$^1C_{10}H_8$ indicates the singlet state) outline appropriate mechanistic possibilities.[26]

In Scheme II, X could result from either proton or electron transfer, as mentioned above. If electron transfer is involved, then a subsequent transfer of a hydrogen atom would be required for hydrogen exchange to occur. The appropriate expressions for ϕ_{ex}, the quantum yield of hydrogen exchange, are given as eq 3 for Scheme I and eq 4 for Scheme II. In these equations, [M] and [D] refer to monomeric and dimeric TFA concentrations, respectively.

$$\phi_{ex} = \left(\frac{k_4}{k_4 + k_5}\right)\left(\frac{k_2[M]}{k_1 + k_2[M] + k_3[D]}\right) \quad (3)$$

$$\phi_{ex} = \left(\frac{k_3}{k_3 + k_4}\right)\left(\frac{k_2[D]}{k_1 + k_2[D]}\right) \quad (4)$$

We argue in favor of the second possibility as follows. Equation 3 can be transformed into eq 5, where $\alpha = k_4/(k_4 + k_5)$.

$$k_2\tau = \left(\frac{\phi_r}{\alpha - \phi_r}\right)\left(\frac{1 + K_{SV}K[M]^2}{[M]}\right) \quad (5)$$

Since ϕ_r is found experimentally to increase with the stoichiometric concentration of TFA[5,27] the value of $\phi_r/(\alpha - \phi_r)$ increases with [TFA]. Likewise, the value of $(1 + K_{SV}K[M]^2)/[M]$ must increase with increasing [TFA]. Consequently, this model can never compute a constant value for $k_2\tau$, and in practice the calculated value of $k_2\tau$ rises monotonically with [TFA].

By contrast, a good fit to Lodder's data[27] ($r = 0.997$) is found when $1/\phi_{ex}$ is plotted against 1/[D] as required by eq 4. Scheme II thus accounts for the experimental data.

Spillane[7] has raised the question that it may be the excimer of naphthalene that undergoes hydrogen exchange rather than the monomeric singlet. This possibility is clearly excluded by Lodder's data,[27] which show the relationship $1/\phi_{ex} \propto [C_{10}H_8]$, which is to be expected if the monomer is reactive and the excimer unreactive. The reverse situation leads to a linear relationship between $1/\phi_{ex}$ and $1/[C_{10}H_8]$.

We conclude that both fluorescence quenching and hydrogen exchange in the system naphthalene–TFA in alkane solvents involve the dimer of TFA and not the monomer. Further insight into the mechanism of hydrogen exchange in this system must await more information on the nature of the intermediate formed in the initial interaction between the TFA dimer and the naphthalene singlet.

Acknowledgment. We thank the NSERC of Canada for financial support, Professor E. Havinga for kindly making available a copy of the thesis of G. Lodder, and Drs. R. K. Boyd and S. Goldman for helpful discussions.

Registry No. Naphthalene, 91-20-3; TFA, 76-05-1; TFA dimer, 40857-16-7.

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[26] For simplicity, the reverse of the quenching steps whose rate constants are k_2 and k_3 (Scheme I) and k_2 (Scheme II) are omitted.

[27] G. Lodder, Thesis, University of Leiden, 1971, pp 110–3. The thesis provides the raw data on which the graphs of ref 4 are based.

Pyrolysis of Nitrobenzene

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The pyrolysis of nitrobenzene was examined over the temperature range of 275–630 °C. Liquid products were determined by using a GC–MS combination. Evaluation of the gaseous products was done by using an on-line IR gas cell. At the lower temperatures, nitrobenzene decomposes via direct rupture of the arene–nitro bond to give phenyl radical and NO_2 as primary products. As the temperature is raised, the yield of NO_2 decreases.

There still exists uncertainty on the question of what are the primary products resulting from the pyrolysis of nitrobenzene. Two reports highlight this question. In the earlier report,[1] Fields and Meyerson, utilizing a flow-through Vycor reactor, postulated that at 600 °C the nitro–arene bond breaks to produce phenyl radical and nitrogen dioxide. This was based on the distribution of liquid products obtained from the pyrolysis and from the similarity of this distribution to the mass spectrum. In the mass spectrum, *m/e* 77, $C_6H_5^+$ is the base peak of the spectrum and *m/e* 77 and 123, the molecular ion for nitrobenzene, are related by a metastable transition. Although noncondensable gases were caught in a gas bulb for analysis and analyzed with a mass spectrometer, nitrogen dioxide was not detected. However, given the difficulty experienced by Friedel in analyzing for NO_2 with a mass spectrometer,[2] its absence is not too surprising. In a parallel study,[3] nitrobenzene was examined over the temperature range 400–600 °C by utilizing a stainless-steel-tube reactor on-line with a gas chromatograph. The effluent of the chromatograph was allowed to flow directly into a mass spectrometer. Here, no nitrogen dioxide was detected. Its absence was established by monitoring *m/e* 46, the molecular ion of nitrogen dioxide, during passage of the effluent through the mass spectrometer. (It was also necessary to simultaneously monitor *m/e* 44, the molecular ion of carbon dioxide. The latter, ever-present in a pyrolysis, would contribute to *m/e* 46 via the species $CO^{16}O^{18}$.) From the variation of the concentration of nitrosobenzene, one of the products of pyrolysis, with temperature and the similarity of the distribution of products to those obtained from the pyrolysis of nitrosobenzene

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[1] E. K. Fields and S. Meyerson, *J. Am. Chem. Soc.*, **89**, 3224 (1967).

[2] R. A. Friedel, A. G. Sharkey, J. L. Shultz, and C. R. Humbert, *Anal. Chem.*, **25**, 1314 (1953).

[3] C. W. Hand, C. Merritt, Jr., and C. DiPietro, *J. Org. Chem.*, **42**, 841 (1977).

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itself, Merritt concluded that the primary products were nitrosobenzene and atomic oxygen. Because of our own interest in the pyrolysis of nitroaromatics and also because our pyrolysis apparatus contained an infrared gas cell which we felt permitted a fairly straightforward analysis of gaseous products, we decided to reexamine the pyrolysis. During the course of the pyrolysis, the on-line IR cell in series with the pyrolysis apparatus can be removed for analysis. We believe the IR cell, because of its smaller dimensions and glass construction, is conditioned more easily than the mass-spectrometer inlet used earlier. Because our pyrolysis apparatus is very similar to that used by Fields, we believe our results directly address the question of whether NO_2 is one of the primary products in this type of reactor.

Experimental Section

The pyrolysis were carried out in a Vycor tube filled with glass helices which was continually flushed with argon. The tube was positioned vertically in an electric furnace. In each experiment 25 mL of nitrobenzene was added dropwise from the top at a rate of 25–30 drops/min. The residence time of the nitrobenzene was 10 s. Temperatures were measured with a thermocouple with the bead positioned about halfway along the length of the Vycor tube. The argon used contained less than 1 ppm oxygen. This was determined in a separate experiment using an oxygen analyzer which monitored the argon as it emerged from the bottom of the apparatus. After the vapors eluted from the hot tube, they were cooled by passage through a water-cooled spiral condenser. The condensate was then allowed to collect in a round-bottom flask. This flask had a side arm to which the entrance stopcock of a glass-bodied infrared gas cell was attached via a ball joint. The effluent from the flask would flow into the cell, along its length, and then out the exit stopcock. The cell was 10-cm long and had a volume of 145 cm^3. The window materials were 1-mil polyethylene backed by spectroscopic-grade potassium bromide. The glass-window gaskets were made of neoprene or Teflon. During the addition of the last 5 mL of nitrobenzene, the exit stopcock was closed and the vapors were allowed to pressurize the cell. This was done to ensure that sufficient sample was in the cell for infrared measurements. At completion of addition, the entrance stopcock was closed and the cell was detached from the apparatus. The spectrophotometer used was a Beckman Model 12 equipped with a 2-cm spectral slit width. The liquid contents of the round-bottom flask were examined with a GC/MS combination. Two different SE-30 columns were utilized. The first was a 10 ft × 0.25 in. Cu column packed with 20% SE-30. The other was a 6 ft × 0.25 in. Cu column packed with 3% SE-30. The former was especially useful in resolving the lower-boiling components of the reaction mixture. The effluent from the gas chromatograph was allowed to flow directly into an AEI MS 902 mass spectrometer.

Above the tube furnace, all standard-taper glass connections were lubricated with Apiezon T. Below the furnace, connections were fitted with Teflon-sleeve inserts in order to minimize contact of the hot vapors with any grease. After each run, the furnace temperature was raised to 600 °C and purged with oxygen to ensure that any carbonaceous deposits would be burned out.[4]

Discussion

The results of the infrared determinations of the relative abundance of the gaseous products at the various temperatures are listed in Table I. The spectral data were corrected to relative abundance by using published absorbance ratios[7,8] since pure reference samples were not available during these tests. Any systematic error induced, except for nitrous oxide, will be very small. The error in the N_2O value would be no more than 2% absolute by using the limiting-case data. This would not cause a major change in the relationships. Infrared spectra corresponding to low and high values of NO_2 are shown in Figures 1 and 2, respectively. (See paragraph at the end of paper about supplementary material.)

Table I. Volatile Products from Nitrobenzene

temp, °C	flow rate, cm^3/min	relative abundance, %				
		NO_2	NO	N_2O	CO	CO_2
475	20	81	12	0.4	5	1
475	20	57	27	0.4	13.2	3
475	20	33	42	1.1	19	5
475	20	36	28	1	27	9
475	20	38	20	1.5	33	8
475	40	23	45	0.6	26	6
525	20	7	35	1.6	49	8
550	20	0.5	36	1.9	53	9
550	20	0.3	34	0.2	54	9
550	60	(nd)	36	1.5	58	5
550	60	0.3	38	1.4	53	7
625	20	(nd)	30	2.3	59	9
625	20	1.2	28	1.2	61	8
630	90	(nd)	34	1.9	59	5

Table II. Liquid Products from Nitrobenzene[a]

product	relative concn[b]
benzene	21.3
phenol	18.8[c]
benzonitrile	5.3[d]
aniline	1.0[d]
nitrobenzene	100
quinoline	0.1
biphenyl	7.8
dibenzofuran	8.5
diphenylamine	1.5
benzoquinoline	2.5
nitrobiphenyl	2.5
terphenyls	5.9
phenylnaphthalene	0.7
methylterphenyls	2.0

[a] 600 °C, contact time 10 s. [b] Normalized areas from chromatograms. [c] To resolve phenol from the benzonitrile/aniline combination it was necessary to use the heavier loaded column (see Experimental Section). [d] It was not possible to resolve benzonitrile from aniline. Estimate of the relative concentrations was made from the relative abundance of the respective molecular ions in the composite mass spectrum.

As can be seen from Table I, NO_2 is the main gaseous decomposition product at the lower temperatures. As the temperature is raised, CO and NO begin to predominate. The decreasing NO_2 concentration could be attributable to an accelerated buildup of carbonaceous material as the temperature is raised. Here the carbon could provide a surface for reduction of the NO_2. Some evidence for this was obtained in a separate experiment at 525 °C. Here, a value of 8% NO_2 was obtained after the addition of the 25 mL of nitrobenzene. Then, without the customary oxygen purge an additional 75 mL was added. The NO_2 level was found to have decreased to 2%. Also possible is an alternative mode of decomposition at higher temperatures.

Since our apparatus is very similar to that used by Fields and Meyerson, the appearance of NO_2 in the effluent offers some evidence for their suggestion that one of the primary

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(4) It had been found in an earlier study (ref 3) that carbon deposits can remove nitrogen dioxide, i.e., $C + NO_2 \rightarrow CO + NO$.

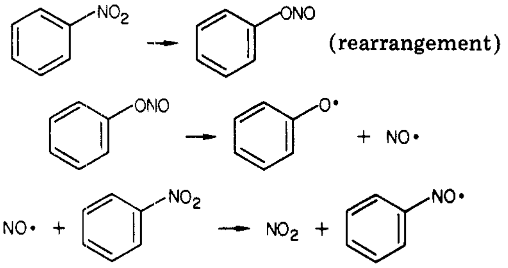
(5) We are indebted to Professor M. J. S. Dewar for this suggestion.

(6) Interestingly enough, in the earlier study (ref 1), when nitrobenzene was pyrolyzed with excess benzene only 1% phenol was found.

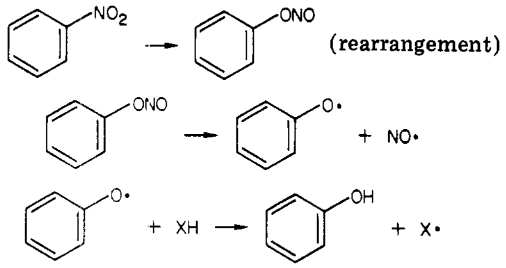
(7) R. H. Pierson, A. N. Fletcher, and E. St. Clair Gantz, *Anal. Chem.*, **25**, 1218 (1956).

(8) M. V. Zeller, "Infrared Methods in Air Analysis", Report no. 993-9236, Perkin-Elmer Corp., 1975.

processes of nitrobenzene pyrolysis is the breaking of the arene–nitro bond to produce NO_2 and phenyl radical. This appearance of NO_2 is not, however, conclusive proof that NO_2 is a primary product. NO_2 could be a secondary product, formed via the following set of reactions:[5]



The liquid product distribution of our 600 °C nitrobenzene pyrolysis is presented in Table II. As expected, this distribution resembles that obtained earlier. In both studies, phenol and benzene are found to be major products. This contrasts with the stainless-steel-tube experiments where no phenol was detected.[6] The presence of phenol would indicate that some rearrangement of nitrobenzene to phenyl nitrite does precede decomposition.



Also, the presence of benzofuran and diphenyl ether could be due to an intermediate phenoxy radical. The presence of benzene and the di- and triphenyls may result from the direct decomposition of the nitro–arene bond to produce a phenyl radical which can subsequently combine with other phenyl radicals. In contrast to the result of Fields, we find a significantly higher ratio of benzene to biphenyl (2.7 vs. 0.3). The most obvious difference in experimental conditions which might cause such a change would be the contact times, 10 vs. 20 s. Another parameter affecting the liquid product distribution could be the total amount of nitrobenzene added during the course of a single experiment. We would expect conditions at the helical surfaces to be continually varying as liquid is added at 600 °C. If so, then the final product distribution should reflect the total amount of liquid added. In our experiments, 25 mL was added. The amount added by Fields was not mentioned in their paper. Aniline, the major product of the steel-tube reactor, here accounts for about 1% of the liquid products.

Conclusions

We believe that our finding of nitrogen dioxide in the pyrolysis off-gases, in conjunction with liquid products from phenyl radical reactions, requires that consideration be still given to the possibility for direct arene–nitro bond cleavage in the pyrolysis of nitrobenzene.

Registry No. Nitrobenzene, 98-95-3.

Supplementary Material Available: Figure 1, infrared spectrum for 2.4% NO_2 level; Figure 2, infrared spectrum for 20% NO_2 level (2 pages). Ordering information is given on any current masthead page.

Autoxidation of Ethyl Phosphinite, Phosphonite, and Phosphite Esters[1]

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The AIBN-initiated autoxidations in benzene of triethyl phosphite, $P(OEt)_3$, diethyl ethylphosphonite, $EtP(OEt)_2$, and ethyl diethylphosphinite, Et_2POEt, were studied at 50 °C. The quantitative conversion of $P(OEt)_3$ to triethyl phosphate obeys the rate law rate = $(2.0 \times 10^{-4}\ \text{atm}^{-1}\ \text{s}^{-1})[\text{AIBN}]P_{O_2}$ and is zero order in phosphite. Autoxidation of $EtP(OEt)_2$ and Et_2POEt gives the complete mixture of intermediates and products predicted by Buckler's mechanism for the autoxidation of trialkylphosphines. At 1 atm of oxygen pressure and 0.02 M AIBN the pseudo-first-order rate law is rate = k'[organophosphorus ester], ester], with $k' = 7.49 \times 10^{-4}\ \text{s}^{-1}$ for $EtP(OEt)_2$ and $2.37 \times 10^{-4}\ \text{s}^{-1}$ for Et_2POEt.

The autoxidation of low molecular weight aliphatic tertiary phosphites (eq I) requires heat and catalysis, e.g.,

$$2P(OR)_3 + O_2 \rightarrow 2P(O)(OR)_3 \qquad \text{(I)}$$

aluminum oxide at 120 °C[2] or radical [3-5] or photoinitiation.[6,7] At room temperature, in the absence of initiation, triethyl phosphite gives no reaction with air[8] or oxygen.[5] Only very limited rate studies of phosphite autoxidation have been reported. The rate of air autoxidation of triisopropyl phosphite was independent of phosphite concentration over much of the range with γ-ray initiation and enough water to give initiating radicals on radiolysis but not enough to cause extensive hydrolysis.[9] Under UV photoinitiation, tri-*n*-butyl phosphite underwent more rapid oxidation in pure oxygen than in air,[6] and the rate

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[1] Taken from a portion of the Dissertation submitted by W.S.H. to the Graduate School of Oregon State University in partial fulfillment of the requirements for the Ph.D. degree. Supported in part by NSF Grant MPS75-05782, which is acknowledged with thanks.

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