Picosecond Translent Absorption Studies of Dinitrotoluenes in Solution

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Employing picosecond transient spectroscopy, we have studied the photochemistry of 2,6-, 2,4-, and 3,4-dinitrotoluenes in solution. With 266-nm excitation (ca. 1 mJ, 22 ps) similar broad transient absorptions in the 420–650-nm region are observed for each isomer. They are assigned to their lowest $n\pi^*$ excited triplet states. For the 2,6 and the 2,4 compounds, the initial triplet absorptions evolve to yield spectra characteristic of the *aci*-quinoid species, which are formed following intramolecular hydrogen transfer from the methyl group to the ortho nitro group. Intramolecular hydrogen abstraction rates of 0.5×10^9 and 0.6×10^9 s⁻¹ are estimated for the 2,6 and 2,4 isomers, respectively.

Introduction

Intramolecular hydrogen transfer reactions, between a nitro and an ortho substituted group, are among the earliest known photoreactions of aromatic nitro compounds.¹ The generally proposed mechanism for hydrogen abstraction is given in eq 1.



In recent nanosecond laser studies, we have characterized spectrally the aci-quinoid forms and the dinitrobenzyl anions of 2,6- and 2,4-dinitrotoluenes (DNT).² The aci species b is observed at low pH (<2.0) or in nonpolar media following intramolecular hydrogen transfer. At pH > 3.0 or in polar solvents the aci form undergoes deprotonation to yield the corresponding anion c. The nature of the reactive excited states, the mechanism (vis-a-vis the role of intermediates, such as a), and the rate of the hydrogen abstraction process remain unclear. In attempting to resolve these issues, we have undertaken picosecond spectroscopic studies of DNT in solution. Recently, this technique has been successfully employed by Yip et al.³ to characterize the lowest triplet state of nitrobenzene and of alkyl nitrobenzenes. The $T_1 \rightarrow T_n$ spectra may provide a useful probe for unraveling the important photochemistry⁴ of o-nitrobenzyl systems. For phenyl o-nitrobenzyl ether and pcyanophenyl o-nitrobenzyl ether, it was concluded that the aciquinoid intermediates were formed from the singlet excited state at a rate much faster than that for triplet decay.^{3b} In this paper, our findings are presented for 2,6-, 2,4-, and 3,4-DNT.

Experimental Section

The active-passive mode-locked Nd:YAG laser system has been described previously.⁵ A more detailed description of our im-

proved dual-beam picosecond spectrometer and method of data collection will be given here. After one stage of amplification and beam splitting 70% of the fundamental 1064-nm pulse (ca. 22 ps, ca. 2.5 mJ) was apodized, spatially filtered, and further amplified to give a maximum energy of ca. 30 mJ. Efficient frequency doubling and redoubling in KD*P crystals generated a fourth harmonic photolyzing pulse (266 nm, ca. 22 ps) of up to 4 mJ (for the current studies ca. 1 mJ was employed). The UV beam, isolated with a LiF prism and a harmonic splitter, was focused with a 60-cm silica lens to a 1.5-2-mm spot diameter in a sample cell (MgF₂ windows) of 2-mm path length.

The remaining 30% of the fundamental beam, after spatial filtering and amplification, passed through a variable delay and was focused with a 1-m lens into a 15-cm cell containing a $D_3PO_4/D_2O(1/1 (v/v))$ mixture. The emergent white-light continuum beam passed through a 400- μ m pinhole, mounted on a Schott KG 3 filter (to remove the residual 1064 nm), and was imaged to a ca. 500-µm-diameter spot, which interrogated the central portion of the photolyzed region. In addition, the probe beam was apertured to isolate the central, relatively homogeneous, core of the continuum light. A Corning 1-61 filter was placed in the white-light path to attenuate preferentially the green to red region of the probe continuum, which is generated more efficiently than the blue. A metal 0.3 neutral density filter diverted a replica of the focused probe beam to generate a second spot in the sample cell. The signal and reference beams were focused onto the entrance slit of a monochromator (Instruments SA, HR 320, 152 g/mm) and were dispersed onto the face of an ISIT vidicon detection system (PAR Model 1216, 1215, 1257).

Of several liquids employed in the continuum cell, the D_3PO_4/D_2O mixture gave the most reproducible and least spectrally structured probe source. Streak camera (Hamamatsu C1587) measurements indicated that the continuum pulse had a double-pulse structure with an overall fwhm of ca. 60 ps. In contrast to the observations of Masuhara et al.⁶ for H₃PO₄, we observed no significant wavelength dependence of the continuum pulse. Employing 450- and 700-nm 80 Å band-pass filters, we measured average pulse widths of 64 and 58 ps, respectively. Also, it was determined that the blue pulse was delayed with respect to the red by only ca. 7 ps.⁷

The induced absorption log (I_0/I) was computed for each channel (a total of 500 corresponding to ca. 235 nm). I_0 is the ratio of the reference beam to the signal beam (after dark current subtraction) in the absence of UV excitation and I is the same ratio in its presence. To improve the signal-to-noise ratio, this

See, e.g.: Morrison, H. A. In The Chemistry of Functional Groups. The Chemistry of the Nitro and Nitroso Groups; Feuer, H., Ed.; Wiley: New York, 1969; Chapter 4. Döpp, D. O. In Top. Curr. Chem. 1978, 55, 49.
 (2) (a) Craig, B. B.; Atherton, S. J. Proc. SPIE, Int. Soc. Opt. Eng. 1984,

^{(2) (}a) Craig, B. B.; Atherton, S. J. Proc. SPIE, Int. Soc. Opt. Eng. 1984, 482, 96.
(b) Atherton, S. J.; Craig, B. B. Chem. Phys. Lett. 1986, 127, 7.
(3) (a) Yip, R. W.; Sharma, D. K.; Giasson, R.; Gravel, D. J. Phys. Chem.

^{1984, 88, 5770; (}b) 1985, 89, 5328.
(4) See, e.g.: Amit, B.; Zehavi, U.; Patchornik, A. Isr. J. Chem. 1974, 12,

⁽⁴⁾ Sec. e.g., Ann, B., Zenavi, G., Faculonik, A. 157. J. Chem. 1974, 12, 103. Reichmanis, E.; Smith, B. C.; Gooden, R. J. Polym. Sci., Polym. Chem. Ed. 1985, 23, 1.

⁽⁵⁾ Craig, B. B.; Faust, W. L.; Goldberg, L. S.; Schnur, J. M.; Schoen, P. E.; Weiss, R. G. Fast Reactions in Energetic Systems; Capellos, C., Walker,

<sup>R. F., Eds.; Reidel: Dordrecht, Netherlands, 1981; p 419.
(6) Masuhara, H.; Miyasaka, H.; Karen, A.; Uemiya, T.; Mataga, N.;</sup>

Koishi, M.; Takeshima, A.; Tsuchiya, Y. Optics Commun. **1983**, 44, 426. (7) The corresponding value for our D₂O continua (fwhm 40 ps) was ca.

⁽⁷⁾ The corresponding value for our D_2O continua (form 40 ps) was ca. 14 ps; this suggests that the mechanism of continuum generation in D_2O and D_3PO_4 is different.



Figure 1. Representative transient absorption spectra recorded 33 ps after laser photolysis (266 nm, ca. 1 mJ) of aerated ca. 5×10^{-3} M solutions of dinitrotoluene in methanol; average of 12 laser pulses. Solid

line, 2,6-DNT; broken line, 3,4-DNT.

data collection/reduction cycle was repeated several times, and the resulting spectra were averaged. In order to minimize any systematic deviations associated with I_0 , a base-line spectrum was computed after each UV shot. This was calculated in the same manner (using the same I_0) as the induced absorption, except that the ratio I was measured with the UV beam blocked. An averaged base line was thus obtained for each averaged absorption measurement. Typically, the deviation of the base line from zero was no more than 0.01 absorbance units. In presentation of our transient spectra the averaged base-line spectra have been subtracted from the averaged absorption; no smoothing has been applied. For every shot, the pulse train was monitored with a silicon photodiode and Tektronix 7104 oscilloscope. The recorded data were restricted to a relatively well-defined UV energy range (monitored with a Laser Precision RJ 7200 energy ratiometer).

The zero time delay between the photolyzing and the probe pulse was determined by measuring the rise of the peak absorbance of the $S_1 \rightarrow S_n$ absorption spectrum of pyrene (λ_{max} ca. 470 nm) and by measuring the photobleaching of rhodamine 6G. The time at which the signal was half of its maximum value was defined as the origin of the time axis. There was good agreement between the two methods.

2,6-, 2,4-, and 3,4-DNT (Aldrich) were recrystallized from water/ethanol solutions. Solvents were spectrophotometric grade. Since the observed transient absorption spectra and kinetic data are unaffected by the presence of dissolved oxygen, aerated solutions have been employed throughout this work. Solutions were prepared to have an OD_{266} of ca. 2 for a 2-mm path length.

Results

Following 266-nm excitation, all three isomers of DNT yield similar transient absorption spectra at early times. Representative spectra for 2,6- and 3,4-DNT in methanol are given in Figure 1. The spectra are characterized by a band at ca. 450 nm and a very broad red absorption. The early-time spectra for the 2,6 compound exhibit a larger blue absorption than for the 3,4 isomer. A similar excess of signal was also observed for 2,4-DNT, although it was of smaller magnitude. Similar spectra were obtained in *n*-hexane; this is evidence that the spectra are characteristic of a dinitrotoluene excited state and are not associated with the solvent or solvent impurities. Further, the appearance of the red absorption in *n*-hexane solutions rules out the possibility that this absorption can be attributed to a solvated electron produced through a nonlinear process. In fact, the absorption signals display a linear dependence upon laser pulse energy.

Figure 2 shows absorption spectra for 2,6-DNT in methanol for a sequence of probe pulse delays. After the initial signal growth, there is a gradual loss of intensity in the red (to a residual level) accompanied by a slight increase in the blue. This spectral evolution is essentially complete by the 1587-ps frame in Figure 2: spectra recorded out to 15 ns (the maximum delay of our picosecond system) show no further change. Also, the 1587-ps spectrum agrees well with the spectrum in the bottom frame, which



Figure 2. Time-resolved absorption spectra following laser photolysis of 2,6-DNT; conditions as in Figure 1. Spectra have been normalized for the UV excitation energy. The bottom frame is the spectrum recorded 9 μ s after nanosecond laser photolysis (266 nm) of a 2.5 × 10⁻⁴ M solution of 2,6-DNT in methanol in the presence of 2.5 × 10⁻³ M HCl; taken from ref 2b.

is a normalized spectrum recorded 9 μ s after nanosecond 266-nm excitation of 2,6-DNT in methanol in the presence of 2.5 × 10⁻³ M HCl. This latter spectrum has previously been attributed to the *aci*-quinoid form of 2,6-DNT.^{2b} It is concluded that within a few nanoseconds of short-pulse excitation the predominant transient species is the aci -form of 2,6-DNT.⁸ We have shown

⁽⁸⁾ It is possible that other transients are present that do not absorb over our probe wavelengths.



Figure 3. Time dependence of integrated absorption signals following laser photolysis of 2,6-DNT; conditions as in Figure 1. (O) 415-460 nm, (\triangle) 535-625 nm. (a) Note that the normalized signals exhibit essentially the same rise time as the S₁ \rightarrow S_n absorption from pyrene (\blacksquare). (b) Decay of signal in the red is accompanied by a slight increase of signal in the blue.

previously that in methanol this aci species undergoes deprotonation with a rate of ca. 5×10^4 s⁻¹ to yield an [anion]:[aci] ratio of ca. $1.1.^{2b}$

Figure 3 illustrates the time dependence of integral absorption signals in the blue and red for 2,6-DNT in methanol. Figure 3a also includes the rise time of the $S_1 \rightarrow S_n$ absorption of pyrene in methanol. Since production of the S_1 state is known to be very rapid,⁹ this curve represents the system response time. Evidently the rise times of the initial spectra in both the blue and red are instrumentally limited. The difference in the long-time behavior of these spectral regions, which is apparent in Figure 2, is more clearly demonstrated in Figure 3b. While the blue signal shows a very slight increase with time, the red signal decays substantially to a residual level. A semi-logarithmic plot of the decay is given in Figure 4, where the residual component of absorption has been subtracted from each ΔOD_t measurement. From the slope in Figure 4, we determine a first-order decay constant of $(2.1 \pm 0.2) \times 10^9 \text{ s}^{-1}$.

The gross kinetic features are very similar for the 2,4 compound: the rise time of the initial species was instrumentally limited and there was a decay of signal in the red while the blue signal remained essentially constant. The late term absorption, attributed to the aci species, was somewhat weaker than that for 2,6-DNT, which is consistent with our nanosecond studies.² Further, there was no residual signal in the red. A semi-logarithmic plot of absorbance vs. time yielded a rate constant of $(2.2 \pm 0.2) \times 10^9$ s⁻¹ for removal of the red absorption from 2,4-DNT in methanol.

The overall signal-to-noise ratio for the transient signals from 3,4-DNT was inferior to those obtained from the other isomers. Nevertheless, we were able to determine that they show the same instrumentally fast rise time. In our previous nanosecond laser studies² we were unable to detect any long-lived transients from 3,4-DNT. Consistent with these observations, the initial picosecond absorptions from 3,4-DNT exhibited a concomitant decay in both the blue and the red to a zero signal level. A decay constant of $(1.7 \pm 0.2) \times 10^9$ s⁻¹ was measured in methanol.

We have also studied the picosecond photolysis of 2,6-DNT in neutral aqueous solution. Under these solvent conditions, it has previously been shown that the immediate product on nanosecond time scales is the 2,6-dinitrobenzyl anion (λ_{max} 490 nm).² This raised the question as to whether production of the anion in aqueous solutions (at pH >7) may actually circumvent the aci species; i.e., the excited state equilibrium may become significant

$$DNT^* \rightleftharpoons A^{-*} + H^+$$
 (2)

where A^- is the anion. Unfortunately, a detailed kinetic study of these processes on picosecond time scales is severely encumbered by the spectral overlap of the early time absorption, the aci form, and the anion. Certainly, our data indicate the presence of the aci species as an essential intermediate to the anion. However,



Figure 4. Semi-logarithmic plot of the change in absorption in the red (from Figure 3) vs. time. The residual signal level has been subtracted from each point. From the slope, a first-order rate constant of $(2.1 \pm 0.2) \times 10^9 \text{ s}^{-1}$ is determined for the decay of the lowest triplet state of 2,6-DNT.

we are unable to rule out unequivocally the presence of a minor channel yielding the anion directly from an excited state of 2,6-DNT.

Discussion

Yip et al.3ª have employed picosecond absorption spectroscopy to identify the lowest triplet state of nitrobenzene and of alkylnitrobenzenes. With excitation at 355 nm, the triplet lifetimes of nitrobenzene, o-nitrotoluene, and o-nitroethylbenzene were determined to be 770 \pm 90, 690 \pm 140, and 420 \pm 35 ps, respectively. The $T_1 \rightarrow T_n$ spectra are characterized by two absorption bands at ca. 440 and 625-650 nm.¹⁰ The aci forms of these nitrobenzene derivatives, however, do not absorb in the spectral region probed by the continuum;^{2a,11} thus their formation was not detected. However, in a more recent study^{3b} of several oxygen-substituted o-nitrobenzylic compounds, aci-quinoid intermediates were identified. In the case of phenyl o-nitrobenzyl ether and *p*-cyanophenyl *o*-nitrobenzyl ether, both the triplet excited state and the aci species were observed at early times. For these two compounds, it was concluded that the aci-quinoid intermediate is formed from the excited singlet state at a rate much faster than the decay of the triplet.

In general, aromatic nitro compounds do not fluoresce; intersystem crossing is known to proceed both rapidly and efficiently.^{1,12} In the present study, no emission was detected from solutions of DNT. Previously, we have speculated that the photochemically reactive state supporting the intramolecular hydrogen-transfer process is a triplet.² Certainly, the early-time absorptions from DNT share similar spectral and kinetic properties with the $T_1 \rightarrow$ T_n spectra of nitrobenzyl compounds (cf. our instrumentally limited rise times and lifetimes of 470, 450, and 600 ps for 2,6-, 2,4-, and 3,4-DNT, respectively). The fact that the 3,4 compound, which has no intramolecular hydrogen-transfer channel, exhibits the same early-time spectra rules against their assignment to a biradical species (such as a). Our preferred assignment of the early spectra then is to the lowest triplet state of each DNT. Our lifetime measurements suggest that the triplet states are of $n\pi^*$ character.¹³

⁽¹⁰⁾ We have also observed rapid production of the characteristic $T_1 \rightarrow T_n$ absorption following 266-nm excitation of *p*-nitrobenzyl derivatives: Craig, B. B.; Weiss, R. G.; Atherton, S. J. J. Am. Chem. Soc., submitted.

 ⁽¹¹⁾ Wettermark, G. Nature (London) 1962, 194, 677; J. Am. Chem. Soc.
 1962, 84, 3658; J. Phys. Chem. 1962, 66, 2560.

⁽¹²⁾ Hurley, R.; Testa, A. C. J. Am. Chem. Soc. 1968, 90, 1949.

⁽¹³⁾ Nitroaromatic triplet states of $n\pi^*$ character tend to have lifetimes <5 ns, whereas those of $\pi\pi^*$ or charge-transfer character are in the microsecond range. See, e.g., ref 14.

⁽⁹⁾ Miyasaka, H.; Masuhara, H.; Mataga, N. Laser Chem. 1983, 1, 357.

The lack of a substantial change in the blue absorption with time for 2,6- and 2,4-DNT can be rationalized in terms of a decay of the triplet absorption superimposed upon a concomitant growth of an aci-like absorption, the intensity of the initial triplet signal being very similar to that of the final aci absorption. The larger triplet decay rates for 2,6- and 2,4-DNT are consistent with these molecules possessing an additional deactivation channel, i.e., intramolecular hydrogen transfer. If we assume that the lowest triplet state of each isomer has a common radiationless decay rate (the 3,4-DNT value of 1.7×10^9 s⁻¹), then the rate of intramolecular hydrogen abstraction for the 2,6- and 2,4-DNT can be estimated to be 0.5×10^9 s⁻¹ and 0.6×10^9 s⁻¹, respectively. Evidently the rate is not enhanced by the presence of an additional ortho nitro group. For 2,6-DNT, increased steric interactions could cause at least one of the nitro groups to be twisted out of the plane of the benzene ring; this may affect its reactivity in the hydrogen abstraction process. The intramolecular hydrogen abstraction rate for dinitrotoluenes lies between the values determined for onitrotoluene (ca. $\leq 0.1 \times 10^9 \text{ s}^{-1}$) and o-ethylnitrobenzene (ca. 0.9 $\times 10^9$ s⁻¹).³ This is consistent with a larger rate of reaction for a secondary vs. a primary hydrogen and with an electron-withdrawing substituent at the ortho or para position producing an enhanced rate of reaction. From the rate of intramolecular hydrogen abstraction and the overall triplet decay rate, we determine that ca. 25% of the triplet states of 2,6- and 2,4-DNT undergo reaction to yield the aci species. Aromatic nitro compounds generally have a high quantum yield of triplet formation ϕ_{T} : e.g., nitrobenzene, 0.67,¹² 1-nitronaphthalene, 0.63;¹² 1-nitropyrene, 0.6.15 Assuming a ϕ_T of 0.6, we estimate a quantum yield of ca. 0.15 as an upper limit for hydrogen abstraction through the triplet states of 2,6- and 2,4-DNT.

Our data support a triplet-state mechanism as the major pathway for production of the aci species; this demands the intermediacy of a triplet biradical. The transient spectra suggest that the aci forms of both 2,6- and 2,4-DNT evolve progressively from the initial triplet spectra; there is no discernible intermediate. We conclude that (i) the biradical collapses to the aci form very rapidly (<10 ps) and may not absorb in our probe wavelength region or (ii) the biradical is spectrally indistinguishable from the aci form. The early-time spectra from 2,6- and 2,4-DNT systematically exhibit an excess of signal in the blue with respect to those from the 3,4 compound. This may simply reflect larger exctinction coefficients in the blue for the triplet states of 2,6and 2,4-DNT. Alternatively, the excess signal may be attributed to the aci species. This would represent a minor singlet channel for rapid production of the aci species, possibly through a concerted process.

 $T_1 \rightarrow T_n$ rise times for various aromatic nitro compounds have been correlated with the electronic nature of the initial and final states of the intersystem-crossing process.^{14,16} For nitrobenzenes (<5 ps),^{3a} 1-nitronaphthalene (ca. 10 ps),¹⁷ and 2-nitronaphthalene (10-22 ps),¹⁷ the rapid triplet rise times have been interpreted in terms of production of an $n\pi^*$ singlet state followed by fast intersystem crossing to a $\pi\pi^*$ triplet, which subsequently relaxes to the lowest $n\pi^*$ triplet state. Slower rates of rise are anticipated for nitro compounds undergoing intersystem crossing from $\pi\pi^*$ or charge-transfer singlet states to $\pi\pi^*$ or charge-transfer triplet states. 9-nitroanthracene, which has a $T_1 \rightarrow T_n$ rise time of 50 ps,¹⁶ falls into this latter category. In the current work 266-nm excitation initially addresses a $\pi\pi^*$ singlet state; the dinitrotoluene $T_1 \rightarrow T_n$ triplet rise times are instrumentally limited. Our results then are consistent with rapid internal conversion to an $n\pi^*$ singlet state followed by a fast intersystem-crossing process analogous to that for nitrobenzene.

In summary, we believe that triplet-mediated intramolecular hydrogen abstraction is the major pathway for generation of the aci forms of 2,6- and 2,4-dinitrotoluene in methanolic solutions. There may also exist a minor rapid channel of hydrogen abstraction occurring via a singlet-state mechanism. In constrast, the singlet-state mechanism is dominant for certain oxygen-substituted o-nitrobenzylic compounds.³ In neutral aqueous solutions, the aci form is the preponderant intermediary in the production of dinitrobenzyl anions, although we can not rule out their direct production at a minor level from an excited state of dinitrotoluene.

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Registry No. 2,6-DNT, 606-20-2; 2,4-DNT, 121-14-2; 3,4-DNT, 610-39-9; 2,6-DNT (*aci*-quinoid form), 24431-33-2; 2,4-DNT (*aci*-quinoid form), 42849-59-2.

⁽¹⁴⁾ Varma, C. A. G. O.; Plantenga, F. L.; Huizer, A. H.; Zwart, J. P.;
Bergwerf, Ph.; Van der Ploeg, J. P. M. J. Photochem. 1984, 24, 133.
(15) Scheerer, R.; Henglein, A. Ber. Bunsen-Ges. Phys. Chem. 1977, 81, 1234.

⁽¹⁶⁾ Ohtani, H.; Kobayashi, T.; Suzuki, K.; Nagakura, S. Bull. Chem. Soc. Jpn. 1980, 53, 43.

⁽¹⁷⁾ Anderson, R. W., Jr.; Hochstrasser, R. M.; Lutz, H.; Scott, G. W. Chem. Phys. Lett. 1974, 28, 153.