[Contribution from the Chemical Laboratory of the Johns Hopkins University]

The Thermal Decomposition of Organic Compounds from the Standpoint of Free Radicals. XIII. The Decomposition of Ethyl Nitrite

By F. O. Rice and Edward L. Rodowskas

According to the theory of free radicals discussed in previous papers[1] of this series, the thermal decomposition of ethyl nitrite should be represented by the primary decomposition

$$CH_3CH_2ONO \longrightarrow NO + CH_3CH_2O\text{—} \quad (1)$$

Since the stable nitric oxide molecule is one of the products, this decomposition probably occurs in preference to others which would yield two free radicals. The primary decomposition should be followed by[2]

$$CH_3CH_2O\text{—} + CH_3CH_2ONO \longrightarrow CH_3CH_2OH + CH_3CH(ONO)\text{—} \quad (2)$$

$$CH_3CH(ONO)\text{—} \longrightarrow NO + CH_3CHO \quad (3)$$

or, if the decomposition occurs at low pressures, one might expect

$$CH_3CH_2O\text{—} \longrightarrow HCHO + CH_3\text{—} \quad (4)$$

$$CH_3\text{—} + CH_3CH_2ONO \longrightarrow CH_4 + CH_3CH(ONO)\text{—} \quad (5)$$

followed by reaction (3).

The over-all decomposition at higher pressures would be

$$CH_3CH_2ONO \longrightarrow NO + {}^1/_2CH_3CH_2OH + {}^1/_2CH_3CHO \quad (6)$$

while at lower pressures the final result would be

$$CH_3CH_2ONO \longrightarrow NO + {}^1/_2HCHO + {}^1/_2CH_4 + {}^1/_2CH_3CHO \quad (7)$$

From an analysis of the products formed in a run at 235° with an initial pressure of 270 mm., Steacie and Shaw[3] have concluded that equation (6) represents the over-all decomposition.

The free radical mechanism leads to the curious conclusion that the substrate itself terminates chains and that therefore the decomposition cannot be expected to occur through a chain mechanism. Even if a free radical were introduced into ethyl nitrite it would be immediately removed and replaced by molecules according to the equations

$$R + CH_3CH_2ONO \longrightarrow RH + CH_3CH(ONO)\text{—} \quad (8)$$

$$CH_3CH(ONO)\text{—} \longrightarrow CH_3CHO + NO \quad (9)$$

It occurred to us that an experimental test of this mechanism was possible by passing ethyl nitrite at low pressures through a furnace and then over a metallic mirror. Using a technique previously described[4] we found that ethyl nitrite is decomposed to a considerable extent at 425° but that there is no noticeable effect on metallic mirrors. That the mirrors were not deactivated was proved by the fact that they were subsequently readily removed by the fragments formed from butane or acetone passed through the furnace heated in the range 800–900°. The non-removal of metallic mirrors by ethyl nitrite may be explained by assuming that reactions (1) and (4) occur in the furnace and that they are followed by reactions (5) and (3), which remove the methyl groups before they reach the mirror.

We then diluted the ethyl nitrite with various gases in an attempt to reduce the rate of the bimolecular reaction (5) and thus permit the methyl groups to reach the mirrors. We found that 1% of ethyl nitrite carried in carbon dioxide removed mirrors with great readiness even as low as 400°. When the gases leaving the furnace passed over a tellurium mirror we obtained pure dimethylditelluride[5] (m.p. −19.5°) so that it seems probable that methyl groups are the only fragments that escape from the furnace. We obtained the same effect when we diluted the ethyl nitrite with butane or ether; mirrors were readily removed when the furnace was heated in the range 400–500° although none of the pure substances used remove mirrors at these temperatures.

Activation Energy Measurements.—We next measured the activation energy of the primary dissociation into free radicals. Carbon dioxide was used as carrier gas in a quartz tube of 1.3 cm. diameter fitted with a furnace 15 cm. long. Standard antimony mirrors were placed at different measured distances from the end of the furnace and the time of removal was noted for different furnace temperatures. The results are shown in Table I. Steacie and Shaw[3] obtained 37.7 Cal.

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[1] Rice, This Journal, 53, 1959 (1931); *Trans. Faraday Soc.*, 30 (1934).

[2] We have omitted consideration of the reactions $R + CH_3CH_2ONO \longrightarrow RH + CH_2CH_2ONO$ because the reaction of the free radical with the more loosely bound secondary hydrogen atom in the α position to the —ONO group probably predominates. Furthermore the decomposition $CH_2CH_2ONO \longrightarrow NO + CH_2CH_2O \longrightarrow NO + CH_3CHO$ would lead to the same final result.

[3] Steacie and Shaw, *J. Chem. Physics*, 2, 243 (1934).

[4] Rice, Johnston and Evering, This Journal, 54, 3529 (1932). The observations recorded for pure ethyl nitrite apply only to mirrors placed at distances greater than 1.5–2.0 cm. from the end of the furnace. Mirrors nearer the furnace were slowly removed.

[5] Rice and Glasebrook, *ibid.*, 56, 2472 (1934).

TABLE I

ACTIVATION ENERGY OF THE DISSOCIATION OF ETHYL NITRITE INTO FREE RADICALS

Pressure at entrance to furnace, mm.	0.75		
Pressure gradient, mm./cm.	.015		
Furnace temperature, °K.	703	743	803
t_m, sec.	25.5	7.2	1.2
E (Cal.)	34.3 ± 3		

t_m is the extrapolated time of the disappearance of a standard mirror at the end of the furnace.

for the activation energy of the over-all decomposition. Our measurement[6] of 34.3 ± 3 is in satisfactory agreement with this figure and supports the conclusion of these authors that they were really measuring the activation energy of the primary dissociation into a molecule of nitric oxide and the ethoxy radical.

Identification Experiments.—The identification of the fragments as dimethyl ditelluride has already been mentioned. This was further confirmed by combining the fragments with mercury[7] and identifying methyl mercuric bromide. We have developed recently an improved technique for this method which avoids some of the difficulties of the older method. At the end of a run the contents of the liquid air trap are allowed to warm up to approximately 0°, some pure ether is added and the solution is filtered from suspended mercury. An excess of an alcoholic solution of mercuric bromide is added and after standing for ten to fifteen minutes, the solution is evaporated to dryness in a vacuum below room temperature. The white solid remaining is steam distilled and the white crystalline alkyl mercuric bromide that distils over is filtered, washed with alcohol and dried in a vacuum. Our preparation melted sharply at 160°, either alone or mixed with methyl mercuric bromide made by the Grignard reaction. We have found this method very convenient for separating alkyl mercuric bromides from the excess of mercuric bromide. Separate experiments showed that mercuric bromide is not volatile with steam.

Discussion.—If our mechanism for the decomposition of ethyl nitrite is correct we have the important conclusion that this substance should terminate chains. According to reactions (8) and (9), a free radical reacts with a molecule of ethyl nitrite to produce a molecule and the radical $CH_3CH(ONO)$—which decomposes into the two molecules NO and CH_3CHO. The introduction therefore of a small quantity of ethyl nitrite into an organic substance (RH) decomposing according to a chain mechanism should inhibit the reaction to a greater or less extent by shortening the chains. The efficiency of ethyl nitrite as an inhibitor will be determined by the activation energies of reactions (8) and (9) as well as by the energy of activation of the reaction between the CH_3CH (ONO)— radical and the organic substance (RH)

$$CH_3CH(ONO){-} + RH \longrightarrow R + CH_3CH_2ONO \quad (10)$$

Judging from the failure of our attempts to remove mirrors with pure ethyl nitrite, reaction (8) probably has an activation energy of less than 10 Cal. which is appreciably less than the activation energies of similar reactions in which the ethyl nitrite is replaced by other organic molecules.[8] Reaction (9) is very probably strongly exothermic and may be expected to occur with little or no activation energy; consequently the regeneration of free radicals through reaction (10) should not be appreciable and ethyl nitrite should act as an inhibitor of chain reactions. We have done some preliminary experiments with butane containing 1% of ethyl nitrite but we found the rate of decomposition to be unaffected. This is of course to be expected in this case because the life of an ethyl nitrite molecule is exceedingly short in the temperature range in which butane decomposes at a measurable rate.

From Steacie and Shaw's analytical results we may conclude that at pressures higher than about one-third of an atmosphere, reaction (2) occurs to the almost complete exclusion of reaction (4). Our own results indicate that at pressures of approximately 1 mm., reaction (4) predominates: under these conditions methyl groups are formed in abundance and can be identified by combination with either tellurium or mercury. It is possible to estimate[9] the relative activation energies

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[6] In the experiments in which the ethyl nitrite was diluted with carbon dioxide, a methyl radical produced in the furnace could not make more than a few hundred collisions with ethyl nitrite molecules before reaching the mirror. It seems unlikely therefore that our measurement of the activation energy of reaction (1) is affected by reaction (5) to any marked extent. The effect of diluting the ethyl nitrite with carbon dioxide or other inert gas is probably to be ascribed to reactions occurring outside the furnace, *i. e.*, between the end of the furnace and the mirror. Reaction (1), the primary decomposition, ceases immediately the gases leave the furnace but reactions (2) or (5) presumably having much lower activation energies combine and when pure ethyl nitrite is used cause the removal of all radicals 1–2 cm. from the end of the furnace. On the other hand, dilution of the ethyl nitrite with an inert gas permits the radicals to reach the mirror by diminishing the number of collisions they make outside the furnace with the ethyl nitrite.

[7] Rice and Evering, THIS JOURNAL, **56**, 2105 (1934); see also Ref. 4.

[8] Rice, *ibid*., **56**, 488 (1934).

[9] See Rice and Herzfeld, *ibid*., **56**, 284 (1934).

of these two reactions from the two rate equations

$$k_2[\mathrm{CH_3CH_2O}—]\,[\mathrm{CH_3CH_2ONO}] \sim 10^9\,e^{-E_2/RT}\,[\mathrm{CH_3CH_2O}—]\,[\mathrm{CH_3CH_2ONO}]$$

$$k_4[\mathrm{CH_3CH_2O}—] \sim 10^{14}\,e^{-E_4/RT}\,[\mathrm{CH_3CH_2O}\,-]$$

Equating these and solving for the concentration of ethyl nitrite we obtain

$$[\mathrm{CH_3CH_2ONO}] = 10^5\,e^{-(E_4-E_2)/RT}$$

If we make a very rough approximation and assume that the two rates are equal at 0.01 atmospheres when the temperature is 500°K. we have

$$10^{-2} = 10^5 \times 10^{-(E_4-E_2)/4.6\times 500} \text{ or } E_4 - E_2 = 16 \text{ Cal.}$$

It is probable that reaction (2) requires a somewhat higher activation energy than does reaction (5); taking this into account as well as previous estimates[7] for analogous reactions, it seems plausible to assume that E_2 and E_4 have values in the range 12–18 Cal. and 28–34 Cal., respectively.

We wish to thank Dr. O. K. Rice for suggestions received in connection with the interpretation of these experiments.

Summary

When pure ethyl nitrite vapor at low pressures is decomposed in a flowing system, cold metallic mirrors are not affected by the gases leaving the furnace. On the other hand, if the ethyl nitrite is diluted with an inert gas, mirrors are readily removed, even when the furnace is at temperatures as low as 425° and this behavior may be explained by assuming that the interaction of a free radical with ethyl nitrite results in the production of molecules only.

The activation energy of the primary dissociation of ethyl nitrite was found to be 34.3 ± 3 Cal.

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[CONTRIBUTION FROM THE GOESSMANN CHEMISTRY LABORATORY, MASSACHUSETTS STATE COLLEGE]

The Synthesis of 5,5-Alkylphenylbarbituric Acids[1,2]

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The syntheses of ethylphenylbarbituric acid, Luminal or Phenobarbital, by Rising and Stieglitz,[3] by Rising and Zee,[4,5] and by Cretcher and Nelson,[6] all start with phenylacetonitrile and by three to five steps obtain alkylphenylmalonic ester. This is then condensed with urea, by heating under pressure or at the high boiling point of the mixture, the product being the desired alkylphenylbarbituric acid. In the synthesis of Cretcher and Nelson and according to Hessler[7] and Bodreux,[8] phenylacetonitrile condenses with diethyl carbonate in ether solution, with sodamide, yielding cyanophenylacetic ester (phenylmalonic nitrile). Hörlein[9] ethylates this ester to cyanoethylphenylacetic ester and Conrad[10] and Tabern and Volwiler[11] have condensed the cyanoethylphenyl-(or cyanodialkyl)-acetic ester with urea yielding iminobarbituric acids which readily hydrolyze to the barbituric acids.

The present investigation consists of the preparation, by means of this general series of reactions, of four hitherto unprepared alkylphenylbarbituric acids. The results may be summarized as follows.

(1) The condensation of phenylacetonitrile with diethylcarbonate is best effected by using sodamide as condensing agent in absolutely anhydrous ether, with continued stirring and efficient refluxing. The product is ethyl cyanophenylacetate.

(2) A by-product results from the probable reaction of two molecules of the nitrile with one molecule of the carbonate and its formation is favored by non-anhydrous conditions and by too long refluxing. The compound proved to be α,α'-dicyano-α,α'-diphenylacetone.

(3) Alkylation of the cyanophenylacetate and the condensation of the resulting cyanoalkylphenylacetate with urea take place in ether–alcohol and in absolute alcohol in the presence of sodamide or sodium ethylate. The product of the

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(1) The work reported in this paper represents part of the material contained in theses presented by Messrs. Chap, Doyle and Spaulding to the Graduate School of the Massachusetts State College in 1933 and 1934 for advanced degrees, and is published with the consent of the Director of the Graduate School.

(2) Presented before the Division of Organic Chemistry at the Cleveland Meeting of the American Chemical Society, Sept. 10–14, 1934.

(3) Rising and Stieglitz, THIS JOURNAL, **40**, 723 (1918).

(4) Rising and Zee, *ibid.*, **49**, 541 (1927).

(5) Rising and Zee, *ibid.*, **50**, 1208 (1928).

(6) Cretcher and Nelson, *ibid.*, **50**, 2758 (1928).

(7) Hessler, *Am. Chem. J.*, **32**, 119 (1904).

(8) Bodreux, *Compt. rend.*, **151**, 1358 (1910).

(9) Hörlein, *C. A.*, **6**, 3312 (1912).

(10) Conrad, *Ann.*, **340**, 310 (1905).

(11) Tabern and Volwiler, THIS JOURNAL, **56**, 1139 (1934).