The transient spectrum obtained in pure liquid hydrazine shows a broad absorption extending from 500 to 1100 nm which has been attributed to the solvated electron; its maximum wavelength is located beyond 1100 nm. A small uv band is also found, probably due to oxidizing species. The recombination rate constant of the solvated electron with the acidic ion N2H5+ is \( (5 \pm 3) \times 10^7 \text{ M}^{-1} \text{s}^{-1} \) and hence is not diffusion controlled. The electron yield \( (G = 3.4) \) in the nanosecond time range has been obtained by scavenging with biphenyl. The rate constant of the scavenging reaction is \( 1.7 \times 10^{10} \text{ M}^{-1} \text{s}^{-1} \) and the extinction coefficient of the solvated electron is \( \epsilon = 1.85 \times 10^4 \text{ M}^{-1} \text{cm}^{-1} \) at 1000 nm. The high value of electron yield is interpreted in terms of the slowness of the recombination with the cation \( \text{N}_2\text{H}_5^+ \).

Hydrazine was distilled over quick lime under reduced pressure of inert gas according to the procedure described in ref 15. Hydrazine contained less than 0.5% water and 0.3% ammonia which corresponds to a negligible concentration of basic and acidic ions. Hydrazinium chloride was from Prolabo. Zone refined biphenyl was from Merck.

Hydrazine samples and solutions were degassed by the freeze-pump-thaw technique (77 K, 10^-7 Torr). Samples were irradiated at room temperature and repetitive pulsing had no effect on results. The experimental dose was \( 4.7 \times 10^{17} \text{ eV} \text{ ml}^{-1} \text{ pulse} \) as determined from the initial absorption of the hydrated electron, taking \( G_{\text{h}} = 3.0^{15} \) and \( \epsilon_{\text{h}} = 13 000 \text{ M}^{-1} \text{ cm}^{-1} \) at 600 nm. Biphenyl concentrations were measured spectrophotometrically after extraction by hexane from hydrazine solutions.

**Results**

1. **Transient Spectra and Kinetic Data.** Figures 1 and 2 show the transient absorption spectra obtained in pure liquid hydrazine at the end of a 3-ns pulse and at time 4 as after irradiation. Transient spectrum was not extended below 310 nm because of the strong absorption of hydrazine. For the wavelength range 450-1100 nm, a similar spectrum has been previously observed by the use of a 4.5-µs electron pulse and has been attributed to the solvated electron in hydrazine. Evidence for such an assignment results from scavenging experiments in the presence of biphenyl and hydrazinium chloride. In the uv range, there is a relatively small absorption peaking near 390 nm.

In Figure 3 absorption decays vs. time have been plotted for convenience on a semilog scale. The decay of the solvated electron as recorded at 900 nm lasts 10 µs and apparently obeys no simple kinetics. From Figure 3 the half-time \( t_{1/2} \), i.e., the time at which the optical density equals half of the initial optical density is 570 ns. In spite of experimental errors and assuming the decay to be due to homogeneous concurrent pseudo-first- and second-order reactions, numerical calculations based upon nearly equal initial concentrations of the solvated electron and reacting species for the second-order reaction yield \( k_{\text{pseudo first}} = 2 \times 10^5 \text{ s}^{-1} \) and \( k_{\text{second}} = 1.75 \times 10^{11} \text{ M}^{-1} \text{s}^{-1} \). At 400 nm the absorbing species decays more slowly than does the solvated electron except within the first microsecond during which the decay seems to parallel that of \( \epsilon_{\text{h}}^- \).

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**Introduction**

Theoretical models based on diffusion attempt to predict the fate of radiation induced species as a function of time and space, and of parameters related to the initial space distribution and to the physical properties of the solvent such as diffusion coefficients, dielectric constants, and relaxation times. In fact diffusion models imply that the solvated electron only reacts with the cation and that this neutralization effectively occurs at each encounter. This assumption could be incorrect and experimental results on liquid ammonia afford an example which favors consideration of collision efficiency. Indeed the yield of the ammoniated electron\(^{14} \) is much higher than expected by comparing with the electron yields obtained from solvents of similar static dielectric constant. We explained\(^2 \) this peculiarity by the marked slowness of the neutralization of the ammoniated electron by the acidic cation \( \text{NH}_4^+ \) (\( k = 10^6 \text{ M}^{-1} \text{s}^{-1} \)). This explanation is also that given by Farhataziz, Perkey, and Hentz\(^4 \) and confirmed by their results on the electron yield dependence on pressure.\(^5 \)

The aim of this paper is to extend the "G value-rate constant" correlation to hydrazine. Its physical properties are comparable to those of water whereas its chemical properties resemble those of liquid ammonia (amine function and the proton affinity).

The transient spectrum obtained in pure liquid hydrazine shows a broad absorption extending from 500 to 1100 nm which has been attributed to the solvated electron; its maximum wavelength is located beyond 1100 nm. A small uv band is also found, probably due to oxidizing species. The recombination rate constant of the solvated electron with the acidic ion \( \text{N}_2\text{H}_5^+ \) is \( (5 \pm 3) \times 10^7 \text{ M}^{-1} \text{s}^{-1} \) and hence is not diffusion controlled. The electron yield \( (G = 3.4) \) in the nanosecond time range has been obtained by scavenging with biphenyl. The rate constant of the scavenging reaction is \( 1.7 \times 10^{10} \text{ M}^{-1} \text{s}^{-1} \) and the extinction coefficient of the solvated electron is \( \epsilon = 1.85 \times 10^4 \text{ M}^{-1} \text{cm}^{-1} \) at 1000 nm. The high value of electron yield is interpreted in terms of the slowness of the recombination with the cation \( \text{N}_2\text{H}_5^+ \).

**Experimental Section**

The radiation source was a 706 Megatron delivering a 3-ns pulse of 600-keV electrons and providing about \( 10^{14} \) electrons per pulse. The pulse radiolysis set-up will be described in detail elsewhere.\(^12 \) Because of the catalytic decomposition of hydrazine by metals, instead of using a stainless steel cell,\(^13 \) an entire silica cell has been designed\(^14 \) with a 0.2-mm silica window for entrance of the electron beam. The optical path length is 1 cm and the cross section of the analyzing beam is 0.05 × 1 cm². The fast spectroscopic and electronic equipment enables us to detect transient absorbing species from 200 to 1100 nm and to record kinetics with a 3.7-ns risetime. A light beam splitting technique is used for determination of spectra, except for biphenyl experiments for which the spectrum has been normalized with respect to that of the solvated electron.
Concentrations higher than 0.5 M hydrazinium chloride are necessary to obtain a change of kinetics. In the presence of acidic ions $\text{N}_2\text{H}_5^+$, the decay of the solvated electron follows a pseudo-first-order law due to the reaction

$$e^- + \text{N}_2\text{H}_5^+ \rightarrow \text{N}_2\text{H}_3 + \text{H}_2$$  \hspace{1cm} (1)$$

Table I shows the concentration dependence of the rate constant due to the effect of ionic strength. Because of the high value of the dielectric constant of hydrazine ($\varepsilon = 53$ at 20 °C), the Debye–Hückel theory\textsuperscript{17} applies and the dependence of the rate constant $k_1$ on ionic strength $I$ reads

$$\log k_1 = \log k_{10} - \frac{2B\sqrt{I}}{1 + aC\sqrt{I}} + 2CI$$

where $k_{10}$ is the rate constant at zero ionic strength, $a = 4.5 \times 10^{-8}$ cm the distance of closest approach, $C$ a semiempirical parameter, $B = 0.935$ M$^{-1/2}$/s, and $a = 0.403 \times 10^{10}$ M$^{-1/2}$ cm$^{-1}$.

<table>
<thead>
<tr>
<th>[N$_2$H$_5$Cl] M</th>
<th>$k_{1/2}$, 10$^{-9}$ s$^{-1}$</th>
<th>$k_1$, 10$^6$ M$^{-1}$ s$^{-1}$</th>
<th>$k_2$, 10$^{10}$ M$^{-1}$ s$^{-1}$</th>
<th>$G(\text{Phz}^-)$, anions/100 eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Phz}]$, M</td>
<td>$t_{1/2}$, 10$^{-9}$ s</td>
<td>$k_1(\text{Phz})$, 10$^6$ s$^{-1}$</td>
<td>$k_2(\text{Phz})$, 10$^{10}$ s$^{-1}$</td>
<td>$G(\text{Phz}^-)$, anions/100 eV</td>
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<tr>
<td>-----------------</td>
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<td>-------------------</td>
</tr>
<tr>
<td>0.5</td>
<td>570</td>
<td>7.85</td>
<td>1.57</td>
<td>1.97</td>
</tr>
<tr>
<td>0.8</td>
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<td>9.9</td>
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<td>1.45</td>
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<tr>
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</tr>
<tr>
<td>0.6</td>
<td>3.4</td>
<td>7.85</td>
<td>16.8</td>
<td>1.97</td>
</tr>
</tbody>
</table>

$^a$ $t_{1/2}$ is the time at which the optical density equals half of the initial optical density.
and in water. The fact that there is no absorption near 950 nm at the highest biphenyl concentration excludes the presence of the solvated electron. Moreover as the absorption beyond 950 nm increases with the biphenyl concentration, the absorption cannot be due to the solvated electron in equilibrium with the biphenyline anion as recently pointed out in tetramethylhydrazine. Therefore the absorption beyond 950 nm has been assigned to the biphenyline anion.

Figure 2 (inserts) shows typical traces of the absorption recorded respectively at 400 and at 1000 nm in a 1.8 × 10⁻³ M biphenyl solution. At 400 nm the initial absorbance reaches a maximum over a time corresponding to the disappearance of the absorption at 1000 nm. Therefore the growth of the biphenyline anion is correlated to the decay of the solvated electron accordingly to the reaction

\[ e^- + Ph_2 \rightarrow Ph_2^- \]  

(2)

Assuming no decay of biphenyline anion during the buildup because its lifetime is comparatively long (10 μs), the maximum of absorbance corresponds to solvated electrons scavenged at a specified biphenyl concentration. Table I gives the concentration dependence of the observed pseudo-first-order rate constant \( k_f \) and of the \( G/\langle Ph_2^- \rangle \) value. The observed rate constant was calculated from the electron decay at 1000 nm and from the growth of biphenyline anion at 400 nm. The \( G/\langle Ph_2^- \rangle \) value was obtained from the maximum absorbance recorded at 640 nm and is based on an extinction coefficient \( \varepsilon (Ph_2^-) = 1.21 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1} \) at 640 nm, the mean value from ref 19 and 25.

At the highest biphenyl concentration, the half-time of the solvated electron is 14 ns. Compared to the pulse duration (3 ns) and to the half-time of the solvated electron in pure hydrazine (570 ns) it can be assumed that all solvated electrons present at the end of the pulse are scavenged by \( 3.4 \times 10^{-3} \) M biphenyl. Therefore the value \( G/\langle Ph_2^- \rangle = 3.4 \pm 0.2 \) obtained at the highest concentration can be considered as close to the yield \( G_{e^-} \) in pure hydrazine in the nanosecond time range. Therefore the extinction coefficient \( \varepsilon (e^-) = (1.85 \pm 0.10) \times 10^4 \text{ M}^{-1} \text{ cm}^{-1} \) at 1000 nm has been calculated from the experimental value of the product \( G \times \varepsilon \). From the observed pseudo-first-order rate constant the specific second-order rate constant of the scavenging has been found: \( k_f = (1.7 \pm 0.3) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1} \).

**Discussion**

The observed absorption spectrum of the solvated electron in pure hydrazine has no maximum in the wavelength range 450–1100 nm. As previously pointed out, such an electron absorption spectrum would be probably due to electrons interacting more weakly with surrounding hydrazine molecules than in the case of water or alcohols in spite of the fact that the hydrazine dielectric constant (\( \varepsilon = 53 \)) is between that of water and those of alcohols. However assuming the reaction of the solvated electron with biphenyl to be diffusion controlled, the comparatively low value of the specific rate constant \( k_f = 1.7 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1} \) corresponds to a diffusion coefficient of the solvated electron similar to that in water in or in liquid ammonia. Therefore the maximum of the spectrum would be expected to be located in the same wavelength range as in ammonia or in amines.

As concerns the decay of the solvated electron in pure hydrazine, some mechanisms can be ruled out. Indeed, in spite of the exploding character of alkali metal solutions in hydrazine, the blue color due to the solvated electron (possibly associated with metal) can be observed during a few seconds; this implies very low rate constants for the reactions of solvated electron with another electron or with hydrazine. This fact incidentally excludes the reaction of the solvated electron with the solvent previously suggested to explain the first-order kinetics of the electron decay observed in early pulse radiolysis experiments. On the other hand the reaction of the solvated electron with the acidic cation \( \text{NH}_2\text{H}_2^+ \) cannot account for the electron decay because the rate constant \( k_1 \) is too low as is the corresponding rate constant of the hydrated electron.

Contrastingly \( H \) atoms generated either by excitation processes or by ion recombination promptly react with hydrazine and then they cannot be involved in the electron recombinations. Then it follows that the solvated electron will disappear by reacting with oxidizing species, probably \( \text{N}_2\text{H}_3^+ \).

As concerns the electron yield related to a 3-ns pulse, the \( G \) values in hydrazine (3.4) and in ammonia (3.0) were calculated relatively to the \( G \) value in water (3.3) so that our results are self-consistent. Under the circumstances, it seems that hydrazine is a singular case for which the electron yield is slightly higher than that in water. Similar to liquid ammonia, the value \( G = 3.4 \) can be reasonably explained by the slowness of the electron–\( \text{NH}_2\text{H}_3^+ \) recombination, which increases the escape probability of the solvated electron.

Supposing an initial electron yield near 5, we have to ask ourselves which reactions can lead to a yield of 3.4 at 3 ns. Recent picosecond results in water clearly demonstrate the occurrence of spur reactions between electron, \( \text{H}_2\text{O}^- \), and \( \text{OH}^- \), thus explaining a decrease in the yield of electron from 4.8 to 3 in the nanosecond time range. In hydrazine, once the electron is solvated, its capture by the cation or by another electron is excluded as shown in this work. We mentioned above the scavenging by radicals being responsible for the decay after the pulse. This reaction is already effective at early times, especially as the primary species are concentrated in the spurs, and therefore lowers the escape probability of the solvated electron.

Hydrazine is thus an example illustrating the fact that chemical reactivity of ions must be taken into consideration as well as physical properties of the solvent. Consequently the knowledge of rate constants of the electron–cation neutralization would enable us to appreciate the extent to which present theoretical models are adapted to liquids.

**Acknowledgment.** The authors wish to thank Drs. J. C. Goudou and M. Broussely for valuable discussions.

**References and Notes**

13. P. Cordier and J. Delaire, to be submitted for publication.

The equilibrium and the kinetics of disproportionation of sodium tetracenide (Te\(^-\),Na\(^+\)) in benzene containing small amounts of tetrahydrofuran (THF) was investigated. It was shown that the equilibrium is represented by the stoichiometric equation, \(2\text{Te}^-,\text{Na}^+,(\text{THF})_{2n-2} \rightarrow \text{Te}^2-,2\text{Na}^+,(\text{THF})_{2n-2} + 2\text{THF}\) and the formal equilibrium constant \(K_{\text{dispr}} = [\text{Te}][\text{Te}^2-,2\text{Na}^+] / [\text{Te}^-,\text{Na}^+]^2\) varies from 400 at very low concentration of THF to 10\(^{-5}\) in bulk THF. The kinetics of disproportionation was investigated by flash-photolytic technique leading to the value of \(k_{\text{dispr}}\) of 1.5 \times 10\(^{5}\) M\(^{-1}\) s\(^{-1}\) for the reaction \(\text{Te}^2-,2\text{Na}^+,(\text{THF})_{2n-2} + \text{Te} \rightarrow 2\text{Te}^-,\text{Na}^+,(\text{THF})_{n-1}\).

It is generally believed that the disproportionation of planar aromatic radical anions, a reaction that yields dienes and the neutral hydrocarbons, is highly endothermic and its equilibrium constants are very low.\(^1\)\(^-\)\(^3\) Examples to the contrary are known,\(^4\)\(^-\)\(^6\) but all of them refer to systems in which the geometry of at least some of the reacting species is drastically changed; this allows us to understand the preference in these systems for dienes over the radical anions. It was surprising, therefore, to find out\(^7\) that the disproportionation of the planar tetracenide radical anions (Te\(^-\),Cat\(^+\)), derived from the planar hydrocarbon, is favored in diethyl ether, e.g., \(K_{\text{dispr}}\) of lithium tetracenide in this solvent exceeds 1

\[
2\text{Te}^-,\text{Cat}^+ = \text{Te} + 2\text{Te}^2-,2\text{Cat}^+ \quad K_{\text{dispr}}
\]

In fact, as shown by the data collected in Table I, the disproportionation equilibrium of Te\(^-\),Cat\(^+\) is strongly affected by the nature of cation, and even more by the nature of solvent for reasons discussed elsewhere\(^8\) (see also ref 2 and 3).

We wish now to report that the disproportionation constant of sodium tetracenide is even larger in benzene and its value exceeds 400. Moreover, we wish also to describe the spectacular changes in the value of \(K_{\text{dispr}}\) in benzene resulting from the addition of small amounts of tetrahydrofuran (THF).

**Results**

Tetracenide in THF solution was reduced on a sodium mirror. The reduction was not carried out to completion and the concentrations of the radical anions and of the unreduced hydrocarbon in the resulting solution were determined spectrophotometrically. Thereafter, THF was distilled off and an equal volume of benzene was distilled in. All these operations were performed on a high-vacuum line.

The change of solvent led to a dramatic result. The concentration of the hydrocarbon in the benzene solvent substantially increased (the increase corresponded to about one-half of the original concentration of Te\(^-\),Na\(^+\)). For example, a prepared THF solution was 1.6 \times 10\(^{-5}\) M with respect to Te and 6.1 \times 10\(^{-5}\) M with respect to Te\(^-\),Na\(^+\). After replacement of THF by benzene the concentration of Te increased to 4.8 \times 10\(^{-5}\) M, while the conversion of 2Te\(^-\),Na\(^+\) to Te + Te\(^2\),2Na\(^+\) would make the concentration of tetracenide equal to [1.6 + (0.5)6.1] \times 10\(^{-5}\) = 4.65 \times 10\(^{-5}\) M. This implies that the reaction

\[
2\text{Te}^-,\text{Na}^+ \rightarrow \text{Te} + \text{Te}^2-,2\text{Na}^+
\]

converts nearly all the Te\(^-\),Na\(^+\) into Te\(^2\),2Na\(^+\). Due to its low solubility, only a fraction of the formed Te\(^2\),2Na\(^+\) was dissolved, its concentration was found to be 0.22 \times 10\(^{-5}\) M. However, in spite of the large excess of Te, no Te\(^-\),Na\(^+\) was detected in the investigated solution, while a concentration \(\sim 5 \times 10^{-7}\) M still could be measured. From such spectrophotometric data we conclude that the disproportionation constant in benzene is greater than 400.

Reduction of tetracenide in benzene containing small...