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SELECTIVE REDUCTION OF DINITROTOLUENE ISOMERS BY ASCORBATE ION.--ETC(U)
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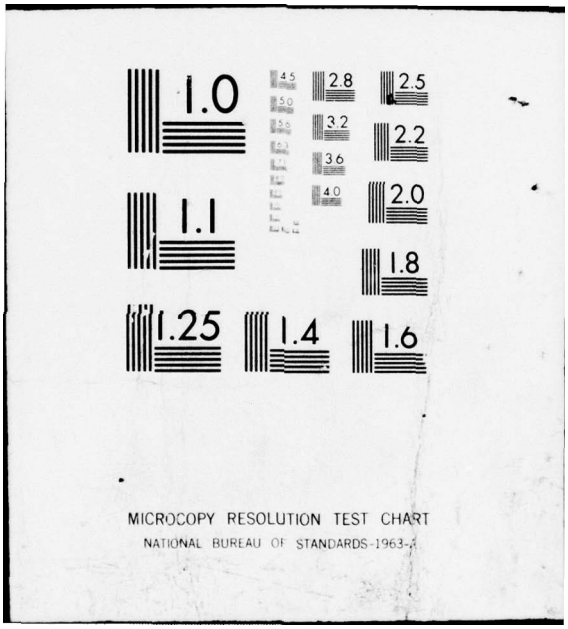
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SELECTIVE REDUCTION OF DINITROTOLUENE ISOMERS BY ASCORBATE ION. RELATIVE RATES IN HOMOGENEOUS SOLUTION

by

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Research Division

February 1978

US ARMY ARMAMENT RESEARCH AND DEVELOPMENT COMMAND
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(18) SBIE (19) AD-E400 084

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SECURITY CLASSIFICATION OF THIS PAGE (When Date Entered)

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REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER: ARCSL-TR-77069	2. GOVT ACCESSION NO. / 3. RECIPIENT'S CATALOG NUMBER
(6) 4. TITLE (and Subtitle): SELECTIVE REDUCTION OF DINITROTOLUENE ISOMERS BY ASCORBATE ION. RELATIVE RATES IN HOMOGENEOUS SOLUTION.	(9) 5. TYPE OF REPORT & PERIOD COVERED: Technical Report, Nov 72–Apr 76
	6. PERFORMING ORG. REPORT NUMBER
(10) 7. AUTHOR(s): Leon J. Schiff, Harold Z. Sommer, George T. Davis	8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS: Director, Chemical Systems Laboratory, Attn: DRDAR-CLB-CA, Aberdeen Proving Ground, Maryland 21010	(16) (17) 10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: Task 1L762720D04803
(11) 11. CONTROLLING OFFICE NAME AND ADDRESS: Director, Chemical Systems Laboratory, Attn: DRDAR-CLJ-R, Aberdeen Proving Ground, Maryland 21010	12. REPORT DATE: Feb 78
	13. NUMBER OF PAGES: 27 → 26 pp
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	15. SECURITY CLASS. (of this report): UNCLASSIFIED
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE: NA

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

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17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Dinitrotoluene isomers	Water soluble reduction products
Selective reduction	Pollution abatement
Ascorbic acid	TNT process
Purification of dinitrotoluenes	Specification grade TNT

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Investigations were conducted with the objective to reduce waste products and the associated water pollution problems arising from the manufacture of trinitrotoluene (TNT). The approach was to remove undesired dinitrotoluene (DNT) isomers by selective reduction with inexpensive carbohydrates, such that the resulting mixture, upon subsequent nitration, would yield specification grade TNT. Using ascorbic acid as a model compound, kinetic studies were performed on five DNT isomers in aqueous acetonitrile at different pH's. Appreciable differences

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20. ABSTRACT (Contd)

in the rates of reduction of the five DNT isomers were obtained indicating that the undesired DNT isomers could be preferentially removed from a crude mixture of DNT. Furthermore, experiments were performed to simulate process conditions. When actual mixtures of DNT isomers were stirred in a basic ascorbic acid solution, the undesired DNT isomers were considerably reduced, whereas the desired 2,4- and 2,6-DNT's were virtually unaffected.

PREFACE

The work described in this report was authorized under Task 1L762720D04803, Environmental Quality Research and Development; Solid Waste. This work was started in November 1972 and completed in April 1976. The experimental data are recorded in notebooks MN2508 and MN2521.

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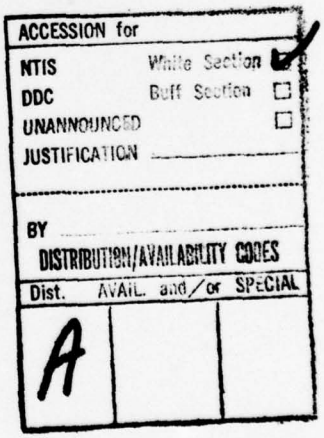

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I. INTRODUCTION.

In the final step of the present trinitrotoluene (TNT) process, the undesired TNT isomers are removed by washing the crude TNT mixture with a hot solution of sodium sulfite (sellite).[1] Disposing of the huge volumes of heavily concentrated and intensely red-colored waste that is generated in the sellite treatment is a major problem in pollution control. Incineration of this red water (one approach to disposal) produced an accumulation of vast stores of solid waste which are considered potentially hazardous to the environment.

Other difficulties in the sellite method include formation of substantial amounts of byproducts and losses of approximately 3% of 2,4,6-trinitrotoluene (α-TNT) product.[2]

In the present configuration of TNT production, purification after the final nitration achieves a high quality product. An alternative to this method is application of a purification treatment at an earlier, intermediate stage of the TNT process. This approach is rendered more credible by the recent development of the Stanford Research Institute (SRI) process, incorporating low-temperature nitration for production of intermediate dinitrotoluenes free of trinitrotoluenes.[3] Chemical treatment of this intermediate mixture can be successful only with selective action directed against the undesirable isomers of dinitrotoluene (DNT). Furthermore, this approach becomes very attractive, because a mixture of pure 2,4- and/or 2,6-DNT should nitrate exclusively to provide high quality α-TNT. The present research is concerned with fundamental development of such a method, which is based upon the chemistry of reduction (not previously considered) of *nitroaromatics.*

Crude DNT consists of five isomers in the approximate quantities shown in figure 1. The isomers in greatest abundance (97% to 98%) are 2,4- and 2,6-DNT. The remaining three unwanted isomers are composed of 3,4-DNT (50% of the group of three), lesser quantities of 2,3-DNT, and even smaller quantities of 2,5-DNT. Although 3,5-DNT is also hypothetically present, the amount is insignificant.

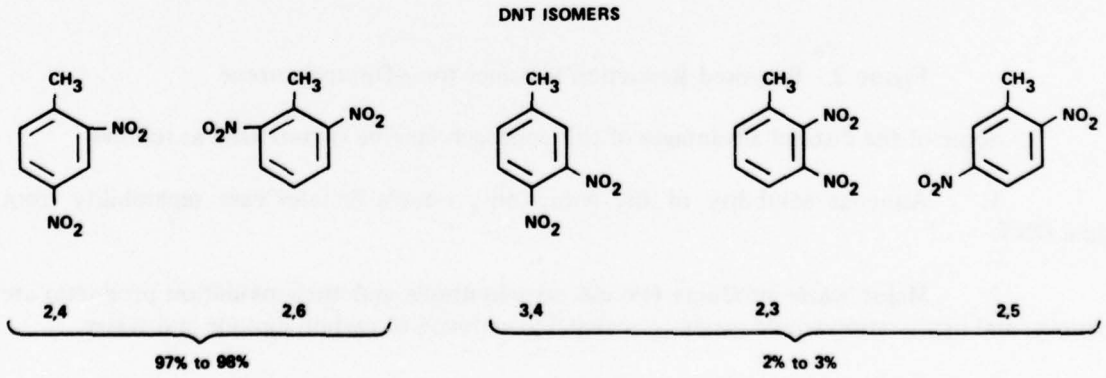

Figure 1. Composition of Crude Dinitrotoluene

Our approach was based upon predicted reactivity differences owing to variation in the disposition of nitro groups on the aromatic nucleus. It was postulated that reductants will attack isomers containing *ortho* dinitro or *para* dinitro groups rather than *meta* dinitro groups. (Similar reactivity differences have been found for nucleophilic attack of the isomers, but sluggishness of the reactions hinders development of practical systems.[1])

A literature search confirmed the approach, as reports of extensive *qualitative* tests (colorimetric) for reducing sugars (e.g., glucose or ascorbic acid) were found.[4-6] Provided the reactions are conducted under basic conditions, *o*-dinitrobenzene (o-DNB) is converted into a water soluble anionic species. Studies of this reaction resulted in the proposal of two different reaction paths and reaction products (figure 2). In the first scheme, two hydrogen atoms are added to *o*-DNB followed by base-induced enolization to the salt of *o*-diaci-dihydro-dinitrobenzene.[7] Another investigator suggested reduction of *o*-DNB to *o*-nitrophenylhydroxylamine followed by base-induced isomerization to the acid form of *o*-nitrosonitrobenzene.[8] Regardless of the precise mechanism and product structure, application of this apparently facile reaction for purification of DNT isomers seemed feasible, i.e., if reducing sugars could be detected by oxidation with *o*-dinitro compounds (thereby reducing the nitro compounds), why not use reducing sugars (in excess) to selectively reduce unwanted DNT isomers with *o*- or *p*-dinitro groups?

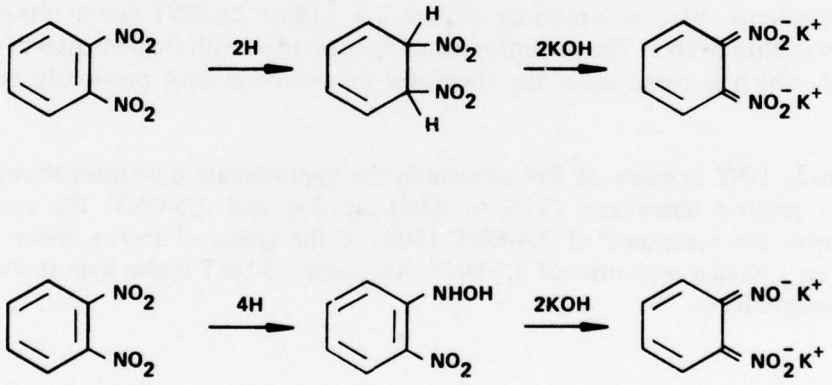

Figure 2. Proposed Reduction Schemes for *o*-Dinitrobenzene

Some of the distinct advantages of this approach may be summarized as follows:

1. Aqueous solubility of the reduction products dictates easy separability from residual DNT.

2. Major waste products (excess carbohydrates and their oxidation products) are innocuous, and incineration would generate acceptable emission of carbon dioxide and water.

3. Reagent sugars are relatively inexpensive and available in bulk.

This report describes studies for evaluating the reactivity of DNT isomers towards ascorbic acid, a model carbohydrate reducing agent. As a result of these studies, additional heterogeneous and homogeneous chemical and electrochemical studies were undertaken, and will appear in a separate report.*

Initially a homogeneous system was chosen, since feasibility of a heterogeneous system rests partly on rates in *homogeneous* solution. Additional uninterpretable design variables appear in heterogeneous systems which normally must be evaluated empirically for a set configuration. Since DNT's are very slightly soluble in water, it was necessary to incorporate a cosolvent. Acetonitrile was chosen because it is commercially available as high-purity material. Further, as compared with organic solvents in general, the dielectric constant of acetonitrile is high. Acetonitrile is also comparatively "inert" towards acids, bases, and reducing reagents. Therefore, an 80–20 acetonitrile water medium was chosen.

Addition of external buffers proved not to be practical because of solubilities in the desired-buffering range or ionic strength effects which could not be assessed. Therefore, ascorbate ion-hydroxide was used as the buffering system (internal), with a high background (0.5 M) of sodium chloride to provide a constant "swamping" ionic strength. The overall medium poses several difficulties in accurate and interpretable readings, however. The dissociation constant of ascorbate ion to the dianion is lowered by the reduction in dielectric constant. Hence, solutions of high alkalinity were required for dissociation to dianion. (Prior to actual commencement of studies, it was ascertained that, qualitatively, reduction proceeded at reasonably fast rates only at relatively high alkalinity. It was, therefore, postulated that the dianion of ascorbic acid must be the most active species in reduction).

Potentiometric measurement of pH with the glass electrode-calomel system in this medium also presents several problems. First, measurements at high alkalinity may produce pH-dependent junction potentials which will affect values in a systematic, but unpredictable way. Also, pH measurements in this medium are only "operationally" defined as pH, since standardization requires external *aqueous* buffers. To provide pH measurements in the absolute sense of the definition requires establishment of electromotive force (EMF) response patterns to $[H^+]$ with the electrode system employed, followed by establishment of true pKa values in the medium for buffer systems utilized for standardization. Finally, there would be desired a determination of Kw for the system at the ionic strength employed. Investigation of these pH considerations is a separate research problem and was not pursued. Operational pH values were employed throughout and, for the purposes of kinetics, it should have been possible to derive an operational pKa for ascorbic acid dianion. However, sodium (or other cation) response to the glass electrode is undefined in 80–20 acetonitrile water, so that corrections for this effect could not be applied.

These combined difficulties prevented the actual establishment of an operational pKa for ascorbate ion which could be applied to interpretation of the kinetic data (see appendix A). The chosen system also limits the range of data obtained, and this self-limiting feature hinders the establishment of rate laws, particularly if complex expressions involving more than one rate coefficient are required.

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*Davis, G. T., Schiff, L. J., Gorrell, J., and Sommer, H. Z. Further Studies on the Selective Reduction of Dinitrotoluenes. Report in preparation.

II. PROCEDURES AND RESULTS.

Initial efforts described herein were concerned with a study of the rates of ascorbic acid reduction of the individual DNT isomers. Experiments were conducted at 25°C under pseudo first-order conditions over a range of basic pH values in an aqueous acetonitrile (80/20) medium whose ionic strength was maintained constant by the addition of 0.5 M sodium chloride. The buffering point was controlled by varying the amounts of standardized carbonate-free sodium hydroxide added to the sodium ascorbate solutions. Equal volumes of ascorbate stock solutions and DNT stock solutions were mixed to produce a reaction medium containing 0.01 M total ascorbate species.

As 2,3-, 3,4-, and 2,5-DNT isomers produced highly colored reaction products, rates of reduction of these isomers were determined spectrophotometrically. The spectrophotometer was set at 550 nm for 2,3-DNT, and 540 nm for 3,4-DNT.

Reduction of 2,5-DNT was followed at 540 nm in an Aminco-Morrow stopped-flow apparatus. Rate constants and half lives for the 2,3-, 3,4-, and 2,5-DNT isomers are recorded in table 1.

Since the 2,4- and 2,6-DNT isomers did not produce a colored reaction product, their rates of reduction were determined by following their disappearance on a gas chromatograph. Rate data for these isomers are also displayed in table 1.

To evaluate the practical utility of selective reduction, a few experiments simulating process conditions were performed. In these experiments 1.0 gram of a mock, crude DNT mixture was treated with 10 ml of a pH 11.49 solution containing 1.0 gram of sodium ascorbate. Starting material disappearance was analyzed by gas chromatography. Data are recorded in table 2. After 10 minutes, significant losses of the undesired isomers had occurred while the 2,4- and 2,6-DNT isomers were completely recovered. A 20-minute contact time was sufficient to remove 2,5-DNT completely, and reduce the amounts of 3,4- and 2,3-DNT substantially. Although full retention of 2,4-DNT was realized, a 20-minute exposure did have a small effect upon the 2,6-DNT isomer.

III. EXPERIMENTATION.

A. Preparation of Solutions.

1. DNT Isomers.

For 2,3-, 3,4-, and 2,5-DNT, 0.00455 gram of the DNT isomer (10^{-4} M) and 7.31 grams of sodium chloride (0.5 M) were added to a 250-ml volumetric flask which was filled to the mark with 80/20 aqueous acetonitrile.

For 2,4- and 2,6-DNT, 0.09107 gram of the DNT isomer (10^{-3} M) and 14.61 grams of sodium chloride (0.5 M) were added to a 500-ml volumetric flask which was filled to the mark with 80/20 aqueous acetonitrile.

2. Ascorbate Solutions.

To a 250-ml volumetric flask were added 1.98 grams (0.04 M) of sodium ascorbate and 14.62 grams of sodium chloride (1 M). The flask was filled to the mark with 80/20 aqueous acetonitrile.

Table 1. Pseudo First-Order Rates of Reduction of Dinitrotoluene Isomers

pH	2,5-DNT rate	Half life $t_{1/2}$	3,4-DNT rate*	Half life $t_{1/2}$	2,3-DNT rate*	Half life $t_{1/2}$	2,4-DNT rate*	Half life** $t_{1/2}$	2,6-DNT rate*	Half life $t_{1/2}$
	sec^{-1}	sec	sec^{-1}	sec	sec^{-1}	sec	hr^{-1}	hr	hr^{-1}	hr
11.560	9.93×10^{-2}	7	9.38×10^{-3}	74	2.41×10^{-4}	2878				
11.723	1.72×10^{-1}	4	1.73×10^{-2}	40	4.52×10^{-4}	1535				
11.865	2.71×10^{-1}	3	2.83×10^{-2}	25	6.62×10^{-4}	1047	0.11	6.2		
12.155	3.37×10^{-1}	2	3.98×10^{-2}	17	1.42×10^{-3}	488	0.28	2.5		
12.333	3.82×10^{-1}	2	6.21×10^{-2}	11	2.10×10^{-3}	330	0.45	1.5	1.75×10^{-2}	39.6
12.473	3.68×10^{-1}	2	8.52×10^{-2}	8	2.69×10^{-3}	258	1.26	0.6	2.35×10^{-2}	29.5

*Imperfect first-order plots under pseudo first-order conditions.

** First-order plots improved when run under an argon atmosphere. Also, the derived rate constants were somewhat greater.

Table 2. Analysis of Dinitrotoluene (DNT) Isomer Solutions Before and After Reduction

Reaction time	2,4-DNT		2,6-DNT		3,4-DNT		2,3-DNT		2,5-DNT		Weight percent loss
	Weight percent	Percent recovered	Weight percent	Percent recovered	Weight percent	Percent recovered	Weight percent	Percent recovered	Weight percent	Percent recovered	
min											
0	83.20	–	13.84	–	1.72	–	0.94	–	0.30	–	–
10	83.15	100	13.73	99	0.60	35	0.51	45	0.06	20	1.95
20	83.20	100	12.52	90	0.35	20	0.31	33	–	–	3.62

A 25-ml aliquot of the 0.04 M ascorbate solution was placed in a 50-ml volumetric flask. To this a measured volume of 0.8725 M carbonate free sodium hydroxide and a quantity of acetonitrile equivalent to 20% of the added base were added. This solution was diluted to the mark with 80/20 aqueous acetonitrile. The ascorbate concentration was reduced to 0.02 M.

B. Determination of Rates.

1. Spectrophotometric Determinations.

To provide a final concentration of 0.01 M ascorbate, 2.5 ml of the 2,3- or 3,4-DNT solution and 2.5 ml of the 0.02 M basic ascorbate were added to a 2-cm cell. After shaking, the cell was placed in a Cary 14 spectrophotometer and measurements were started within 15 seconds of mixing. The 2,3-DNT was observed at 550 nm and the 2,4-DNT was observed at 540 nm. The reactions were followed to completion and the rates and half lives were calculated using a computer program for pseudo first-order kinetics.

2. Stopped-Flow Kinetics of 2,5-DNT with Ascorbate Ion.

The reactions were followed in an Aminco-Morrow stopped-flow apparatus at 540 nm. The apparatus was fitted with a thermostat set at 25.0°C. Solutions were prepared to give (on 1:1 mixing of two reaction solutions) a final reaction solution containing 0.01 M total ascorbic acid species, ionic strength of 0.5 M (compensated with sodium chloride), 1.0×10^{-4} M 2,5-DNT, all in a medium of 20% (by volume) acetonitrile and 80% (by volume) water. For example, stock solution (A) of 2×10^{-4} M DNT was prepared in 20% acetonitrile and 80% water containing 0.50 M sodium chloride. Then, a primary stock solution (B) was prepared of 0.0400 M sodium ascorbate in 1.00 M sodium chloride in 20% acetonitrile and 80% water. Secondary stock solutions (C) were constructed using 25 ml of (B) with varying amounts of 1 M sodium hydroxide (0.100 to 0.800 ml) and diluted to a final volume of 50 ml with 20% acetonitrile and 80% water. In the stopped-flow apparatus, equal volumes of (A) were mixed with equal volumes of (B). The apparent pH of the mixed reactant solution was measured on a Beckman Research pH meter with glass/saturated calomel electrodes. The kinetic data were computer-analyzed by a program for pseudo first-order kinetics.

C. Potentiometric Determination of the Second Ionization Constant of Ascorbic Acid in 80/20 Water-Acetonitrile.

Solutions were prepared to contain the total ascorbic acid species of 0.0100 M with accurately measured sodium hydroxide contents and enough sodium chloride to provide 0.50 ionic strength. Apparent pH values were measured on a Beckman pH meter equipped with glass and saturated calomel electrodes. Parallel solutions containing all species except sodium ascorbate were prepared. The background pH obtained from the latter solutions provided the molarity of sodium hydroxide necessary to titrate the medium to a given pH. The medium titration was conducted from 1.00×10^{-4} to 2.5×10^{-3} M sodium hydroxide. From these data the apparent pKa and ascorbate dianion concentration were calculated.

D. Treatment of Crude DNT with Ascorbate.

To 1 gram of mock crude DNT mixture (composition: 2,4-DNT, 83.20%; 2,6-DNT, 13.84%; 3,4-DNT, 1.72%; 2,3-DNT, 0.94%; and 2,5-DNT, 0.30%) in a 25-ml round-bottom flask

was added 10 ml of a pH 11.49 ascorbate solution prepared by dissolving 5 grams of sodium ascorbate in 50 ml of 0.8725 M sodium hydroxide. In one experiment the mixture was stirred for 10 minutes and in the other experiment the mixture was stirred for 20 minutes. The solids were filtered, washed with water until the wash was colorless, and placed in a vacuum dessicator to dry.

For the 10-minute experiment, 28.93 mg of product was placed in 1.5 ml of benzene containing dinitroxylene as an internal standard. A 31.19-mg sample in the same volume of solution was used for the 20-minute experiment. These solutions, along with a solution of the starting mixture, were analyzed by gas chromatography on a Hewlett-Packard 7610 equipped with a 4-inch by 1/4-inch column filled with 5% Carbowax 20 M on Chromosorb W AW, 60/80 mesh. The following conditions were used: column, 200°C; FID, 300°C; injector, 200°C; and helium carrier flow, 60 ml/min. The data were processed and the concentrations calculated by an Autolab System IV Computing Integrator.

IV. DISCUSSION.

The data in table 1 show that for all isomers the rates were pH dependent, increasing as the solutions became more basic. All of the data may have also been influenced by atmospheric oxygen. This effect has been inadequately examined, and may contribute to uncertainty in the determination of rate laws for the processes. Furthermore, at all pH's the reaction rates decreased in the order of 2,5-DNT > 3,4-DNT > 2,3-DNT > 2,4-DNT > 2,6-DNT, as illustrated in figure 3. These results confirmed our expectations that the undesirable 2,5-, 3,4-, and 2,3-DNT isomers are more easily reduced than the isomers we wish to retain.

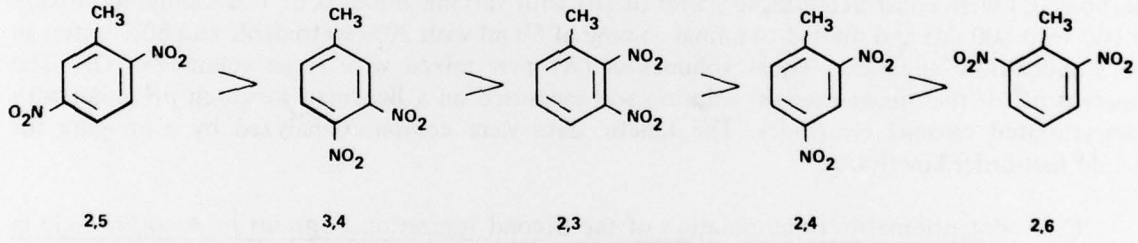

Figure 3. Decreasing Order of Reduction Rates of Dinitrotoluene Isomers with Sodium Ascorbate

The observed differences in the rates of reduction of the three unwanted isomers (table 1) can be explained by invoking steric considerations. The electronic configuration of the reduction products (figure 4) requires that the two nitro groups be coplanar with the aromatic ring. Thus, 2,3-DNT, the most crowded of the three isomers, exhibits the slowest rate in this group. The 3,4-isomer reacts, depending upon pH, about 30 to 40 times as fast as the 2,3-isomer. Although the nitro groups are still adjacent, their separation from the methyl group has a pronounced effect upon the rate. A fivefold to tenfold increase in rate over that of the 3,4-isomer was observed for 2,5-DNT. Apparently, a nitro group adjacent to a methyl group has an easier time becoming coplanar with the ring than a nitro group adjacent to another nitro group that also wishes to adopt the same configuration. Greater charge separation (figure 4) in the reduction product of the para-substituted isomer might also account for the 2,5-DNT being the most reactive isomer.

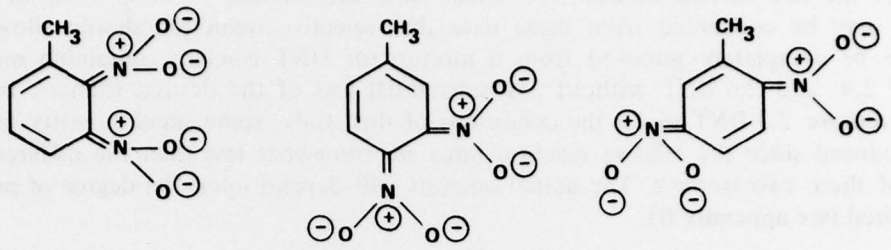

Figure 4. Possible Structures of the Reduction Products of Unwanted Dinitrotoluene Isomers

If resonance forms of the type needed for one or two electron transfers are important contributors, then steric inhibition of resonance which is a unique feature of ortho-disubstituted systems could also explain the difference in reactivity between the ortho- and para-substituted compounds.

In the case of the 2,4- and 2,6-DNT isomers, resonance forms in which the positive charge resides on a carbon atom attached to a nitro group cannot be realized (figure 5). This might explain why these isomers behave in a totally different manner under the reaction conditions. Reduction products derived from the 2,4- and 2,6-isomers consist of insoluble material rather than water-soluble colored species.

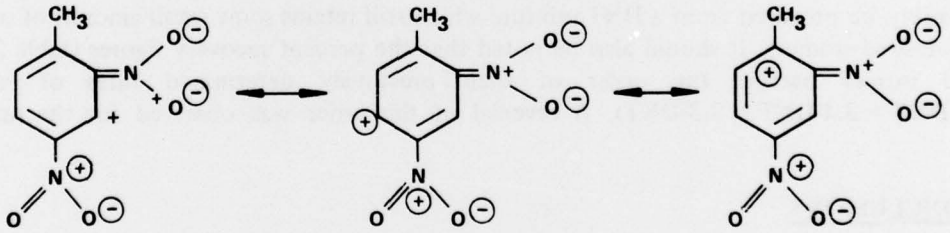

Figure 5. Resonance Forms of 2,4-Dinitrotoluene

Another important aspect of this particular system is the large difference between the amounts of the unwanted and desired isomers that constitute the crude DNT mixture. Thus, not only must the unwanted isomers be more easily reduced, but their rates must be tremendously faster than those of the desired DNT isomers. This condition is necessary so that none of the 2,4- and 2,6-DNT will be affected in the course of removing unwanted DNT isomers (see appendix B).

In table 3 the ratios of the rates of the 2,3-, 3,4-, and 2,5-isomers relative to 2,4-DNT, the faster of the two desired isomers, are listed. Note the increase in these ratios as the pH is lowered. It may be concluded from these data that selective reduction should allow 2,5- and 3,4-DNT to be completely removed from a mixture of DNT isomers containing much larger amounts of 2,4- and 2,6-DNT without any substantial loss of the desired isomers. In order to completely remove 2,3-DNT under the conditions of this study, some small quantity of 2,4-DNT would be reduced since the relative reaction rates are somewhat less than the difference in the quantities of these two isomers. The actual amount will depend upon the degree of purification which is desired (see appendix B).

Table 3. Rates of Reduction of 2,5-, 3,4-, and 2,3-Dinitrotoluene (DNT), Relative to 2,4-Dinitrotoluene

pH	2,5-DNT	3,4-DNT	2,3-DNT
11.865	8856	925	22
12.155	4332	512	18
12.333	3056	497	17
12.473	1051	243	8

The failure to observe excessive loss of the desired isomers when a crude DNT mixture is treated with ascorbate is very significant. The data in table 2 demonstrate the high selectivity of this system in which the undesired isomers exhibit a much greater sensitivity towards the reducing agent. This type of heterogeneous treatment, in effect, simulates the approach that would have to be utilized if selective reduction is adapted to a manufacturing process. Another consideration is that complete removal of the undesired isomers might not be necessary. Specification grade TNT could possibly be prepared from a DNT mixture which still retains some small amount of one or all of the undesired isomers. It should also be noted that the percent recovery figures (table 2) of the undesired isomer parallel the order of their previously determined rates of reduction (i.e., 2,5-DNT > 3,4-DNT > 2,3-DNT). A reversal of the order was observed for the other two isomers.

V. CONCLUSIONS.

Our efforts have shown that, in a basic ascorbate solution, dinitro aromatic compounds in which the nitro groups are ortho or para to each other are more easily reduced than those compounds in which the nitro groups are meta to one another. This difference in reactivity has been utilized to selectively remove undesired DNT isomers from crude mixtures of DNT. The reduction products, being water soluble, are easily separable from the unreacted isomers. Further studies are required to improve the efficiency of this process; that is, finding the minimum quantity of reducing agent that will be necessary to effect complete removal of the undesired isomers in the shortest possible time.

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APPENDIX A

MECHANISTIC RELATIONSHIPS TO CONJUGATIVE ELECTRONIC EFFECTS. FAILURE TO OBTAIN RATE LAW BEARING ON MECHANISM. HYPOTHETICAL MODELS

Ascorbic acid is dibasic, providing a monoanion, $HAsc^{\ominus}$, at slightly basic pH values and a more reactive dianion at higher pH values. The steady increase in rates of reduction with increasing pH suggested that the ascorbate dianion, $Asc^{\ominus}$, was the active species in this system. To determine the extent of the $Asc^{\ominus}$ participation in the reduction, its concentration as a function of pH had to be established (i.e., its second dissociation constant). Attempted determination of pKa was conducted potentiometrically at the same ionic strength and in the same medium as the reaction system for kinetics. The difference between total added hydroxide ion concentration and the hydroxide ion concentration corresponding to titration of the medium to the given pH corresponded to the concentration of ascorbate dianion. The pK_a was then calculated from the formula:

$$pK_a = pH + \log \left[\frac{HAsc^{\ominus}}{Asc^{\ominus}} \right]$$

Five values over the pH range 11.534 to 12.671 gave an average pK_a of 11.85 ± 0.03. When these data were incorporated into calculations to determine the order with respect to ascorbate dianion for the three unwanted isomers, no satisfactory first- or second-order fit was obtained. Mixed first and second orders were also unsatisfactory. More complicated expressions were not sought, for the precision and range of the data do not warrant determination of several independent parameters.

In another attempt to elucidate the role of the ascorbate dianion, a model was postulated in which it was assumed that the reaction was first order with respect to ascorbate dianion and exhibited no dependency upon the other variable species (other than DNT) in the reaction medium. The following equation could then be derived:

$$\frac{[Asc]_T}{R_o} = \frac{H^{\oplus}}{R_2 K_a} + \frac{1}{R_2} \qquad (1)$$

R_o = observed pseudo first-order coefficient

R_2 = derived second-order coefficient

K_a = second dissociation constant for ascorbic acid

Asc_T = total ascorbate concentration

Treatment of the 2,5-dinitrotoluene (DNT) rate data (21 values), according to this equation (by least squares), gave no significant intercept (small negative value). Hence, pK_a could not be derived. However, the plot was linear (correlation coefficient 0.996) and provided an

apparent value for R_2K_a of 2.94×10^{-11}. The value of the linear correlation coefficient may be misleading since variables are transformed to obtain linear treatment. (The actual equation is nonlinear with respect to the experimental variables.)

An alternative method of plotting (statistically, even less interpretable) is derived from the following equation (with the same physical model):

$$R_o[H^+] = R_2K_a[Asc]_T - (R_o)(K_a) \qquad (2)$$

The equation would be linear with respect to the plot of $R\,[H^+]$ versus R_o. However, these variables are not independently separated. Linear treatment of this data (least squares provided a value from a scatter diagram) for K_a of $3 \pm 2 \times 10^{-3}$. (The $pK_a = 12.5$.) This is an exceedingly high pK_a value and would be difficult to determine by any method. The intercept provides $R_2K_a = 3.11 \times 10^{-11}$, a value consistent with the reciprocal plot (equation 1). This would give $R_2 = 1 \times 10^2\ M^{-1}\ sec^{-1}$. The poor fit of the data could result from an incorrect model, *or* systematic mathematical derivations produced by the many inherent faults in the system (as previously described). Consequently, the data cannot establish the rate law or mechanism unambiguously. However, the strong pH dependency at high alkalinity points to the heavy involvement of ascorbate dianion in the reduction process. The inadequacy of the model (or data) is emphasized by utter failure when applied to data from 3,4-DNT kinetics. Here, the dissociation constant from the model is, from a total scatter diagram, completely undefined. Reciprocal plot (as in equation 1) produces curvature, especially near the intercept where it is least desired.

Although the increase in rate at high pH values suggests that the active reducing species is probably the dianion of ascorbic acid, there may be a significant contribution from the monoanion. Inability to establish the rate law for the processes prohibits selection of a mechanism from a number of reasonable hypothetical models, some of which are shown in figure A.

Either a stepwise or concerted electron transfer from ascorbate dianion to the aromatic system is possible. Nucleophilic addition followed by internal scission with a two-electron transfer is also reasonable. Complex chain mechanisms with stepwise electron transfers could occur, with anion radical carriers. These possibilities are illustrated in figure A. Depending upon the rate law, kinetics should be able to reduce the number of applicable models, but a better working system must be found to increase the range and quality of data obtainable for these interpretations to be made.

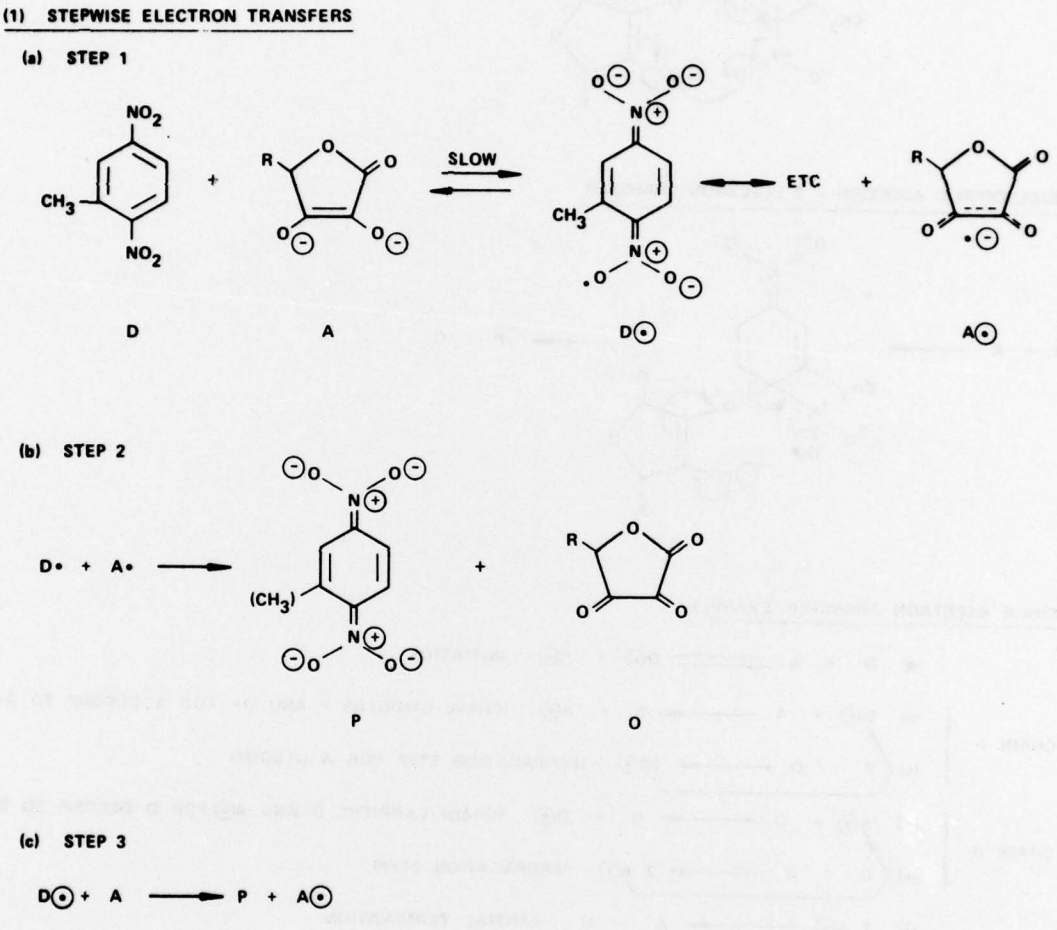
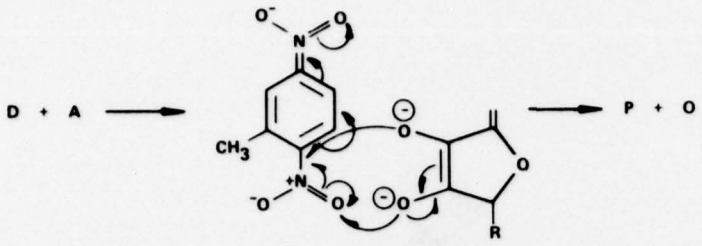
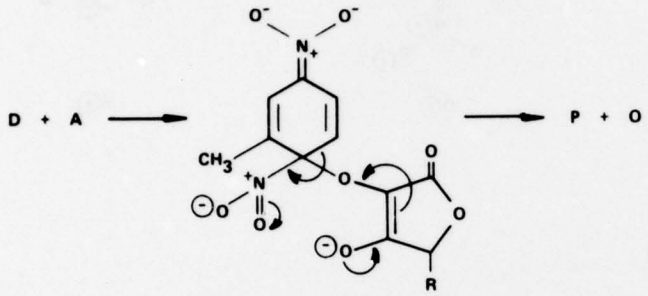


Figure A. Some Hypothetical Mechanisms for Ascorbate Reduction of Dinitrotoluenes

(2) TWO-ELECTRON CONCERTED TRANSFER



(3) NUCLEOPHILIC ADDITION – 2 ELECTRON TRANSFER



(4) CHAIN ELECTRON TRANSFER EXAMPLE

(a) D + A ⇌ D⊙ + A⊙ INITIATION

CHAIN I

(b) D⊙ + A → P + A⊙ (CHAIN CARRIERS P AND D• FOR A DECOMP TO A•)

(c) P + D → 2D⊙ (PROPAGATION STEP FOR A DECOMP)

CHAIN II

(d) A⊙ + D → O + D⊙ (CHAIN CARRIERS O AND A⊙ FOR D DECOMP TO D⊙)

(e) O + A → 2 A⊙ (PROPAGATION STEP)

(f) 2 A⊙ → A + O PARTIAL TERMINATION

(g) 2D⊙ → D + P PARTIAL TERMINATION

(h) A⊙ + D⊙ → P + O TERMINATION

Figure A. (Contd)

APPENDIX B

REQUIREMENTS FOR A SELECTIVITY FACTOR FOR TRINITROTOLUENE MIXTURES IN HOMOGENEOUS SOLUTIONS UNDER PSEUDO FIRST-ORDER CONDITIONS

Let U be an undesired isomer and D be a desired isomer. Then the following parameters can be defined:

R_1 = pseudo first-order rate constant for U

R_2 = pseudo first-order rate constant for D

(U_o) = initial concentration of U

(D_o) = initial concentration of D

Then the ratio any time, t, will be given the selectivity factor for any time:

$$D/U = (D_o)e^{-R_2 t}/(U_o)e^{-R_1 t} \tag{B1}$$

In order to evaluate the usefulness of the system it is necessary to consider the selectivity independent of initial concentrations, i.e.,

$$(D/U)/(D_o)/(U_o) = e^{-R_2 t}/e^{-R_1 t} = e^{(R_1 - R_2)t} \tag{B2}$$

We set standards for the improvement in ratio and for the degree of attack upon D. Let the improvement be 10X and attack upon D be 1%.

$$\log 10 = \frac{(R_1 - R_2)t}{2.303} \tag{B3}$$

$$2.303 = (R_1 - R_2)t \tag{B4}$$

Now suppose the allowable attack upon D is 1%.

$$\frac{D}{D_o} \cong \frac{99}{100} = e^{-R_2 t} \tag{B5}$$

$$-0.00436 = -\frac{R_2 t}{2.3} \qquad (B6)$$

$$R_2 t = 0.0100 \qquad (B7)$$

$$R_1 t = 2.303 + 0.01 = 2.313$$

The equation (B7) defines the *ratio* R_1/R_2 as 2.31×10^2, which is the minimum by which the result may be obtained. Equation B4 defines a different requirement, namely that, $R_1 t - R_2 t = 2.3$. Combining the two conditions, we can prepare table B.

Table B. Reaction Time, as a Function of Rate, Required to Meet Specifications

R_2	R_1	Reaction time for desired result
sec^{-1}	sec^{-1}	sec
1×10^{-4}	2.31×10^{-2}	100
1×10^{-3}	2.31×10^{-1}	10
5×10^{-3}	1.055×10^{-1}	5
1×10^{-2}	2.31	1
5×10^{-2}	1.055	0.5
1×10^{-1}	23.1	0.1

Preparation of such a table leads to several obvious conclusions. First, the stated time for the desired result becomes very critical with fast reactions (to prevent loss of D simultaneously with achievement of the desired ratio). Accurate timing will be necessary if R_1/R_2 fulfills only the minimum requirements, in any case. (Although further reaction would improve the product ratio, it would exceed the attack requirement for the desirable material.)

The equation (B7) described can be used to obtain *minimum* (R_1/R_2)'s for any homogeneous case where the reductant is in excess and follows pseudo first-order kinetics, once the practical limit of attack of the desirable isomers has been established. The data (table 1, text) show that the selectivity has easily been achieved by the system under study for all of the undesirable isomers versus the desirable ones.

However, this result is not generally applicable (even in homogeneous solution) when reductants are not present in large excess.

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