

gested will be done. Of course, EHT is a very crude MO theory, and we would further suggest that other more accurate MO schemes be investigated. Some

such work has recently appeared for the CNDO model,<sup>4</sup> and in a separate paper we shall discuss our own CNDO studies.<sup>5</sup>

## Pulse Radiolysis Study of Succinonitrile in the Rotator Phase<sup>1,2</sup>

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**Abstract:** A transient absorption spectrum ( $t_{1/2} = 0.23 \mu\text{sec}$ ) has been detected in the pulse radiolysis of succinonitrile, a plastic crystal at room temperature. This absorption is not produced in the presence of 1 mol % tetracyanoethylene (TCNE) and the spectrum of TCNE $\cdot^-$  is observed instead. The value of  $\lambda_{\text{max}}$  (450 nm) for the transient corresponds to the absorption maxima observed in the low-temperature spectra of monomer radical anions from acetonitrile and adiponitrile. On the basis of these results, the transient spectrum is assigned to a monomer radical anion of succinonitrile although the possibility of a dimer species similar to that observed at low temperature cannot be excluded. The first-order decay of the radical anion is attributed to the unimolecular dissociation to  $\cdot\text{CH}_2\text{CH}_2\text{CN}$  and  $\text{CN}^-$ . In addition to the radical anion, a long-lived species is produced which absorbs most strongly in the ultraviolet.

In the pulse radiolysis of organic liquids, studies of transient ions by optical absorption spectroscopy have been largely restricted to solvated electrons and to ions produced by reactions with suitable charge scavengers.<sup>4</sup> The detection of these ions is facilitated by a  $G \epsilon_{\text{max}}$  product which frequently exceeds  $1 \times 10^4$ , where  $G$  is the 100-eV yield of species with lifetimes exceeding the resolution time of the equipment and  $\epsilon_{\text{max}}$  is the extinction coefficient in  $M^{-1} \text{cm}^{-1}$  at the absorption maximum ( $\lambda_{\text{max}}$ ). Two pulse radiolysis studies of acetonitrile solutions containing aromatic hydrocarbons such as biphenyl<sup>5</sup> and anthracene<sup>6</sup> have been reported in which transient absorption spectra were readily observed and identified as belonging to the radical anion and triplet state of the solute. For pure acetonitrile, however, there is only a brief report<sup>5</sup> of a short-lived transient ( $t_{1/2} < 5 \mu\text{sec}$ ) with a very weak absorption at 660 nm which was tentatively attributed to a solvated electron. Even this observation is in doubt because in a later study of the pulse radiolysis of oxygen-free acetonitrile,<sup>6</sup> no absorption could be detected between 280 and 800 nm despite high sensitivity and a resolution time of 100 nsec.

By contrast, esr and optical studies of  $\gamma$ -irradiated acetonitrile in the solid state at low temperature have

definitely shown that the dimer and monomer radical anions of acetonitrile are produced and stabilized in crystal I and crystal II, respectively.<sup>7</sup> The optical absorption spectrum of the dimer radical anion in a polycrystalline sample has two bands with  $\lambda_{\text{max}}$  at 510<sup>8,9</sup> and 310 nm,<sup>9</sup> whereas the corresponding spectrum of the monomer radical anion has only one clearly defined band with  $\lambda_{\text{max}}$  at 430 nm.<sup>9</sup> In similar low-temperature irradiation studies, the dimer radical anion of succinonitrile was identified in both crystalline phases.<sup>10</sup> Its powder esr spectrum is identical with that of the acetonitrile dimer radical anion<sup>11</sup> and  $\lambda_{\text{max}}$  for the optical absorption is located at 540 nm.<sup>10</sup>

Succinonitrile differs from other simple organic cyanides in having a relatively high melting point (331°K). Also, the solid phase above 233°K (crystal I) is a transparent plastic crystal in which the rotational motion of the individual molecules is more characteristic of a liquid than of a solid.<sup>12</sup> It was thought that the physical properties of this plastic crystal<sup>13</sup> which are intermediate between those of a liquid and a solid might favor the detection by pulse radiolysis of a succinonitrile radical anion (or solvated electron) at room temperature. This finding would be of particular interest in view of the close resemblance between the  $\gamma$ -irradiation results for acetonitrile and succinonitrile at low temper-

(1) (a) Kinetics of Ionic Processes in the Radiolysis of Liquids. VI; (b) part V: R. B. Taylor and F. Williams, *J. Amer. Chem. Soc.*, **91**, 3728 (1969).

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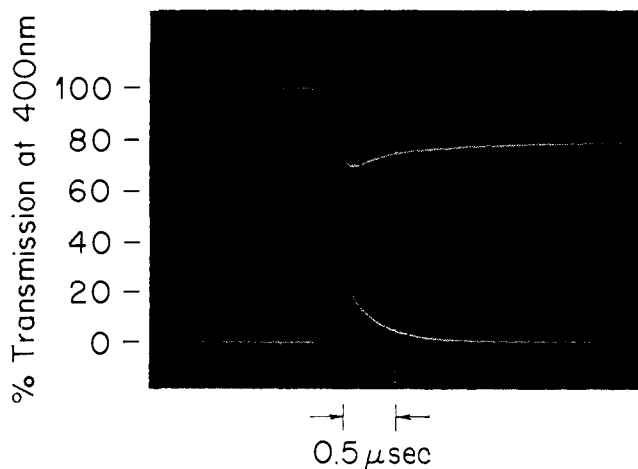


Figure 1. Oscilloscope showing the absorption in pure succinonitrile at 400 nm. The upper trace is the composite absorption signal, and the lower trace shows the emission from the sample cell.

ature and the absence of any significant information about the reactions of electrons with alkyl cyanides in the liquid phase.<sup>14</sup>

### Experimental Section

**Materials and Preparation of Samples.** Succinonitrile (Matheson Coleman and Bell) was distilled at reduced pressure and stored under vacuum in breakseals. The material was either redistilled *in vacuo* or transferred manually into the sample cell and subsequently degassed before the cell was sealed. The pulse radiolysis results were the same regardless of the method of sample preparation. Tetracyanoethylene (TCNE), obtained as a White Label grade from Eastman Organic Chemicals, was used as received. Samples of succinonitrile containing a weighed amount of TCNE (~1 mol %) were prepared by placing both compounds in a cell after which the mixture was degassed by several cool-pump-melt cycles. The resulting solid solution was quite transparent, suggesting that the TCNE was uniformly incorporated.

**Irradiation Cells.** The Suprasil cells used in this investigation were the same as those which have been employed in this laboratory for low-temperature optical studies.<sup>9</sup> The flat portion of the cell containing the sample is rectangular (1.2 cm width  $\times$  1.5 cm height) with a path length of 0.1 cm and is fused to the quartz section of an 8-mm quartz-to-Pyrex graded seal.

**Pulse Radiolysis.** The irradiation cell, mounted on an aluminum plate, was inserted into the sample holder of the apparatus.<sup>15,16</sup> A 1.2-cm aperture in the plate accommodates the four passes of the analytical light which are collinear with the electron beam, thereby giving a total optical path length of 0.4 cm. A high-pressure Hg-Xe arc (Hanovia Model 901B-1) was used as the source of analytical light. This lamp was pulsed to an intensity approximately 50 times that obtainable in dc operation to minimize the correction for emission from the Suprasil cell during the first microsecond after the pulse. The lamp was not pulsed in experiments which did not require microsecond time resolution. To minimize the photolytic effects of the analytical light, a Corning CS 0-51 filter, which does not transmit below 400 nm, was placed between the lamp and the sample. In studying the decay of TCNE $^{\cdot-}$ , Corning filters CS 3-73 and CS 1-56 were used to transmit a narrow band centered at 440 nm.

Through the use of the McPherson Model 216 polychromator and a double slit mechanism, it was possible to monitor the absorption at two wavelengths simultaneously. For 3-mm slits and a grating

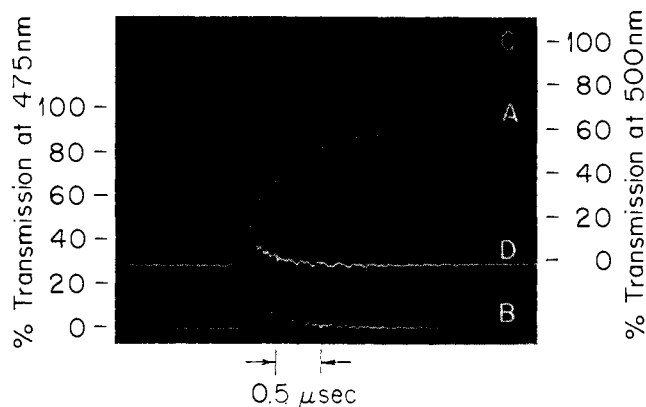


Figure 2. Oscilloscope showing absorption and emission at 475 nm (traces A and B) and 500 nm (traces C and D).

with 1200 lines/mm, the band width of the light beam reaching the photomultiplier is 2 nm.

The calculation of the dose received by the sample was based on measurements of the energy absorbed in a thin aluminum calorimeter placed at the sample position.<sup>16</sup> After correcting for the depth-dose effect<sup>16</sup> and the estimated ratio ( $1.20 \pm 0.10$ ) of the mass stopping powers of succinonitrile and aluminum,<sup>17</sup> the average dose per pulse was calculated to be  $9.0 \times 10^{18}$  eV g $^{-1}$  ( $1.44 \times 10^5$  rad). The dose per pulse has been shown to be reproducible within 5% from pulse to pulse.

### Results

Initial experiments revealed an absorption in the 350–600-nm region after the pulse. Examination of the oscillograms showed that the absorption was composed of two components, a transient absorption with a microsecond lifetime and a much longer lived absorption which persisted for at least 5 min and will henceforth be referred to as the permanent absorption. In addition, by pulsing the Febetron with no analytical light, it was found that the oscilloscope trace was further complicated by light emission of *ca.* 1- $\mu$ sec duration. This emission was also observed from an empty irradiation cell indicating that it originates from the Suprasil windows through which the electron beam penetrates.

Figure 1 shows a typical oscilloscope with the monochromator set at 400 nm. The upper trace is the composite signal and the lower trace is the emission signal recorded in the subsequent pulse on the same transmission scale. The net absorption signal was obtained by subtraction. In order to correct for the permanent absorption, it was assumed that this signal reached its maximum value at the same time (0.2  $\mu$ sec) as that of the transient signal and then remained constant. The validity of this assumption was verified in subsequent experiments on solid solutions of TCNE in succinonitrile, as will be discussed later. Accordingly, the absorbance of the transient was evaluated as the difference between the net and permanent absorbances.

Since repetitive pulsing of the same sample led to a marked decrease in the signal intensity of the transient, the spectrum was derived by the simultaneous recording of the absorption signals at two wavelengths, one of which was fixed at 475 nm to serve as a reference and the other was varied from pulse to pulse to cover the range from 350 to 550 nm. A typical oscilloscope obtained by using this technique is shown in Figure 2.

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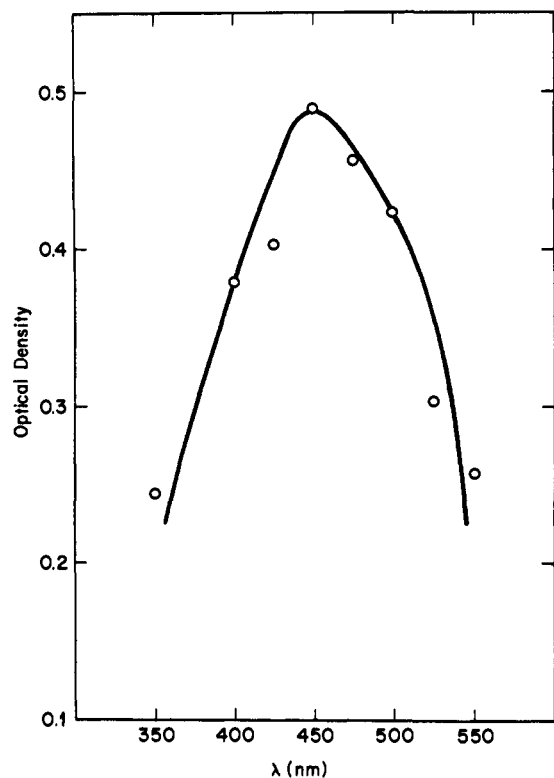


Figure 3. Optical spectrum of the transient radical anion produced by pulse radiolysis of succinonitrile at room temperature. Optical densities were measured at  $0.2 \mu\text{sec}$  after the beginning of the pulse.

The traces A and B refer to the absorption and emission, respectively, at  $475 \text{ nm}$ , and the traces C and D are the corresponding signals at  $500 \text{ nm}$ . It is evident that the transient species is completely formed within  $0.2 \mu\text{sec}$  after the beginning of the pulse, and optical densities were measured after this time. By taking the ratio of the optical densities at the monitoring wavelength and  $475 \text{ nm}$  from each oscillogram, the spectrum of the transient was obtained at  $0.2 \mu\text{sec}$  and normalized to the optical density at  $475 \text{ nm}$  in the first pulse. This spectrum is shown in Figure 3 and  $\lambda_{\text{max}}$  is in the region of  $450 \text{ nm}$ . The  $G \epsilon_{\text{max}}$  product is  $8.2 \times 10^3$  (molecules/ $100 \text{ eV}$ )  $M^{-1} \text{ cm}^{-1}$ .

Evidence that the transient spectrum results from only one species is provided by the decay kinetics. Excellent first-order plots were obtained at all wavelengths between  $350$  and  $550 \text{ nm}$ . Measurements were made at intervals of  $25 \text{ nm}$ . The first-order rate constants were in good agreement and gave an average value of  $3.0 \pm 0.6 \times 10^6 \text{ sec}^{-1}$  over this range. It was also clearly demonstrated that the decay of the transient species proceeds by a thermal and not a photochemical reaction, for reducing the intensity of the incident analytical light by a factor of  $2.5$  did not alter the first-order rate constant.

In an attempt to establish the nature of the transient species, experiments were carried out with solutions of TCNE which is known to be an excellent electron scavenger. The monochromator was set at  $550 \text{ nm}$  where TCNE $\cdot^-$  does not absorb but where the transient species shows a significant absorption (Figure 3). A comparison of the results for pure succinonitrile and a TCNE solution (Figure 4) shows that the presence of the TCNE eliminates the transient but has no effect on

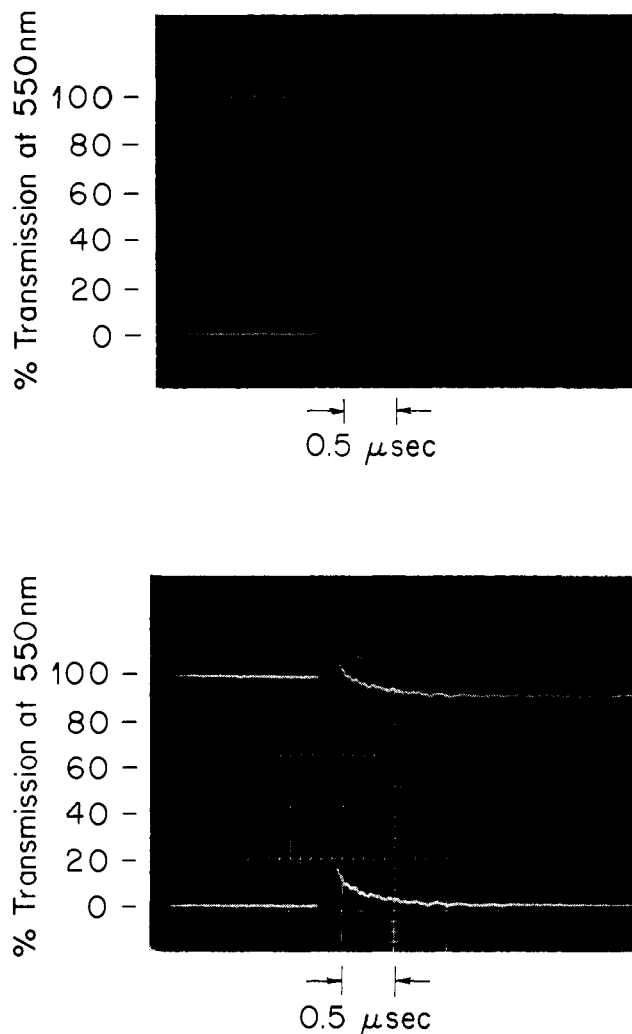


Figure 4. Oscillograms showing absorption and emission at  $550 \text{ nm}$ . The traces in the upper photograph are for pure succinonitrile and those in the lower photograph are for succinonitrile doped with  $1 \text{ mol } \%$  tetracyanoethylene.

the appearance of the permanent absorption. It is from this experiment, where no transient is observed, that the permanent absorption signal is seen to grow in during the first  $0.2 \mu\text{sec}$  after the pulse and to maintain a constant value for the subsequent  $2 \mu\text{sec}$ . This justifies the previous assumption that the permanent absorption remains unchanged during the decay of the transient in pure succinonitrile.

The identification of TCNE $\cdot^-$  in the above experiment proved to be a relatively simple task. A strong long-lived absorption below  $500 \text{ nm}$  was detected on the oscilloscope and *ca.*  $1 \text{ min}$  after the pulse, the sample was removed from the apparatus and plunged into liquid nitrogen. The optical spectrum recorded at  $77^\circ\text{K}$ , where there was no decay, is shown in Figure 5, and the positions of the well-resolved peaks correspond to those reported<sup>18,19</sup> for TCNE $\cdot^-$ . In the light of this result, a detailed examination of the decay of TCNE $\cdot^-$  at room temperature was made by following the absorption peak at  $438 \text{ nm}$ . Although some decay occurred in the millisecond region, most of the absorp-

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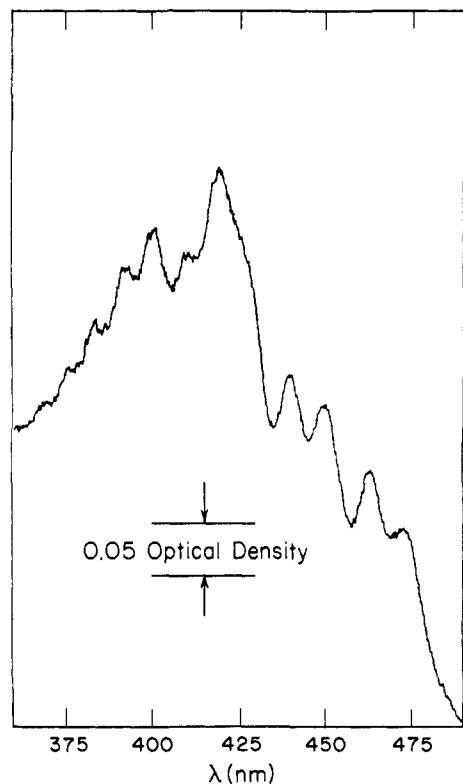


Figure 5. Optical absorption spectrum of the tetracyanoethylene radical anion in polycrystalline succinonitrile at 77°K. The radical anion was produced by pulse radiolysis of succinonitrile containing 1 mol % tetracyanoethylene at room temperature and then stabilized at 77°K.

tion disappeared according to first-order kinetics with  $t_{1/2} = 9.3$  min.

As indicated by the oscilloscope traces (*cf.* Figures 1 and 4), the rapidly induced permanent absorption in succinonitrile is more intense at shorter wavelengths. This absorption increases only slightly on standing at room temperature for several minutes after the pulse, and its uv spectrum recorded with a conventional spectrophotometer exhibits a sharp rise to shorter wavelengths with a well-defined shoulder at 245 nm. A similar feature is observed at 265 nm in the spectrum of  $\gamma$ -irradiated succinonitrile crystal II after photo-bleaching at 77°K.

## Discussion

As a result of the TCNE experiments, it has been clearly established that the transient species in succinonitrile originates by electron capture. Its absorption spectrum ( $\lambda_{\max}$  450 nm) differs from that of the dimer radical anion ( $\lambda_{\max}$  540 nm) produced at low temperature<sup>10</sup> but is remarkably similar to the spectra of the monomer radical anions of acetonitrile<sup>9</sup> and adiponitrile<sup>20</sup> for which  $\lambda_{\max}$  is between 430 and 440 nm. On the basis of this correlation, and in view of the suggestion<sup>21</sup> that a solvated electron in acetonitrile would have an absorption peak in the near infrared,

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the transient spectrum is assigned to a succinonitrile monomer radical anion, although the choice between the monomer and dimer radical anion cannot be made with absolute certainty owing to the broad nature of the absorption bands. Since the monomer is likely to be the precursor of the dimer, it is possible that the conditions favoring the formation of the dimer may not exist at room temperature. In this connection, the rotational motion characteristic of succinonitrile at room temperature<sup>13a</sup> could prevent the precise alignment of the cyanide groups required for dimer formation.<sup>7</sup>

The short lifetime ( $t_{1/2} = 0.23$   $\mu$ sec) of the transient species is most likely to be determined either by ionic recombination or by dissociation. The other possibility that the species disappears by reaction with neighboring molecules in the lattice is considered improbable in view of the well-known stability of many radical anions in aprotic media.<sup>14a</sup> Since the decay of TCNE $\cdot^-$  occurs on a much longer time scale than that of the transient, this would appear to exclude ionic recombination as a mechanism for the disappearance of the transient. Hence, the most reasonable path is suggested to be simple dissociation of the monomer radical anion to give CN $^-$  and  $\cdot$ CH<sub>2</sub>CH<sub>2</sub>CN. This is consistent with the instability of isostructural molecules such as HCN $\cdot^-$ <sup>22</sup> and CH<sub>3</sub>CO $^{\cdot-}$ <sup>23</sup> at elevated temperatures. Confirmation of the dissociation reaction by direct observation of the  $\cdot$ CH<sub>2</sub>CH<sub>2</sub>CN would have been desirable but was prevented by the intense permanent absorption in the ultraviolet.

The formation of the permanent absorber is unaffected by the incorporation of TCNE so it can be safely assumed that it does not arise from a reaction involving electrons liberated in the ionization process. Its optical spectrum showing a high intensity in the uv and a long tail in the visible region is indicative of a highly conjugated structure, as would be produced by the polymerization of  $-C\equiv N$  groups. From the fact that the yield of the transient species diminished on repeated pulsing, it is conceivable that the permanent absorber acts as a competitive electron scavenger.

Based on the value of  $\epsilon = 7.1 \times 10^3$   $M^{-1} \text{ cm}^{-1}$  for TCNE $\cdot^-$  at 435 nm,<sup>18</sup>  $G(\text{TCNE}\cdot^-)$  is 4.0 which demonstrates very efficient trapping of electrons. Unfortunately, an estimate of the  $G$  value for the transient radical anion cannot be made since there has been no independent determination of  $\epsilon_{\max}$  for species of this type. However, the  $G \epsilon_{\max}$  product of  $8.2 \times 10^3$  (molecules/100 eV)  $M^{-1} \text{ cm}^{-1}$  in this pulse radiolysis study is comparable to the range of values ( $4 \times 10^3$ – $1 \times 10^4$ )<sup>9a,10</sup> obtained for monomer and dimer radical anions of nitriles at 77°K, implying that electron capture is as efficient in succinonitrile at room temperature as it is at low temperature, although the thermal stability of the ion is much less in the former case. As a concluding remark, the failure to observe radical anions in the pulse radiolysis of pure liquid acetonitrile<sup>6</sup> could perhaps be attributed to the greater instability of these ions at elevated temperatures, particularly in the absence of an ordered lattice.

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