Thermal Decomposition of Simple Nitrite Esters

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Studies of the thermal decomposition of nitrite esters have been extended to *tert*-butyl, isopropyl, and *n*-propyl nitrites to examine the generality of ideas developed in earlier studies. Thermal decomposition of *tert*-butyl nitrite, which yields acetone, nitric oxide, *tert*-butyl alcohol, formaldoxime, and hydrogen cyanide but no nitrous oxide as products, is sharply decelerated by addition of nitric oxide. In the presence of nitric oxide, hydrogen cyanide is replaced in the products by nitromethane. For isopropyl nitrite the products are acetone, acetaldehyde, isopropyl alcohol, nitric oxide, hydrogen cyanide, and a trace of nitrous oxide. The addition of nitric oxide results in the elimination of acetaldehyde and hydrogen cyanide with a concurrent sharp rise in nitrous oxide. For *n*-propyl nitrite the products are propionaldehyde, *n*-propanol, formaldehyde, nitric oxide, and a product tentatively identified as nitroethane. In the presence of nitric oxide, nitrous oxide becomes a product. These results offer strong support for the mechanism proposed earlier.

BECAUSE of the importance of nitrate esters as propellants, the thermal decomposition of simple nitrate esters has been under study in this laboratory for the past few years (*4*). The observation that nitrite esters were important reaction products led to a re-examination of the thermal decomposition of ethyl nitrite in the gas phase at 160° to 200° C. (*3*). This article extends these studies to *tert*-butyl nitrite, isopropyl nitrite, and *n*-propyl nitrite.

Experimental Part

Chemicals. The nitrite esters used were prepared in standard fashion, distilled, and middle fractions taken. They were stored by sealing small amounts, 1 to 2 ml., in glass ampules under their own vapor pressure. The boiling points were: *tert*-butyl nitrite, 64–64.5° C.; *n*-propyl nitrite, 47.5–48° C.; and isopropyl nitrite, 40° C.

For experiments with nitric oxide where the nature of the reaction products was important, the nitric oxide was prepared from potassium nitrate, sulfuric acid, and mercury. No nitrous oxide was ever observed in the product prepared in this fashion. For experiments with nitric oxide where only the reaction kinetics were involved, the source was a cylinder of gas purchased from Matheson Co. To use the nitric oxide, it was condensed into a tube on the vacuum line and the tube warmed only slightly in order to generate nitric oxide free of any nitrogen dioxide. Then when cooled with liquid nitrogen the nitric oxide condensed to a white solid.

Procedure. The procedures follow those used in earlier work (*4*), and the decompositions were carried out in glass bulbs of about 600-ml. capacity, which were immersed in baths of liquid salt mixtures for appropriate periods of time.

The carbonyl absorption at 5.7 microns was used to determine acetone whereas the peak at 12.40 was used for the *tert*-butyl nitrite analysis and that at 14.05 microns used for hydrogen cyanide. The analyses were carried out on a Perkin-Elmer Model 12-C infrared spectrometer, but spectra for qualitative examination of the products were taken on a Perkin-Elmer Model 21 double beam infrared spectrometer.

Results

***Tert*-Butyl Nitrite.** When this work was begun only the photolytic decomposition of *tert*-butyl nitrite had been investigated (*1*). The results were explained on the basis of the one-step breakdown

$$(CH_3)_3CONO \rightarrow CH_3NO + (CH_3)_2CO$$

However, recently Yoffe (*7*) has reported that when *tert*-butyl nitrite was passed through a hot tube at 340° C. in a stream of helium the products obtained were acetone, nitric oxide, and formaldoxime along with traces of ethane, methane, and methyl ethyl ketone.

The spectrum of the products from a sample of *tert*-butyl nitrite carried to complete decomposition at 181° C. is shown in Figure 1. The peaks at 5.57, 8.25, and 7.30 microns identify acetone as a product of the reaction, and the peak at 14.05 microns identifies hydrogen cyanide as a product. This identification was confirmed by absorbing the reaction products in water and testing the resultant solution for cyanide ion using the Prussian blue test (*2*). A positive test was obtained. The presence of nitric oxide and *tert*-butyl alcohol in the products is established by the admission of air to the system. As shown in Figure 1 the *tert*-butyl nitrite peaks at 12.4 and 13.2 microns appeared on the admission of air. At the same time the peaks at 8.8 and 10.9 microns, which are due to *tert*-butyl alcohol, became less intense. These changes occur because the admission of air oxidizes the nitric oxide to nitrogen dioxide which then converts the alcohol to the nitrite ester. In addition to the above products the presence of a nitroalkane is suggested by the small peak at 6.3 microns, but there is no indication of any peak at 4.5 microns where nitrous oxide absorbs.

When *tert*-butyl nitrite was heated for shorter periods of time it was possible to identify formaldoxime as a reaction product from the infrared spectrum. On the longer heating the disappearance of its absorptions was accompanied by an increase in the hydrogen cyanide peak intensity.

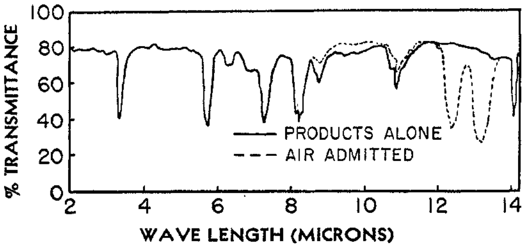

Figure 1. Decomposition products of *tert*-butyl nitrite (P_o = 35 mm.) at 181° C., t = 1020 minutes

When the thermal decomposition of *tert*-butyl nitrite was carried out in the presence of excess nitric oxide, certain qualitative changes in the infrared spectrum of the products were observed (Figure 2), although the time of heating and initial pressure of *tert*-butyl nitrite are about the same as for the experiment of Figure 1. The strong *tert*-butyl nitrite peaks in Figure 2 show that the decomposition has proceeded to a lesser extent than in the preceding experiment. In addition the product distribution has been affected by the addition of nitric oxide. In Figure 2 the hydrogen cyanide peak at 14.05 microns is much less intense relative to the 6.3-micron peak than is the case in Figure 1. When the 6.3-micron peak was examined in detail it became evident that the peak was due to the presence of nitromethane in the mixture. Thus, it appears that one effect of nitric oxide is to favor a reaction which gives nitromethane at the expense of the one that gives hydrogen cyanide. Quantitative results obtained for the *tert*-butyl nitrite decomposition at 201° C. are given in Table I.

Table I. Thermal Decomposition of *tert*-Butyl Nitrite at 201° C.

	Initial Pressure (Mm.)				
Run	Nitrite	Nitric oxide	% Reaction	Acetone Yield, %	10^3k^a (Sec.$^{-1}$)
1	28.0	0	15.0	100	..
2	19.5	0	30.2	100	3.33
3	19.5	0	59.7	99	3.02
4	17.6	0	80.5	87	2.83
5	17.6	0	86.6	88	2.02
6	28.0	0	100.0	88	..
7	19.9	17.0	57.0	..	0.70
8	22.0	52.0	24.8	..	0.31
9	15.0	77.8	49.5	..	0.23
10	19.5	127.5	18.3	..	0.13

[a] For runs 1 to 5 this is the apparent first-order rate constant calculated between successive runs—for example, between runs 1 and 2 or runs 2 and 3. This method of calculation points up the trend of apparent rate constants. For runs 7 to 10 the apparent first-order rate constant was calculated for each point from zero time.

A few analyses for hydrogen cyanide were carried out for reaction times such that the formaldoxime apparently was used up. The hydrogen cyanide yields observed were 20 to 25%. No analyses were made for *tert*-butyl alcohol, methane, or ethane. Since *tert*-butyl alcohol and acetone are alternative products it is assumed that where the acetone yield is less than 100% the deficiency is due to the formation of *tert*-butyl alcohol. As Table I indicates, *tert*-butyl alcohol appeared as a product only in the later stages of the reaction.

Isopropyl Nitrite. The thermal decomposition of isopropyl nitrite was examined only from the point of view of the reaction products. The spectrum of the products obtained when isopropyl nitrite was heated to almost complete decomposition at 181° C. is shown in Figure 3. It is possible to identify hydrogen cyanide by its absorption at 14.05 microns and acetone by the peaks at 5.75, 7.30, and 8.25 microns. The 5.75-micron peak is more intense relative to the 8.25-micron peak than it would be if acetone alone were absorbing there. Moreover there is a small shoulder at 3.7 microns which is characteristic of aldehydes. It thus appears that acetaldehyde is responsible for the additional absorption at 5.75 microns. The presence of isopropyl alcohol in the products was established by observing the changes in the spectrum when air was admitted to the cell. The appearance of the isopropyl nitrite spectrum was observed along with a decreased absorption at 9.4 microns where isopropyl alcohol absorbs most strongly. The presence of a nitroalkane is suggested by the small peak at 6.3 microns, whereas the absence of absorption at 4.5 microns indicates that nitrous oxide is not a product.

The spectrum of the products resulting when isopropyl nitrite was heated at 181° C. in the presence of excess nitric oxide is also shown in Figure 3. Comparison of the two spectra shows that one effect of the nitric oxide is the elimination of the aldehydic product presumed to be acetaldehyde. The 3.7-micron shoulder is not found, and the relative intensities of the 5.75- and 8.25-micron peaks are those expected for acetone alone. In addition the hydrogen cyanide yield is greatly lowered, whereas nitrous oxide becomes a significant product.

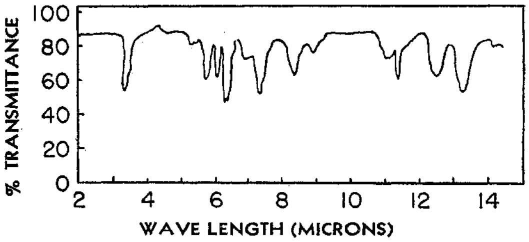

Figure 2. Decomposition products of *tert*-butyl nitrite (P_o = 36 mm.) in presence of nitric oxide (P_o = 65 mm.) at 181° C., t = 1022 minutes

N-**Propyl Nitrite.** For this ester, too, only qualitative experiments on the nature of the reaction products were carried out. The spectra of the products obtained are shown in Figure 4. In the absence of added nitric oxide it is possible to identify an aldehyde by the absorptions at 5.75 and 3.70 microns; this is assumed to be propionaldehyde, and comparison with the spectrum of propionaldehyde supports this assumption. The appearance of the *n*-propyl nitrite spectrum on the admission of air was used to show the presence of *n*-propyl alcohol and nitric oxide in the products. The small peak at 6.3 microns suggests the presence of nitroalkane. Neither hydrogen cyanide nor nitrous oxide can be detected as products. In the presence of the nitric oxide the only observable difference is that nitrous oxide appears as a product.

Discussion

The results obtained in the study of ethyl nitrite (*2*) led to the proposal of the mechanism:

$$C_2H_5ONO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C_2H_5O\cdot + NO \qquad (a)$$

$$C_2H_5O\cdot + NO \xrightarrow{k_2} CH_3CHO + NOH \qquad (b)$$

$$C_2H_5O\cdot + NOH \rightarrow C_2H_5OH + NO \quad (c)$$

$$2NOH \rightarrow N_2O + H_2O \quad (d)$$

The rate expression derived for the sequence was

$$\frac{-d \ln (C_2H_5ONO)}{dt} = \frac{k_1k_2}{k_{-1} + k_2}$$

The results for *tert*-butyl nitrite, isopropyl nitrite and *n*-propyl nitrite may be considered in terms of the above mechanism.

***Tert*-Butyl Nitrite–Reaction Products.** For the thermal decomposition of *tert*-butyl nitrite, the mechanism may be written

$$t\text{-}C_4H_9ONO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} t\text{-}C_4H_9O\cdot + NO \quad (e)$$

$$t\text{-}C_4H_9O\cdot \xrightarrow{k_2} (CH_3)_2CO + CH_3\cdot \quad (f)$$

$$CH_3\cdot + NO \rightarrow CH_3NO \rightarrow CH_2{=}NOH \rightarrow HCN + H_2O \quad (g)$$

In this sequence the reaction products indicated are those found in the early stages of reaction. The appearance of *tert*-butyl alcohol in the later stages of the reaction suggests that its formation involves one of the above reaction products. One possibility which is attractive is

$$t\text{-}C_4H_9O\cdot + (CH_3)_2CO \rightarrow t\text{-}C_4H_9OH + \cdot CH_2COCH_3 \quad (h)$$

In this way, the abstraction of a hydrogen atom from acetone, by a methyl radical, occurs in the decomposition of *tert*-butyl peroxide (*5*). There the fate of the radical formed is

$$\cdot CH_2COCH_3 + CH_3\cdot \rightarrow CH_3CH_2COCH_3 \quad (i)$$

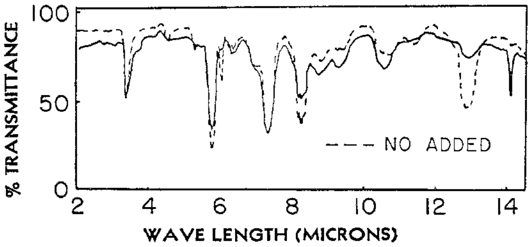

Figure 3. Decomposition products of isopropyl nitrite at 181° C.

Step *g* in this sequence has been used to explain the inhibiting effect of nitric oxide on chain reactions involving methyl radicals. Also, the appearance of formaldoxime when *tert*-butyl peroxide was decomposed in the presence of nitric oxide (*5*) was explained by step *g*, although it may well have involved the transitory formation of the nitrite ester. A study of the dehydration of formaldoxime to hydrogen cyanide and water (*6*) indicated that the reaction would be negligibly slow at temperature involved — ~200° C. However, when samples of formaldoxime were heated, the appearance of the hydrogen cyanide band indicated that the reaction proceeded at a rate consistent with the results observed here. Acceleration of the reaction in the presence of nitric oxide (*6*) has been confirmed by preliminary results obtained in this laboratory.

The effect of nitric oxide on the product distribution was to produce nitromethane at the expense of hydrogen cyanide. The most likely source for this effect seemed to be in the oxidation of the nitrosomethane. When nitrosomethane is heated by itself it isomerizes rapidly to formaldoxime (*1*). However, when samples of nitrosomethane were heated in the presence of nitric oxide the nitrosomethane was converted to nitromethane. This reaction is under further study.

***Tert*-Butyl Nitrite–Reaction Kinetics.** Steps *e–g* yield the rate expression

$$\frac{-d \ln (C_4H_9ONO)}{dt} = k = \frac{k_1k_2}{k_{-1}\,(NO) + k_2} \quad (j)$$

This expression predicts that with increasing amounts of nitric oxide the rate should decrease steadily. Thus, the rate should drop as the reaction proceeds, as shown by runs 1 to 5, Table I. For runs 7 to 10 enough nitric oxide was present initially so that its concentration remained essentially constant over the entire reaction periods involved. Also for these runs the rate constant value would not decrease with reaction time.

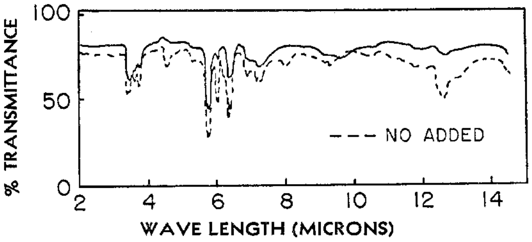

Figure 4. Decomposition products of *n*-propyl nitrite at 181° C.

If expression *j* is put into the form

$$\frac{1}{k} = \frac{k_{-1}}{k_1k_2}\,(NO) + \frac{1}{k_1}$$

it is clear that the above interpretation requires that a plot of $1/k$ versus (NO) give a straight line. Figure 5 illustrates such a plot. Here the data of runs 7 to 10 have been used, and the rate constant from runs 1 to 2 has been taken as equal to k_1. The points fall on a good straight line.

The differing effects of nitric oxide in the ethyl nitrite case (where nitric oxide did not essentially affect the reaction rate) and the *tert*-butyl nitrite cases are due to the fact that ethyl nitrite has an alpha hydrogen so that the reaction of step *b* can occur, whereas in *tert*-butyl nitrite there is no alpha hydrogen and the only thing nitric oxide can do is regenerate the *tert*-butyl nitrite.

On the basis of the inhibiting effect of nitric oxide it is clear that the mechanism proposed for the photolytic decomposition of *tert*-butyl nitrite cannot hold for the thermal decomposition. The photolytic mechanism requires that the rate be independent of the nitric oxide concentration.

Isopropyl Nitrite. For isopropyl nitrite the reaction products observed can be explained in a manner in line with the general reaction mechanism. The opening step would be

$$(CH_3)_2CHONO \rightleftharpoons (CH_3)_2CHO\cdot + NO \quad (k)$$

which would be followed logically by

$$(CH_3)_2CHO\cdot \rightarrow CH_3CHO + CH_3\cdot \quad (l)$$

$$CH_3\cdot + NO \rightarrow CH_3NO \rightarrow CH_2{=}NOH \rightarrow HCN + H_2O \quad (m)$$

This explains the hydrogen cyanide observed in the products and the acetaldehyde whose presence was indicated by the evidence from the spectra in Figure 3.

The acetone formation can be explained by the steps

$$CH_3\cdot + (CH_3)_2CHONO \rightarrow CH_4 + (CH_3)_2CO + NO \quad (n)$$

or by

$$NO + (CH_3)_2CHO. \rightarrow NOH + (CH_3)_2CO \tag{o}$$

The alcohol formation suggests the steps

$$(CH_3)_2CHO. + NOH \rightarrow (CH_3)_2CHOH + NO \tag{p}$$

or

$$(CH_3)_2CHO. + RH \rightarrow (CH_3)_2CHOH + R. \tag{q}$$

where $RH = CH_3COCH_3$ or CH_3CHO

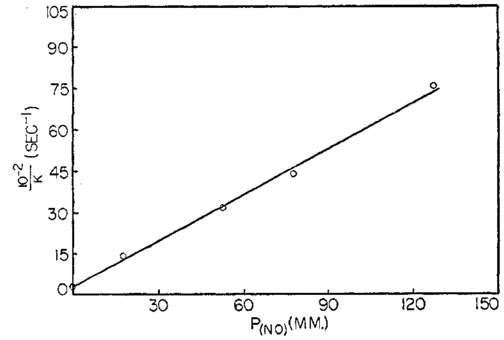

Figure 5. Effect of nitric oxide on thermal decomposition of *tert*-butyl nitrite at 201° C.

The effect of nitric oxide on the product distribution fits in so well with the mechanism that it offers it strong support. The addition of nitric oxide should favor step *o* at the expense of step *l*. In the presence of substantial amounts of nitric oxide step *l* would be eliminated, acetaldehyde and hydrogen cyanide would disappear as products, and nitrous oxide would be found. The only other way in which the addition of nitric oxide could effect these changes would be if it could react directly with isopropyl nitrite by some step

$$NO + (CH_3)_2CHONO \rightarrow (CH_3)_2CO + NOH$$

This would require that the addition of nitric oxide accelerate the reaction. Although this has not been tested for isopropyl nitrite the results for ethyl nitrite indicated that such an acceleration did not occur. It seems most unlikely that it should occur here.

The nitroalkane indicated in the reaction products is probably nitromethane, which is formed just as in the *tert*-butyl nitrite case.

No kinetic studies have been carried out on isopropyl nitrite. It is, in a sense, an intermediate case. For ethyl nitrite, nitric oxide depressed the rate steadily. For isopropyl nitrite, the mechanism predicts that nitric oxide should lower the rate toward a limiting value where further nitric oxide had no effect. This value would be reached when step *l* had been effectively eliminated.

***N*-Propyl Nitrite.** The case of *n*-propyl nitrite is similar to that of its isomer. A point of interest here is that no hydrogen cyanide is formed. This supports the idea that hydrogen cyanide arises from a reaction of methyl radicals. The *n*-propoxyl radical breakdown gives ethyl radicals but not methyl. The appearance of nitrous oxide, when the decomposition is carried out in the presence of nitric oxide, is explained just as in the isopropyl nitrite case and thus offers support for the mechanism written. In line with the mechanism the nitroalkane indicated in Figure 4 should be nitroethane, but this point has not been established.

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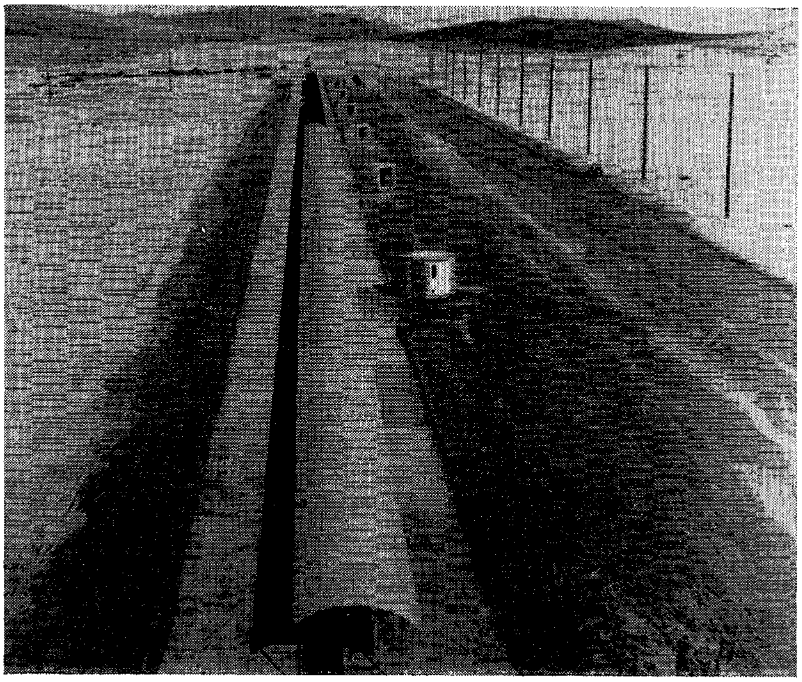

Rail rocket launcher (1500 feet long) in use at Naval Ordnance Test Station, Inyokern, Calif., for testing high speed rockets

U. S. NAVY PHOTO