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Equilibria and Kinetics of Disproportionation of Barium Salts of Radical Anions of Tetraphenylethylene and Tetracene

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Abstract: Disproportionation of barium salts of radical anions of tetraphenylethylene, TPE, and tetracene, T, was investigated in THF and DME. The disproportionation constant for the reaction $Ba^{2+},TPE\cdot^- + TPE\cdot^- \rightleftarrows Ba^{2+}, TPE^{2-} + TPE$ is very high in both solvents, apparently greater than 10^6. The bimolecular rate constant of that reaction taking place in DME was found to be $\sim 10^7\ M^{-1}\ s^{-1}$, the kinetics was studied by flash photolysis technique. The disproportionation constant of $Ba^{2+},T\cdot^- + T\cdot^- \rightleftarrows Ba^{2+},T^{2-} + T$ in THF was found to be ~520, a lower value of ~20 being found in DME. Since the dissociation constant of $Ba^{2+}(T\cdot^-)_2$ in THF was determined at 6×10^{-6} M, the disproportionation constant of the reaction $T\cdot^-, Ba^{2+},T\cdot^- \rightleftarrows T + Ba^{2+},T^{2-}$ is 3×10^{-3} M. Kinetics of the disproportionation of $Ba^{2+},T\cdot^- + T\cdot^-$ was investigated in THF, again by flash-photolytic technique. The results indicate that this reaction proceeds through two routes: (a) (k_a) $Ba^{2+},T\cdot^- + T\cdot^- \rightleftarrows Ba^{2+},T^{2-} + T$ with $k_a = 6 \times 10^8\ M^{-1}\ s^{-1}$, and (b) $T\cdot^- + Ba^{2+},T\cdot^- \rightleftarrows T\cdot^-,Ba^{2+},T\cdot^-$, followed by $T\cdot^-,Ba^{2+},T\cdot^- \rightleftarrows T + Ba^{2+}, T^{2-}$. The merits of this mechanism were discussed. Finally, some striking features of the optical spectrum of Ba^{2+},TPE^{2-} were reported. Their interpretation led us to postulate an unsymmetric structure of the barium salt, namely, $Ba^{2+},Ph_2\overline{C}-\overline{C}Ph_2$, with the cation strongly associated with one but not with the other $-\overline{C}(Ph)_2$ chromophore.

Following our studies of the effect of alkali counterion and of solvent on the equilibrium and rates of disproportionation of radical anions,[1-4] we investigated now the disproportionation of the barium salts of radical anions derived from tetraphenylethylene, TPE, and tetracene, T. The salts of the respective dianions were prepared in THF or DME by reacting solution of the appropriate hydrocarbon with a barium mirror, the latter being formed by the procedure described by Sigwalt et al.[5] All the operations and the subsequent handling of the solutions were performed in high vacuum.

Barium Salts of Radical Anions and Dianions of Tetraphenylethylene. THF or DME solutions of tetraphenylethylene, TPE, contacted with a barium mirror yield the salt of the dianion, Ba^{2+},TPE^{2-}. The disproportionation of the pertinent radical anions is high and only a weak ESR signal could be detected from DME solutions of $\sim 2 \times 10^{-4}$ M Ba^{2+},TPE^{2-} in the presence of $\sim 5 \times 10^{-3}$ M of the unreduced TPE. On this basis the disproportionation constant in DME is estimated to be $\sim 10^6$. The optical spectrum of Ba^{2+},TPE^{2-}, shown in Figure 1, is unaffected by dilution from $\sim 10^{-4}$ to 10^{-6} M. The λ_{max} of the absorption band peaking at 485 nm is unaffected by the solvent. This band appears in the spectra of the sodium salt, $TPE^{2-},2Na^+$ (λ_{max} 485 nm) and the free TPE^{2-} ion formed when the sodium salt is dissolved in hexamethylphosphorictriamide (HMPA). The strong band appearing at shorter wavelength (λ_{max} 345 nm in THF and 350 nm in DME) is absent in the other two spectra, but a similar band (λ_{max} 385 nm) is pronounced in the spectrum of the lithium salt, $TPE^{2-},2Li^+$. Its appearance in the spectrum of the lithium salt, in addition to the "conventional" band (λ_{max} 495 nm), was discussed elsewhere.[6] These two bands do not originate from the chromophore's splitting[7] because the lithium or sodium salts of 1,1,4,4-tetraphenylbutane dianions,

$$Cat^+, \overline{C}(Ph)_2CH_2CH_2\overline{C}(Ph)_2,Cat^+$$

with chromophores identical with those of TPE^{2-}, but placed further apart, again absorb only at ~480 nm and not at ½(385 + 495) = 440 nm. Moreover, the 385-nm band disappears on addition of tetraglyme to the THF solution of $TPE^{2-},2Li^+$ (see ref 6).

The appearance of the new band (385 nm) in the spectrum of $TPE^{2-},2Li^+$ was rationalized[6] by postulating that one of the $-\overline{C}Ph_2$ groups of this skewed-shape salt is tightly associated with Li^+, while the other Li^+ cation is fully solvated and forms a loose ion pair with the second chromophore. The latter pair absorbs like the free $-\overline{C}Ph_2$ anion or the loose sodium salt, i.e., at ~495 nm, whereas the absorbance of the very tight pair is substantially shifted to the shorter wavelength, giving rise to the 385-nm band. Indeed, the integrated extinction coefficient of the 485-nm band of the free TPE^{2-} anion or its loose sodium aggregate is twice as high as that of the 495-nm absorption band of the lithium salt. Other evidence reported in ref 6 corroborates this explanation.

A somewhat similar explanation may account for the

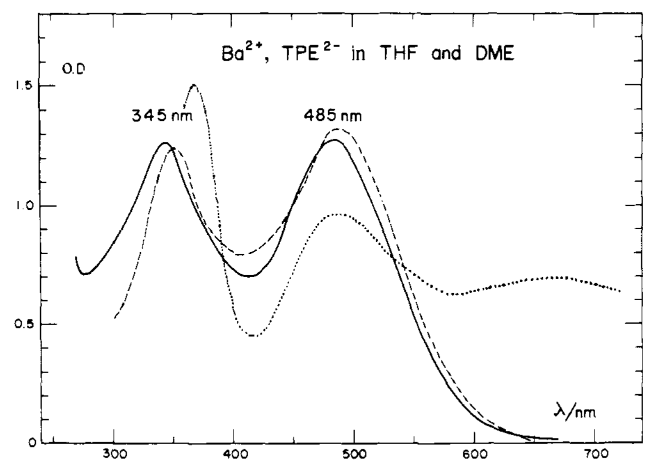
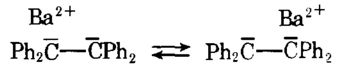


Figure 1. Spectra of Ba^{2+},TPE^{2-} in THF (solid line), in DME (dashed line), and spectrum of $Ba^{2+},TPE\cdot^{-}$ + $TPE\cdot^{-}$, which might contain a small proportion of Ba^{2+},TPE^{2-} (dotted line).

spectrum of the barium salt. Apparently the Ba^{2+} cation is placed asymmetrically, being strongly associated with only one of the $-\bar{C}Ph_2$ centers, but not with the other. Thus, one of the chromophores forms an extremely tight $Ba^{2+},-\bar{C}Ph_2$ pair, while the other behaves as a free $-\bar{C}Ph_2$ anion and absorbs at 485 nm. The association with the doubly charged Ba^{2+} cation results in a very large hypsochromic shift of the absorbance of the $-\bar{C}Ph_2$, namely to 345 nm. This salt therefore demonstrates again how specific could be the structure of ion pairs.

The exchange shown below is probably slow. Unfortunately,



$$\overset{Ba^{2+}}{Ph_2\bar{C}}—\bar{C}Ph_2 \rightleftarrows Ph_2\bar{C}—\overset{Ba^{2+}}{\bar{C}Ph_2}$$

the low solubility of this salt prevents us from studying its rate.

Flash Photolysis of Ba^{2+},TPE^{2-}. Flash photolysis of $\sim10^{-6}$ M DME solution of Ba^{2+},TPE^{2-} containing some unreduced TPE initially leads to about 5–10% bleaching of the 485-nm band and to the appearance of a transient absorption at 660 nm. Typical difference spectra recorded at 20, 60, and 120 ms after a flash are shown in Figure 2. Eventually the spectrum of the photolyzed solution becomes identical with that recorded prior to flash; i.e., the photolyzed system always returns to its initial state.

The absorbance at 660 nm is attributed to the formation of $Ba^{2+},TPE\cdot^{-}$ + $TPE\cdot^{-}$ caused by photoejection of an electron from Ba^{2+}, TPE^{2-} and its capture by the unreduced TPE. The absorbance of the $Ba^{2+},TPE\cdot^{-}$ + $TPE\cdot^{-}$ solution has been recorded. Addition of HMPA to a solution of the dianions containing excess of the unreduced TPE results in their quantitative conversion to radical anions. The spectrum of such a solution shown in Figure 1 closely resembles the spectrum of the sodium or lithium salts of TPE radical anions,[1b,c] and from its intensity the pertinent extinction coefficients of $Ba^{2+}(TPE\cdot^{-})$ + $TPE\cdot^{-}$ were determined relative to those of Ba^{2+}, TPE^{2-}.

Inspection of Figure 2 reveals two isosbestic points at 540 and 420 nm, respectively. Their appearance confirms the stoichiometry of the photolytic process and implies that the reverse dark reaction proceeds directly, without involving appreciable concentration of intermediates. The absorbance of $TPE\cdot^{-}$ in the 480-nm region is responsible for the shift to 450 nm of the λ_{max} of the bleached band of the dianion.

Kinetics of Disproportionation. A flash of visible light perturbs the equilibrium between TPE^{2-} Ba^{2+} and TPE on one hand and the radical anions on the other by increasing the concentration of the latter and decreasing that of the former.

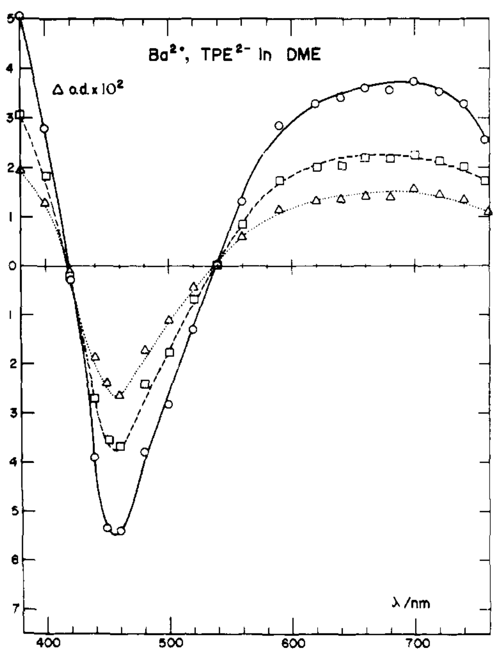


Figure 2. Difference spectra of flashed solution of Ba^{2+},TPE^{2+} + TPE in DME: 20 ms after flash (circles); 60 ms after flash (squares); and 120 ms after flash (triangles).

The equilibrium is reestablished during the dark period following the flash and the changes in the absorbance at 450 (increase in the concentration of dianions) or at 660 nm (decrease in the concentration of radical anions) monitor the return of the system to its equilibrium state.

The reestablishment of the equilibrium monitored by the appropriate Δ(OD) is governed by a second-order process, namely the plots of 1/Δ(OD), whether measured at 450 or 660 nm, are perfectly linear with time, at least up to 85% of conversion (see Figure 3). A complete treatment of the pertinent kinetics leads to the relation:

$$-dx/dt = (k_1 - k_{-1})x^2 + k_1x\{2(bc/K_1)^{1/2} + (b + c)/K_1\} \approx k_1x^2 + k_1x\{2(bc/K_1)^{1/2} + (b + c)/K_1\}$$

because $k_1 \gg k_{-1}$. In this equation $x = \Delta[Ba^{2+},TPE\cdot^{-}] = \Delta[TPE\cdot^{-}] = \Delta(OD)$ (at 450 or 660 nm) multiplied by the appropriate effective extinction coefficient, while b and c are the equilibrium concentrations of Ba^{2+},TPE^{2-} and TPE, respectively. This rate expression is derived on the basis of the following mechanism:

$$\underset{a+x}{Ba^{2+},TPE\cdot^{-}} + \underset{a+x}{TPE\cdot^{-}} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \underset{b-x}{Ba^{2+},TPE^{2-}} + \underset{c-x}{TPE}$$

$$K_1 = k_1/k_{-1} = bc/a^2$$

i.e., the dissociation of $Ba^{2+}(TPE\cdot^{-})_2$ into $Ba^{2+},TPE\cdot^{-}$ + $TPE\cdot^{-}$ is assumed to be virtually quantitative within the investigated range of concentrations of the radical anions, namely 10^{-7} to 10^{-8} M. This is plausible in view of the high value of the dissociation constants of the sodium or lithium salts of TPE radical anions in THF[1a,c] and the high degree of dissociation of $Ba^{2+}(T\cdot^{-})_2$ in THF (see the later part of this paper).

Alternatively, the sequence such as

$$Ba^{2+},TPE\cdot^{-} + TPE\cdot^{-} \overset{K_a}{\rightleftarrows} Ba^{2+}(TPE\cdot^{-})_2$$

$$\overset{k_2}{\rightleftarrows} Ba^{2+}, TPE^{2-} + TPE$$

may account equally well for the overall process. In this case

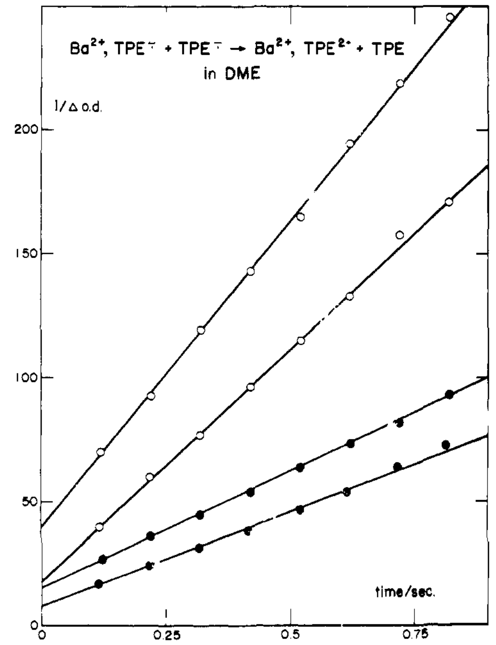


Figure 3. Plot of $1/\Delta$(OD) vs. time for disproportionation of $Ba^{2+},TPE\cdot^-$ + $TPE\cdot^-$ in DME (open circles at 660 nm, full circles at 450 nm).

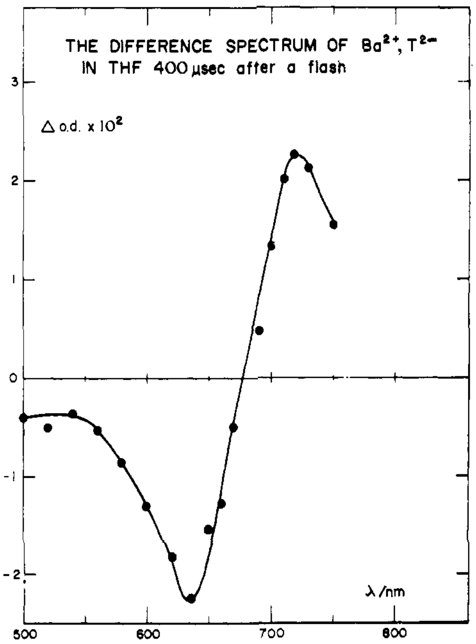


Figure 4. The difference spectrum of photolyzed mixture of Ba^{2+},T^{2-} + T in THF 400 μs after flash.

Table I. Kinetics of disproportionation of $Ba^{2+},TPE\cdot^-$ + $TPE\cdot^-$ in DME

$$Ba^{2+},TPE\cdot^- + TPE\cdot^- \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} Ba^{2+},TPE^{2-} + TPE$$

$[Ba^{2+},TPE^{2-}]_0$, $\times 10^6$ M^{-1}	[TPE], $\times 10^6$ M^{-1}	Slopes of the $1/\Delta$(OD) plots, Δ(OD) s 450 nm	660 nm	Ratio of the slopes 660/450
4.2	<1.0	92	253	2.75
6.3	<1.0	107	215	2.0
8.3	<1.0	79	185	2.34
7.6	5.9	78	170	2.18
4.9	3.8	98	244	2.49
7.0	8.4	82	176	2.15
8.0	85.0	94	182	1.94
5.0	53.4	99	196	1.98
	Av	91 ± 10	203 ± 32	2.23 ± 0.3

k_2K_a would correspond to k_1. In a more general case the forward rate constant is $k_1 + k_2K_a$.

The perfect linearity of the $(1/\Delta(OD)) - t$ plots requires the inequality[11]

$$\{2(bc/K_1)^{1/2} + (b + c)/K_1\} \ll x$$

Typically $b \approx 5\text{-}7 \times 10^{-6}$ M, c was varied from less than 1×10^{-6} M to 53×10^{-6} M, and x could be as low as 4×10^{-8} M. Hence, the above inequality demands $K_1 \geq 5 \times 10^7$, a value larger than that estimated from the ESR study for the disproportionation taking place in DME. The high value of the disproportionation constant is compatible with the other data pertaining to the disproportionation of radical anions of TPE.[1a,c,8] Its largeness is due, at least partially, to changes in the geometry of $TPE\cdot^-$ on its conversion into TPE^{2-} dianions (see ref 9 for a detailed discussion of this point).

The slopes of the lines $1/\Delta$(OD) vs. time are given in Table I, showing that this disproportionation is relatively slow. The sensitivity of the system to minute amounts of impurities, as well as the considerable technical difficulties, lead to a substantial scatter of the data. Nevertheless, it is obvious that k_1 is not affected by the concentration of Ba^{2+},TPE^{2-} and certainly is independent of the concentration of TPE, which was varied by a large factor. The slopes of the lines $1/\Delta$(OD 450 nm) are lower by a factor of about 2.2 than those obtained at 660 nm. This observation implies that the extinction coefficient at 450 nm is by a factor of ~2.2 greater than that at 660, a conclusion supported by the spectral data pertaining to the sodium and lithium salts. The low solubility of Ba^{2+},TPE^{2-} and the high value of the disproportionation constant prevented us from direct determination of the exact extinction coefficients of Ba^{2+},TPE^{2-} and $Ba^{2+},TPE\cdot^-$. The extinction of Ba^{2+},TPE^{2-} was determined at 1.95×10^4 by converting the barium salt into that of lithium, and hence the k_1 value is in the range of 10^7 M^{-1} s^{-1}. The alternative interpretation of the kinetic data would attribute this value to k_2K_a. Since K_a may be as large as 10^4 M^{-1}, k_2 could be as small as 10^3 s^{-1}.

Finally, some remarks about the nature of Ba^{2+},TPE^{2-} solution may be in place. The barium mirror, when contacted with the solution of TPE, becomes eventually coated by some precipitate which could not be dissolved in THF or DME. The clear, cherry-red solution of Ba^{2+},TPE^{2-} decanted from the precipitate slowly decays, over a period of a few days, and a precipitate is formed. It seems that the relatively concentrated solution of Ba^{2+},TPE^{2-} (~10^{-3} M) formed in the preparation is oversaturated. Apparently the salt slowly aggregates and the aggregates coalesce into insoluble particles. No attempts were made to study this phenomenon further; it was ascertained, however, that although the decay of the color reduced the intensity of the spectrum, it did not affect its shape. No decay is observed in dilute solutions (~10^{-6} M) used in our kinetic study.

Barium Salts of Radical Anions and Dianions of Tetracene in THF. The spectrum of the barium salt of tetracene dianions, Ba^{2+},T^{2-}, closely resembles that of the sodium salt. The peculiarities observed in the spectrum of Ba^{2+}, TPE^{2-} are not evident in the absorption of Ba^{2+},T^{2-}; the delocalization of the negative charge through the large tetracene moiety prevents the formation of the very tight pairs. The absorption maximum of Ba^{2+},T^{2-} appears at 630 nm, its extinction coefficient being determined as 3.2×10^4, while the λ_{max} of the sodium salt appears at 620 nm, ϵ being 4.3×10^4. The barium salt of tetracene radical anions, or more correctly a mixture of Ba^{2+},

Table II. Conductance of $Ba^{2+}(T\cdot^-)_2$ in THF at ~25 °C

$[Ba^{2+}(T\cdot^-)_2]_{total}$, $\times 10^6$ M^{-1}	$[Ba^{2+},T^{2-}]$, $\times 10^6$ M^{-1}	Λ, Ω M/cm^2
5.71	28.4	59.0
2.98^a	15.8	70.0
1.54	9.5	77.4
0.74	5.1	85.7
0.38	3.0	97.8
0.25	1.9	90.4

[a] New batch of reagents: Λ_0 = 95 Ω M/cm^2; K_{diss} = 5.7 × 10^{-6} M.

Table III. Conductance Study of Na^+ $T\cdot^-$ in THF

T °C	Λ_0, Ω M/cm^2	$\eta \times \Lambda_0$	K_{diss}, 10^{-5} M
20	99	0.485	2.27 (?)
10	89.5	0.485	3.00
0	80.5	0.489	3.48
−10	71.0	0.489	3.93
−20	61.5	0.486	4.56
−30	53.0	0.485	5.03
−40	45.5	0.487	5.19
−50	38.0	0.486	5.80
−60	31.4	0.487	6.13
−70	25.0	0.478	6.81

$T\cdot^-$ + $T\cdot^-$, is characterized by λ_{max} 715 nm, corresponding to ϵ 1.45 × 10^4.

Studies of the equilibrium of disproportionation required careful determination of the ratios $\epsilon_{630}/\epsilon_{715}$ for each salt. This ratio is calculated for $Ba^{2+},T\cdot^-$ + $T\cdot^-$ from its spectrum to be 0.193 the corresponding value for Ba^{2+},T^{2-} was found to be 0.14. Flash photolysis of the equilibrated mixtures of Ba^{2+},T^{2-} and its parent hydrocarbon demonstrates that the extent of bleaching at 630 nm is the same as the extent of the additional absorption at 715 nm (see Figure 4). This implies the equality

$$\epsilon_{630}(Ba^{2+},T^{2-}) - 2\epsilon_{630}(Ba^{2+},T\cdot^- + T\cdot^-) = 2\epsilon_{715}(Ba^{2+}, T\cdot^- + T\cdot^-) - \epsilon_{715}(Ba^{2+},T^{2-})$$

Accepting the values of the ratios given above and of ϵ_{max}-($Ba^{2+},T\cdot^-$ + $T\cdot^-$), we calculate from this equation ϵ_{max}-(Ba^{2+},T^{2-}) = 3.04 × 10^4, in fair agreement with the directly determined value of 3.2 × 10^4.

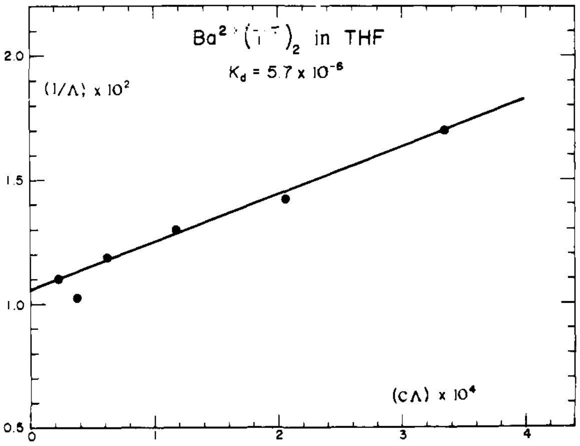


Figure 5. Plot of 1/Λ vs. CΛ for $Ba^{2+},(T\cdot^-)_2$ in THF at ambient temperature.

The ESR Spectrum of $Ba^{2+},T\cdot^-$ + $T\cdot^-$. The well-resolved ESR spectrum of $Ba^{2+},T\cdot^-$ + $T\cdot^-$ in DME shows only one set of sharp lines. The coupling constants 1.15, 1.55, and 4.24 G were determined, each resulting from four identical protons. These values are insignificantly different from the coupling constants of the sodium salt. The Ba nucleus has no spin and hence its presence does not lead to any further splitting of the lines.

Conductance Studies. Conductance of $Ba^{2+},T\cdot^-$ + $T\cdot^-$ was measured in THF using the technique described elsewhere.[10] The results are collected in Table II and the plot of 1/Λ vs. CΛ is shown in Figure 5. From these data Λ_0 was found to be 95 Ω M/cm^2 and K_{diss} = 5.7 × 10^{-6} M. For the sake of comparison, we collected in Table III the conductance data for the $Na^+,T\cdot^-$ in THF determined in our laboratory by Dr. B. Lundgren. These results lead to a similar value of Λ_0 and, not surprisingly, to a value of K_{diss} at 20 °C about a factor of 4 higher. It seems that the latter value should be even higher; the extrapolation from the data obtained at lower temperatures leads to K_{diss}(20 °C) ≈ 2.7 × 10^{-5}.

Equilibrium of Disproportionation. Knowing the extinctions of Ba^{2+},T^{2-} and $Ba^{2+},T\cdot^-$ + $T\cdot^-$ at 630 and 715 nm, we could determine the composition of mixtures of tetracene, its radical anions, and dianions. The results are given in Table IV, where

Table IV. $Ba^{2+},T\cdot^- + T\cdot^- \rightleftarrows Ba^{2+},T^{2-} + T$; K_+ (K_+ is the corrected K_+' taking into account the degree of association); $Ba^{2+},T\cdot^- + T\cdot^- \rightleftarrows Ba^{2+},(T\cdot^-)_2$ (solvent THF at ~25 °C)

Length of the cell, cm	[T], $\times 10^6$ M^{-1}	½[total radical anions], $\times 10^6$ M^{-1}	$[Ba^{2+},T^{2-}]$, $\times 10^6$ M^{-1}	K_+'	K_+
10^b	9.4	0.25	1.85	278	305
10^c	24.0	0.26	2.0	700	770
10^a	36.5	0.35	1.5	447	510
10^c	37.9	0.415	2.9	638	740
10^b	18.7	0.45	2.75	254	300
10^a	68.1	0.52	1.5	372	445
10^a	53.3	0.53	2.0	377	450
10^c	62.8	0.78	5.2	535	690
10^b	39.2	0.94	4.25	190	260 (?)
1^a	307	2.05	5.3	387	660
1^c	236	3.45	16.4	325	700
1^a	345	3.75	10.3	252	570
1^c	186	7.65	32.2	103	350
0.2^b	424	14.7	42.4	83	435
0.2^b	403	22.0	68.6	57	400
			Av for K_+	520 ± 160	

[a] First batch of solution of the reagents. [b] Second batch of solution of the reagents. [c] Third batch of solution of the reagents.

Table V. $\mathrm{Ba^{2+},T\cdot^{-} + T\cdot^{-} \rightleftarrows Ba^{2+},T^{2-} + T}$ in DME at ~25 °C

[T], $\times 10^5$ M^{-1}	½[total radical anions], $\times 10^5$ M^{-1}	[$\mathrm{Ba^{2+},T^{2-}}$], $\times 10^5$ M^{-1}	K_+'
6.0	1.15	2.85	13
7.45	0.79	1.71	20
15.0	1.32	2.29	20
21.0	1.06	1.16	22

K_+' denotes the formal disproportionation constant calculated as

$$4[\mathrm{Ba^{2+},T^{2-}}][\mathrm{T}]/[\text{total of radical anions}]^2$$

and K_+ refers to the correct disproportionation described by the equation

$$\text{(a)}\quad \mathrm{Ba^{2+},T\cdot^{-} + T\cdot^{-} \rightleftarrows Ba^{2+},T^{2-} + T}; \qquad K_+ = 520 \pm 160$$

The conversion of K_+' to K_+ takes into account that some of the radical anions are present in the form $\mathrm{Ba^{2+}(T\cdot^{-})_2}$.

The equilibrium constant of the reaction

$$\text{(b)}\qquad \mathrm{Ba^{2+}(T\cdot^{-})_2 \rightleftarrows Ba^{2+},T^{2-} + T}$$

is given by the product $K_+K_{\mathrm{diss}} \approx 14 \times 10^{-3}$ M^{-1}. The two values, that for reaction a and the other for b, cannot be compared, since they have different dimensions.

Equilibrium of this disproportionation was investigated also in dimethoxyethane. The results of a few experiments, given in Table V, might indicate that the pair $\mathrm{Ba^{2+},T^{2-}}$ is much looser in that solvent than in THF, since K_+' is substantially smaller than K_+' determined in the latter solvent. Lack of the relevant conductance data prevents us from calculating the respective K_+.

Kinetics of Barium Tetracenide Disproportionation. Kinetics of this reaction were investigated in THF, again using the flash-photolytic technique. As revealed by Figure 4, a flash of visible light bleaches the 630-nm band and produces a transient absorption at 715 nm. The system always returns to its initial state after a flash, and the ratio ΔOD(630)/ΔOD(715) ≈ 1:1 remains constant during the dark reaction. Apparently no new transients are formed in this process.

The regeneration of $\mathrm{Ba^{2+},T^{2-}}$ at later stages of the reaction, i.e., 200 μs after a flash, is governed by the first-order law. This virtually linear dependence of ln(ΔOD) on time is observed for the following 3 or 4 ms, until at least 90% of all the species present in excess at the onset of the first-order reaction become consumed. A somewhat faster reaction taking place in the first 200 μs rapidly decays in this period as manifested by Figure 6, while the initial state of the system is fully regenerated during the slower process. The faster reaction seems to consume about 30% or more of the species formed in the flash, but its kinetics is uncertain because of large corrections for stray light.

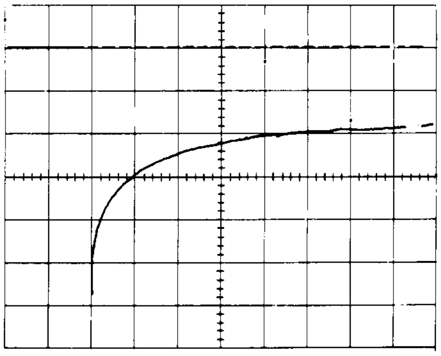


Figure 6. Oscilloscope tracing of the 630-nm transient in the flash photolysis of $\mathrm{Ba^{2+},T^{2-} + T}$ in THF: scale 100 μs/div. Note the initial fast reaction; however, the curve should be corrected to account for the stray light.

A flash of light undoubtedly ejects electrons from $\mathrm{Ba^{2+},T^{2-}}$, and these electrons are captured by the unreduced T, always present in large excess in the investigated solution (see Table VI for the pertinent data). Therefore the photolysis yields additional $\mathrm{Ba^{2+},T\cdot^{-}}$ and $\mathrm{T\cdot^{-}}$ formed in equivalent amounts and their reversible combination restores the initial state of the system. Neither the interaction of two $\mathrm{Ba^{2+},T\cdot^{-}}$ nor of two $\mathrm{T\cdot^{-}}$ is expected to be effective, and hence only the following two routes a and b should be considered:

$$\text{(a)}\quad \mathrm{Ba^{2+},T\cdot^{-} + T\cdot^{-} \overset{k_a}{\rightleftarrows} Ba^{2+},T^{2-} + T}; \qquad K_+ = k_a/k_a'$$

$$\text{(b)}\quad \mathrm{T\cdot^{-} + Ba^{2+},T\cdot^{-} \overset{k_b}{\rightleftarrows} T\cdot^{-}, Ba^{2+},T\cdot^{-}}; \qquad 1/K_{\mathrm{diss}} = k_b/k_b' = K_b$$

followed by

$$\mathrm{T\cdot^{-},Ba^{2+},T\cdot^{-} \overset{k_2}{\rightleftarrows} T + Ba^{2+},T^{2-}}; \qquad K_+K_{\mathrm{diss}} = k_2/k_2'$$

Let us denote by *a*, *b*, and *c* the equilibrium concentrations of $\mathrm{Ba^{2+},T\cdot^{-}}$ (equal to $\mathrm{T\cdot^{-}}$), $\mathrm{Ba^{2+},(T\cdot^{-})_2}$, and $\mathrm{Ba^{2+},T^{2-}}$, respectively, and by *T* the concentration of the unreduced hydrocarbon, the latter being virtually constant in the course of each run. Let *x* denote the depletion of the concentration of

Table VI. Kinetics of Disproportionation

$$\mathrm{Ba^{2+},T\cdot^{-} + T\cdot^{-} \overset{k_1}{\rightleftarrows} Ba^{2+},T^{2-} + T}$$

$[\mathrm{T}]_e$, $\times 10^6$ M^{-1}	$[\mathrm{T\cdot^{-}}]_{\mathrm{total},e}$, $\times 10^6$ M^{-1}	$[\mathrm{Ba^{2+},T^{2-}}]_e$, $\times 10^6$ M^{-1}	x_0,[b] $\times 10^6$ M^{-1}	Slope of the lines,[c] $\times 10^{-3}$ s	
				At 630 nm	At 710 nm
9.4	0.50	1.85	0.23; 0.28	0.43	0.32
18.7	0.90	2.75	0.60; 0.51	0.59	0.54
39.2	1.88	4.25	0.81; 1.00	0.91	0.78
68.0	1.04	1.48	0.10; 0.09	1.00	0.63 (?)
100[a]	1.48	2.84	0.06; -	1.86	(?)
134[a]	1.88	3.42	0.11; 0.10	1.80	1.94
296[a]	2.78	3.39	0.20; 0.17	1.90	1.98

[a] These $[\mathrm{T}]_e$ values were calculated by using the determined values of $[\mathrm{T\cdot^{-}}]_{\mathrm{total},e}$ and $[\mathrm{Ba^{2+},T^{2-}}]_e$ and assuming $K_{\mathrm{dispr}} = 520$. [b] The first value refers to extrapolation using the data at 630 nm, the other refers to those at 715 nm. $[\mathrm{T\cdot^{-}}]_{\mathrm{total},e} = [\mathrm{Ba^{2+},T\cdot^{-}}]_e + [\mathrm{T\cdot^{-}}]_e + [\mathrm{Ba^{2+}(T\cdot^{-})_2}]_e$. [c] Shown in Figure 6.

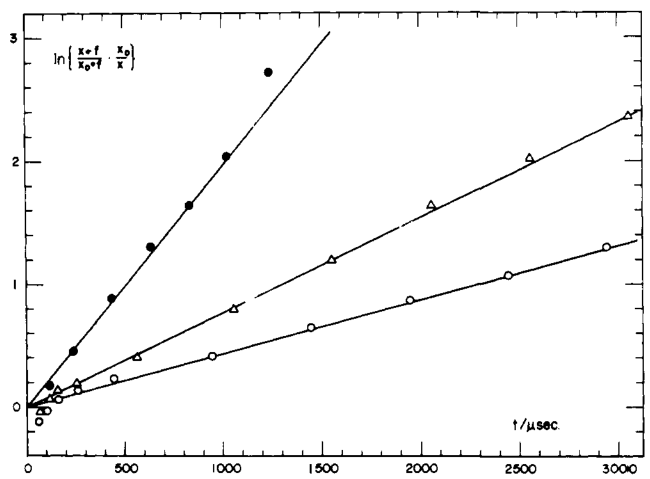


Figure 7. Plot of $\ln\{x_0(x + \alpha)/x(x_0 + \alpha)\}$ vs. time for the disproportionation of $Ba^{2+},T\cdot^- + T\cdot^-$ after flash. The lines refer to: the first experiment (see Table VI), the lowest line; third, the middle line; the last, the upper line.

Ba^{2+},T^{2-} at time t after a flash, y the respective increase in concentration of $Ba^{2+},(T\cdot^-)_2$, while $x - y$ denotes the increase in concentration of $Ba^{2+},T\cdot^-$ or $T\cdot^-$. Thus, the course of the reaction governed by the parallel routes a and b is represented by

$$-dx/dt = \{2ak_a + (k_a' + k_2')T\}x + \{k_2 - 2ak_a\}y$$

and

$$-dy/dt = -\{2ak_b + k_2'T\}x + \{2ak_b + k_b' + k_2\}y$$

provided that the terms square in x and y may be neglected. This scheme leads to two relaxation times, $1/\lambda_1$ and $1/\lambda_2$, determined by the secular equation

$$\begin{vmatrix} \alpha - \lambda, \beta \\ -\gamma, \delta - \lambda \end{vmatrix} = 0$$

where α, β, γ, and δ are the coefficients of x and y in the above equations.

The solutions of the secular equations are

$$\lambda_{1/2} = \tfrac{1}{2}(\alpha + \delta)\{1 \pm \sqrt{1 - 4(\alpha\delta + \beta\gamma)/(\alpha + \delta)^2}\}$$

The limited range of concentrations accessible in our investigation, and the not negligible experimental uncertainties, do not allow us to deduce the pertinent rate constants from this expression. However, the ionic equilibrium, reaction b, seems to be established within 200 μs and maintained thereafter. Then $x/y = 1 + K_{diss}/2a$ and inspection of Table VI reveals that x is greater than y by a factor of from 3 to 7.

We may omit therefore y in the first approximation and treat the kinetics as resulting from reversible reaction a or reversible reaction b, in which the equilibrium with the component ions maintains a minute concentration of $Ba^{2+}(T\cdot^-)_2$, or from both. In either case the relation

$$\ln\{x_0(x + f)/x(x_0 + f)\} = \text{const} \times ft$$

applies for the slow reaction (200 μs after flash). Here $f = 2a + (T/K_+)$ and x_0 denote the value of x extrapolated to zero time. Typical plots of $\ln\{x_0/(x + f)/x(x_0 + f)\}$ vs. time are shown in Figure 7, their slopes being given in Table VI. Monitoring of the reaction progress at 630 and 715 nm yields fairly concordant results. The plot of the slopes vs. f is shown in Figure 8. In spite of the experimental scatter the expected relation slope = const $\times f$ appears to be confirmed, and thus the constant is found to be $(6 \pm 2) \times 10^8\ M^{-1}\ s^{-1}$.

Transfer via route a requires $-dx/dt = 2ak_a\{1 + T/2aK_+\}x \approx 2ak_a x$.[12] A similar expression applies for the other route, k_a being then substituted by k_2K_b. Hence, provided route a is dominant $k_a = (6 \pm 2) \times 10^8\ M^{-1}\ s^{-1}$, and hence $k_a' = 1 \times 10^6\ M^{-1}\ s^{-1}$. For route b to be dominant it is necessary to have $k_2K_b \approx 6 \times 10^8\ M^{-1}\ s^{-1}$, and since K_b is $4 \times 10^4\ M^{-1}$, k_2 should be $\sim 1.5 \times 10^4\ s^{-1}$ and $k_2' \sim 10^6\ M^{-1}\ s^{-1}$. Since both routes might contribute to the overall process $k_a < 6 \times 10^8\ M^{-1}\ s^{-1}$ and $k_2 < 10^4\ s^{-1}$.

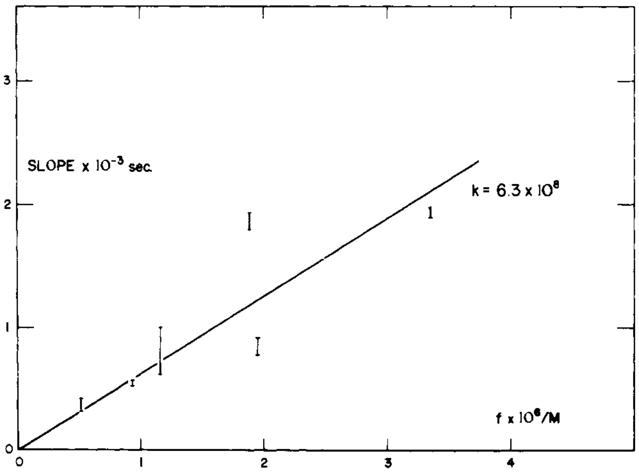


Figure 8. Plot of the slopes of the lines given in Table VI vs. f = [total radical anions]$_c$ + $[T]_c/K_+$. The slope of the line shown gives k_a.

Examination of Figure 5 indicates that the reciprocal of the longer relaxation time, λ_2, is about $10^3\ s^{-1}$. The shorter relaxation time could not be determined reliably, but our results indicate that λ_1 is slightly larger than $10^4\ s^{-1}$. Inspection of our data indicates that such a result demands $\alpha \approx 700$ and $\delta \approx 10^4\ s^{-1}$ for $a = 0.5 \times 10^{-6}$ M. It may be easily verified that $2ak_a + k_2'T$ dominate the expression for α and $2ak_b$ is the leading term for δ. Hence k_b is about $10^{10}\ M^{-1}\ s^{-1}$—a reasonable value for ions association. The partition of the reaction into channel a and b is given by $2ak_a/k_2'T$.

Comparison of Disproportionations Ba^{2+},TPE$\cdot^-$ and Ba^{2+}, $T\cdot^- + T\cdot^-$. While the former reaction proceeds by second-order kinetics, the latter takes place by the first-order process. This different behavior arises from the greatly different values of the respective disproportionation constant. Thus the concentration of TPE$\cdot^-$ formed by flash is much larger than its equilibrium concentration, whereas in the tetracene system $x < a$, at least in later stages of the process.

Accepting our interpretation of the latter reaction, we conclude that the bimolecular rate constant Ba^{2+},TPE$\cdot^-$ + TPE$\cdot^-$ → Ba^{2+},TPE^{2-} + TPE, about $10^7\ M^{-1}\ s^{-1}$, is lower than that of $Ba^{2+},T\cdot^- + T\cdot^- \rightarrow Ba^{2+},T^{2-} + T$, namely $<6 \times 10^8\ M^{-1}\ s^{-1}$. This is reasonable; the changes of geometry affect the first but not the latter reaction.

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Reaction of Diacyl Peroxides with Alumina

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Abstract: Several diacyl peroxides, as well as perbenzoic acid and hydrogen peroxide, react rapidly with alumina surfaces to give a nonextractable oxidant of equivalent oxidizing power. This surface oxidant decomposes to O_2. The only organic product is the carboxylic acid corresponding to the peroxide used. The decay kinetics of the surface oxidant are interpreted in terms of Al_sOOH groups at nonequivalent sites.

When a solution of a diacyl peroxide is placed in contact with alumina, diacyl peroxide disappears from the solution and an equivalent amount of a titratable oxidant appears on the alumina. In most cases the process is complete within a few minutes at 26 °C. The amount of oxidizing power that can be transferred to the alumina depends on the activity of the alumina as an adsorbent. Chromatographic alumina, reacting with benzoyl peroxide, will acquire about 3×10^{-4} equiv of oxidizing power per gram of alumina. This corresponds roughly to N (Avogadro's number) times 100 $Å^2$ per equivalent. For comparison, the area of a benzoic acid molecule lying flat is about 60 $Å^2$.

Even though the amount of oxidant that can be formed on the alumina parallels its adsorptive capacity, the surface oxidant is not adsorbed benzoyl peroxide, contrary to what might be supposed from an earlier report on the removal of peroxidic impurities from solvents by means of alumina.[1] There are several compelling reasons for this conclusion. First, the benzoyl peroxide is not extractable from the alumina by means of ether, unlike compounds such as adsorbed phenyl benzoate. Secondly, the rate of decay of the surface oxidant titer at 26 °C is several orders of magnitude greater than the rate of decomposition of benzoyl peroxide in ordinary solvents. The rate is also nearly independent of the diacyl peroxide used to form the surface oxidant (Figures 1 and 2) and of the nature or continued presence or absence of the solvent with which the peroxide is put on the surface (Figure 3).

Lastly, the products of the reaction are O_2 and benzoic acid with none of the usual CO_2, biphenyl, or phenyl benzoate characteristic of the decomposition of benzoyl peroxide. The oxygen yield is somewhat less than the theoretical 0.5 mol per mole of peroxide because of losses during the removal of the solvent with which the benzoyl peroxide is applied to the surface. Benzoic acid, which can be extracted with considerable difficulty by treating with HCl and ether, was isolated in 86% of the theoretical 2 mol. This is also the amount of benzoic acid recoverable from adsorption on alumina in a control experiment.

Isobutyryl Peroxide. Isobutyryl peroxide reacts with alumina in the same way as benzoyl peroxide, giving a nonextractable surface oxidant with approximately the same oxidant decay kinetics (Figure 1), and isobutyric acid. It is worth noting, however, that isobutyryl peroxide is very much unlike benzoyl peroxide in its behavior in solution. In polar media the decomposition of isobutyryl peroxide is fast even at 40 °C,[2] while the products are mostly carboxyinversion[3] or other ionic products involving the decarboxylation of one of the isobutyroxy moieties. Since carboxyinversion reactions are acid catalyzed,[3-6] the decomposition of isobutyryl peroxide on the surface of acidic alumina should be quite fast. Nevertheless, the decomposition reaction is unable to compete with the reaction that produces surface oxidant unless excess peroxide is used. Thus with 5.7×10^{-4} mol of this peroxide per gram of Merck acidic alumina, not all of the peroxide is removed from the solution. If this same amount of peroxide is forced onto the surface by distilling off the solvent, the ionic products isopropyl isobutyrate and isopropyl alcohol are isolated in 20 and 41% yields, respectively. About half of the peroxide has reacted with the surface in the usual way to give surface oxidant and isobutyric acid. The isobutyric acid blocks the alumina surface and is not mobile enough to permit access of the remaining peroxide before the latter undergoes the ionic decomposition reaction.

The Effect of Benzoic Acid. Benzoyl peroxide is much less subject to Bronsted acid-catalyzed[4] ionic decomposition than is isobutyryl peroxide, although the reaction is catalyzed by $AlCl_3$.[6] We find that if acidic alumina is first covered with benzoic acid, loss of peroxide from the solution is prevented almost entirely. If less benzoic acid is used, so that the total of the benzoic acid and the benzoyl peroxide does not exceed the adsorptive capacity of the alumina, all of the peroxide reacts in the usual way. It is significant that the decay kinetics of the surface oxidant (Figure 4) are indistinguishable from those of an ordinary run at about the same initial concentration of peroxide.

The Use of Different Aluminas. The behavior of benzoyl peroxide on Merck acidic alumina has been illustrated in Figures 1–3. This alumina is of adsorption activity grade II[7] and has 3.0×10^{-4} equiv of acid per gram as titrated with NaOH to a phenolphthalein end point. A different lot from the same source gave the same surface oxidant decay behavior.

Baker acidic alumina, activity grade I and 0.73×10^{-4} equiv of titratable acid per gram, behaves as shown in Figure 4. The major difference from the Merck alumina is that the surface oxidant decay rate is more uniform, i.e., somewhat slower at the beginning of the run but decreasing much less rapidly.

Allied neutral alumina, of low adsorptive capacity (less than grade II), adsorbs only a little benzoyl peroxide, but the small amount of surface oxidant formed still decays rapidly as in the case of the acidic aluminas. If 1.2×10^{-4} mol per gram of