The Radiolysis of Gaseous Trifluoroiodomethane in the Presence of Nitric Oxide

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Nitric oxide reduces the 100-eV yields of tetrafluoromethane and difluorodiiodomethane and increases the yield of iodine in the radiolysis of trifluoroiodomethane. The products nitrogen, nitrogen dioxide, trifluoronitrosomethane, trifluoronitromethane, and hexafluoroethane are also identified. A radical-chain mechanism involving an intermediate diazonium nitrate is proposed to explain the formation of these products and the high value of $G(-NO)$. It is suggested that nitric oxide is acting as a scavenger of excited radicals.

Nitric oxide has been used as a radical scavenger in the radiolysis of hydrocarbons, notably by Yang.[1,2] Yang presents a cogent argument that nitric oxide is a true radical scavenger during methane radiolysis and does not interfere with any ionic or molecular reactions that may be proceeding. This argument is based on a comparison of the effect of nitric oxide and other radical scavengers on $G(H_2)$ in methane radiolysis.

The radiolysis of trifluoroiodomethane in the presence of oxygen as a radical scavenger reduces the 100-eV yields of tetrafluoromethane and difluorodiiodomethane indicating that these products are formed largely by radical processes.[3] Unfortunately the presence of oxygen results in a number of secondary reactions which make a complete interpretation of the results difficult. It was with a view to clarifying this situation regarding the radical nature of the reaction that the present work was initiated.

Experimental Section

Except where otherwise stated, the preparation of trifluoroiodomethane, gas chromatographic analysis, infrared spectroscopic analysis, dosimetry, and radiolysis were carried out as previously described.[3] Nitric oxide was prepared by the reaction of acidified ferrous sulfate with sodium nitrite.[4]

In a typical experiment trifluoroiodomethane (45.45 mmol) and nitric oxide (45.73 mmol) were condensed into a 2.2-l. bulb and irradiated, in the gas phase, on the ^{60}Co source at a dose rate of *ca.* 0.73 Mrad/hr for 15 hr. After irradiation the nitrogen was transferred by means of an automatic Toepler pump[5] into a vessel of known volume and measured. The purity of the nitrogen was checked by gas chromatographic analysis and found to contain only a slight trace of nitric oxide. The condensable gases which remained frozen down during the removal of nitrogen were fractionated *in vacuo* through traps cooled to −63, −96, −131, and −196°, respectively. The fraction condensed at −63° contained iodine together with a trace of nitrogen dioxide. The iodine was determined by titration with sodium thiosulfate solution after destroying the nitrogen dioxide by addition of sulfamic acid. The fraction condensed at −96° was nitrogen dioxide; this was determined by allowing it to react with excess standard sodium hydroxide solution and back-titrating with standard hydrochloric acid. The fraction condensed at −131° consisted mainly of trifluoroiodomethane together with a small amount of trifluoronitromethane. The relative proportions of these two compounds were determined by gas chromatography using an 8 m × 4 mm i.d. column of 30% w/w Kel F oil No. 10 (F & M Scientific Corp.) on 80–120 mesh Celite. The fraction condensed at −196° contained trifluoroiodomethane, tetrafluoromethane, carbonyl fluoride, nitric oxide, hexafluoroethane, and trifluoronitrosomethane. Since nitric oxide has almost the same retention time as tetrafluoromethane, direct analysis of this mixture by gas chromatography was not possible. Oxygen was added to the mixed gases to oxidize the nitric oxide to nitrogen dioxide. Excess oxygen was removed, and the nitrogen dioxide was separated from the other gases by trap-to-trap fractionation *in vacuo* and determined by titration. The remainder of this fraction was analyzed by gas chromatography.

Other experiments using different proportions of reactants and different irradiation times were also carried out. The results are shown in Table I together with results of the radiolysis of trifluoroiodomethane alone for comparison.

Results and Discussion

Examination of the results in Table I shows that the most notable features of this reaction are (a) the high values and dependence of $G(N_2)$ and $G(-NO)$ on the initial pressure of nitric oxide, (b) the marked increase in the value of $G(I_2)$ relative to the value in the absence of nitric oxide, and (c) the marked reduction of $G(CF_4)$ and $G(CF_2I_2)$ compared with the corresponding values for trifluoroiodomethane alone.

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Table I

	Ratio	G values								
Expt no.	$CF_3I:NO$	I_2	CF_4	C_2F_6	CF_3NO	N_2	NO_2	CF_3NO_2	$-NO$	CF_2I_2
1[a]	0.25	12.3	...	...	...	478	...	...	1092	...
2[a]	1	10.1	0.2	0.02	0.32	150	251	3.3	571	...
3[a]	16.6	12.1	0.03	0.03	27.7	...	1.3	...	83	...
4[b]	∞	0.13	1.08	...	...	...	...	...	...	0.82

[a] This work. [b] See ref 3.

The last point substantiates the conclusions from work in the presence of oxygen, namely, that tetrafluoromethane and difluorodiiodomethane are formed mainly by radical reactions. The value of $G(CF_4) = 0.03$ is much less and the value of $G(I_2) = 12$ higher than the corresponding values observed when trifluoroiodomethane is irradiated alone or in the presence of oxygen. This suggests that nitric oxide is a better radical scavenger than either oxygen or iodine, which is in agreement with the work of Yang on hydrocarbons.

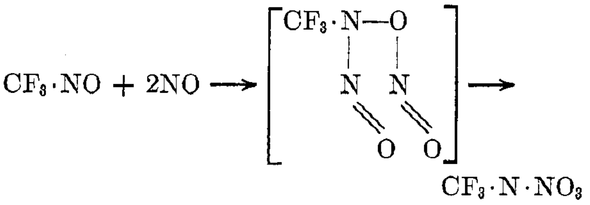
The scavenging of trifluoromethyl radicals by nitric oxide prevents the formation of tetrafluoromethane and $\cdot CF_2I$ radicals by the reaction

$$CF_3\cdot^* + CF_3I \longrightarrow CF_4 + \cdot CF_2I \qquad (1)$$

Hence no difluorodiiodomethane can be formed as is observed in the presence of nitric oxide. The scavenging reaction will form trifluoronitrosomethane

$$CF_3\cdot^* + NO \longrightarrow CF_3NO \qquad (2)$$

but the yield of trifluoronitrosomethane will depend on the relative abilities of nitric oxide and iodine as radical scavengers and on the reactivity and environment of trifluoronitrosomethane. In the presence of 5% molar nitric oxide and at low dose $G(CF_3NO) = 27.7$ whereas at higher dose and 50% molar nitric oxide $G(CF_3NO) = 0.3$. Also under the latter conditions $G(N_2)$ and $G(-NO)$ are markedly increased. The reaction thus has two stages: first scavenging of trifluoromethyl radicals by nitric oxide to give trifluoronitrosomethane, followed by reaction of trifluoronitrosomethane with nitric oxide to give nitrogen, nitrogen dioxide, and trifluoronitromethane. The following chain reaction is suggested



(3)

$$CF_3\cdot N_2\cdot NO_3 \longrightarrow CF_3\cdot + N_2 + \cdot NO_3 \qquad (4)$$

$$\cdot NO_3 + NO \longrightarrow 2NO_2 \qquad (5)$$

$$CF_3\cdot + NO \longrightarrow CF_3\cdot NO \qquad (6)$$

which can lead to the formation of nitrogen and nitrogen dioxide in high yield.

The reaction of monomeric nitroso compounds with nitric oxide was first observed by Bamberger[6] for nitrosobenzene and has subsequently been reported by other workers using nitric oxide as a radical scavenger in photolytic and pyrolytic studies.[7–14] This is the first report of a reaction of this type occurring when nitric oxide is used as a radical scavenger in radiolysis work. The length of each chain will depend on how much nitric oxide is available. Once the concentration of nitrogen dioxide becomes appreciable, the chain-termination reaction

$$CF_3\cdot + NO_2 \longrightarrow CF_3NO_2 \qquad (7)$$

begins to compete with and may eventually take precedence over the scavenging reaction 2. This is probably what is happening in the later stages of expt 2 (Table I) since trifluoronitromethane is produced with $G(CF_3NO_2) = 3.3$. The main over-all effect of this chain reaction is the disproportionation of nitric oxide into nitrogen and nitrogen dioxide

$$4NO \longrightarrow N_2 + 2NO_2 \qquad (8)$$

and so the ratio $G(-NO):G(NO_2):G(N_2)$ should be 4:2:1. The observed ratio in expt 2 of 3.8:1.7:1.0 is of this order and suggests that the chain mechanism outlined above is operating. In expt 1, where an excess of nitric oxide is present, the proportion of nitrogen present in the products is low. It would appear that some other mechanism is operating when nitric oxide is present in excess, and further work is in progress to clarify this point. It should be noted that the value of $G(-NO)$ is limited by the initial concentration of nitric oxide, indicating that a small amount of trifluoroiodomethane can act as an initiator for the radiolytic disproportionation of nitric oxide. The

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irradiation of nitric oxide alone has been carried out by other workers using fission fragments and γ rays,[15,16] but in both cases the $G(-NO)$ value was much lower than when trifluoroiodomethane was present.

The occurrence of this chain reaction propogated by a regenerated trifluoromethyl radical casts doubt on the usefulness of nitric oxide as a radical scavenger in radiolysis work. In the present work the inference is that nitric oxide scavenges the initially formed excited or "hot" trifluoromethyl radicals followed by a chain reaction involving thermalized trifluoromethyl radicals. It has been suggested in the previous work that only excited trifluoromethyl radicals can abstract fluorine from trifluoroiodomethane to give tetrafluoromethane, and this is now substantiated. The eventual fate of the thermal trifluoromethyl radicals is to form trifluoronitromethane, trifluoronitrosomethane, or some as yet unidentified product.

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Mechanism of Reaction of Hydroxyl Radicals with Benzene in the γ Radiolysis of the Aerated Aqueous Benzene System

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The reaction of hydroxyl radicals with benzene in aerated aqueous solutions under γ radiolysis produces phenol and β-hydroxymucondialdehyde (βHMD). The respective G values are 1.7 and 1.2, in 0.8 N H_2SO_4, and 1.78 and 0.7, in neutral solutions, the sum of the two yields accounting for all the OH radicals in each instance. The enhancing effect of ferrous ions on these yields has been correlated with the peroxide chain mechanism advanced originally to account for the influence of organic impurities on the $G(Fe^{3+})$ of the Fricke dosimeter. At a benzene concentration of 10^{-2} M and a ferrous ion concentration of 10^{-3} M, $G(Fe^{3+})$ is $\sim$48; G(phenol) and $G(\beta HMD)$ are 8.8 and 6.6, respectively. This corresponds to a chain length of $\sim$2.

Introduction

A program of study of the formation of phenolic compounds under radiolysis required reexamination of the aerated aqueous benzene system. Earlier work[1-6] has reported the formation of phenol in the γ radiolysis of this system. Three other products, "mucondialdehyde" with a G value ranging from 0.2 to 1.7,[7-10] an unknown phenol-like compound, and an acid, have been notably described. In a previous communication[11] it was shown that these three products are one and the same, *i.e.*, β-hydroxymucondialdehyde (βHMD). Interference due to βHMD accounts for the wide variation in the values of G(phenol) reported earlier.[1-6,9,10,12] This problem has here been solved by effecting a separation of the two compounds before analyzing them, and reliable G(phenol) and $G(\beta HMD)$ values have been obtained.

Ferrous ions have been observed to enhance the yields of phenol and the dial.[9] This effect has been restudied and correlated with the peroxide chain mechanism advanced originally by Kolthoff and Medalia[13] in the case of Fenton's reagent and later by Dewhurst[14,15] to explain the influence of organic impurities on the G

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