leading to an additional bracketing of the uncertainties of both rate constants.

Discussion and Conclusions

The discussed procedure is quite general and can be applied to a variety of situations, where spectral overlapping tends to obscure the experimental results. Advantages can also be taken of the possibility of reducing the complexity of the system when both the concentration as a function of time and the spectrum of a particular species can be known with certainty. The possibility of introducing complementary data obtained by other methods and/or in other conditions is also of value. Even in those cases where the problem of evaluating spectra and concentrations from the experimental data can be accomplished by current procedures, the outlined one constitutes a way by which all the experimental data can be consistently analyzed. Advantage here is taken of the ability of the method for the detection of experimental errors and artifacts.

A further advantage is given in the possibility of introducing hypotheses in a rational way, one at a time, and arriving at partial solutions of the common problem: the establishment of the composition of matrices $[\epsilon]$ and $[c]$. Testing of suitable mechanisms can also be rationally accomplished. Once a mechanism is formulated, the method provides bounded values for the rate constants. This is a consequence of the linear properties of first-order systems and need not be the case when nonlinear systems are considered.

According to the general principles already given, the procedure can be extended in order to include weight factors. At the same time that consistency and stoichiometric tests are performed, others can be developed for the particular system under study.

The application of the procedure is not restricted to the evaluation of time-resolved absorption spectra, as the only property required for the measured quantity is bilinearity with respect to concentrations and some set of component-dependent parameters, as absorption coefficients are for that case. It can be applied, for example, to fluorometrically or conductometrically followed reactions. However, as it is obvious in the last case, the obtained information is limited, but conductometric measurements can be easily combined with spectral data obtained under the same conditions.

Wavelength and time enter in the method only as working parameters. Time, for example, can be replaced by other variables in order to study different phenomena, such as complex equilibria. In this case, temperature or analytical concentrations are suitable parameters. Instead of a set of differential equations, the normal algebraic equations found in equilibrium problems can be used to relate measured absorbances with the selected parameter.

The procedure is particularly suited for processing by interactive computing,[6] and therefore can be used as a standard method in a great variety of applications. Advantage here is taken of the possibility of testing the experimental data under different hypotheses within the same operational mainframe.

It should be emphasized that the outlined procedure puts in a rational way the different aspects of spectral and kinetic analysis. It constitutes a suitable aid for guiding intuition, which is unavoidable when resolving this kind of problem.

Acknowledgment. We thank Dr. E. Castellano for his constructive criticism and helpful suggestions. This research project was supported by the Consejo Nacional de Investigaciones Cientîficas y Têcnicas and by the Comisiôn de Investigaciones Cientîficas de la Provincia de Buenos Aires.

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(6) Programs were developed for a Hewlett-Packard HP1000 minicomputer. A listing can be requested from the authors.

Photochemistry of Aqueous Solutions of Triphenyltetrazolium Chloride

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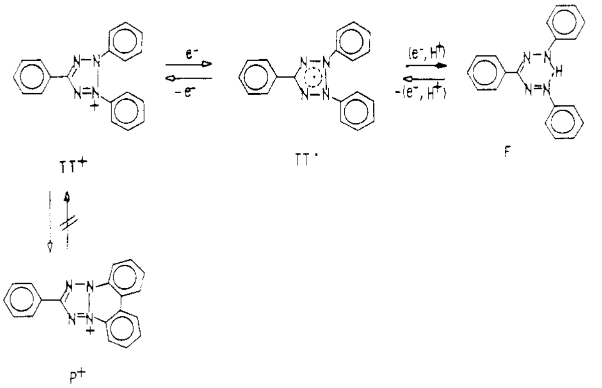
The photodisproportionation of triphenyltetrazolium chloride (TTC) was studied by flash spectrophotometry in aqueous solution at 23–24 °C and pH between 9.0 and 11.5. Several intermediates were found to be involved in the photoreductive pathway and its spectra and decay kinetics obtained as a function of pH. Following the fast formation of tetrazolinyl radicals, two other species coupled by a rapid equilibrium precede formazan formation. Hypotheses about the nature of these intermediates are proposed, and a mechanistic interpretation is given.

Introduction

Tetrazolium salts have been extensively studied since 1941.[1] Emphasis was given to their application in biochemistry as indicators of reductive enzyme activity.[2-5] They have also been used in organic chemistry as reducing agents of sugars and steroids[6-8] and in inorganic chemistry as analytical reagents for the photometric determination of metals.[5]

SCHEME I



Though tetrazolium salts have been widely used as qualitative indicators, their quantitative use has been less successful, partly because of their complex chemistry.[9,10] Information has been

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(1) Kuhn, R.; Jerchel, D. *Chem. Ber.* **1941**, *74*, 941.

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mainly sought from three principal sources: polarographic studies, electron spin resonance spectroscopy, and classical chemical and biochemical experiments,[5-11] but they have been only partially conclusive about the nature of the intermediates leading to formazan formation, the most interesting step when uses of these salts are being considered. Only some evidence on the formation of intermediates has been presented for nitroblue and triphenyltetrazolium salts.[12-14]

In neutral and basic aqueous solutions the triphenyltetrazolium ion (TT^+) can be reversibly converted into the corresponding deep colored formazan (F) by a stepwise reduction with the formation of at least one intermediate, the tetrazolinyl free radical ($TT^\bullet$)[11-13] shown in Scheme I. In acid media 1,2-dihydrotriphenyltetrazolium chloride was reported to be formed instead of formazan.[15]

Aqueous solutions of tetrazolium salts disproportionate when irradiated with UV light, giving equimolecular amounts of formazan and a photooxidation compound.[9] A similar reaction does take place in the dark in strongly basic media.[5,12] Also shown in Scheme I is the nonreversible oxidative pathway conducting to the formation of the photooxidation product cation (P^+). In this case nothing has been said about the nature of the corresponding intermediates.

The time-resolved study of the photochemical reaction could be of importance for the elucidation of both the reduction and oxidation mechanisms of tetrazolium salts. For this purpose, we have undertaken flash photolysis studies on two of the most widely used tetrazolium salts: 2,2′-(*p*-diphenylene)bis(3,5-diphenyl)-tetrazolium chloride (NTC) and 2,3,5-triphenyltetrazolium chloride (TTC). Since preliminary experiments carried out with NTC revealed that two reduction products are formed (the mono- and diformazans),[16] we first report the less complex TTC results.

Experimental Section

Materials. 2,3,5-Triphenyltetrazolium chloride (Riedel-De Haen, analytical grade) was recrystallized from ethanol several times. Its purity was checked by thin-layer chromatography with *n*-BuOH:glacial AcOH:H_2O (78:5:17) as running solvent.[17] Nitrogen (Matheson Co.) or UHP helium (Linde Specialty Gas) were indistinctly used for deoxygenating the solutions. All solutions were prepared with highly purified water which was obtained by passing distilled water through a Millipore ultrapurification system. All buffer reagents were of analytical grade, used without further purification: for pH 9.0–9.5 sodium borate (Mallinckkrodt)–sodium hydroxide (Mallinckkrodt) was used, for pH 10.0–10.5 sodium bicarbonate (Carlo Erba)–sodium hydroxide was used, and for pH 11.0–11.5 sodium phosphate (Carlo Erba)–sodium hydroxide was used. All solutions were adjusted to known ionic strength with potassium chloride (Merck), also used without further purification.

Product Analysis. The photolysis products obtained from both flash experiments and comparative stationary runs were selectively extracted from the aqueous solution with dichloromethane and/or diethyl ether. In this way formazan and eventually its reduction products (amidrazone and its derivatives) were quantitatively extracted, while unreacted TTC and the photooxidation product remained in the aqueous phase. The solvents were vacuum evaporated and the products isolated by TLC, using respectively *n*-hexane:dichloromethane at different ratios for the reduction products and *n*-BuOH:AcOH:H_2O for TTC.[17] The nature of the products was tested by UV–visible absorption spectroscopy, and the obtained spectra were compared with those found in the literature.

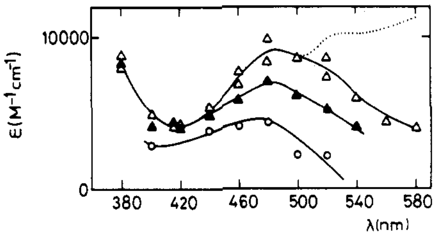

Figure 1. Absorption spectra of formazan (F) at pH 11.0 (△), 10.0 (▲), and 9.0 (○), as obtained from flash photolysis experiments, at low concentrations in order that molecular aggregates do not contribute significantly to the absorbance. The dotted line corresponds to an alkaline aqueous solution of the formazan obtained from a sodium ascorbate reduction of TTC, pH 11.1, [F] = 2.2 × 10^{-5} M (see text).

Apparatus and Technique. Flash photolysis experiments were carried out in a conventional apparatus (Xenon Co., Model 720C) with modified optics and electronics in order to increase its sensitivity.[18] The time resolution was 60 μs and the flash energy 90 J. Two collinear quartz–xenon lamps were used with emission in the range 250–600 nm and maximum at 450 nm. Most of the visible wavelengths that could further complicate the reaction by the cis–trans isomerization of the formazan[9] were filtered out from the flash light by a $NiSO_4/CuSO_4$ liquid filter[19] surrounding the sample cell. The sample cell had a 10-cm optical path length. The monochromator (Bausch & Lomb, high intensity) collecting the analysis beam incoming from a 250-W tungsten lamp was directly coupled to a photomultiplier, whose output was fed into a digital oscilloscope (Leader LBO-5825). Hard copies were obtained with an *X–Y* recorder (Houston Instruments). The analysis wavelength range was 300–800 nm.

All experiments were carried out at room temperature (23–24 °C) under nitrogen or helium atmosphere in order to avoid the presence of oxygen. TTC concentration was varied between 10^{-5} and 10^{-4} M. The pH range was limited to 9.0–11.5, though some experiments were performed at pH 6.0. At pH values lower than 9 the reaction becomes too slow to be followed by our experimental setup. Furthermore, as previously cited, at pH ~6 a colorless product, identified as the 1,2-dihydrotriphenyltetrazolium chloride, is formed instead of formazan.[15] The ionic strength was adjusted between 0.04 and 0.5 M. The spectral analysis was limited to the range 380–580 nm, since at shorter wavelengths the reactant absorbs strongly and at longer wavelengths no appreciable signals were observed.

The obtained formazan is slightly soluble in water. Its spectrum is enhanced at lower wavelengths due to the formation of molecular aggregates. The formation of these entities is strongly dependent on the way solutions are prepared, though they were found both when samples of formazan were obtained by the ascorbate reduction of TTC or when it was formed in situ by photolysis of the parent compound.

The sample cell was carefully washed and refilled with fresh solution every two flashes in order to prevent the formation of aggregates and the possibility of further photoreduction of the dissolved formazan.[20,21] Under these conditions less than 10% TTC conversion was achieved.

Results

Under the above experimental conditions, only the two expected photolysis products were observed: the 2,3-diphenylenetetrazolium ion (P^+) and the formazan (F). The absorption spectra of TT^+

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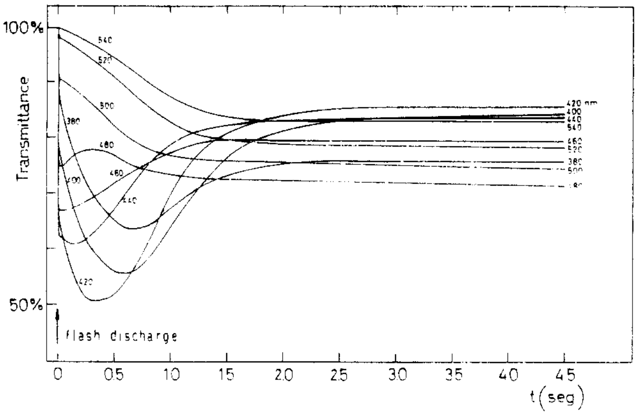

Figure 2. Experimental time-resolved absorption curves at various wavelengths. Runs for first flashes at pH 11.0, [TTC] = 4.4×10^{-5} M, and ionic strength 0.043 M. For drawing purposes, graphs obtained from *X–Y* recorder were hand smoothed. The noise amplitude was in all cases less than 0.5% in transmittance units.

and of P^+ were found to be independent of pH. The absorption spectrum of the formazan could not be quantitatively obtained by direct spectroscopic measurements at longer wavelengths owing to the formation of aggregates. As will be discussed later, formazan spectra could be obtained from flash photolysis experiments. The pH dependence is shown in Figure 1. The corresponding p*K* value is 10.0 ± 0.5.

The presence of small quantities of formazan ($\sim 10^{-5}$ M) showed no influence over the reaction kinetics, while molecular oxygen stabilizes the formed tetrazolinyl radical,[12] leading probably to other reaction products.

The absorption curves obtained at different wavelengths show the formation of at least three species that absorb light through most of the accessible spectra range (see Figure 2). An intermediate A, having a single absorption peak at 440 nm, is formed immediately after the photolysis ($t = 0$). Its spectrum does not change with pH in the range 6.0–11.5. This species gives rise to one or more intermediates, which are in turn transformed into a stable product, later identified as the formazan F. The formation of the photooxidation product could not be followed in the spectral range investigated since its spectrum is superimposed on that of the TTC molecule. The reaction rate increases with pH and is lowered to some extent when the ionic strength is raised. A preliminary kinetic analysis of the decay curves showed that the experimental results could be approximately fitted as a function of time by the difference of two exponentials; an overall mechanism composed essentially by two sequential first-order reactions could then be inferred.

As the overlapping of the absorption spectra, the experimental error, and the probable influence of impurities made very difficult the quantitative evaluation of the results by standard procedures, a regressional method was formulated in order to rationalize and simplify the spectral and kinetic analysis using all the available information. The detailed procedure can be found elsewhere;[22] only the final results are discussed in this paper.

Three species connected through a sequence of two consecutive reactions were retrieved from the regressional analysis. Assuming a one-to-one relationship between these species, the following overall reaction scheme was proposed:

$$\mathrm{A} \rightarrow \mathrm{B} \rightarrow \mathrm{F}$$

The spectra of A and F could be directly obtained from the corrected absorbances at $t = 0$ and $t = \infty$, respectively.[22] Once these spectra were known, it was possible to calculate the concentration of species B as a function of time. The overlapping of the absorption spectra did not allow a direct determination of the concentration of species A. Under the assumption that species B decays following first-order kinetics (later verified), the spectrum of species B and the concentration of species A could be obtained as a function of the decay rate constant of species B, k_B^{obsd}, used here as a bounded adjustable parameter.

The kinetic analysis performed over the calculated concentrations of species A showed that this species also decays following a first-order kinetics, though deviations were registered for first flashes (see later).

Aside from the spectra of species F, readily identified as the formazan (Figure 1), in Figure 3 are given the spectra of the intermediates A and B. Absolute absorption coefficients were obtained by using the cited stoichiometric relation and the known values of formazan absorption coefficients at shorter wavelengths, where aggregates do not contribute to the absorption. Also, in this way the absorption of formazan at longer wavelengths could be calibrated. The pH-dependent spectrum of B was calculated for the most probable value of k_B^{obsd} at the corresponding pH values.

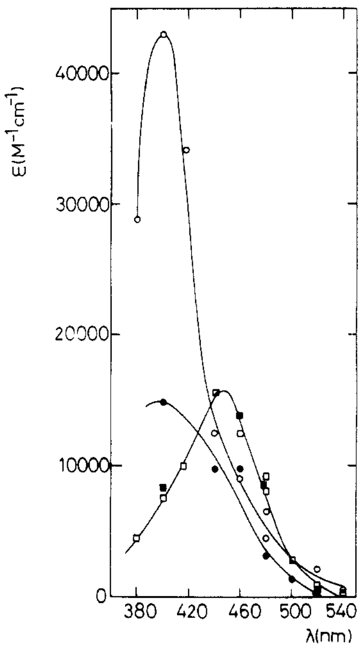

Figure 3. Absorption spectra of species A and B, as obtained from regressional analysis. Species A at pH 11.0 (□) and 9.0 (■); species B at pH 11.0, $k_B^{obsd} = 3.0$ s^{-1} (○) and pH 9.0, $k_B^{obsd} = 0.3$ s^{-1} (●).

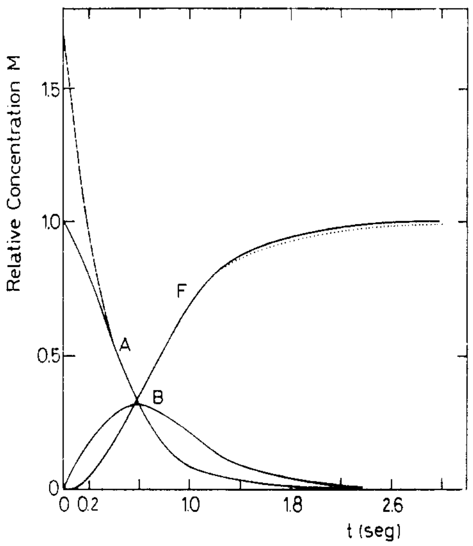

Figure 4. Relative concentrations of A, B, and F as a function of time; first flash, pH 11.1, [TTC] = 4.4×10^{-5} M, ionic strength 0.043 M. Solid lines were obtained from the regressional analysis of experimental time-resolved absorbances for $k_B^{obsd} = 3.0$ s^{-1}. The dashed line represents a first-order decay curve adjusted to fit the calculated concentrations of species A at longer times. The dotted line is normalized experimental time-resolved absorbance at 540 nm (see text).

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(22) San Román, E.; González, M. C. *J. Phys. Chem.*, accompanying paper in this issue.

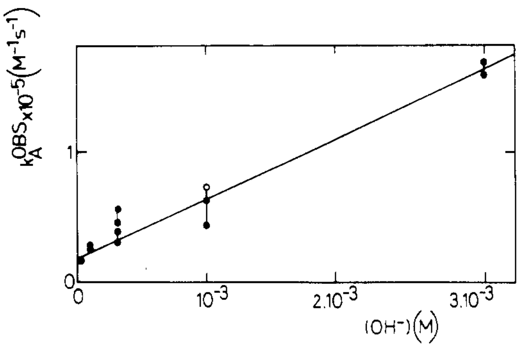

Figure 5. Second-order decay rate constant of species A as a function of the hydroxide ion concentration (upper and lower bounds shown). [TTC] = 3.9×10^{-5} M except for $[OH^-] = 1 \times 10^{-3}$ M, where ● corresponds to [TTC] = 4.4×10^{-5} M and ○ to [TTC] = 9.8×10^{-5} M; ionic strength 0.043 M.

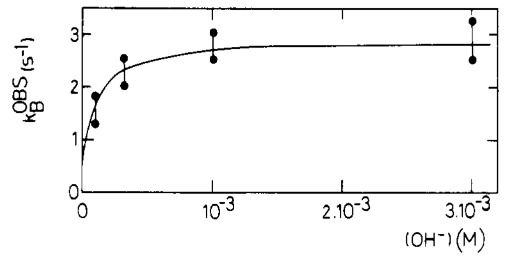

Figure 6. First-order decay rate constant of species B as a function of hydroxide ion concentration (see comments on Figure 5).

Figure 4 shows the concentration profiles of species A, B, and F for a selected example. An excellent agreement can be observed between the calculated concentration of F obtained as a function of time by integration of the known concentration of B under the first-order assumption and the absorbance recorded at 540 nm, where, as can be seen from Figure 3, the other species do not absorb. Also shown in this figure is the first-order fitting of the concentration of species A showing the observed deviation already cited for first flashes.

A full account of the observed results is next given. The spectrum of species A is independent of pH in the range 6.0–11.5, while a pH-dependent spectrum is observed for species B and F between 9.0 and 11.5. The decay rate of species B is independent of TTC, while that of species A is proportional to the initial TTC concentration, pointing to a pseudo-first-order behavior. Finally, the decay rates of species A and B are pH-dependent, and the ionic strength has only a small negative effect over the decay of species A.

As mentioned before, the regressional method allows the determination of bounded values for the observed decay rate constants. These are shown in Figure 5 and Figure 6 as a function of the hydroxide ion concentration. The observed second-order decay rate constant of species A, k_A^{obsd}, is a linear function of the hydroxide ion concentration:

$$k_A^{\mathrm{obsd}} = k_A' + k_A''[OH^-] \qquad (1)$$

The observed first-order decay rate constant for species B, k_B^{obsd}, shows a more complicated dependence:

$$k_B^{\mathrm{obsd}} = k_B'[OH^-]/(k_B'' + [OH^-]) \qquad (2)$$

The best fits for k_A^{obsd} and k_B^{obsd} are represented respectively in Figures 5 and 6.

Discussion and Conclusions

From the above observations the following sequence of reactions was inferred.

Photolysis and Transference of Charge. Previous EPR studies on the reduction of TT^+ and on the oxidation of the corresponding formazan have shown that these reactions give rise to a paramagnetic species identified as the tetrazolinyl radical $TT^\bullet$.[11,12] Considering that species A is also an intermediate in the photoinduced reduction of TT^+ to formazan and that its pH-independent spectrum is similar to the spectra of other tetrazolinyl radicals,[13,14] it is reasonable to identify this species as the $TT^\bullet$ radical. The sequence of reactions leading to its formation is too fast to be observed within our experimental time resolution. Considering that the $TT^\bullet$ radical is a reduced form of the TT^+ ion, another TT^+ ion should have been oxidated by its production:

$$TT^+ + h\nu \xrightarrow{TT^+} TT^\bullet + \text{oxidated intermediates} \qquad (3)$$

where the oxidated intermediates are the precursors of the photooxidation product P^+, not observed in the experimental wavelength range.

Decay of Species A. The dependence of the decay rate constant of species A on the concentration of tetrazolium ions points to the interaction of $TT^\bullet$ with TT^+. This interaction can be direct (first term in eq 1) or through a basic form of either $TT^\bullet$ or TT^+ (second term in eq 1). It is then reasonable to postulate

$$TT^\bullet + TT^+ \rightarrow TT^- + \text{oxidated intermediates} \qquad (4)$$

$$TT^\bullet + (TT^+\cdots OH^-) \rightarrow TT^- + \text{oxidated intermediates} \qquad (5)$$

$$(TT^\bullet\cdots OH^-) + TT^+ \rightarrow TT^- + \text{oxidated intermediates} \qquad (5')$$

where TT^- is a one-electron-reduced form of $TT^\bullet$.

Both basic forms, $(TT^+\cdots OH^-)$ and $(TT^\bullet\cdots OH^-)$, were already proposed.[12,14] If the corresponding equilibrium constants are defined as $K_{TT^+} = [(TT^+\cdots OH^-)]/[TT^+][OH^-]$ and $K_{TT^\bullet} = [(TT^\bullet\cdots OH^-)]/[TT^\bullet][OH^-]$, the following relation is obtained:

$$k_A^{\mathrm{obsd}} = k_4 + (K_{TT^+}k_5 + K_{TT^\bullet}k_{5'})[OH^-] \qquad (6)$$

in accordance with eq 1. From the best fit of Figure 5 can be obtained $k_4 = (2.0 \pm 0.5) \times 10^4$ M^{-1} s^{-1} and $K_{TT^+}k_5 + K_{TT^\bullet}k_{5'} = (4.5 \pm 1.0) \times 10^7$ M^{-2} s^{-1}.

The small negative effect of the ionic strength can be accounted for by the term involving $[OH^-]$ in eq 6.

The deviations observed for first flashes can be accounted for by the presence of small quantities of molecular oxygen. In fact, it is already known that oxygen stabilizes the tetrazolinyl radical,[12] leading probably to reaction products other than formazan. We propose that the formed adduct sensitizes the oxidation of tetrazolium ions and regenerates the tetrazolinyl radical. After oxygen is completely consumed, the decay routes of this radical are reactions 4 and 5 or 5′ and first order is observed.

Decay of Species B and Formazan Formation. The complex acid–base behavior observed for the intermediate B can be interpreted if the observed intermediate is actually a mixture of two species with different absorption spectra coupled by a rapid equilibrium:

$$TT^- + H_2O \rightleftharpoons TTH + OH^- \qquad (7)$$

$$TT^- + H_2O \rightarrow F + OH^- \qquad (8)$$

According to the above proposed scheme, both species, here identified as TT^- and TTH, decay with the same time constant by reaction 8. Solving the above reaction mechanism for the decay of species B (in fact a combination of TT^- and TTH), the following expression can be readily obtained:

$$k_B^{\mathrm{obsd}} = k_8[OH^-]/(K_7 + [OH^-]) \qquad (9)$$

where K_7 stands for the equilibrium constant of reaction 7. This relation is in accordance with eq 2. From the best fit of Figure 6 can be obtained $k_8 = 2.9 \pm 0.3$ s^{-1} and $K_7 = (8.1 \pm 1.0) \times 10^{-5}$ M.

According to the proposed scheme, the acid form of TT^- should be an isomer of the formazan, F. On the other hand, the observed spectrum for TTH as well as its lifetime are similar to the one reported by Hausser et al., also ascribed to an unstable isomeric form of the formazan.[23] (See also ref 9.) These authors, based

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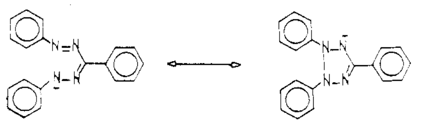
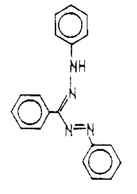
[23] a) Hausser, I., Jerchel, D.; Kuhn, R. *Chem. Ber.* **1949**, *82*, 195. (b) *Ibid.* **1949**, *82*, 515.

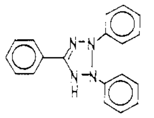
SCHEME II



on analogies with related azo compounds, postulated a nonbridged isomer as responsible for the observed absorption.



However, considering that the rapid equilibrium given in eq 7 imposes the condition that TTH must be formed very rapidly as compared with the formazan, and assuming that two resonance forms should contribute to the structure of TT$^-$ (Scheme II), a cyclic structure for TTH



also warrants serious consideration, specially if it is considered that this species could be easily transformed into 1,2-dihydrotriphenyltetrazolium chloride, observed for the TTC reduction in acid media.

Further work should be performed in order to clarify the nature of these isomers.

As is apparent from the results presented in this paper, the photodisproportionation of TTC in alkaline aqueous solutions is analogous to the tetrazolium salt disproportionation observed in the dark in strongly basic media.[5,12] Jãmbor has already noted this analogy in the early 1950s.[17] In both cases, the strong reducing properties of the basic forms of TT$^+$ (and perhaps TT$^\bullet$) play an essential role.

Opposite to our observations of a pseudo-first-order decay for the TT$^\bullet$ radical, Bielski et al. found a second-order decay in the case of nitroblue tetrazolinyl radicals.[14] On the other hand, preliminary flash photolysis experiments carried out with neotetrazolium chloride indicate also a second-order behaviour.[16]

Assuming that the TT$^\bullet$ radical disproportionates with a rate constant similar to the one found by Bielski et al., $k_{disp} \sim 10^9$ M^{-1} s^{-1}, and that under our experimental conditions [TT$^\bullet$] $\sim 10^{-7}$ M, the second-order process should be 100 times faster than reaction 4, indicating that the actual disproportionation rate constant for the TT$^\bullet$ radicals should be less than 10^7 M^{-1} s^{-1}.

This would indicate that the tetrazolinyl radicals of the ditetrazolium ions are better reducing agents than the parent tetrazolium ions. Whether this is a general rule should be a matter of further research.

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Registry No. TTC, 298-96-4; F, 504-65-4; P$^+$, 236-27-1; NTC, 13146-67-3.

Elementary Reactions of NH($a^1\Delta$) with Atoms and Diatomic Molecules

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The elementary reactions of NH($a^1\Delta$) with the noble gas atoms Kr and Xe and with the diatomic molecules N_2, O_2, and NO were studied in a quasi-static laser flash photolysis cell at room temperature and low pressures. NH(a) was produced by HN_3 laser photolysis at λ_L = 248 and 308 nm. The detection of NH(a) and of the reaction products was achieved by pulsed laser-induced fluorescence (LIF). Time resolution was obtained by the delay between photolysis and probe pulse. For the overall NH(a) depletion NH(a) + R → products, the following rate constants were obtained at T = 296 K: k_1(Kr) $\leq 6 \times 10^9$ cm^3/(mol s); k_1(Xe) = $(7.2 \pm 0.7) \times 10^{12}$ cm^3/(mol s); $k_1(N_2)$ = $(5.0 \pm 0.5) \times 10^{10}$ cm^3/(mol s); $k_1(O_2)$ = $(2.7 \pm 0.3) \times 10^{10}$ cm^3/(mol s); k_1(NO) = $(1.8 \pm 0.3) \times 10^{13}$ cm^3/(mol s). For the reactions of NH(a) with O_2 and N_2, the primary products OH and NH(X) were observed and the branching ratios for the corresponding product channels were determined quantitatively. The elementary processes of NH(a) are discussed and compared with the NH(X) reactions and with the reactions of the isoelectronic species O(^{1}D) and $CH_2(\tilde{a}^1A_1)$.

Introduction

Elementary processes of electronically excited species are of interest from a practical and a theoretical point of view. In contrast to the other degrees of freedom like translational, rotational, or vibrational energy the change of electronic energy, as a general rule, influences the reactivity of the species significantly, due to the change of the energy surface on which the reaction proceeds. Comparison of the experimental results with the calculated potential surfaces makes detailed knowledge of the reaction dynamics feasible. In photolytic systems, for instance in atmospheric photochemistry, the reactions of electronically excited atoms and molecules are of great importance.

NH radicals, which are isoelectronic with O atoms and CH_2 radicals, are much less studied than either of the other two. The first electronic excited state of NH is the ($a^1\Delta$) state which has a long lifetime of about $\tau_0 \simeq 1.7$ s^1 due to the forbidden transition to the ($^3\Sigma^-$)-electronic ground state. The excitation energy of NH(a) of 151 kJ/mol lies between those of O(^{1}D) and $CH_2(\tilde{a})$. The NH radical is a suitable species for studying the effects of electronic excitation in the isoelectronic group O, NH, and CH_2 since both its lowest electronic states, ($a^1\Delta$) and ($X^3\Sigma^-$), can be detected with high sensitivity by laser-induced fluorescence (LIF).

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