Registry No.—**1**, 935-79-5; **2**, 36337-42-5; **3**, 35438-81-4; **4**, 2746-19-2; **5**, 129-64-6; **6**, 56587-29-2; **7**, 56587-27-0; **8**, 56587-28-1; **9**, 24327-08-0.

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(15) We have utilized coordinate averaging rather than shift averaging as a matter of manipulative convenience. A detailed comparison of these methods as well as a more complete description of the PDIGM procedure is contained in ref 5a. The number of different proton shifts utilized in the PDIGM calculation were **1**, 4; **2**, 4; **3**, 3; **4**, 5; **5**, 5; **6**, 5; **7**, 4; **8**, 4; **9**, 4.

(16) The sensitivity of the Servis method to proper models can readily be appreciated in the observation that **9** does not seem *folded* relative to the norbornyl models. That the PDIGM method could give results compatible with those from the Servis method was tested by compressing the computor coordinate system of the cyclohexene moiety of **1** so that the vinyl protons were closer to the anhydride ring (i.e., more resembling the norbornyl system). PDIGM found a minimum *R* of 2.16% at an 80:20 (*folded:open*) mix. Thus, we see that the PDIGM mix starts to approach that observed by the Servis method. And, because a reasonable minimum was found, the importance of good molecular coordinates in conformational work is indicated.

Micellar Effects on the Reaction of 2,4,6-Trinitrotoluene with Amines

Yoshiyuki Okamoto* and Joseph Y. Wang

Department of Chemistry, Polytechnic Institute of New York, Brooklyn, New York 11201

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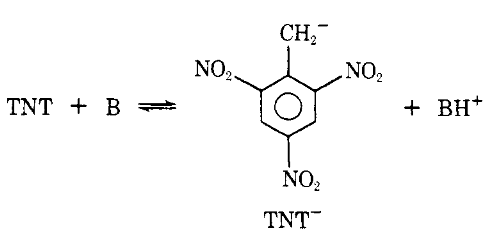
It is known that 2,4,6-trinitrotoluene (TNT) has a limited solubility (~5 × 10^{-4} M) in water at room temperature and produces a highly colored solution when reacted with strong bases.[1-6] The reaction has been interpreted as due to the formation of an intermediate, 2,4,6-trinitrobenzyl anion (TNT^-), which absorbs light in the visible region (at 500–525 nm).



In the presence of pyridine, TNT was found to react with benzaldehyde and 2,4,6-trinitrostilbene was produced. The intermediate was proposed to be TNT^-.[1]

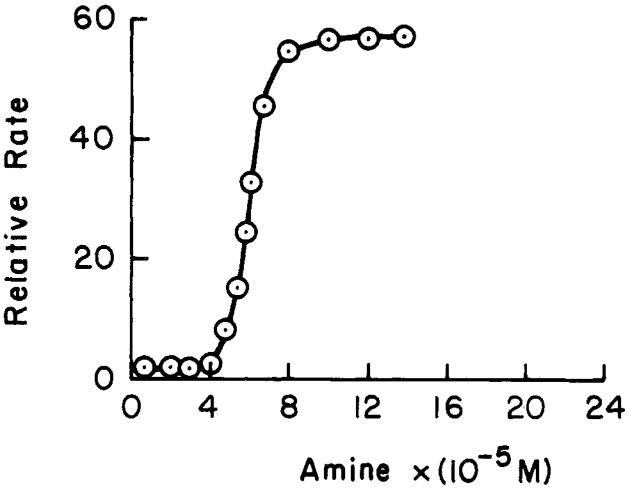


Figure 1. Relative rate of the formation of TNT^- vs. the concentrations of 4-dodecyldiethylenetriamine and 3,3′-diamino-*N*-methyldipropylamine at 25 °C in aqueous solutions. Initial concentration of TNT was 2.5 × 10^{-4} M.

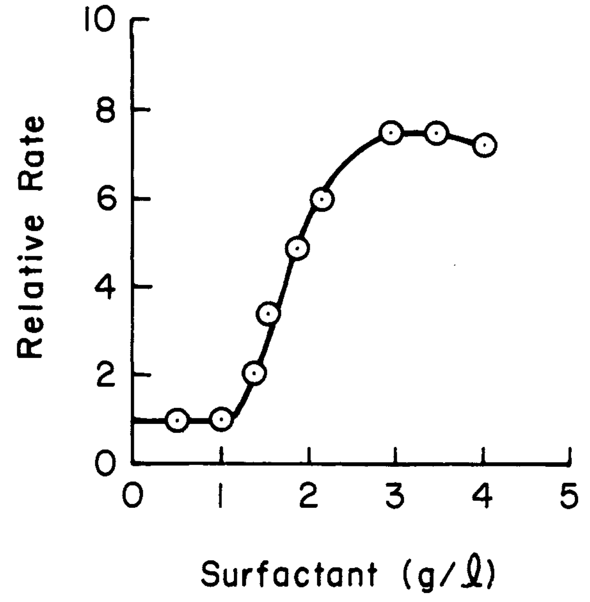


Figure 2. Relative rate for the formation of TNT^- in the reaction of TNT with II as a function of the concentration of alkylphenoxypolyethoxyethanol in aqueous solution at 25 °C. Initial concentrations of TNT and II were 2.5 × 10^{-4} and 1 × 10^{-3} M, respectively.

In the present work we investigated the reaction kinetics of TNT in aqueous solutions with two amines, i.e., 4-dodecyldiethylenetriamine (I), which is a surfactant, and a non-surface-active triamine, 3,3′-diamino-*N*-methyldipropylamine (II). The results are shown in Figure 1. It was observed that I has a critical micelle concentration at about 5 × 10^{-5} M.[7] Below this concentration, the reaction rates of TNT with I and II were identical. However, above the critical micelle concentration of I, the reaction rate of TNT with I increases sharply and eventually levels off. The rate increase is about 55-fold compared to the same reaction of TNT with II and the enhancement is accounted for by the micellar effect.[8]

In order to study the micellar effect further, the reactions of TNT with II were explored in the presence of both nonionic and ionic surfactants. Surfactants used were alkylphenoxypolyethoxyethanol and hexadecyltrimethylammonium bromide. These results are summarized in Figures 2 and 3. The rates were found to be increased in the presence of both sur-

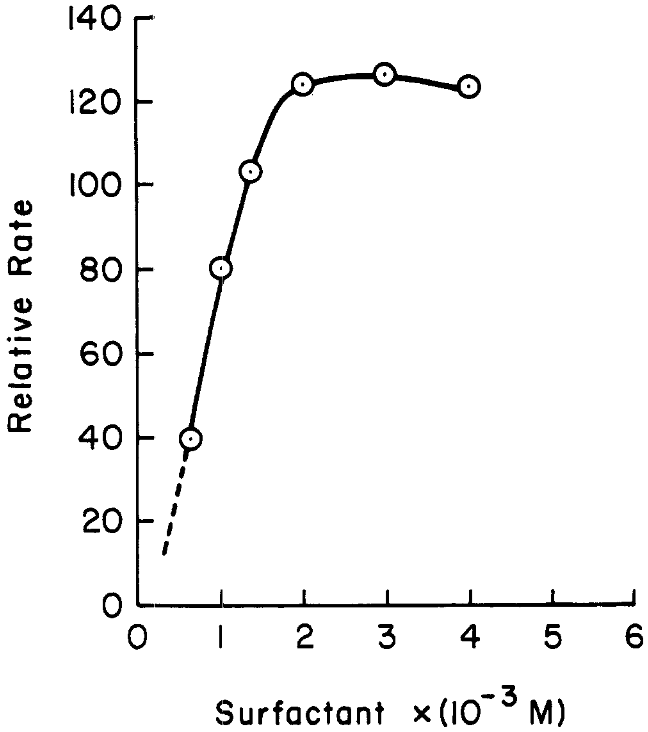


Figure 3. Relative rate for the formation of TNT$^-$ in the reaction of TNT with II as a function of the concentration of hexadecyltrimethylammonium bromide in aqueous solution at 25 °C. Initial concentrations of TNT and II were 2.5×10^{-4} and 1×10^{-3} M, respectively.

factants. The enhanced rate was more pronounced with the cationic surfactant than the nonionic one (cf. 130 vs. 8). The critical micelle concentration of hexadecyltrimethylammonium bromide is 9.2×10^{-4} M.[9] It was observed that the rate was greatly increased above this concentration. For low concentrations of hexadecyltrimethylammonium bromide ($<9 \times 10^{-4}$ M), the reaction rate of TNT with II cannot be detected since precipitation was observed.

Experimental Section

Materials. 2,4,6-Trinitrotoluene was purchased from Eastman Kodak Co. and purified by recrystallizing twice from ethanol. 4-Dodecyldiethylenetriamine and hexadecyltrimethylammonium bromide were also purchased from Eastman Kodak Co. and used without further purification. Alkylphenoxypolyethoxyethanol, Triton X-100, and 3,3′-diamino-*N*-methyldipropylamine were obtained from Rohm and Haas Co. and Jefferson Chemical Co., Inc., respectively.

Reaction Rate Measurements. The reaction rates of TNT with I and II were measured at 25 °C in 1- or 10-cm UV cells by following the absorbance at 525 nm using a Cary 14 spectrophotometer.

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Registry No.—I, 4182-44-9; II, 105-83-9; 2,4,6-trinitrotoluene, 118-96-7.

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Reactions of α-Phenylpolynitrotoluenes. 4. Ortho-Nitro Rearrangements in the Polynitrodiphenylmethanes

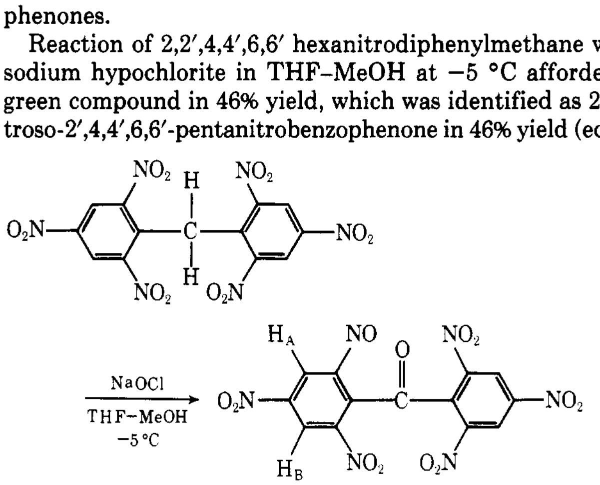
Lloyd A. Kaplan,[1] Isaac A. Angres,*[2] and Kathryn G. Shipp

Explosives Chemistry Branch, Naval Surface Weapons Center, White Oak Laboratory, Silver Spring, Maryland 20910

Received September 8, 1976

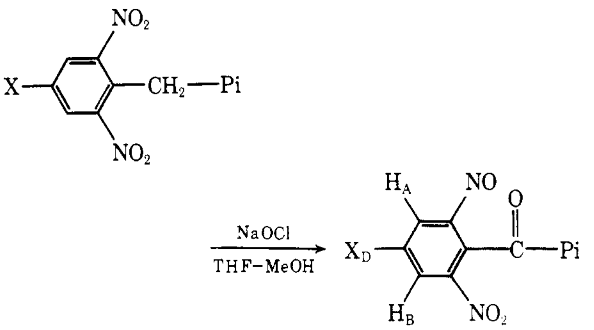
The previous paper in this series[3] described the preparation of some polynitrodiphenylmethanes. In our efforts to synthesize from these compounds tetrakis(polynitrophenyl) ethylenes,[3b] in analogy to the preparation of hexanitrostilbene[3b] from 2,4,6-trinitrotoluene, we investigated their reaction with sodium hypochlorite. The products from these reactions were, however, found to be nitrosopolynitrobenzophenones.

Reaction of 2,2′,4,4′,6,6′ hexanitrodiphenylmethane with sodium hypochlorite in THF–MeOH at −5 °C afforded a green compound in 46% yield, which was identified as 2-nitroso-2′,4,4′,6,6′-pentanitrobenzophenone in 46% yield (eq 1).



(1)

Similarly, 4-substituted pentanitrodiphenylmethanes afforded the corresponding nitroso ketones in 40–50% yield, the results being summarized in eq 2. Proof of structure of the above compounds was obtained by elemental analyses, by NMR measurements, and by IR and mass spectroscopy. Evidence for the carbonyl and nitroso groups came from the infrared spectra in which absorptions in the range 1650–1700 (C═O) and 1550 and 1600 cm^{-1} (NO_2 and NO) were observed; and the fact that all the compounds were emerald green (aromatic nitroso) in color. The NMR spectra show that the 2,4,6-trinitrophenyl (Pi) group remained intact during the course of the reaction (singlet, 2 H, in the region 9.30–9.44 ppm relative to Me_4Si) as previously observed for other picryl derivatives,[3] and that the nitroso group was formed in the other ring (see eq 2). The hydrogens of the ring containing the nitroso function show the expected splitting pattern for nonequivalent hydrogen (see Experimental Section). The mass spectra are also in agreement with the proposed structures as the molecular weights obtained exactly matched the expected theoretical values.



(2)

Pi = 2,4,6-trinitrophenyl
X = H, C≡N