were low. Therefore, a quantitative analysis was made, on a fresh reaction mixture, making use of Beer's law as applied to certain distinct bands in the ir spectra of the mixture and pure samples of the products.[14] The bands employed were 820 and 1690 cm^{-1} (mesitoin and mesitil) and 852 cm^{-1} (all three compounds). The percentage yields thereby obtained were 45, 2, and 53% for mesitoin, mesitil, and the other compound, respectively. The other compound was shown to be identical with the dimeric compound reported by Fuson from hypochlorite oxidation of 2,2-dimesitylvinyl alcohol.[9] Its ir spectrum showed a carbonyl band at 1720 cm^{-1}, but no hydroxyl band. Its nmr spectrum and characterization as the dimer (XV) of radical XII were discussed earlier. When a solution of the dimer approached room temperature, it lost its color, but the color reappeared when the solution was warmed to 45° or higher.

Ozonation of 2,2-dimesitylvinyl alcohol at −78° gave a faint pink color, but no dimer was observed. The major product was mesitoin (XIII).

References and Notes

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Electron Paramagnetic Resonance Studies of Ion Pairs in Solutions of Cation Radicals

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Abstract: Effects due to the formation of ion pairs between the 1,2,4,5-tetramethoxybenzene (TMB) cation radical and halide anions in solution have been observed by esr spectroscopy. In particular the g shift ($g_{\text{free}} - g_{\text{ion pair}}$) is much greater in iodine oxidized systems than in bromine oxidized systems. The g shift also increases as the solvent becomes less polar. A consideration of the oxidation mechanism suggests that the counteranion is I_3^- for iodine oxidized systems and is a mixture of Br_3^- and Br^- for bromine oxidations. The effects of halogen concentration, addition of halide ions, and temperature are also indicative of the existence of equilibria, possibly of the contact ion pair $\rightleftarrows$ solvent separated ion pair variety.

The literature concerned with the study of anion radical-metal cation ion pairs (A^-M^+) by esr spectroscopy is considerable.[1] By contrast there is almost no work in the literature on cation radical–counteranion ion pair (C^+X^-) interactions. There has been one study in which direct effects on the esr spectrum of C^+X^- ion pairs have been postulated,[2] and there have been two studies in which ion pair formation has been suggested as effecting information derived from esr spectra.[3,4] There is also a report of the interaction of halide ions with metalloporphyrin cation radicals in which hyperfine splitting from the halide ions has been detected, although the species present in these studies are thought to be complexes rather than ion pairs.[5]

Due to this obvious lack of information on C^+X^- ion pairs and because of the current growing interest in the chemistry of cation radicals,[6] as well as their importance as intermediates in many oxidation processes (see for example ref 7-10), it seemed important to explore the possibility, given the right set of conditions, of observing effects in the esr spectrum of a cation radical due to ion pair formation. Our first consideration was how to optimise conditions so that effects due to ion pairing would be most likely to occur. In general, cation radicals have been prepared by oxidation

with compounds such as H_2SO_4, $AlCl_3$, $SbCl_5$, BF_3, etc., in solvents of high dielectric constant (CH_3NO_2, CH_3CN, CF_3COOH). Under these conditions not only are the solvents likely to strongly solvate the ions but the counteranion is probably a complicated species. Obviously one needs to carry out the oxidations in solvents of lower dielectric constant with an oxidant which will produce a relatively simple anionic species, if one is to observe any effects due to ion-pair formation. The oxidants of choice are therefore molecular bromine or iodine, since they are known to act as one-electron oxidants toward some easily oxidized compounds and the counteranions should be relatively simple species. The compound to be oxidized, 1,2,4,5-tetramethoxybenzene (TMB), was selected for several reasons. The oxidation potential of TMB is 0.82 V[11] which indicates that oxidation by bromine, at least, should be successful. In addition the cation radical of TMB had been previously investigated by electrochemical oxidation[11] and by chemical oxidation in H_2SO_4 or $AlCl_3$–CH_3NO_2[12] and had been shown to be a relatively stable species as compared to other cation radicals. The esr spectrum of TMB·$^+$ is also relatively simple consisting of 13 groups of triplets ($a^H_{OCH_3} = 2.20$, $a^H_{CH} = 0.85$ G) and is easily recognizable (see Figure 1).

Experimental Section

1,2,4,5-Tetramethoxybenzene (TMB) was prepared by treatment of p-benzoquinone with fused $ZnCl_2$ in absolute methanol to obtain 2,5-dimethoxy-1,4-benzoquinone which was then converted to 2,5-dimethoxyhydroquinone as described by Baker.[13] The product was then treated with dimethyl sulfate as described by Benington, et al.,[14] to give TMB (mp 102–103°, lit. 102.5°[13]), which was further purified by sublimation. An alternative source of TMB was as an impurity in commercially available 1,2,4-trimethoxybenzene. The solvents used in this study were all the best available commercial samples which were dried over molecular sieves, distilled, and carefully degassed by repeated freeze-pump-thaw cycles before use.

Samples were prepared in the usual way for aluminum chloride oxidations.[15] When bromine was used as oxidant, solutions of TMB in the desired solvent were prepared and degassed in the esr cell. Bromine was also degassed in a separate container on the vacuum line; this was connected to an evacuated compartment whose volume (1.05 cm^3) represented 1 unit of bromine in our study. Bromine vapor at room temperature was allowed to flow freely into this compartment and was then transferred through the vacuum line to the frozen TMB solution. Initially the minimum number of bromine units necessary to produce a detectable and resolved esr signal was transferred, and then, as required, excess bromine was added.

Oxidation with iodine was achieved by preparing saturated solutions of iodine in the different solvents. To these or diluted solutions one or two drops of 1,2,4-trimethoxybenzene (containing TMB as impurity) were added.

The esr spectra were recorded on a Varian E-15 x-band spectrometer. The g factors were measured in a dual sample cavity using the perylene radical anion ($g = 2.002671 \pm 0.000003$)[16] as a standard. The field difference between the two cavities was small ($ca.$ 0.02 G), and although no attempt was made to obtain absolute g values, relative values being of primary interest, the numbers quoted should be within ± 0.00002 of the absolute values. The magnetic field was typically scanned at 0.3 G/min with chart speeds corresponding to 0.066 G/cm; these conditions gave a shift in g of 3.9×10^{-5} per centimeter shift of the center of the spectrum relative to the center of the perylene spectrum. For each sample at least four spectra were recorded and the g values reported are the average of the four measurements.

The absorption spectra were measured at room temperature with a Cary-14 spectrophotometer, using a 1-cm path length cell. In some measurements, a special accessory was used so that the solution containing TMB·$^+$ radicals could be transferred directly from the esr cell to a uv–visible air-free cell.

Results and Discussion

Initial Observations. Our initial experiments were concerned with a comparison of the TMB·$^+$ esr spectra when oxidized with aluminum trichloride, bromine, or iodine in a variety of solvents of different polarity. The results are presented in Tables I and II. The major difference found in these experiments was the change in g factor measured for TMB·$^+$. The hyperfine splittings were relatively invariant to the conditions employed (to within a few per cent), and no attempt was made to accurately measure them. In Tables I and II the Δg values listed represent the shift in g between the value for TMB·$^+$ in the solvent–oxidant system of interest minus the value for TMB·$^+$ in $AlCl_3$–CH_3NO_2. This latter value was chosen as a reference since the conditions were thought to be most favorable for the existence of solvated "free" ions in solution. This g value of 2.003959 ± 0.000003 is still quite different from the free spin value and this residual difference can be attributed to contributions from spin density on the oxygen atoms. As shown by Stone[17] the deviation of the g factor from the free spin value in a series of related radicals can be written as the summation of contributions from the different atoms in the molecule. Thus for TMB·$^+$, $\Delta g_F = \Sigma_o \rho_o \gamma_o + \Sigma_c \rho_c \gamma_c$, where $\Delta g_F = g_{\text{free ion}} - g_{\text{electron}}$ and ρ_i is the spin density on atom
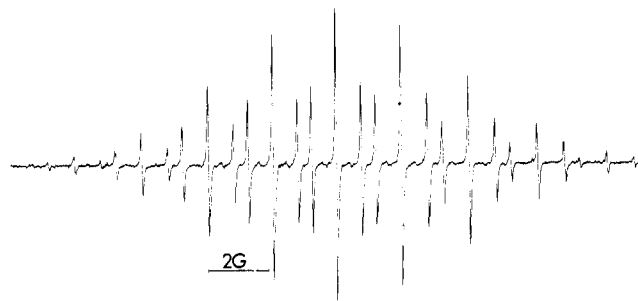

Figure 1. The esr spectrum of the 1,2,4,5-tetramethoxybenzene cation radical in $AlCl_3$–CH_3NO_2 at $-20°$.

Table I. g Shifts and Line Widths for TMB·$^+$ Oxidized with Aluminum Trichloride in the Appropriate Solvent ($T = -20°$)

Solvent	g^a	Δg^b ($\times 10^5$)	Line width^c (G)
Chloroform	2.004030	7.1 ± 0.5	0.080
1-Chloropropane	2.003944	-1.5 ± 0.5	0.117
Dichloromethane	2.003940	-1.9 ± 0.2	0.141
1,2-Dichloroethane	2.004045	8.6 ± 0.2	0.051
1,1-Dichloroethane	2.004039	8.0 ± 0.2	0.041
n-Heptyl cyanide	2.003979	2.0 ± 0.2	0.069
Hexanenitrile	2.003977	1.8 ± 0.2	0.049
Valeronitrile	2.003984	2.5 ± 0.3	0.059
Butyronitrile	2.003960	0.2 ± 0.2	0.044
Proprionitrile	2.003970	1.1 ± 0.2	0.048
Acetonitrile	2.003980	2.1 ± 0.2	0.045
1-Nitrohexane	2.003956	-0.3 ± 0.2	d
1-Nitropentane	2.003952	-0.7 ± 0.6	d
1-Nitrobutane	2.004010	5.1 ± 0.2	d
1-Nitropropane	2.003954	-0.5 ± 0.2	d
Nitroethane	2.003998	1.2 ± 0.3	0.048
Nitromethane	2.003959	0	0.040

^{a} Relative to perylene radical anion $g = 2.002671$. $^b \Delta g = g(AlCl_3\text{–nitromethane}) - g(AlCl_3\text{–solvent})$, error limits represent the errors involved in the determination of Δg from four measurements. ^{c} Peak to peak line widths. ^{d} Not measured.

i and the γ's are factors which depend upon both the spin-orbit coupling parameters and the orbital energy of the unpaired electron. One can illustrate the validity of this expression by calculating g for TMB·$^+$ from the known g value of the related compound p-dimethoxybenzene[18] (DMB). g(DMB) = 2.00368 and $a^H_{OCH_3} = 3.45$ G, whereas $a^H_{OCH_3} = 2.21$ G for TMB. The expressions for Δg_F are given as

$$\Delta g_F(\text{DMB}) = 2\rho_o \gamma_o + \Sigma \rho_c \gamma_c$$

$$\Delta g_F(\text{TMB}) = 4\rho_o \gamma_o + \Sigma \rho_c \gamma_c$$

Since the contributions of the oxygen atoms are much greater than those of the carbon atoms (spin–orbit coupling constants $\xi_o = 151$, $\xi_c = 28$ cm^{-1}), one can neglect the contributions from the carbon atoms. If one further assumes that ρ_o^π is proportional to $a^H_{OCH_3}$, one obtains

$$\frac{\Delta g_F(\text{TMB})}{\Delta g_F(\text{DMB})} = \frac{4(2.21)\gamma_o}{2(3.45)\gamma_o}$$

which if the γ_o's are taken to be equal gives $\Delta g_F(\text{TMB}) = 17.7$ or $g(\text{TMB}) = 2.00409$, in reasonable agreement with the experimental value of 2.00396, considering the approximations made.

Returning to Table I it is seen that Δg for $AlCl_3$ oxidized systems is quite small. Since it is believed that the effect of the counteranion in these systems is negligible this implies that the effects observed are attributed to the solvents, which have only a small effect on the g factor of TMB·$^+$.

On oxidation with bromine the observed g shifts are much larger than the shifts in $AlCl_3$ oxidized systems, espe-

Table II. g Shifts and Line Widths for TMB·$^+$ Oxidized with Bromine and Iodine in the Appropriate Solvent ($T = -20°$)

Solvent	Dielectric constant[a] $-20°$	Dielectric constant[a] $+20°$ (or as indicated)	Bromine oxidations g	Bromine oxidations Δg ($\times 10^5$)	Bromine oxidations Line width[c] (G)	Iodine oxidations g	Iodine oxidations Δg ($\times 10^5$)	Iodine oxidations Line width[c]
Chloroform	5.58	4.80	2.004656	77.8 ± 0.2	0.252	2.006631	267.2 ± 0.4	0.502
1-Chloropentane	b	6.6 (11)	2.004755	79.6 ± 0.2	0.302	2.005791	183.2 ± 1.0	0.441
1-Chloropropane	b	7.7	2.004520	56.1 ± 0.2	0.178	2.005570	161.1 ± 1.9	0.438
Dichloromethane	10.85	9.1	2.004316	35.4 ± 0.2	0.326	2.005473	151.4 ± 0.5	0.646
1,2-Dichloroethane	13.25	10.6	2.004108	14.9 ± 0.2	0.134	2.005203	124.4 ± 0.3	0.387
1,1-Dichloroethane	13.72	10.45	2.004371	41.2 ± 0.3	0.216	2.005311	135.2 ± 0.3	0.486
n-Heptyl cyanide	b	13.89 (25)	2.004320	36.1 ± 0.1	0.153	2.004511	55.2 ± 0.2	0.381
Hexanenitrile	b	17.26 (25)	2.004285	32.6 ± 0.4	0.091	2.004440	48.1 ± 0.3	0.224
Valeronitrile	24.2	19.71 (25)	2.004156	19.7 ± 0.6	0.280	2.004608	64.9 ± 0.3	0.200
Butyronitrile	b	20.3 (21)	2.004213	15.4 ± 0.2	0.234	2.004501	54.2 ± 0.2	0.247
Propionitrile	b	27.2	2.004086	12.7 ± 0.2	0.047	2.004711	75.2 ± 0.2	0.237
Acetonitrile	43.55	37.5	2.004001	4.2 ± 0.2	0.076	2.004361	40.2 ± 0.2	0.127
1-Nitrohexane	b	b	2.004022	6.3 ± 0.2	0.249	2.004500	54.1 ± 0.2	0.336
1-Nitropentane	b	b	2.004020	6.1 ± 0.1	0.075	2.004490	53.1 ± 0.2	0.188
1-Nitrobutane	b	b	2.004004	4.5 ± 0.2	0.064	2.004469	51.0 ± 0.2	0.288
1-Nitropropane	b	23.2 (30)	2.004009	5.0 ± 0.2	0.093	2.004299	34.0 ± 0.2	0.384
Nitroethane	b	30.0 (18)	2.003983	2.4 ± 0.2	0.064	2.004238	27.9 ± 0.2	0.154
Nitromethane	45.70	39.40	2.003978	1.9 ± 0.2	0.047	2.004128	16.9 ± 0.2	0.088

[a] From Landolt-Bornstein, Band II, Teil 6; Riddick and Bunger, "Organic Solvents," Wiley-Interscience, New York, N.Y., 1970. [b] Not available. [c] $\pm 10\%$

cially in the solvents of lower dielectric constant. The results listed in Table II represent the g shift observed when a minimum amount of bromine has been added to the solvent-TMB mixture so that a signal of reasonable intensity and resolution is obtained.

Oxidation with iodine gave even larger g shifts as shown in Table II. The actual oxidation was in itself initially somewhat surprising since the standard reduction potential of I_2/I^- is 0.535 V which would suggest that iodine should not be capable of oxidizing TMB to any extent. However, when saturated solutions of iodine in the appropriate solvents are used, esr signals corresponding to TMB·$^+$ are detected. The results in Table II correspond to the oxidation of TMB with saturated solutions of iodine in the appropriate solvent. The actual mechanism of this oxidation will be considered later.

Several general observations can be made about the results in Tables I and II. The observed g shift in a given solvent always follows the order I_2 oxidation > Br_2 oxidation > $AlCl_3$ oxidation. The g shifts are approximately the same for all solvents in $AlCl_3$ oxidations; in Br_2 and I_2 oxidations the g shifts generally increase as the dielectric constant of the solvent decreases. Plots of Δg vs. ϵ for Br_2 and I_2 systems are, however, fairly scattered and are not reproduced. (Plots of Δg vs. Z or Δg vs. E_T where the appropriate Z and E_T values are available are also somewhat scattered.) The line widths show no apparent trends in the $AlCl_3$ oxidized systems; however, for Br_2 and I_2 systems the line widths tend to increase as ϵ decreases and the line widths for I_2 systems are generally larger than those of Br_2 systems. All of these results are consistent with the existence of ion-pair interactions between TMB·$^+$ and a halide anion, these interactions becoming stronger in solvents of lower solvating power.

g **Shifts in Ion Pairs.** The large positive g shifts observed above are, as first suggested by Symons,[1,19] precisely what one would expect to observe on ion-pair formation between cation radicals and halide anions. It is perhaps useful at this point to compare the effects of ion-pair formation for anion radicals and alkali metal cations (A^-M^+) to that of cation radicals and halide anions (C^+X^-). It is well known that in the case of A^-M^+ ion pairs the most obvious possible effect on the esr spectrum is the appearance of additional splittings due to a hyperfine interaction of the metal ion.[1] This splitting arises from the presence of spin density in an alkali

metal s orbital and is most simply visualized as arising from an electron transfer from A^- to M^+. In the case of C^+X^- ion pairs one requires the transfer of spin density from X^- to C^+ leaving a hole in the p shell of the halide. Before any hyperfine interaction could occur the inner s electrons would have to be polarized. It is therefore not likely that hyperfine splittings from X^- would be detected in C^+X^- ion pairs except under unusual conditions.

It is also known that the formation of A^-M^+ ion pairs can result in g shifts from the "free ion" g value. It should be noted, however, that electron transfer into the valence s orbital of the alkali metal will not itself affect the g value. If the molecular orbital of the unpaired electron does have some small contribution from the metal p_z orbital then coupling to the metal p_x and p_y orbitals will result in a shift of the g value. The shifts of the diagonal elements of the g tensor are calculated to be[20]

$$\Delta g_{ii} = K\xi \sum_n \frac{\langle \psi | \hat{L}_i | \psi_n \rangle \langle \psi_n | \hat{L}_i | \psi \rangle}{E_n - E_0}$$

where K is a factor depending upon the amount of mixing, ξ is the spin-orbit coupling constant for the metal atom, ψ is the ground state wave function and ψ_n's are the excited state wave functions, and E_n and E_0 are the energies of the excited and ground state orbitals. Considering only the p_x, p_y, and p_z orbitals one finds $\Delta g = \frac{2}{3}K\xi/(E_z - E_x)$. Since ξ and K are positive quantities and since one considers the p_z orbital to be perturbed by ion pairing so that $E_z < E_x = E_y$, the g shift is therefore predicted to be negative and should be roughly proportional to the spin-orbit coupling constant. This was shown to be the case for the alkali metal naphthalene anion pairs[21] as indicated in Table III.

Considering the g shifts of C^+X^- ion pairs one notes that in this case electron transfer occurs directly out of the filled p shell of the halide ion resulting in a much stronger coupling of the p_x and p_y orbitals. Additionally the energy term $E_z - E_x$ must now become positive since we are dealing with a hole in the p shell. The g shift is therefore expected to be positive and much larger than that of the A^-M^+ ion pairs since not only does the electron transfer take place directly out of the p shell but also the spin-orbit coupling constant of a halide ion such as bromine or iodine is much larger than that of an alkali metal ($\xi_{Br} = 2400$, $\xi_I = 5050$

Table III. g Shifts for Naphthalene Anion Radicals with Various Alkali Metals in Dimethoxyethane[a]

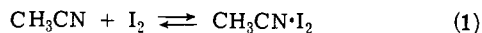| Cation	Δg^b ($\times 10^5$)	Spin–orbit coupling constant of cation (cm^{-1})
Li$^+$	-0.07	0.29
Na$^+$	-1.13	11.5
K$^+$	-1.19	38.5
Rb$^+$	-4.84	158.4
Cs$^+$	-18.66	369.4

[a] Taken from ref 21. [b] $\Delta g = g(\text{free ion}) - g(\text{ion pair})$.

cm^{-1}). The results in Table II are entirely consistent with this reasoning, showing large positive g shifts, with the TMB–I$_2$ shifts being much larger than the TMB–Br$_2$ shifts.

The structure of the TMB·$^+$X$^-$ ion pair is intuitively expected to be similar to the structure of benzene–halogen charge transfer complexes,[22] that is with halogen anion situated above the plane of the benzene ring and able to overlap with the p–π orbitals on the carbon and oxygen atoms. This presumes that the TMB·$^+$ molecule is a planar species; this is substantiated by the magnitude and temperature independence of the methoxyl group proton splitting constant since it is known that nonplanar methoxyl groups have greatly reduced splitting constants and are generally quite temperature dependent.[18] The actual structure of TMB·$^+$ is unknown but is probably in a trans–trans configuration.

Oxidation Mechanism and Nature of the Halide Anions. In view of the somewhat unexpected oxidation of TMB by iodine, it became apparent that some consideration should be given to the mechanism of the oxidation and the nature of the halide ion in solution. The half-wave and standard oxidation potentials have been reported by several workers[11,23,24] for TMB and for the halogen–halide or halide–halide couples that are presumably involved in the oxidation of TMB. Thus for example the standard potentials vs. a saturated calomel electrode have been reported in acetonitrile[23] as Br$_2$|Br$^-$ = 0.7 V, Br$_2$|Br$_3^-$ = +1.1 V, I$_2$|I$^-$ = +0.26 V, and I$_2$|I$_3^-$ = +0.65 V. The actual half-wave potentials in a given solution may of course change considerably with the concentration of the ions in the solution. Thus Popov and Deskin[25] have shown that iodine forms 1:1 complexes with acetonitrile with a formation constant of 0.57; the complexes then dissociate in solution according to eq 2

$$CH_3CN + I_2 \rightleftharpoons CH_3CN\cdot I_2 \qquad (1)$$

$$CH_3CN\cdot I_2 \rightleftharpoons (CH_3CNI)^+ + I^- \qquad (2)$$

$$I^- + I_2 \rightleftharpoons I_3^- \qquad (3)$$
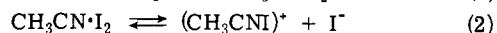
and 3. Reaction 1 is slow and steps 2 and 3 are rapid. Further studies[24] showed that in a typical solution of I$_2$ in CH$_3$CN only 0.9% of the total iodine is present as I$_3^-$ immediately after preparation. From the formation constant for I$_3^-$ in acetonitrile, $10^{6.6}$,[23] the concentration of I$^-$ in a 0.1 M solution is ca. 2.25×10^{-9} M. These ionic concentrations give a half-wave potential of 0.89 V for the I$_2$–I$_3^-$ couple. This compares with a half-wave oxidation potential of 0.81 V for TMB in CH$_3$CN.[11] One can therefore justify the oxidation of TMB by iodine in acetonitrile if the anionic species produced in solution is I$_3^-$. In the case of the bromine oxidations it is reasonable to assume from the potentials reported that both Br$^-$ and Br$_3^-$ ions may be present in solution, the relative amounts of each being dependent on the initial concentration of molecular bromine. One presumes that similar considerations apply to the other solvents studied.

A plausible oxidation mechanism of TMB by iodine may then be proposed as follows. The first step (eq 4) represents

$$TMB + I_2 \rightleftharpoons TMB\cdot I_2 \qquad (4)$$

$$TMB\cdot I_2 + I_2 \rightleftharpoons TMB\cdot{}^+I_3^- + I\cdot \qquad (5)$$

$$TMB\cdot{}^+I_3^- + S \rightleftharpoons TMB\cdot{}^+(s) + I_3^-(s) \qquad (6)$$

the formation of a charge transfer complex (an outer complex in Mulliken's terms[26]). This complex reacts with another molecule of iodine which acts as an auxilary acceptor to produce the TMB radical cation and the I$_3^-$ ion.[27] Equation 6 then represents the solvation of these species in solution. In support of these ideas some absorption spectra of TMB–I$_2$ systems showed the presence of bands from I$_3^-$ (λ_{max} 360 nm) and from TMB·$^+$ (λ_{max} 450 nm)) in the more polar solvents. In less polar solvents bands were seen which might be attributed to the charge-transfer complex. More quantitative studies of the absorption spectra are in progress. Additional support is also provided by the fact that several compounds are known to form solid paramagnetic semiconducting complexes with iodine having stoichiometries of 2 mol of compound to 3 mol of iodine (e.g., perylene,[28] phenothiazine,[29] and carotene.[30] It seems likely that the complexes also involve the I$_3^-$ ion (eq 7).

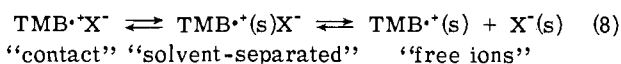$$2M + 3I_2 \rightleftharpoons 2M\cdot I_3^- \qquad (7)$$
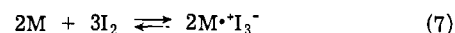
It might also be noted that the mechanism outlined is similar in principle to the mechanisms proposed for the oxidation reactions of cobalt(III) trifluoroacetate[10] and AlCl$_3$[31] and seems therefore to suggest a general mechanism for one-electron oxidations leading to cation radicals.

Effect of X$_2$ Concentration. Increasing amounts of Br$_2$ beyond the minimum resulted in larger g shifts, being particularly pronounced for the solvents of higher dielectric constant. For example doubling the amount of Br$_2$ in butyronitrile resulted in an increase of Δg from 15.4 to 26.9 $\times$ 10^{-5}, while doubling the bromine concentration in chloroform resulted in a negligible change in Δg. The addition of excess bromine tended to decrease the line widths in solvents of higher polarity while in solvents of lower polarity the line widths remained about the same. An interesting observation was the presence of additional splittings in the esr spectra (see Figure 2) on the addition of excess bromine to TMB solutions in methylene chloride, n-heptyl cyanide, hexanenitrile, valeronitrile, butyronitrile, nitrobutane, nitropropane, and nitromethane. The origin of these splittings has not been definitely attributed to the halide ions, although this is certainly an attractive possibility.[32] However, the splittings may also arise from secondary radicals. Further work is required to clarify this point.

The effect of I$_2$ concentration on the spectra is similar to Br$_2$. Thus increased I$_2$ concentrations in low polarity solvents resulted in little change in Δg or in the line widths. In high polarity solvents, increased concentrations of I$_2$ caused increases in Δg (i.e., doubling the I$_2$ concentration in butyronitrile changes Δg from 35.1 to 54.2 $\times$ 10^{-5}) and also caused increased line widths.

The above results are certainly indicative of equilibrium shifts possibly represented by eq 5 or 6 or by shifts between ion pairs of the type (eq 8)

$$TMB\cdot{}^+X^- \rightleftharpoons TMB\cdot{}^+(s)X^- \rightleftharpoons TMB\cdot{}^+(s) + X^-(s) \qquad (8)$$
"contact"   "solvent-separated"   "free ions"

where X$^-$ may represent I$^-$, Br$^-$, I$_3^-$, or Br$_3^-$. This type of equilibria has of course been observed previously for anion radical ion pairs.[1]

Effect of Added X$^-$. If trihalide anions X$_3^-$ are indeed the counterions in solution, then addition of X$^-$ ions to the TMB–X$_2$ solutions should increase the concentration of X$_3^-$ (eq 9). This in turn should cause the equilibrium repre-
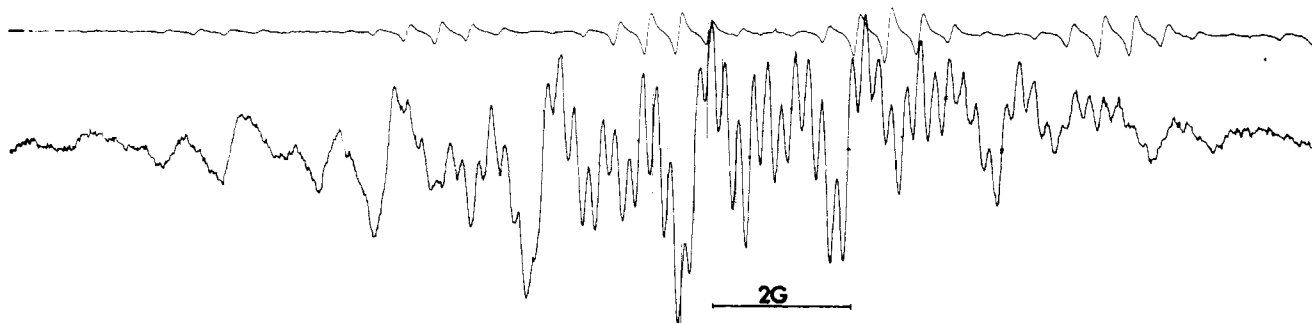
$$X_2 + X^- \rightleftharpoons X_3^- \qquad (9)$$
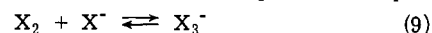
Figure 2. The esr spectrum (lower) of the 1,2,4,5-tetramethoxybenzene-bromine system in methylene chloride at −20°.
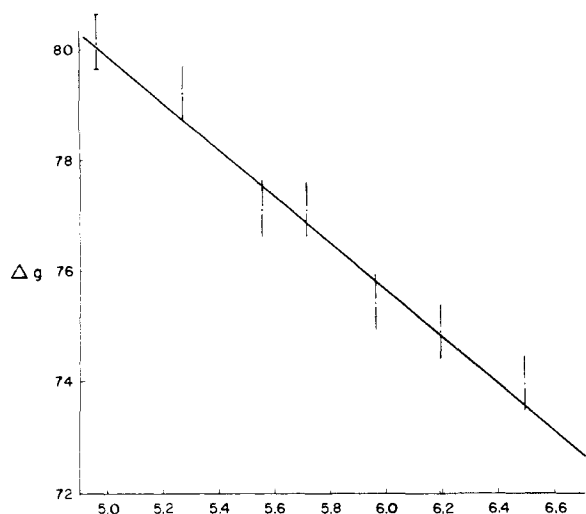

Figure 3. A plot of Δg vs. dielectric constant of chloroform at various temperatures for the TMB–Br$_2$–chloroform system.

sented by eq 8 to move toward the contact ion pairs thus resulting in an increase in Δg. Attempts to add sodium bromide to TMB$\cdot^+$–Br$_2$ solutions were unsuccessful due to the low solubility of the bromide. However, the addition of sodium iodide to the TMB–Br$_2$ system in nitropropane was successful. The spectra showed increasing Δg values as the amount of added NaI increased; thus for TMB–Br$_2$ Δg was 15.3×10^{-5} and this value increased with added NaI to 63.9×10^{-5} before the signal finally disappeared. One presumes that the polyhalide ion Br$_2$I$^-$ is formed under these conditions (K_f for Br$_2$I$^-$ 370[33]), and therefore in addition to moving the equilibrium more toward the contact ion pairs the presence of the iodine atom also causes a larger g shift. On adding sufficient I$^-$ the TMB$\cdot^+$ is finally reduced and the esr signal disappears.

The addition of NaI to TMB–I$_2$ solutions always resulted in an increase in Δg, of about 20–80%, the percentage increase being smaller for the lower polarity solvents. The effect of the added I$^-$ on the line width depended on the solvent being used; for dichloromethane, 1,1-dichloroethane, and 1,2-dichloroethane the line width was reduced (i.e., in 1,1-dichloroethane from 0.60 to 0.40 G), whereas for solvents of higher polarity the line width either increased or remained the same on addition of NaI.

Effect of Temperature on Δg. A change in temperature is expected to shift any equilibria occurring in the solution; it may also cause a drastic change in the structure of the ion pair. The former situation is likely to result in a small but smooth change in Δg, whereas the latter might cause a large and perhaps discontinuous change.

Initial experiments on the TMB–Br$_2$ system in chloroform indicate that the former situation prevails. Thus Δg

varies smoothly from 80.1×10^{-5} at +20° to 74.2×10^{-5} at −60°. The shift is well represented as a linear function of the dielectric constant as shown in Figure 3. This strongly suggests that there is a rapid equilibrium in this solution between contact and some sort of solvent separated ion pair. Interestingly the line width seems to pass through a maximum at about −20°, decreasing somewhat on either increasing or decreasing the temperature from this value. However, Δg does not always decrease with decreasing temperature; for example, in TMB–Br$_2$–hexanenitrile Δg is found to increase from 32.9×10^{-5} at +20° to 37.1×10^{-5} at −40°. Obviously the effects occurring in different solvents must be studied independently.

Conclusions

The above results strongly support the existence of ion pairs in solutions of the TMB cation radical with halide anions. The nature of the counterion is thought to be I$_3^-$ in the case of iodine and possibly a mixture of Br$_3^-$ and Br$^-$ in the case of bromine. The experiments describing the effects of added halogen, halide ion, or temperature, while qualitative, are indicative of the occurrence of various possible types of equilibria. No attempt has been made to rigorously define these equilibria at this stage although possibilities have been mentioned. It is anticipated that more quantitative measurements in the future will address themselves to this problem in detail.

References and Notes

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Aliphatic Semidiones. XXV.
Bicyclo[n. 2.1]alkane-2,3-semidiones[1]

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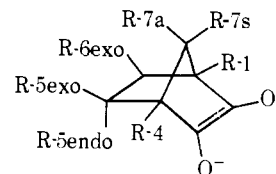*Received May 16, 1974*

Abstract: The esr spectra of a number of bicyclo[2.2.1]heptane-2,3-semidiones and bicyclo[3.2.1]octane-2,3-semidiones are reported, including tri- and tetracyclic derivatives. Assignments of hyperfine splitting constants have been made by studies of deuterium and alkyl derivatives. A number of long range transoid, coplanar interactions between protons and the electron spin are reported, discussed, and analyzed in terms of valence bond resonance structures. Extended Hückel and/or INDO calculations are reported for bicyclo[2.2.1]heptane-2,3-semidione and several alkyl derivatives, the corresponding semifuraquinone, bicyclo[2.2.1]hept-5-ene-2,3-semidione, and the semifuraquinone derivative and *exo*- and *endo*-tricyclo[3.2.1.0^{2,4}]octane-6,7-semidiones.

Esr hyperfine splittings (hfs) by hydrogen atoms separated from a center of spin density by three or four bonds have been reported for a few monocyclic species such as cyclobutyl, cyclopentyl, and cyclohexyl radicals,[4] piperidine nitroxide,[5,6] and cycloheptanesemidione.[7] Resolution of these long range hfs requires a frozen conformation for the monocyclic system. Rigid bicyclic structures are often rich in such long range hfs.[8,9] Since our original report of such long range hfs in bicyclic 1,2-semidiones,[8,9] similar observations have been reported for other spin centers including alkyl radicals,[10-12] nitroxides,[13,14] semiquinones,[15,16] semifuraquinones,[17] dicyanoethylene radical anions,[18] dimethyldialkylhydrazine radical cations,[19] and 1,4-semidiones.[16,20]

The present results complement previous reports on long range splittings in 2,3-semidiones derived from bicyclo[n.1.0]alkanes,[21] bicyclo[n.1.1]alkanes,[22] bicyclo[2.2.2]alkanes,[23,24] bicyclo[3.2.0]octanes,[7,9,23] bicyclo[3.2.2]nonanes,[9,25] bicyclo[3.3.1]nonanes,[9] bicyclo[3.3.2]decanes,[25] and a variety of polycyclic derivatives of cyclobutanesemidione.[26]
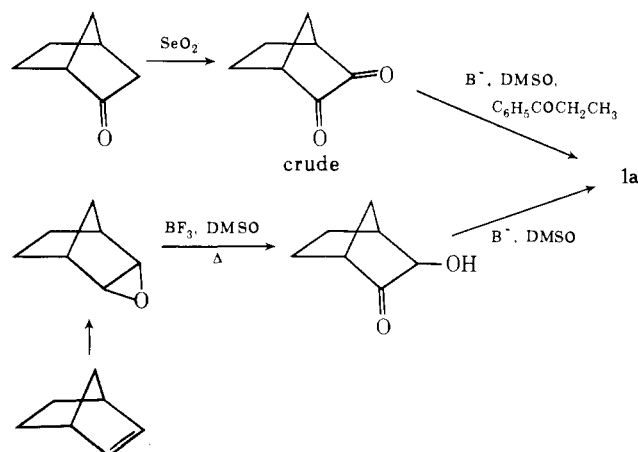
Synthesis of Bicyclo[2.2.1]heptanesemidiones. Treatment of bicyclo[2.2.1]heptan-2-one with traces of oxygen in basic DMSO solution failed to yield the esr signal of the semidione although this technique can be applied to a wide variety of cyclohexanone derivatives.[27,28] Reaction of this ketone, and most other bicyclo[2.2.1]heptan-2-ones not containing a *syn*-7 substituent with selenium dioxide, failed to yield significant amounts of the α-diketone although the crude product from norcamphor did yield the esr signal of **1a** when treated with the propiophenone enolate ion in DMSO.[8]

An *in situ* preparation of 3-hydroxy-2-norbornanone from norbornene oxide in DMSO containing a trace of boron trifluoride etherate (80°, 24 hr)[29] yielded **1a** when the DMSO solution was treated with potassium *tert*-butoxide (Scheme I), but this method gave mixtures of radicals


```
              R-7a    R-7s
        R-6exo           R-1
    R-5exo                     O·
                               
    R-5endo   R-4
                          O⁻
```

1a, unsubstituted
   (R unspecified = H)
b, R-7a = D
c, R-7s = D
d, R-5,6exo = D
e, R-7 = CH₃O
f, R-1,4 = D; R-7 = CH₃O
g, R-1 = CH₃
h, R-7a = CH₃

i, R-7a = CD₃
j, R-7s = CH₃
k, R-1,7s = CH₃
l, R-7 = CH₃
m, R-1,7,7 = CH₃
n, R-1,7s = CH₃; R-7a = CD₃
p, R-5,6exo = CH₃
q, R-5,6endo = CH₃

Scheme I

when applied to other substituted norbornenes. 3-Bromo-norcamphor in basic DMSO also yielded **1a** but this method[30] failed for 3-bromocamphor itself.