Disproportionation of Monosodium Tetraphenylethylene[1]

By John F. Garst,[2] Ernest R. Zabolotny, and Ronald S. Cole

The extent of disproportionation of monosodium tetraphenylethylene at room temperature varies with solvent in the order (diethyl ether, dioxane) > tetrahydrofuran > diglyme ≈ 1,2-dimethoxyethane. The factors influencing the equilibrium are discussed.

Introduction

Examples of hydrocarbons for which the disproportionation equilibrium (I) for the monoalkali adducts lies in any position except far to the left have been rare.[3,4]

$$2(RH^-, M^+) \overset{K}{\rightleftharpoons} RH + RH^{-2}, 2M^+ \qquad (1)$$
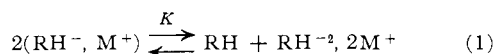
Tetraphenylethylene (TPE) has long been known as an anomalous example,[4-8] monoalkali adducts being unknown until recently.[1,9-11]

The present work is concerned with the influence of the solvent on the magnitude of $K_{TPE,Na}$. We have employed spectrophotometric methods, primarily, and have examined the solvents diethyl ether, dioxane, tetrahydrofuran, 1,2-dimethoxyethane, and diglyme.

Experimental

Quartz optical cells of 1.00 cm. and 0.119 or 0.020 cm. path lengths were attached to a 10-ml. Pyrex solvent reservoir and a 10-ml. Pyrex reaction vessel. To the reaction vessel was attached a 20 cm. length of 7 mm. Pyrex tubing, constricted in several places, which acted as a distilling column for the sodium. About a mg. of zone refined TPE was placed in the solvent reservoir. The whole system was evacuated to 10^{-6} mm. and baked periodically during a 12-hr. period. After coating the reaction vessel with a sodium mirror by distilling the sodium, the ethereal solvent was distilled into the solvent reservoir from storage over the disodium adduct of benzophenone. The reaction vessel and contents were cooled in liquid nitrogen and sealed off from the vacuum system. The progress of reaction was followed spectrophotometrically, concentrations being adjusted by tipping and distilling.

The concentration of TPE was accurately determined via its absorption spectrum. Frequently the initial disappearance of TPE did not generate a colored solution. By following the initial disappearance spectrophotometrically until a stable, faintly colored solution did result, the extent of "wastage" of TPE through these side reactions, probably with impurities, was estimated. For the more concentrated solutions, ca. 10^{-3} M, the wastage was about 3% or less. For more dilute solutions, 10^{-4} M or less, varying amounts of wastage were observed, but could be accurately measured, as evidenced by the fact that the extinction coefficients calculated for TPE^{-2}, by measurement of the spectrum when all TPE was converted to TPE^{-2}, were consistent

for experiments in which the final concentration of TPE^{-2} was taken to be the same as TPE concentration after the wastage period.

The use of two optical cells on the same reaction vessel permitted the accurate determination of widely varying optical densities. All spectra were taken on a Cary Model 14 recording spectrophotometer at room temperature (ca. 23°). Examination of the temperature coefficients, to be reported later with results on other alkali metals, indicated that ambient temperature fluctuations about room temperature have only slight effects on the spectra of the solutions, although part of the experimental scatter in $K_{TPE,Na}$ may be due to these fluctuations.

Results

The dashed curves of Fig. 1 show the experimentally determined shapes of the absorption bands of TPE and TPE^{-2}. No distinct solvent dependence of the positions, shapes, or extinction coefficients of these bands was noted. The extinction coefficient of TPE in 1,2-dimethoxyethane, tetrahydrofuran, diethyl ether, and diglyme is $(1.35 \pm 0.04) \times 10^4$ at 3070 Å. The extinction coefficient of TPE^{-2} is $(3.4 \pm 0.1) \times 10^4$ at 4900 Å.[12] The wave lengths cited correspond to band maxima.

In diethyl ether and dioxane, the dissolution of sodium in a TPE solution leads to spectra consisting of the superimposed bands of TPE and TPE^{-2}. In 1,2-dimethoxyethane, diglyme, or tetrahydrofuran additional bands at 3700 and 6600 Å. are present. The bulk of our data are from experiments in 1,2-dimethoxyethane. Until otherwise stated, the following summary of results will refer to that solvent.

The solid line of Fig. 1 is a typical spectrum containing all four bands. As sodium is dissolved, initial growth of the 3700 and 6600 Å. bands is followed by their decline, the 4900 Å. band growing at their expense. The intensities at 3700 and 6600 Å. vary linearly with one another (after allowance for overlapping bands).

(1) J. F. Garst and R. S. Cole, *J. Am. Chem. Soc.*, **84**, 4352 (1962), have previously reported some of the preliminary results on the present topic.

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(3) G. J. Hoijtink, E. deBoer, P. H. van der Meij, and W. P. Weijland, *Rec. trav. chim.*, **75**, 487 (1956).

(4) N. S. Hush and J. Blackledge, *J. Chem. Phys.*, **23**, 514 (1955).

(5) W. Schlenk, J. Appenrot, A. Michael, and A. Thal, *Ber.*, **47**, 473 (1914); W. Schlenk and E. Bergmann, *Ann.*, **463**, 1 (1928).

(6) N. B. Keevil and H. E. Bent, *J. Am. Chem. Soc.*, **60**, 193 (1938).

(7) H. Gilman and R. V. Young, *J. Org. Chem.*, **1**, 315 (1936).

(8) (a) D. W. Ovenall and D. H. Whiffen, Special Publication No. 12, The Chemical Society, London, 1958, p. 139; (b) discussion of M. J. S. Dewar, *ibid.*, p. 164; (c) discussion of N. S. Hush, *ibid.*, p. 164; (d) discussion of P. Gray, *ibid.*, p. 166.

(9) H. P. Leftin and W. K. Hall, *J. Phys. Chem.*, **64**, 382 (1960).

(10) (a) A. G. Evans, J. C. Evans, E. D. Owen, B. J. Tabner, and J. E. Bennett, *Proc. Chem. Soc.*, 226 (1962); (b) *J. Chem. Soc.*, 3954 (1963); (c) A. G. Evans and B. J. Tabner, *ibid.*, 4613 (1963).

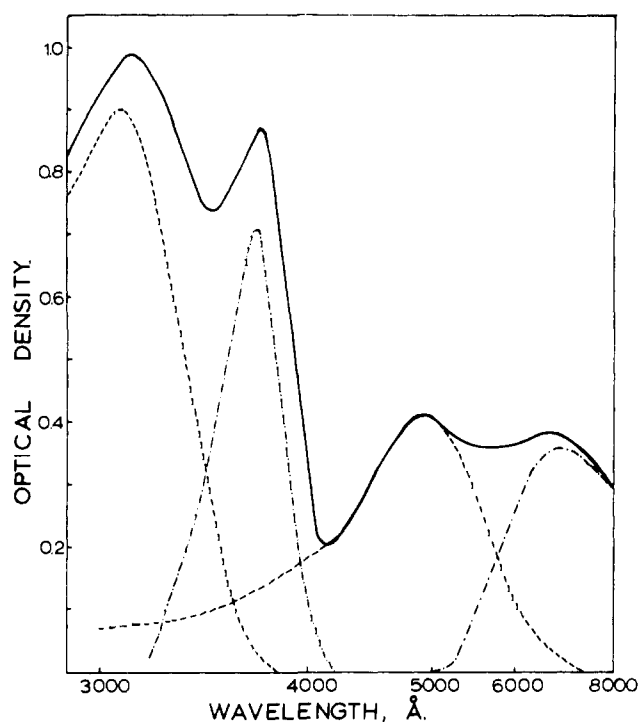(11) A. V. Tobolsky and D. B. Hartley, *J. Am. Chem. Soc.*, **84**, 1391 (1962).

(12) Results reported recently by Evans and co-workers[10] differ from ours in several respects. They report extinction coefficients of Na$_2$TPE and Li$_2$TPE in tetrahydrofuran as 1.8 and 2.7 $\times 10^4$, respectively. We consider our observed variations in the extinction coefficient of TPE^{-2} with metal ion and solvent to be within experimental error, and in no case did we obtain a value less than 3.1×10^4. While it is easy to imagine reactions of the TPE anions, probably during their initial formation period (see Experimental), which might lead to low estimates of the extinction coefficient of TPE^{-2}, it is more difficult to imagine such processes leading to high estimates. The fact that the direct determination of each substance through the use of extinction coefficients gave good accounts of mass balance over a wide range of relative concentrates substantiates the values we employ.

Evans and co-workers also report variations in the band maximum of TPE^{-2} with metal ion, their maxima being up to 250 Å. on the high energy side of those obtained in our laboratories. Variations of about 100 Å. were observed in our work, and we consider such variations to be of doubtful significance, in view of the breadth of the band. We observed the appearance of a new band at 4300 Å. in preparations in which extensive decomposition had obviously occurred. Some experiments which led to band maxima at energies higher than 4900 Å. showed distinct evidence of the presence of both bands, being broader than normal and having discernible shoulders. Such runs were discarded. They were met steadily decreasing frequency as our techniques were perfected.

In spite of these differences, the chemical regularities which emerge from the work of the two groups are in agreement.

Fig. 1.—Typical spectrum of the sodium adducts of TPE in 1,2-dimethoxyethane (solid curve); dashed curves, bands due to TPE (3100 Å.) and TPE^{-2} (4900 Å.), actual shapes; dash-dotted curves, speculated shapes of bands at 3700 and 6600 Å., due, presumably, to TPE^{-} (see text).

Clearly, at least two species are being formed initially, with the material(s) absorbing at 3700 and 6600 Å. being ultimately converted to TPE^{-2}. Spectra obtained by converting all TPE to TPE^{-2}, then admitting more TPE by means of a break seal, were identical in form with those obtained by dissolution of sodium in a TPE solution, equilibrium being achieved immediately upon a mixture of TPE and TPE^{-2}.

Assuming that TPE, TPE^{-2}, and a third material (X), absorbing only at 3700 and 6600 Å., are the only species present, knowledge of the extinction coefficients of TPE and TPE^{-2} permits the calculation of the extinction coefficients of X at 3700 and 6600 Å. by mass balancing. This procedure involves uncertainty in curve analysis (see Fig. 1), but fortunately the bands under consideration are spaced so that the problem is not extremely serious. Extinction coefficients of compound X obtained in this manner are 1.3×10^4 and 2.8×10^4 at 6600 and 3700 Å., respectively.

Compound X is logically TPE^{-}. If so, solutions containing X should be paramagnetic, as indeed they are. Solutions of TPE^{-2} in diethyl ether and dioxane gave no e.s.r. signals in the $g = 2$ region.[1,8a] Electron spin resonance spectra of TPE^{-} have been reported and a coupling constant analysis in fair agreement with both the e.s.r. spectrum and a McLachlan calculation of spin densities has been given.[1,10,13,14]

If a simple equilibrium of the type I is assumed, differences in the degrees of ionic dissociation not being

(13) A. D. McLachlan, *Mol. Phys.*, **3**, 233 (1960). In our calculation λ was employed as calculated, λ = 1.14, and was not treated as adjustable. The resolution of the spectrum would probably not justify a more detailed calculation.

(14) E.s.r. spectra showing considerably more fine structure have been obtained in the laboratories of Dr. W. G. Schneider, National Research Council, Canada, for the potassium adduct in tetrahydrofuran and 1,2-dimethoxy-ethane. Although our spectra showed no changes in fine structure with variation of metal ion, it is quite possible that better resolved spectra might
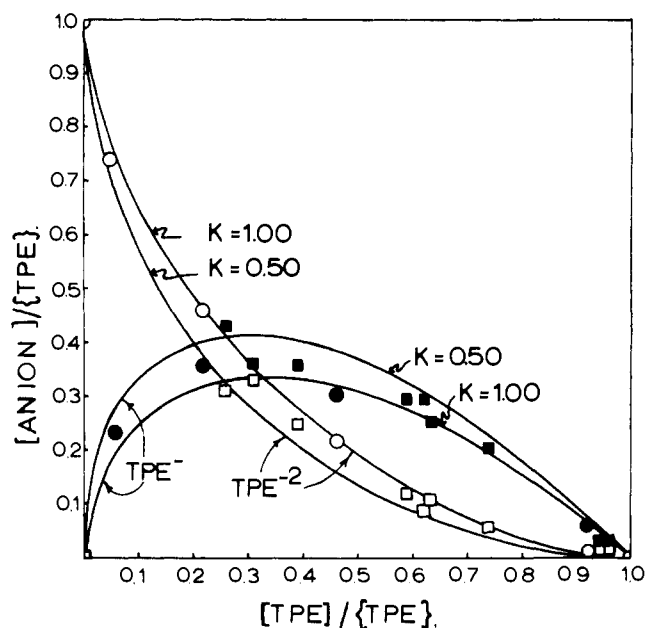

Fig. 2.—Conformance of the data to eq. 2: O, TPE^{-2} in experiment 95. ●, TPE^{-} in experiment 95; □, TPE^{-2} in other experiments; ■, TPE^{-} in other experiments. All values of concentrations for anions have been divided by $\{TPE\}$ appropriate to the experiment being plotted (see text).

taken into account, the forms of the variations of the concentrations of all three species with successive dissolution of sodium in a TPE solution can be calculated. The appropriate relations are

$$2x = (z/K) + 2(w - z) - \sqrt{(z/K)((z/K) + 4(w - z))} \quad (2)$$

and

$$w = x + y + z \quad (3)$$

where $w = \{TPE\}$, $x = [TPE^{-2}]$, $y = [TPE^{-}]$, and $z = [TPE]$. The circles of Fig. 2 show the conformance of some typical data to these relationships. They correspond to a single run (experiment 95) in which $\{TPE\}$, formal concentration of TPE, remained constant. For reasons which will appear later, all concentrations were divided by $\{TPE\}$, in this case, $3.35 \times 10^{-4} M$, before plotting. The points closely fit the theoretical curve for a value of $K_{TPE,Na}$ near 1.00. As a check on the extinction coefficients and curve analyses, $\{TPE\}$ can be calculated from the measured concentrations of TPE, TPE^{-}, and TPE^{-2}. For the four points (of experiment 95) shown, $\{TPE\}$ is calculated in this fashion to be 3.35, 3.26, 3.47, and $3.41 \times 10^{-4} M$, while the end points (all TPE or TPE^{-2}) indicate $3.35 \times 10^{-4} M$. This scatter gives an indication of the magnitude of the errors involved in our procedure. Table I gives the values of $K_{TPE,Na}$ calculated directly from the equilibrium expression.

Employing a method previously described,[15] Beer's law was tested for all four bands at typical concentration ratios and absolute concentrations in the ranges about 10^{-4}–$10^{-5} M$, with the result that all bands appear to obey Beer's law. However, when the concentration of a given solution containing the equilibrium mixture of hydrocarbon and anions was varied

(15) J. F. Garst, D. Walmsley, C. Hewitt, W. R. Richards, and E. R. Zabolotny, *J. Am. Chem. Soc.*, **86**, 412 (1964).

by a factor of 34 (from $\{TPE\} = 8.87 \times 10^{-5}\ M$ and $\{Na\} = 5.68 \times 10^{-5}\ M$ to $\{TPE\} = 2.98 \times 10^{-3}\ M$ and $\{Na\} = 1.87 \times 10^{-3}\ M$), variations in the relative intensities of the bands were observed. The equilibrium "constant," calculated as if eq. 4 correctly represented

$$2NaTPE \underset{\longleftarrow}{\overset{K_{TPE,Na}}{\longrightarrow}} TPE + Na_2TPE \qquad (4)$$
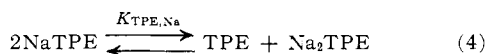
the equilibrium, was 0.91 in the dilute solution and 2.1 in the more concentrated solution. This direction of variation is the expected one if the ion pairs (NaTPE) are more ionically dissociated than the triple ions (Na$_2$TPE), as the work of Hoijtink's group indicates.[3,16]

The variation of $K_{TPE,Na}$ with concentration appears to be insufficient to disturb seriously the plot shown in Fig. 2, even though the formal concentration of sodium ions varies during experiment 95. Further, experiment 95 can be compared with other experiments of rather different over-all concentrations by dividing all concentrations by $\{TPE\}$ before plotting the resulting points on the graph of Fig. 2. If Beer's law were perfectly obeyed, the resulting data should fit the relationship established by experiment 95. The squares of the figure show that the agreement is surprisingly good, nearly all points falling between the theoretical curves for $K_{TPE,Na} = 0.50$ and $K_{TPE,Na} = 1.00$ with more near the latter value. The agreement of this figure with our previous estimate ($K_{TPE,Na} < 1.8$; the calculated figure, assuming no errors in measurement, was 0.4),[1] employing a different and independent method (e.s.r. intensity measurements), is gratifying. Data from which the points of Fig. 2 can be identified and from which the original concentrations of all species can be computed, with the aid of Fig. 2, are given in Table I.

TABLE I

DISPROPORTIONATION OF MONOSODIUM TETRAPHENYLETHYLENE

Experiment	Solvent	$\{TPE\}^a \times 10^5$	$\{TPE\}/TPE$	$K_{TPE,Na}^b$
95	1,2-Dimethoxyethane	33.5	0.94	7
		33.5	.46	1.1
		33.5	.22	0.77
		33.5	.05	.72
108		8.56	.62	.71
109		12.5	.59	.81
		6.0	.31	.80
113		12.7	.74	1.2
115		116	.94	9.0
		10.7	.63	1.1
		9.88	.39	0.73
		4.48	.26	0.45
116		158	.96	11.5
	1,2-Dimethoxyethane average			0.84^c
80	Diglyme	180	0.64	1.0
107	Tetrahydrofuran	15.8	0.64	42^d
	Dioxane, $K_{TPE,Na}$ too large for measurement^e			
	Diethyl ether, $K_{TPE,Na}$ too large for measurement^f			

^{a} $\{TPE\}$ = formal concentration of TPE. ^{b} Evaluated directly from the equilibrium expression. ^{c} Average omits those points corresponding to $[TPE]/\{TPE\}$ greater than 0.90. ^{d} Reference 10c reports $K_{TPE,Na}$ at 30° as 2800, in pronounced disagreement with the value given here.[12] ^{e} Estimated from the sensitivity of the spectrophotometric method as being greater than 10^5. ^{f} Estimated from e.s.r. sensitivity[1] as being greater than 10^5 and probably greater than 10^6.

The results in solvents other than 1,2-dimethoxyethane are less extensive. No equilibrium constant

(16) A. C. Aten, V. Dieleman, and G. J. Hoijtink, *Discussions Faraday Soc.*, **29**, 182 (1960).

could be measured for dioxane or diethyl ether, since no band assignable to TPE$^-$ could be detected. We estimate that such a band would be detectable for values of $K_{TPE,Na}$ up to about 5×10^4, assuming that the extinction coefficient of TPE$^-$ derived from the 1,2-dimethoxyethane data is applicable. This assumption is supported by the fact that the same extinction coefficient gives good accounts of mass balance in diglyme and tetrahydrofuran.[12] (There are indications from work with Li adducts of TPE that the band at 3700 Å. may be due to a different material from the band at 6600 Å. If so, the values of $K_{TPE,Na}$ reported should be raised by a factor of about 2.) We have previously estimated $K_{TPE,Na}$ in diethyl ether as being greater than 10^5, from considerations of the sensitivity of e.s.r. This estimate is probably conservative, a lower limit of 10^6 being more likely.

The values tabulated for tetrahydrofuran and diglyme stem from experiments considered to be least susceptible to errors owing to curve analysis and the anomalies associated with very large relative excesses of TPE (see below). In each case, the value given is substantiated by several other experiments.

In 1,2-dimethoxyethane the directly determined values of $K_{TPE,Na}$ scatter between 0.45 and 1.2 for most of the points reported, which are typical of many more actually obtained. At values of $[TPE]/\{TPE\}$ greater than 0.90, larger equilibrium constants resulted, in spite of the fact that the simultaneous use of thin and thicker cells permitted the accurate determination of widely different optical densities. Similar variations appear in the tetrahydrofuran and diglyme data. While this scatter seems at least semisystematic, it is difficult to account for the trends in any reasonable fashion. The variations are too large to be a result of simple curve analysis errors.

One possibility which seems capable of accounting for the 1,2-dimethoxyethane data, at least, is that TPE$^-$ has a hidden band at 4900 Å. with an extinction coefficient comparable to that at 6600 Å. If so, values of $K_{TPE,Na}$ calculated for ratios $[TPE]/\{TPE\}$ near 1.0 would be significantly larger than those calculated from data corresponding to smaller ratios $[TPE]/\{TPE\}$, which would be more precise. For this reason we have chosen to omit the largest values in our averaging of $K_{TPE,Na}$ in Table I. This possible factor was also considered in evaluating the reliability of $K_{TPE,Na}$ determined in solvents tetrahydrofuran and diglyme (see above) from various experiments.

While there is evidence that NaTPE ion pairs, at least, may be to some extent dissociated, the system comes surprisingly close to obeying the simple equilibrium law related to eq. 4. We will assume eq. 4 as the basis for our present discussion.[17]
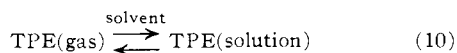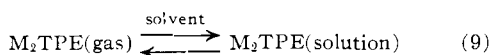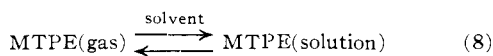
Discussion

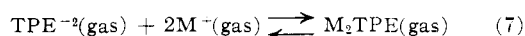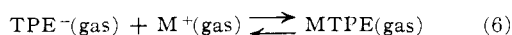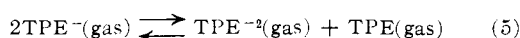Four factors have been previously mentioned as possibly contributing to the anomalously large value for $K_{TPE,Na}$: (1) solvation energies could favor the dianion, a corollary being that more polar solvents would lead to an increase in $K_{TPE,Na}^{4,8c}$; (2) ionic aggregation effects could favor the dianion[8a]; (3) the difference be-

(17) If NaTPE ion pairs are appreciably dissociated, but Na$_2$TPE triple ions are not,[3,16] the interpretation of the solvent and metal ion influences discussed below follows along nearly identical lines and leads to the same conclusions.

tween the electron–electron repulsion energies in planar TPE^{-2} and those in TPE^{-1} could be less than the similar differences for other hydrocarbons[4]; and (4) the energy of TPE^{-2} might be even lower than predicted for a planar molecule, due to possible changes (not available to other hydrocarbon anions) in geometry.[4,8b-d]

The order of polarities of the ethers employed in the present investigation appear to be diethyl ether < dioxane < tetrahydrofuran < 1,2-dimethoxyethane < diglyme.[15] Thus, the trend of $K_{TPE,Na}$ with solvent is the opposite of that predicted by hypothesis 1 above. If solvation effects are important, one may reasonably conclude that it is the ion pair and triple ion solvation energies which should be considered, since there is a distinct metal ion effect on K_{TPE}.[1,10e,11,18] The facts are consistent with hypothesis 2 above, and it is quite likely that the factors of hypotheses 3 and 4 may also apply to the consideration of the magnitude of $K_{TPE,Na}$.

Aggregation and Solvation Effects.—The following scheme affords one view of the factors influencing the equilibrium constant and provides a basis for the discussion of the effects involved. The ΔF°'s corresponding to the following series of hypothetical reactions are viewed as components of ΔF°_4. For convenience of discussion, parenthetical groupings of terms have been indicated (eq. 11a) and the resulting four terms have

$$2TPE^-(gas) \rightleftarrows TPE^{-2}(gas) + TPE(gas) \quad (5)$$

$$TPE^-(gas) + M^+(gas) \rightleftarrows MTPE(gas) \quad (6)$$

$$TPE^{-2}(gas) + 2M^+(gas) \rightleftarrows M_2TPE(gas) \quad (7)$$

$$MTPE(gas) \xrightarrow{\text{solvent}} MTPE(\text{solution}) \quad (8)$$

$$M_2TPE(gas) \xrightarrow{\text{solvent}} M_2TPE(\text{solution}) \quad (9)$$

$$TPE(gas) \xrightarrow{\text{solvent}} TPE(\text{solution}) \quad (10)$$

been given numerical symbols (eq. 11b). If δ^s is a difference operator reflecting a change to a *more polar* solvent,[19] eq. 12 applies, δ^s1 is zero, and δ^s4 is neglected.

$$\Delta F^\circ_4 = \Delta F^\circ_5 + (\Delta F^\circ_7 - 2\Delta F^\circ_6) +$$
$$(\Delta F^\circ_9 - 2\Delta F^\circ_8) + \Delta F^\circ_{10} \quad (11a)$$

$$\Delta F^\circ_4 = 1 + 2 + 3 + 4 \quad (11b)$$

$$\delta^s \Delta F^\circ_4 = \delta^s2 + \delta^s3 \quad (12)$$

While the symbol F° will be employed in the following discussion, most of the deductions will actually be based on considerations of potential energy, the tacit assumption being that the free energies will reflect these variations. The analysis may therefore be in error for any situation for which that assumption fails.

If eq. 6 and 7 are understood to relate to products which adopt geometries of minimum free energy in the gas phase, δ^s2 is zero. For the purposes of this discussion, however, we presume that the ionic configurations of the aggregates may be different in solution from those

(18) Unpublished results from the author's laboratories.

(19) Following J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York N. Y., 1963, p. 22 ff., δ has been employed as a symbol for a medium effect difference operator, rather than Δ, which is reserved for a change associated with a chemical reaction. The restriction of δ^s to always indicate an increase in solvent polarity makes the above discussion a little more convenient without removing generality. It further assumes the existence of an appropriate polarity scale.

adopted in the gas phase, and may vary from one solvent to another. The ionic aggregates of eq. 6 and 7 are considered here to have the same interionic geometries as those finally adopted by the same aggregates in the solvent in question. If there should be no differences between the geometric dispositions of the ions of aggregates of minimum free energy in various solvents, δ^s2 will vanish.

If the ions were completely dissociated in some solvent, δ^s2 would vanish and δ^s3 would be predicted, on the basis of the Born charging model, to be negative, reflecting solvation energy of a dianion (TPE^{-2}) which is larger than that of two monoanions (TPE^-) of the same size.[4] An increase in solvent polarity would therefore lead to a larger value of $K_{TPE,M}$.[4] This is not in accord with observation.

If the ions were completely associated and if there were no changes in the interionic geometry from one solvent to another, δ^s2 would again vanish from eq. 12, leaving only δ^s3 for consideration. Term 3 is zero in the gas phase and should be positive in solvent, since the solvation energies of higher aggregates (which probably have no dipole moments) should be less than the solvation energies of ion pairs. Furthermore, if the solvation energies are simply proportional to some function reflecting solvent polarity, as is commonly presumed, δ^s3 will also be positive, terms 3 becoming monotonically more and more positive in more and more polar media. Thus it is predicted that $K_{TPE,M}$ should be smaller in more polar solvents, in accord with observation.

Situations which might involve incomplete ionic association are more complex, but can be treated in the same general fashion outlined here. Simple considerations suggest that higher degrees of ionic dissociation ought to correspond to lower values of $K_{TPE,M}$.

The consideration of possible solvent dependent interionic geometry variations in aggregates introduces another complication. "Loosening" of the aggregates is the major such variation which might be important. "Loosening" will occur only if the accompanying increase in solvation energy (due to increased electric moments of the aggregate and to decreased steric hindrance to the solvation of the ions by their partners) compensates for it. It is difficult to estimate rationally the magnitude or sign of δ^s2, but its appearance in eq. 12 reflects a possible mechanism by which the direction of the solvent effect might be reversed. Since the direction is properly accounted for by the assumption that δ^s2 is zero, we assume that its actual value is smaller than and/or of the same sign as δ^s3.

It should be noted that since term 3 of eq. 11 is *positive*, and since ΔF°_4 in solution is *much less* than predicted from neglecting terms 2, 3, and 4, it is clear that either term 2 plays a dominant role in the determination of ΔF°_4 in solution or that the estimation of term 1 did not take into account some pertinent factor, or both.

Term 2 should be negative, as required from electrostatics, if the distances of separation of counterions are about the same in the ion pair as in the triple ion. It is instructive to consider the approximate magnitudes of some of the terms of eq. 11. Term 1 has been estimated as above 110 kcal./mole.[4] Term 2 depends upon the interionic radii, the detailed geometry of the aggregates, and the charge distribution in the anion.

Using simple spherical charges as models for the ions, the order of magnitude of 2 can be estimated with reference to Fig. 3. Term 2 is seen to be of the same order of magnitude as 1 (Table II), but of opposite sign, and may easily outweigh 1, leading to $K_{\text{TPE,Na}} > 1$ for the gas phase disproportionation of NaTPE. Solvation effects, discussed above, tend to decrease $K_{\text{TPE,Na}}$.

TABLE II
COULOMBIC ENERGETICS OF GAS PHASE ION PAIR DISPROPORTIONATION[a]

r, Å.	Term 2, kcal./mole[b]	r, Å.	Term 2, kcal./mole[b]
2	−249	6	−83
3	−166	7	−71
4	−125	8	−62
5	−100	9	−55
		10	−50

[a] For the significance of r and the geometry assumed for the ions see Fig. 3. The energies tabulated here are due strictly to interionic coulombic interaction and do not include internal electron–electron repulsive interactions. [b] Term 2 of eq. 11.

Geometric Changes in the Dianion.—The resemblance of the electronic structure of TPE^{-2} to that of hydrazine derivatives has been taken as a basis for the possibility that TPE^{-2} might not be (nearly) planar, but might instead possess tetrahedral geometries about the two central carbon atoms.[8b–d] Such a change in bond hybridization might be accompanied by a substantial decrease in the energy of the molecule, as compared to the energy of the planar molecule. Another similar kind of distortion of the (nearly) planar molecule would simply involve twisting by 90° about the central bond.[4,8]

To the previous discussions[4,8] may be added the following remarks. The loss of conjugation energy upon twisting the two halves of TPE^{-2} so that their planes are perpendicular is calculated by Hückel MO theory as 0.5β or about 10 kcal/mole. The further loss of conjugation energy (compared to the twisted form) upon complete localization of electron pairs on the central carbon atoms is similarly calculated as 2.6β, or about 52 kcal./mole. Acting in a compensatory fashion will be substantial decreases in the electron–electron repulsion energies in the dianion, accompanying twisting and rehybridization, in addition to the orbital and bond energy changes. It is not unreasonable that the favorable energetic terms accompanying geometry changes could outweigh the loss of conjugation energy, leading to a larger $K_{\text{TPE,Na}}$ than would have otherwise been estimated.

Since the same considerations should be applicable to stilbene,[3,20] one might ask why its behavior seems qualitatively different from tetraphenylethylene. The
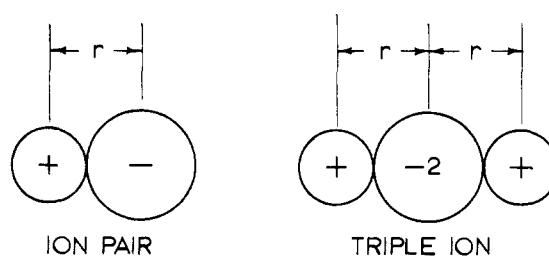

Fig. 3.—Geometries of ionic aggregates assumed in the calculation of the electrostatic contribution to term 2 of eq. 11.

answer could lie in the quantitative considerations of Hush and Blackledge, who concluded that while ΔE for the gas phase disproportionation of TPE^- to planar TPE^{-2} is about 110 kcal./mole, the similar energy for stilbene$^-$ is 127 kcal./mole. If the other factors affecting K were about the same for the two compounds, the 17 kcal./mole difference could account for K's differing by a factor of about 10^{12} at room temperature. Furthermore, the solvents in which stilbene anions have been examined are restricted to the more polar ethers,[20] favoring a smaller K.

Although we have referred to the disporportionation behavior of TPE as "anomalous," it may be that this judgment is the result of a biased viewpoint, and that the reference compounds employed in making the judgment are not the most satisfactory ones. Most of the hydrocarbons for which $K \ll 1$ are condensed aromatic hydrocarbons whose rigidity may prohibit deviations from planarity in the dianion. Olefins do not fall into this class.[21] To the extent that TPE can be thought of as a perturbed ethylene, there is perhaps no sound basis for viewing the disproportionation behavior of TPE^- as anomalous, since the appropriate data for ethylene$^-$ are not available. A similar remark could be applied to cyclooctatetraene.[22]

(20) (a) D. E. Paul, D. Lipkin, and S. I. Weissman, *J. Am. Chem. Soc.*, **78**, 116 (1956); (b) J. V. B. Reesor, V. G. Smith, and G. F. Wright, *J. Org. Chem.*, **19**, 940 (1954).

(21) Although Hush and Blackledge calculated a very large ΔE for the disproportionation of gas phase, unaggregated ethylene$^-$ to ethylene and planar ethylene^{-2} (205 kcal./mole), the compensating energies accompanying rehybridization and ionic aggregation should also be larger than for other hydrocarbons (including TPE). This follows from the facts that geometric changes in ethylene^{-2} would involve no loss in conjugation energy and that the small size and high charge density in ethylene^{-2} would imply *both* a great sensitivity of electron–electron repulsion energies to geometric changes *and* exaggerated energetics of ionic aggregation (corresponding to entries near the top of Table II).

(22) (a) T. J. Katz, *J. Am. Chem. Soc.*, **82**, 3784 (1960); (b) H. L. Strauss, T. J. Katz, and G. K. Fraenkel, *ibid.*, **85**, 2360 (1963).