graphite networks.[18]

The second implication of the present study concerns the speculative design of a novel type of polymers with potentially extreme properties for which the crystal structure of **1** provides a model. The interlocking diamondoid lattices of **1** may be viewed as weakly (hydrogen-) bonded crystalline polymers with an extremely high degree of three-dimensional cross-linking. By analogy, the ultrastrong diamond itself may be looked upon as a tightly (covalently) bonded crystalline polymer three-dimensionally maximally cross-linked. The role of the monomers in the two cases is played by the individual molecules of **1** and the carbon atoms, respectively. Replacing the weak hydrogen bonds in **1** by chains of covalent bonds would lead to more conventional novel polymers consisting of interpenetrating firmly bonded diamondoid networks ("diamondoid polymers"). Consequently, diamondoid properties such as extremely high strength, modulus and hardness, high refractive index and density, as well as extreme thermal stability and chemical inertness, could be foreseen for such hypothetical polymers. Moreover, diamondoid polymers would be expected to represent high-performance polymers with *isotropic* extreme properties in contradistinction to linear fibrous high-performance polymers such as aromatic polyamides (aramid fibers, Kevlar), which display extreme properties only *anisotropically*, i.e., parallel to the (fiber) axis of polymerization.

Figure 10a shows some hypothetical possibilities of constructing diamondoid polymers based upon 1,3,5,7-tetrafunctional adamantanes. For example, a diamondoid polyamide ("nylamant") would result through replacing the pairs of hydrogen bonds and carboxylic groups interlinking the adamantane nuclei of **1** by the covalent bridging chain B = $-(CH_2)_xCONH(CH_2)_y-$ with x, y = 0, 1, 2, ...[19] Similarly, hypothetical diamondoid polymers may be designed on the basis of tetrafunctional methanes (Figure 10b). The spirobis(lactam) shown in Figure 10c (a double ε-caprolactam) would, for instance, represent an attractive monomer for generating a nylon-6-type (perlon) diamondoid polyamide ("superlon"). This spirobis(lactam) is unknown yet should be readily obtainable from the known dioxime[20b] of spiro[5.5]undecane-3,9-dione.[20,21]

Whether diamondoid polymers of the type outlined briefly above can actually be made, or whether they are merely hypothetical concoctions of no practical use, is open to speculation. An ordered diamondoid polymerization of the tetrafunctional monomers is statistically/entropically a rather unfavorable process. In addition, crystalline diamondoid polymers are expected to display poor solubility properties and will not exist in the melt. The prospects for realizing highly ordered crystalline diamondoid polymers with interpenetrating three-dimensional lattices are therefore rather unfavorable unless suitable special polymerization techniques can be found. Possibly, less ordered glasslike polymeric structures formed in the primary polymerization process can be made to rearrange to thermodynamically more favorable crystalline diamondoid architectures of higher order by (catalytic) equilibration and annealing procedures at elevated temperatures.[22]

Acknowledgment. We thank the Fonds der Chemischen Industrie for financial support.

Registry No. 1, 100884-80-8.

Supplementary Material Available: List of observed and calculated X-ray structure amplitudes of **1** (6 pages). Ordering information is given on any current masthead page.

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(18) (a) Herbstein, F. H.; Kapon, M.; Reisner, G. M. *Proc. R. Soc. London, A* **1981**, *376*, 301. (b) Davies, J. E. D.; Finocchiaro, P.; Herbstein, F. H. in *Inclusion Compounds*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Eds.; Academic: New York, 1984; Chapter 11, p 407.

(19) A diamondoid polymeric hydrocarbon made up of adamantane cores with directly covalently linked bridgehead carbon atoms is also conceivable [poly(1,3,5,7-tetradehydroadamantane); last entry of Figure 10a, $x = 0$]. For a structure of this sort with a single undistorted diamondoid lattice, which would suffer from severe nonbonded H···H repulsions, a density of about 1.37 g cm^{-3} may be estimated (r = 4.70 Å).[5]

(20) (a) Farges, G.; Dreiding, A. S. *Helv. Chim. Acta* **1966**, *49*, 552. (b) Rice, L. M.; Scott, K. R. *J. Org. Chem.* **1967**, *32*, 1966. (c) Anteunis, M.; Geens, A.; van Cauwenberghe, R. *Bull. Soc. Chim. Belg.* **1973**, *82*, 573.

(21) On first thought, one would expect the spirobis(lactam) of Figure 10c to form chains of doubly hydrogen-bonded molecules in the crystal. However, a distorted diamondoid crystal structure appears also possible provided neighboring molecules are linked by single rather than pair-wise hydrogen bonds. Diamondoid crystal packing could perhaps help favor diamondoid polymerization of the spirobis(lactam). Experimental work is pursued.

(22) We thank G. Wegner, Mainz, for a discussion (Nov 4, 1986) concerning the prospects of realizing diamondoid polymers.

Homogeneous Gas-Phase Formation and Destruction of Anthranil from *o*-Nitrotoluene Decomposition

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Abstract: Dilute quantities of *o*-nitrotoluene and anthranil have been pyrolyzed in comparative rate single pulse shock tube experiments. Rather than C–NO$_2$ bond cleavage and NO$_2$ isomerization found as major channels in *p*-nitrotoluene decomposition, we demonstrate that the important pathway for pyrolysis involves the formation of anthranil with the following overall rate expression: k(*o*-nitrotoluene → anthranil) = $1.2 \times 10^{13} \exp(-26020/T)$/s. The anthranil that is formed is very unstable under our conditions; the rate expression for disappearance has been found to be the following: $k(\text{anthranil})_d = 3.7 \times 10^{15} \exp(-25800/T)$/s. Arguments are presented that suggest that the first rate expression is representative of a retroene reaction and the second expression is for the breaking of the N–O bond in anthranil. These conclusions emphasize the difference in results from shock tube and laser pyrolysis experiments. Their implications on the initiation reactions in the decomposition of nitroaromatic explosives are discussed.

In an earlier study on the decomposition of *o*-nitrotoluene[1] under single pulse shock tube conditions, we found that only one-third of the lost reactant could be accounted for in terms of products from an initial C–NO$_2$ bond split. This is in striking contrast to the situation for nitrobenzene or *p*-nitrotoluene where over two-thirds of the products are accounted for in this manner and the remainder could be reasonably interpreted in terms of an isomerization of the nitro compound to the nitrite. At that time we were not able to identify the principal channel for *o*-nitrotoluene

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[†] Guest Scientists: Permanent Address, Institute of Mechanics, Academia Sinica, Beijing, China.

(1) Tsang, W.; Robaugh, D.; Mallard, W. G. *J. Phys. Chem.* **1986**, *90*, 5968.

decomposition. In addition, our observations were not in conformity with the results of laser pyrolysis studies.[2] We have now carried out further experiments and are able to confirm our previous observations and deduce a mechanism which at lower temperatures is probably the sole channel for the decomposition of any nitroaromatic compound with an adjacent methyl grouping. This has important implications with respect to the initiating processes during the decomposition of nitroaromatic explosives. The key intermediate in this mechanism is anthranil and the principal quantitative aspect of this study will deal with its formation and stability. With such information we will demonstrate that we can account for substantially all the channels for *o*-nitrotoluene decomposition under the present reaction conditions.

It is well-known that *o*-nitrotoluene is less thermally stable than other nitrotoluenes.[3] In lower temperature pyrolysis studies of nitrotoluenes there are major changes in the nature of the decomposition products. Unlike the case with the other nitrotoluenes, where products are explicable in terms of C–NO_2 bond cleavage, Fields and Meyerson[3] detected aniline and anthralinic acid as major products. Dacons et al.[4] found dinitroanthranil as an important reaction product during the liquid phase decomposition of trinitrotoluene at 200 °C. It is known that *o*-nitrotoluene when heated in aqueous or alcoholic base is converted to anthralinic acid.[5] Although anthranil has not been detected, there has been much indirect evidence that it is an important intermediate.[6,7] One would expect that for a purely gas phase reaction, where there is no possibility of intervention by solvents or surfaces, such base-catalyzed processes will be effectively suppressed. This is the conclusion from the laser pyrolysis studies of Gonzales and co-workers,[2] who find the main reaction in *o*-nitrotoluene decomposition to be, as in the other nitroaromatic compound they studied, C–NO_2 bond cleavage. Nevertheless, they do note that methyl substitution increases the rate of decomposition over that for nitrobenzene by an order of magnitude. Furthermore, only 75% of the products were recovered as toluene, in contrast to the much larger recovery for the other compounds.

Thermal decomposition experiments on complex organic molecules, when properly carried out in a single pulse shock tube, are much easier to interpret in terms of elementary processes than similar studies with classical techniques. The experimental configuration is such that most of the complications that are characteristic of pyrolytic studies are eliminated. There are no possible contributions from surface processes since the walls are cold and in the short time available for reaction molecules cannot diffuse to the walls.[8] The short reaction time when coupled with studies of reactants in high dilutions and the use of a radical scavenger to prevent chain processes isolates the initial decomposition processes for study. Although the reaction time is short, it is nevertheless long enough (10^7 collisions) and with conditions sufficiently well defined to assure a properly thermally equilibrated mixture. We have successfully used this technique to determine the rates and mechanisms of decomposition of many organic compounds.[8]

Experimental Section

The experiments are carried out in a single pulse shock tube that is heated to 100 °C.[9] All of the gas handling lines are similarly heated. This permitted the introduction and extraction from the shock tube of low volatility substances. Analysis of the products was by programmed temperature capillary gas chromatography using a 60 m bonded methyl, phenyl, and vinyl silicone capillary column. Detection is by hydrogen flame ionization. With such a column very detailed analysis of the higher boiling components can be made. We give up information on the light hydrocarbons. We have reported on their product distributions in an earlier study.[1] In this and the earlier study yields of toluene are given and this can serve as a bridge for linking the two sets of data.

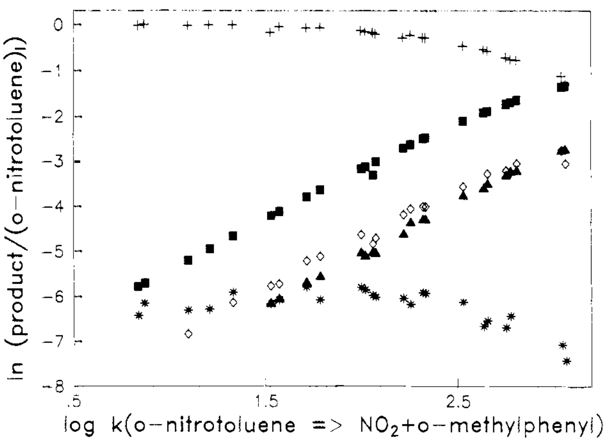

Figure 1. Larger products formed during the decomposition of 282 ppm *o*-nitrotoluene in 4.81% cyclopentane and argon: temperature 1000–1170 K, pressure 2–4 atm, heating time ~450 μs; (+) *o*-nitrotoluene, (■) toluene, (◇) *o*-cresol, (*) anthranil, (▲) "cyanocyclopentadiene".

Isolation of the initial process for study was achieved by adding into the system very large quantities of cyclopentane. Under our conditions the cyclopentane furnishes an abstractable hydrogen for the reactive radicals. The resulting cyclopentyl radical decomposes rapidly into ethylene and an allyl radical. Within the time scale of these experiments the latter is fairly stable. All the above claims with respect to inhibition are in accord with well-established rate constants in the literature and have been verified by direct measurements over wide ranges of cyclopentane concentrations. Detailed discussions of these factors can be found in an earlier paper[6] and the references therein. Quantitative results are based on the internal standard method that have proved to be highly successful in single pulse shock tube studies. For the present studies we used the toluene that is formed as the marker for the extent of decomposition and the rate expressions for the breaking of the C–NO_2 bond in *o*-nitrotoluene and *p*-nitrotoluene as the internal standard. These have been determined in our earlier study and the validity of such an approach has been demonstrated.[1] From these rate expressions we can derive an average temperature for the decomposition processes. In order to demonstrate explicitly our independence from a temperature measurement we have chosen to plot our results in terms of the logarithm of the unimolecular decomposition rate constants for the two bond breaking process. For a rate expression in the Arrhenius form, this is proportional to $-1/T$.

Our results are based primarily on studies on two separate mixtures, (a) 285 ppm *o*-nitrotoluene in 4.81% cyclopentane and argon and (b) 182 ppm anthranil and 84 ppm *p*-nitrotoluene in 4.91% cyclopentane and argon. Ancillary experiments have also been carried out to verify various aspects of the reaction mechanism, and this will be mentioned in the course of the paper. The anthranil and *o*-nitrotoluene have been obtained from Aldrich Chemicals. The cyclopentane is from Wiley Organics,[10] and the argon is of Ultra High Purity and is from Matheson. Except for vigorous degassing of the organics all of the substances are used without further purification. Anthranil samples showed some instability over the period of days during which we carried out our experiments. However, they did not lead to any new detectable products, and the results of experiments over different periods of time are reproducible.

Results

Figure 1 gives the product distribution from the gas chromatographic analysis of the mixtures obtained from shocking dilute mixtures of *o*-nitrotoluene in cyclopentane. As noted earlier, with our column we lose information on the light hydrocarbon products. Also, with such excesses of cyclopentane as we have in this system, the first of the heavier compounds that we can reliably quantify is toluene. Also present in small amounts are compounds such as picoline, aniline, and diazobenzene. Except for the anthranil, the compounds listed in Figure 1 are the major large organic

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[2] Gonzalez, A. C.; Larson, C. W.; McMillen, D. F.; Golden, D. M. *J. Phys. Chem.* **1985**, *89*, 4809.

[3] Fields, E. K.; Meyerson, S. *Adv. Free-Radical Chem.* **1965**, *5*, 101.

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[7] Willadsen, P.; Zerner, B. *J. Org. Chem.* **1973**, *38*, 3411.

[8] Tsang, W. In *Shock Waves in Chemistry*; Lifshitz, A., Ed.; Marcel Dekker: New York, 1981; p 59.

[9] Robaugh, D.; Tsang, W. *J. Phys. Chem.* **1986**, *90*, 5363.

[10] Certain commercial materials and equipment are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the national Bureau of Standards, nor does it imply that the material or equipment is necessarily the best available for the purpose.

products. Anthranil is present in extremely small quantities. The reason for its inclusion will become clear subsequently. In separate experiments with *p*-nitrotoluene under the same reaction conditions we confirmed our earlier results with regard to the recovery of close to 70% of the product as toluene and 10–15% as *p*-cresol. Particularly important is the fact that unlike the situation with *o*-nitrotoluene no anthranil or cyanocyclopentadiene could be detected.

The presence of all of the compounds except for cyanocyclopentadiene, which is not commercially available, has been verified with neat samples. Our identification of cyanocyclopentadiene is based on the fact that, as can be seen in Figure 7, it is the expected final product from the decomposition of anthranil and this was confirmed directly. Furthermore, in the hydrogen atom induced decomposition of aniline at high temperatures a large peak was located in exactly the same region of the chromatogram. Attempts to generate cyanocylopentadiene from benzenetriazole were unsuccessful since this compound did not survive storage in our mixing vessel. For our present purposes, the nature of the peak that we assigned to cyanocyclopentadiene is not important since all we require is that this peak is also formed in the decomposition of anthranil. This was verified by shocking mixtures of anthranil and cyclopentane in argon where in all cases we observed the formation of the chromatographic peak that we assign to cyanocyclopentadiene. Quantitatively, although virtually total destruction of anthranil was easily achieved under the conditions of these experiments ($T > 800$ K), it was not until the highest temperatures ($T > 1150$ K) that we recovered over 50% of the decomposed anthranil as cyanocyclopentadiene. At lower temperatures yields of the cyanocyclopentadiene were as low as 5%.

For our purposes it is necessary to relate measured cyanocylopentadiene concentration to the actual amount of anthranil that is formed during *o*-nitrotoluene decomposition, since the mass balance is unsatisfactory when cyanocyclopentadiene is considered by itself. Accordingly, we carried out experiments with anthranil and *p*-nitrotoluene in cyclopentane and argon mixtures using the decomposition of the *p*-nitrotoluene as the internal standard to determine the temperature. The rate expression for the decomposition of *p*-nitrotoluene is

$$k(p\text{-}NO_2C_6H_4CH_3 \rightarrow NO_2 + p\text{-}CH_3C_6H_4) = 7.7 \times 10^{14} \exp(-32305/T)\ s^{-1}$$

The results are given in Figure 2. Note that all the anthranil that has disappeared does not show up as cyanocyclopentadiene. However, as the temperature is increased the recovery gets better. We will use Figure 2 as a calibration curve in order to convert the measured cyanocyclopentadiene (see Figure 1) into the amount of anthranil produced by decomposition of *o*-nitrotoluene. To do this we need to know the temperature of the experiment and to take into account the continuous production of anthranil in the *o*-nitrotoluene experiments. The temperature is calculated from the rate of decomposition of the *o*-nitrotoluene

$$k(o\text{-}NO_2C_6H_4CH_3 \rightarrow NO_2 + o\text{-}CH_3C_6H_4) = 6.4 \times 10^{14} \exp(-30888/T)\ s^{-1}$$

The difference between the experiments with anthranil and those with *o*-nitrotoluene is that in the latter anthranil is continuously formed. In the former one starts with the maximum amount of anthranil. If we now assume that the decomposition from anthranil to cyanocyclopentadiene is a sequential process, that is, given sufficient time all the anthranil will be converted to cyanocyclopentadiene, then the yield of cyanocyclopentadiene from the *o*-nitrotoluene decomposition will imply twice the amount of anthranil being formed than that deduced from experiments where the anthranil is the initial reactant.

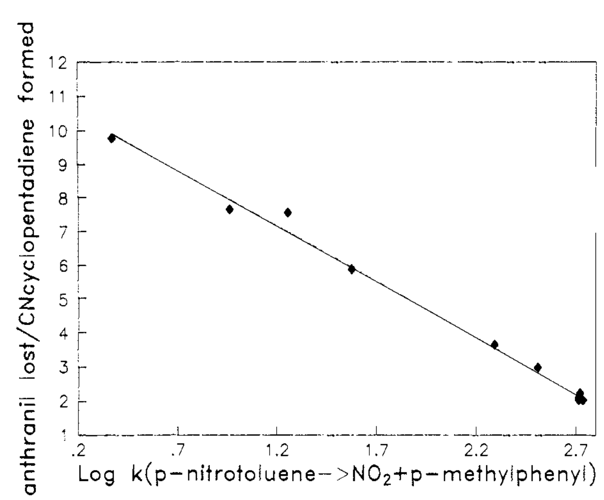

Figure 2. Ratio of anthranil disappeared to "cyanocyclopentadiene" formed during the decomposition of 185 ppm anthranil and 85 ppm *p*-nitrotoluene in 4.91% cyclopentane and argon: temperature 1000–1150 K, pressure, 2–4 atm, heating time ~450 μs. $-k(p\text{-}NO_2C_6H_4CH_3 \rightarrow NO_2 + p\text{-}CH_3C_6H_4) = \ln(1 - ([\text{toluene}]{*}X/[p\text{-}NO_2C_6H_4CH_3]_i))/tX$ where $X = 1 + 2(p\text{-cresol})/\text{toluene}$ and $k(p\text{-}NO_2C_6H_4CH_3 \rightarrow NO_2 + p\text{-}CH_3C_6H_4) = 7.7 \times 10^{14} \exp(-32305/T)\ s^{-1}$.

This can be demonstrated more formally by considering the following sequence of reactions,

$$N \rightarrow A \rightarrow I \rightarrow C$$

where N, A, and I are the nitrotoluene, anthranil, and reaction intermediate and C is the peak that we designated as cyanocyclopentadiene, and the rate constants are k_1, k_2, and k_3. k_2 is very fast. This is seen by the very small concentration of anthranil. The total anthranil that is produced in the course of the reaction is $N_0(1 - \exp(-k_1 t))$ where N_0 is the initial nitrotoluene concentration. Practically all of it is immediately destroyed and I is formed. The rate-determining step for the formation of C is therefore the decomposition of I. The differential equation for the formation of C can be written as

$$dC/dt + k_3C = k_3N_0(1 - \exp(-k_1t)) = k_3N_0k_1t$$

where the last term is based on the assumption that we are in the linear regions of the decomposition process. This leads to

$$C/N_0 = k_3k_1t^2/2$$

where we have also linearized the decay process. However, the total amount of anthranil that is formed is $N_0k_1t = N_t$. Therefore $C = N_tk_3t/2$. Conrast this with the situation when C is formed from an initial amount of anthranil (N_i). The linear relation for cyanocyclopentadiene formation is $C = N_itk_3$. Then for any tk_3, $N_t = 2N_i$.

Some error is introduced by the linearization procedure, but the error is only meaningful at the highest temperature where our anthranil yields may be overestimate by about 20%. This drops off quite rapidly, so that at the lowest temperatures no errors can occur. It should be noted that the above represents a working hypothesis. As will be seen below it leads to results that are in reasonable accord with experimental observations with regard to mass balance and rate constants and expressions.

It can be seen in Figure 3 that with the corrected anthranil concentration the mass balance is excellent. Even if we take into account the possibility of a 20% overestimate, we will still have recovered about 90% of the products at the highest temperature. This is not unsatisfactory and is probably within the limits set by our assumptions and the uncertainties of our measurements. In contrast (also in Figure 3) if we make use of only the directly measured values the mass balance is less satisfactory. There is also the possibility that instead of the sequential reaction, an undetected product from anthranil decomposition is formed in parallel with cyanocyclopentadiene. In that case, for a given yield of cyanocyclopentadiene the anthranil lost from our calibration experiment will be equal to the anthranil formed during the *o*-nitrotoluene experiments. At the highest extents of reactions this will mean 70% recovery of the reaction products. This is not as good as the results derived on the assumption of sequential reactions. Even with this lower number it is clear that anthranil formation is an important reaction channel. Note that at the lower temperatures (or equivalently smaller rate constants for C–NO$_2$ bond breaking in *o*-nitrotoluene decomposition) the low conversions

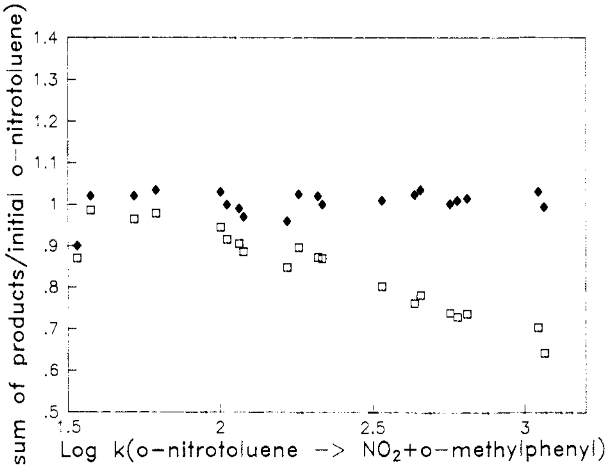

Figure 3. Tests of mass balance during the decomposition of 282 ppm *o*-nitrotoluene in 4.81% cyclopentane and argon: temperature 1000–1170 K, pressure 2–4 atm, heating time ~450 μs. $-k(o\text{-}NO_2C_6H_4CH_3 \rightarrow NO_2 + o\text{-}CH_3C_6H_4) = 6.4 \times 10^{14} \exp(-30888/T)$ s^{-1}. (□) From products in Figure 1, (◆) after correction for anthranil production.

make it difficult to carry out proper mass balances. A major problem in single pulse shock tube experiments is the inability to vary reaction time. Thus the accuracy of the mass balance data for low extent of reactions is limited by the uncertainty in our chromatographic measurements. In Figure 3 we have assumed that the cresol that is detected accounts for only half of the *o*-methylphenoxy radicals that are initially formed. The rationale for this is from our earlier paper where from mass balance considerations it appeared that only half the phenoxy type radicals are trapped by the amount of cyclopentane that we have in the reaction mixture. Since NO_2 isomerization is only a very minor channel in this reaction any error we may have introduced here is minuscule.

On this basis we can now calculate the relative rates for the production of anthranil and *o*-methylphenyl radicals in *o*-nitrotoluene decomposition. The rate constants can be calculated from the relations

$$-k(o\text{-}NO_2C_6H_4CH_3 \rightarrow NO_2 + C_6H_4CH_3) = \ln(1 - ([\text{toluene}]X/[o\text{-}NO_2C_6H_4CH_3]_i))/tX$$

and

$$k((o\text{-}NO_2C_6H_4CH_3 \rightarrow NO_2 + C_6H_4CH_3)/k(o\text{-}NO_2C_6H_4CH_3 \rightarrow \text{anthranil}) = [\text{toluene}]/[\text{anthranil}]_c$$

where t is the residence time and is of the order of 450 μs, $X = 1 + [\text{anthranil}]_c/\text{toluene} + 2(\text{cresol})/\text{toluene}$ is the factor that takes into account the various channels in *o*-nitrotoluene decomposition and $[\text{anthranil}]_c$ is the anthranil concentration if decomposition did not occur and 2(cresol) takes into account our estimate that only half the *o*-methylphenoxy radicals are converted to cresol. The comparative rate plot can be found in Figure 4 and the relation between the two reaction channels have been found to be

$$\log(k((o\text{-}NO_2C_6H_4CH_3 \rightarrow NO_2 + C_6H_5CH_3)) = (0.843 \pm 0.017)\log(k(o\text{-}NO_2C_6H_4CH_3 \rightarrow \text{anthranil})) + (0.598 \pm 0.039)$$

Substituting into the above the rate expression for the breaking of the C–NO_2 bond in *o*-nitrotoluene, we find

$$k(o\text{-nitrotoluene} \rightarrow \text{anthranil} + H_2O) = 1.2 \times 10^{13} \exp(-26038/T)/\text{s}$$

As written this is not an elementary single step reaction. In a subsequent section, we will identify this rate expression with a particular process. The least squares uncertainty lead to an error limit of the order of 5 kJ/mol in the activation energy. Note that our rate expression is also based on our treatment of how anthranil disappears. We estimate that the actual uncertainty is more in the 14 kJ/mol range, where the most likely direction of error is toward higher values.

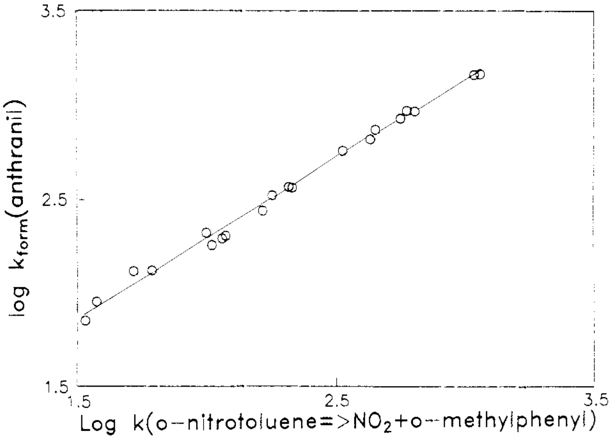

Figure 4. Comparative rate plot for the breaking of the C–NO_2 bond in *o*-nitrotoluene in 4.81% cyclopentane and argon: temperature 1000–1170 K, pressure 2–4 atm, heating time ~450 μs. $-k(o\text{-}NO_2C_6H_4CH_3 \rightarrow NO_2 + o\text{-}CH_3C_6H_4) = \ln(1 - ([\text{toluene}]X/[o\text{-}NO_2C_6H_4CH_3]_i))/tX$ where $X = 1 + [\text{anthranil}]_c/\text{toluene} + 2(o\text{-cresol})/\text{toluene}$ and $k(o\text{-}NO_2C_6H_4CH_3 \rightarrow NO_2 + o\text{-}CH_3C_6H_4) = 6.4 \times 10^{14} \exp(-30888/T)$ s^{-1}.

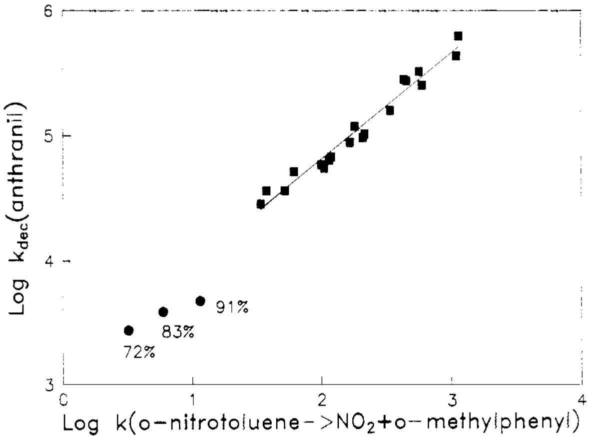

Figure 5. Comparative rate plot for anthranil decomposition and C–NO_2 bond cleavage (a) during the decomposition of 282 ppm *o*-nitrotoluene in 4.81% cyclopentane and argon (■) and (b) 700 ppm anthranil in 6% cyclopentane and argon (■): pressure 2–4 atm, temperature 900–1170 K, heating time ~450 μs. Percentage refers to anthranil decomposed. $-k(o\text{-}NO_2C_6H_4CH_3 \rightarrow NO_2 + o\text{-}CH_3C_6H_4) = \ln(1 - ([\text{toluene}]X/[o\text{-}NO_2C_6H_4CH_3]_i))/tX$ where $X = 1 + [\text{anthranil}]_c/\text{toluene} + 2(o\text{-cresol})/\text{toluene}$ and $k(o\text{-}NO_2C_6H_4CH_3 \rightarrow NO_2 + o\text{-}CH_3C_6H_4) = 6.4 \times 10^{14} \exp(-30888/T)$ s^{-1}.

The very small yield of anthranil (see Figure 1) is due to its relative instability our system. Since anthranil is present in steady state, the formation and decomposition of anthranil as represented by the subscripts f and d can be related as follows,

$$k(\text{anthranil})_d/k(\text{anthranil})_f = [o\text{-nitrotoluene}]_i \exp(-k(o\text{-nitrotoluene})t)/[\text{anthranil}]$$

where $k(o\text{-nitrotoluene})$ can be expressed as the sum of the three modes of decomposition, C–NO_2 bond cleavage, NO_2 isomerization to form the nitrite and anthranil formation, t is the residence time of approximately 450 μs, and $[o\text{-nitrotoluene}]_i$ is the initial concentration. The comparative rate plot relating anthranil decomposition with C–NO_2 bond cleavage in *o*-nitrotoluene decomposition can be found in Figure 5. The comparative rate expression is

$$\log k(\text{anthranil})_d = (0.840 \pm 0.038)\log(k(o\text{-}NO_2C_6H_4CH_3 \rightarrow NO_2 + C_6H_4CH_3)) + (3.130 \pm 0.088)$$

and this leads to the rate expression

$$k(\text{anthranil})_d = 3.7 \times 10^{15} \exp(-25945/T)/\text{s}$$

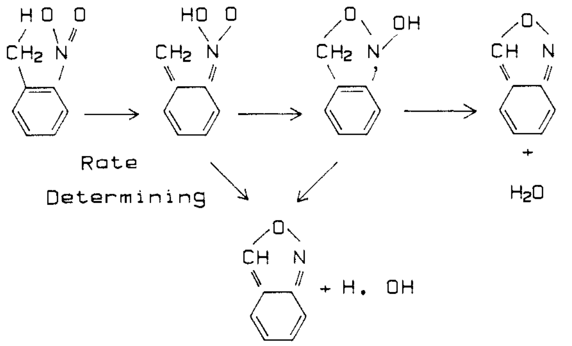

Figure 6. Possible mechanism for anthranil formation during *o*-nitrotoluene decomposition.

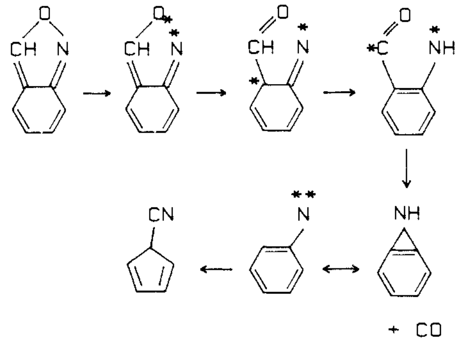

Figure 7. Possible mechanism for the decomposition of anthranil.

The comparative rate data show considerable scatter. This is a reflection of the derivative nature of the determination and the very low yields of anthranil that were detected. Unlike the situation with respect to anthranil formation, we will show subsequently that it is relatively easy to assign this rate expression to the breaking of the N–O bond in anthranil.

Also included in Figure 5 are data from comparative rate studies with anthranil and *o*-nitrotoluene. The anthranil is present in sufficiently large concentrations so that the small amount produced in *o*-nitrotoluene decomposition does not make any contributions. The experiments are rendered difficult by the great differences in stability between the two compounds. Practically all the anthranil will have disappeared before *o*-nitrotoluene starts to decompose. We have been able to carry out a few experiments that are meaningful. It can be seen that our extrapolated rate expression passes very close to the point where there is the lowest extent of decomposition from thd direct studies (72%). At the higher decomposition ranges, the discrepancy becomes more serious. This is completely understandable in terms of the anthranil that is in the boundary layer (next to the cool wall). Since it is not at the reaction temperature, decomposition cannot occur. It is the equivalent of a dead space effect in static experiments. This has been observed by other workers.[11] The present results represent a satisfactory consistency check of our rate expression for anthranil decomposition. Indeed, if we just use our results from the lowest extent of reaction (72%) as a fixed point and estimate the *A*-factor by analogy (for example, from the decomposition of C_6[12] and C_5[13] ring compounds) we would obtain a rate expression very similar to that which we obtained here. We can then reverse the process and derive the rate expression for anthranil formation without recourse to the quantity of cyanocyclopentadiene that we measured. It also follows that we can obtain the satisfactory mass balance displayed in Figure 1 by this alternative manner. This is then an added consistency check of our interpretation of the decomposition mechanism.

Discussion

The results of our study show that in these experiments there are three modes for the decomposition of *o*-nitrotoluene. The most important of these channels involves anthranil formation and is specific with respect to the presence of the methyl group adjacent to the NO_2 moiety. The low activation energy for this process means that at lower temperatures this will be even more important. We have noted earlier that our rate expression certainly does not represent the direct process of anthranil formation. Undoubtedly a number of consecutive reactions are involved. The rate expression is reflective of the rate-determining process. The value of the *A*-factor suggests a relatively tight complex, and it would appear that a retroene reaction involving hydrogen atom transfer would not be incompatible with our results.[12] Indeed our rate expression is very much in line with other such processes. The mechanism is outlined in Figure 6. An important question is the nature of the secondary reactions. Is there a mechanism for the direct formation of the anthranil from the acid through the ejection of water? Or is there a sequential series of reactions which releases OH and the H atoms in the system. We note from our earlier study the increased yields of light hydrocarbons from that which can be expected purely on the basis of *o*-methylphenyl and NO_2 radicals released into the system.

The rate expression for the decomposition of anthranil is reflective of the breaking of the =N—O– bond. The activation energy is in the range of values for the decomposition of an oxime.[12] The larger than "normal" *A*-factor is in line with the increased entropy in the transition energy as a result of the loosening of the more rigid stable ring state. It can be assumed that the subsquent reactions will follow the sequence of processes as given in Figure 7. This leads to nitrene formation and its decomposition to form cyanocyclopentadiene.

It is interesting to extrapolate our results to the low-temperature region where Dacons et al. carried out their experiments. From our rate expression we find at their reaction temperature (200 °C) a rate constant of 1.54×10^{-11} s^{-1}. This leads to a conversion of (8.76×10^{-5})% for their reaction time of 16 h. This is about five orders of magnitude smaller than that which has been observed. Of course there is a considerable difference between trinitrotoluene and *o*-nitrotoluene, so that the differences may be strictly a substituent effect. Alternatively and probably most likely there may be very strong catalytic effects in TNT solution. In a similar fashion we can compare our results with those of Bakke and co-workers.[6] In the presence of Vycor chips they obtained 30% destruction of *o*-nitrotoluene at 500 °C and a residence time of 10 s. Extrapolating our results leads to a prediction of 33% conversion. Although the exact agreement is probably deceptive, we conclude that under the conditions of the flow experiments with vycor chips surface reactions are relatively unimportant and the decomposition of nitrotoluene under these conditions is not proceeding via a chain mechanism.

These results have important implications on the nature of the initial process in the decomposition of trinitrotoluene. Certainly, it is no longer possible to assume that it involves C–NO_2 bond cleavage. Instead all evidence points to a sequence of reactions during which anthranil is an important reaction intermediate. At the lower temperatures where initiation occurs, the lower activation energy process will be much more favored than in the present situation. Furthermore one notes the evidence for a condensed phase catalytic process that also yields anthranil. The direction of future work must be to investigate the effects of nitro substitution on anthranil formation and then to better understand the nature of catalytic effects for reactions in the condensed phase. We plan to carry out some of these experiments in the near future.

Our results emphasize the quantitative discrepancies between this work and the data of Gonzales and co-workers using laser pyrolysis. Summarizing briefly, the differences are as follows, Gonzales and co-workers report 75% recovery of their products as toluene and rate constants for *o*-nitrotoluene decomposition which if interpreted in terms of purely C–NO_2 bond cleavage is a factor of five higher than our value for that process. On the other hand, the sum of rate constants from our experiments is only a factor of 2 smaller than theirs. Coupling this with the fact that

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their 75% product recovery in *o*-nitrotoluene decomposition is significantly smaller than their product recovery in *p*-nitrotoluene decomposition, thus suggesting differences in mechanisms, it is possible to claim some degree of qualitative agreement. The validity of our experiments is now buttressed by the very satisfactory mass balance and the determination of rate expressions that are clearly explicable in terms of thermokinetic considerations. We have previously noted[1] our difficulty in understanding how all the *o*-methylphenyl radicals can be trapped in the laser experiments and our failure to do so using the same inhibitor as used by Gonzales and co-workers when the conditions for doing so are in fact more favorable. Aside from the possibility of experimental artifacts, the only remaining possibility is the definition of reaction conditions in the laser studies. That is, the stated temperatures are too low and the results will discriminate against the lower activation energy process. Note that aside from *o*-nitrotoluene decomposition the laser studies also led to some very novel and unexpected substituent effects. We have commented on these in our earlier paper.[1] This suggests the need for caution in the quantitative interpretation of laser pyrolysis data. In view of the recent development of the laser technique this caveat is hardly surprising. We note that in general the many advantages with regard to unambiguity in the determination of reaction mechanisms which are inherent to appropriate single pulse shock tube studies should also hold for the laser experiments. Furthermore, by the proper selection of internal standards and through variation of reaction conditions such as laser intensities, sensitizer concentrations, reaction pressures, etc., it may well be possible to factor out some of the quantitative discrepencies that we have noted.

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Reversible One-Electron Generation of 4a,5-Substituted Flavin Radical Cations: Models for a Postulated Key Intermediate in Bacterial Bioluminescence

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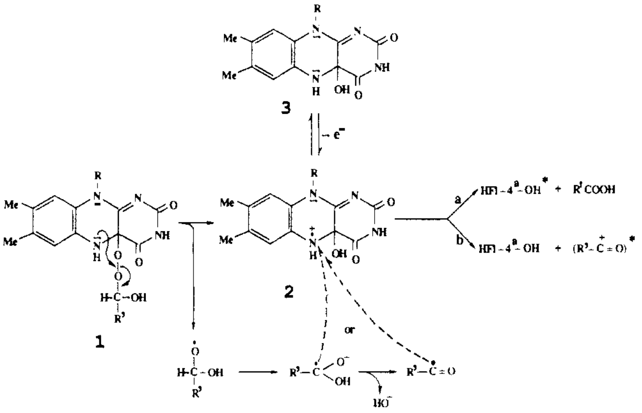
Abstract: A chemically initiated electron-exchange luminescence (CIEEL) mechanism is proposed for the bacterial bioluminescent reaction in which a 4a-hydroxyflavin radical cation is postulated to be a key intermediate. As model compounds, the electrochemical generation of 4a,5-substituted flavin radical cations from 5-ethyl-4a-hydroxy-3-methyl-4a,5-dihydrolumiflavin and 5-ethyl-4a-methoxy-3-methyl-4a,5-dihydrolumiflavin is demonstrated for the first time. These reversible one-electron oxidations were characterized in acetonitrile by cyclic voltammetry, controlled-potential coulometry, and spectroelectrochemistry. The electrogenerated radical cations can also undergo a one-electron oxidation and, after a subsequent chemical transformation, lead to the formation of a 5-ethyl-3-methyllumiflavinium cation. Both the intermediates and the final products of electrooxidation were spectrally and electrochemically identified.

The formation of a 4a-hydroperoxyflavin intermediate in the bioluminescent reaction catalyzed by bacterial luciferase has been well documented.[2-4] The flavin peroxide is proposed to react with an aliphatic aldehyde substrate to form a dihydroflavin 4a-peroxyhemiacetal **1**.[5] The decay of **1** leads to bioluminescent emission,[5,6] but the mechanism for the generation of the primary excited species is still not understood.

Schuster has elegantly demonstrated that a CIEEL (chemically initiated electron-exchange luminescence) mechanism can account for certain chemiluminescent, and possibly also for some bioluminescent, reactions.[7] Subsequently McCapra has shown that chemiluminescence derived from 10a-flavin adducts probably also follows a CIEEL mechanism.[8] Following these pioneering studies, Mager and Addink have proposed a detailed CIEEL mechanism for the bacterial bioluminescence reaction (Scheme I).[9] Starting from dihydroflavin 4a-peroxyhemiacetal **1**, the first step is postulated to be an intramolecular one-electron rearrangement to give a 4a-hydroxyflavin radical cation **2** [$(HFl\text{-}4a\text{-}OH)^{\cdot +}$]. This latter

Scheme I



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