Table III. Comparison of Experimental and Estimated E_{RSE}

	CSC(R·)	CSC(RH)	E_{RSE} (eq 3)	E_{RSE} (exptl)	Exptl ref
Allyl	2	1	11.6	10.0 ± 1.5	*a*
Cyclohexen-3-yl	2	1	11.6	12.5 ± 1.0	*b*
Methylallyl	2	1	11.6	12.5 ± 1.5	*a*
1,3-Hexadien-5-yl	3	1	18.4	18 ± 3	*a,c*
1,3-Cyclohexadien-5-yl	3	1	18.4	24 ± 6	*d,e*
Cyclopentadienyl	5^h	1	27.0	17.5 ± 2.5	*f*
Cyclopentadienyl	$5/2^i$	1	15.4	17.5 ± 2.5	*f*
Cycloheptatrienyl	7^h	1	32.6	21.5	*g*
Cycloheptatrienyl	$7/2^i$	1	21.0^g	21.5	*g*

[a] Reference 8. [b] S. Furuyama, D. M. Golden, and S. W. Benson, *Int. J. Chem. Kinet.*, **3**, 93 (1970). [c] K. W. Egger and M. Jola, *ibid.*, **2**, 265 (1970); H. M. Frey and A. Krantz, *J. Chem. Soc. A*, 1159 (1969). [d] D. G. L. James and R. D. Suart, *Trans. Faraday Soc.*, **64**, 2752 (1968). [e] S. W. Benson, "Thermochemical Kinetics", 2d ed, Wiley, New York, N.Y., 1976. [f] S. Furuyama, D. M. Golden, and S. W. Benson, *Int. J. Chem. Kinet.*, **3**, 237 (1971). [g] G. Vincow, H. J. Dauben, F. R. Hunter, and W. V. Volland, *J. Am. Chem. Soc.*, **91**, 2823 (1969). [h] CSC has not been previously defined for such nonalternant systems; it is assumed to be equal to the total number of distinct resonance structures. [i] E_{RSE} (eq 3) is derived using CSC(R·) defined as one-half of the number of resonance structures.

mental uncertainty. The current paucity and inaccuracy of existing data, however, make a convincing test of these methods impossible. For nonalternant conjugated radicals, the proposed estimation method yields E_{RSE} substantially higher than measured values. By halving the total structure count to yield a corrected structure count for these radicals, E_{RSE} predictions accurately match the measured values.

Acknowledgment. This work has been supported by the U.S. Energy Research and Development Administration, Office of Coal Research, under Contract E(49-18)-2202.

Registry No.—Benzyl, 2154-56-5; 3-phenanthryl, 61062-76-8; 2-triphenylenyl, 61062-77-9; 1-triphenylenyl, 61062-78-0; 2-naphthyl, 10237-50-0; 1-phenanthryl, 61062-79-1; 1-naphthyl, 2510-51-2; 9-phenanthryl, 20199-82-0; 6-chrysyl, 61062-80-4; 2-anthryl, 61062-81-5; 1-anthryl, 27735-76-8; 1-pyrenyl, 27735-78-0; 9-anthryl, 27735-77-9; 2-phenanthryl, 61062-82-6; 4-phenanthryl, 61062-83-7; 2-pyrenyl, 61062-84-8; 4-pyrenyl, 61062-85-9; 1-chrysyl, 61062-86-0; 2-chrysyl, 61062-87-1; 3-chrysyl, 61062-88-2; 4-chrysyl, 61062-89-3; 5-chrysyl, 61062-90-6; 1-naphthacenyl, 61062-91-7; 2-naphthacenyl, 61062-92-8; 5-naphthacenyl, 61062-93-9; 1-perylenyl, 61062-94-0; 2-perylenyl, 61092-32-8; 3-perylenyl, 61062-95-1; allyl, 1981-80-2; cyclohexen-3-yl, 15650-80-3; methylallyl, 15157-95-6; 1,3-hexadien-5-yl, 61062-96-2; 1,3-cyclohexadien-5-yl, 15819-51-9; cyclopentadienyl, 2143-53-5; cycloheptatrienyl, 3551-27-7.

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(9) Table I also shows the results of optimizing an equation of the form $E_{\pi RSE} = A \ln [CSC(R\cdot)]/[CSC(RH)]$. Equation 3 is better.

Production of Nitric Oxide in the Pyrolysis of Aromatic Nitro Compounds

C. W. Hand*

University of Alabama, University, Alabama 35486

C. Merritt, Jr., and C. DiPietro

Pioneering Research Laboratory, U.S. Army Natick Laboratories, Natick, Massachusetts 01760

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The pyrolysis of nitrobenzene in the temperature range 400–600 °C was studied in a continuous-flow apparatus consisting of pyrolyzer, gas chromatograph, and mass spectrometer. Several of the observed products (benzene, biphenyl, naphthalene) could arise from phenyl radical, but, in contrast to earlier suggestions, there is no evidence supporting a primary fission to phenyl radical and nitrogen dioxide. Pyrolysis of nitrosobenzene yields products similar to those from nitrobenzene, and a two-step mechanism, nitrobenzene → nitrosobenzene → phenyl, is proposed. Although the details of the mechanism are not conclusively proven, there is considerable evidence for a heterogeneous mechanism and none supporting a homogeneous mechanism.

Recent experience in this laboratory[1] and others[2] has shown that nitric oxide is a prominent product of the pyrolysis of aromatic nitro compounds, and that nitrogen dioxide is not produced in detectable quantities. This is not necessarily a surprising result inasmuch as the possible rearrangement to an aryl nitrite leads to compounds which should readily undergo homolytic fission to nitric oxide plus aryloxy radicals. Photochemical nitro–nitrite rearrangements are known,[3] and the analogous rearrangement of the positive ion occurs in the mass spectrum of nitrobenzene.[4] Even though there is little evidence that such a process takes place by thermal stimulus at ordinary temperatures, it is quite possible that it occurs readily at high temperature.

The bond dissociation energy corresponding to the homolytic fission of phenyl nitrite into nitric oxide and phenoxy radicals is 23.7 kcal/mol.[5] By comparison, the homolytic fission of an aromatic nitro compound to an aryl radical and NO_2 should be less favorable; a lower limit to $D(PhNO_2)$ of 63 ± 3 kcal may be estimated from the heats of formation of phenyl radical,[6] NO_2, and nitrobenzene.[7] Thus, if the nitro–nitrite rearrangement is not a rapid one, the production of NO_2 should compete favorably with the production of NO in the pyrolysis of nitrobenzene, and by extension, of other aromatic nitro compounds as well. If on the other hand the thermal nitro–nitrite rearrangement is a facile one, little, if any, NO_2 would be expected in the pyrolysis of an aromatic nitro compound.

Several recent publications[2,8,9] concern the pyrolysis of nitrobenzene in a packed-tube reactor at 600 °C. The products of pyrolysis under these conditions were explained on the basis of primary fission of the C–N bond, yielding phenyl radical and nitrogen dioxide. However, as in our experience, no NO_2 was observed in the reactor effluent. The available evidence does not, therefore, favor primary C–N fission over other possibilities for the formation of phenyl radical.

Experimental Section

Nitrogen dioxide was purchased from Matheson, and subjected to several freeze–thaw cycles at −78 °C before use. Nitrobenzene and nitrosobenzene (reagent grade) were purchased from Eastman, and used as received. Samples to be pyrolyzed were injected into a Fisher-Victoreen pyrolyzer, and passed directly into a gas chromatograph and thence into the ion source of a Bendix MA-2 time-of-flight mass spectrometer.

In the Fisher-Victoreen instrument the pyrolysis chamber is a straight stainless steel tube of 0.6 cm i.d. and length 10 cm; the tube is rapidly (<1 s) raised from room temperature to a preselected pyrolysis temperature by resistive heating and held there for a preselected time. In our experiments that hold time always exceeded the reactor residence time (~20 s). Samples were either directly injected through a rubber septum, or else introduced via small stainless steel boats inserted into the reactor. All connecting tubing was maintained at a temperature (100 °C) insufficient for pyrolysis, as shown by blank runs. The GC column was stainless steel, 6 ft × 0.125 in., 10% SE-30 on Chromosorb W, or in some experiments, a dummy column (10 ft × 0.125 in. stainless steel tubing, no packing). Helium carrier gas was used at a flow rate of 10 ml/min.

The quantity to be determined in most experiments was the amount of NO_2 produced in pyrolyses. Monitoring of the mass spectral intensity at *m/e* 46 is not an adequate test for the presence of *trace* quantities of NO_2: CO_2, which is produced in the pyrolyses and/or present as impurity or background, also has a peak (isotopic) at *m/e* 46. The natural abundance of ^{18}O is such that, in the mass spectrum of pure CO_2, the ratio I_{46}/I_{44} should be close to 4×10^{-3}.

The mass spectrometer was therefore arranged for simultaneous monitoring of the intensities at *m/e* 44 and 46, and any increase of the ratio $R = I_{46}/I_{44}$ from the value obtained from a sample of pure CO_2 was taken as evidence of the presence of NO_2. Several calibration runs with pure CO_2 were made before each nitrobenzene pyrolysis in order to establish the relative instrumental response factors for the two output channels; the relative sensitivities were such that for pure CO_2 $I_{46}/I_{44} = 3.7 \times 10^{-3}$.

Results

Loss of NO_2 in the Column and Pyrolyzer. Preliminary runs were made to determine whether NO_2, if produced in pyrolyses, would survive the journey to the mass spectrometer ion source. Several 10-µl samples of NO_2/N_2O_4 at atmospheric pressure were injected into the pyrolyzer, which in these experiments was held at room temperature. The results were uniform and unambiguous: NO_2 is completely consumed, and large quantities of NO appear during the ca. 1.5-min journey through the SE-30 column at 100 °C. Conversely, when the packed column was replaced with the dummy column and no other element of apparatus or procedure was changed, large amounts of NO_2 survived. Little, if any, NO was formed under these conditions: the peak heights at *m/e* 46 and 30 were in proportion appropriate to the mass spectrum of pure NO_2, but the reliability of this type of measurement is such that up to perhaps 10% of the original NO_2 could have been converted to NO. In any case, it is clear that NO_2 survives the dummy column but not the packed column.

The possibility that NO_2 is consumed in the pyrolyzer itself was also checked, by the introduction of several 10-µl samples of NO_2 into the pyrolyzer at 400 °C; the dummy column was used for these runs. The results of five determinations were $0.002 < R < 0.004$, showing clearly that NO_2 is entirely consumed. (That R is in fact less than that expected for CO_2 may be due to the presence of some N_2O, for which $R = 0.002$. However since these results were obtained from rather small peak heights, the results should not be taken to prove the presence of N_2O.) Similar determinations with the same sample and the pyrolyzer at room temperature gave $500 < R < 1700$, showing that NO_2 survives.

These observations could be explained if carbonaceous deposits from previous pyrolyses of organic samples remained in the pyrolyzer and thus provided an efficient surface for the heterogeneous reduction of NO_2, e.g., $C + NO_2 \rightarrow CO + NO$. Accordingly the surface was treated with pure oxygen flowing at ca. 60 ml/min through the pyrolyzer, held at 600 °C. This treatment was continued for 0.5 h, and produced a marked effect on NO_2 survival.

When several 10-µl samples of NO_2 were injected into the oxygenated pyrolyzer at 400 °C, values of R were obtained which were greater by 3–4 orders of magnitude than the values obtained with the unoxygenated pyrolyzer. The R values varied, probably owing to varying amounts of CO_2 in the NO_2 sample,[10] and/or variable surface effects. On the two different days this experiment was carried out, average values of 2.5 and 2.0 were obtained. Control experiments with the pyrolyzer at room temperature yielded values of 4.3 and 7.3 on two different days. Apparently some NO_2 is destroyed at higher temperatures, but for the most part it survives. Similar experiments with the pyrolyzer at 500 °C yielded lesser values of R (~1.0) showing increasing NO_2 destruction as the pyrolyzer temperature is raised. Subsequent NO_2 determinations were therefore done only at 400 °C, a temperature sufficiently great for pyrolysis but not so high as to cause complete destruction of NO_2.

Pyrolysis of Nitrobenzene. When 0.1-µl samples of neat nitrobenzene were injected into the pyrolyzer at 400 °C two distinct results were obtained, depending on the temperature of the dummy column. If the column was at 125 °C, all material was eluted in a single peak, which showed a 46/44 ratio of about 0.7. If the dummy column temperature was 50 °C, some separation took place and three peaks were eluted. These are (1), CO_2, NO, and benzene; (2), nitrosobenzene; and (3), unpyrolyzed nitrobenzene. Any NO_2 present would be eluted with the $CO_2/NO/C_6H_6$ fraction. The value of R obtained for this fraction in four separate determinations was in the range 0.002–0.004. That is, no NO_2 was observed.

It has been suggested[8] that NO_2 is produced in pyrolyses, but is converted to NO via a nitrous acid mechanism:

$$NO_2 + RH \rightarrow HNO_2 + R$$

$$2HNO_2 \rightarrow H_2O + NO_2 + NO$$

where the H-atom donor in the first step is primarily nitrobenzene itself. In the present work this possibility was checked by the 400 °C pyrolysis of a mixture of NO_2 (4×10^{-7} mol) and nitrobenzene (10^{-5} mol), under conditions such that the NO_2 and nitrobenzene fractions were well separated by the dummy column. The resulting intensity ratio 46/44 of 7.8 indicates

Table I. Products of Nitrobenzene Pyrolysis

Product	Pyrolysis temp, °C				
	400	450	500	550	600
NO_2 + NO[a]	0.7[b] (0.8)	0.8 (0.7)	2.9 (2.4)	7.5 (6.9)	14.8 (19.0)
Benzene	0.3 (0.03)	0.6 (0.2)	1.9 (1.6)	7.0 (5.5)	15.5 (14.8)
Nitrosobenzene	3.1 (1.3)	2.2 (0.3)	(0.2)	0.08 (0.03)	0.2 (<0.5)
Aniline	9.6 (0.03)	4.1 (0.5)	7.0 (3.1)	12.2 (7.5)	15.1 (17.9)
Nitrobenzene	86.3 (93.6)	92.3 (94.7)	74.6 (84.4)	44.3 (57.5)	14.5 (7.4)
Naphthalene			(0.4)	1.6 (1.1)	4.3 (4.0)
Biphenyl + phenyl ether[a]	(1.7)	(1.0)	3.5 (2.9)	6.3 (5.1)	10.8 (9.7)
Dibenzofuran	(2.5)	(0.8)	3.8 (2.6)	6.5 (6.0)	10.5 (9.8)

[a] Not separated under these chromatographic conditions. [b] Percentage of the total integrated area of the chromatogram. Numbers in parentheses are the results of a repeated determination.

that much of the NO_2 survived in spite of the 25-fold excess of nitrobenzene. Thus the above mechanism cannot explain the absence of NO_2 in pure nitrobenzene pyrolyses.

Products of Nitrobenzene Pyrolysis. Several pyrolyses of 0.1 μl of nitrobenzene were carried out with the SE-30 column rather than the dummy, in order to identify and measure the products. The column was temperature programmed for 2 min at 70 °C, then 25 °C/min to 240 °C, with a helium flow rate of 20 ml/min. Under these conditions the residence time in the reactor was about 10 s. Quantitative analysis was obtained by digital integration of the GC peak areas, using the mass spectrometer total ion current monitor as the detector. These results are collected in Table I. Not shown in Table I is some high molecular weight material formed in amounts too small for mass spectral identification.

Discussion

Several points should be made in regard to the results in Table I. In the first place, the extent of agreement between the results of repeated determinations indicates that attention should be focussed on general trends rather than on numerical results. Lack of precise agreement is expected if there is a variable heterogeneous contribution to the pyrolysis mechanism, and we have already demonstrated a variable heterogeneous effect on NO_2 consumption (reactor oxygenation experiments, vide supra).

The lack of reproducibility of product distribution is more striking and significant when the results of previous investigations are considered. For example, in nitrobenzene pyrolysis at 700 °C, Patterson et al.[9] found the ratio of dibenzofuran to aniline among the products to be 83:1; the same ratio observed by Fields and Myerson[2] at 600 °C was 11:1 and in this work at 600 °C, 0.8:1. In both the other laboratories the pyrolysis chamber was quartz or Vycor, whereas in our experiments it was stainless steel. Secondly, the relatively large amount of aniline formed at all temperatures in the present work also indicates a significant heterogeneous contribution, since this product could hardly be formed via a homogeneous mechanism.

It is interesting that the results from three laboratories are in much better agreement when the dibenzofuran–biphenyl ratios are considered, since both these compounds could be formed homogeneously. Patterson et al. found 0.85:1, Fields and Myerson found 0.75:1, and we found 0.97:1.

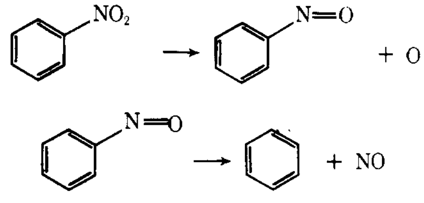
Thirdly, the behavior of nitrosobenzene is unique: it alone is produced to a decreasing extent as the reaction temperature is increased. When this fact is considered together with our finding that NO_2 is not produced in significant quantities, it lends support to the hypothesis that the mechanism of nitrobenzene pyrolysis involves a nitrosobenzene intermediate rather than the direct cleavage to NO_2 and phenyl radical.

In order to confirm the hypothesis of the intermediacy of nitrosobenzene, several experiments were performed in which nitrosobenzene itself was pyrolyzed. These experiments differed from the nitrobenzene pyrolyses in that the sample, solid at room temperature, was dissolved in benzene (~170 mg of nitrosobenzene/ml benzene); 0.3 μl of the solution was then injected into the pyrolyzer. Thus there was present in the nitrosobenzene pyrolyses a larger amount of benzene than in the case of nitrobenzene pyrolysis. A second difference was that much lower temperatures sufficed for nitrosobenzene pyrolysis, as might be expected from the behavior of the nitrosobenzene produced in nitrobenzene pyrolyses.

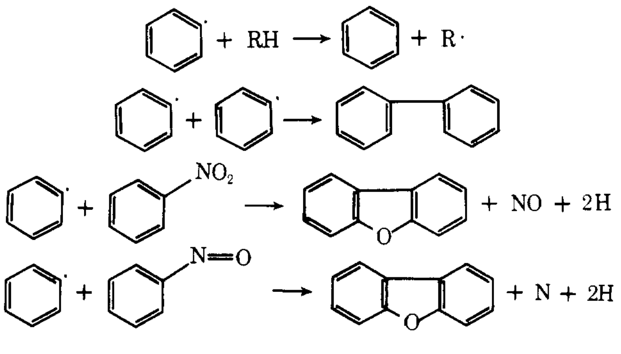
The results of these experiments were striking in their similarity to nitrobenzene pyrolysis, and lend strong support to the hypothesis of nitrosobenzene intermediacy. In the pyrolysis of nitrosobenzene (in benzene solution) at 275 °C the products were CO_2 + NO (3.4), benzene (62.9), nitrosobenzene (8.4), aniline + phenol (3.1), nitrobenzene (1.9), naphthalene (trace), biphenyl (6.7), dibenzofuran (1.7), and hydroxyphenylbenzene (3.9). The numbers in parentheses give the percentage of the total integrated area of the chromatogram. Also, the identification of hydroxyphenylbenzene is probable rather than certain, since it is not confirmed by comparison with literature or authentic sample spectra. As in the case of nitrobenzene pyrolysis, some high molecular weight material was formed, in amounts insufficient for mass spectral identification.

Conclusion

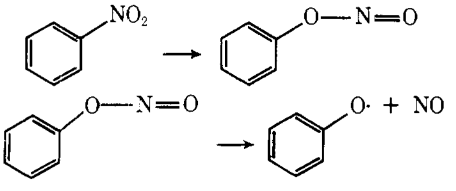
We propose that the initial phase of nitrobenzene pyrolysis is the formation of phenyl radical via the intermediate formation of nitrosobenzene:



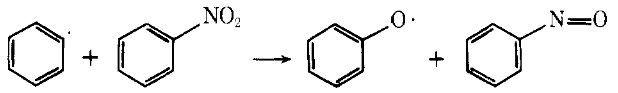
The major products benzene, biphenyl, and dibenzofuran are the expected products of phenyl radical reactions:



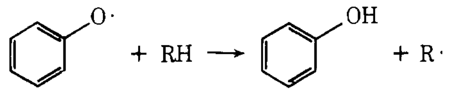
The major difference between this mechanism and that proposed by Fields and Meyerson[8] is that we do not postulate as a primary step the direct fission of nitrobenzene to NO_2 and phenyl radical, a step which, in our view, is not supported by the evidence. Also, in our experiments phenol was not observed as a product of nitrobenzene pyrolysis under any circumstances, whereas Fields and Meyerson reported phenol as the most prominent product at 600 °C. This again supports the conclusion that heterogeneous processes are of great importance in pyrolyses of aromatic nitro compounds. Formation of phenolic products most probably involves the prior production of phenoxy radical, either by



or by



followed by



without specifying whether these are homo- or hetereogeneous processes.

As we have stressed, surface reactions play a dominant role in pyrolyses. It might therefore be asked, what is the evidence for a *homogeneous* mechanism. The answer, considering both present and previous results, is that even though many of the reactions discussed above could proceed as uni- or bimolecular gas phase reactions, there is *no* evidence that nitrobenzene pyrolysis takes place to any extent by a homogeneous mechanism.

Registry No.—Nitric oxide, 10102-44-0; nitrobenzene, 98-95-3.

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(10) The NO_2 was stored in a flask equipped with a rubber septum, which after a time was degraded by the NO_2, with the resulting production of CO_2. As described above, our test for NO_2 was not affected by the presence of CO_2, even in relatively large amounts.

Dry Ozonation of Amines. Conversion of Primary Amines to Nitro Compounds

Ehud Keinan and Yehuda Mazur*

Department of Organic Chemistry, The Weizmann Institute of Science, Rehovot, Israel

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An efficient synthetic method for the conversion of primary amines into their nitro derivatives is described. The amines, adsorbed on dry silica gel, are ozonized to give mainly the corresponding nitro compounds. The dependence of the product yields on several experimental factors was investigated.

Saturated primary amines undergo oxidation reactions by ozone in solution.[1,3] These reactions, thoroughly investigated by Bailey and his co-workers[1,2] result in the corresponding nitroalkanes accompanied by several other compounds depending on the reaction conditions. The by-products are derived mainly from the partially oxidized amines, which react with the solvent, with the solvent oxidation products, or with each other. In addition, competitive reactions of ozone with C atoms were intermittently observed. Therefore nitroalkanes are formed in modest yields and their isolation necessitates separation from the accompanying by-products limiting the preparative value of ozonation in solution.

In order to overcome these drawbacks, we have applied our recently described method of ozonation on silica gel.[4] We have used this dry ozonation method to convert primary amines (alkyl, alkyl aryl, and aryl) into the corresponding nitroalkanes.

The oxidation procedure is carried out as follows. The amine is absorbed on the silica gel ca. 100 times its weight, either by mixing the dry materials in a closed flask or by impregnation using volatile solvent. The adsorbed silica gel is then cooled to −78 °C and ozone is passed through it (3 equiv of ozone is needed). After warming to room temperature, the product may be eluted from the silica gel with an appropriate solvent or by direct vacuum distillation.

Ozonation of Alkyl and Alkyl Aryl Amines. Table I lists the primary amines which were ozonized by our method. Elution of the silica gel with either ether or chloroform gave in all cases, as a major product, the corresponding nitroalkanes, whose yields were between 44 and 70%. The only by-product isolated (except for *tert*-butylamine, whose sole product is the *tert*-nitrobutane) was the respective α-carbonyl derivative (Table I) formed in yields between 2 and 6%. No other products were eluted from the silica gel neither with the solvents mentioned above nor with ethyl acetate.

To obtain optimal conditions for the formation of nitroalkanes we have determined the dependence of the yields of the two reaction products as a function of four experimental factors: concentration of the amine in the silica gel, concentration of water absorbed on the silica gel, reaction temperature, and reaction time. In the first three experiments *sec*-