delta^{2-} = (k^-\phi_{-} - k^0\phi_{2-}K_{\mathrm{dispr}})[\mathrm{Te}{\cdot}^{-},\mathrm{Cat}^{+}]_0{}^2/(k^0[\mathrm{Te}]_0 \\ + k^-[\mathrm{Te}^{-},\mathrm{Cat}^{+}])\end{aligned}$$

Thus, Δ^{2-} is positive when $k^-\phi_{-} - k^0\phi_{2-}K_{\mathrm{dispr}} > 0$ and negative for $k^-\phi_{-} - k^0\phi_{2-}K_{\mathrm{dispr}} < 0$, *independently* of the ratio $[\mathrm{Te}{\cdot}^{-},\mathrm{Cat}^{+}]_0/[\mathrm{Te}^{2-},2\mathrm{Cat}^{+}]_0$. However, since ϕ_{-} and ϕ_{2-} depend on the spectral distribution of the photolyzed radiation, the nature of the actinic light is a factor determining which species is bleached and which is formed.

In conclusion, electron photoejection may result in bleaching of a radical anion and in the formation of a dianion or vice versa. The nature of the system, i.e., of the parent compound, counterion, and solvent, as well as the spectral characteristics of the actinic radiation determine which of the two species (radical anion or dianion) is bleached and which is formed. However, the results obtained for a system and a light source are independent of the $[\mathrm{A}^{2-}]/[\mathrm{A}{\cdot}^{-}]$ ratio. For a sufficiently low value of K_{dispr} the electron photoejection leads to bleaching of radical anions and the formation of dianions.

These conclusions apply to the system in which *all* the photoejected electrons have been captured by the hydrocarbon or its radical ion.

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Structural Effects in Solvolytic Reactions. 15. Solvolysis of 1-Arylcyclohexyl and 1-Arylcyclohex-2-enyl *p*-Nitrobenzoates. Effect of Increasing Electron Demand on the Contributions of an Allylic Double Bond in the Solvolysis of Tertiary Cyclohex-2-enyl Derivatives

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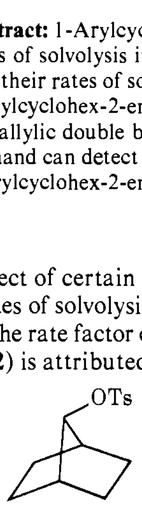
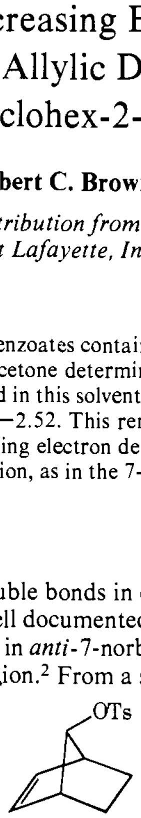
Abstract: 1-Arylcyclohexyl *p*-nitrobenzoates containing representative substituents in the aryl ring were synthesized and their rates of solvolysis in 80% aqueous acetone determined. The corresponding cyclohex-2-enyl derivatives were also synthesized and their rates of solvolysis measured in this solvent. The value of ρ^+ for the 1-arylcyclohexyl system is -4.60 and that for the 1-arylcyclohex-2-enyl derivatives is -2.52. This remarkable change in ρ^+ is attributed to increased π conjugation, involving the allylic double bond, with increasing electron demand at the cationic center. Consequently, the tool of increasing electron demand can detect both π participation, as in the 7-aryl-*anti*-norbornenyl derivatives, and developing π conjugation, as in the 1-arylcyclohex-2-enyl derivatives.

The effect of certain homoallylic double bonds in enhancing the rates of solvolysis reactions is well documented.[2,3] For example, the rate factor of 10^{11} observed in *anti*-7-norbornenyl tosylate (**2**) is attributed to π participation.[2] From a study of the solvolysis of 7-aryl-*anti*-norbornenyl *p*-nitrobenzoates (**3**) and the corresponding saturated derivatives (**4**), Gassman and Fentiman established that the contribution of the π electrons to the stabilization of the electron-deficient center increases with increasing electron demand.[3] On the other hand, the tool of increasing electron demand establishes the absence of π participation in the cyclopent-3-enyl system[4] (**5**).

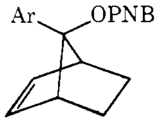


1

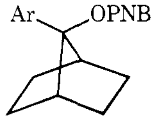


2

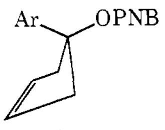
Rel rate (25°) 1.0 10^{11}



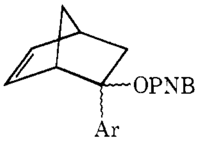
3 (ρ^+ -2.30)



4 (ρ^+ -5.27)



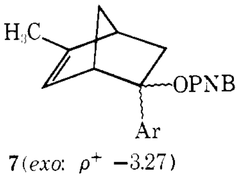
5 (ρ^+ -3.92)



6 (*exo*: ρ^+ -4.21)
(*endo*: ρ^+ -4.17)

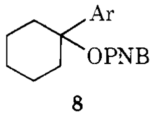
In contrast, the 2-aryl-2-norbornenyl system (**6**) appears to be a borderline case.[5] With the less electron-demanding substituents (*p*-CH_3O, *p*-H, *p*-CF_3) the exo:endo rate ratio remains sensibly constant, indicating the absence of π participation. However, with the more deactivating 3,5-$(CF_3)_2$ substituent, there is observed a modest increase in the exo:endo rate ratio, suggesting the initiation of π participation. Steric hindrance to ionization of the endo isomers arising from the π cloud of the double bond has been proposed for the relatively high, essentially constant exo:endo rate ratio observed in the 2-aryl-2-norbornenyl derivatives.[5,6]

Activation of the double bond by a methyl group (**7**) converts the system (**6**) from a borderline case to one that clearly involves π participation.[7]

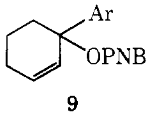


7 (*exo*: ρ^+ -3.27)
(*endo*: ρ^+ -4.19)

It was of interest to examine the question of whether the tool of increasing electron demand could detect π conjugation as well as π participation. To this end we undertook a study of the solvolysis of the 1-arylcyclohexyl (**8**) and the 1-arylcyclohex-2-enyl (**9**) *p*-nitrobenzoates.



8



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