



The kinetics of dye formation by pulse radiolysis of pararosaniline cyanide in aqueous organic solution

McLaughlin, W.L.; Kosančić, M.M.; Marković, V.M.; Nenadović, M.T.; Holcman, J.; Sehested, Knud

Publication date:
1979

Document Version
Publisher's PDF, also known as Version of record

[Link back to DTU Orbit](#)

Citation (APA):
McLaughlin, W. L., Kosančić, M. M., Marković, V. M., Nenadović, M. T., Holcman, J., & Sehested, K. (1979). *The kinetics of dye formation by pulse radiolysis of pararosaniline cyanide in aqueous organic solution*. Risø National Laboratory. Risø-M No. 2202

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Risø-M-2202

THE KINETICS OF DYE FORMATION BY PULSE RADIOLYSIS OF
PARAROSANILINE CYANIDE IN AQUEOUS OR ORGANIC SOLUTION

W.L. McLaughlin, M.M. Kosanić^a, V.M. Marković^b,
M.T. Nenadović^b, J. Holcman, and K. Sehested.

^aFaculty of Science, University of Novi Sad,
21000 Novi Sad, Yugoslavia.

^bRadiation Chemistry Dept., Boris Kidrić Institute of
Nuclear Sciences, Vinča, 11001 Belgrade, Yugoslavia.

Abstract. The radiation-induced conversion of the leuco-
cyanide of pararosaniline dye, $[H_2N \text{ (benzene ring) }]_3 \equiv C-CN$, to the
highly colored salt-isomer of the dye, $[H_2N \text{ (benzene ring) }]_2 = C = \text{ (quinonoid ring) }] = NH_2^+ + CN^-$, in acidic aqueous solution (wavelength of
maximum absorption $\lambda_{\max} = 540 \text{ nm}$) or polar organic solu-
tion ($\lambda_{\max} = 550 \text{ nm}$), takes place in two separate pro-
cesses. The first is very fast (within $< 50 \text{ ns}$), and the
second much slower following first-order kinetics with
a rate constant that varies from $4 \times 10^3 \text{ s}^{-1}$ to $\sim 10^6 \text{ s}^{-1}$,
as the acidity or concentration of an oxidizing agent
increases. In oxygen-free acidic aqueous or organic
solutions (argon saturated) there is an unstable transient
species ($\lambda_{\max} = 380 \text{ nm}$). When using O_2 or N_2O -saturated

November 1979

Risø National Laboratory, DK 4000 Roskilde, Denmark

aqueous or organic solution, there is no intermediate absorption band at 380 nm, but the slow process of dye formation at 540 or 550 nm is still sequential to the initial fast process having somewhat faster kinetics than in Ar-saturated solution.

INIS descriptors: ABSORPTION SPECTRA, ANILINE, AQUEOUS SOLUTIONS, CHEMICAL REACTION KINETICS, CHEMICAL REACTION YIELD, CYANIDES, DOSE RATES, DYES, ORGANIC SOLVENTS, PULSED IRRADIATION, RADIO-LYSIS, TRIPHENYLMETHANE DYES.

UDC 668.855.1 : 541.15

ISBN 87-550-0630-2

ISSN 0418-6435

Risø Repro 1979

CONTENTS

	Page
1. INTRODUCTION	1
2. RADIOLYTIC DYE FORMATION	2
3. EXPERIMENTAL PROCEDURES	3
3.1. Pulse Radiolysis Equipment	3
3.2. Dosimetry	3
3.3. Pulse Monitoring	4
3.4. Solutions of Pararosaniline Cyanide (PR-CN)	4
4. EXPERIMENTAL RESULTS	5
4.1. Absorption Spectra	5
4.2. Kinetics of the Decay of Intermediate Species	8
4.3. Kinetics of Dye Formation	8
4.4. The Effect of Acidity	9
4.5. The Effect of Oxygen or Nitrobenzene	10
4.6. The Effect of Polarity of Solvent	11
5. CONCLUSIONS	11
ACKNOWLEDGEMENTS	12
REFERENCES	13
FIGURE LEGENDS	15
TABLES	17

1. INTRODUCTION

Photochemical studies of solutions of substituted triphenyl-methanol or triphenyl-acetonitrile have shown that the absorption of short-wave ultraviolet photon energy results in triphenylmethane dye production as salt formation due to cleavage of OH^- or CN^- (1-15). The resulting highly colored dye cation is stable in a weakly acidic polar environment and unstable in a non-polar solvent or in any basic solvent. In the presence of excess OH^- or CN^- ions, the reverse reactions to colorless derivatives of the dye follow pseudo first-order kinetics, with rate constants that vary with $[\text{OH}^-]$, $[\text{CN}^-]$, ionic strength, and the dielectric properties of the system (16-18). If the dielectric constant of the solvent is below ~ 4 , the colored species is shortlived (15).

Recent radiolysis studies of dye formation have been made using gamma rays and electrons over a wide range of intensities (19-21). It was shown that weakly-acidic polar-organic solutions of tris-(4-amino phenyl)acetonitrile, namely pararosaniline cyanide, that are sufficiently oxygenated can be used as accurate radiation dose meters for absorbed doses in the range $10^3 - 10^6$ rads and dose rates up to at least 10^{14} rad \cdot s $^{-1}$. Acidic aqueous solutions of the same dye derivative may also be used for dosimetry; however, at dose rates greater than $\sim 10^{18}$ rad \cdot s $^{-1}$, the dye yield becomes diminished and rate dependent.

Flash ultraviolet photolysis of alcohol solutions of leuco derivatives of triphenylmethane dyes shows a fast initial reaction occurring in less than 40 ns, with no apparent rate dependence of dye yield (12,15,22). The production of dye in this case is complete within 100 μ s after the UV flash.

Although there have been pulse radiolysis studies of related compounds such as Wurster's blue (23-25) and triphenylcarbinol (26), no such examination has been made of the kinetics of ionizing radiation-initiated reactions of solutions of leucocyanide dyes of amino-substituted triarylmethane. The present work provides an analysis of the kinetics of dye formation due to pulse radiolysis of a typical symmetric form of these leuco dyes, namely

pararosaniline cyanide in aqueous or organic solution. The results give insight to reasons for the radiolytic dye yield being constant over large variations of absorbed dose rate, for some forms of the dye precursor in polar organic solutions.

2. RADIOLYTIC DYE FORMATION

The leucocyanide does not revert to the dye spontaneously in the presence of acid, but is stable in a moderately protonated environment until ionized by irradiation^(2,6,7). For a simple symmetric form of this class of leucocyanide dyes, namely tris-(4-aminophenyl)acetonitrile (H_2N )₃≡C-CN, referred to in dye nomenclature as the cyanide of pararosaniline or basic red (Colour Index of the parent dye, pararosaniline, is 42500)⁽²⁷⁾, the bond strength of ≡C-CN is approximately 3.8 eV, and the radiation threshold for cleavage of this bond is correspondingly in the ultraviolet at about 330 nm wavelength^(6,15).

The main radiation products of pararosaniline cyanide (PR-CN) in a mildly acid polar solvent are CN^- and the highly-colored carbonium cation. The latter is the triaminotriphenylmethyl salt which is the parent dye, namely the tris-(4-aminophenyl) methylum ion, with the positive charge being highly delocalized into the para-amino moiety at the quinonoid ring having extended conjugation: (H_2N )₂-C-- NH_2^+ . The wavelength maximum of the absorption band of the dye in slightly acidic polar organic solvent is 550 nm and in 20% acetic acid in water is 540 nm. In photolysis studies using ultraviolet radiation, the production of dye in such environments occurs with a quantum efficiency of approximately 1.0^(1,7,8,12). With ⁶⁰Co gamma radiation, the G-value is proportional to concentration of the leucocyanide at low concentrations and decreases with increasing O₂ concentration⁽¹⁹⁾. An O₂-saturated solution of 2 mM PR-CN in 2-methoxy ethanol, with acetic acid added at a concentration of 17 mM, has a G-value of 0.062 molecules per 100 eV, for absorbed dose rates of gamma radiation or electron radiation ranging from 1 to 10¹⁴ rad · s⁻¹)⁽²¹⁾. Oxygenated aqueous solutions of PR-CN containing 20% acetic acid, on the other hand, show a marked variation of dye yield as an inverse function of dose rate (10¹² to 10¹⁴ rad ·

s^{-1})⁽²¹⁾. A possible explanation for this is the greater probability of back reactions of radiolytic free radicals with radical ions at these very high dose rates.

3. EXPERIMENTAL PROCEDURES

3.1 Pulse Radiolysis Equipment.

A 10-MeV electron linear accelerator (Haimson, Inc.) was used to supply 1- μ s pulses with a pulse radiolysis set-up described previously⁽²⁸⁾. A field emission accelerator (Febetron 707) was used as the other high-intensity source of radiation. It produced single pulses of electrons having a maximum energy of about 2 MeV and a maximum current output of ~ 3000 A in approximately a Gaussian-shape pulse with a full width at half maximum of ~ 30 ns. Kinetic spectrophotometry provided a means for analysis of optical density changes in the ultraviolet and visible spectra, with a time resolution of 50 ns. The optical apparatus consisted of a continuous stabilized xenon lamp (Osram X130450/y), a device for pulsing the lamp with a resulting 20-fold increase in light intensity for a period of ~ 0.5 ms, high-purity silica optical components, a pulse radiolysis quartz cell equipped for automatic filling and flushing, a double quartz prism monochromator (Opton MM 12), a fast rise-time photomultiplier (RCA-1P28) with the sensitivity over a broad UV and visible spectrum (240-650 nm). The two fast-response oscilloscopes (Tektronix 454 and 564B) were equipped with Polaroid cameras, and were used to display spectral changes in optical density for short times after electron pulses. Long-term stability afforded analysis after the pulses for time periods up to several seconds.

3.2 Dosimetry.

Measurement of absorbed dose in the contents of the cell along the optical path (5.1 cm) was accomplished by using 5 mM $K_3Fe(CN)_6$ aqueous solution saturated with N_2O with a small amount of air added after saturation⁽²⁹⁾. The calculation of absorbed dose was based on the following values of ferricyanide yield due to oxidation of ferrocyanide by the OH radical:

$G[\text{Fe}(\text{CN})_6^{3-}] = G[e_{\text{aq}}^-] + G[\text{OH}] = 6.0$ ions of absorbing species per 100 eV energy absorbed, where the molar absorptivity $\epsilon_{420} = 1000 \text{ M}^{-1} \text{ cm}^{-1}$

3.3 Pulse Monitoring.

In order to monitor variations in electron beam intensity from pulse to pulse, a thin aluminum foil (0.03 mm thickness) was placed 20 cm from the accelerator window perpendicular to the beam axis. The front surface of the pulse radiolysis cell was approximately 5 cm behind this foil. The foil was isolated from ground by three 6.8-nF capacitors in parallel, each with very high internal resistance. Since the charge deposited (or associated voltage reading) on the foil during each electron pulse leaked only very slowly, it could be measured at a convenient time after the pulse, even after several minutes.

3.4 Solutions of Pararosaniline Cyanide (PR-CN)

The dye derivative PR-CN was synthesized from an industrial batch of the hydrochloride salt of the parent dye* by combining in a ball mill with NaCN. It was purified (as shown by loss of color) by repeated cycles of dissolution in triethylphosphate and precipitation of the hydrophobic leucocyanide with cold distilled water. When dried in a desiccator with P_2O_5 , the final product consisted of a fine white crystalline powder.

Solutions of PR-CN were 0.1 to 5 mM concentrations of the dye derivative in (1) triply distilled water containing 3.5 M acetic;** or (2) 2-methoxy ethanol, reagent grade devoid of peroxides, containing different amounts of glacial acetic acid or NaOH. Using 20-minute bubbling in a sealed vessel, the solutions were saturated with oxygen or argon or combinations of these gases mixed in order to vary the molecular oxygen concentration. Alternatively, various concentrations of nitrobenzene were dissolved in

* Supplied by Eastman Organic Chemicals, Rochester, NY

** 3.5 M acetic acid was required for sufficient solubility of pararosaniline cyanide in water at room temperature

argon-saturated solutions in order to study the effect of this weak oxidizing agent on the kinetics of radiolytic dye production. The solutions could also be saturated with nitrous oxide or could be used with methanol added, which served to scavenge solvated electrons or hydroxyl radicals, respectively.

To prevent photolysis of the solutions by the ultraviolet analyzing light, a uv cut-off filter (Schott WG-360) was used between the lamp and the cell. Pulse radiolysis was carried out with analyzing light ranging in wavelength from 310 nm to 630 nm and over a time scale from 0.1 μ s to several minutes. Over this spectral region and time scale, the organic solvents alone did not supply appreciable transient absorbing species, which would add to the absorption of dye-related species of interest. The irradiated solvents, in fact, did not exhibit optical absorption in the wavelength region being studied.

4. EXPERIMENTAL RESULTS

4.1 Absorption Spectra.

The absorption spectra due to irradiation of 2 mM PR-CN in O_2 -saturated water containing 3.5 M acetic acid are shown in Fig. 1, at two different times after irradiation. The molar extinction coefficient values were based on measured values at the maximum of the main dye absorption band, using μ M concentrations of the hydrochloride salt of the parent dye, pararosaniline⁽¹⁹⁾. For solutions in O_2 -saturated water containing 3.5 M acetic acid, $\epsilon = 1.3 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$; for solutions in 2-methoxy ethanol containing 17 mM acetic acid, $\epsilon = 1.4 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$. Also shown are unstable absorption bands formed for short times. The ordinate is given in terms of molar absorptivity, which is proportional to the yield of absorbing species. Similar values of molar absorptivity as determined previously by γ -ray radiolysis⁽¹⁹⁾ can be used for subsequent calculations of dye yield.

The main absorption band at the longer wavelengths ($\lambda_{\text{max}} = 540 \text{ nm}$) is due to the conjugated quinonoid chromophore of the dye ion and is formed by two processes: (1) a minor fast process occurring within 50 ns; (2) a relatively slow major process lasting

during the first 100 to 300 μ s after the pulse, depending on the dose rate. The shoulder or superimposed band in the short wavelength side of the main visible band (~ 480 nm) is due to the electronic system of a less-symmetric, less-planar geometric form of the trihedral molecular isomer rather than to the main dye species absorbing at 540 nm. The two forms have different dichroic axes and thus have different relaxation resonances⁽¹⁵⁾.

If O_2 -saturated acidic aqueous solutions are used, the main absorption band once formed is stable for long periods, even over several years, whereas the absorption bands in the ultraviolet are rather unstable. A broad weak absorption appears in O_2 -saturated solution in the blue and near-UV part of the spectrum, but this fades slowly over several hours as slight buildup occurs in the ultraviolet absorption below 350 nm. A short-lived intermediate species forms a prominent band in this region of the spectrum ($\lambda_{\max} = 330$ nm) for O_2 -saturated solutions, and then decays simultaneously with dye formation. A similar-unstable band ($\lambda_{\max} = 380$ nm) is formed within $\ll 50$ ns in Ar-saturated acidic aqueous solutions.

In the unirradiated leucocyanide solute there is negligible absorption at wavelengths greater than 350 nm. At lower wavelengths, however, two prominent stable bands were found in neutral 2-methoxy ethanol solution of PR-CN, with maxima at 257.5 nm ($\epsilon = 3.8 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$) and 295 nm ($\epsilon = 6.2 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$). After adding 17 mM acetic acid to the solution, a slow increase in the molar absorptivity was observed at 295 nm. After about 24 hours, it remained constant ($\epsilon = 9.6 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$). The stable absorption bands at the shorter wavelength without radiolysis is probably due to π, π^* transition in the aryl groups held in polar solution⁽¹⁵⁾. The increase of absorption in the longer wavelength region with the addition of acid probably indicates the slow development of proton charge-transfer states with the aniline groups, causing reorientation of their steric configuration due to n, π^* transition⁽¹⁶⁾.

Figure 2 shows the absorption bands induced in 2 mM PR-CN in slightly acid 2-methoxy ethanol, both under oxygen-free and

oxygen-saturated conditions. Unlike acidic aqueous solution, there is no absorption induced just below 350 nm wavelength. The unstable intermediate ($\lambda_{\text{max}} = 380 \text{ nm}$) is produced only in oxygen-free conditions within 0.1 μs and disappears within 100 μs . During this period a slow component of dye formation is added to the small fast component of dye formation with first-order kinetics, reaching fairly high absorbance with a maximum at 550 nm wavelength. As will be seen later, however, the decay of the intermediate at 380 nm does not occur with simple first-order kinetics, although the time scales for this decay and the slower component of dye formation are about the same. The main absorption band of the radiation-produced dye is slightly narrower in oxygenated solution at all stages, with a shoulder forming at about 500 nm due to the slow component of dye formation. This is also a first-order process. The slow formation of the shoulder on the dye absorption band suggests diffusion-controlled protonation from the solvent, causing tautomeric distortion of the otherwise relatively symmetric propeller-shaped trihedral ions.

The presence of oxygen can contribute to scavenging of reducing radicals produced in the solvent and acid by irradiation. Without such an agent to scavenge these nucleophilic radicals, saturation in dye production would be expected to occur at fairly low dose levels^(19,21). Such effects are seen in the oscilloscope traces shown in Fig. 3, for PR-CN solution in oxygen-free organic solutions. Several successive pulses cause a change in the transient absorbance of both the low wavelength absorption band ($\lambda_{\text{max}} = 380 \text{ nm}$) and the main dye absorption band ($\lambda_{\text{max}} = 550 \text{ nm}$). The decay of the absorbing species at 380 nm and the dye formation having a maximum at 550 nm become slower and slower with successive pulses. The amplitudes of the fast components at these two wavelengths are not affected by successive pulses. In oxygenated solution, the exhaustion of dye production by successive pulses was not observed. The same kinetics and yields were repeated for many successive pulses, similar to the first pulse traces of Fig. 3.

Figure 4 shows the effect of N₂O saturation on the kinetics of dye formation due to irradiation of deaerated 2-mM solution of PR-CN in 2-methoxy ethanol containing 17 mM acetic acid. By effectively scavenging solvated electrons in this manner, the intermediate absorption at 380 nm is quenched, which is similar to the effect of saturating with oxygen. The fast component of dye yield at 550 nm is approximately the same as with Ar-saturation. Although the total yield is greatly diminished, there is essentially no difference in the kinetics of the slow component of dye formation due to the presence of the electron scavenger. Exhaustion of dye production by successive radiation pulses also does not occur at this mild acidity, but it is shown in Fig. 4 that lowering the pH introduces such exhaustion effects in N₂O-saturated solutions similar to those shown in Fig. 3 for less acidic Ar-saturated solutions.

By adding 10 mM methanol to air-saturated acidic aqueous solutions, a severe exhaustion effect occurs in the slow components at the two wavelengths. Although the first pulse gives typical kinetics of decay of the intermediate absorption at 380 nm and dye formation at 550 nm, a second pulse results in much slower decay at 380 nm and much slower dye formation at 550 nm, also with significantly reduced yield.

4.2 Kinetics of the Decay of Intermediate Species.

For O₂-saturated aqueous acetic acid solutions of PR-CN, the short-lived absorption band produced within 0.1 μs at short wavelengths ($\lambda_{\text{max}} = 330 \text{ nm}$) decays in at least two processes. This decay is displayed in Fig. 5 for two different absorbed doses given in a 30-ns pulse. A fast decay is complete within 10 μs, while a slower component of decay in the first-order process occurs with a rate constant $k = 5.5 \times 10^4 \text{ s}^{-1}$ and $\tau_{1/2} = 13 \text{ μs}$. A similar decay occurs for the quickly formed intermediate species in Ar-saturated solution of PR-CN ($\lambda_{\text{max}} = 380 \text{ nm}$), as shown in Fig. 3.

4.3 Kinetics of Dye Formation.

Radiolytic dye formation in both aqueous and organic solutions consists of both a fast and a slower process. The fast process

occurs in a time scale $\tau \ll 50$ ns. In acidic aqueous solution, although the slower component is dose-rate dependent, it forms with apparent first-order kinetics with $\tau_{1/2}$ of about 20 to 40 μ s depending on the dose rate. Figure 6 shows the buildup of the slow component ($\lambda_{\text{max}} = 540$ nm) of dye formation in aqueous solution containing 3.5 M acetic acid and saturated with O_2 . In this solvent the rate constant increases with dose rates for doses of 1.5 to 31.5 krad in a 30-ns pulse, as shown in Table I. The G-value for the final dye production 300 μ s after the pulse (G_{∞}) decreases with dose rate, but G_0 for the fast component of dye formation (~ 0.1 μ s after the pulse) does not vary with dose rate. This is illustrated in Fig. 7, where G_{∞} and G_0 for dye production in oxygenated acidic aqueous solution are plotted as a function of dose administered in a 30 ns pulse. The value of G_{∞} for 5×10^{10} rad \cdot s $^{-1}$ is nearly as great as that for ^{60}Co γ radiation at $\sim 10^2$ rad \cdot s $^{-1}$ (20,21).

For O_2 -saturated solutions of PR-CN in 2-methoxy ethanol containing small concentrations of acetic acid (17 mM), the slow component of dye formation also follows first-order kinetics. As shown in Fig. 8, however, the rate constant does not vary with dose rate or with concentration of PR-CN. The rate constant [$k = 7.9 \pm 0.5 \times 10^4$ s $^{-1}$ ($\tau_{1/2} = 9$ μ s)] is greater than that for aqueous acetic acid solutions at the lower dose rates, whereas the value of G is smaller.

Whereas the rate constant is independent of concentration of PR-CN, the value of G_{∞} (after 100 μ s) is strongly dependent on concentration; on the other hand, G_0 (after 0.1 μ s) does not vary significantly with concentration, as shown in Table II. As was observed in earlier work (20,21), both values of G_0 and G_{∞} for the oxygenated solutions of PR-CN in 2-methoxy ethanol are independent of dose rate, at least up to $\sim 10^{14}$ rad \cdot s $^{-1}$.

4.4 The Effect of Acidity.

It was shown previously that the photolytic production of dye from colorless leucocyanide progenitors is most efficient in neutral to slightly acid solution (30). The same work shows that at very low pH the substituted triphenylmethane leuco-salt base

is formed preferentially with release of CN^- due to UV irradiation. At very high pH the colorless leuco-carbinol is the predominate species.

We have shown earlier that both the G-value for radiolytic dye production from PR-CN in organic solution and the molar extinction coefficient (ϵ) are pH-sensitive⁽¹⁵⁾. Maximum values of G and ϵ occur with a fairly weak acid (e.g. low molecular weight carboxylic acid such as acetic acid or substituted acetic acid) in concentrations of acid corresponding to about three molecular equivalents of PR-CN concentration.

Solutions of 2 mM PR-CN in 2-methoxy ethanol were studied by varying the concentration of acetic acid from 85 mM to neutral or the concentration of NaOH up to 1 mM. Table III shows the results of this study. Note that although the G-value is relatively large for dye formation at high pH at $\sim 100 \mu\text{s}$ after irradiation, the dye is not stable for periods exceeding a few seconds, because of recombinations to leucocyanide and leuco-carbinol forms⁽¹⁸⁾ in the absence of H^+ ions. The first-order dye formation has a rate constant that varies from $2 \times 10^4 \text{ s}^{-1}$ for the most acidic condition (85 mM acetic acid) to $5 \times 10^3 \text{ s}^{-1}$ for neutral solutions. The spectrum of the unstable intermediate species under oxygen-free conditions and the absorption band of the dye have shapes that do not change appreciably with pH over the range of mild acidity and alkalinity studied here. The absorption at 380 nm wavelength increases slightly with increase of pH.

4.5 The Effect of Oxygen or Nitrobenzene.

The oxygen content of the 2-methoxy ethanol solutions of PR-CN was varied by adding small concentrations of O_2 -saturated solution to Ar-saturated solutions. The dye yield was found to decrease with increasing O_2 concentration, and the first-order rate constant of dye formation increased with increasing oxygenation.

Table IV shows that the effects of varying the concentration of a weak oxidizing agent (e.g. nitrobenzene) are similar to those of varying the O_2 concentration. The rate constant varies from

about $4 \times 10^3 \text{ s}^{-1}$ to 10^5 s^{-1} as O_2 or $\text{C}_6\text{H}_5\text{NO}_2$ is added in small amounts. By adding small amounts of O_2 to solutions containing 0.1 mM $\text{C}_6\text{H}_5\text{NO}_2$, the rate constant increases to about $2 \times 10^5 \text{ s}^{-1}$. The intermediate absorption ($\lambda_{\text{max}} = 380 \text{ nm}$) produced at very short times decreases with increasing $[\text{C}_6\text{H}_5\text{NO}_2]$ and $[\text{O}_2]$ and vanishes altogether for fully aerated or oxygenated solutions. Parallel to this spectral change is a reduction in fatigue effects at large radiation doses as $[\text{O}_2]$ or $[\text{C}_6\text{H}_5\text{NO}_2]$ is increased.

4.6 The Effect of Polarity of Solvent.

Using a solvent with greatly reduced polarity such as ethyl acetate inhibits the photolytic formation of dye^(10,15,31). By using an Ar-saturated solution PR-CN in ethyl acetate, we found that the yield of dye with $\lambda_{\text{max}} = 550 \text{ nm}$ and the yield of the intermediate with $\lambda_{\text{max}} = 380 \text{ nm}$ are an order of magnitude less than in polar organic solution, using 2-methoxy ethanol as solvent. In addition, the kinetics are of a higher order, and the kinetics of the decay of the intermediate form are also more complicated.

5. CONCLUSIONS

Upon irradiation of para-triaminotriphenylacetonitrile in acidic polar solution, the intense absorption band formed in the visible spectrum is generally assumed to be due to a change in the tetrahedral form of the dye precursor to a trihedral one that is asymmetric and highly conjugated in one of the aniline groups. In a strong polar field the positive charge of the carbonium cation resides at the electronic system associated with the molecule in its dipolar ground state, namely at the NH_2 end of the highly conjugated aniline group⁽³²⁾. The radiolytic process is accompanied by hydrolysis or solvent protonation of the CN^- ion.

The triphenylmethane dye is formed by two separate processes:

- (1) a minor but fast intramolecular internal conversion lasting much less than 50 ns;
- (2) a major pseudo first-order process involving much slower reactions between the dye molecule and radiolytic products, whereby the highly polarized quinonoid structure of one of the aniline groups, $-\text{C}-\text{C}_6\text{H}_4-\text{NH}_2^+$, forms the chromophore of the dye.

The mechanisms by which these processes occur are still under study.

ACKNOWLEDGEMENTS

The authors are grateful for valuable discussions with G.M Meaburn of the National Marine Fisheries Service, National Oceanic and Atmospheric Administration, Charleston, DC, N. Klein of the U.S. Army Aberdeen Proving Ground, MD, and L. Chalkley of La Jolla, CA.

REFERENCES

1. J. Lifschitz and C.L. Joffe, Ber. 1921, 97, 426.
2. L. Chalkley, Chem. Rev. 1929, 6, 217.
3. E. Weyde, W. Frankenberger, and W. Zimmerman, Z. Phys. Chem. 1932, B 17, 276.
4. L. Harris, J. Kaminsky, and R.G. Simard, J. Am. Chem. Soc. 1935, 57, 1151.
5. F.E.E. Germann and G.L. Gibson, J. Am. Chem. Soc. 1941, 63, 110.
6. L. Chalkley, J. Am. Chem. Soc. 1941, 63, 987.
7. J.G. Calvert and H.E. Rechen, J. Am. Chem. Soc. 1952, 74, 210.
8. E.O. Holmes, Jr., J. Phys. Chem. 1957, 61, 434.
9. A.H. Sporer, Trans. Faraday Soc. 1961, 57, 893.
10. G.H. Brown, S.R. Adisesh, and J.E. Taylor, J. Phys. Chem. 1962, 66, 2426.
11. W. Luck and H. Sand, Angew. Chem. 1964, 76, 463.
12. M.L. Herz, J. Am. Chem. Soc. 1975, 97, 6777.
13. G.J. Fisher, J.C. LeBlanc, and H.E. Johns, Photochem. Photobiol. 1967, 6, 757.
14. R.N. Macnair, Photochem. Photobiol. 1967, 6, 779.
15. R.C. Bertelsen, in Photochromism, Techniques of Chemistry, Vol. III, edited by G.H. Brown, Wiley-Interscience, New York, 1971, p. 294.
16. S.S. Katiyar, Bull. Chem. Soc. Japan 1970, 43, 601.
17. S.K. Sinha and S.S. Katiyar, Indian J. Chem. 1971, 9, 1115.
18. M.L. Herz, D. Feldman, and E.M. Healy, J. Org. Chem. 1976, 41, 221.
19. W.L. McLaughlin and M.M. Kosanić, Int. J. Appl. Rad. Isotopes 1974, 25, 249.
20. B.B. Radak, M.M. Kosanić, M.B. Šešić, and W.L. McLaughlin, in Biomedical Dosimetry, International Atomic Energy Agency, Vienna, 1975, p. 633.

21. M.M Kosanić, M.T. Nenadović, B.B. Radak, V.M. Marković, and W.L. McLaughlin, Int. J. Appl. Rad. Isotopes 1977, 28, 313.
22. J.F. Dreyer, R.W. Harries, R.N. Macnair, and D. Feldman, "Investigation of materials and systems for protection against flashblindness effects of nuclear detonations, Phase I," U.S. Army Natick Laboratories Techn. Rep. 68-38-CN, AD688692, Contract No. DA 19-129-AMC-112 N, Natick, Mass. 01760, 1968.
23. T.J. Kemp, J.P. Roberts, G.A. Salmon, and G.F. Thompson, J. Phys. Chem. 1968, 72, 1464.
24. C. Capellos and A.O. Allen, J. Phys. Chem. 1968, 72, 4265.
25. R. Cooper and J.K. Thomas, Radiation Chemistry - II Advanced Chem. Ser. 1968, 81, 351.
26. C. Capellos and A.O. Allen, Science 1968, 160, 302.
27. The Colour Index, 2nd ed., Soc. Dyers and Colourists, and Am. Assoc. Textile Chemists and Colourists, Lowell, Mass., 1956.
28. H.C. Christensen, G. Nilsson, P. Pagsberg, and S.O. Nielsen, Rev. Sci. Instr. 1969, 40, 786.
29. G.E. Adams, J.W. Boag, and B.D. Michael, Trans. Faraday Soc. 1965, 61, 492.
30. P.C. Henriquez, Rec. Trav. Chim. Pays-Bas 1933, 52, 991.
31. G.H. Brown (Kent State University, Kent, Ohio), "Kinetic studies of the phototropic reactions of triphenylmethane leuconitriles," Rep. AMRL-TDR-62-84, AD287451, Aug. 1962.
32. F.C. Adam and W.T. Simpson, J. Molec. Spectros. 1959, 3, 363.

FIGURE LEGENDS

- Fig. 1. Absorption spectra of 2-mM pararosaniline cyanide in aqueous solution containing 3.5 M acetic acid at different times after irradiation (Ar- and O₂-saturated solutions).
- Fig. 2. Absorption spectra of 2-mM pararosaniline cyanide in 2-methoxy ethanol, at different times after irradiation (Ar- and O₂-saturated solutions).
- Fig. 3. Oscilloscope traces of the relative change in absorbance of 2-mM PR-CN in Ar-saturated 2-methoxy ethanol containing 17 mM acetic acid, at two wavelengths (380 and 550 nm), as a function of time after 1 μs electron pulses (dose = 1 krad per pulse). Time scale: a - 10 μs per division; b - 100 μs per division.
- Fig. 4. Oscilloscope traces of the relative change in absorbance of 2-mM PR-CN in Ar- and N₂O-saturated 2-methoxy ethanol containing either 17 mM or 430 mM acetic acid, at two wavelengths (380 and 550 nm), as a function of time after 1 μs electron pulses (dose = 1 krad per pulse). Time scale: a - 10 μs per division; b - 100 μs per division.
- Fig. 5. Kinetics curves of decay of the intermediate ($\lambda_{\max} = 330$ nm) for pararosaniline cyanide in O₂-saturated aqueous solution containing 3.5 M acetic acid at two dose rates. Dose per 30 ns pulse: (1) 31.5 krad; (2) 11.2 krad.
- Fig. 6. Kinetics curves of dye formation ($\lambda_{\max} = 540$ nm) for pararosaniline cyanide in O₂-saturated aqueous solution containing 3.5 M acetic acid at two dose rates. Dose per 30 ns pulse: (1) 1.5 krad; (2) 18 krad.
- Fig. 7. Variations of initial and final yields of dye (G_0 and G_{∞}) in O₂-saturated aqueous solution containing 3.5 M acetic acid, as a function of dose rate.

Fig. 8. Kinetics curves of dye formation ($\lambda_{\text{max}} = 550 \text{ nm}$) for pararosaniline cyanide in O_2 -saturated 2-methoxy ethanol solution containing 17 mM acetic acid at two dose rates. Dose per 30 ns pulse: (1) 13.5 krad; (2) 1.6 krad.

TABLE I

Variation of rate constant for slow component of dye formation, and initial and final dye yields, with absorbed dose per 30-ns pulse in O₂-saturated 2-mM PR-CN aqueous solution containing 3.5 M acetic acid.

Dose/pulse (krad)	Approx.		k(s ⁻¹)	G ₀ (molecules/100 eV)	G _∞	G _∞ [*] / G ₀
	Ave. Dose Rate (rad/s)					
1.5	5 x 10 ¹⁰		1.3 x 10 ⁴	0.023	0.115	4.8
2.5	8 x 10 ¹⁰		1.35 x 10 ⁴	0.025	0.100	4.1
7.5	2.5 x 10 ¹¹		-	0.023	0.090	3.8
13.0	4 x 10 ¹¹		2.2 x 10 ⁴	0.023	0.072	3.0
18.0	6 x 10 ¹¹		3.4 x 10 ⁴	0.027	0.070	2.9
31.5	3 x 10 ¹²		4.0 x 10 ⁴	0.022	0.058	2.4

*G_∞/G₀ was calculated using G₀ = 0.024.

TABLE II

Variation of the dye yield with concentration of pararosaniline cyanide in O₂-saturated 2-methoxy ethanol solution.

[PR-CN] (mM)	G ₀ (molecules/100 eV)	G _∞	(number of determ.)	G _∞ /G ₀
1	0.013	0.031	± 0.002 (21)	2.4
2	0.014	0.059	± 0.004 (14)	4.2
5	0.015	0.119	± 0.008 (21)	8.0

TABLE III

Variation of rate constant for slow component of dye formation and initial and final dye yields with acidity in Ar-saturated 2 mM PR-CN solution in 2-methoxy ethanol.

Acidity	$k(s^{-1})$	G_o (molecules/100 eV)	G_∞	G_∞/G_o^*
85 mM acetic acid	2×10^6	0.013	0.069	5.3
17 mM acetic acid	0.9×10^6	0.014	0.134	9.6
neutral	0.5×10^6	0.015	0.085	5.7
1.0 mM NaOH	**	0.015	0.093	6.2

* G_∞/G_o was calculated using $G_o = 0.014$.

** Not first-order.

TABLE IV

Variation of rate constant for slow component of dye formation and initial and final dye yields with concentrations of nitrobenzene, in Ar-saturated 2 mM PR-CN solution in 2-methoxy ethanol containing 17 mM acetic acid.

$[\text{C}_6\text{H}_5\text{NO}_2]$ (mM)	$k(\text{s}^{-1})$	G_0 (molecules/100 eV)	G_∞	G_∞/G_0
0	0.86×10^6	0.014	0.134	9.6
0.001	0.38×10^6	0.015	0.122	8.1
0.01	0.36×10^6	0.014	0.100	7.1
0.1	1.0×10^6	0.014	0.088	6.3
1.0	6×10^6	0.014	0.064	4.6
10	10×10^6	0.014	0.029	2.1

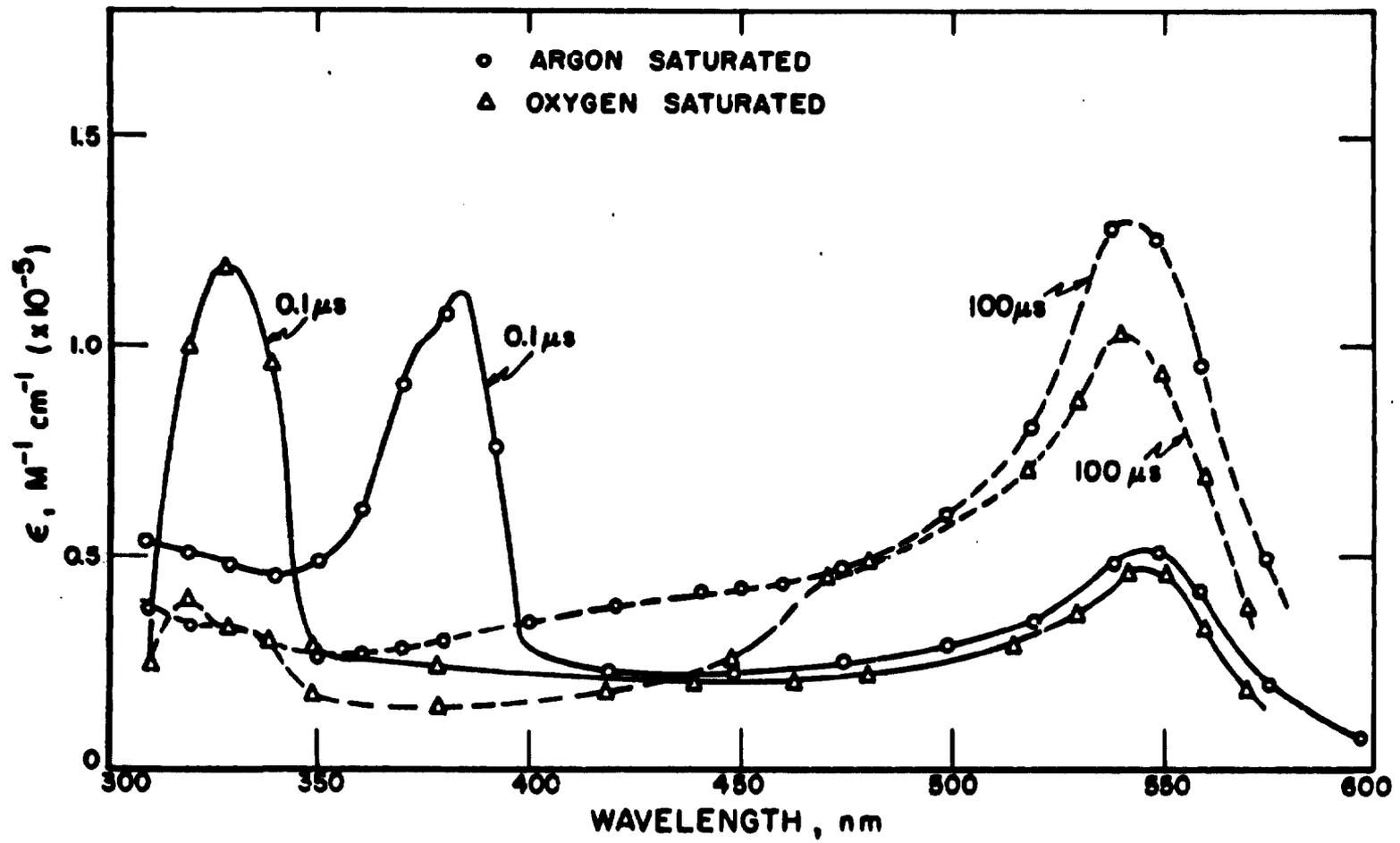


Fig. 1

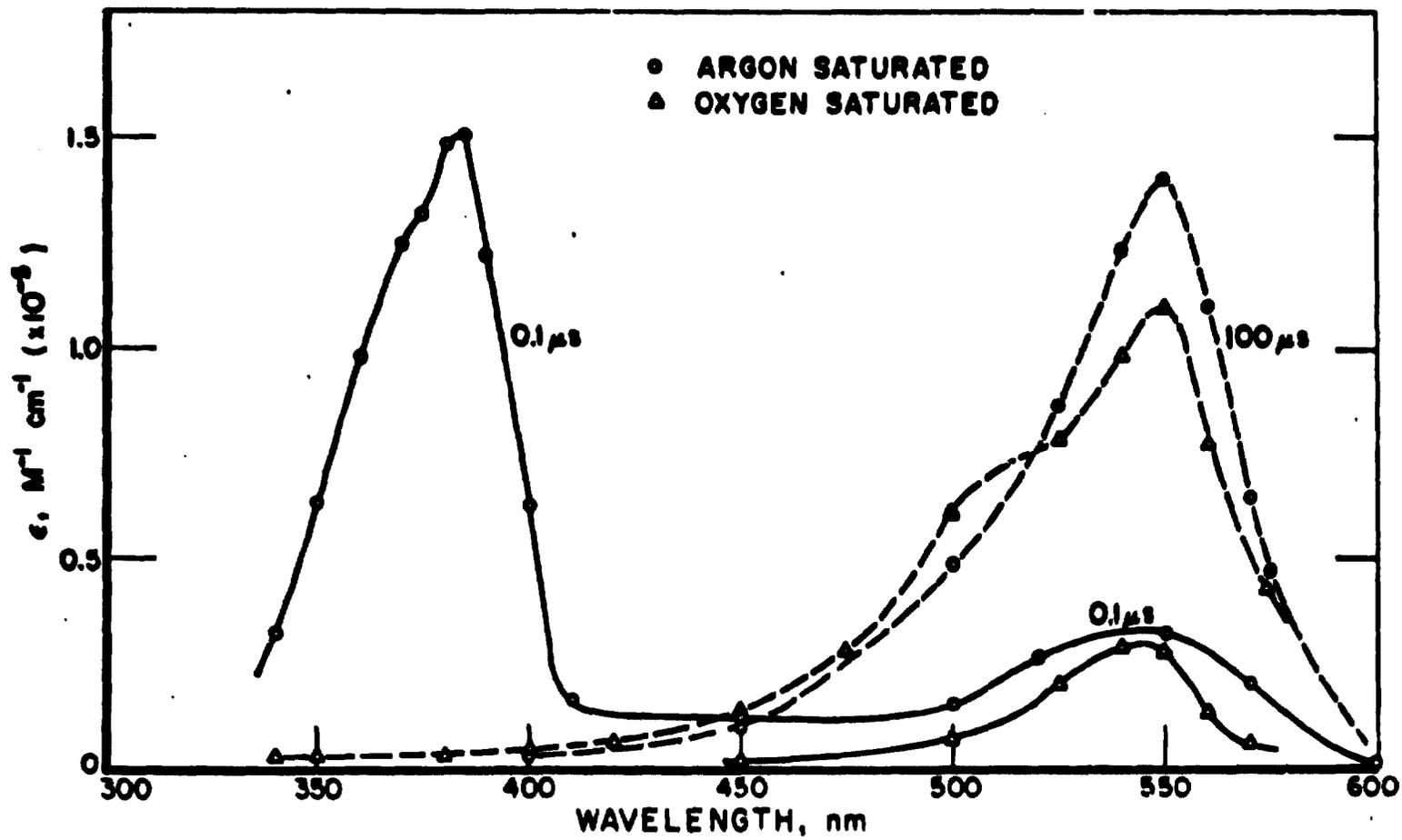


Fig. 2

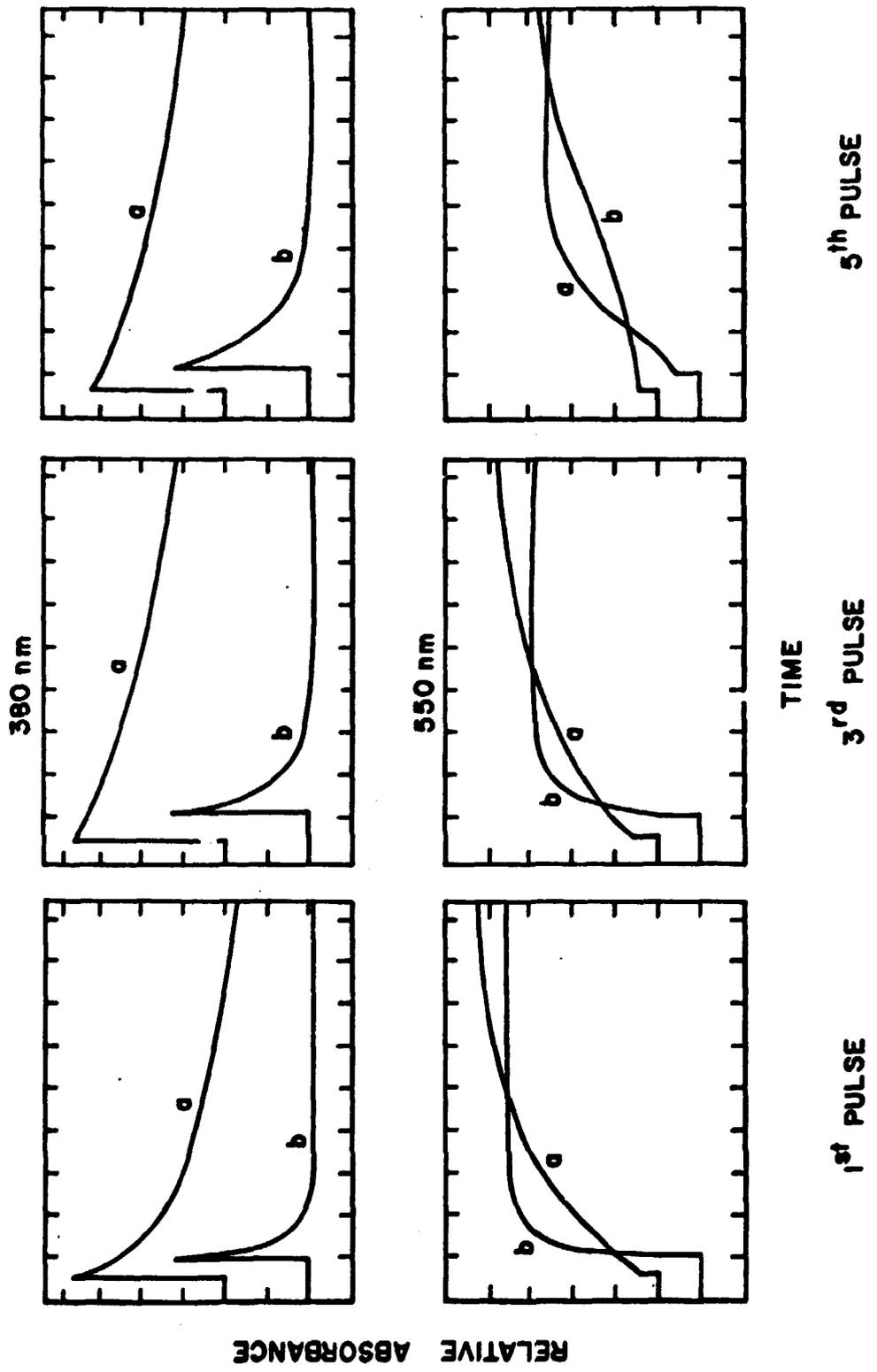


Fig. 3

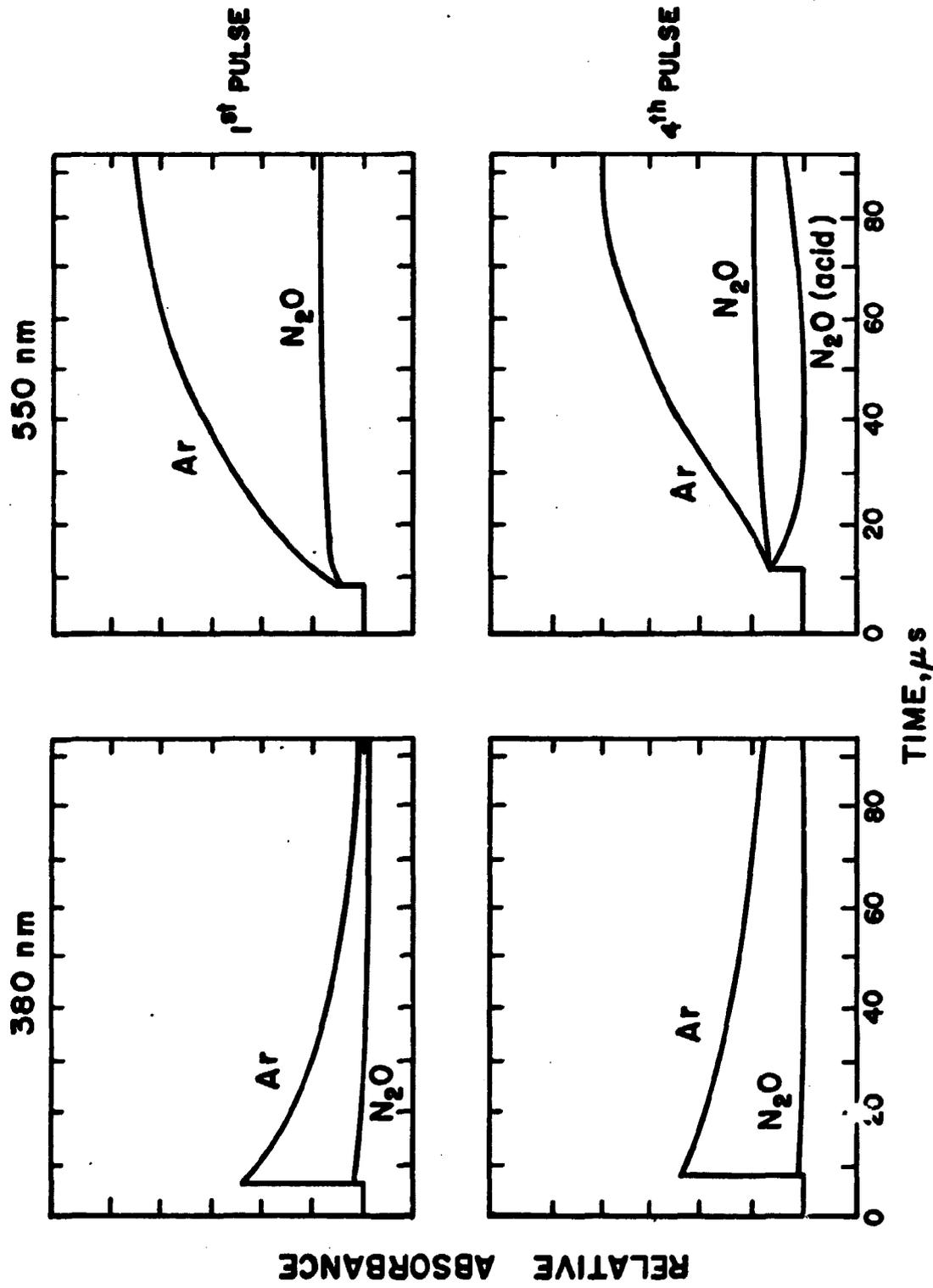
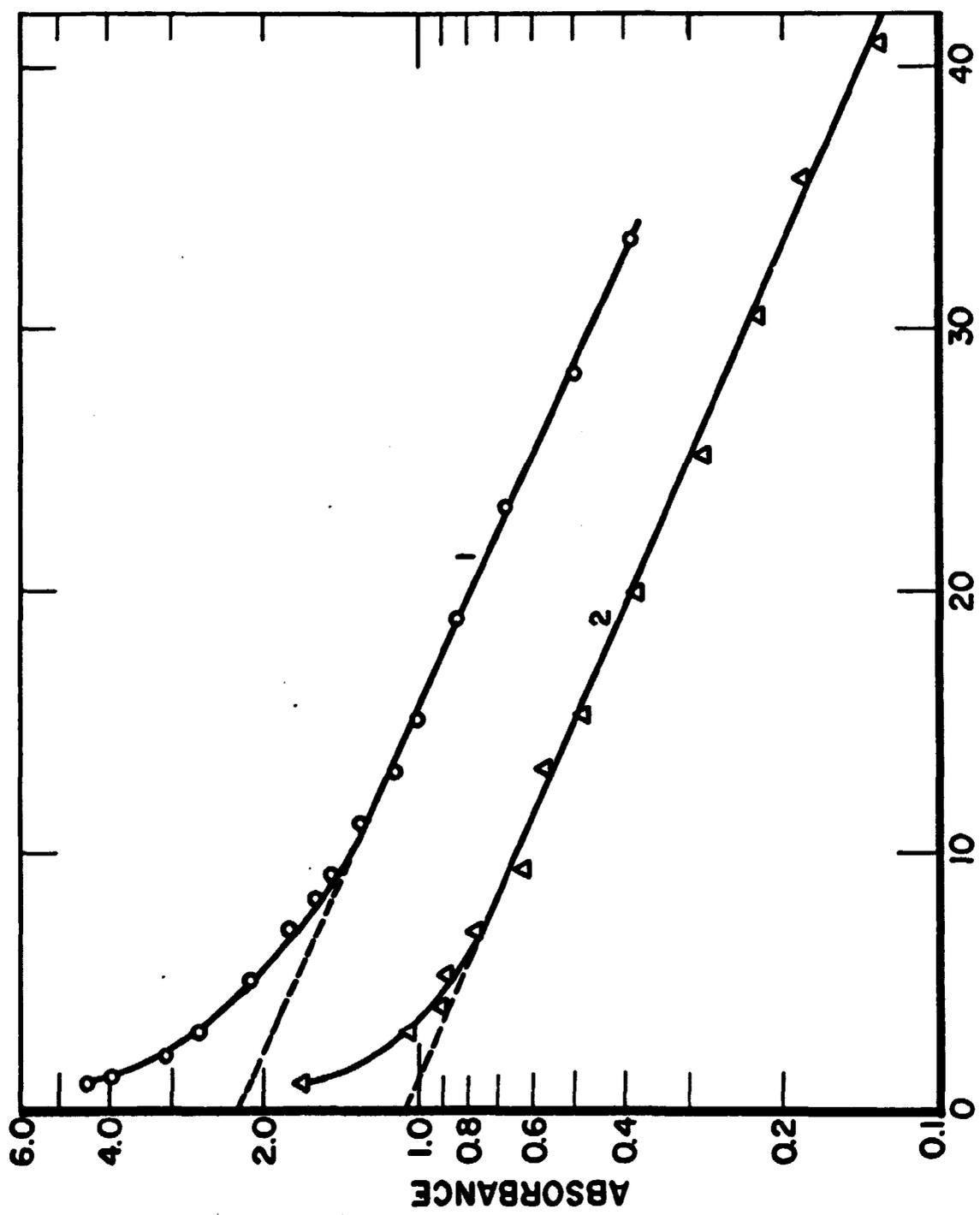


Fig. 4



TIME, μ s
Fig. 5

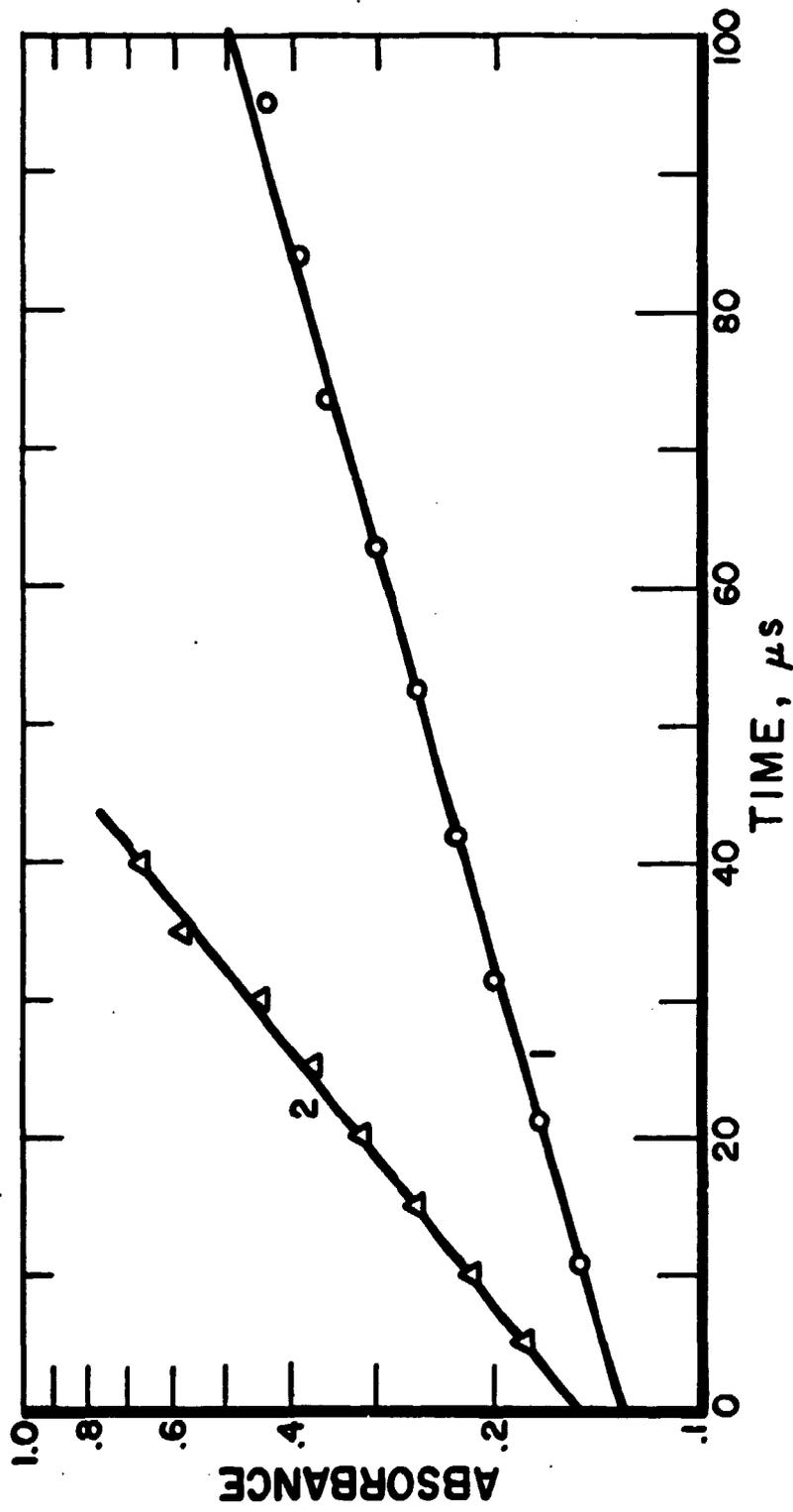


Fig. 6

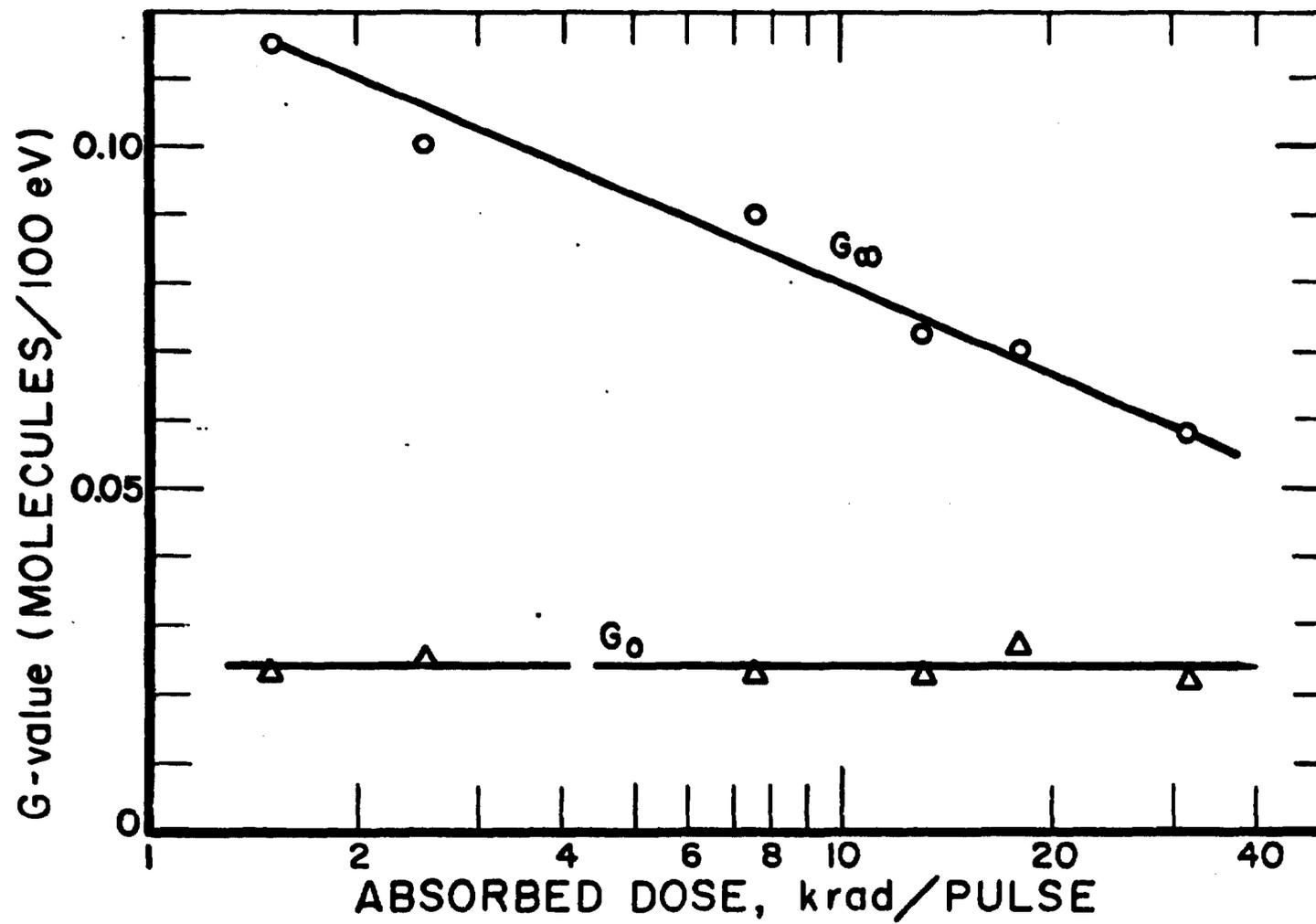


Fig. 7

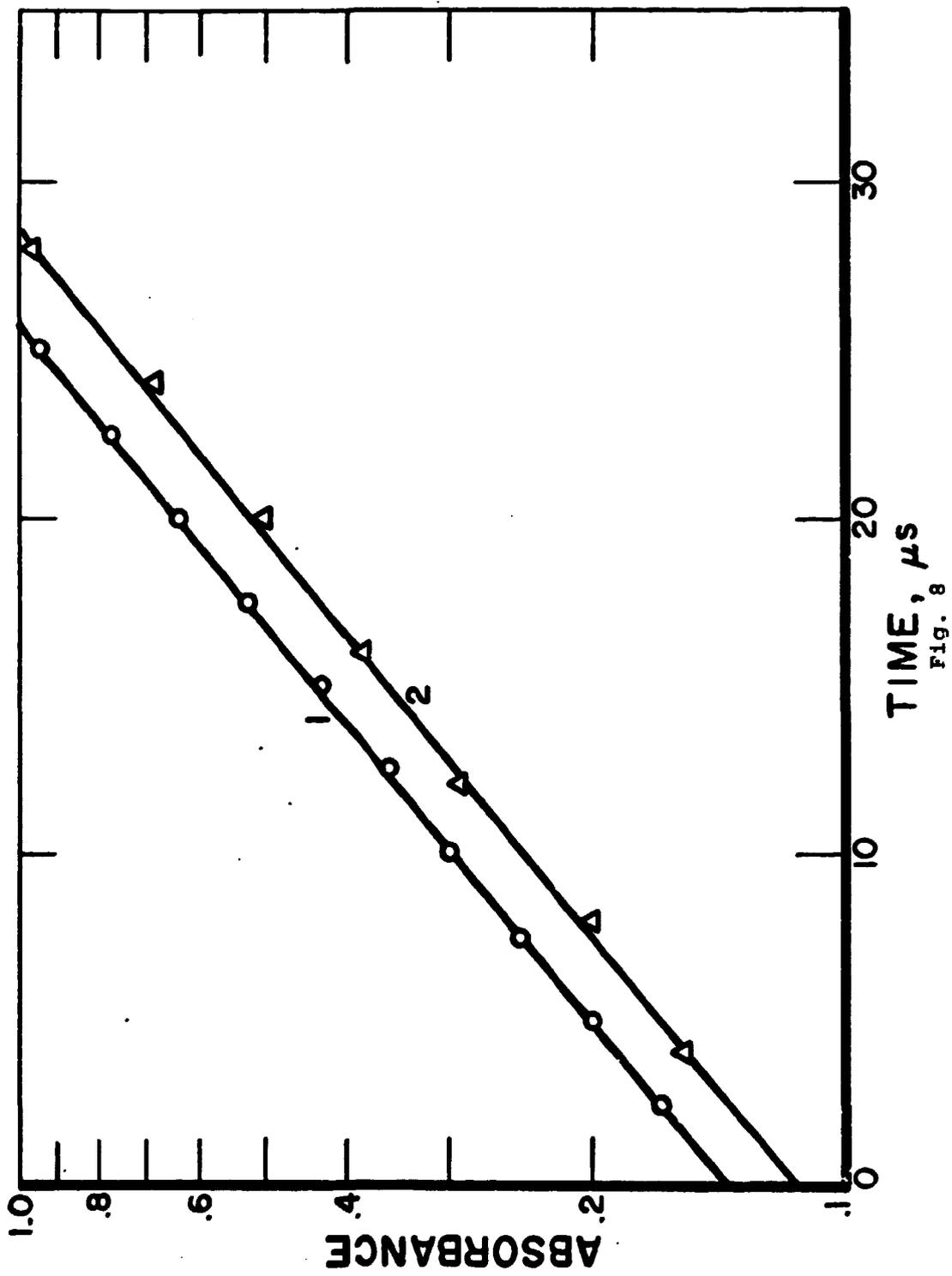


Fig. 8

2202

Rise - M -

<p>Title and author(s) The Kinetics of Dye Formation by Pulse Radiolysis of Pararosaniline Cyanide in Aqueous or Organic Solution.</p> <p>W.L. McLaughlin, M.M. Kosanić^a, V.M. Marković^b, M.T. Nenadović^b, J. Holcman, and K. Sehested.</p> <p>^aFaculty of Science, University of Novi Sad, 21000 Novi Sad, Yugoslavia.</p> <p>^bRadiation Chemistry Dept., Boris Kidrić Inst. of Nuclear Sciences, Vinča, 11001 Belgrade, Yugoslavia.</p>	Date November 1979
pages + 4 tables + 8 illustrations	Department or group Accelerator
<p>Abstract</p> <p>The radiation-induced conversion of the leuco- cyanide of pararosaniline dye, $[H_2N \langle \text{C}_6H_4 \rangle]_3C-CN$, to the highly colored salt-isomer of the dye, $[H_2N \langle \text{C}_6H_4 \rangle]_2C=C \langle \text{C}_6H_4 \rangle =NH_2^+ + CN^-$, in acidic aqueous solution (wavelength of maximum absorption $\lambda_{max} =$ 540 nm) or polar organic solution ($\lambda_{max} = 550$ nm) takes place in two separate processes. The first is very fast (within <50 ns), and the second much slower following first-order kinetics with a rate constant that varies from $4 \times 10^3 s^{-1}$ to $\sim 10^6 s^{-1}$, as the acidity or concentration of an oxidizing agent increases. In oxygen-free acidic aqueous or organic solutions (argon satu- rated) there is an unstable transient species ($\lambda_{max} = 380$ nm). When using O_2 or N_2O-saturated aqueous or organic solution, there is no inter- mediate absorption band at 380 nm, but the slow process of dye formation at 540 or 550 nm is still sequential to the initial fast process having somewhat faster kinetics than in Ar- saturated solution.</p> <p>Available on request from Rise Library, Rise National Laboratory (Rise Bibliotek), Forsøgslab Rise), DK-4000 Roskilde, Denmark Telephone: (03) 37 12 12, ext. 2262. Telex: 43116</p>	Group's own registration number(s)
	Copies to