Organic and Biological Chemistry

Electron Transfer Equilibria. IV. Effects of Metal Ion and Temperature on the Disproportionation of Monoalkali Tetraphenylethylenes[1,2]

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The metal ion dependence of the formal equilibrium constant for the disproportionation of monoalkali tetraphenylethylenes in ethers can be rationalized in terms of competing solvation and coulombic aggregation effects. The temperature coefficients of K_F are positive in each case examined, and the trends in the values of formal $\Delta H°$ and formal $\Delta S°$ are also indicative of competing effects.

Introduction

The factors influencing the disproportionation of the mononegative ion of tetraphenylethylene (TPE⁻) in solution have been under investigation in our labora-

$$2\text{TPE}^- \rightleftharpoons \text{TPE} + \text{TPE}^{-2} \qquad (1)$$

tories.[2] Our previous reports have been confined to solutions in which the counterion was sodium and the temperature was *ca.* 23°. A pronounced solvent effect among ethers was found. The effects of variations of the alkali metal and the temperature, as well as the solvent, are now reported.

The metal ion effects may be of particular interest in connection with the problem of the influence of metal cations on the reactivity and mode of reaction of anions in alkylation and related reactions in ethers and other aprotic solvents, not because of detailed similarities, but rather because both problems must involve the same general kinds of considerations. The disproportionation of TPE⁻ may prove to be a model system, in some respects, for these reactions, since it is a reaction of a rather different and perhaps fundamentally simpler type, studied here as an equilibrium rather than a rate problem. These features suggest that the present results might provide insight applicable to other reactions, and *vice versa.* In all such cases it should be clear that metal ion and solvent effects will generally be interwoven, since both the presence and the nature of the cation may exert controlling influences on the details of solvation phenomena.[4-8]

Experimental

The general techniques were previously described.[2b] Potassium mirrors were created by direct distillation, in the same manner as previously described for sodium. Cesium was introduced to reaction vessels by distillation from a Ca–CsCl mixture. Lithium mirrors were created by the evaporation of ammonia from lithium–ammonia solutions.

Cells of 1.00-, 0.119-, and 0.020-cm. path lengths were employed as the occasion demanded. All spectra were obtained using a Cary Model 14 spectrophotometer. The temperatures of the heating or cooling agents employed for the temperature variation studies were determined near the jacketed optical cells by means of a thermocouple.

Results

K_F is the formal equilibrium constant for disproportionation of TPE⁻. It is related to eq. 1 in the usual fashion, but the formal concentrations of the ionic species, which are directly measured, are employed. If ionization and aggregation factors are important, as our data show them to be, K_F indexes the position of a complex set of equilibria rather than the very simple situation implied by eq. 1.

In our previous report of spectrophotometric studies of the disproportionation of monosodium tetraphenylethylene at room temperature, we noted that K_F was reasonably constant (near 0.8) for many runs, but was determined at rather high values (7, 9, and 12) when large excesses of TPE were present.[2b] Except for this point, all the data seemed consistent with the simplest and most direct interpretation of the visible spectra of sodium–TPE solutions, namely, that the band at 4900 Å. is due to TPE⁻² while those at 3700 and 6600 Å. are due to TPE⁻. It was suggested, however, that if the spectrum of TPE⁻ had a band coincident with that of TPE⁻² at 4900 Å., the peculiar variation in the apparent values of K_F might be accounted for. We

(1) Supported by funds provided through grants from the National Science Foundation and through the Director of General Research of the University of Georgia.

(2) (a) Part I: J. F. Garst and R. S. Cole, *J. Am. Chem. Soc.*, **84**, 4352 (1962); (b) part II: J. F. Garst, E. R. Zabolotny, and R. S. Cole, *ibid.*, **86**, 2257 (1964); (c) part III: E. R. Zabolotny and J. F. Garst, *ibid.*, **86**, 1645 (1964); see also ref. 3.

(3) (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).

(4) A comprehensive discussion, with references, of the role of cations in the alkylation of ambident anions, including their role with regard to solvent effects, is given by N. Kornblum, R. Selzer, and P. Haberfield, *J. Am. Chem. Soc.*, **85**, 1148 (1963).

(5) H. D. Zook and T. J. Russo, *ibid.*, **82**, 1258 (1960); H. D. Zook and W. L. Gumby, *ibid.*, **82**, 1386 (1960).

(6) H. E. Zaugg, B. W. Horrom, and S. Borgwardt, *ibid.*, **82**, 2895 (1960); H. E. Zaugg, *ibid.*, **82**, 2093 (1960); **83**, 837 (1961).

(7) J. F. Garst, D. Walmsley, C. Hewitt, W. R. Richards, and E. R. Zabolotny, *ibid.*, **86**, 412 (1964); J. F. Garst, C. Hewitt, D. Walmsley, and W. Richards, *ibid.*, **83**, 5034 (1961).

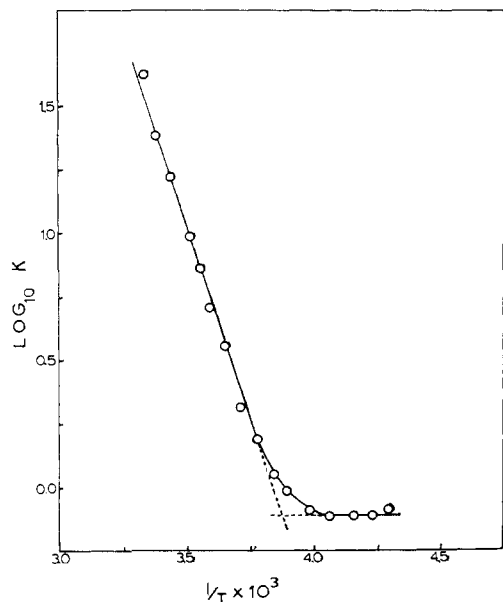(8) A. Streitwieser, Jr., and J. I. Brauman, *ibid.*, **85**, 2633 (1963).

Figure 1. Log K_F vs. $1/T$ plot for the sodium adducts of TPE in tetrahydrofuran (expt. 118b), on the basis of the simple band analysis previously employed.[2b,3] Similar plots were observed in all cases in which the apparent value of K_F dropped below 1.0, the region of zero slope being longer than that shown in this figure in several cases. The straight line portion of the curve shown has a slope corresponding to a $\Delta H_F{}^\circ$ of 14 kcal./mole. This does not compare unreasonably with the 11 kcal./mole reported in ref. 3c, and, in fact, we obtained 11 kcal./mole in another experiment employing different concentration conditions.
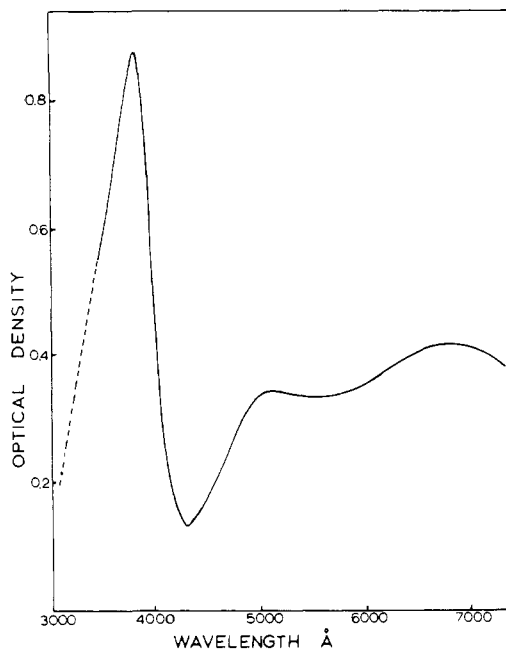

Figure 2. Limiting spectrum obtained by driving equilibrium 1 far to the left either by having present a very large excess of TPE or by sufficiently lowering the temperature, and, thereby, K_F.

have found convincing evidence in studies of the temperature dependence of the spectra, combined with the results previously reported, that *both* TPE^{-2} and TPE$^-$ have significant bands at 4900 Å.

If the band at 4900 Å. is treated as resulting entirely from absorption by TPE^{-2}, and equilibrium constants are calculated on that basis, the resulting log K_F vs.
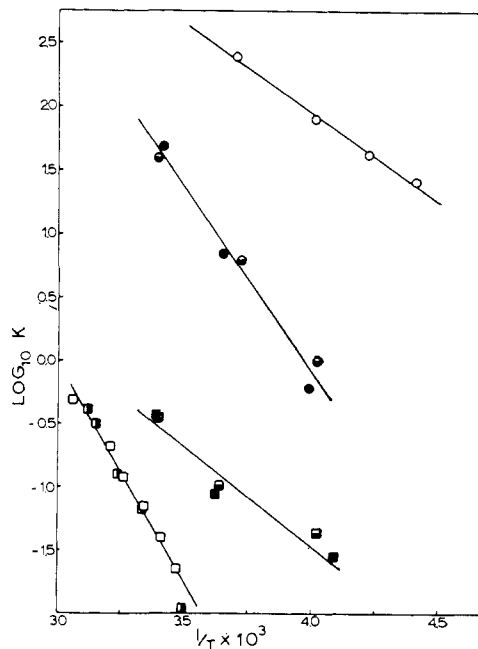

Figure 3. Log K_F vs. $1/T$ plots for the disproportionation of mono-alkali tetraphenylethylenes in 1,2-dimethoxyethane. Key to alkali metals: O, Cs, expt. 120; ●, K, expt. 110; ◒, K, expt. 122; □, Na, expt. 115a; ◨, Na, expt. 115b; ▣, Li, expt. 114 (1); ■, Li, expt. 114 (2).
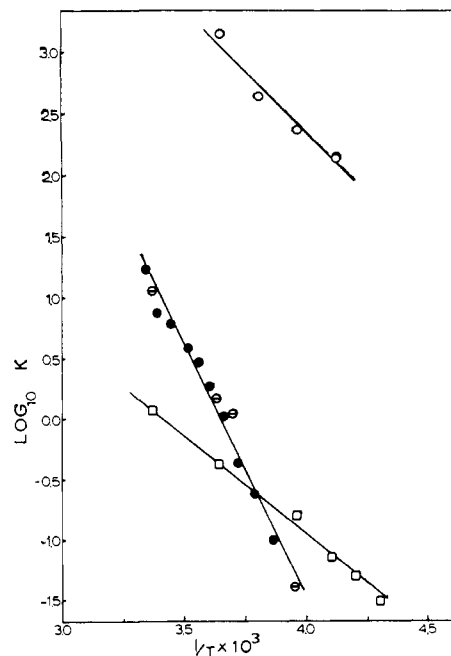

Figure 4. Log K_F vs. $1/T$ plots for the disproportionation of mono-alkali tetraphenylethylenes in tetrahydrofuran. Key to alkali metals: O, K, expt. 112; ●, Na, expt. 118 (4); ◒, Na, expt. 118b; □, Li, expt. 117 (3).

$1/T$ plots have the form shown in Figure 1 in every case in which K_F reaches values notably less than 1.0.[9, 10]

(9) The assumption of a band at 4900 Å. for TPE$^-$ will, of course, alter the calculated extinction coefficient for TPE$^-$ at 6600 Å. (see later). The *form* of the log K_F vs. $1/T$ plot is insensitive to the value of the extinction coefficient employed, since the use of other values simply displaces the entire curve up or down.

(10) Evans and co-workers apparently did not obtain the peculiar forms of the log K_F vs. $1/T$ plots that we report, although they used a simple band analysis which assigned the band at 4900 Å. to TPE^{-2} alone.[3] It is quite reasonable that they would not observe the phe-

Table I. Typical Analytical Product Balances

Action	[TPE]^a	{TPE^{-2}}^{a}	{TPE$^-$}^{a}	{TPE}^{a}	{Na$^+$}^{a}	$1/T^b$
Dissolution of	3.45	0.00	0.00	3.45	0.00	3.38
Na in 1,2-	1.43	0.39	1.73	3.55	2.51	3.38
dimethoxy-	0.75	0.98	1.74	3.47	3.70	3.38
ethane solu-	0.31	1.55	1.51	3.37	4.61	3.38
tion of TPE	0.00	3.48	0.00	3.48	6.96	3.38
at room tem-						
perature						
Change in	0.313	0.073	0.054	0.440	0.200	3.40
temperature	0.313	0.066	0.068	0.447	0.200	3.50
of a solution	0.319	0.055	0.096	0.470	0.206	3.60
of Na adducts	0.314	0.036	0.135	0.485	0.207	3.70
of TPE in	0.311	0.019	0.177	0.507	0.215	3.80
tetrahydro-	0.311	0.008	0.207	0.526	0.223	3.90
furan	0.316	0.003	0.221	0.540	0.227	4.00

^{a} 10^4 times actual concentrations in moles/l. {TPE} is the sum of concentrations of all species containing TPE residues. {Na$^+$} is the formal concentration of dissolved sodium, computed from the formal concentrations of TPE$^-$ and TPE^{-2}. ^{b} 10^3 times actual values.

The lower portion of the curve always has zero slope, even in different solvents and with different cations. In fact, the spectra simply do not change with changing temperature in the regions of zero slope, as should be the case if the only alkali adduct of TPE measurably present throughout this region is TPE$^-$. The latter condition will prevail whenever K_F is sufficiently small.

Since the presence of a large excess of TPE should drive the equilibrium to the side of TPE$^-$, the same explanation applies to the large values of apparent K_F obtained at room temperature with sodium in 1,2-dimethoxyethane; e.g., a band (at 4900 Å.) due to TPE$^-$ was interpreted as being due to TPE^{-2}, resulting in the overestimation of TPE^{-2} and, thus, K_F. That the spectrum of TPE$^-$ is the one shown in Figure 2 is confirmed by the fact that for the sodium adduct in 1,2-dimethoxyethane the *same* limiting visible spectrum (Figure 2) is obtained by shifting the equilibrium sufficiently toward TPE$^-$ either by having a large excess of TPE present *or* by lowering the temperature sufficiently. Moreover, the *same* limiting spectrum is similarly achieved for other cations and other solvents.

Both the unusual dependence of calculated K_F values on large excesses of TPE and the peculiar forms for log K_F vs. $1/T$ plots vanish when the spectrum of TPE$^-$ is assumed to be that given in Figure 2 (see Figures 3 and 4). The extinction coefficient of TPE$^-$ is then recalculated to be 1.0×10^4 at 6600 Å. and 0.75×10^4 at 4900 Å. Recalculation of K_F values alters the previously reported values (except the ones with large excesses of TPE, which are more affected) by factors near 0.1–0.3, but has no consequences affecting the significance of the previously reported results.[2b,11]

Table I shows typical analytical data. For the upper part of the table the formal concentration of TPE ({TPE} = [TPE] + {TPE$^-$} + {TPE^{-2}}) should be a

nomenon, since the aberrations appear only in regions for which K_F is actually quite small, and their solvent and temperatures confined their studies to regions of larger values of K_F.

(11) For an individual run the conformance of the data to eq. 2 of ref. 2b is slightly improved upon recalculation. The scatter between K_F values for different runs is slightly increased, however, due to slightly increased dependences of recalculated K_F values on both temperature and concentration. The concentration effect is detailed in a later section. Recalculation of K_F values previously reported gives the values recorded in Table II. The spectra recorded in diglyme appear to have so little TPE^{-2} present that recalculation is inaccurate; values near 0.08 are obtained if this inaccuracy is ignored.

constant. For the lower part of the table both {TPE} and {Na$^+$} should increase slightly (and proportionately) with lowering of temperature due to the contraction of the solvent. The fact that the measured {TPE} increases proportionately more than the measured {Na$^+$} is probably an indication that our analysis for [TPE] is less accurate, when there is not a substantial excess of TPE, than our analyses for the ionic species, since the increase in {Na$^+$} is about what it should be, judged from independent experiments. The experiment tabulated in the lower part of the table is actually one of our poorer runs of this type in regard to the constancy of the ratio {TPE}/{Na$^+$}; it was chosen to illustrate the point made in the preceding sentence.

Table II records some values of K_F obtained for various alkali metals in three ethers at 25°. Upper and lower observed limits are given in some cases, since the value of K_F is dependent, in those cases, on concentration conditions.[2b] The variation of K_F with concentration is probably due to the fact that some of the ionic species are ionized or aggregated to various degrees in different concentration ranges. Consequently, the form written for K_F, which ignores aggregation and ionization, does not correspond to the complex set of equilibria which may be appropriate to an exact description of the system (see a later section).

Table II. Formal Disproportionation Constants at 25°

| Metal | Solvent | | |
	Diglyme	DME^a	THF^b
Li	. . .	0.3, 1.3^c	0.7, 1.2
Na	. . .^{d}	0.05, 0.3	8, 30
K	9, 12	40, 50	6000
Cs	200, 400	2700	Large

^{a} 1,2-Dimethoxyethane. ^{b} Tetrahydrofuran. ^{c} Where two figures are given, these represent the limits encountered in our experiments, in which the concentrations of all species were usually within an order of magnitude of 10^{-4} M. Where one figure is given the observed variation, over a small number of experiments, was slight. ^{d} Recalculation of the previously reported value would be very inaccurate because of the very small amount of TPE^{-2} present.

The lithium spectra exhibit a feature the sodium spectra do not; the band at 3700 Å. does not always stand in constant ratio to the band at 6600 Å., implying that more than one species must be responsible for these bands. The deviation is not apparent until

Table III. Formal Thermodynamic Quantities for Disproportionation[a]

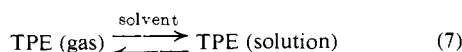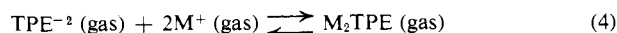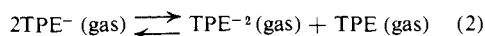| Expt.	Solvent	Metal	$\Delta H_F^{\circ b}$	$\Delta S_F^{\circ c}$	$\{TPE\}^d$	$\{M\}^d$
114 (1)	1,2-Dimethoxyethane	Li	7.5	23	2.4	0.61
115a		Na	16	47	1.4	0.80
110		K	13	53	6.8	0.28
120		Cs	6.4	35	14.3	0.45
117 (3)	Tetrahydrofuran	Li	7.4	25	0.96	0.54
118 (4)		Na	19	68	1.2	0.33
112		K	9	48	13.0	0.39

[a] From Figures 3 and 4. [b] Formal enthalpy of reaction in kcal./mole. [c] Formal entropy of reaction in e.u. [d] 10^4 times the formal concentrations of TPE and alkali metal in moles/l.

considerable lithium is dissolved, and is accompanied by a distortion of shape and position of the 4900-Å. band. This is reminiscent of the situation which occurs when any alkali TPE solutions decompose, presumably through reaction with solvent. An alternative is that the new bands reflect new species (aggregates perhaps), or that the spectrum of TPE^{-2} is quite sensitive to the proximity of Li^+ but less sensitive to other alkali ions, so that the spectra of the different ionized forms become distinguishable. Further, it may be that the spectra of the different ionized forms are different for TPE^{-2} in all cases, but that only the triple ion is present in most situations. All these alternatives are consistent with the findings of Bushow (see ref. 19). We have not further resolved the situation at present, but for the present purposes we have discarded those runs in which the 3700- and 4900-Å. bands show marked deviations from their normal appearance and relationship and have calculated the remaining data in the usual fashion.

Table III tabulates some values of ΔH_F° and ΔS_F° derived from the plots of Figures 3 and 4. Again, these are formal values, and should be expected to vary with $\{TPE\}$ and $\{M\}$ if ionization or aggregation is important. ΔH°_F is invariably positive in these experiments. Excepting lithium, a decreasing trend in ΔH_F° with increasing alkali metal radius is indicated. Even this trend is not clear in the values of ΔS_F°.

Discussion

Metal Ion Effects on K_F. The reports of Hoijtink and co-workers indicate that ionic dissociation of monoalkali adducts of hydrocarbons in ethers can be significant, but that dissociation of dialkali adducts is usually much less extensive.[12] The direction of the concentration effect on K_F is consistent with these considerations.[2b,11] The following equations would be applicable to the consideration of ΔF_F° if ionization of both MTPE and M_2TPE were negligible.

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

$$TPE^- \text{ (gas)} + M^+ \text{ (gas)} \rightleftarrows MTPE \text{ (gas)} \quad (3)$$

$$TPE^{-2} \text{ (gas)} + 2M^+ \text{ (gas)} \rightleftarrows M_2TPE \text{ (gas)} \quad (4)$$

$$MTPE \text{ (gas)} \underset{}{\overset{solvent}{\rightleftarrows}} MTPE \text{ (solution)} \quad (5)$$

$$M_2TPE \text{ (gas)} \underset{}{\overset{solvent}{\rightleftarrows}} M_2TPE \text{ (solution)} \quad (6)$$

$$TPE \text{ (gas)} \underset{}{\overset{solvent}{\rightleftarrows}} TPE \text{ (solution)} \quad (7)$$

(12) G. J. Hoijtink, E. deBoer, P. H. van der Meij, and W. P. Weijland, *Rec. trav. chim.*, **75**, 487 (1956); A. C. Aten, J. Dieleman. and G. J. Hoijtink, *Discussions Faraday Soc.*, **29**, 182 (1960).

The effect of ionization of MTPE can then be introduced as a perturbation term **(I)** appended to the otherwise idealized relationship (eq. 8), ionization of M_2TPE being neglected.

$$\Delta F_F^\circ = \Delta F_2^\circ + (\Delta F_4^\circ - 2\Delta F_3^\circ) + (\Delta F_6^\circ -$$
$$2\Delta F_5^\circ) + \Delta F_7^\circ + I \quad (8a)$$

$$\Delta F_F^\circ = 1 + 2 + 3 + 4 + I \quad (8b)$$

If δ^M is a difference operator corresponding to an *increase* in the alkali metal ion radius, the effect of such a change on ΔF_F° can be expressed as in eq. 9.

$$\delta^M \Delta F_F^\circ = \delta^M 2 + \delta^M 3 + \delta^M I \quad (9)$$

From simple electrostatics, $\delta^M 2$ should be positive,[2b] so that if this term dominated the right side of eq. 9 K_F would be expected to be smaller for alkali metal ions of larger radii. Since the metal ion effect is in the opposite direction (with the exception of the apparent inversion of values for Li and Na in 1,2-dimethoxyethane), $(\delta^M 3 + \delta^M I)$ must be of the opposite sign from $\delta^M 2$.

It can be reasonably argued that $\delta^M 3$ should be negative. The first term of **3** pertains to the solvation energies of triple ions, while the second relates to the solvation energies of ion pairs. Since triple ions (M_2TPE) probably adopt configurations minimizing their dipole moments, their solvation energies should be much less than those of the related ion pairs (MTPE). Consequently, differences among the solvation energies of triple ions ($\delta^M \Delta F_6^\circ$) should be smaller in absolute value than the corresponding differences among ion pairs ($\delta^M \Delta F_5^\circ$), so that the sign of $\delta^M 3$ is reasonably expected to be determined by the sign of $\delta^M \Delta F_5^\circ$.

A metal ion effect lending a negative value to $\delta^M 3$ can be rationalized by considering the solvation energy of an ion pair as the sum of contributions from the individual ions of the pair. The solvation of each ion of a pair is shielded both electrostatically and sterically by the partner ion. If one ion is small and the other sufficiently large, solvation of the larger ion will be negligible, as will be the electrostatic shielding of solvation of the smaller ion. Unless the larger ion somehow engulfs the smaller, steric shielding of the smaller ion should remove from consideration about half the effectively oriented and/or polarized solvating molecules which would otherwise surround the free smaller ion. Thus, the solvation energies of ion pairs of this type may be expected to parallel the solvation energies of the smaller ions, the solvation energies of the pairs being about half those of the free ions. If MTPE ion pairs fall into this class (as does not seem unreasonable), the solvation energies of the ion pairs

would parallel those of the free corresponding cations, that is, $\Delta F_5°$ would be a larger negative number for lithium than for sodium, etc. Restated, $\delta^M \Delta F_5°$ would be positive, with the consequence that $\delta^M 3$ would be negative.

Since ionic dissociation of the ion pairs, at least, is probably extensive in some of our solutions, we will consider the sign of the term $\delta^M I$. Ionic dissociation is accompanied (as is any other spontaneous chemical change at constant temperature and pressure) by a decrease in the free energy of the system. In this case, dissociation is accompanied by a decrease in the partial molar free energy of the formal dissociating species (formal MTPE, consisting actually of TPE⁻, M⁺, and actual MTPE). The result of dissociation of MTPE is therefore that a smaller K_F will be observed than would have been in the absence of dissociation. Since the tendency to dissociate presumably varies with counterion in the direction Li > Na > K > Cs,[12] $\delta^M I$ should be negative, paralleling $\delta^M 3$.

If our interpretation is correct, variation in the sign of $\delta^M \Delta F_F°$ (or of $\delta^M K_F$) is possible, the sign depending on which of the terms of eq. 9 dominates. Indeed, the direction of the effect between lithium and sodium in 1,2-dimethoxyethane does appear to be opposite from that for all the other pairs of metals considered in Table I. Further, distinct reversals in the metal ion effect, as compared with that which is usual for tetraphenylethylene, have been noted for two other systems, stilbene[2c] and triphenylethylene.[13]

The view adopted here, that the observed direction of the metal ion effect is the result of parallel ion and ion pair solvation and dissociation effects which override (gas phase) coulombic aggregation effects, bears a formal resemblance to that put forth by Streitwieser and Brauman,[8] who employed similar competitive coulombic aggregation and ion pair solvation factors to account for an unusual order of metal ion effects on the spectra of alkali salts of fluorenes in cyclohexylamine. Considerations of this type are applicable to many systems, and it may be worthwhile to formulate a general principle, of which the following paragraph is one statement. For convenience, the statement will be formulated so as to apply to ion pair systems in which cationic solvation is considered to outweigh anionic solvation, either by virtue of the nature of the solvent or the relative sizes of the cation and anion. The roles of cation and anion could, of course, be exchanged. All the generalities stated may not apply to certain kinds of intermediate ion pair situations in which both ions may be solvated significantly. Further, the statement could be generalized to include other aggregates.

If state I of an ion pair involves more interionic charge separation or anionic charge dispersion than state II, coulombic forces between the ions will energetically favor the latter state, while solvation energies of the ion pairs will favor the former. Three notable consequences are: (1) ΔE ($E_{II} - E_I$), or ΔF, will be algebraically larger in more polar solvents[14]; (2) ΔE, or ΔF, can be either greater or less than the corresponding quantity for free anions; (3) $\delta^M \Delta E$, or $\delta^M \Delta F$, can

be either greater or less than zero, more polar solvents favoring more algebraically negative values.

All three of these consequences follow from the kinds of arguments given earlier, the triple ions M₂TPE playing the same role as type II ion pairs in the above statement, and ion pairs MTPE playing the role of type I ion pairs. The ΔE and ΔF values could relate to spectral, equilibrium, or rate phenomena, depending on whether states I and II were ground and excited states, reactants and products, or reactants and transition state.

In the application of the generalization to the prediction of the behavior of the rates of alkylation of anions in ion pairs by alkyl halides it is presumed that the negative charge is more dispersed in the transition states than in the reactants. Ion pair transition states are then identified as type II ion pairs relative to the type I reactant ion pairs. Thus, where the generalization is applicable, alkylation of ion pairs will be faster in more polar solvents, can be either faster or slower than alkylation of free anions, and can be faster or slower for lithium cations than for sodium, with lithium ion pairs reacting more rapidly, relative to sodium, in more polar solvents.

A similar application can be made to the competition between C- and O-alkylation of alkali β-naphthoxide ion pairs,[4] of which Kornblum and co-workers have recently reported an important study. Adopting their model, the transition state for O-alkylation is a type I ion pair as compared to the type II transition state for C-alkylation. Applying consequence 3, lithium may favor either C- or O-alkylation over sodium for the ion pairs, but will tend to favor O-alkylation in more polar solvents relative to the less polar solvents provided that the generalization is applicable to the media involved (i.e., provided that the aprotic solvents which might be employed are indeed good cation solvators and poor anion solvators). Data against which to test this prediction are not available.

$\Delta H_F°$ and $\Delta S_F°$. In view of the formal nature of the K_F under discussion, and especially in view of the fact that the extent of ionic dissociation probably varies with temperature, too literal an interpretation of $\Delta H_F°$ and $\Delta S_F°$ is to be avoided. With this qualification, the values obtained nonetheless deserve some comment.

It is notable that $\Delta S_F°$ ranges up to rather large values. Values of the same order have been observed for entropies of activation or of chemical change involving other alkali metal adducts in ethers,[15] and presumably reflect extensive changes in solvation.

Both $\Delta H_F°$ and $\Delta S_F°$ are nearly the same, respectively, in 1,2-dimethoxyethane and tetrahydrofuran for lithium, although this is not true for the other alkali metals. Correspondingly, the energy of a solvent-sensitive transition of 1,1-diphenylhexyllithium is about the same in both solvents, while the energy of a similar transition in sodium benzophenone ketyl varies in such a fashion that 1,2-dimethoxyethane appears to be the more polar solvent of the pair,[7,16] suggesting the possibility of a variation in the relative polarities of the two solvents with the metal ion in-

(13) Unpublished results of E. R. Zabolotny in these laboratories.
(14) Here, as elsewhere in this paper, it is assumed that potential energy and free energy parallel one another. Where this is not the case, the considerations given may fail.

(15) (a) N. M. Atherton and S. I. Weissman, J. Am. Chem. Soc., 83, 1330 (1961); (b) A. Mathias and E. Warhurst, Trans. Faraday Soc., 56, 348 (1960).
(16) R. Waack and M. A. Doran. J. Phys. Chem., 67, 148 (1963).

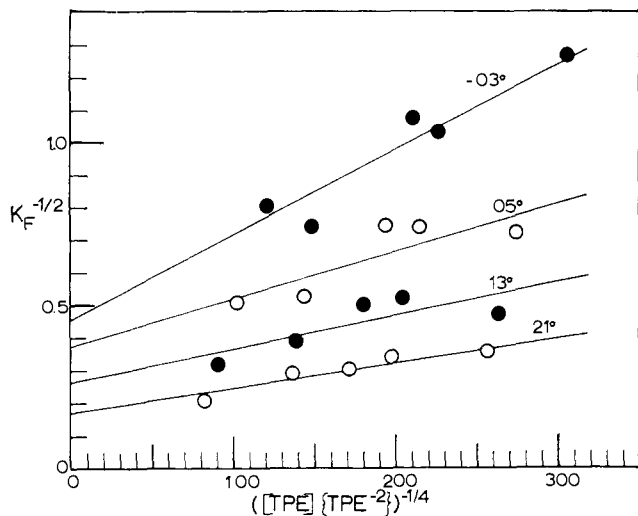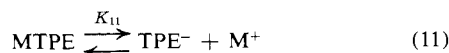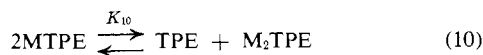Figure 5. Conformance of the data for sodium TPE adducts in tetrahydrofuran at various temperatures to eq. 12.

Figure 6. Log K_F vs. $1/T$ plots for K_{10} and K_{11} for sodium adducts of TPE in tetrahydrofuran. The values of K_{10} and K_{11} are taken from Figure 5.

volved.[17] In contrast, other data indicate that the extent of ionization of lithium adducts of hydrocarbons increases in going from tetrahydrofuran to 1,2-di-methoxyethane[12,18] so that either the concept of solvent polarity is not applicable in considerations of the experimental systems just cited, or the phenomena observed in connection with these systems are not all reflections of solvent polarity, or both.

Explicit Tests of Concentration Dependence of Data. The above discussion presumes that ion pairs MTPE are partly dissociated while triple ions M₂TPE are undissociated. The system is reduced by these assumptions to two equilibria.

$$2MTPE \xrightleftharpoons{K_{10}} TPE + M_2TPE \qquad (10)$$

$$MTPE \xrightleftharpoons{K_{11}} TPE^- + M^+ \qquad (11)$$

Assuming that activity coefficient changes may be neglected over the range studied, the equilibrium expressions corresponding to eq. 10 and 11 lead to eq. 12. Equation 12 is in the form of a straight line for which

$$(1/K_F)^{1/2} = (K_{11}^{1/2}/K_{10}^{1/4})(1/\{TPE^{-2}\}[TPE])^{1/4} + (1/K_{10})^{1/2} \quad (12)$$

the variables are measureable quantities and the constants are combinations of the unknown equilibrium constants K_{10} and K_{11}. Figure 5 shows the conformance of the data for sodium TPE adducts in tetrahydrofuran at several temperatures.

Data for sodium and lithium adducts of TPE in 1,2-dimethoxyethane at room temperature definitely follow a linear trend of the form required by eq. 12, but show even more scatter than is apparent in Figure 5, making the separation of K_{10} and K_{11} more uncertain.

(17) Professor K. Dimroth has kindly communicated some of his unpublished results on solvent effects on the spectra of betaines to the authors, pointing out that in ethers there is a nearly linear relation between the energies of transition of certain bands of the betaines and those of the visible band of sodium benzophenone ketyl.[7] Since there is no metal ion involved in the case of the betaines, but rather a quaternary nitrogen positive site, the absence of specific metal ion solvation effects in the ketyl is suggested. This point does not bear on ionoid lithium compounds, however.

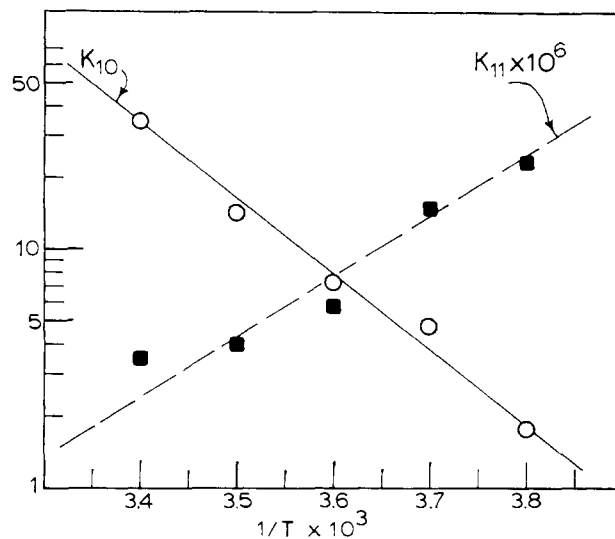(18) H. L. Strauss, T. J. Katz, and G. K. Fraenkel, *J. Am. Chem. Soc.*, 85, 2360 (1963).

There are several possible sources for this scatter other than random experimental errors. Among these are the likely possibilities of activity coefficient variation and dissociation of triple ions M₂TPE.[19]

Values of K_{10}, K_{11}, and Related Thermodynamic Quantities. For the sodium adducts of TPE in tetrahydrofuran the plots of Figure 5 afford estimates of K_{10} and K_{11} at various temperatures. Figure 6 shows plots of log K_{10} and log K_{11} vs. $1/T$, for which values of $\Delta H°$ and $\Delta S°$ for the two reactions may be derived.

For reaction 10, the disproportionation of ion pairs, $\Delta H°$ and $\Delta S°$ are found to be 14.6 kcal./mole and 57 e.u., respectively. We know of no previous data with which these values could be compared for purposes of checking reasonability. The large value of $\Delta S_{10}°$ is consistent with the hypothesis that the ion pairs are much more highly solvated than the triple ions, this entropy change being considered as a reflection of a substantial increase in the available degrees of freedom of solvent molecules tightly bound in the reactants but free (or nearly free) in the products.

For reaction 11, ionization of ion pairs, $\Delta H°$ and $\Delta S°$ are found to be -11.6 kcal./mole and -65 e.u., respectively. An estimate of a concentration equilibrium constant and related thermodynamic quantities is available for a similar ionization of a sodium adduct of an aromatic hydrocarbon in tetrahydrofuran–sodium naphthalene. The values reported by Atherton and Weissman for the ionization of sodium naphthalene, determined by an e.s.r. technique, are $\Delta H° = -7.5$ kcal./mole and $\Delta S° = -51.6$ e.u.[15a] The similarity of these values to those we obtained for reaction 11 constitutes support for our analysis of the situation. Even more striking is a comparison of the values of K(dissociation of ion pairs) at 25°: $K_{11} = 2 \times 10^{-6}$;

(19) K. H. J. Bushow, Thesis, Free University, Amsterdam, 1963, has demonstrated that ionization of the aggregates M₂R, where R is pentacene or tetracene, may be essentially zero at room temperature but becomes significant at lower temperatures, in some cases reaching complete dissociation to the free dianion R⁻² at liquid air temperature, in the modestly polar ether methyltetrahydrofuran. In the much more polar ether 1,2-dimethoxyethane, some dissociation of similar triple ions at room temperature is quite possible.

K(dissociation of sodium naphthalene) $= 1.7 \times 10^{-6}$.[15a]

One would gather from the values of ΔS° obtained for reactions 10 and 11 that solvation changes accompanying reaction of a triple ion to give two ion pairs are roughly comparable with those accompanying dissociation of a single ion pair to free ions.

Table IV gives such estimates of K_{10} and K_{11} as our data afford. Values for Li and Na in 1,2-dimethoxyethane are based on plots similar to those of Figure 5, for which we must make the reservation that the scatter prohibits a very accurate separation of K_{10} and K_{11}, possibly due to the ionization of triple ions. For K and Cs we assume that ionization is not very significant so that $K_F \simeq K_{10}$. The solvent effects on K_{10} and K_{11} are both in the expected direction. The metal ion effect on K_{10} appears to be generally opposite in direction from that which would be predicted on a strictly coulombic basis, a trend we view as reflecting solvation factors, discussed above.

Table IV. Estimated Values of K_{10} and K_{11} at 25°

| Metal | K_{10} | | K_{11} | |
	DME[a]	THF[b]	DME	THF
Li	>2.4	...	10^{-3}–10^{-5}	...
Na	1	42	$\sim 3 \times 10^{-4}$	2×10^{-6}
K	45	6000	...	....
Cs	3000	Large	...	...

[a] 1,2-Dimethoxyethane. [b] Tetrahydrofuran.

Extent of Disproportionation of MTPE. Reference to eq. 12 discloses that a possible explanation for the unusually large extent of disproportionation of alkali adducts of TPE is that K_{11} is abnormally small, not that K_{10} is abnormally large. The comparison of K_{11} with the value found by Atherton and Weissman for dissociation of sodium naphthalene ion pairs (see above)[15a] suggests that this is not the case, and that K_{10} must be unusually large instead. Thus, while disproportionation probably would not occur in the absence of association, ion association in itself is probably not the cause for the unusual behavior of MTPE. Previous speculations as to this cause remain applicable.[20,20a]

(20) See ref. 2b and citations therein.

(20a) NOTE ADDED IN PROOF. Examples of directly measureable spontaneous disproportionation of monoalkali adducts of aromatic hydrocarbons in ethers have recently come to our attention from two groups.

J. Dieleman reports that monosodium p-terphenyl and monosodium p,p'-quaterphenyl disproportionate in methyltetrahydrofuran at room temperature with K (presumably analogous to our K_{10}) values of 0.29 and 6.9, respectively. Disproportionation of the same species occurs in tetrahydrofuran to a lesser extent (J. Dieleman, Thesis, Free University, Amsterdam, 1962).

By employing selected metal ions and solvents, Shatenstein and co-workers found conditions under which the spontaneous disproportionation of naphthalene radical anion occurs, namely, with lithium in diethoxyethane or dioxane (A. I. Shatenstein, E. S. Petrov, and M. I. Belouseva, *Organic Reactivity* (Tartu State University, Tartu, Estonian S.S.R.), 1, 191 (1964). Since this publication is probably unavailable in most libraries, and since it is apparently bilingual, with a detailed English summary appearing in this case beginning on p. 199, we give here both the title of the paper, "Reaction Equilibria of Sodium and Lithium with Biphenyl and Naphthalene in Electrondonating Solvents," and the address, L. Y. Karpov Institute of Physical Chemistry, Moscow, of Prof. Shatenstein, from whom reprints can probably be obtained. We are grateful to Prof. Shatenstein for such a reprint.

Equilibria of Substituted Semiquinones at High pH

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The equilibrium constants, K', of a number of substituted semiquinones with the corresponding quinones and doubly ionized hydroquinones have been measured by a flow method. The calculation of K' necessitates the consideration of the reversible quinone–hydroxide addition reaction in some cases. Inductive effects have been shown to be an important factor in the position of equilibrium.

The oxidation of hydroquinones is known to involve semiquinone free-radical intermediates,[1,2] which themselves are stable at high pH, owing to the equilibrium with the corresponding quinone and doubly ionized hydroquinone (eq. 1).[1,3-6] However, most quinones

$$T + R^{-2} \rightleftharpoons 2S \qquad (1)$$

where

$$T = \quad, R^{-2} = \quad, S =$$

react rapidly and irreversibly with hydroxide ion, causing the position of equilibrium to change with time and making quantitative determinations difficult. Tetramethylquinone (duroquinone) is one of the few exceptions, and the semiquinone equilibria were first investigated in this less reactive system by a static method.[4] More recently, the p-benzosemiquinone equilibria were

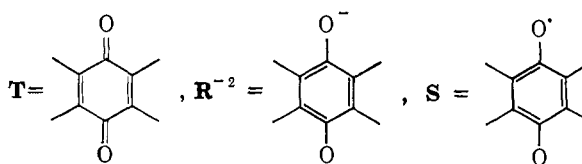(1) L. Michaelis, M. P. Schubert, R. K. Reber, J. A. Kuck, and S. Granick, *J. Am. Chem. Soc.*, 60, 1678 (1938).

(2) T. H. James, J. M. Snell, and A. Weissberger, *ibid.*, 60, 2084 (1938); G. Kornfeld and A. Weissberger, *ibid.*, 61, 360 (1939); J. E. LuValle and A. Weissberger, *ibid.*, 69, 1567 (1947).

(3) L. Michaelis, *Chem. Rev.*, 16, 243 (1935).

(4) J. H. Baxendale and H. R. Hardy, *Trans. Faraday Soc.*, 49, 1433 (1953).

(5) N. K. Bridge and G. Porter, *Proc. Roy. Soc.* (London), A244, 276 (1958).

(6) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957.