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PHOTOLYSIS OF RDX IN AQUEOUS SOLUTION, WITH AND WITHOUT OZONE

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This report describes an investigation of the products of the photolysis of RDX, in the presence and absence of ozone. RDX in tap water reacts with UV radiation to produce nitrite ion, ammonia, and organic nitro compounds. When this complex mixture was treated with ozone, there was found carbon dioxide, cyanic acid, nitrate ion, and ammonia.

If the RDX solution is simultaneously exposed to UV radiation and ozone, there is found carbon dioxide, carbon monoxide, nitrate ion, and ammonia.

In addition, two organic nitro compounds were found, which were different from those found in the absence of ozone.

SUMMARY

This report describes the identification of some of the products of the photolysis of RDX in tap water, in the presence and absence of ozone. The work was performed under Task Number SF57-572-391, Pollution Potential of Explosives in Water.

Julius W. Enig
JULIUS W. ENIG
By direction

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I. INTRODUCTION

Kubose and Hoffsommer (1a) have investigated the initial products formed in the photolysis of aqueous RDX with radiation greater than 220 nm (no pyrex filter). As many as seven compounds were extracted from the aqueous solution with benzene, and one of these was 1-nitroso-3,5-dinitro-1,3,5-triazacyclohexane (1b,c). These compounds were formed in the first minutes of reaction, and had disappeared when the RDX concentration was not detectable.

The present report describes an investigation of the products of the photolysis of RDX after the RDX is not detectable. The same photolysis geometry was used as in the previous investigation (1a). In addition to ultraviolet (UV) radiation, ozone was also used as a reactant in an effort to produce non-toxic products. As an aid in following the distribution of products, uniformly labelled carbon-14 RDX was used (2).

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(1) (a) D. A. Kubose and J. C. Hoffsommer, NSWC/WOL TR 77-20, "Photolysis of RDX in Aqueous Solution. Initial Studies," 22 February 1977.

(b) This mono-nitroso compound was not found by Smetana and Bulusu (TR ARLCD-TR-77039, "Photochemical Studies of Secondary Nitramines. Part II. Ultraviolet Photolysis and Ozonolysis of RDX in Aqueous Solutions," ARRADCOM, June 1977, p 8).

(c) Dimethylnitrosamine was found when dimethylnitramine was photolysed (K. Suryanarayanan and S. Bulusu, TR 4068, "Photochemical Studies of Secondary Nitramines I. Absorption Spectra of Nitramines and Photolysis of Dimethylnitramine in Solution," Picatinny Arsenal, Dover, N. J., September 1970).

(2) Courtesy of Sharon Bradley, Armed Forces Radiobiological Research Institute, Bethesda, Maryland.

II. EXPERIMENTAL AND RESULTS

Analytical Methods

RDX was determined by extraction with benzene, followed by injection of an aliquot of the benzene into a Hewlett-Packard Model 5750 research gas chromatograph equipped with a nickel-63 electron capture detector. The 4-ft x 1/4-inch glass column was packed with 3.52% Dexsil GC on 80/100 mesh Chromosorb W AW DMCS. The carrier gas was 95/5 (v/v) argon/methane at 200 ml/min. and the column temperature was 180°.

Mass spectra were obtained on a Varian Mat III gas chromatograph/mass spectrometer (gc/ms). Two columns were used: (1) An 8-ft x 1/8-inch stainless steel packed with 10% Carbowax 20M on 60/80 mesh on Chromosorb W AW DMCS, and (2) a 5-ft x 1/8-inch stainless steel packed with Polypack I (80/120 mesh).

Nitrate ion was determined by conversion to nitrobenzene followed by gc analysis of nitrobenzene (3). Nitrite ion was determined by the Griess method (4).

Formaldehyde was determined by the chromotropic acid method (1a),(5).

Ammonia was determined with an Orion ammonia gas electrode, and pH was determined with a Beckman Model G pH meter.

RDX Stock Solutions

A stock solution of the carbon-14 RDX (0.015 millicurie per milligram) was prepared by accurately weighing 1 mg into a 25-ml volumetric flask and dissolving it in about 10 ml of acetone. The acetone was completely removed by warming the solution while passing a stream of nitrogen over it. Water was added to the RDX-coated flask, which was warmed to about 80°C in a water bath. When the RDX appeared to be in solution, the flask was allowed to cool to room temperature, diluted to volume with water, and mixed. The solution was analyzed by extracting 50 microliters with 10 ml of benzene to which was added 25 microliters of a 100 ppm solution

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(3) D. J. Glover and J. C. Hoffsommer, J. Chromatog., **94**, 334 (1974).

(4) Described in "Colorimetric Methods of Analysis," F. D. Snell and C. T. Snell, Vol. 2, Van Nostrand, New York, 3rd ed., 1949, pp. 802-804.

(5) J. W. Cares, Amer. Ind. Hyg. Assoc. **29**, 405 (1968).

of TNT in benzene (reference compound). An aliquot of this 10-ml benzene solution was injected into the GC and compared with a standard prepared from the same TNT solution and an accurately weighed RDX sample in acetone (40 ppm). The GC analysis of the aqueous carbon-14 RDX agreed with the weight (40 ppm). A stock solution of carbon-12 RDX in tap water was prepared by stirring an excess of RDX in 2 liters of water for several days at room temperature, then filtering through a glass fiber filter.

Preparation of Reaction Mixture of Carbon-14 and Carbon-12 RDX

To an aliquot (1 to 5 ml) of the carbon-14 RDX stock solution was added enough carbon-12 stock solution to make a volume of 100 to 125 ml. The pH was measured and a 100-microliter aliquot was added to 15 ml of Aquasol (scintillating liquid, New England Nuclear) containing Cab-O-Sil, and 50 microliters were extracted with 10 ml of benzene for RDX analysis.

Reaction Set-up and Conditions

The reaction mixture was put in a quartz tube mounted next to the UV source, a 450 watt medium pressure lamp which was shielded until exposure was desired. The quartz tube was fitted with a rubber stopper containing an inlet for ozone (generated by passing oxygen through a PCI Ozone Corp. (N.J.) generator) or oxygen, which passed through a coarse frit at the bottom of the tube. This allowed thorough mixing during reaction. The stopper was also fitted with a dropping funnel for adding 1 to 2 ml of 18 N sulfuric acid in order to remove all of the carbon dioxide from the reaction mixture. An exit tube led from the stopper to a trap containing approximately 23% aqueous potassium hydroxide.

Experiment 1. Photolysis of RDX in the presence of ozone; carbon-14 distribution and carbon dioxide formation

This experiment was set up to follow the carbon-14 distribution only. As carbon dioxide was expected as a major product, a second KOH trap was put in line to be sure all carbon dioxide was trapped. A previous run with carbon-12 RDX showed that less than 0.1 ppm remained after five minutes, so ozone was bubbled for five minutes through the carbon-14 RDX solution while the solution was also being exposed to UV radiation (no Pyrex filter). The ozone generator was then turned off, but the oxygen continued for an additional 15 minutes, then stopped. The system was vented and 1 ml of 18 N sulfuric acid added. Oxygen was again bubbled through for about one hour.

An aliquot of the reaction mixture was counted for carbon-14. To each KOH solution was added 0.5 ml of saturated solution of sodium carbonate, followed by 5 ml of a saturated solution of barium nitrate. The precipitated barium carbonate was allowed to settle over night, and the solution decanted from the precipitate. An aliquot of the supernate was counted for carbon-14. The precipitate was washed with water, decanted, etc. until the supernate was neutral to litmus. All of the precipitate was then counted for carbon-14.

The carbon-14 distribution for this experiment was:

Remaining in the reaction mixture	32.9%
1st KOH trap; in barium carbonate precipitate:	50.6%
in supernate	2.5%
2nd KOH trap; in barium carbonate precipitate:	0.01%
in supernate	0.53%
TOTAL	86.5%
lost as volatiles	13.5%

The conclusions drawn from this experiment were: (1) only one KOH trap is necessary to trap carbon dioxide, and (2) some other oxidized carbon species is in and has passed through the second trap. Carbon monoxide seemed a likely suspect.

Experiment 2. Photolysis of RDX in the presence of ozone; carbon monoxide and other carbon compound formation

The second KOH trap of experiment 1 was replaced with a trap containing 7.5 g of cuprous chloride dissolved in 60 ml of concentrated hydrochloric acid, and diluted to 100 ml with water (a known absorbent for carbon monoxide). Better carbon-14 counting is obtained if cuprous chloride is in ammoniun hydroxide, which also absorbs carbon monoxide. The hydrochloric acid solution is dark, and therefore, scintillation is largely quenched. After a twelve minute exposure to UV plus ozone, the carbon-14 distribution was:

Remaining in the reaction mixture:	52.3%
KOH trap, in barium carbonate precipitate:	37.7%
Cuprous chloride trap (carbon monoxide):	3.9%
TOTAL	93.9%
lost as volatiles	6.1%

The supernate of the KOH trap was not analysed, but it probably contained 1-2% of the carbon-14. The lack of reproducibility between experiments 1 and 2 may be due to a change in ozone flow (the ozone concentration was not measured).

Chemical Analysis of Reaction Mixture

The reaction mixture of this experiment was analysed, with the following results:

$(RDX)_o = 31$ ppm (1.40×10^{-4} M); $(RDX)_{final} = 0.005$ ppm

Formaldehyde:	not detected
Nitrate ion:	5.53×10^{-4} M
Ammonia	3.10×10^{-4} M
TOTAL N	8.63×10^{-4} M
calculated total N ($6 \times (RDX)_o$)	8.40×10^{-4} M
Nitrate ion/RDX	4.0

Extraction Experiments of Reaction Mixture: Variation of Nitrate Ion Remaining

An aliquot of this acidic reaction mixture was extracted three times with equal volumes of benzene: carbon-14 extracted, 3% of the 52%. The remaining aqueous solution was extracted three times with equal volumes of ethyl acetate: carbon-14 extracted, 23% of the 52%. The aqueous solution remaining was analyzed for nitrate ion: found, 4.24×10^{-4}M. (An aqueous solution of sodium nitrate containing 2 ml of 18 N sulfuric acid per 100 ml was extracted three times with equal volumes of ethyl acetate: no nitrate was extracted.).

The acidity of another 25 ml aliquot of this reaction mixture was increased by adding another 2 ml of 18 N sulfuric acid. Extraction of this aliquot with an equal volume of ethyl acetate gave a loss of 29% of the carbon-14 and the resulting aqueous solution was 3.84×10^{-4}M in nitrate ion. This aqueous extract was extracted twice more with equal volumes of ethyl acetate: 50% of the carbon-14 was extracted (of the 52%); nitrate ion = 2.61×10^{-4}M; nitrate ion/RDX = 1.9. The three aliquots of ethyl acetate were combined and evaporated to 50 microliters. Of the 50% carbon-14 extracted, there remained 5.4%.

Mass Spectra of Compounds Extracted from Reaction Mixture

The gc/ms of the 50-microliter solution was obtained on 10% Carbowax 20 M. The column was initially at 40°, and after ethyl acetate eluted, the temperature was programmed to 200° at 20°/min. A blank was prepared from ethyl acetate/tap water in the same manner. When the two runs were compared, there remained from the reaction mixture three compounds: m/e 142, m/e 114, and m/e 89 (Figures 1, 2, and 3). After three hours, these products were no longer detectable.

Experiment 3. Photolysis of RDX in the Absence of Ozone. Photolysis and Ozonolysis of RDX Products

In this experiment, the RDX solution was exposed to UV plus oxygen for 12 minutes. One half the solution was removed for analysis, and the other half was again exposed to UV radiation with ozone bubbling through for 12 minutes. An aliquot of this latter half was taken for carbon-14 analysis before acidification. The reaction mixture was acidified, and oxygen bubbled through for one hour.

This third experiment was analyzed with the following results.

First half, Experiment 3. RDX Photolysis in the Absence of Ozone: Product Distribution.

Carbon-14 analysis:	Remaining in reaction mixture	98.7%
	KOH trap; in barium carbonate precipitate:	0.42%
	Cuprous chloride trap (ammonia) as carbon monoxide	0.03%
	TOTAL	99.2%

Chemical analysis:

Initial pH = 7.26; final pH = 7.03

$(RDX)_o = 27$ ppm (1.23×10^{-4}M); $(RDX)_{final} = 0.014$ ppm

Nitrate ion = 0.33×10^{-4}M
Nitrite ion = 3.91×10^{-4}M
ammonia = 2.5×10^{-4}M
(nitrate + nitrite)/RDX = 3.4

Formaldehyde = 0.53×10^{-4}M

Extraction Experiments of Reaction Mixture. Variation of Nitrite Ion and Carbon-14 Products with Extraction Solvent

An aliquot of the neutral reaction mixture of experiment 3 was extracted with an equal volume of benzene, followed by an equal volume of ethyl ether, and then an equal volume of ethyl acetate. After each extraction, the aqueous phase remaining was analysed for nitrite ion and carbon-14. There was no loss of nitrite ion after benzene extraction, a 6.4% loss after ether extraction, and a further 6.3% loss after the ethyl acetate extraction. The corresponding carbon-14 losses were 4.6%, 7.4%, and 3.4%.

To 15 ml of the reaction mixture was added 0.5 ml of 18 N sulfuric acid. This acid solution was extracted with three 15-ml portions of ethyl acetate: carbon-14 extracted, 28%. The ethyl acetate extract was evaporated to 50 microliters: carbon-14 remaining, 3.6% of the 28%.

GC/MS Analysis of Ethyl Acetate Extracts of Acidified Reaction Mixture

To get better peak separation, the column temperature was increased in approximately 15° intervals and was kept at a given temperature for five minutes. The initial temperature was 43° and the final temperature was 200°. After correcting for the blank, there was found:

(1) on 10% Carbowax 20 M: formaldehyde, m/e 44 (not CO_2 or N_2O) (Figure 4), m/e 89 (same as from Exp. 2).

(2) on Polypak I: after ethyl acetate eluted (120°), two compounds each having m/e 117 (Figures 5 and 6).

Experiments with the Aqueous Layer from Ethyl Acetate Extraction

Test for urea: Urea is known to react with nitrous acid to form carbon dioxide. To 1 ml of the neutral aqueous extract (above) was added 0.2g solid sodium nitrite and the solution was acidified with 18 N sulfuric acid. There was a loss of 6% of the carbon-14 after one hour.

Volatility test: A 10-ml aliquot of the aqueous extract was allowed to evaporate to dryness in the hood at room temperature. The residue was dissolved in water and an aliquot counted for carbon-14. There was a loss of 75% of carbon-14.

Second half, Experiment 3. Photolysis and Ozonolysis of RDX Products

Carbon-14 analysis:	Before acidification (pH = 7.0)	
	58.4% in reaction mixture	
	41.6% loss as volatiles (as CO_2, see KOH trap below)	
	After acidification (pH = 0.98)	
	Remaining in reaction mixture	36.4%
	KOH trap; in barium carbonate precipitate:	54.4%
	Cuprous chloride trap (ammonia) as carbon monoxide	0.80%
	TOTAL	91.6%
	loss as volatiles	8.4%

Chemical Analysis of Acidified Reaction Mixture

Nitrate ion: 4.91×10^{-4} M
Ammonia: 2.5×10^{-4} M
Nitrate ion/$(RDX)_o = 4.0$

Extraction Experiments of Acidified Reaction Mixture Mass Spectra

(1) Ethyl Acetate

A 25-ml aliquot of this acidified reaction mixture was extracted with three 25-ml portions of ethyl acetate: carbon-14 extracted, 59%; nitrate ion, unchanged. The ethyl acetate was evaporated to 40 microliters: carbon-14 remaining, 10% of the 59%; gc/ms (after correcting for the blank): Polypak I: Two compounds having m/e 43 (Figures 7 and 8), both eluting before ethyl acetate, and m/e 60 (Figure 9), eluting after ethyl acetate (minor product).

(2) Methyl Formate

To 15 ml of the acidified reaction mixture, was added 6 g of sodium chloride, in an effort to reduce the amount of water extracted. This aqueous-solid mixture was extracted with three 15-ml portions of methyl formate. Approximately 15 ml of this methyl formate extract was evaporated to 150 microliters, when further evaporation became very slow (probably because of the presence of formic acid); gc/ms: Polypak I: m/e 43 corresponding to the first m/e 43 eluted in the ethyl acetate extract.

Experiments with the Aqueous Phase after Extraction

Solid sodium nitrite (0.2g) was added to a 1-ml aliquot of the aqueous phase after ethyl acetate extraction. The solution was acidified with 18 N sulfuric acid, and after one hour, the carbon-14 was counted. There was no loss in carbon-14.

Carbon-14 Distribution. Summary for Experiments 1, 2, and 3

Table 1 below summarizes the carbon-14 distribution found in the products and reactants of experiments 1, 2, and 3.

Table 1. Photolysis of RDX. Carbon-14 Distribution

		Percent Carbon-14				
Experiment	Conditions	Initial	Final in Reaction Mix	CO_2	CO	Volatiles
1	UV + O_3 for 5 min. After photolysis, acidified to 0.3N in sulfuric acid	100	32.9	53.6	--	13.5
2	UV + O_3 for 12 min. Acidified as in (1)	100	52.3	37.7	3.9	6.1
3 First half	UV + O_2 for 12 min. Not acidified	100	98.7	0.42	0.03	0.8
3 Second half	UV + O_3 for 12 min. Not acidified, pH = 7.03	98.7	58.4	--	--	41.6
	Acidified, pH = 0.98		36.4	54.4	0.80	8.4

III. DISCUSSION

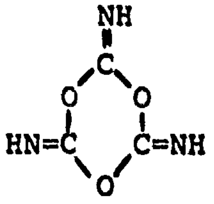
Identification of m/e 43 (I) and fragment ion m/e 43

More carbon-14 was extracted with ethyl acetate, than with benzene, or ethyl ether. Consequently, ethyl acetate was the solvent of choice for extraction, concentration and for obtaining gc/ms data.

The appearance in all of the mass spectra of a m/e 43 ion was thought, at first, to be due to $(CH_3CO)^+$ from reactions of the products with ethyl acetate. However, there is no m/e 43 peak in the mass spectrum of methyl formate, and this is the reason the extraction was also made with this solvent. It seemed likely that one of the compounds, m/e 43 (I) or m/e 43 (II), was cyanic acid. To test this, a 0.6-M solution of potassium cyanate in water was acidified with 18 N sulfuric acid, and immediately extracted with an equal volume of ethyl acetate. By gc/ms analysis on Polypak I, there eluted only one compound having m/e 43 - identical with m/e 43 (I) (major product) (6). This synthetic product was not stable, the concentration decreasing within several hours. At the same time, this ethyl acetate solution became cloudy and a white solid separated. This solid from synthetic cyanic acid proved to be a mixture of urea and m/e 129 (cyanuric acid or cyamelide) (by mass spectral analysis using the solid probe). These known reactions of cyanates may be summarized as follows.

---

(6) Whether this synthetic cyanic acid is HOCN or HNCO is not known. Urbanski (7) states that isocyanic acid is HCNO, and most textbooks call HOCN cyanic acid. All sources seem to agree that acidified alkali cyanates also give cyanuric acid and cyamelide. Urbanski gives the structure of cyamelide as

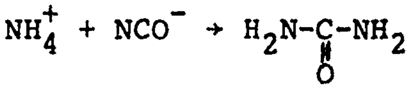


MW = 129

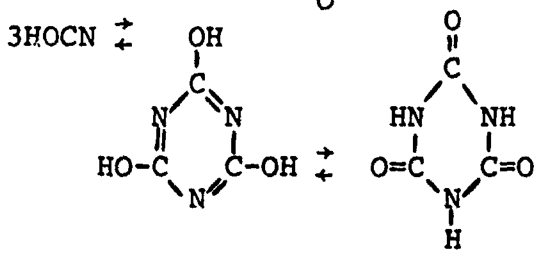
(7) T. Urbanski, "Chemistry and Technology of Explosives," Pergamon Press, Oxford; Polish Scientific Publishers, Warsaw, 1967, Vol. III, p 132-4.

$$NCO^- + H_3\overset{+}{O} \rightleftarrows HOCN + H_2O \qquad (a)$$

$$HOCN + H_3\overset{+}{O} \rightarrow CO_2 + NH_4^+ \qquad (b)$$

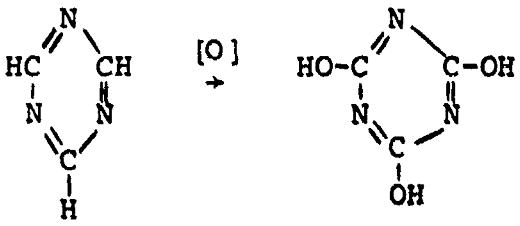


$$NH_4^+ + NCO^- \rightarrow H_2N\text{-}\underset{\underset{O}{\|}}{C}\text{-}NH_2 \qquad (c)$$



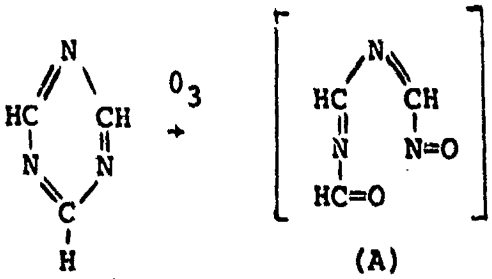
(d)

The cyanic acid is found in the reaction of RDX products with ozone after exposure to UV radiation only (experiment 3). Thus, it is attractive to consider that the major product from the UV radiation only is s-triazine (equation (e)). This product might be oxidized by ozone to cyanuric acid directly, and/or may undergo ozonolysis of the -CH=N- linkage (8) followed by decomposition to cyanic and fulminic acids:



(e)

s-triazine



(A)

(f)

(A) →2HOCN + CNOH (fulminic acid) (g)

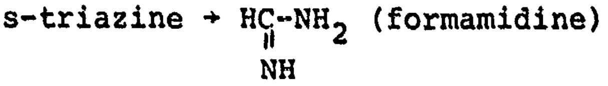
---

(8) A. Riebel, R. Erickson, C. Abshire, and P. Bailey, J. Amer. Chem. Soc., 82, 1801 (1960).

Two moles of cyanic acid would be expected, for the oxidation of the remaining HCN moiety would likely be at the carbon atom as it is in alkali cyanides. From equation (g), fulminic acid (oxygen attached to nitrogen) would be expected, and may be m/e 43 (11) observed from RDX (9).

Decomposition of cyanic acid by equation (b) could account for the formation of carbon dioxide and ammonia in the RDX reaction, at least in part.

The reactions of s-triazine under our reaction conditions are being investigated in this laboratory at the present time. If present from RDX, s-triazine apparently is not extracted with ethyl acetate, or if extracted, it decomposes when the ethyl acetate is concentrated. Its reported (12a) decomposition in aqueous solution to ammonia and formic acid has been confirmed by us, but contrary to the reported rapid decomposition, s-triazine is still present (gc/ms) after at least one hour. Another decomposition product reported (12b) is formamidine. Formamidine has a molecular weight of 44, and may be the transient m/e 44 found in the RDX decomposition. (The reactions of formamidine are also presently under investigation.). It should be noted that the m/e 44 product from RDX also has a m/e 43 fragment, which may be $(CN_2H_3)^+$.



$$\text{s-triazine} \rightarrow \underset{\underset{\text{NH}}{\|}}{\text{HC}}\text{-NH}_2 \text{ (formamidine)} \qquad \text{(h)}$$

The formation of formamidine and ammonia from s-triazine would be expected to be accelerated in the presence of hydroxide ion, for example under the conditions of determining ammonia by the specific ion electrode: 10 M sodium hydroxide is added to give a final solution which is 0.1 M in sodium hydroxide.

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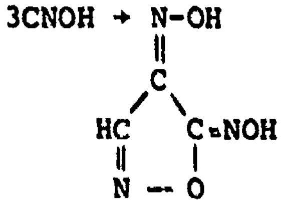
(9) Fulminic acid is also known to polymerize, forming "metafulminic acid" (10a), or "metafulminuric acid" (11)(same compound):



(10) (a) P.A.S. Smith, "Open-Chain Nitrogen Compounds," W. A. Benjamin, INC., N.Y., 1966, Vol. II, p 102.
(b) Ibid., p 362.

(11) H. Wieland and H. Hess, Ber., 42, 1346; Chem. Abstracts, 3, 2166 (1909).

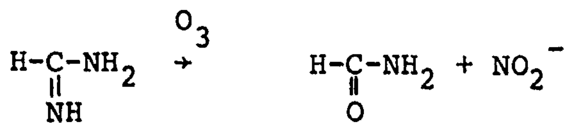
(12) (a) C. Grundman and A. Kreutzberger, J. Amer. Chem. Soc., 76, 632 (1954).
(b) C. Grundman and A. Kreutzberger, Ibid., 76, 5646 (1954).

If, indeed, s-triazine is one of the initial products from RDX by reaction with UV radiation in the absence of ozone, then nitrite ion must be formed at the same time. If ammonia only comes from s-triazine, then the minimum amount of nitrite ion by the reactions that formed s-triazine would be equal to the ammonia. There is more nitrite ion than ammonia, and this nitrite ion probably arises from the reactions of RDX which also produce m/e 89, m/e 117 (I), and m/e 117 (II). In addition, when the neutral aqueous reaction mixture was extracted with ether and ethyl acetate, some of the "nitrite ion" was extracted. This indicates that one or more of the products has a N-nitroso group which is hydrolysed under the analytical conditions to give nitrite ion. That it is not an N-nitro group that is being hydrolysed to nitrite ion is shown in the following section.

Formation of nitrate ion

It has been noted previously (1) that it is necessary to completely remove RDX before analyzing for nitrate ion, as the strongly acid solution used to convert nitrate ion to nitrobenzene hydrolyzes RDX. In experiment 2, it was found that the nitrate ion decreased 50% after extracting the reaction mixture with ethyl acetate, and that this was not due to extraction of nitric acid. Thus, it is presumed that one or more of the products has a $N-NO_2$ linkage which hydrolyzes in aqueous sulfuric acid to yield nitrate ion and a N-H linkage. When an aliquot of 33 ppm solution of RDX was analyzed for nitrate ion by formation of nitrobenzene in aqueous sulfuric acid (3), none was found immediately. After standing 24 hours, this acidic RDX solution was again analyzed for nitrate ion and residual RDX. One-third of the RDX had reacted, and the molar ratio of nitrate ion present to RDX reacted, was 2.6 (87% yield of nitrate ion). No nitrosobenzene, which is formed when nitrite ion is present (3), was observed. This would rule out the $N-NO_2$ hydrolysis to NO_2^-.

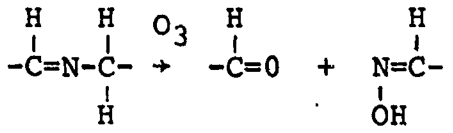
Another source of nitrate ion is the oxidation of nitrite ion by ozone, as observed in experiment 3. The third source of nitrate ion comes from the ozonolysis of the -CH=N- linkage. Bailey (8) and his students have shown that Schiff bases, as well as N-substituted oximes (nitrones), are cleaved by reaction with ozone. The carbon atom is oxidized to an aldehyde, which may then be oxidized to the carboxylic acid. The nitrogen atom is oxidized to a nitro group, if the N-substituent is aryl. If, however, the N-substituent is a proton, as it is in formamidine, it would seem that a final ozone product would be nitrate ion. Consequently, a solution of formamidine acetate (Aldrich) was prepared in water and treated with ozone for 12 minutes (after adjusting to pH 8 with sodium bicarbonate). When the solution was analyzed, a 58% yield of nitrate ion was found. Nitrosobenzene was also found indicating the presence of nitrite ion.



$$\mathrm{H{-}\underset{\underset{NH}{\|}}{C}{-}NH_2 \xrightarrow{O_3} H{-}\underset{\underset{O}{\|}}{C}{-}NH_2 + NO_2^-} \qquad \text{(i)}$$

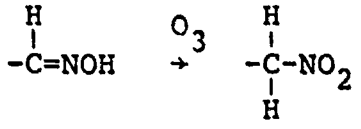
$$\mathrm{NO_2^- \xrightarrow{O_3} NO_3^-} \qquad \text{(j)}$$

If the N-substituent is alkyl, the first formed nitroso-group would rearrange to the oxime (10b):

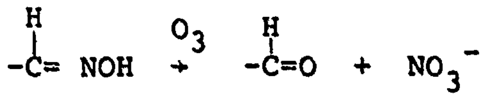


$$\mathrm{-\overset{H}{\overset{|}{C}}{=}N{-}\overset{H}{\overset{|}{\underset{\underset{H}{|}}{C}}}- \xrightarrow{O_3} -\overset{H}{\overset{|}{C}}{=}O + \underset{\underset{OH}{|}}{N}{=}\overset{H}{\overset{|}{C}}-} \qquad \text{(k)}$$

Consequently, reaction of the resulting oxime with ozone could lead to the C-nitro compound, or cleavage:

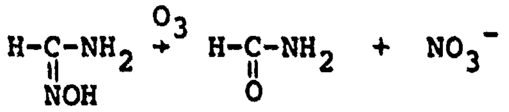


$$\mathrm{-\overset{H}{\overset{|}{C}}{=}NOH \xrightarrow{O_3} -\overset{H}{\overset{|}{\underset{\underset{H}{|}}{C}}}{-}NO_2} \qquad \text{(l)}$$



$$\mathrm{-\overset{H}{\overset{|}{C}}{=}\ NOH \xrightarrow{O_3} -\overset{H}{\overset{|}{C}}{=}O + NO_3^-} \qquad \text{(m)}$$

A solution of formamidoxime (Aldrich) in water (pH 6) was treated with ozone for 12 minutes, and a 69% yield of nitrate ion was obtained. No attempt was made to identify any other products.



$$\mathrm{H{-}\underset{\underset{NOH}{\|}}{C}{-}NH_2 \xrightarrow{O_3} H{-}\underset{\underset{O}{\|}}{C}{-}NH_2 + NO_3^-} \qquad \text{(n)}$$

Attempted identification of m/e 60 (Figure 9)

The appearance of m/e 60 in the same extract as contained cyanic acid was thought to indicate the presence of urea. However, a comparison of the mass spectrum of m/e 60 with that of urea (solid probe) showed some differences, particularly in the ratio of m/e 28 to m/e 60. The unknown m/e 60 is not formamidoxime either, because it does not have a m/e 33 ion fragment as does formamidoxime.

Formation of Carbon Monoxide - Possible Precursors

The appearance of carbon monoxide in the presence of ozone was surprising. However, the oxidation of carbon monoxide by ozone has been studied (13) in the gas phase. Although some carbon dioxide forms, the best yields were found when the carbon monoxide concentration exceeded the ozone concentration.

The mechanism for the formation of carbon monoxide from RDX is not clear. There have been studies of the photolysis of "isocyanic acid" vapor (prepared from inorganic cyanates) (14) in the UV. Carbon monoxide is a product. Whether this reaction occurs in solution is not known.

It has already been shown above (see also (12a)) that formic acid is formed in the decomposition of s-triazine. In experiment 2, it may be that some of the non-extractable carbon species (50%) is formic acid. This could be the precursor of carbon monoxide.

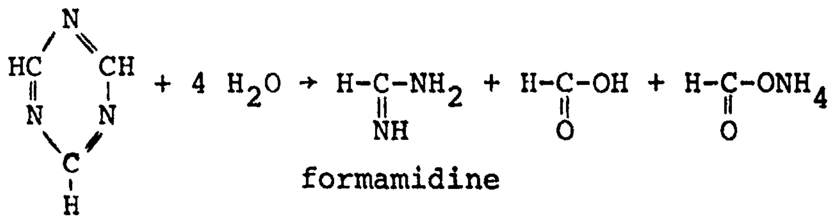
Other RDX Decomposition Products

The formation of s-triazine involves the loss of three moles of nitrous acid from RDX. Some of the other products can be explained as coming from an intermediate formed after the loss of only two moles of nitrous acid. For example, the mass spectrum of m/e 89 (Figure 3), shows the loss of 30 mass units to give m/e 59, and a loss of 46 mass units to give m/e 43. Alternatively, m/e 59 can lose 16 mass units to give m/e 43. These mass losses are characteristic of a nitro compound, although in some instances, for example 1,3,5-trinitrobenzene, the first mass loss is 16. Because m/e 89 forms from RDX whether or not ozone is present, it is presumed to form (in a manner similar to formamidine from s-triazine) from either intermediate (A) or (B):

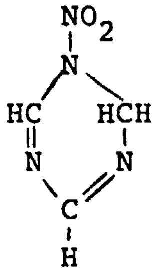
---

(13) D. Garvin, J. Amer. Chem. Soc., 76, 1523 (1954).

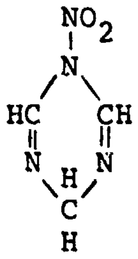
(14) W. Woolley and R. Back, Can. J. Chem., 46, 295 (1968). See also, N. Friswell and R. Back, Ibid., 46, 527 (1968); R. Back and R. Ketcheson, Ibid., 46, 531 (1968).



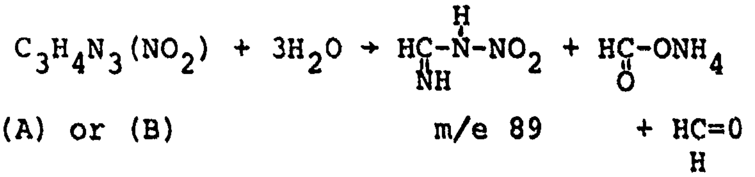
(o)



(A)

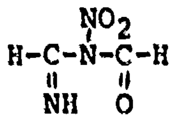


(B)



$$\underset{\text{(A) or (B)}}{C_3H_4N_3(NO_2)} + 3H_2O \rightarrow \underset{m/e\ 89}{\underset{\underset{NH}{\|}}{HC}-\overset{H}{N}-NO_2} + H\underset{\underset{O}{\|}}{C}-ONH_4 + H\underset{H}{C}{=}O \quad \text{(p)}$$

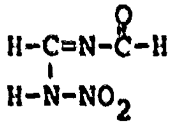
The two m/e 117 compounds (Figures 5 and 6) also form in the absence of ozone. The spectra of each indicate the presence of a nitro group (P - 46) and possibly, a formate linkage (HC=O, P - 29). Considering that P - 29 yields m/e 88 (m/e 89 minus one), one of the m/e 117 compounds may have the structure



$$H-\underset{\underset{NH}{\|}}{C}-\overset{NO_2}{N}-\underset{\underset{O}{\|}}{C}-H$$

(C) m/e 117

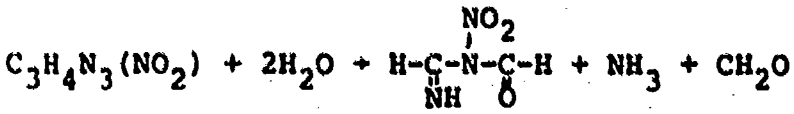
where the HC=O group has replaced the hydrogen atom in m/e 89. One isomeric structure of (C) is



$$\underset{H-N-NO_2}{H-C}{=}N-\overset{O}{\overset{\|}{C}}-H$$

(D) m/e 117

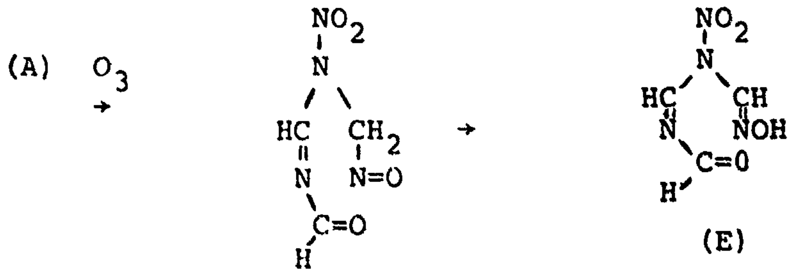
The fragment m/e 60 in the mass spectrum of m/e 117 (II) could be due to the grouping $N-NO_2$. Thus, the structure (D) is probably m/e 117 (II) and the structure (C) is m/e 117 (I). Presumably, one isomer comes from the intermediate (A) and the other isomer from (B).



$$\underset{\text{(A) or (B)}}{C_3H_4N_3(NO_2)} + 2H_2O \rightarrow H-\underset{\underset{NH}{\|}}{C}-\overset{NO_2}{N}-\underset{\underset{O}{\|}}{C}-H + NH_3 + CH_2O \quad \text{(q)}$$

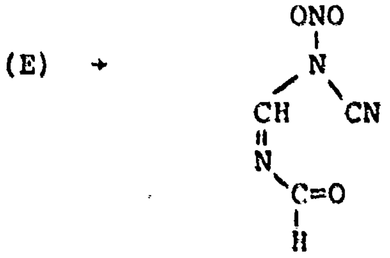
Note also, that formaldehyde is a product of reactions (p) and (q).

The reaction of RDX with both ozone and UV radiation produced m/e 142 (Figure 1). From the mass spectrum, there is a loss of 27 mass units to give m/e 115. The loss of 27 mass units suggest the loss of the elements of HCN. For example, s-triazine has the ions m/e 81, 54, and 27 as the major peaks in its mass spectrum. From mass considerations only, m/e 142 can be viewed as m/e 117 minus a hydrogen atom plus a nitrile group. Intermediate (A) would be expected to add ozone as follows:



(r)

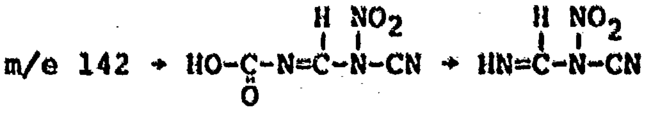
If (E) loses a molecule of water, a compound having a molecular weight of 142 results:



m/e 142 (s)

The structure of this product can explain the mass spectrum of m/e 142 (Figure 1). For example, P - 27 would be the loss of the elements of HCN, which when followed by loss of NO from the nitro group, would give m/e 85. The loss of the elements of CNO would give m/e 100, which followed by loss of CHO, would give m/e 71. The presence of m/e 43 would be due to HCNO.

Furthermore, oxidation of m/e 142 to the carbamic acid, followed by loss of carbon dioxide, would lead to m/e 114 (Figure 2):



$$\text{m/e 142} \rightarrow HO\text{-}\underset{\overset{\|}{O}}{C}\text{-}N{=}\overset{\overset{H}{|}}{C}\text{-}\overset{\overset{NO_2}{|}}{N}\text{-}CN \rightarrow HN{=}\overset{\overset{H}{|}}{C}\text{-}\overset{\overset{NO_2}{|}}{N}\text{-}CN$$

m/e 114 (t)

From Figure 2, m/e 88 is the loss of CN; m/e 71 is the loss of the elements of HCNO from m/e 114, or, more likely, the loss of OH from m/e 88; m/e 58 is the loss of NO from m/e 88, and m/e 43 is due to HCNO.

IV. SUMMARY

When RDX in tap water is reacted with a mixture of ozone and UV radiation, there is formed carbon dioxide, nitrate ion, ammonia, and at least three organic nitro compounds. Also, there is formed as a minor product, carbon monoxide, and 26% (based on carbon-14 analysis) of unidentified, non-extractable carbon compounds. The major non-extractable compound is thought to be formic acid.

Exposure of RDX in tap water to UV radiation in the absence of ozone, gave as major products nitrite ion, ammonia (or ammonia-producing compounds), and at least three organic nitro compounds. There is also produced some formaldehyde, and there is evidence for an organic nitroso compound. There remained as non-extractable, 72% of carbon-containing compounds (based on carbon-14 analysis), the main component of which is thought to be formic acid.

When RDX in tap water is exposed to UV radiation, and then allowed to react with ozone, there is found carbon dioxide, cyanic acid, nitrate ion, ammonia, and 41% of non-extractable carbon-containing compounds (based on carbon-14 analysis). Presumably, the non-extractable is mostly formic acid.

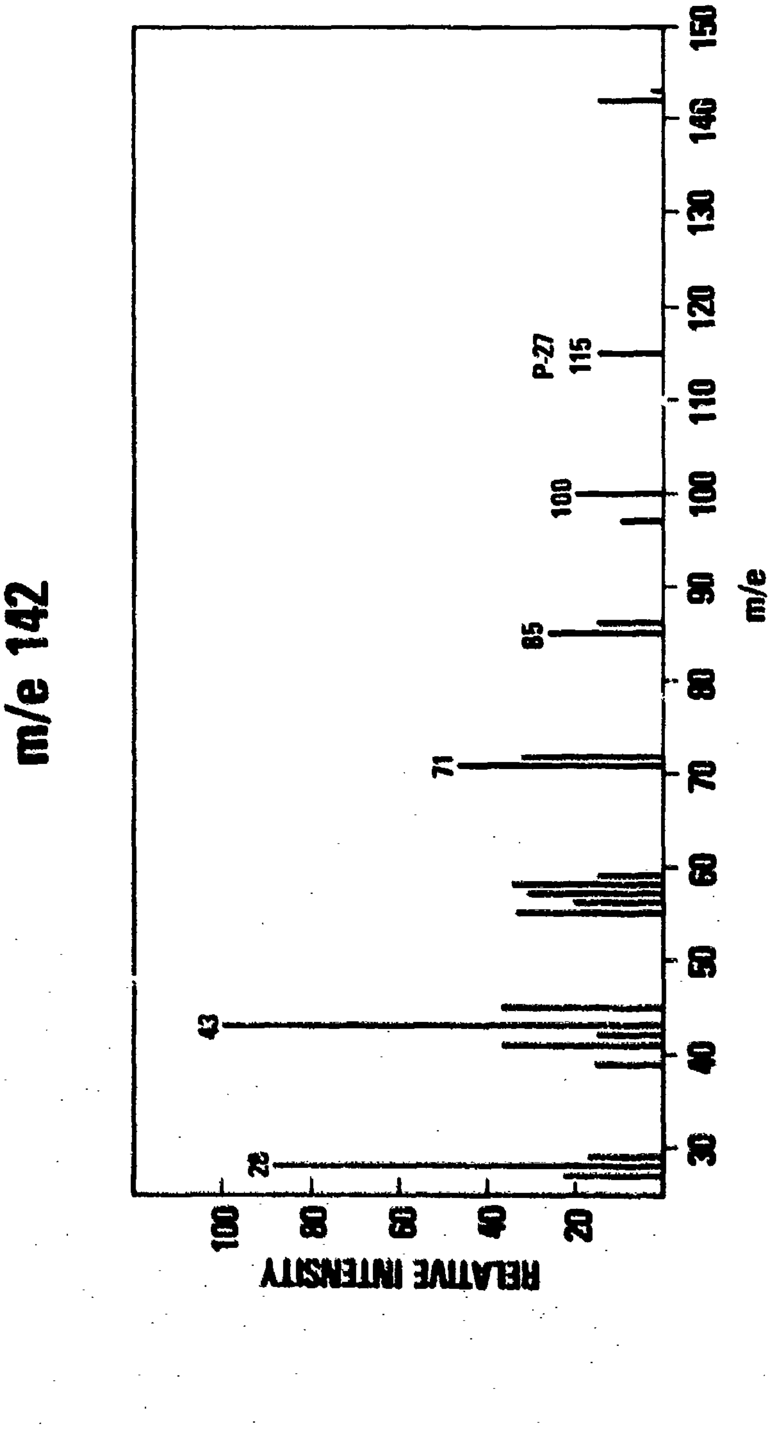


FIGURE 1. MASS SPECTRUM OF m/e 142 PRODUCT FROM REACTION OF RDX WITH A COMBINATION OF UV RADIATION AND OZONE

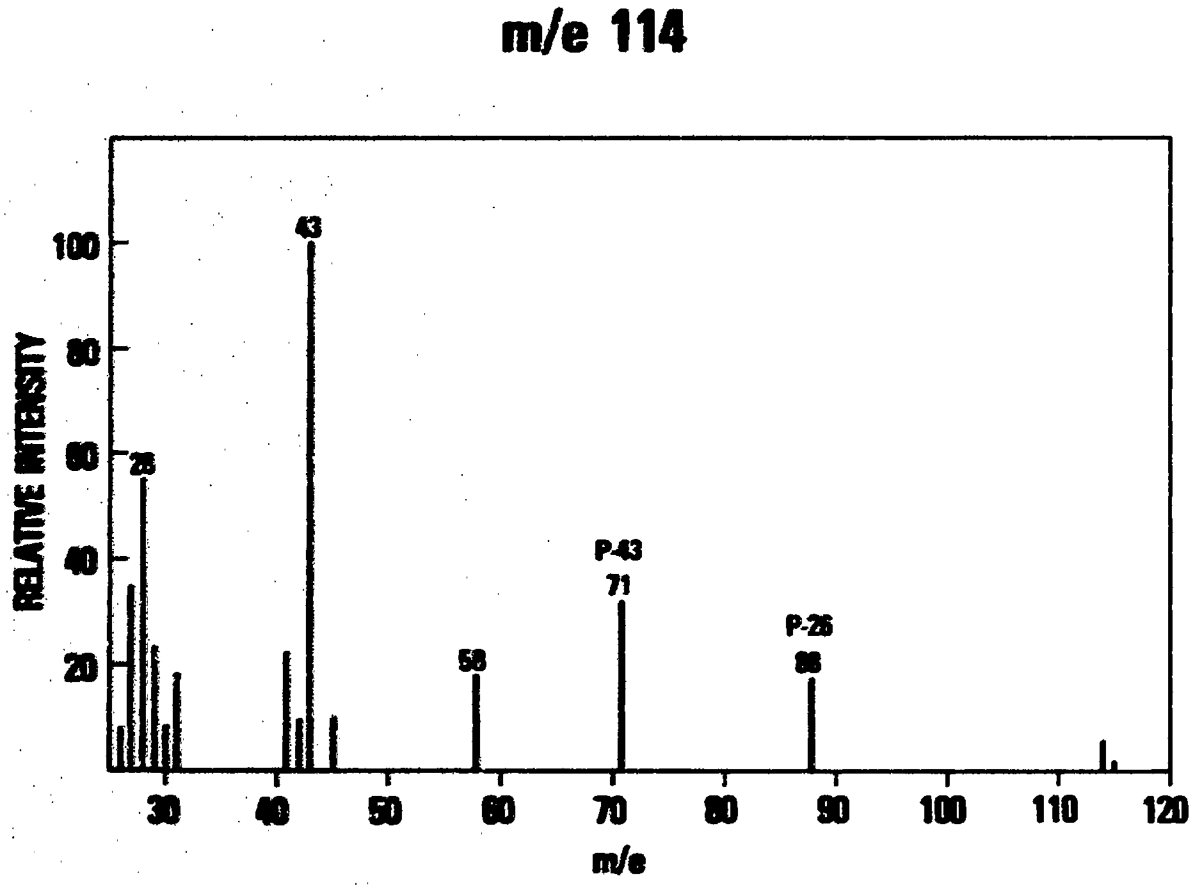


FIGURE 2. MASS SPECTRUM OF m/e 114 PRODUCT FROM REACTION OF RDX WITH A COMBINATION OF UV RADIATION AND OZONE

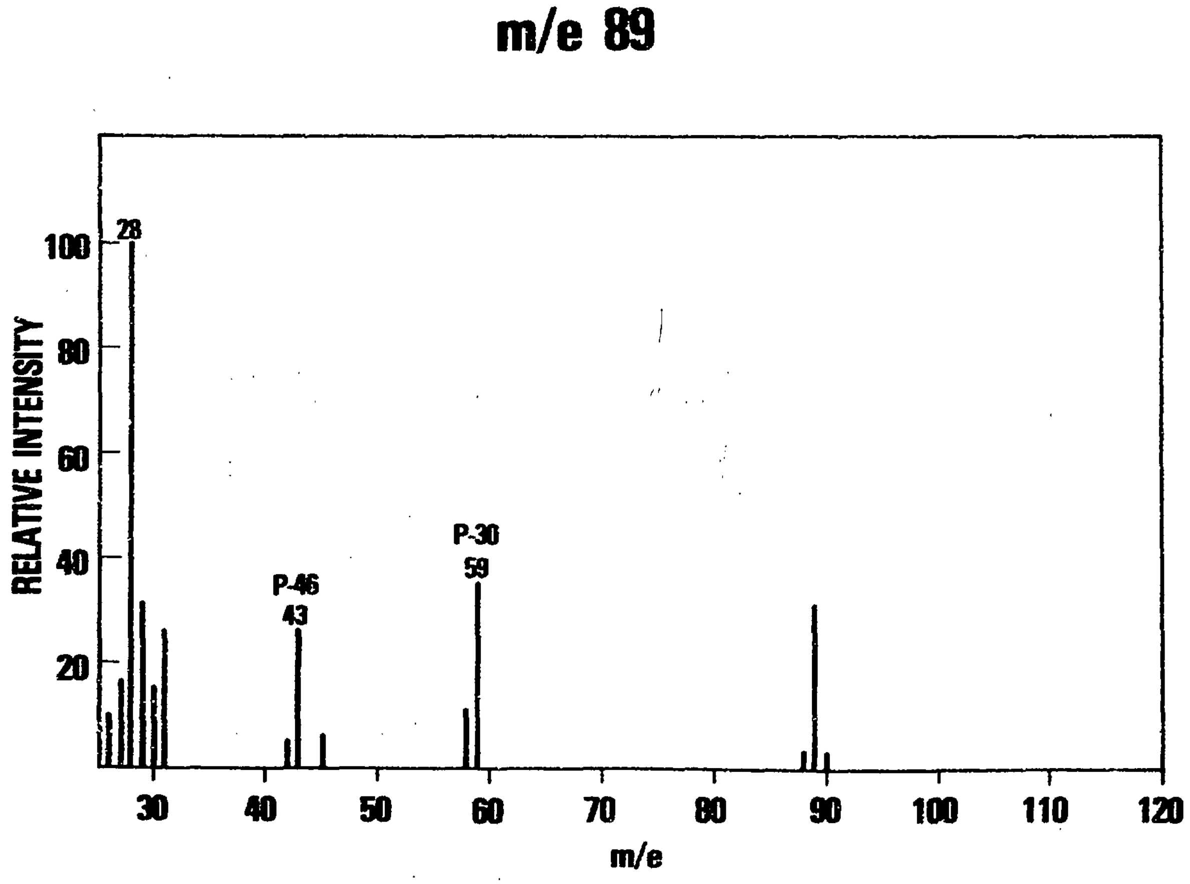


FIGURE 3. MASS SPECTRUM OF m/e 89 PRODUCT FROM REACTION OF RDX WITH EITHER A COMBINATION OF UV RADIATION AND OZONE, OR UV RADIATION ONLY

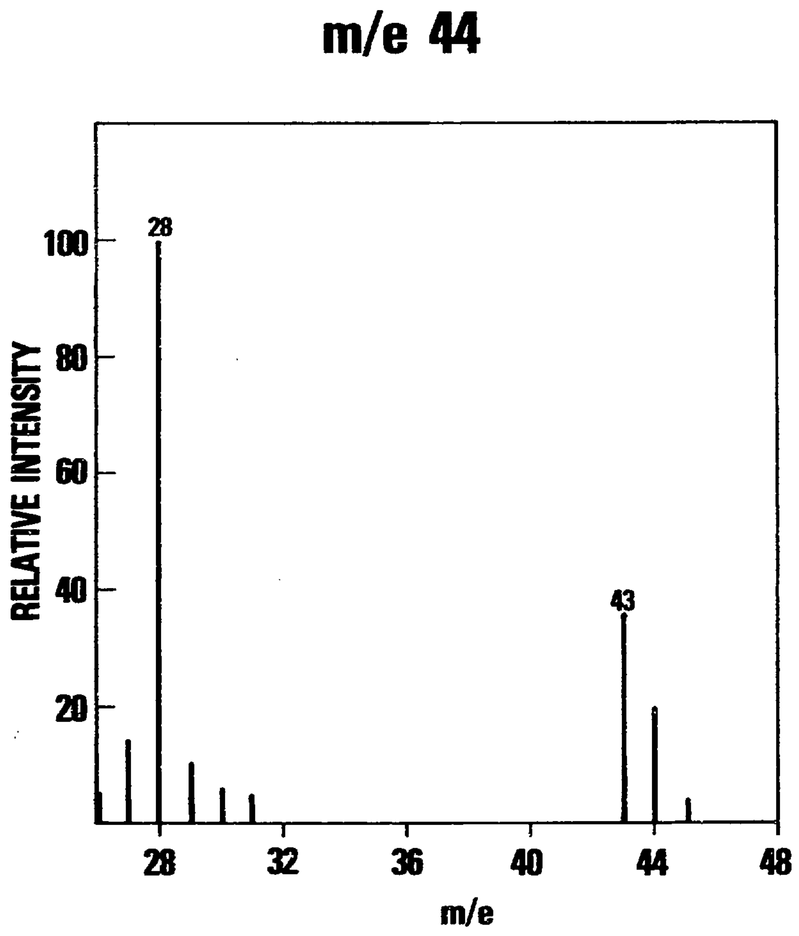


FIGURE 4. MASS SPECTRUM OF m/e 44 PRODUCT FROM REACTION OF RDX WITH UV RADIATION ONLY

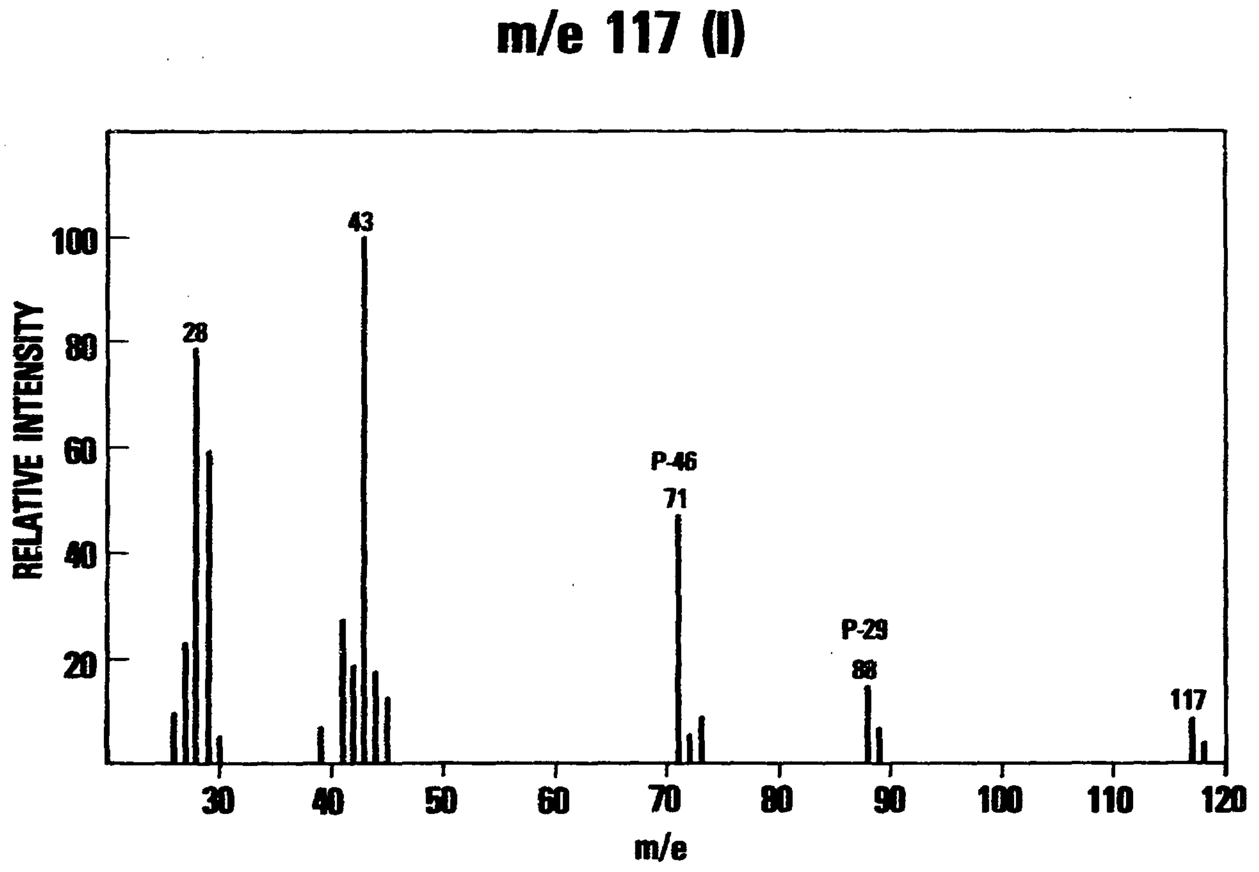
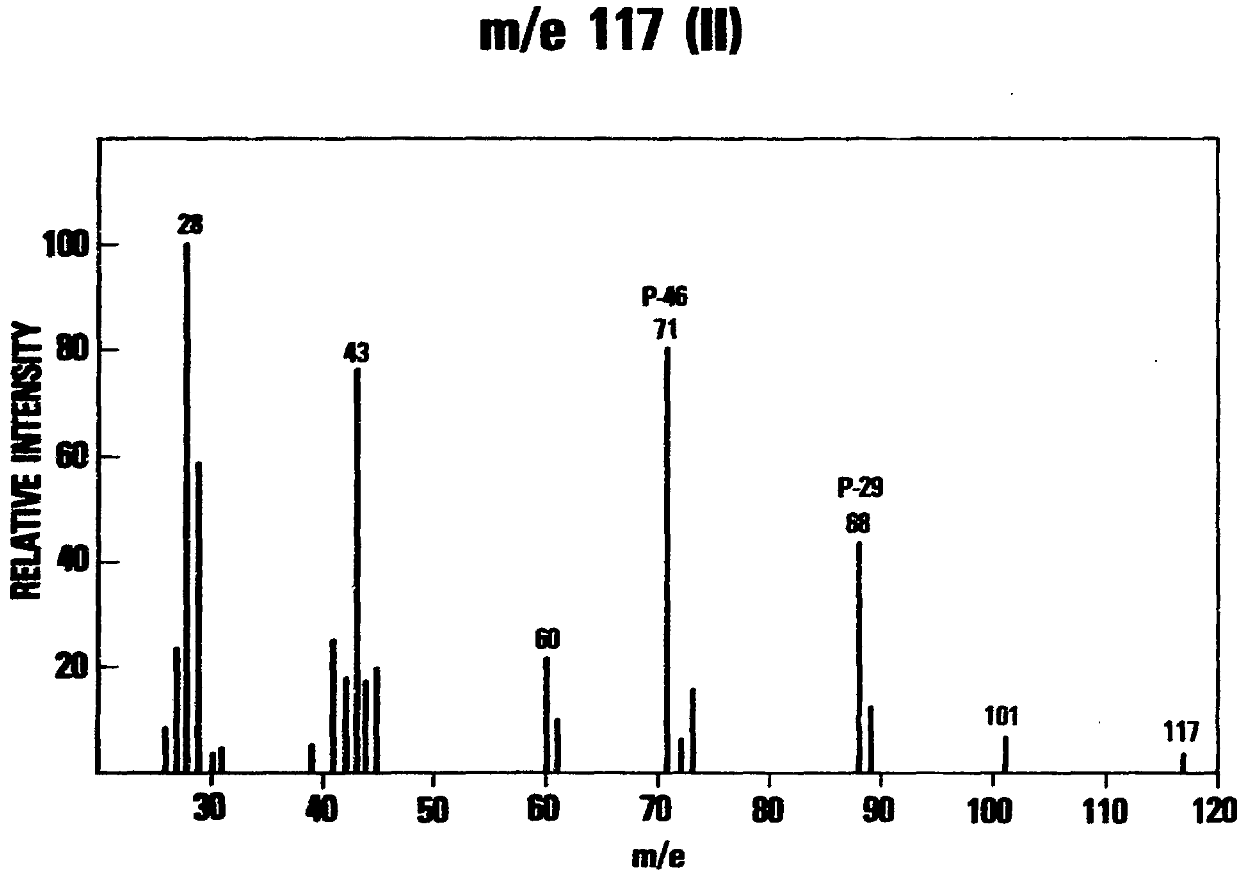


FIGURE 5. MASS SPECTRUM OF m/e 117(I) PRODUCT FROM REACTION OF RDX WITH UV RADIATION ONLY



m/e 117 (II)

FIGURE 6. MASS SPECTRUM OF m/e 117 (II) PRODUCT FROM REACTION OF RDX WITH UV RADIATION ONLY

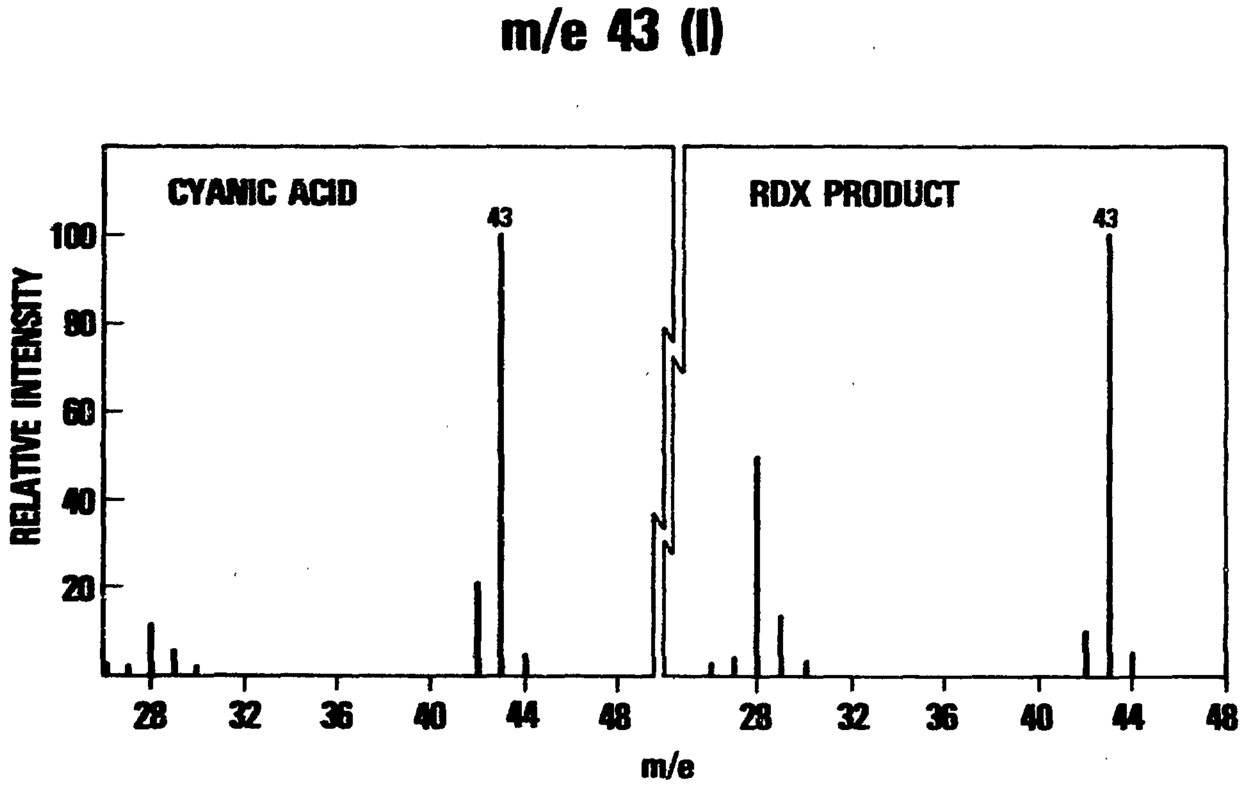


FIGURE 7. MASS SPECTRUM OF CYANIC ACID AND OF m/e 43 (I), THE OZONOLYSIS PRODUCT AFTER RDX REACTION WITH UV RADIATION ONLY

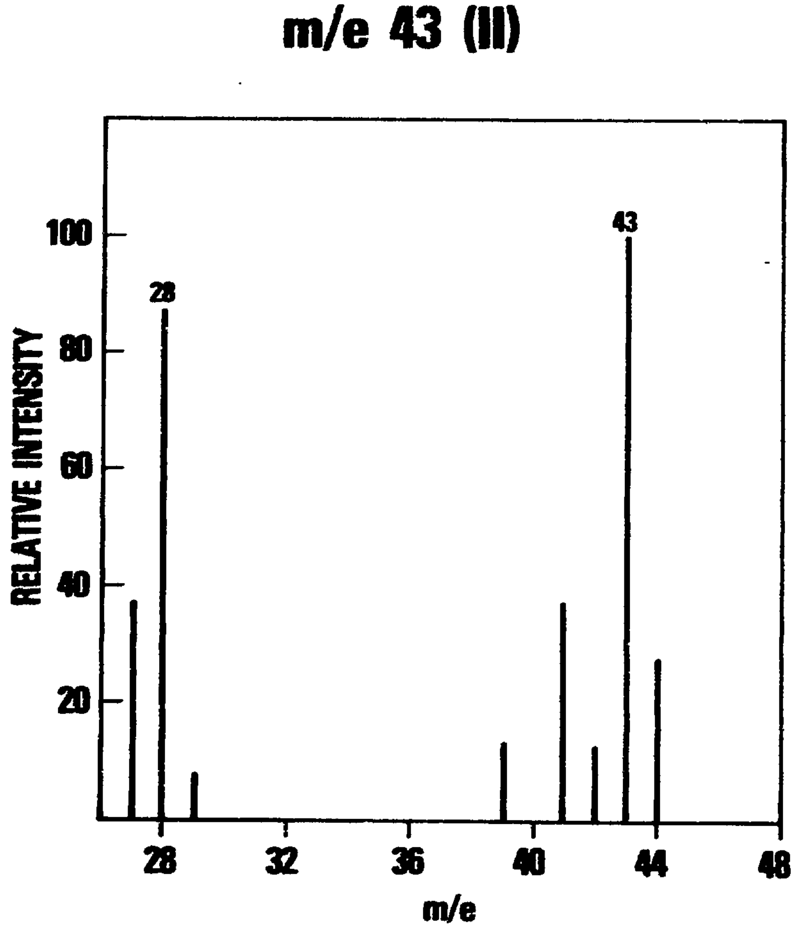


FIGURE 8. MASS SPECTRUM OF m/e 43 (II) OZONOLYSIS PRODUCT AFTER RDX REACTION WITH UV RADIATION ONLY

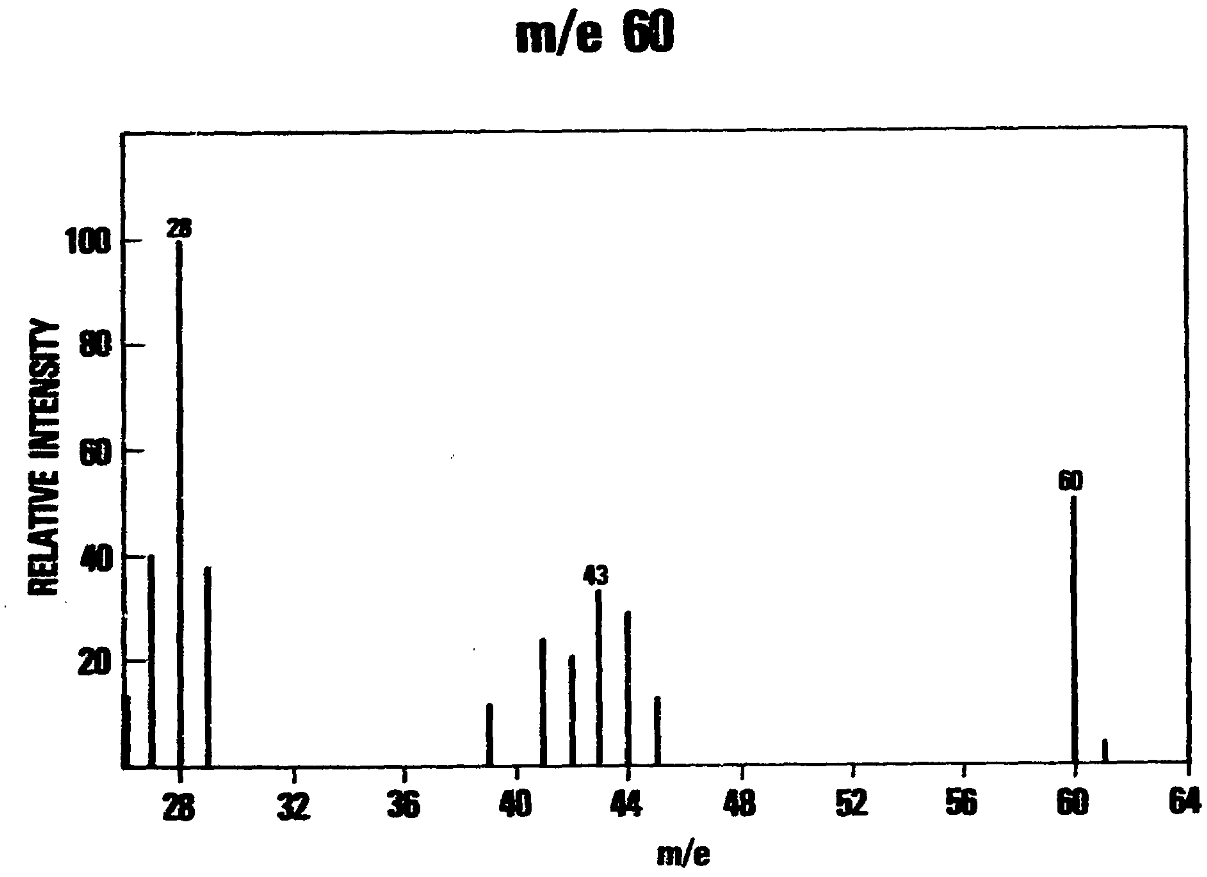


FIGURE 9. MASS SPECTRUM OF m/e 60 OZONOLYSIS PRODUCT AFTER RDX REACTION WITH UV RADIATION ONLY

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