to oxygen. However, oxygen was not absorbed and indigo was not formed. Acidification with aqueous hydrochloric acid produced 2-(*p*-nitrobenzal)indolinone, mp 273°. Recrystallization from acetonitrile gave 190 mg (35%), mp 285–286° (lit.[28] mp 273–274°); ir (KBr) 3340 (NH), 1680 (C=O), and 1510 and 1335 cm^{-1} (NO_2); mass spectrum (70 eV), parent peak at *m/e* 266.

Anal. Calcd for $C_{15}H_{10}N_2O_3$: C, 67.66; H, 3.79; N, 10.52. Found: C, 67.70; H, 3.84; N, 10.54.

Reaction of Tetramethylhydrazine with Iodine

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Abstract: In nonpolar solvents tetramethylhydrazine (TMH) and iodine form a charge-transfer complex. At low TMH to iodine ratios the complex probably has 1:1 stoichiometry but at higher ratios a 2:1 TMH to iodine comcomplex may be formed. In middle polarity solvents solutions of TMH and iodine yield esr spectra which are broadened by electron exchange due to the reaction of $TMH\cdot^{+}I_2\cdot^{-}$ ion pairs with uncomplexed TMH. The rate constant for electron exchange is estimated to be 9×10^9 l./mol sec. The change in *g* factor as a result of ion pairing is noted. In polar solvents the solutions give highly resolved esr spectra characteristic of $TMH\cdot^{+}$. It is postulated such spectra are due to the free, solvated $TMH\cdot^{+}$ ion. The mechanism of the one-electron oxidation of TMH by iodine appears to be as shown in eq 7.

The esr spectrum of the tetramethylhydrazine radical cation ($TMH\cdot^{+}$) has been published.[2,3] In our earlier communication[3] we showed that $TMH\cdot^{+}$ could be generated by the reaction of tetramethylhydrazine (TMH) with iodine. It is the intent of this paper to discuss this reaction in greater detail.

The interaction of N,N,N′,N′-tetramethyl-*p*-phenylenediamine (TMPD) with tetracyanoethylene (TCNE) was studied by Liptay, Briegleb, and Schindler.[4] They found that in nonpolar solvents the two reactants formed a change-transfer complex. In polar solvents the uv visible spectra showed that only the radical cation and radical anion of TMPD and TCNE, respectively, were formed. In solvents of intermediate polarity, however, the charge-transfer complex, radical-ion pairs, and free, solvated radical ions were in simultaneous equilibrium (eq 1). The conclusions of Briegleb and his coworkers were based on an involved analysis of electronic spectra. They were also able to estimate K_1, K_2, and K_3 as a function of the solvents used.

$$\mathrm{TMPD} + \mathrm{TCNE} \xrightleftharpoons{K_1} \mathrm{TMPD}\cdot\mathrm{TCNE} \xrightleftharpoons{K_2} \mathrm{TMPD}\cdot^{+}\mathrm{TCNE}\cdot^{-} \xrightleftharpoons{K_3} \mathrm{TMPD}\cdot^{+} + \mathrm{TCNE}\cdot^{-} \quad (1)$$

There is considerable current interest in one-electron oxidations because of their importance in biological processes. Several other groups[5] presented electronic absorption and esr data consistent with the type of reaction shown in eq 1 but none of these studies showed all the steps of the equilibrium. Recently the oxidation of magnesium octaethylporphin with iodine and several other one-electron oxidizing agents was reported.[6] A qualitative dependence of the oxidation on solvent was noted.

The present study describes the system of TMH and iodine. Our data indicate an equilibrium similar to the type observed by Briegleb, *et al.*,[4] but there are significant differences in techniques and conclusions.

Experimental Section

Materials. Tetramethylhydrazine was prepared by the method of Beltrami and Bissell.[7] The compound was purified by distillation (bp 68–69° (730 mm)) and before each run by glpc (5 ft × 0.25 in. Apiezon L column, operated at 62°, 50 cc/min He flow rate). The purity was checked by nmr (singlet at 2.22 ppm in CCl_4, internal TMS).

Iodine was sublimed and was stored over phosphorus pentoxide.

Solvents. Chloroform (reagent grade) was passed through a column of aluminum oxide to remove ethanol. **Dichloromethane** and **acetonitrile** were heated at reflux over phosphorus pentoxide, then distilled. **Dimethoxyethane** was heated at reflux with sodium and was then distilled. **Dioxane** was purified according to method a given by Fieser.[8] **Carbon tetrachloride, 2-propanol, *t*-butyl alcohol, acetone, methanol,** and ***n*-hexane** were either reagent grade or spectroscopic quality and were used without further purification.

Diphenylpicrylhydrazyl (DPPH) (Aldrich Chemical Co.) was recrystallized from benzene. The first crystals formed were discarded and the remaining crystals were dried *in vacuo* at 80° for at least 16 hr, mp 127–128°.

Anal. Calcd for $C_{18}H_{12}N_5O_6$: C, 54.85; H, 3.05; N, 17.70. Found: C, 55.4; H, 3.1; N, 17.1.

Tetracyanoethylene (TCNE) (Eastman White Label) was recrystallized from methylene chloride and then sublimed *in vacuo*, mp 194–200° in a sealed tube.

Measurements. Ultraviolet spectra were obtained on a Cary Model 14 spectrophotometer. The sample compartment was thermostated by circulation of water from a constant temperature bath. Both 1- and 10-cm matched fused silica cells were used in the measurements.

Electron spin resonance spectra were obtained with a JEOLCO 3BSX spectrometer employing 100-KHz field modulation. The modulation amplitudes were small with respect to line widths unless otherwise noted.

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[1] To whom requests for reprints should be addressed.

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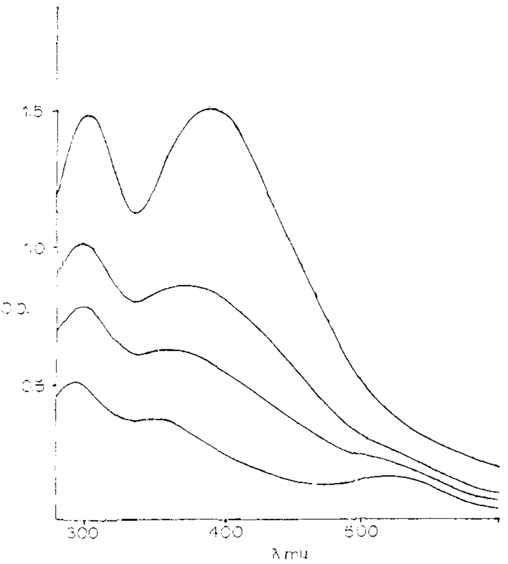

Figure 1. Ultraviolet spectra of TMH and I_2 in *n*-hexane when [TMH] > [I_2]. Concentrations: [I_2] = 1.996 × 10^{-5} *M* in all curves; [TMH] = 3.02 × 10^{-4}, 4.83 × 10^{-4}, 7.25 × 10^{-4}, and 1.45 × 10^{-3} *M*, in order from the bottom to the top curve. Fused silica cells (10 cm) were used for the measurements.

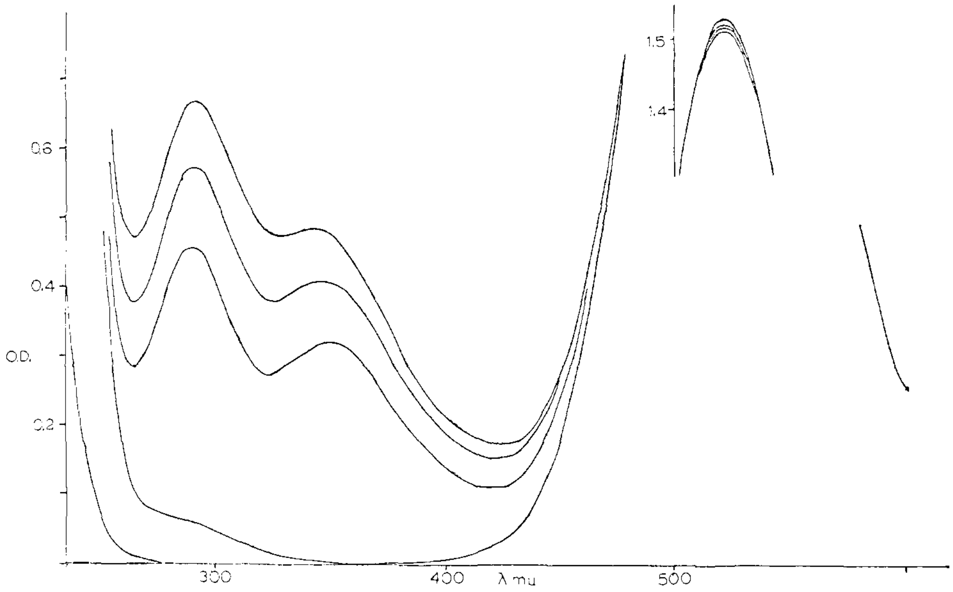

Figure 2. Ultraviolet spectra of TMH and I_2 in *n*-hexane when [I_2] > [TMH]. The bottom curve is the spectrum of TMH with no I_2 added. The next curve is the spectrum of I_2 (1.68 × 10^{-4} *M*) with no TMH added. In the upper three curves [I_2] = 1.68 × 10^{-4} *M* and [TMH] = 1.60 × 10^{-5}, 2.88 × 10^{-5}, and 4.11 × 10^{-5} *M* from bottom to top. The insert shows the maximum of the 520-mμ I_2 band, which was off-scale relative to the complex bands.

The samples were prepared in specially designed tubes. A solution of iodine in a given solvent was placed into one compartment and was degassed on a vacuum line employing three freeze–pump–thaw cycles and then sealed. A solution of TMH in the same solvent was placed in a second compartment separated from the first by a breakseal. This solution was also degassed and sealed. Attached to one of the compartments was a capillary tube[9] which was inserted into the esr cavity during the measurement. Just before insertion into the cavity the breakseal was broken, the reactants were mixed thoroughly, and the resulting solution was allowed to flow into the capillary. The experiments utilizing TCNE as the acceptor were carried out in the same manner.

Spin counts were determined in the following manner. The esr spectrum of a mixture of TMH and I_2 in a given solvent and an esr spectrum of a known concentration of DPPH in the same solvent were recorded using the same modulation width, the same attenuation, and the same sweep width. A normalization factor was computed according to the ratio

$$\frac{\text{theoretical intensity of center line TMH}\cdot^{+}}{\text{theoretical intensities of all lines of TMH}\cdot^{+}} = 0.188$$

To increase the precision of the measurement the spectra were recorded so that the largest possible peak areas were obtained. This resulted in slightly different gain settings for the two spectra. To correct for this the ratio of the two gain settings was incorporated into the calculation. The concentration of TMH$\cdot^{+}$ could then be calculated from the expression

$$[\text{TMH}\cdot^{+}] = \frac{\text{area of 0.5 center line TMH}\cdot^{+}\ \text{gain DPPH}}{0.188(\text{area of 0.5 DPPH spectrum})\ \text{gain TMH}\cdot^{+}}[\text{DPPH}]$$

The areas were computed by graphical integration of the derivative esr curves.

This technique is subject to large error and hence the concentrations reported should be considered approximate.

Results and Discussion

Low Polarity Solvents. Solutions of TMH and iodine in *n*-hexane, cyclohexane, or carbon tetrachloride do not exhibit esr spectra near room temperature. Examination of ultraviolet spectra, however, reveals that a strong charge-transfer complex of TMH and iodine is formed. The equilibrium is a complex one. Figure 1 shows the changes in the ultraviolet spectrum in *n*-hexane solution produced by varying the TMH concentration at constant iodine concentration which was lower than any of the TMH concentrations. Three maxima are observed—at least at lower TMH concentrations. The small long-wavelength band (λ_{max} 520 mμ) is due to uncomplexed iodine. The short-wavelength band we assign to the C–T transition (λ_{max} 295 ± 2 mμ). The middle band can be assigned to the blue-shifted iodine absorption in analogy with the bands observed in the triethylamine–iodine complex.[10] This band is due to the excitation of iodine

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[9] A capillary tube was used to minimize dielectric loss, particularly with the more polar solvents.

Table I[a]

Solvent	Modulation amp., G	ε (25°)	Line width, Gauss	Appearance of spectrum[b]
Chloroform	0.51	4.8	4.41	Broad
Dichloromethane	0.51	9.08	2.84	
2-Propanol	1.02	18.3	2.00	
t-Butyl alcohol	0.51	10.9 (30°)	1.87	
Dimethoxyethane	0.51	7.21	1.74	
Acetonitrile	0.05	36.2	0.38	Resolved
Acetone[c]	0.51	20.7	0.35	
Methanol	0.13	32.63	0.32	
Water[d]	0.10	78.4	0.34	

[a] [TMH] = 2.16×10^{-2} *M*, [I_2] = 7.39×10^{-2} *M*. [b] See text for definitions of "broad" and "resolved." [c] The spectrum in acetone was overmodulated. The correction, however, is small. [d] The line width was taken from a spectrum of solution which was 4.5×10^{-2} *M* in TMH and saturated with iodine.

bound in a complex. It can be seen readily from Figure 1 that the relative intensities of the C–T band and the blue-shifted iodine band are not constant; the intensity of the blue-shifted I_2 band increases relative to the C–T band as the concentration of the TMH is increased. Moreover, the λ_{max} of the blue-shifted I_2 shifts toward the red with increasing TMH concentration. Finally, it may be noted that the curves do not pass through an isosbestic point. These data suggest that at these relative concentrations of the reactants more than one complex is formed. Examination of Figure 2 lends further support to this conclusion. The relative concentrations of TMH and iodine in this figure have been reversed. The iodine concentration was higher than TMH. The relative intensities of the C–T band and the blue-shifted I_2 band are constant and position of the λ_{max} (348 ± 1 mμ) of the blue-shifted I_2 band remains fixed. The curves in Figure 2 pass through an isosbestic point at ~475 mμ. This suggests that in this region of relative concentrations only one complex is formed. Attempts to evaluate the equilibrium constant for complex formation by the Benesi–Hildebrand method[11] gave erratic results. This method was used successfully in the determination of the constant of the 1:1 complex of triethylamine and iodine.[11] The equilibrium constant for a 1:1 complex was estimated from the curves in Figure 2 by assuming that the decrease in intensity of the 520-mμ band represented the iodine used up by complex formation. The value thus obtained was $4.5 \pm 1.7 \times 10^2$ l./mol (25°). This is not unreasonable in view of the value for the triethylamine–iodine complex of 4.68×10^3 l./mol (25°), which was obtained from a Benesi–Hildebrand plot.[11]

The results thus indicate that at least two complexes can be formed depending on the relative TMH and I_2 concentrations. The stoichiometry cannot be assigned with certainty from our data but the equilibrium shown in eq 2 seems reasonable.

$$\mathrm{TMH} + \mathrm{I_2} \rightleftharpoons \mathrm{TMH}\cdot\mathrm{I_2} \overset{\mathrm{TMH}}{\rightleftharpoons} (\mathrm{TMH})_2\cdot\mathrm{I_2} \qquad (2)$$

There is some support in the literature for the formation of (amine)$_2\cdot I_2$ complexes. The complex of (γ-picoline)$_2\cdot I_2$ actually has been isolated and characterized.[12] More recently, calorimetric experiments have shown that the following type of equilibrium exists between triethylamine and iodine, particularly at higher amine concentrations.[13] These authors view

$$\mathrm{Am} + \mathrm{I_2} \overset{K_1}{\rightleftharpoons} \mathrm{Am}\cdot\mathrm{I_2}$$

$$K_1 = 4.7 \times 10^3 \text{ l./mol}$$

$$\mathrm{Am}\cdot\mathrm{I_2} + \mathrm{Am} \overset{K_2}{\rightleftharpoons} \mathrm{Am_2}\cdot\mathrm{I_2}$$

$$K_2 \approx 20\text{–}50 \text{ l./mol}$$

the $Am_2\cdot I_2$ complexes as the "inner" complexes of Mulliken,[14] *i.e.*, [Am_2I^+][I^-]. We, as yet, do not have sufficient data to hazard a guess as to the structure of $(TMH)_2\cdot I_2$. It is, *a priori*, a little surprising that a complex of the type $TMH(I_2)_2$ does not seem to form in our system. The recent study of Halpern and Weiss[15] indicates that diamines such as 1,4-diazobicyclo[2.2.2]-octane (DABCO) and N,N,N,N-tetramethylethylenediamine form complexes of the type $Am\cdot(I_2)_2$ with great facility. Although, formally, TMH is a diamine the fact that the two nitrogens are bonded to each other means that complexation of one nitrogen by an acceptor probably deactivates the other toward further complexation. This does not preclude the fact that stronger acceptors such as TCNE may coordinate both nitrogens. Indeed, this may explain the behavior of TMH in the presence of TCNE in some solvents (*vide infra*).

Middle Polarity Solvents. The solutions of TMH and iodine in this group of solvents exhibit esr spectra. Table I lists several solvents in which esr signals have been observed. In this section the esr spectra produced by solutions corresponding to the first five entries in Table I will be discussed. In these solvents the spectrum appears as 15 equally spaced lines spread over approximately 180 G. All the spectra reported in this paper could be calculated by assuming that the line shapes were Lorentzian and that the hyperfine coupling constants were: $a_N = 13.5 \pm 0.1$ G and $a_H = 12.7 \pm 0.1$ G. The only variable used was the line width. The coupling constants can be extracted directly from the fully resolved spectra.[2,3] Figure 3 shows a typical spectrum in dichloromethane and the corresponding computer-simulated spectrum. For the sake of bookkeeping the "broad line" spectrum will refer to the type of spectrum illustrated in Figure 3.

Table I indicates that there are significant variations in line widths with change in solvent (4.41 G in chloro-

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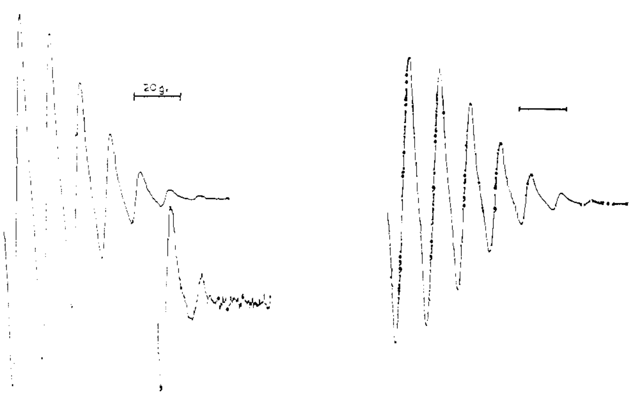

Figure 3. The esr spectrum of TMH^+ in dichloromethane. Only one-half of the spectrum is shown. The experimental spectrum is on the left and the computer-simulated spectrum is on the right. The insert shows the last two lines at higher gain. $[I_2] = 7.39 \times 10^{-2}$ *M*, $[TMH] = 2.16 \times 10^{-2}$ *M*. Line width = 2.84 G, modulation = 0.51 G.

Table II. Effect of Changing Composition of Solvent on the Line Width of the Esr Spectrum of $TMH\cdot^+$

Dioxane–H_2O system[a]			Chloroform–methanol system[b]		
Water, %	Modulation width, G	Line width, G	Methanol, %	Modulation width, G	Line width, G
0	0.51 – 0.25	2.11	0	0.52	4.38
10	0.25 – 0.13	1.80	20	0.52	2.64
15	0.25	1.61	30	0.52	1.95
20	0.25	1.44	40	0.52	1.56
30	0.25	0.38[c]	50[d]	0.12	0.47

[a] $[TMH] = 4.50 \times 10^{-2}$ *M*, $[I_2] = 4.05 \times 10^{-2}$ *M*. [b] $[TMH] = 6.70 \times 10^{-2}$ *M*, $[I_2] = 1.18 \times 10^{-2}$ *M*. [c] At this H_2O concentration the spectrum was fully resolved. [d] At this point the spectrum was partially resolved.

form, 1.74 G in DME). It is difficult to correlate the line width with any solvent parameter because of the wide differences in the chemical characteristics of the solvents used. A better correlation can be obtained from the data summarized in Table II. Here the line widths are presented as a function of the composition of two sets of mixed solvents: dioxane–water and chloroform–methanol. It is clear from these data that in a given solvent mixture the line width is a smooth function of the composition of the solvent.

At the present time there is not enough information to correlate the line widths with a specific solvent parameter such as the *Z* value,[16] but such a correlation is not excluded.

Further examination of Table II reveals that at 30% water in dioxane and >50% methanol in chloroform the spectrum becomes fully resolved (*vide infra*). Before these conditions are reached, however, some hyperfine structure does begin to appear. There is thus a gradual transition from the broad line spectrum to the fully resolved spectrum.

Table III. Spin Count as a Function of the Composition of Dioxane–Water Solvent[a–c]

H_2O, %	Line width, G	$[THM\cdot^+] \times 10^4$ *M*
10	2.20	1.5
15	2.05	2.4
20	1.90	3.1
30	0.38	3.3

[a] $[TMH]_0 = 4.50 \times 10^{-2}$ *M*, $[I_2]_0 = 2.21 \times 10^{-2}$ *M*. [b] The spectra were taken ~450 sec after mixing. Addition of water causes a marked increase in the rate of decay of the radical. This rate did not seem to change (at least qualitatively) over the range of water concentrations examined. [c] The spectra from which this table was derived were probably slightly overmodulated. The trend in line widths is correct (see Table II).

Table IV. Line Width as a Function of I_2 Concentration[a]

$[I_2]_0 \times 10^3$ *M*	$[TMH\cdot^+] \times 10^5$ *M*	Line width, G
2.35	1.1	4.80
8.50	4.7	4.12
13.0	6.6	3.58
13.5	6.1	3.54
16.9	14.0	2.98

[a] $CHCl_3$ solution, $[TMH]_0 = 1.30 \times 10^{-2}$ *M*.

It could be argued that the decrease in line width and eventual complete resolution with increasing solvent polarity are caused by a decrease in the rate of spin–spin exchange. That this is not so is indicated by the data in Table III, which show the variation of line width and spin count as a function of water–dioxane composition. Although the radical concentrations given are approximate (see Experimental Section) the trend indicated in the table is real. Since the rate of spin–spin exchange should increase with increasing radical concentration, this phenomenon cannot account for the line narrowing. This is further indicated by the data in Table IV. In this experiment the concentration of TMH in chloroform was held constant but the iodine concentration was varied. Note that as the iodine concentration increases so does the spin count but there is also a concomitant decrease in line width. The decrease in the line width with an increase in iodine concentration is a clue to the understanding of the line width variations observed in this work. It has already been established that TMH and iodine form charge-transfer complexes. The ultraviolet spectrum of iodine and TMH in chloroform has essentially the same appearance as the spectra shown in Figure 2. It can be assumed that, as in *n*-hexane, two complexes are formed in chloroform if the concentration of TMH is higher than iodine concentration. For the sake of the initial argument assume that only the 1:1 complex is important. As the iodine concentration increases relative to TMH there will be less uncomplexed TMH in solution. We suggest that in solvents indicated in Table I the charge-transfer complex dissociates into radical ion pairs according to eq 3. In solvents in which the radical exhibits the broad line

$$TMH\cdot I_2 \rightleftharpoons [TMH\cdot^+ I_2\cdot^-]_{solv} \qquad (3)$$

spectrum the radicals remain substantially in the form of solvated ion pairs.

A direct indication of the presence of ion pairs is afforded by the data in Table V. Careful measurement of the *g* factor of the $TMH\cdot^+$ radical formed by the reaction of TMH with I_2 in chloroform shows that it is significantly higher than that of the same radical generated in water. The reaction of tetramethyl-

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Table V. g Factor for $TMH\cdot^+$ as a Function of Solvent and Gegenion[a]

Method of formation of $TMH\cdot^+$	Solvent	g value	Line width, G
$Me_2NN{=}NNMe_2 + Me_2SO_4$[b]	$CHCl_3$	2.00357	0.36
$TMH + I_2$	H_2O	2.0036	0.34
$TMH + I_2$	$CHCl_3$	2.00380	3.48
$TMH + I_2$	CH_2Cl_2	2.00367	2.84
$TMH + I_2$	DME	2.00362	1.97

[a] Precision of measurement = ±0.00003; standard: peroxylaminedisulfonate g = 2.00540. [b] The reaction of tetramethyltetrazene with methyl sulfate in chloroform gives $TMH\cdot^+$ whose esr spectrum is fully resolved. This and related reactions will be published in a separate paper.

tetrazene with methyl sulfate gives the $TMH\cdot^+$ radical whose gegenion is presumably the methyl sulfate anion. The spectrum of this radical is fully resolved and its g factor is indistinguishable from that of the aqueous $TMH\cdot^+$. Moreover, the $TMH\cdot^+$ radicals described by Nelsen[2] also seem to have the "aqueous" g factor. In Nelsen's case the gegenions were carboxylate anions derived from anhydrides; his spectra were fully resolved in DMF, THF, and acetonitrile solutions. Table V also shows that the g factor decreases as the line width decreases from chloroform to methylene chloride to dimethoxyethane (DME). In fact, the g factor in DME is indistinguishable from the aqueous solution. Thus it seems that the higher g factor is characteristic of the TMH–I_2 system in the "broad line" region. Changes in the g factor have been observed in the spectra of naphthalenide–alkali metal ion pair systems in several solvents.[17] At the present time not enough is known about the effect of ion pairing on the g factors to explain the differences observed. It is difficult to predict the direction of the change, *a priori*. It is well known that radicals containing heavy atoms generally have higher g factors than those which do not, due, in part, to spin–orbit coupling. Naively, one could explain our data in the same manner, *i.e.*, spin–orbit coupling with iodine increases g value relative to the free $TMH\cdot^+$, but it should be noted that Reddoch[17] observed the opposite effect—his g values decreased in going from K to Rb to Cs. Whatever the detailed mechanism of the change in g is, the data seem to support the ion-pair hypothesis in the TMH–I_2 system. The changes in g are not simply a solvent effect as can be seen by comparing the first and the third entries in Table V. Solvent effects on g factor have been observed in hydrocarbon radicals.[18]

The question of the mechanism of the line broadening cannot be answered with certainty from our data. It seems, however, that the *probable* cause of line broadening is electron exchange between the solvated ion pair and uncomplexed TMH, as shown in eq 4. The data in Table IV lend partial support to this hypothesis.

$$[TMH\cdot^+I_2\cdot^-]_{solv} + TMH \rightleftharpoons TMH + [I_2\cdot^-TMH\cdot^+]_{solv} \quad (4)$$

Since an increase in iodine concentration produces a decrease in uncomplexed TMH there should be a decrease in the rate of exchange which would result in line narrowing. Further support for this idea can be obtained from the data in Table VI. Here the concentration of iodine was held fixed while the TMH concentration was varied. As would be predicted from eq 4 the line width increases with the increasing TMH concentration.

In principle these data can be used to calculate the bimolecular rate constant for eq 4. The problem is made difficult for several reasons. Although the natural line width for the free $TMH\cdot^+$ ion is known (*vide infra*), the natural line width for the ion pair can only be estimated (see footnote b in Table VI). The concentration of uncomplexed TMH can be calculated only by assuming an equilibrium constant for charge-transfer complex formation in chloroform (see footnote a in Table VI). The relationship to calculate the bimolecular rate constant was derived by Ward and Weissman.[19]

Table VI. Line Width as a Function of TMH Concentration[a]

$[TMH]_0 \times 10^2\ M$	$[TMH]_{calcd}$[b] $\times 10^2\ M$	Line width, G	$\Delta\Delta H$[c]
0.109	0.039	2.89	0.13
0.140	0.059	3.12	0.36
0.175	0.065	3.20	0.44
0.240	0.094	3.34	0.58
0.295	0.119	3.44	0.68
0.326	0.132	3.53	0.77
1.18	0.720	4.30	
1.75	1.21	4.47	
2.39	1.82	4.60	
4.78	4.16	5.10	

[a] $CHCl_3$ solution; $[I_2]_0 = 6.70 \times 10^{-3}\ M$. [b] This is a tabulation of uncomplexed TMH concentrations. This was calculated by assuming that $K_{equilib}$ for charge-transfer complex formation in $CHCl_3$ is 3×10^2 and by neglecting the dissociation into radicals. The equilibrium constant for the latter process is estimated to be about 1×10^{-2}. [c] The $\Delta\Delta H$ values are the exchange contributions to the line width. The estimated natural line width for the ion pair in $CHCl_3$ was obtained by plotting the observed line width *vs.* $[TMH]_{calcd}$. The intercept of that line (calculated by the least-squares method) was 2.76 G. The $\Delta\Delta H$ values are the observed line widths minus 2.76.

$$k = \frac{1.2 \times 10^7 \Delta\Delta H}{[TMH]_{calcd}}$$

In deriving this equation an assumption was made that there is no overlap between the broadened lines. This unfortuantely is not the case in this system. Only the first six entries in Table VI could be used in the calculation; in the other entries the line widths shown are not the true line widths because of heavy overlap. The least-squares treatment of the data in Table VI gives the bimolecular rate constant for the exchange reaction: $k = 9.1 \times 10^9$ l./mol sec. The data in Table IV may be treated in a similar manner and the rate constant calculated from that is $k = 5 \times 10^9$ l./mol sec. The agreement is heartening although since the same approximations were made the same error may be present in both. It is probably reasonable to assume that the value is correct within an order of magnitude; however, since the calculation of the rate constant is crude at best it should be pointed out that any con-

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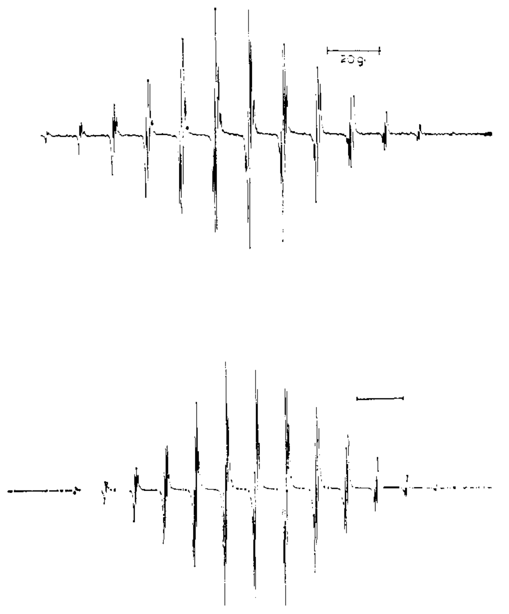

Figure 4. Upper trace is the experimental curve obtained from 2.16×10^{-2} *M* TMH and 7.39×10^{-2} *M* I_2 in acetonitrile. The lower curve is the corresponding computer-generated trace. The spectrum was run from left to right; notice the decay of the radical during the scan.

clusions based on its magnitude should be considered tentative.

An exchange reaction of this kind would be expected to show temperature dependence. The data in Table VII show that the line width changes inversely with the change in temperature. A plot of the log ΔH *vs.* $10^3/T$°K is curved. This is not surprising because all the equilibria in the system would show temperature dependence and hence a linear relationship should not be expected.

Table VII. Line Width as a Function of Temperature[a]

$10^3/T$°K	Modulation width, G	Line width, G
3.36	1.02	4.72
3.54	1.02	4.57
3.69	1.02	4.31
3.92	0.75	3.94
4.12	0.75	3.27
4.31	0.75	2.62

[a] $[TMH]_0 = 1.75 \times 10^{-2}$ *M;* $[I_2]_0 = 6.70 \times 10^{-3}$ *M* in $CHCl_3$.

Radical-ion pairing has been explored extensively in systems involving alkali metals and organic substrates.[20] Frequently in such cases the interaction of the cation with the anion can be detected. In our case we do not observe a signal from the anion ($I_2\cdot^-$). The reasons for this are not clear but similar behavior has been observed by other workers.[21,21a] Although the chlorine[22] and fluorine[23] negative ions have been detected in X-irradiated crystals at low temperatures, the iodine negative ion has not been reported. Indeed, at the temperatures used in this study the free ion probably has a short lifetime (*vide infra*). In the ion pair which is in equilibrium with the diamagnetic charge-transfer complex, the iodine negative ion must have an appreciatively longer lifetime. It is not completely stable because the spectra decay slowly, even in the nonpolar solvents such as chloroform. Some experimental evidence pertaining to the gegenion was obtained in the oxidation of TMH by tetracyanoethylene (TCNE). In acetonitrile solution a spectrum was observed which was the result of superposition of the resolved spectrum of $TMH\cdot^+$ and the characteristic nine-line pattern[24] of the TCNE radical anion. Interestingly enough in aqueous solution only the spectrum of $TCNE\cdot^-$ was obtained; no $TMH\cdot^+$ could be detected. The reason for this may be that $TMH\cdot^+$ is oxidized a second time by TCNE to form the diamagnetic TMH^{2+} ion. This type of oxidation is not unreasonable in view of Hünig's work on the "violene" systems.[25]

Polar Solvents. Table I lists several solvents in which fully resolved spectra such as shown in Figure 4 were obtained. One common feature of these solvents is that they are more polar than the ones discussed above. The line width (measured as the peak to peak separation of the most intense line in the major splittings) was constant in all these solvents, the value being 0.35 ± 0.03 G. Another important feature of these solvents is that the radical cation is much less stable. Addition of the polar solvents to the middle polarity solvents increases the rate of decay noticeably even when the broad line spectrum is observed. The constancy of the line width suggests that in these solvent little or no electron exchange takes place between $TMH\cdot^+$ and TMH, and hence 0.35 G represents the natural line width for $TMH\cdot^+$. It was suggested above that the electron exchange occurred *only* with the ion pair and that it involved the transfer of iodine from one TMH to another. In the polar solvents we postulate that the ion pairs are destroyed. The ions become solvated independently (eq 5). We suggest further that this process is virtually irreversible because the iodine negative ion would not be expected to have an appreciable independent lifetime. A decomposition reaction

$$[TMH\cdot^+I_2\cdot^-]_{solv} \longrightarrow [TMH\cdot^+]_{solv} + [I_2\cdot^-]_{solv} \qquad (5)$$

as shown in eq 6 is not unreasonable, although at the present time there is no independent evidence for it.

$$[I_2\cdot^-]_{solv} \longrightarrow [I^-]_{solv} + I\cdot \qquad (6)$$

Conclusion

The results presented in this paper strongly support the mechanism shown by eq 7 for the one-electron oxidation of tetramethylhydrazine by iodine. The arguments are mainly qualitative but all the data are in general agreement. This mechanism is similar to the

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(20) M. C. R. Symons, *J. Phys. Chem.*, 71, 172 (1967). This paper is a review of ion-pairing phenomena in radical anion–alkali metal systems.

(21) W. H. Bruning, R. F. Nelson, K. S. Marcoux, and R. N. Adams, *ibid.*, 71, 3055 (1967).

(21a) Note Added in Proof. Prof. R. S. Mulliken suggested to us that $TMH\cdot^+I_2\cdot^-$ should have triplet character; since our system does not he suggested further that our ion pair is actually $TMH\cdot^+I_3^-$. The I_3^- would be formed in the following reaction: $TMH\cdot I_2 + I_2 \rightleftarrows TMH\cdot^+I_3^- + I\cdot$. It is difficult to refute or confirm this idea on the basis of our present data. Experiments from which that information can be extracted are now in progress and will be reported later.

(22) H. Ueda, *J. Chem. Phys.*, 41, 285 (1964).

(23) W. Kanzig, *J. Phys. Chem. Solids*, 17, 80 (1960).

(24) W. D. Phillips, J. C. Rowell, and S. I. Weissman, *J. Chem. Phys.*, 33, 626 (1960).

(25) S. Hünig in "Free Radicals in Solution," Plenary Lectures IUPAC Symposium, Ann Arbor, Mich., 1966, Butterworth and Co. (Publishers), Ltd., London, 1967, p 109. It may be noted that $TMH\cdot^+$ is the proper parent radical of the "violene" class.

$$\begin{tikzcd}
TMH + I_2 \arrow[r, shift left] & TMH\cdot I_2 \arrow[l, shift left] \arrow[r, shift left] \arrow[d, shift left, "TMH"] & {[TMH\cdot^{+}I_2\cdot^{-}]_{solv}} \arrow[l, shift left] \arrow[r] & {[TMH\cdot^{+}]_{solv} + [I_2\cdot^{-}]_{solv}} \\
& 2TMH\cdot I_2 \arrow[u, shift left] & &
\end{tikzcd} \qquad (7)$$

$$[I_2\cdot^{-}]_{solv} \longrightarrow [I^{-}]_{solv} + I\cdot$$

one proposed by Briegleb, *et al.*[4] (eq 1), except that in our case the last step is probably virtually irreversible. It is likely that mechanisms of this type are important in many biological oxidations.[26]

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[26] *Cf.* A. Szent-Györgyi, *Discussions Faraday Soc.*, 27, 111 (1959).

The Mechanism of the Hydrochlorination of *t*-Butylethylene and Styrene in Acetic Acid[1]

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Abstract: The hydrochlorination of *t*-butylethylene in acetic acid yields 3-chloro-2,2-dimethylbutane (**SC**), 2-chloro-2,3-dimethylbutane (**TC**), and 3-acetoxy-2,2-dimethylbutane (**SA**) in the approximate ratio 2:2:1. Since **SC** and **SA** are stable to the reaction conditions, rearrangement is a kinetically controlled process; however, 2-acetoxy-2,3-dimethylbutane (**TA**) is rapidly converted to **TC** so that either **TA** or **TC** (or both) may be primary product(s). Although the rate of reaction varies significantly with chloride salt concentration (0–1.5 *M* $(CH_3)_4NCl$), water concentration (0–2.5 *M*), and temperature (25–125°), there is little accompanying change in the product composition. The hydrochlorination of styrene in acetic acid yields α-methylbenzyl chloride (**C**) and α-methylbenzyl acetate (**A**) in the approximate ratio 13:1 under conditions of kinetic control. The reaction is first order in [HCl] at low acid concentration (<0.1 *M*) and linear in effective acidity at high acid concentration. The ratio **C**/**A** varies little with [HCl] (0.006–0.5 *M*), with $[(CH_3)_4NCl]$ (0–0.3 *M*), or with temperature (16.5–50°). From studies of the reactions in DCl–DOAc, kinetic isotope effects $k_H/k_D = 1.2$ and 1.4 were determined for addition to *t*-butyl ethylene and styrene, respectively. The results are discussed in terms of rate-limiting protonation of olefin by HCl to form a carbonium–chloride ion pair; collapse or rearrangement of the ion pair occurs at rates faster than or comparable to that of a diffusion-controlled process.

The addition of hydrogen halides to olefins has long been considered to occur *via* carbonium ions as intermediates.[3] The most compelling evidence for this view comes from studies like those of Whitmore and coworkers who showed that rearranged products are formed in the reaction of hydrogen halides with 3-methyl-1-butene[4] and *t*-butylethylene.[5]

The stereochemistry of hydrogen halide addition is very much dependent upon the structure of the olefin.[6] Arenes[7] and dienes[8] add hydrogen halides preferentially (but not exclusively) *cis* (*syn*)[9] in weakly dissociating solvents, an observation attributed to ion-pairing phenomenon. Norbornene derivatives[10] and other strained bicyclic olefins[11] also add hydrogen halides largely or entirely *cis* (*syn*) for reasons which are as yet not entirely clear—concerted reactions may be involved in at least some cases. However, nonconjugated olefins such as 1,2-dimethylcyclohexene,[12] 1,2-dimethylcyclopentene,[13] and cyclohexene[14] undergo very predominant *trans* (*anti*)[9] addition upon reaction with hydrogen halides. Such *trans* additions have been most often rationalized in terms of a protonium ion intermediate (**1**) but no definitive demonstration of the existence of this species as a discrete reaction inter-

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[2] (a) Alfred P. Sloan Foundation Fellow, 1966–1968; (b) National Defense Education Act Predoctoral Fellow.

[3] P. B. D. de la Mare and R. Bolton, "Electrophilic Additions to Unsaturated Systems," Elsevier Publishing Co., New York, N. Y., 1966, Chapter 5.

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[9] It has been pointed out by E. L. Eliel (*cf.* ref 6, p 238) that in describing the steric course of addition use of the terms "*syn*" in place of "*cis*" and "*anti*" in place of "*trans*" is desirable in order to avoid the confusion which arises when the reacting olefin or the addition product exhibits *cis–trans* isomerism. Since this usage is as yet not widespread, both designations are used in this paper.

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