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Kinetic Study of

$H_2O + NH_3 + HNO_3 \xrightarrow{\text{Acid-Base}} NH_4NO_3 + H_2O$

NH_4OH

12 June 1952

U. S. NAVAL ORDNANCE LABORATORY
WHITE OAK, MARYLAND

A KINETIC STUDY OF THE THERMAL DECOMPOSITION OF ETHYL NITRATE

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ABSTRACT: The thermal decomposition of ethyl nitrate in the vapor phase has been studied at 161-201°C and pressures below 200 mm Hg. An analytical technique has been developed using the infrared spectrometer and the ultraviolet spectrophotometer which has made it possible to follow the disappearance of ethyl nitrate directly.

It has been found that ethyl nitrite is an important reaction intermediate. The formation and disappearance of ethyl nitrite and of nitrogen dioxide over the course of the reaction have been followed using the new techniques. The effect of nitrogen dioxide, ethyl nitrite and mercury on the reaction have been studied.

The mechanism of nitrate ester decomposition is examined in the light of the results found in this work.

Explosives Research Department
U. S. NAVAL ORDNANCE LABORATORY
WHITE OAK, MARYLAND

NAVORD Report 2313 12 June 1952

The research reported herein was done under Task Assignment, NOL-Re2d-02-1-52. The optical techniques developed for the study of propellant decomposition have been applied to the study of the thermal decomposition of ethyl nitrate. Valuable new information on the decomposition of nitrate esters has been uncovered, which it is hoped will lead to a complete understanding of the decomposition mechanism.

W. G. SCHINDLER
Rear Admiral, USN
Commander

Paul M Fye
Paul M. Fye
By direction

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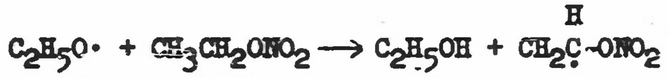
A KINETIC STUDY OF THE THERMAL DECOMPOSITION OF ETHYL NITRATE

INTRODUCTION

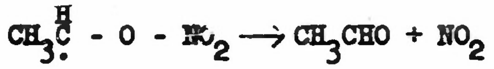
1. Nitric acid esters play a very important role in the field of explosives and propellants; thus glyceryl trinitrate (nitroglycerin) and cellulose nitrate (nitrocellulose) are two of the most important representatives of this class of compounds. Accordingly it has long been of great interest to study the manner in which this type of compound decomposes thermally. Such knowledge is of great usefulness both from the point of view of finding measures for insuring the stability of nitrate ester explosives in storage and from the point of view of understanding the way they decompose in a gun or motor and perhaps improving their performance.

2. In recent years, (a,b,c,d,e) the kinetics of the thermal decomposition of nitrate esters has been the object of much study. In general, due to the complexity of compounds like nitroglycerin and nitrocellulose, simpler compounds like ethyl and methyl nitrates have been chosen as models. On the basis of these kinetic studies a picture of the mechanism of nitric acid ester decomposition has emerged which seems quite plausible. The way in which the reaction is believed to go is expressed by the equations, (d), written for ethyl nitrate:

$$C_2H_5ONO_2 \rightleftarrows C_2H_5O\cdot + NO_2 \qquad (1)$$



$$C_2H_5O\cdot + CH_3CH_2ONO_2 \longrightarrow C_2H_5OH + CH_2\overset{H}{\underset{\cdot}{C}}\text{-}ONO_2 \qquad (2)$$



$$CH_3\overset{H}{\underset{\cdot}{C}} - O - NO_2 \longrightarrow CH_3CHO + NO_2 \qquad (3)$$

Certain additional observations have been made with ethyl nitrate which are of great interest. Nitrogen dioxide, which has been observed visually as one of the products, has been found to inhibit the reaction when present in moderate amounts but to accelerate it when present in larger amounts, (d,e,f). It has also been claimed that the nitrogen dioxide in the reaction seems to build up to a maximum and then drop off again (b,d,e).

3. All of the kinetic studies which were the basis of the above ideas on the decomposition reaction were carried out using manometric techniques in which the rate of pressure development was followed when the organic nitrate was heated in a closed system. This method has the great advantages of simplicity and versatility. It is based on the assumption that the rate of pressure rise is a true measure of the decomposition rates, however, and in the case of a reaction as complex as the decomposition reaction, this assumption is open to question. In most cases, (c,d,e) the kinetics did not follow a simple rate law over the whole course of the decomposition and it was necessary to select a portion of the curve for the rate calculation. Furthermore this technique, although in some cases accompanied by chemical analysis, gives an overall picture of what is going on and is not capable either of measuring the disappearance of the nitrate directly, which is very desirable for a kinetic study, or of detecting and measuring intermediates in the reaction. Since it was felt that the manometric technique did suffer from certain drawbacks

and had been well explored, it seemed best to devise kinetic techniques which permitted a more intimate examination of the reaction. The method chosen was that of infrared spectrophotometry supplemented by spectrophotometry in the visible region.

4. As had been done by the previous investigators, a simple compound, ethyl nitrate, was selected for study to serve as a model for the more complicated nitrate esters actually in practical use. The simplest choice would have been methyl nitrate but this was avoided because of its undue sensitivity. Ethyl nitrate has been studied by others, (c,e) and hence a comparison between results obtained here and those obtained elsewhere by other methods would be possible.

5. In a previous report (g) the development of a spectroscopic analytical technique for the complete analysis of mixtures of ethyl nitrate, acetaldehyde and nitrogen di-and tetroxide has been described. This technique has since been adapted to the analysis of actual gas mixtures arising from the decomposition of ethyl nitrate. The results of these studies and their interpretation are the subject of this report.

APPLICATION OF INFRARED TECHNIQUES

Examination of Infrared Spectra of Decomposition Mixtures

6. Although it had been established, (g) that it was feasible to analyze gaseous mixtures of ethyl nitrate, acetaldehyde and nitrogen di-and tetroxide for all the components, it remained to be seen whether this analysis could be directly applied to the decomposition mixtures obtained from ethyl nitrate or whether the scheme would have to be extended to include other things. Accordingly, the next step was to carry out some decompositions and examine the infrared records to see what, if any, other things were present.

7. In Figure 1, there is reproduced a record taken on a Perkin-Elmer Model 21 double-beam recording spectrophotometer of a sample of ethyl nitrate heated at 181°C until about 60% of the starting material had been decomposed. It is of great interest to examine this record and to identify the various absorption peaks with specific compounds. Although this may be done by reference to the spectra of pure ethyl nitrate, acetaldehyde and nitrogen di-and tetroxide, Figures 3, 4 and 5, it clarifies the problem somewhat if this figure is compared with Figure 2 which shows the record of a sample heated at 180-190°C until the ethyl nitrate had been completely decomposed. A comparison of these two figures shows that the characteristic peaks of ethyl nitrate at 11.73 μ, 9.75 μ, and 7.75 μ have completely disappeared while its contribution to the 6 μ, the 11 μ and the C-H 3.6 μ peaks are also gone. Comparison of Figure 1 with the record for pure acetaldehyde shows that the absorption at 5.65 μ can be attributed to the carbonyl absorption in this compound. Further examination of Figures 1 and 2 shows that there are several absorption peaks which cannot be attributed to ethyl nitrate, acetaldehyde or nitrogen di-and tetroxide. These appear at 12-13 μ, 6 μ, 9.7 μ, 10.8 μ and 7-7.75 μ. The nature of these absorptions is revealed clearly in Figure 2 where they are freed of the interference of the ethyl nitrate absorption. It thus appears that there is something present in the decomposition mixtures other than the compounds postulated in the mechanisms which have been written for the reaction.

Identification of Unknown Absorbent in Decomposition Mixture

8. Although the decomposition of ethyl nitrate is a rather complex reaction, the molecule itself is not very complex and the number of products which could arise from its decomposition is limited. After a number os possibilities had been considered, it was established that the molecule responsible for the unidentified absorption peaks was ethyl nitrite. The record for pure ethyl nitrite in Figure 6 shows very clearly that it is responsible for the peaks at 5.95μ, 6.15μ, 7.25μ, 9.5μ, 10.7μ and the broad absorption peak between 12 μ and 13.25μ. Thus the absorptions due to ethyl nitrate, acetaldehyde, nitrogen di- and tetroxide and ethyl nitrite account for about all of the major absorptions found in the decomposition mixture.

Extension of Analytical Scheme

9. At this point it seemed desirable to attempt to include ethyl nitrite in the analytical scheme and a point in the center of the broad absorption at 12-13.25μ was chosen for the analysis of ethyl nitrite, to wit 12.85μ. The Beer's law constants for the four components at the wavelengths used for analysis are given in Table I. Using the bulb expansion technique described in the previous report (g) tests were carried out on synthetic mixtures of the four components to show whether it was possible to analyze such mixtures for all the components. The results are given in Table II and it was concluded that the analysis was satisfactory.

TABLE I

Beer's Law Constants

(unit pressure = 1 mm., unit cell length = 1 mm.)

Wavelength	Ethyl Nitrate	Ethyl Nitrite	Acetaldehyde	Nitrogen Dioxide	Nitrogen Tetroxide
5.70 μ	0.000021± 0.000006	---	0.000436± 0.000005	---	0.00298± 0.00008
11.73 μ	0.00108± 0.00004	0.000046± 0.000006	---	---	---
12.85 μ	0.00003± 0.000002	0.000347± 0.00002	---	---	---
0.4050 μ	---	---	---	0.000888± 0.000014	---

TABLE II

Four Component Analyses

Compound	Pressure in mm. As Made Up	Optical	% Error
Ethyl Nitrate	8.16	7.80	4.4
Ethyl Nitrite	9.7	9.4	3.1
Acetaldehyde	1.93	1.94	0.5
Nitrogen Dioxide	3.09	2.89	6.5

Compound	Pressure in mm. As Made Up	Optical	% Error
Ethyl Nitrate	13.8	13.9	0.7
Ethyl Nitrite	2.76	2.86	3.6
Acetaldehyde	12.5	12.0	4
Nitrogen Dioxide	3.20	3.10	3
Ethyl Nitrate	3.74	3.50	6.4
Ethyl Nitrite	12.4	12.5	0.8
Acetaldehyde	12.7	11.3	11
Nitrogen Dioxide	8.30	7.60	8
Ethyl Nitrate	3.62	3.64	0.7
Ethyl Nitrite	25.0	23.5	6.0
Acetaldehyde	14.0	14.8	5.7
Nitrogen Dioxide	8.10	8.60	5.8
Ethyl Nitrate	2.90	3.08	6.2
Ethyl Nitrite	2.70	2.56	5.2
Acetaldehyde	19.1	11.3	4.1
Nitrogen Dioxide	24.3	23.1	4.9

The Effect of Pressure on the Absorption Peaks

10. Although it seemed safe to conclude that the analytical method developed was free from objection, further proof was desirable. In other attempts at the application of infrared spectroscopy to analytical problems it has been found that the intensity of absorption of certain compounds, particularly simple molecules, is markedly affected by the presence of other gases, (h). Although the tests already carried out had demonstrated the absence of such effects for the pressures and gases used, it still remained to show definitely that the actual gases and pressures encountered in the decomposition mixtures did not bring about such effects.

11. One test that was applied is illustrated in Figures 7 and 8. In the former are shown the records for 2 mm of nitrous oxide and the same partial pressure of the gas when air was admitted to the cell at atmospheric pressure. The effect is very noticeable here. In Figure 8, are shown the records for a decomposition mixture carried to 92% decomposition and for the same mixture after air had been admitted at atmospheric pressure. Here a comparatively slight change is found. This change furthermore is due to about 1 atm. of added pressure while in the decomposition mixtures the total pressure never exceeded 100 mm.

Comparison of the Decomposition Mixture Records With Those for Synthetic Mixtures

12. A group of experiments was undertaken to check the soundness of the analytical scheme and to determine how well ethyl nitrate, ethyl nitrite, acetaldehyde and nitrogen dioxide accounted for the absorptions found in the actual decomposition mixture. Decomposition of ethyl nitrate was halted at various stages. The resulting gas mixtures were analyzed from their infrared records. A synthetic mixture was made up to duplicate each analysis, and its infrared record compared with the original.

13. Figures 9, 10, 11 and 12 illustrate the results of such experiments. In these the infrared record of the synthetic mixture has been taken on the same chart that bears the record for the corresponding decomposition mixture. As will be explained later, the analysis for acetaldehyde in the decomposition mixture is in doubt. In addition there is no peak for nitrogen dioxide <u>in</u> the 2-15μ region which could be used to check its analysis in this fashion. The nitrogen dioxide pressure was never more than 2-3 mm. For this reason attention was focused principally on ethyl nitrate and ethyl nitrite. In Figures 9 and 11 only these two components are present while in Figure 10 only ethyl nitrate, ethyl nitrite and acetaldehyde are present.

14. It is most instructive to examine these figures both from the point of view of the regions where the two records in each figure agree and from the point of view of their discrepancies. For the validity of the analysis it is clear that the two curves should show good agreement at the peaks used in the analytical scheme, and in fact, at all other peaks where compounds other than those represented in the synthetic mixture do not interfere.

15. The agreement for the peaks due to ethyl nitrate will be considered first. The peak at 11.73μ was that used in the analysis and in all four figures the agreement shown at this point is good. Part of the discrepancy is due to the fact that the synthetic mixture did not duplicate the decomposition mixture exactly because of experimental difficulties. A calculation to compensate for this may be made wherein the optical density (Log I_0/I) of the synthetic mixture curve at the particular point is multiplied by the factor P_d/P_s. (P_d= pressure in decomposition mixture; P_s= pressure in synthetic mixture). When this is done the agreement is improved and at 11.73μ the difference in the two curves is 2.2%, 1.9%, 0% and 2.1% for figures 9, 10, 11 and 12 respectively. Ethyl nitrate also has a strong absorption at 7.75μ which is apparently free of interference. Here, too, agreement is good although the neighboring very strong cell face absorption[1] makes a quantitative discussion unreliable. The ethyl nitrate peak at 6μ is at the same

---

[1] This absorption has been mentioned in the literature (i, j) and is due to sodium nitrate which is formed by the reaction

$$2NO_2 + NaCl \rightarrow NOCl + NaNO_3$$

In the present work (g) a sharp double pointed absorption at 5.52-5.60μ had been found when spectra of nitrogen dioxide were taken. It is clear that this is due to the nitrosyl chloride formed in the above reaction. Pulford and Walsh (k) report a strong absorption for nitrosyl chloride at 1800 cm.$^{-1}$ or 5.55μ.

It is known that the above reaction requires the presence of water (l). This explains why it was possible to carry out the complete analysis of quartenary mixtures of ethyl nitrate, ethyl nitrite, acetaldehyde and nitrogen dioxide without interference by this reaction.

It will be noted that in some of the spectra of the decomposition products e.g. Figures 8, 9, 11 and 13, nitrosyl chloride is present. Since nitrogen dioxide was determined in the glass cell, no errors are introduced into the analyses by this reaction.

place as an ethyl nitrite peak; so again a simple discussion is not possible. The agreement here should be pretty close, however. As the figures show, it is.

16. The peak used for the analysis of ethyl nitrite is at 12.85μ. When figures 9, 10, 11 and 12 are examined it is found that at 12.85μ the agreement is good. When a correction is made for the small pressure differences between the analysis and the synthetic mixture composition, the 12.85μ peaks check to 0.7%, 3.6%, 4.6% and 3.1% for Figures 9, 10, 11 and 12. The 9.5μ peak shows fair agreement while as mentioned above the 5.97μ peak cannot be considered apart from the 6μ ethyl nitrate peak.

17. When the region between 12 and 13μ is examined more closely, certain discrepancies appear. While agreement is good in each case at 12.85μ the agreement in the region from 12-12.75μ is poor and the contour of the decomposition curve does not match that of the synthetic mixture well at all. This suggests that an additional absorption not due to ethyl nitrite is present in the 12-12.75μ region. By subtracting the optical density of the synthetic mixture curve from that of the decomposition mixture curve at various points the contour of that absorption could be found. It is clear that the discrepancy is much smaller at the lower percent reactions. A more exact picture of the difference between the synthetic mixture and the decomposition mixture can be gained by comparing the two in the double beam infrared spectrometer. A cell containing the decomposition mixture is placed in one beam and a cell with the synthetic mixture in the other. The spectrum observed is that of the decomposition mixture minus the synthetic mixture. Figures 13 and 14 show such records for the mixtures of Figures 9 and 11 respectively. The absorption in the 12-12.5μ region is small but noticeable. An additional experiment was carried out to 93.3% decomposition of the ethyl nitrate. The record for the decomposition mixture plus the record for the comparison of the decomposition mixture with the synthetic mixture appear in Figure 15. The 12-12.5μ absorption is present but it is poorly defined. When this region was recorded again at low speeds and high resolution the results shown in Figure 16 were found. Here the shape of the spectrum is well defined. It is clear that an additional compound absorbing in the region 12-12.5μ is present and it is necessary to inquire as to what the nature of the compound is and what its effect on the analysis is.

Additional Absorbents

Methyl Nitrite

18. The 12-12.5μ absorption has not noticeably affected the ethyl nitrate or ethyl nitrite analyses since, as discussed above, the peaks used for their analysis check well in the comparison records in Figures 9, 10, 11 and 12. It may be noted too that in Figures 13, 14 and 15 the absorption at 10.5-11μ due to ethyl nitrate and ethyl nitrite have been completely blanked out giving a further check on the analyses of these two compounds. When the nature of the absorbent responsible for the peak in Figure 16 is considered it is noted that this peak is very reminiscent of the methyl nitrite peak in this region. The record for this compound is shown in Figure 17 at two pressures. It is seen that its absorption in the 12-13μ region does indeed look very much like the unknown absorption of Figure 16. Since methyl nitrite also shows absorptions at 10-10.25μ and in the 5.9 and 6.2μ regions it is pertinent to examine Figure 15 to see whether any absorptions at these points which can be correlated to the methyl nitrite can be found. It is clear that there is

absorption at 10-10.25μ which resembles that found for methyl nitrite, and which cannot be due to ethyl nitrate, cf figure 3. In addition absorption is also found in the 5.9 - 6.5μ region which cannot be due to ethyl nitrate entirely, and which could very well be due in part to methyl nitrite. The absorption here extends to longer wavelengths than could be explained by either methyl nitrite or ethyl nitrate. It will be shown later that this additional absorption may be attributed to the presence of still another absorbent. When one examines the comparison spectra in each case it is found that absorption by the decomposition mixture is more intense at each of the regions where methyl nitrite absorbs than the synthetic mixture can explain. Hence it seems fairly certain that methyl nitrite is present in the decomposition mixtures. As the comparison Figures 9, 10, 11 and 12 show it is present in quite small amounts in the earlier stages of the reaction (Figures 9 and 10) and becomes noticeable, but not large, in the final stages of the reaction.

Nitromethane

19. With the inclusion of methyl nitrite in the analysis of the experiments illustrated in Figures 9, 10, 11 and 12, only the region of 6.2 - 6.7μ shows a distinctly greater absorption for the decomposition mixture than for the synthetic mixture. This is just the region where nitromethane and nitroethane show absorption; cf. Figures 18 and 19. Ethyl nitrate, nitrite and possibly methyl nitrite show absorptions which make it difficult to find the nitromethane doublet at 6.30μ, 6.37μ. Nitromethane is very stable thermally compared to these compounds. If a decomposition were carried out for a time long enough to bring about the destruction of all of these esters, nitromethane should still persist and its absorption spectrum should be clear. In Figure 20 is shown the record for a sample of ethyl nitrate heated at 161°C for 7120 minutes. It is clear that nitromethane is present and it probably is responsible for the difference in the two curves in Figures 9, 10, 11 and 12 in the 6.2-6.7μ region. A point that should be emphasized is, that since nitromethane is so relatively stable the amount shown in Figure 20 represents an accumulation of all that was formed over the whole course of the reaction. A rough estimate of the amount present based on a comparison with the record for the pure compound at P = 12 mm, Figure 18, places it at about 3-4 mm.

20. The record for nitroethane, Figure 19, is included. Although its absorption is similar to that for nitromethane, the difference is great enough to rule it out as the cause for the absorptions discussed here.

Consideration of Other Compounds as Intermediates or Products

21. Although it is clear that all the major absorbents have now been accounted for, it is still of interest to see whether by further examination of these figures it is possible to draw any conclusions as to the presence or absence of other compounds which have been associated with this reaction.

Ethyl Alcohol

22. An examination of the reaction mechanism on Page 1 shows that one of the molecules involved in the scheme, ethyl alcohol, has not been considered as yet.

In the spectrum for ethyl alcohol, Figure 21, the main absorption peak is around 9.4 μ while weaker absorptions appear at 3.4 μ, 7.2 μ, and 8 μ. Examination of Figures 9, 10, 11 and 12 at these points shows that at all of them agreement between the synthetic mixture record and the decomposition mixture record is close. Thus it appears that ethyl alcohol does not build up to any appreciable concentration in the reaction mixture assuming that it is formed. There is other chemical evidence to support this view and this will be discussed in another connection elsewhere in this report (See discussion page 23).

Nitrous Oxide

23. One of the products reported for the decomposition of nitrate esters is nitrous oxide, (b,e). This presumably results from the reaction of nitrogen dioxide with the acetaldehyde or possibly ethyl alcohol formed. The spectrum for nitrous oxide is shown in Figure 22. Its most intense absorptions are found at 4.5 μ, 7.7 μ and 7.8 μ. Examination of Figures 9, 10, 11 and 12 at these points gives no evidence that nitrous oxide is present. Although nitrous oxide is not a very strong absorbent it has been found that its absorption intensity is greatly increased by the presence of other gases. Thus in Figure 7, it is seen that when air is admitted to a cell containing 2 mm of nitrous oxide the absorption is very greatly increased. Figure 8 is a record of a decomposition mixture at 161°C carried to about 92% decomposition of the ethyl nitrate. Here the admission of air has not shown the presence of nitrous oxide. Figure 8 should show an accumulation of the total amount of nitrous oxide formed over 92% of the decomposition of the ethyl nitrate. Hence it seems doubtful that it has been formed or that it is present in appreciable quantity in the reaction mixture.

Formaldehyde

24. In the decomposition of ethyl nitrite (n) the ethoxy radical is assigned a role similar to that assigned to it in the ethyl nitrate decomposition.

$$C_2H_5ONO \longrightarrow C_2H_5O\cdot + NO$$

$$C_2H_5O\cdot + C_2H_5ONO \longrightarrow C_2H_5OH + CH_3.CHONO$$

In addition, however, it has been demonstrated, (o) that at lower pressures the reaction

$$C_2H_5O\cdot \longrightarrow CH_3\cdot + CH_2O$$

also occurs and hence the reaction

$$CH_3\cdot + C_2H_5ONO \longrightarrow CH_4 + CH_3.CHONO$$

must also be considered.

25. This makes it necessary to consider the possible formation of formaldehyde and methane in the ethyl nitrate decomposition.

26. The spectrum for formaldehyde is shown in Figure 23. The characteristic carbonyl absorption falls between 5.5μ and 5.9μ. Acetaldehyde has a carbonyl absorption, (Figure 4), at about the same place. In most of the decomposition mixtures analyzed the absorption in this region was quite small, cf. Figure 1. Although the shapes of the acetaldehyde and formaldehyde absorptions in the 5.5-5.9μ region are quite different, with small amounts of absorption in this region it was not clear that the shape corresponded to one or the other. For some cases, in the later stages of the reaction, cf. Figure 2, the contour definitely was that of acetaldehyde. Thus although it seems safe to say that acetaldehyde is formed sometime in the reaction, the data do not allow the exclusion of formaldehyde from a role in the decomposition.

Nitric Oxide

27. Nitric Oxide is a very likely product in the reaction. It has been reported by others (c,e) and its origin has generally been attributed to the reduction of nitrogen dioxide by acetaldehyde. Since it has been found here that ethyl nitrite is a major intermediate in the reaction, another possible source for nitric oxide is by the decomposition of ethyl nitrite. Unfortunately nitric oxide is a comparatively weak absorbent and it is not possible to draw any conclusions on its presence or absence from the infrared records. It was clear, however, that nitric oxide was present. When air was admitted to the decomposition mixtures a noticeable intensifying of the known nitrogen dioxide color was observed which can only be explained by the oxidation of nitric oxide by air to nitrogen dioxide. On the basis of this reaction some estimate of the amount of nitric oxide present could be obtained. The results of these estimates are reported in a later section of this report. Since nitric oxide is such a weak absorbent, it did not interfere at all in the analytical scheme.

Methane

28. The spectrum of methane is shown in Figure 24. Since its absorption is so weak it is not possible from the data obtained in this work to draw any conclusions on the presence or absence of methane in the mixtures. It is safe to say that it would not interfere with the analyses of the other components.

Other Compounds

29. There is no doubt that there are other compounds present in the decomposition mixtures. Water and carbon dioxide are almost certainly present but no attempt has been made at their analysis.

30. Another compound which it is of interest to consider is nitric acid. This could be formed via the reactions

$$3NO_2 + H_2O \rightleftarrows 2HONO_2 + NO$$

$$2NO_2 + C_2H_5OH \rightarrow C_2H_5ONO + HONO_2$$

It is possible to get some idea of the amount of nitric acid that would be left undissociated by considering the equilibria

$$(1)\quad 3NO_2 + H_2O \rightleftarrows 2HONO_2 + NO$$

$$(2)\quad 2HONO_2 \rightleftarrows H_2O + 1/2\ O_2 + 2NO_2$$

At 298.1°A the equilibrium constant for (1) is $K_{(1)} = 1.37 \times 10^{-2}\ atm^{-1}$ and that for (2) is $K_{(2)} = 6.9 \times 10^{-5}\ atm^{-3/2}$, (1). From these two, the equilibrium constant for

$$(3)\quad NO_2 \rightleftarrows NO + 1/2\ O_2$$

is $K_1K_2 = 9.5 \times 10^{-7}\ atm^{-1/2}$. Since NO is found to be present over almost the entire reaction period it will be seen that only equilibrium (1) need be considered.

31. If the pressures of nitric oxide, nitrogen dioxide and water are taken as being about 0.01 atm., which seems a reasonable assignment, an estimate of the nitric acid pressure can be made. This comes out to be about 1×10^{-4} atm. Hence the nitric acid present can be dismissed as negligible. It will be shown later, that ethyl nitrate, ethyl nitrite nitrogen dioxide and nitric oxide account for all the nitrogen present so that little if any could be tied up otherwise.

Comments on the Application of the Infrared Technique to the Decomposition Mixture

32. From the preceding discussion it seems clear that the decomposition mixtures can be analyzed for the ethyl nitrate and ethyl nitrite content within the limits of the accuracy found in the preliminary experiments with synthetic four-component mixtures. The analysis for acetaldehyde, however, is open to serious doubt due to the possible interference of formaldehyde. It seems clear that in the later stages of the reaction acetaldehyde is present for here the 5.65 μ peak definitely has the acetaldehyde contour. For the major part of the reaction there is uncertainty as to the source of the absorption in this region, however, and hence no interpretation of the measurements made at this point will be attempted.

33. Since the nitrogen dioxide content of the decomposition mixtures was always small and since there is no clear infrared absorption peak for nitrogen dioxide, free of interference, it has not been possible to test the validity of the nitrogen dioxide analyses in the same way as the validity of the ethyl nitrate and ethyl nitrite analyses were tested. At the wavelength used for the nitrogen dioxide analysis, 4050 Å, it is the only absorbing molecule present in the mixture. For this reason it seems safe to assume that its analysis in the decomposition mixtures is as good as in the artificial four-component mixtures used in the preliminary experiment.

The Material Balance

34. It is of interest to make a further check on the analytical method by means of a material balance. Since neither carbon dioxide, water or aldehydes were determined, a balance cannot be made on the basis of carbon or oxygen. It is believed that ethyl nitrate, ethyl nitrite, nitrogen dioxide and nitric oxide account for most of the nitrogen. In the late stages of the reaction, methyl

nitrite appears while nitro compounds are formed in small amount sometime during the reaction. A material balance for nitrogen should show good agreement however for most of the reaction period. Since data for nitric oxide are complete only for 181°C the nitrogen balance for the data at that temperature are given in Table III.

TABLE III

The Material Balance for Nitrogen for the Thermal Decomposition of Ethyl Nitrate at 181°C

Moles per Mole of Ethyl Nitrate Present Initially

Time (min.)	Ethyl Nitrate	Ethyl Nitrite	Nitrogen Dioxide	Nitric Oxide	Total
5.0	0.952	0.065	0.039	0.0	1.056
13.0	0.770	0.130	0.056	0.0	0.956
25.0	0.696	0.236	0.044	0.015	0.991
40.0	0.500	0.353	0.079	0.051	0.983
40.0	0.525	0.432	0.076	0.023	1.056
50.0	0.431	0.458	0.089	0.033	1.011
60.0	0.335	0.544	0.075	0.044	0.998
70.0	0.249	0.576	0.071	0.081	0.977
80.0	0.197	0.605	0.066	0.105	0.973
90.0	0.145	0.614	0.053	0.097	0.909
100.0	0.075	0.608	0.010	0.142	0.835
110.0	0.067	0.571	0.015	0.215	0.878

35. It is seen that the agreement is very good over most of the reaction but that not all of the nitrogen is accounted for toward the end of the reaction. This is in harmony with the ideas expressed above and is excellent support for the validity of the analysis.

EXPERIMENTAL PART

Apparatus and Chemicals

36. For the analysis of the gas mixtures a Perkin-Elmer Model 12-B infrared spectrometer equipped with a rock salt prism was used. The visible region measurements were made on a Beckman Model DU Spectrophotometer. The infrared records shown here were taken on a Perkin-Elmer Model 21 double-beam spectrometer equipped with a rock salt prism.

37. Ethyl Nitrate was Eastman Kodak white label grade which was redistilled. A fraction boiling at 87.5-87.8°C was used.

38. Acetaldehyde was Eastman Kodak white label grade. It was redistilled and a middle fraction taken. It was stored in a sealed ampule.

39. Ethyl alcohol was USP absolute alcohol and was used directly from the bottle.

40. The nitrogen dioxide was purchased from the Matheson Company and was certified as better than 95% pure, the impurities being other oxides of nitrogen. It was distilled into the vacuum system through a tube of anhydrous calcium sulfate.

41. The nitric oxide used was purchased from the Matheson Company and was rated as 99%pure. It was used without further treatment.

42. The bath used as the constant temperature medium contained a mixture of potassium nitrate, sodium nitrate and sodium nitrite (p). The temperature was maintained constant to ± 0.2°C.

43. The timing device was a Precision Time-it Timer which could be read to hundredths of a minute.

The Rate Measurements

44. Rate measurements were carried out by filling a glass bulb with ethyl nitrate vapor, heating the bulb for a specified time and then cooling the bulb suddenly by immersing it in a container of cold water. The bulb contents then were expanded into an infrared cell and an ultra violet cell and the analytical measurements carried out. The bulb filling operations were carried out on a vacuum line as shown in Figure 25. In the tube T was placed ethyl nitrate. This was then cooled by a Dewar flask with liquid nitrogen and the entire apparatus pumped down by a Cenco Magavac Pump. Enough ethyl nitrate was allowed to vaporize into the system to give a suitable pressure reading on the manometer M. The three bulbs were closed off from the system by their stopcocks and the system re-evacuated by the pump. The bottom of one of the bulbs was cooled by a Dewar flask with liquid nitrogen and with stopcock S_M closed. The stopcock to this particular bulb was then opened. If the ethyl nitrate has completely condensed no pressure was registered on M when the bulb stopcock was opened. If there was any non-condensible gas in the system, it was found that the ethyl nitrate would not condense completely and hence it was possible at this point to check on the completeness with which the system had been evacuated earlier. If it was found that the ethyl nitrate had been completely condensed the bulb was sealed off at the points indicated by arrows and pulled off from the apparatus. This process was repeated with the other bulbs. When the sealed part of the glass had cooled the bulbs were removed from the liquid nitrogen vessels, warmed to room temperature and immersed in the bath. A timer was started as the bulbs were immersed. At the end of an appropriate time the bulbs were removed from the bath and plunged into cold water.

45. The bulb contents were expanded into the two cells by the apparatus pictured in Figure 26. The bulb was placed in the apparatus by means of the ground

glass interjoint on it, the end of which has been pulled out to a thin tube for an appropriate length. The apparatus was evacuated and by turning the interjoint tube T the "golf club" head broke off the thin tube and the gas expanded into the two cells and the apparatus. It was an easy matter to measure the expansion ratio of the bulb volume to the total volume by filling the bulb with air at a measured pressure and expanding it in the same way. As changes are made in the above apparatus the volume changes and this must be accounted for. In general the ratio of the total volume including the bulb, apparatus and cells, to the bulb volume was in the range 1.3 to 1.5. The measurements were then carried out on the cells in the usual way, (g).

46. There are a few points in the above procedure which require comment. When the bulb is plunged into the bath the question arises as to how long it takes for the bulb and its contents to attain the bath temperature. This has been tested in the following way. A bulb was connected by rubber tubing to a large U tube manometer and the pressure at room temperature reduced to about 40 mm. The bulb was then plunged into the bath at 201°C and pressure readings taken with time. It was found that the pressure readings leveled off in 0.5 minutes. It is clear that this order of time is within the accuracy of the experiment especially at 181°C and 161°C and it was not considered further. As far as the quenching of the reaction goes, the removal and immersion operations took only about 5 or 10 seconds. It seems certain that the temperature drop would be rapid and since the rate drops rapidly with cooling it seems that this factor too need not be considered further.

47. Another point checked was the procedure of removing the bulbs from the vacuum line after they had been filled with ethyl nitrate. To test this manometers were sealed on to the bulbs shown in Figure 25 and they were filled and removed in the usual way. When the bulbs had warmed up to room temperature the pressure was checked with that initially measured out and was found to be the same.

48. It seemed advisable to see whether it was sufficient merely to evacuate the bulbs before filling them with the ethyl nitrate. It is possible that moisture or gases absorbed on the bulb walls might persist through evacuation and exercise some influence on the reaction. To test this three experiments were carried out in which the bulbs were heated thoroughly under vacuum with a luminous flame, allowed to cool under vacuum and then filled. In Table IV, the results so obtained are compared with the results of experiments where this procedure was omitted.

TABLE IV

The Effect of Flaming the Bulbs on the Reaction at 181°C

	P/P_o for Ethyl Nitrate		P/P_o for Ethyl Nitrite	
t(min)	Flamed	Unflamed	Flamed	Unflamed
20.0	0.724	0.720	0.183	0.198
40.0	0.514	0.500 0.525	0.377	0.353 0.432
75.0	0.223	0.223	0.584	0.593

49. It is clear that the results are essentially the same for both procedures. For this reason flaming the bulbs was not made a part of the standard procedure. With this last test it was concluded that the procedure was satisfactory and it was used in the experiments reported here.

The Measurement of the Nitric Oxide Pressures

50. It was noticed quite early in the research that when air was admitted to the decomposition mixture a brown color formed. This was attributed to the presence of nitric oxide in the mixture and was the basis for the determination of nitric oxide in the mixture. The procedure was simply to measure the absorption at 4050 Å due to the nitrogen dioxide present and then to admit air and measure the absorption again. The increase in the absorption was attributed to the oxidation of nitric oxide and its pressure calculated accordingly. After air had been admitted, readings were taken until the absorption became constant, a matter of twenty minutes to half an hour.

51. It is necessary in such a determination to see what effect the admission of air had on the absorption intensity of nitrogen dioxide alone and in Table V below the results of some measurements are shown. Here a 50.00 mm cell was filled with nitrogen dioxide at various pressures, the readings taken at 4050 Å, air admitted and readings taken again.

TABLE V

The Effect of Air on the Absorption of Nitrogen Dioxide

P_{NO_2}(mm)	Optical Density		
	NO_2 Alone	NO_2 & Air	% Increase
1.46	0.065	0.075	15
2.20	0.098	0.115	17
9.30	0.415	0.460	11
10.1	0.447	0.510	14

52. In the above the increase in the absorption of about 10-17% may be due to an impurity of nitric oxide in the nitrogen dioxide or to some pressure effect on the absorption. No effort is made in this report to treat the nitric oxide analyses as quantitative. It may be pointed out that the amounts of nitric oxide found (Figure 30) were in general much greater than the above effect could explain and there is no doubt that the figures reported represent a reliable estimate of the amount of nitric oxide present.

Calculations

53. An examination of Table I shows that at each of the wavelengths used only two of the components had to be considered. It is true that at 5.70 μ ethyl nitrate, acetaldehyde and nitrogen dioxide all absorbed but since in every case

TABLE VI

Rate Constants for Ethyl Nitrate Decomposition (min-1)

	161°C	181°C	201°C
$K_{\text{initial part}}$	0.00226 ± 0.00009	0.0165 ± 0.0014	
$K_{\text{later part}}$	0.00410 ± 0.00005	0.0271 ± 0.0002	0.149 ± 0.004

57. From the three rate constants obtained from the later part of the reaction it is possible to calculate the energy of activation and the temperature independent factor. It is found that

$$k = 10^{14.44} e^{\frac{-36,630}{RT}} \text{ sec.}^{-1}$$

$E = 36,630 \pm 342$ cal./mole where the precision indicated is the deviation from the mean.

58. These results may be compared with those of Phillips (e) and those of Adams and Bawn (c). For the temperature range 179.5-207.95°C, Phillips reports

$$k = 10^{13.86} e^{\frac{-36,000}{RT}} \text{ sec.}^{-1}$$

This is in good agreement with the results reported here. Adams and Bawn studied the reaction over the range 180-215°C and report

$$k = 10^{15.8} e^{\frac{-39,000}{RT}} \text{ sec.}^{-1}$$

This corresponds to a much slower reaction rate than was observed here for the "later" parts of the reaction.

59. It is of some interest that when the general rate expression is calculated from the "initial" slopes obtained in this work the expression that results is

$$k = 10^{15.11} e^{\frac{-39,300}{RT}} \text{ sec.}^{-1}$$

60. No interpretation of this data will be made here except to point out that Adam and Bawn make no mention of two parts to their curves but merely state that they were first order out to 60% reaction.

61. These present results are further similar to those reported by Phillips in that he too found a change in the rate curves. He found an initial period wherein reaction was rather slow followed by a later period which followed first order kinetics and where reaction was more rapid. This phenomenon became less pronounced at higher temperatures: thus at 183.7°C this initial part of the curve

the amount of nitrogen dioxide present was very small the amount of nitrogen tetroxide present was insignificant. It may be further noted that at each wavelength only one component absorbed very strongly. The procedure used in calculating was to use approximations.

54. The ethyl nitrate pressure was obtained approximately by assigning all the absorption at 11.73 μ to it. The pressure so obtained was used to calculate the ethyl nitrate contribution at 5.70 μ and 12.85 μ. From these values the absorptions at 12.85 μ and 5.70 μ could be corrected to give the absorption at these points due to ethyl nitrite and acetaldehyde respectively and the pressures of these components calculated. Using these pressures the contributions of ethyl nitrite and acetaldehyde to the 11.73 μ absorptions could be calculated and a corrected ethyl nitrate pressure found. This process could of course be repeated but it was found that the one approximation gave an accurate solution. Since only the nitrogen dioxide absorbed at 4050 Å the calculation of its pressure was uncomplicated. The pressure of the nitrogen tetroxide was found using the equilibrium constants of Verhoek and Daniels (q). The bulbs and cells were protected from exposure to light to eliminate the danger of photochemical decomposition of the nitrogen dioxide (cf. g).

RESULTS AND DISCUSSION

55. The thermal decomposition of gaseous ethyl nitrate has been studied at the temperatures 161°C, 181°C and 201°C. The rates of change of the pressures of ethyl nitrate, ethyl nitrite and nitrogen dioxide have been measured quantitatively while the variation of the nitric oxide pressure has been followed in a semi-quantitative fashion as described in the Experimental Part. The results of these studies are shown graphically in Figures 27, 28, 29, 30, 31 and 32. In all cases the quantity used for plotting the data has been P/P_o, the pressure of the particular component divided by the initial ethyl nitrate pressure. This was necessary since the initial ethyl nitrate pressures used varied over the range 10-50 mm. as measured at room temperature. They were chosen so that the pressure of ethyl nitrate to be analyzed was at a suitable value - i.e. about 5-10 mm.

The Kinetic Data

56. In Figures 27, 29 and 31 the data have been plotted as if the reaction were first order. The results at 161°C and 181°C fall into two parts - an initial linear portion and a later linear portion of higher slope. The slopes for each of these portions have been determined by the method of least squares. The data at 201°C exhibits too much scatter to allow a division into two parts and the slope reported was determined by a least squares calculation made on the basis of all the data. In the 181°C curves, the points at 100 and 110 minutes were not used in the calculations since they deviated markedly from the preceding points. Thus the data involved in the calculations extended out to 85% reaction only. At 161°C and 201°C as may be seen, the data extend out to about 95%. Table VI below summarizes the results calculated from Figures 27, 29 and 31.

TABLE VI

Rate Constants for Ethyl Nitrate Decomposition (min-1)

	161°C	181°C	201°C
$K_{\text{initial part}}$	0.00226 ± 0.00009	0.0165 ± 0.0014	
$K_{\text{later part}}$	0.00410 ± 0.00005	0.0271 ± 0.0002	0.149 ± 0.004

57. From the three rate constants obtained from the later part of the reaction it is possible to calculate the energy of activation and the temperature independent factor. It is found that

$$k = 10^{14.44} e^{\frac{-36,630}{RT}} \text{ sec.}^{-1}$$

$E = 36,630 \pm 342$ cal./mole where the precision indicated is the deviation from the mean.

58. These results may be compared with those of Phillips (e) and those of Adams and Bawn (c). For the temperature range 179.5-207.95°C, Phillips reports

$$k = 10^{13.86} e^{\frac{-36,000}{RT}} \text{ sec.}^{-1}$$

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$$k = 10^{15.8} e^{\frac{-39,000}{RT}} \text{ sec.}^{-1}$$

This corresponds to a much slower reaction rate than was observed here for the "later" parts of the reaction.

59. It is of some interest that when the general rate expression is calculated from the "initial" slopes obtained in this work the expression that results is

$$k = 10^{15.11} e^{\frac{-39,300}{RT}} \text{ sec.}^{-1}$$

60. No interpretation of this data will be made here except to point out that Adam and Bawn make no mention of two parts to their curves but merely state that they were first order out to 60% reaction.

61. These present results are further similar to those reported by Phillips in that he too found a change in the rate curves. He found an initial period wherein reaction was rather slow followed by a later period which followed first order kinetics and where reaction was more rapid. This phenomenon became less pronounced at higher temperatures: thus at 183.7°C this initial part of the curve

extended out to about 40 minutes while at 201.5°C it is barely noticeable (e). Phillips has indicated that the initial portion of the curve is zero order. We have tested this possibility at 181°C. In a zero order reaction the absolute amount that reacts in a given time is independent of the pressure of the reactant. In a first order reaction the fraction that reacts in a given time is independent of the pressure. In Table VII below are shown the results for three kinetic runs at 181°C.

TABLE VII

The Effect of Ethyl Nitrate Pressure on the Rate of Decomposition at 181°C

Initial Pressure of Ethyl Nitrate (mm)	Absolute Amount Reacted (mm)	Fraction Reacted
22.0	11.0	0.500
31.1	15.0	0.486
45.0	21.3	0.475

62. Hence it is plain that it is the fraction reacting which is constant, and not the absolute amount and the reaction is first order.

63. No explanation for the occurrence of two portions in the rate curve has yet been found. At 161°C and 181°C, where the two portions are distinct, the change in slope occurs at about the same point in the reaction, i.e. 50% and 57% respectively. The general tendency in cases of this sort is to give greater weight to the initial rates since later variations are attributed to the effect of the reaction products. In the results reported here, however, the so-called initial portion persists out into regions where the reaction products are present in substantial amounts. It hardly seems tenable to suppose that this portion is immune to the effects of the products while the later section is not. The later section was chosen as the basis of the thermodynamic calculations because the 201°C data fell in line with the data from it rather than with the data from the earlier section.

The Effect of Additives on the Rate of Decomposition of Ethyl Nitrate

64. Nitrogen Dioxide. Phillips has reported (e) that nitrogen dioxide, when added to ethyl nitrate, lowers its decomposition rate. This has since been confirmed by Pollard, Wyatt and Marshall (f) who reported in addition that larger amounts of nitrogen dioxide caused an acceleration of the rate. As Table VIII demonstrates similar behavior was encountered here.

TABLE VIII

The Effect of Nitrogen Dioxide on the Amount of Ethyl Nitrate Decomposition at 161°C

Initial Pressure (mm)				
Nitrogen Dioxide	**Ethyl Nitrate**	**t**	**Log P_o/P**	**k[1]**
32.2	21.8	180	0.139	0.00178
59.6	23.2	180	0.126	0.00162
158.0	23.2	180	0.261	0.00332

At 161°C, the initial part, which covered the time period out to 250 minutes, was 0.00226 min.$^{-1}$. This was lowered by the first two amounts shown in Table VIII but when still further nitrogen dioxide was present the rate observed had increased to 0.00332 min.$^{-1}$.

65. The above data together with those reported in Table IX are only preliminary results but certain features merit some discussion

TABLE IX

The Effect of Nitrogen Dioxide on the Kinetics of Ethyl Nitrate Decompositon at 161°C

	Initial Pressures (mm)			
t (min.)	**Nitrogen Dioxide**	**Ethyl Nitrate**	**Log P_o/P**	**k[1] (min.$^{-1}$)**
180	32.2	21.8	0.139	0.00178
325	31.8	25.2	0.230	0.00158
1200	37.1	24.8	0.870	0.00167

In Table IX where the ratio of nitrogen dioxide added to ethyl nitrate initially present was about the same for the three cases reported the first order rate constant found was the same for all three intervals as far out as 1200 minutes. This is in marked contrast to the data in the absence of added nitrogen dioxide, where the change in slope occurred at about 250 minutes. The rate found for the three measurements with added nitrogen dioxide was lower than the initial rate found with none added - 0.00178 min.$^{-1}$, as compared to 0.00226 min.$^{-1}$. It may be that the nitrogen dioxide acts to destroy whatever it is that causes the change in slope in the decomposition reaction rate curves or it may be that it changed the course of the reaction. Further experiments will be necessary before an explanation of this effect will be forthcoming.

---

[1] Calculated for the single point as $k = \frac{2.303}{t} \log \frac{P_o}{P}$

66. Phillips (d) has suggested that the inhibition of the decomposition by nitrogen dioxide is due to its effect on the equilibrium

$$C_2H_5ONO_2 \rightleftarrows C_2H_5O\cdot + NO_2$$

There are two consequences of such an explanation which may be considered in the light of the data of Tables VIII and IX . First, it may be shown that when nitrogen dioxide does inhibit the reaction the rate of disappearance of ethyl nitrate should be second order in nitrate (r). Although the data in Table IX are by no means complete, they indicate very strongly that the kinetics remain first order in nitrate.

67. The second consequence of the above explanation is that it should be possible by adding more and more nitrogen dioxide to depress the rate indefinitely. Actually the accelerating effect of larger amounts of nitrogen dioxide limits this factor and complicates the situation. It is hoped, however, that a quantitative study of the effect of nitrogen dioxide on the reaction kinetics will be fruitful and Table VIII represents the preliminary results of such a study. It is striking that almost doubling the amount of nitrogen dioxide, i.e. 32.2 mm. increased to 59.6 mm., has little effect on the rate.

68. Nitrogen dioxide could also inhibit the reaction by reacting with the ethoxy radical. This would compete with step 2 in the mechanism, (see page 1) and could lower the rate of decomposition of ethyl nitrate. Here the lower limit of the rate would be half the uninhibited rate. A possible reaction would be

$$NO_2 + CH_3CH_2O\cdot \rightarrow CH_3NO_2 + CH_2O$$

Further experiments like those of Table V may shed some light on this possibility and such are in prospect.

69. Ethyl Nitrite. As Table X shows, the addition of substantial amounts of ethyl nitrite had no noticeable effect on the rate of decomposition of ethyl nitrate.

TABLE X

The Effect of Ethyl Nitrite on the Kinetics of Ethyl Nitrate Decomposition at 161°C

Ethyl Nitrite	Initial Pressures (mm) Ethyl Nitrate	t (minutes)	Log P_o/P	Log P_o/P (as read from least squares slope)
15.0	19.2	75	0.075	0.075
13.0	19.2	150	0.136	0.150

From the point of view of the mechanism on page 1, this is a bit surprising. Ethyl nitrite in its decomposition

(1) $C_2H_5ONO \longrightarrow C_2H_5O\cdot + NO$

(2) $C_2H_5O\cdot + C_2H_5ONO \longrightarrow C_2H_5OH + CH_3\underset{\cdot}{C}HONO$

(3) $CH_3\underset{\cdot}{C}HONO \longrightarrow CH_3CHO + NO$

acts both to furnish ethoxy radicals and to use them up. It would seem that it should have some effect on ethyl nitrate acting either to retard its decomposition by the consumption of ethoxy radicals or to accelerate it by furnishing them. The fact that it does neither is hard to explain. According to Steacie and Shaw, (n), its rate constant is given by

$$k = 1.39 \times 10^{14}\ e^{\frac{-37,700}{RT}}\ \text{sec.}^{-1}$$

which at 161°C gives k = 0.0008 min.$^{-1}$. This compares to 0.00226 min.$^{-1}$ for ethyl nitrate in the initial part of the reaction rate curve. It would seem that the rate of decomposition of ethyl nitrite relative to ethyl nitrate should be great enough to show an effect. It is possible too that ethyl nitrite takes up ethoxy radicals at a rate such that this counterbalances the effect of its supplying them. Since the results in Table X do indicate that ethyl nitrite is not responsible for the slope change however no further experiments have been carried out with it as yet.

70. Mercury. The presence of mercury, as Table XI shows, results in an increased decomposition rate. The mercury can do at least two things. It can reduce the nitrogen dioxide to nitric oxide. Since this reaction is fast at room temperature, it must be very fast at 161°C. It is conceivable also that mercury reacts directly with ethyl nitrate to reduce it. Either explanation could explain the results of Table XI.

TABLE XI

The Effect of Mercury on the Kinetics of Ethyl Nitrate Decomposition at 161°C

Time (min.)	Log P_o/P	k^1(min.$^{-1}$)
180	0.307	0.00394
322	0.624	0.00436

---

[1] Calculated for the single point as $k = \frac{2.303}{t} \log \frac{P_o}{P}$

Since in the two experiments represented in Table XI liquid mercury was always present, the pressure of mercury in the gas phase was a constant. By varying the mercury pressure and observing the decomposition rate it would be possible to see whether a direct reaction of the mercury with the ethyl nitrate occurred. Such experiments are in prospect here.

The Variation of Nitrogen Dioxide

71. In the data reported here it can be seen that nitrogen dioxide never built up to a large extent in the reaction. Examination of Figures 28, 30 and 32 shows that in general it was less than 10% of the initial ethyl nitrate at all times. Although it does seem to go through a maximum concentration as reported, (c,d,e) it has such low values that this feature is not very striking. This behavior of the nitrogen dioxide pressure may be accounted for if there are two reactions present, one producing nitrogen dioxide and the other consuming it. If it is assumed that the decomposition of ethyl nitrate yields nitrogen dioxide it only remains to find a reaction which uses it up. One reaction which has been suggested, (e), is its reaction with aldehydes. Presumably the aldehydes are formed simultaneously with the nitrogen dioxide however and there is no obvious reason why any concentration should build up. One would rather expect that the nitrogen dioxide would be used up as formed. The way in which the ethyl nitrite pressure varies suggests a reasonable alternative. Ethyl nitrite builds up from zero pressure to a maximum. One of its dissociation products is ethyl alcohol which reacts rapidly with nitrogen dioxide. At the start of the reaction when the ethyl nitrite pressure is small the rate of formation of the ethyl alcohol and hence the rate of consumption of the nitrogen dioxide would be small. The ethyl nitrate pressure is large at the start, however, and the rate of formation of nitrogen dioxide would be comparatively large. Hence at the start of the reaction the nitrogen dioxide would build up. As the ethyl nitrite pressure increased and the ethyl nitrate pressure decreased, a point would be reached where the nitrogen dioxide would be used up faster than it was formed and its pressure would drop off. This, it is suggested, explains the actual behavior found.

The Variation of the Nitric Oxide Pressures

72. This has been reported only for the 181°C experiments. Actually similar phenomena were observed at 161°C and 201°C but measurements were carried out systematically only at 181°C and for this reason only these results are included here.

73. It can be seen from Figure 30 that the nitric oxide values remain rather small over most of the reaction but start to rise rather steeply at the end. It was noted in the Experimental Part that the nitric oxide results are not quantitative. It may be that the earlier, low values are in some doubt but in the later stages of the reaction where the nitric oxide values found are large and the nitrogen dioxide values are small it would seem that the analytical results are quite reliable.

74. The type of behavior shown in Figure 30 would indicate that the main source of the nitric oxide is by the direct decomposition of ethyl nitrite.

$$C_2H_5ONO \longrightarrow C_2H_5O\cdot + NO$$

It is only in the later stages of the reaction where the ethyl nitrite pressures are rather high that the nitric oxide pressure becomes appreciable. If the nitric oxide were being formed via the nitrogen dioxide-acetaldehyde reaction its pressure should build up steadily over the entire reaction time and not, as it does, rather steeply at the end.

The Formation of Methyl Nitrite and Nitromethane

75. Although no quantitative analyses for these two compounds were made their presence had been established toward the end of the reaction. It is plausible that this would be when the reaction

$$CH_3CH_2O \longrightarrow CH_3\cdot + CH_2O$$

would be favored since there would be comparatively little ethyl nitrate and ethyl nitrite present to react with the ethoxy radical. The reaction

$$CH_3\cdot + NO_2 \longrightarrow CH_3NO_2$$

has been suggested before (s). It is possible that it is the source of the nitromethane and that a similar reaction is the source of the methyl nitrite. On this basis, the appearance of these compounds may be harmonized with the mechanism on page 1.

The Variation of Ethyl Nitrite

76. As can be seen from Figures 28, 30 and 32 at all three temperatures the ethyl nitrite pressure curve goes through a maximum. Since the data are rather scattered at 201°C the discussion will be confined to the 161°C data and the 181°C data. It can be seen that rather smooth curves are described here which rise to a maximum of about 62% of the initial ethyl nitrate at 181°C and about 70% at 161°C. Thus it is a major intermediate in the reaction, although it has received little attention as far as its having a role in the ethyl nitrate decomposition goes. It has been reported as a product of the decomposition of ethyl nitrate by Theile, (t) but the equations written for its formation had been considered quite unlikely, (c) and since no experimental detail had been given by Theile, it had been discounted as being of any importance in the decomposition of ethyl nitrate.

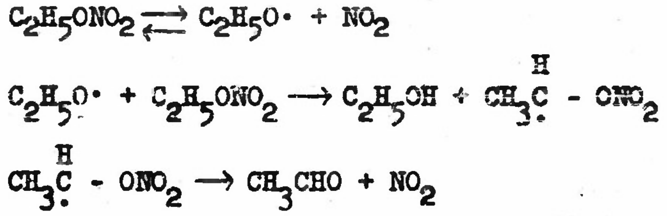
77. Since in the present work, ethyl nitrite has been found to be so important a constituent of the decomposition mixture, it is of some interest to inquire why it was that it was not reported by Adams & Bawn, (e) or by Phillips, (e). It seems quite likely that the explanation for this lies in the reagents used by these workers to estimate nitrogen dioxide. In both cases the analysis for nitrogen dioxide depended on its hydrolysis to nitrous acid

$$2\ NO_2 + H_2O \rightarrow HNO_2 + HNO_3$$

and the subsequent reaction of the nitrous acid with an analytical reagent. Phillips used the Griess reagent with which nitrous acid gives a pink color and Adams and Bawn used amidosulphonic acid from which nitrous acid liberates nitrogen. In each case since only one mole of nitrous acid is formed from two moles of nitrogen dioxide the amount of nitrous acid found had to be multiplied by two to give the amount of nitrogen dioxide originally present. It is well known (u) that ethyl nitrite hydrolyzes to give nitrous acid and water. This hydrolysis is very rapid in acid solution and moderately rapid in base. It seems quite plausible that in both the above cases ethyl nitrite would give a positive test, i.e. it would give a color with Griess reagent and would liberate nitrogen from amidosulfonic acid. In both the above procedures the reaction products were separated out by a system of traps at different temperatures. Since nitrogen dioxide (bp 21.3°C) and ethyl nitrite (bp 17°C) have boiling points very close to one another both would be caught in the same trap. In Phillips procedure the material in the trap was first treated with dilute KOH solution and then with the Griess reagent. It is difficult to repeat his procedure exactly but we have made the simple test of passing ethyl nitrite vapor directly into the Griess reagent. The deep pink color formed immediately and could not be distinguished from the color produced by nitrogen dioxide. Hence it seems quite probable that in Phillips procedure some, and perhaps all, of any ethyl nitrite present would be included in the analysis for nitrogen dioxide. The same may be said for the analysis used by Adams and Bawn. Since one mole of ethyl nitrite produces one mole of nitrous acid it would be twice as effective as nitrogen dioxide in both of these analyses. These facts, it is logical to assume, explain why the above workers did not report ethyl nitrite on the one hand, and why their analyses for nitrogen dioxide on the other hand were much higher than those reported here.

Possible Modes of Formation of Ethyl Nitrite

78. When the mechanism for the ethyl nitrate decomposition is re-examined:



$$C_2H_5ONO_2 \rightleftarrows C_2H_5O\cdot + NO_2$$

$$C_2H_5O\cdot + C_2H_5ONO_2 \longrightarrow C_2H_5OH + CH_3\overset{H}{\underset{\cdot}{C}} - ONO_2$$

$$CH_3\overset{H}{\underset{\cdot}{C}} - ONO_2 \longrightarrow CH_3CHO + NO_2$$

a source for the formation of ethyl nitrite can easily be found. Among the postulated products are nitrogen dioxide and ethyl alcohol. A common method for the preparation of nitrous esters is by the action of "nitrous fumes on the alcohols" (u), and it was thought that this might be the source for the ethyl nitrite found here, i.e., the reaction between nitrogen dioxide and ethyl alcohol. Accordingly these two gases were mixed and the infrared record of the product taken. This is shown in Figure 33. It is obvious that ethyl nitrite is a product. At the time that this work was being done there was no definite mention of this reaction as such in the literature. Harris and Siegel had obviously encountered it when they found that methyl alcohol and nitrogen dioxide react very rapidly in the vapor phase (v). They reported that nitric oxide was not a product but were unable to say anything further. Obviously methyl nitrite had been formed. Recently Yoffe and Gray (w) have reported on this reaction directly, however, and have written it as

$$C_2H_5OH + 2NO_2 \longrightarrow C_2H_5ONO + HNO_3$$

This is then one way by which ethyl nitrite could be formed in the reaction mixture.

79. Before considering the above reaction in somewhat more detail, one other possible route for the formation of ethyl nitrite will be considered. Reference to the reaction mechanism for the decomposition of ethyl nitrate shows that nitrogen dioxide and acetaldehyde are among the products. It is well known, (x), that these react together quite rapidly at these temperatures to give, among other products, nitric oxide. It is possible to write the reaction:

$$C_2H_5O\cdot + NO \rightarrow C_2H_5ONO$$

as a source for ethyl nitrite since ethoxy radicals are also found in the mechanism. Arguments against this idea stem from work done on the decomposition of the nitrites themselves. The above reaction is the reverse of the one written as the rate determining step in the decomposition of ethyl nitrite. If it occurred one would expect that nitric oxide would have a retarding effect on the rate of decomposition of ethyl nitrite. This point has been carefully considered, (n,r), and it has been found that even in the presence of added nitric oxide no effect is found. It therefore seems that the above route to the formation of ethyl nitrite in the decomposition of ethyl nitrite must be discarded.

80. The reaction between nitrogen dioxide and ethyl alcohol thus emerges as the only plausible route for the formation of ethyl nitrite which can be derived from the mechanism written for the ethyl nitrate decomposition. It is of interest to examine this in somewhat greater detail. Ethyl nitrite itself undergoes thermal decomposition at these temperatures, (n).

81. Its rate constant is reported as

$$k = 1.39 \times 10^{14} e^{\frac{-37,700}{RT}} \text{ sec.}^{-1}$$

At 181°C this value becomes $k = 0.00535 \text{ min.}^{-1}$ and at 161°C it is $k = 0.0008 \text{ min.}^{-1}$. The rates are then substantially smaller than those for ethyl nitrate. It is of interest to consider the situation

$$C_2H_5ONO_2 \xrightarrow{k_1} \alpha\, C_2H_5ONO$$

$$C_2H_5ONO \xrightarrow{k_2} \text{products}$$

Here ethyl nitrate yields ethyl nitrite by some first order process having a rate constant k_1. The ethyl nitrite then decomposes to its products by a first order process having a rate constant k_2. Here α represents the fraction of ethyl nitrate molecules that yield ethyl nitrite. It may be pointed out that if ethyl nitrate decomposes to products which react very rapidly to give ethyl nitrite then the first condition is satisfied. Although ethyl nitrate does not give a simple first order decomposition over its entire range it is of interest to treat the above simplified situation mathematically. It may be shown, (y) that at any time t the pressure of ethyl nitrite P is given by

$$P = \frac{\alpha k_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t})$$

The general shape which such a function takes is shown in Figure 34 where it is plotted for $\alpha = 1$, $k_2 = 0.00535$ min.$^{-1}$ and $k_1 = 0.0252$ min.$^{-1}$. The latter figure represents a rate between the value found at 181°C for the initial part of the reaction and the value found for the latter part. The value for ethyl nitrite is the one calculated for 181°C from the data of Steave and Shaw. It is seen that the curve goes through a maximum about at a value of ethyl nitrite equal to 0.657 and at a time = 80 min. A glance at the curve for ethyl nitrite found in Figure 30 shows that it is similar in shape to the above calculated curve. Here the maximum is at 0.61 at t_2 = 90 minutes.

82. When the ethyl nitrate decomposition mechanism is examined it is clear that if the ethyl nitrite is formed via the nitrogen dioxide -- ethyl alcohol reaction $\alpha = 0.5$. This would seem to be the upper limit for α since there is no plausible route for the conversion of acetaldehyde to ethyl nitrite. If the ethyl nitrite were thermally stable, 0.5 moles of it would form per mole of ethyl nitrate decomposed. Since however, it does decompose at a measurable rate the maximum amount that would form would be less than 0.5. If the rate constants used for Figure 34 were correct the maximum amount of ethyl nitrite formed would be 0.329 moles per mole of ethyl nitrate decomposed.

83. Actually the maximum is 0.61 at 181°C and 0.7 at 161°C and both maxima are reached at points where only part of the ethyl nitrate has decomposed. At 181°C the 0.61 moles of ethyl nitrite has been formed from the decomposition of 0.86 moles of ethyl nitrate while at 161°C the 0.70 moles of ethyl nitrite at the maximum has been formed from 0.88 moles of ethyl nitrate. Clearly much more ethyl nitrite has been formed than the above mechanism can account for and it remains an important problem to establish just how this substance arises. It may be noted parenthetically here that since ethyl nitrite is known to yield acetaldehyde, (n), in its decomposition, acetaldehyde would have to be a product of the decomposition of ethyl nitrate and would show up in the later part of the reaction.

Tests of the Modes of Formation of Ethyl Nitrite

84. Two experiments have been carried out in an effort to get more information on the mode of formation of the ethyl nitrite. From the ease and great rapidity with which ethyl alcohol and nitrogen dioxide react in the vapor phase it seems certain that if they form in the decomposition of ethyl nitrite they will react to give ethyl nitrite. In both the experiments described below an effort was made to test the occurrence of this reaction by initially adding to the ethyl nitrate a component which would compete with the ethyl alcohol for the nitrogen dioxide.

The Use of Mercury as a Competitive Reagent

85. It is well known that mercury rapidly reduces nitrogen dioxide to nitric oxide at room temperatures. It was felt that mercury might compete favorably with ethyl alcohol for the nitrogen dioxide. At 181°C mercury has a vapor pressure of 8.6 mm. At the start there is no ethyl alcohol present and since it forms as the reaction proceeds it seemed that at least towards the beginning of the reaction mercury might compete favorably with the ethyl alcohol and reduce the amount of

ethyl nitrite formed. Accordingly excess mercury (enough so that there was always liquid mercury present) was added to a sample of ethyl nitrate and the two heated in a bulb in the usual way at 181°C for 87.1 minutes. The time chosen was that at which the ethyl nitrite pressure would be about at its maximum value. The value for ethyl nitrite found for this experiment is indicated in Figure 30 by a triangle. It is found that somewhat more ethyl nitrite was formed in the presence of mercury than in its absence.

86. If the ethyl nitrite pressure had been markedly lowered by the presence of the mercury it would have indicated strongly that the nitrogen dioxide - ethyl alcohol reaction was largely responsible for the ethyl nitrite formation. The larger value for the ethyl nitrite may however be explained in other ways. For one thing the reaction of ethyl alcohol and nitrogen dioxide is so fast at room temperature that it may be that at 181°C it is fast enough so that the reaction with mercury cannot effectively compete with it. Another alternative is that the mercury may react directly with the ethyl nitrate to give ethyl nitrite viz.

$$C_2H_5ONO_2 + Hg \rightarrow C_2H_5ONO + HgO$$

This latter alternative is susceptible to testing by kinetics since it would be a bimolecular reaction and give corresponding kinetics in the absence of liquid mercury. This has not as yet been attempted.

The Use of Methyl Alcohol as a Competitive Reagent

87. Experiments involving the reaction of nitrogen dioxide with methyl alcohol and with t-butyl alcohol had indicated that it was a general reaction for alcohols. Accordingly it seemed that an effective competitor for ethyl alcohol might be found in the use of another alcohol. The alcohol chosen was methyl alcohol. In order that such an experiment be practical it was necessary for the infrared records of the two nitrites, methyl nitrite and ethyl nitrite, to be sufficiently different to be distinguishable. Fortunately the characteristic bands in the 12-13 μ region were distinctly different. The record for methyl nitrite in this region is shown in Figure 17 and comparison of it with the record for ethyl nitrite in Figure 6 illustrates this point.

88. An experiment was carried out in which 35.5 mm of ethyl nitrate and 30.0 mm of methyl alcohol were heated together at 201°C for 17 minutes. The record for the product is shown in Figure 35. It is clear that methyl nitrite is the predominant nitrite present. It is not possible to rule out ethyl nitrite completely of course. There is however one objection to this experiment which had to be tested. It is well known that the nitrite esters readily undergo trans-esterification. Methyl nitrite is readily prepared by adding methyl alcohol to amyl nitrite at room temperature. The possibility existed that ethyl nitrite and methyl alcohol might react in the vapor phase at 201°C to give methyl nitrite and ethyl alcohol. To test this 25 mm of methyl alcohol were heated with 23 mm of ethyl nitrite at 199°C for 17 minutes. The results are illustrated in Figure 36. It is clear that methyl nitrite is formed and hence this test for the mode of ethyl nitrite formation in the ethyl nitrate decomposition did not help to solve the problem.

The Status of the Problem of the Ethyl Nitrite Formation

89. At the time of this writing no further experiments designed to study the ethyl nitrite formation have been completed. It is interesting to speculate whether the ethyl nitrite can be formed directly from the ethyl nitrate without cleavage of the CO-N band. This might conceivably occur by reaction of the nitrate ester with one of the decomposition products. The result of a direct transformation of ethyl nitrate to ethyl nitrite is reduction and it may be indeed that nitrate esters can function effectively as oxidizing agents and be themselves reduced to nitrites. Amond the decomposition products acetaldehyde, or formaldehyde are likely subjects for oxidation. This remains to be tested.

90. A further attack on this problem which is under consideration involves the study of the decomposition of t-butyl nitrate. In the mechanism written for the decomposition of ethyl nitrate the formation of ethyl alcohol depends on the presence of a hydrogen alpha to the nitrate group. Such a hydrogen is not found in the t-butyl nitrate molecule and it is felt that there would be no way for an alcohol to be formed; if t-butyl nitrite were to be found in the decomposition products of t-butyl nitrate it is hard to see how it could form except by direct reduction of the nitrate ester. This compound is of further interest from the general point of view of the mechanism as a whole. From studies on di-t-butyl peroxide (z) much is known about the way in which t-butoxy radicals behave. If t-butyl nitrate decomposes to give t-butoxy radicals it should be possible to determine this by seeing whether the typical products produced by such radicals are found.

General Comments on the Role of Nitrite Esters in Nitrate Ester Decompositions

91. It is of great interest whether or not nitrite ester formation is general for all nitrate ester decompositions. It is hoped that this problem may be studied in this laboratory in the future. The transformation of nitrate esters to nitrite esters may be of great importance in the storage problems involved with such compounds and in their performance as fuels, propellants and explosives.

General Comments on the Thermal Decomposition of Ethyl Nitrate

92. The mechanism for the decomposition of ethyl nitrate on page 1, is the one which on inspection would seem to be inherently the most plausible. The O-N bond which is broken in the rate determining step would appear to be the weakest bond in the molecule and hence the one prone to break first. Furthermore the activation energies found are in the same range, 36-39 kcal. as those found for the nitrite esters. The fragments formed in the initial decomposition, it would seem, should react as postulated.

93. There remain, however, three important facets of this problem which are not fully explained by the above mechanism and which need to be explained before the problem can be considered to be solved. One facet is the behavior of the rate data. Both in the work reported here and in Phillips' work a change in rate after an initial period has been encountered. In this work the fact that the rate change only occurs after about half the ethyl nitrate has decomposed makes it impossible to discuss this on the basis of small amounts of initial impurities and implies that it is a true part of the reaction.

94. A second facet to be considered is the effect of nitrogen dioxide in inhibiting the rate. Phillips has suggested that this may be explained on the basis of an equilibrium dissociation in the first step. This may well be the correct explanation. The fact that no such phenomenon is encountered with the alkyl nitrites is rather puzzling and for this reason alternative explanations are still desirable. It is possible that a more quantitative examination of the phenomenon may elucidate its nature and as has been mentioned before such an examination is in prospect here.

95. The third facet that is at odds with the mechanism postulated is the amount of ethyl nitrite that is formed. The nitrogen dioxide-ethyl alcohol reaction is such a ready solution for the formation of ethyl nitrite that if it had been formed in lesser amount its presence would fit in readily with the mechanism as written. The fact that the mechanism cannot account for the amount actually formed, however, suggests very strongly that the mechanism is either incorrect or incomplete.

96. The way in which the nitric oxide pressure varied at 181°C is also of interest. It has been pointed out that this variation is more what would be expected if the nitric oxide were being formed by the dissociation of the ethyl nitrite rather than via the dissociation of ethyl nitrate to acetaldehyde and nitrogen dioxide and their subsequent reaction. It seems that any explanation for the ethyl nitrite formation will explain the above behavior as well.

97. It frequently happens with reaction mechanisms or theories of science in general that they are plausible and that they satisfy the main requirements of the fields with which they deal. Yet there are often some discrepancies that are not explained. It is these discrepancies that are important clues to an extension or revision of the parent theory or mechanism to one which better fits the facts. It is believed that the points discussed above are in the nature of such clues and that through them a more complete understanding of the decomposition of nitrate esters may yet be reached.

SUMMARY

98. The decomposition of ethyl nitrate has been studied at 161°C, 181°C and 201°C using spectrophotometric methods in both the infrared and visible region. The rate of decomposition of ethyl nitrate at these temperatures has been measured. At 161°C and 181°C the rate curve falls into two parts, one from 0 to about 50% and the second from 50 to about 90%. The initial part has a smaller slope. On the basis of the higher slopes the rate expression

$$k = 10^{14.44} e^{\frac{-36,630}{RT}} \text{ sec.}^{-1}$$

has been found.

99. The techniques employed here have also revealed that ethyl nitrite is a major intermediate in the reaction and is formed in amounts greater than can easily be explained by the generally accepted mechanism for the decomposition of

nitrate esters. In addition the formation of methyl nitrite and nitromethane in the decomposition mixture has been demonstrated.

100. The variation of nitrogen dioxide with time as the ethyl nitrate decomposes has also been measured and an explanation offered. The effect of nitrogen dioxide, ethyl nitrite and mercury on the rate has been subject to preliminary study and the results discussed.

101. On the basis of the above results and the rate data the accepted mechanism for nitrate ester decomposition has been examined and certain inadequacies pointed out. Some experimental procedures designed to elucidate further the nature of the mechanism have been indicated.

ACKNOWLEDGMENTS

102. The spectra illustrated in the figures in this report were taken on a Perkin Elmer Model 21 Double Beam Recording Spectrometer. I am much indebted to Dr. Robert M. Talley of the Physical Optics Department for making this instrument available to me and to Mrs. Marion B. Glickman of the same department for taking the many spectra that were required.

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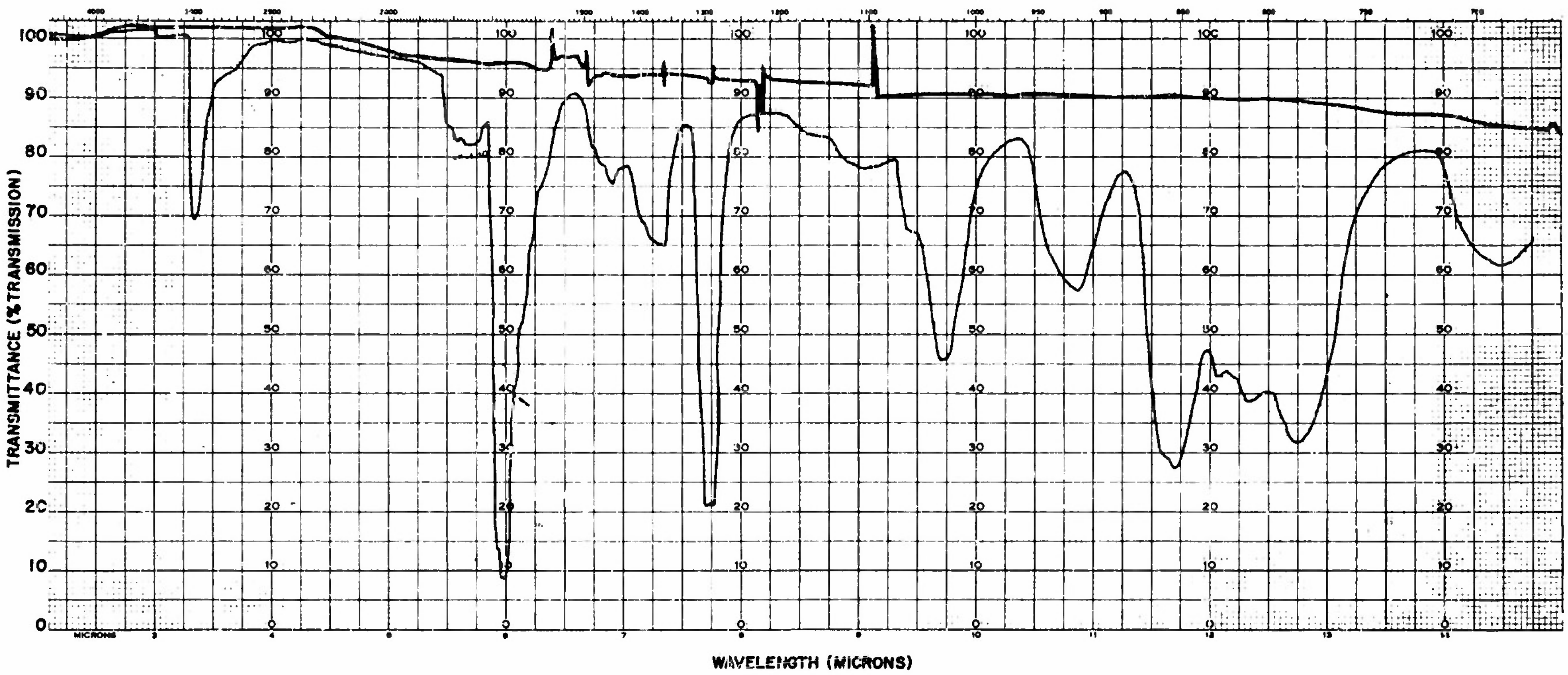


FIG. I PRODUCTS FROM 60% THERMAL DECOMPOSITION OF ETHYL NITRATE AT 181° C

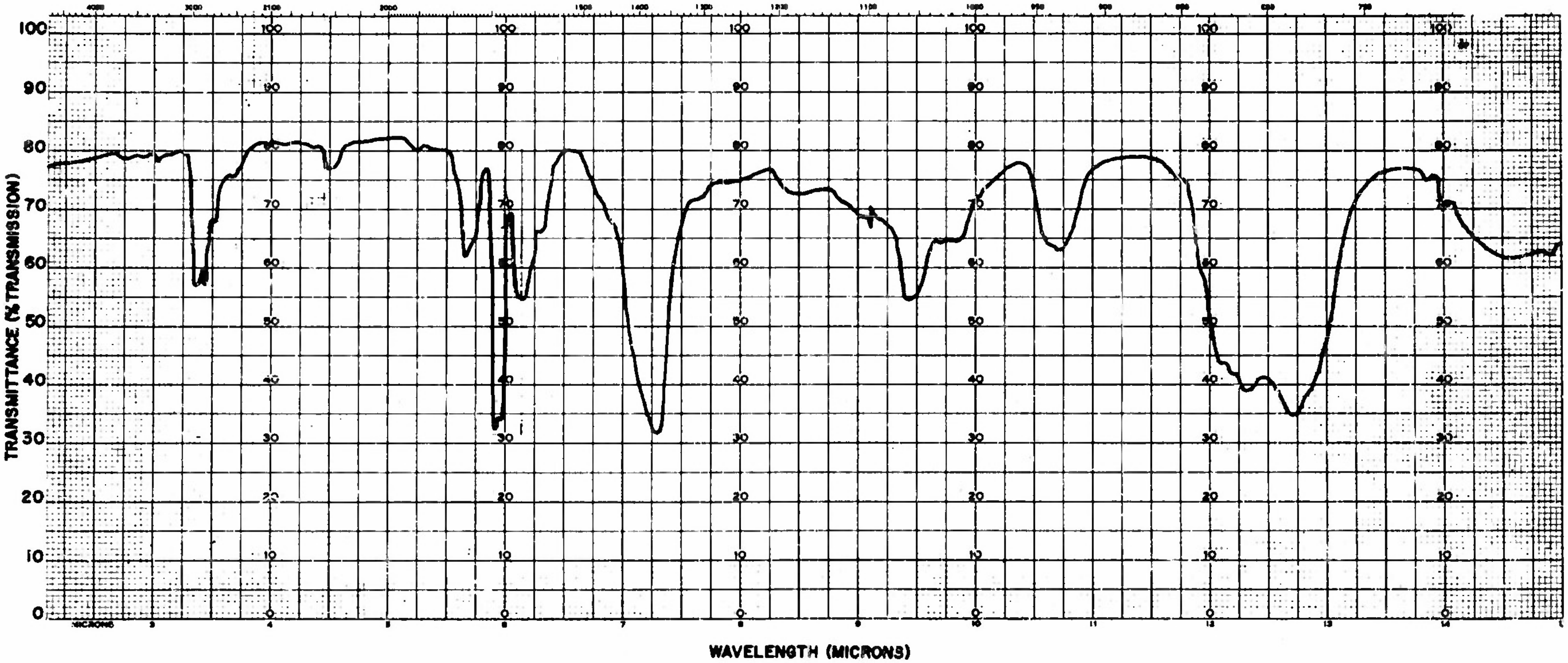


FIG. 2 PRODUCTS FROM COMPLETE THERMAL DECOMPOSITION OF ETHYL NITRATE AT 180-190°C

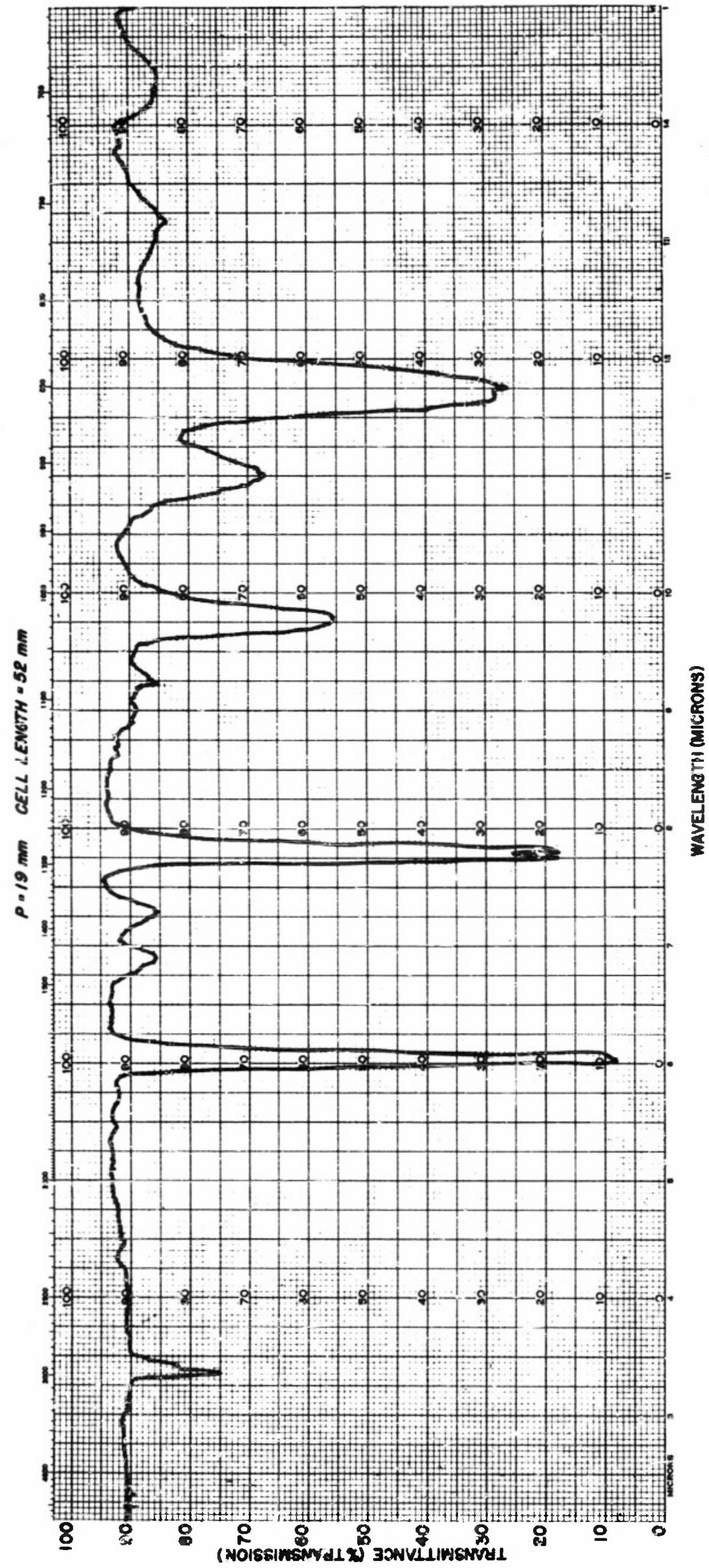
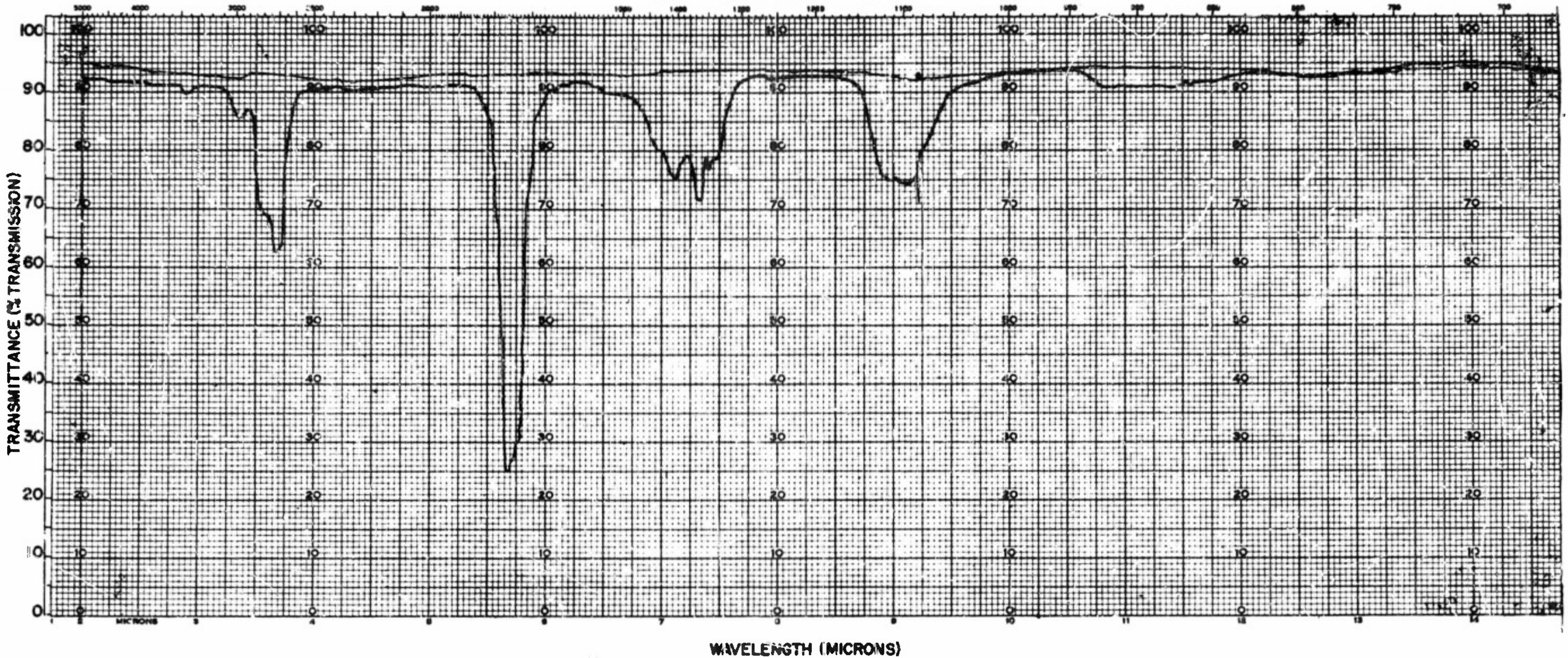

P = 19 mm CELL LENGTH = 52 mm

FIG. 3 ETHYL NITRATE



P = 19 mm CELL LENGTH = 52 mm

FIG. 4 ACETALDEHYDE

$P_{NO_2} = 18.0$ $P_{N_2O_4} = 3.0$ *CELL LENGTH = 52 mm*

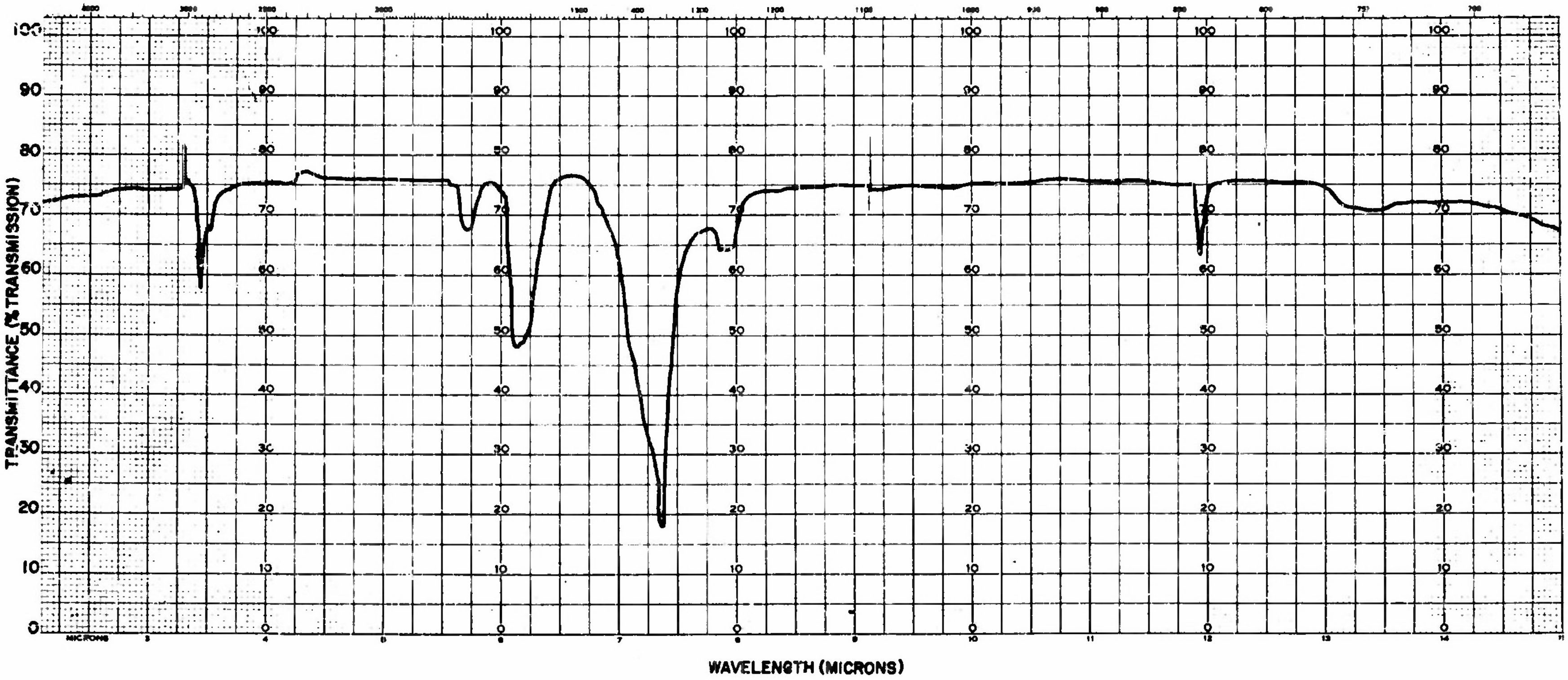


FIG. 5 NITROGEN DI-AND TETROXIDE

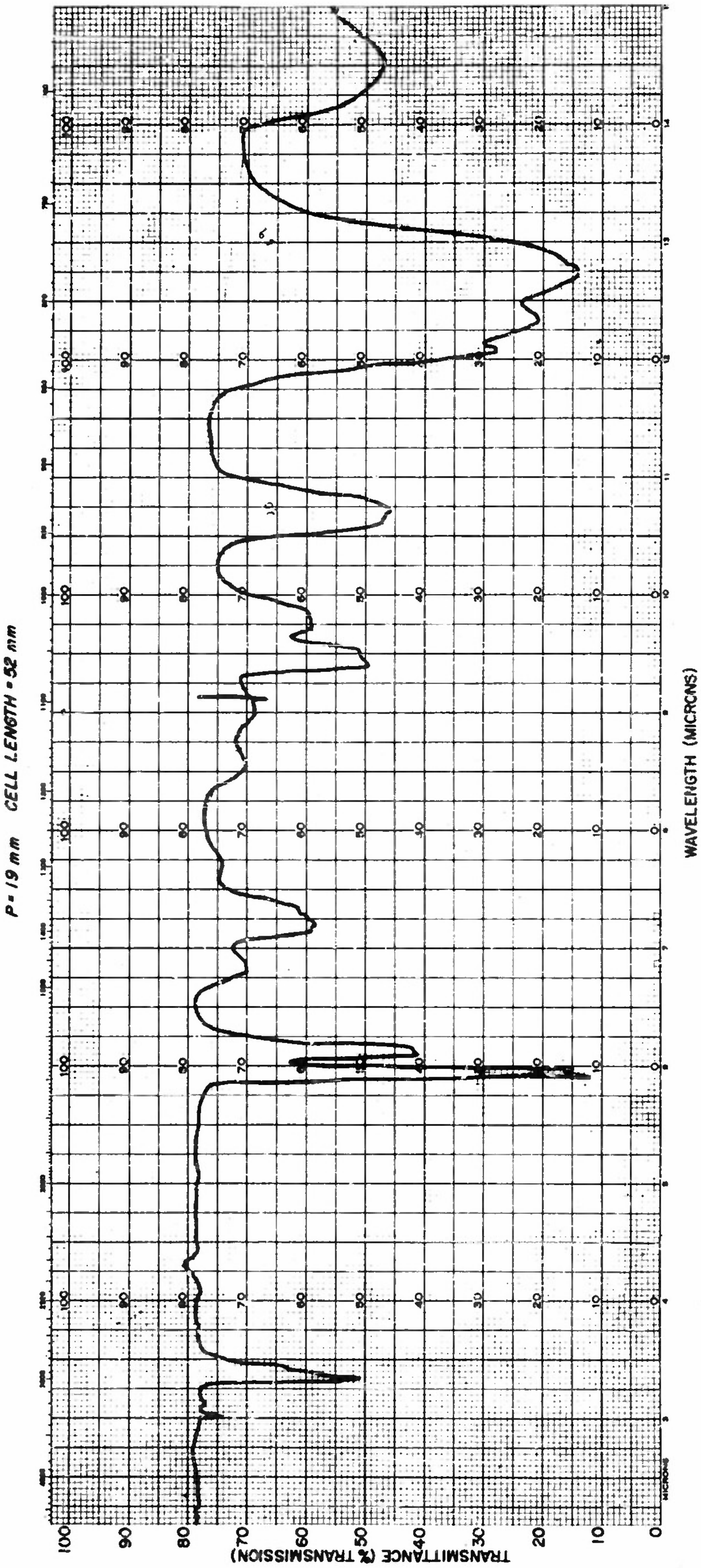


FIG. 6 ETHYL NITRITE

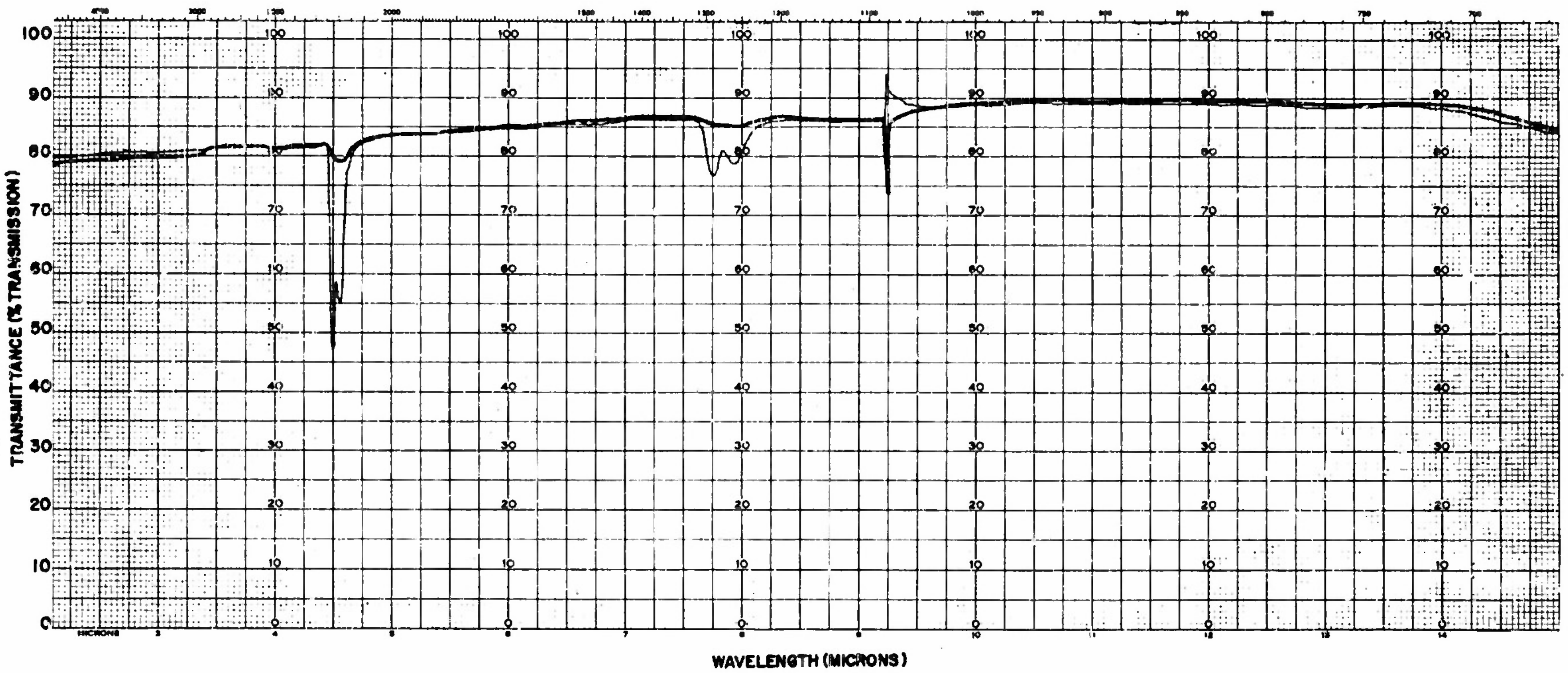

HEAVY LINE - NITROUS OXIDE ALONE P = 2 mm
LIGHT LINE - NITROUS OXIDE, P = 2 MM. PLUS AIR TO MAKE ATMOSPHERIC PRESSURE

FIG. 7 THE EFFECT OF PRESSURE ON THE ABSORPTION OF NITROUS OXIDE

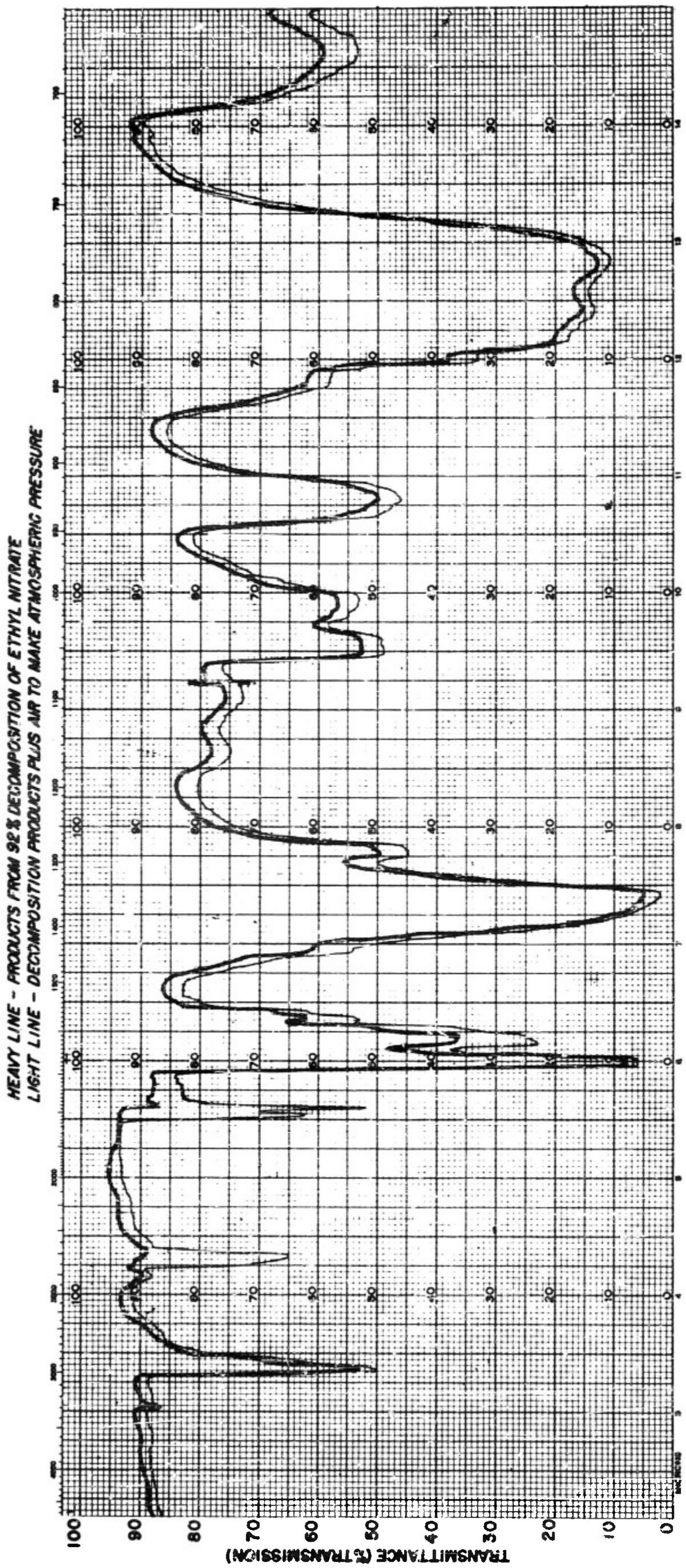


FIG. 8 THE EFFECT OF PRESSURE ON THE ABSORPTION OF THE DECOMPOSITION PRODUCTS

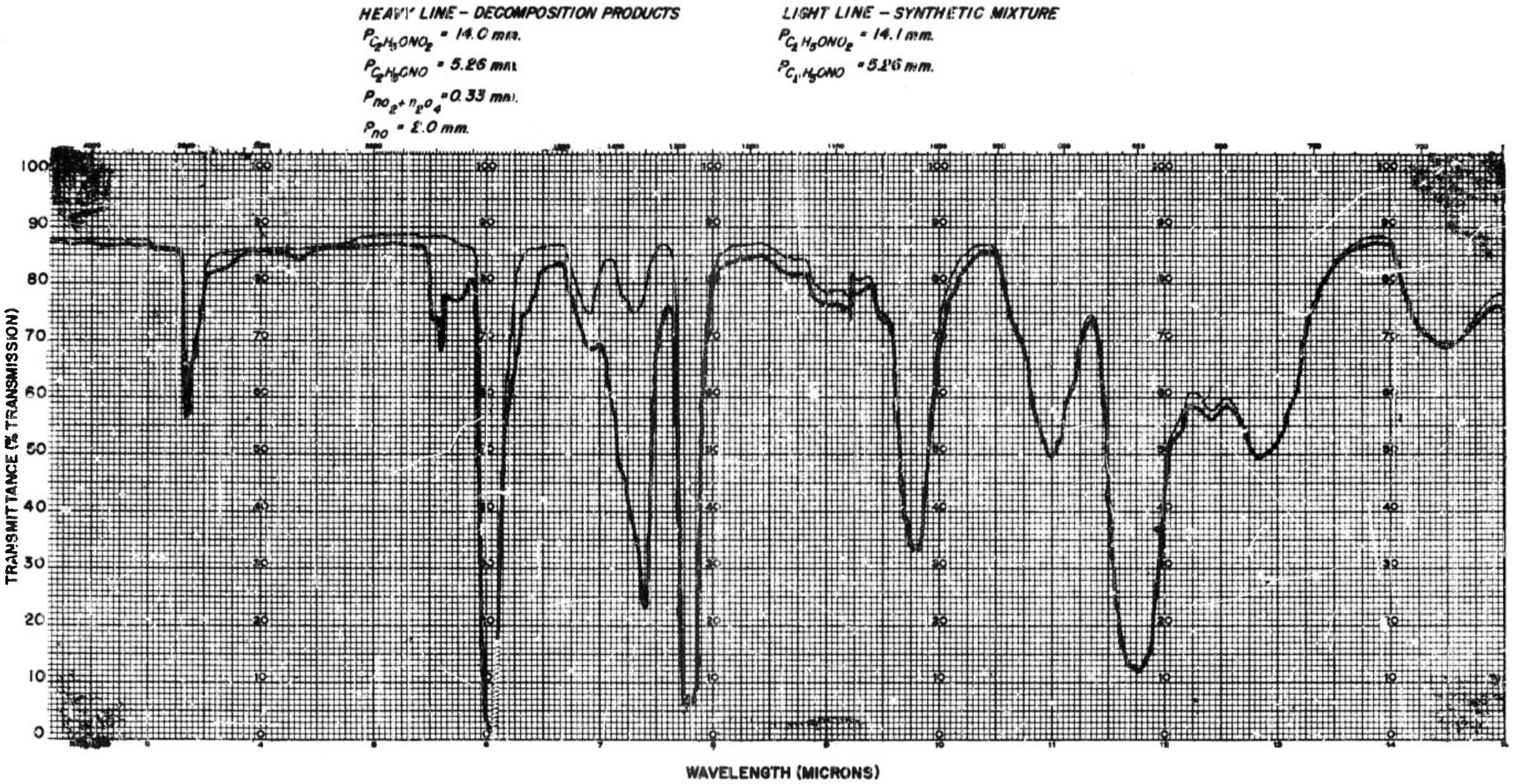


FIG. 9 DUPLICATION OF SPECTRUM OF PRODUCTS OF ETHYL NITRATE DECOMPOSITION. 33.4 % DECOMPOSITION

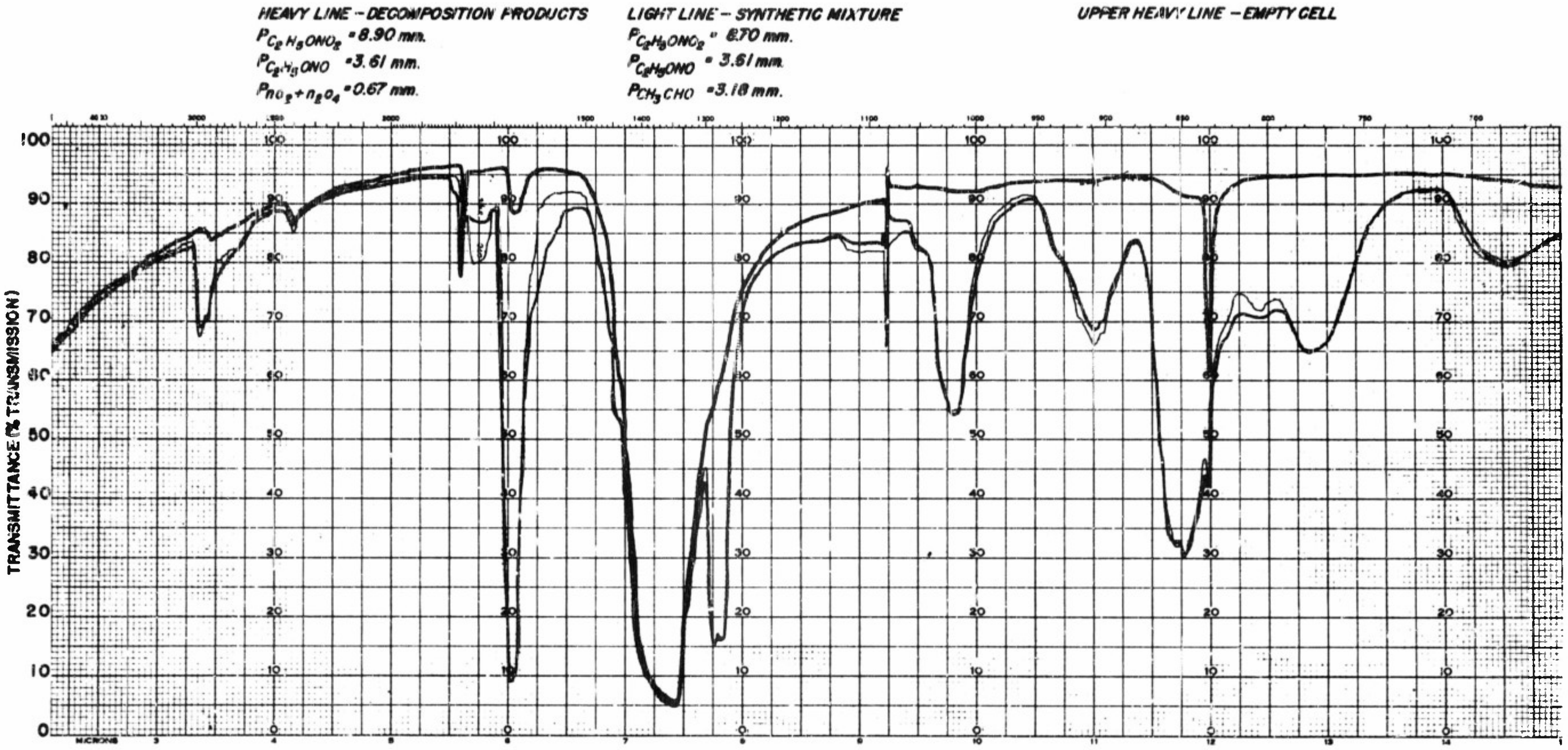


FIG. 10 DUPLICATION OF SPECTRUM OF PRODUCTS OF ETHYL NITRATE DECOMPOSITION 44.0% DECOMPOSITION

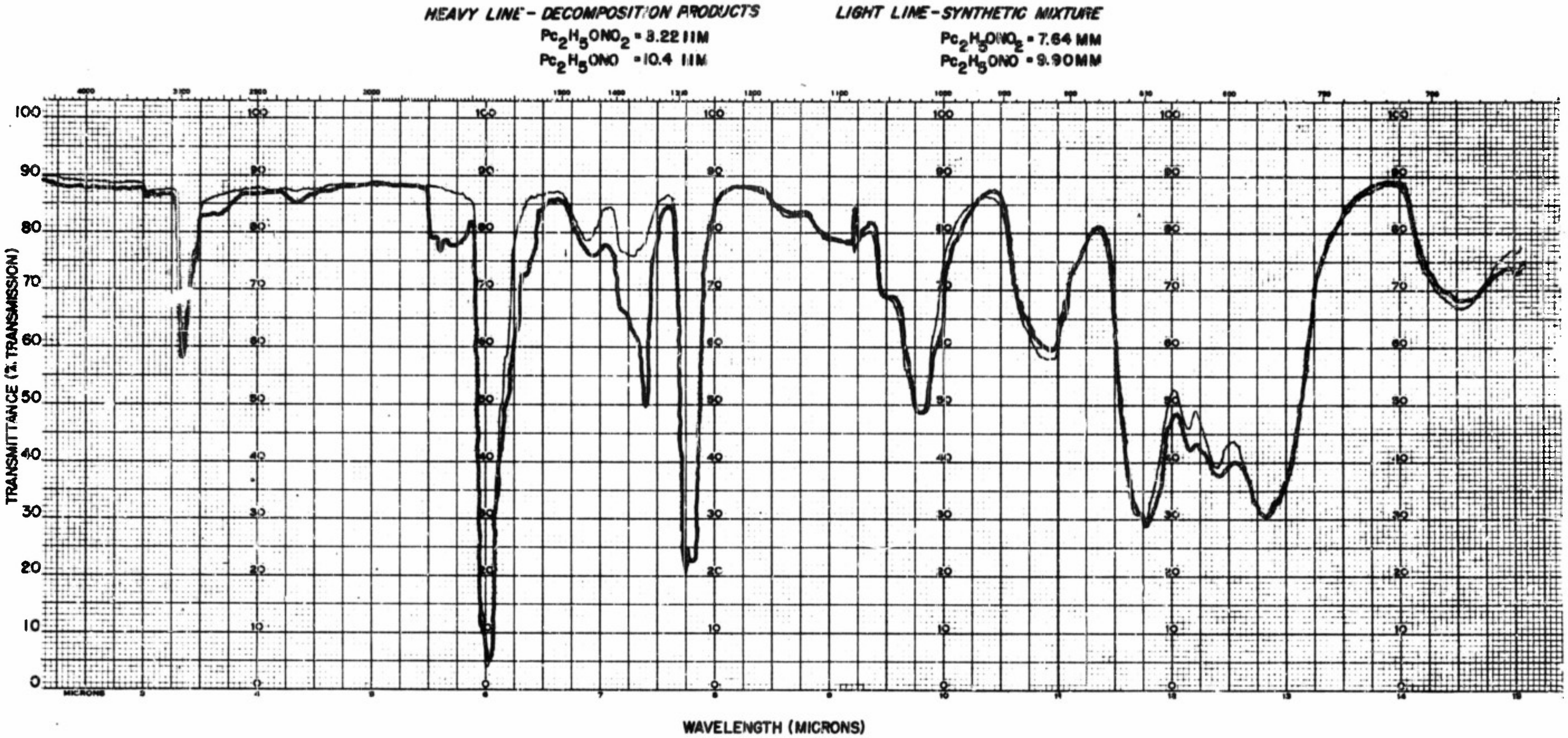


FIG. 11 DUPLICATION OF SPECTRUM OF PRODUCTS OF ETHYL NITRATE DECOMPOSITION 61.5 % DECOMPOSITION

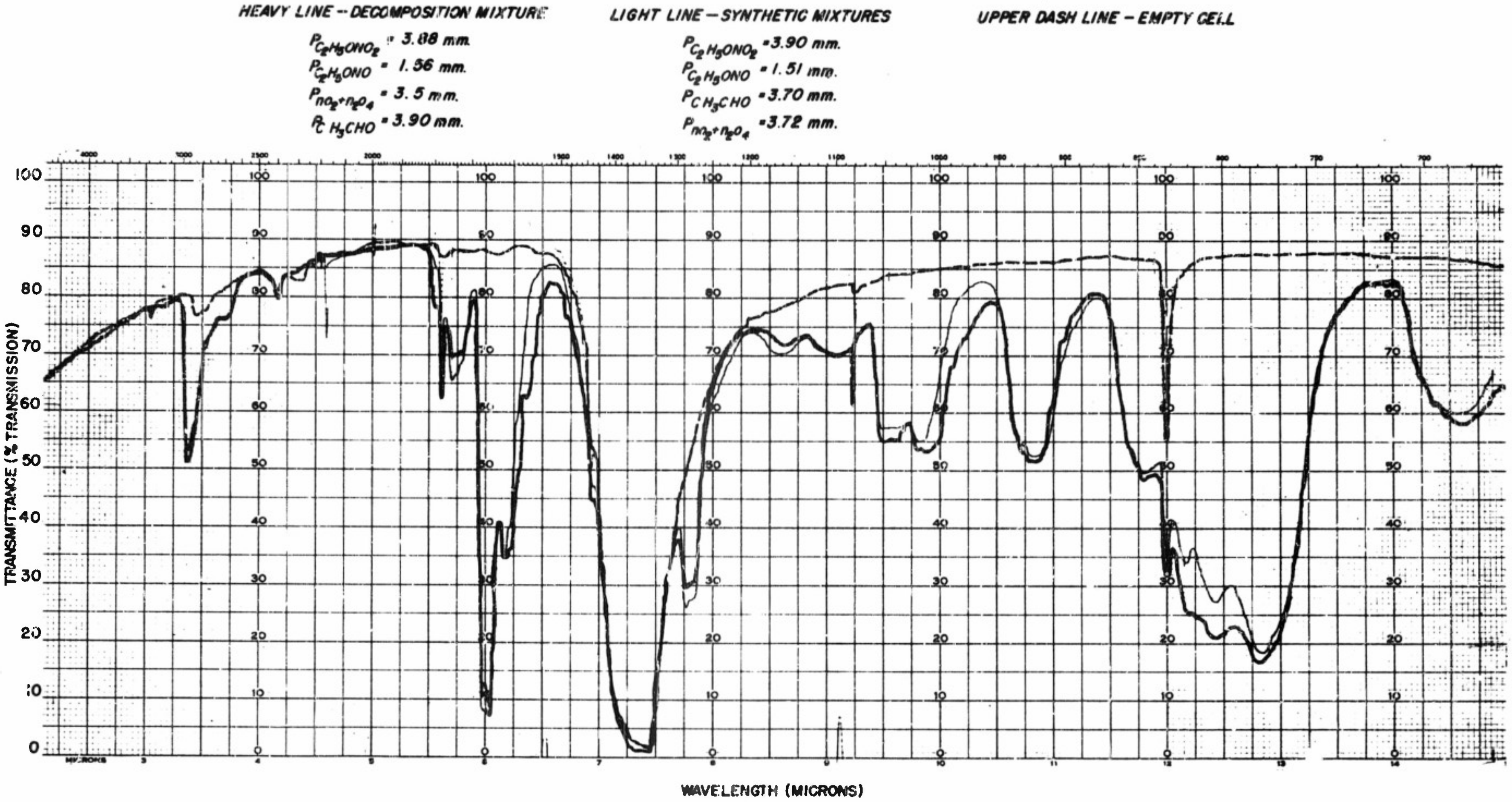


FIG. 12 DUPLICATION OF SPECTRUM OF PRODUCTS OF ETHYL NITRATE DECOMPOSITION. 86.0% DECOMPOSITION

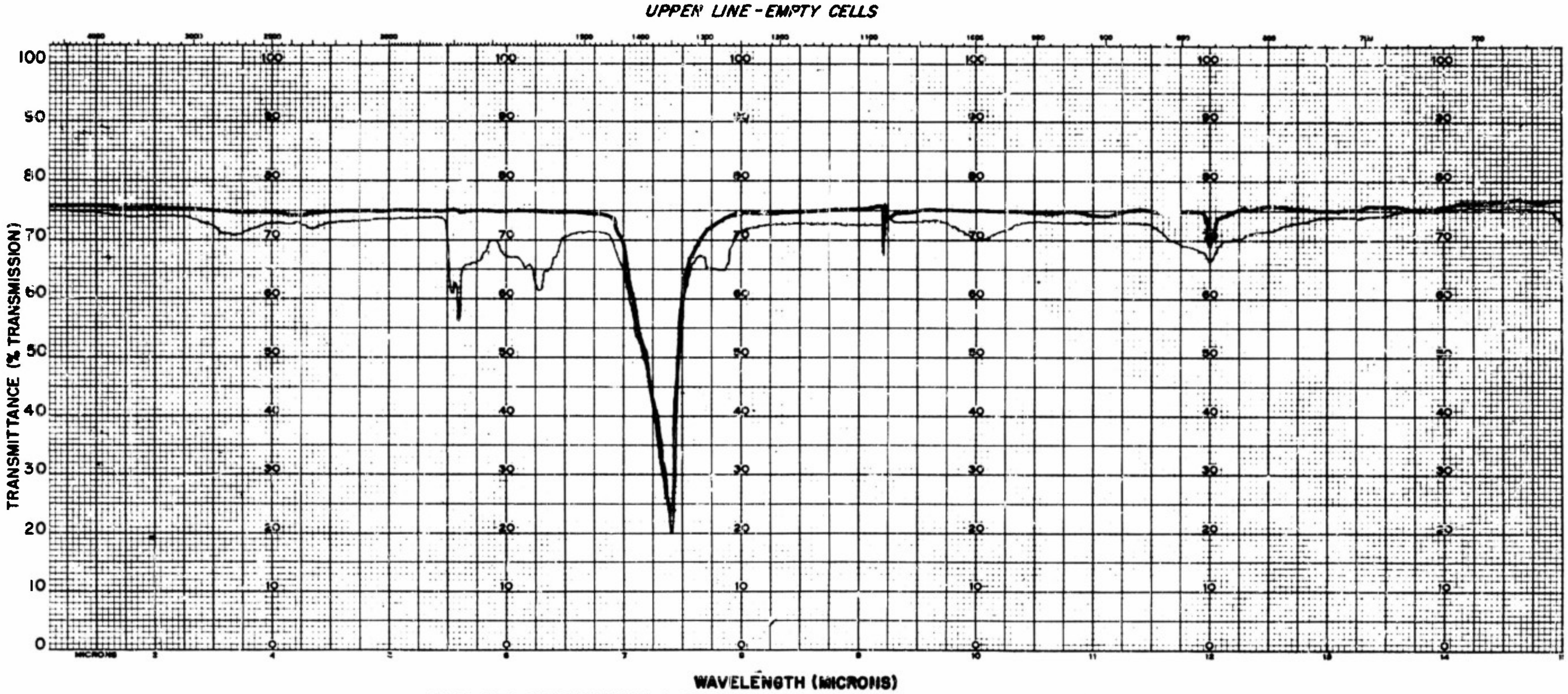


FIG. 13 SPECTRUM OF 33.4% DECOMPOSITION MIXTURE
ETHYL NITRATE AND ETHYL NITRITE BLANKED OUT

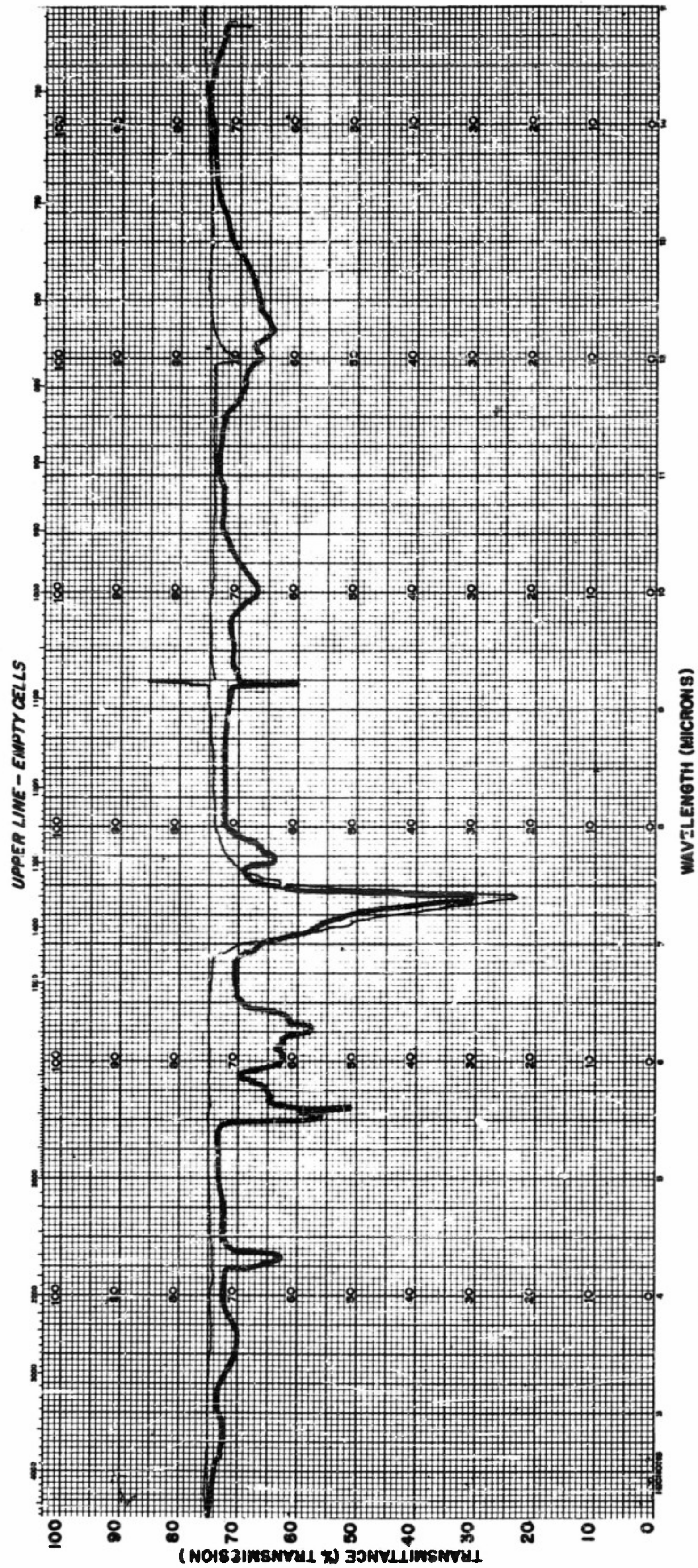


FIG. 14 SPECTRUM OF 61.5% DECOMPOSITION MIXTURE WITH ETHYL NITRATE AND ETHYL NITRATE BLANKED OUT

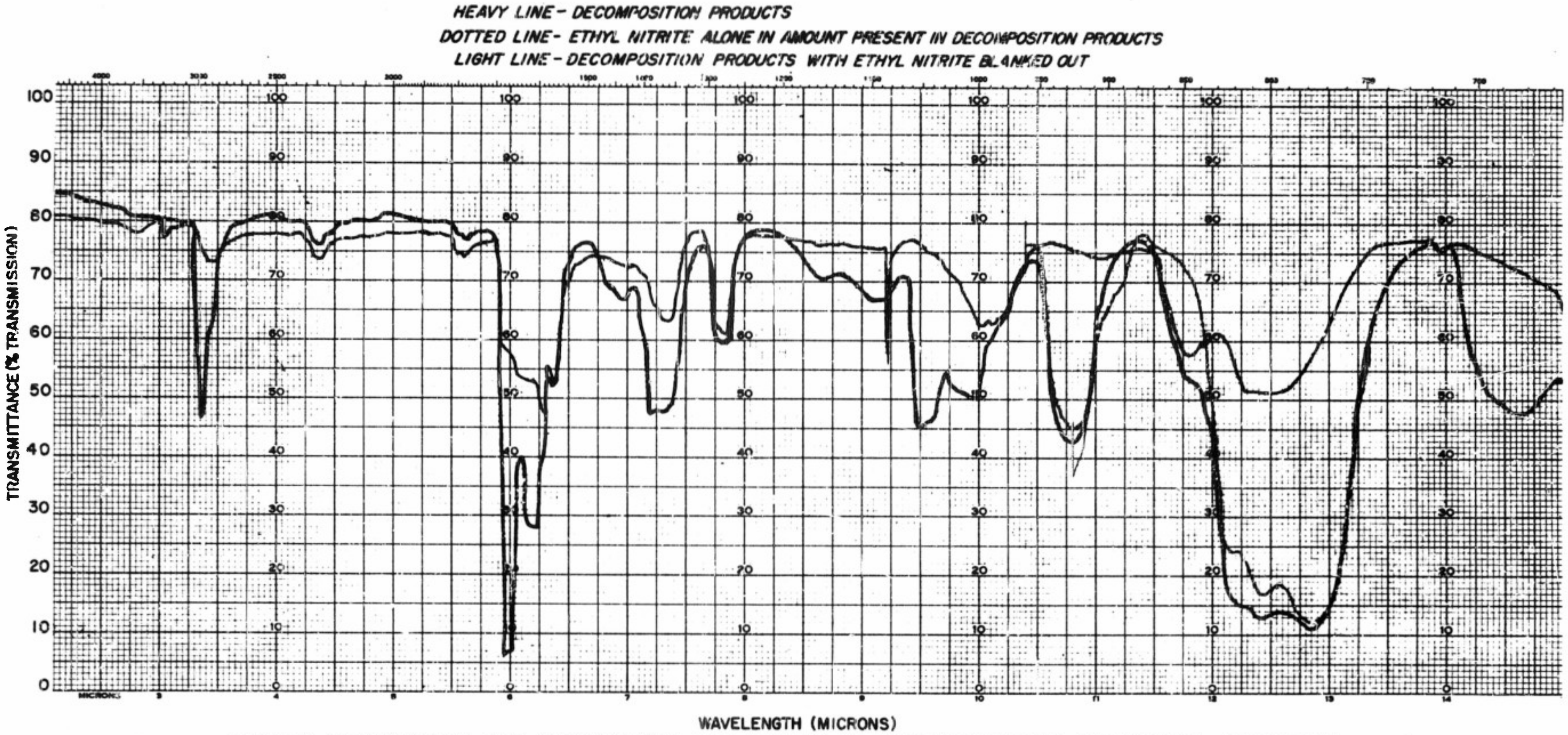


FIG. 15 SPECTRUM OF PRODUCTS OF 93.3% DECOMPOSITION OF ETHYL NITRATE

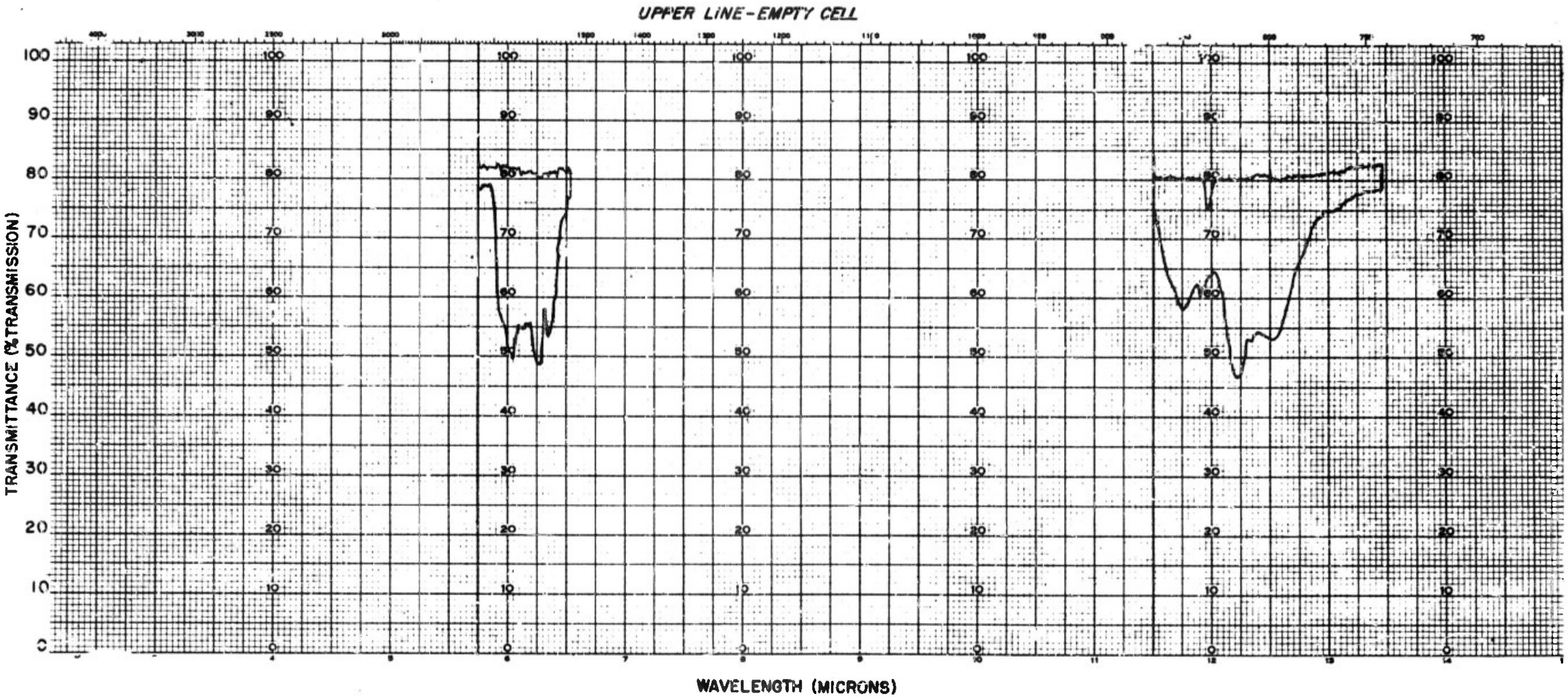


FIG. 16 SPECTRUM OF 93.3% DECOMPOSITION MIXTURE WITH ETHYL NITRITE BLANKED OUT. LOW SPEEDS. HIGH RESOLUTION.

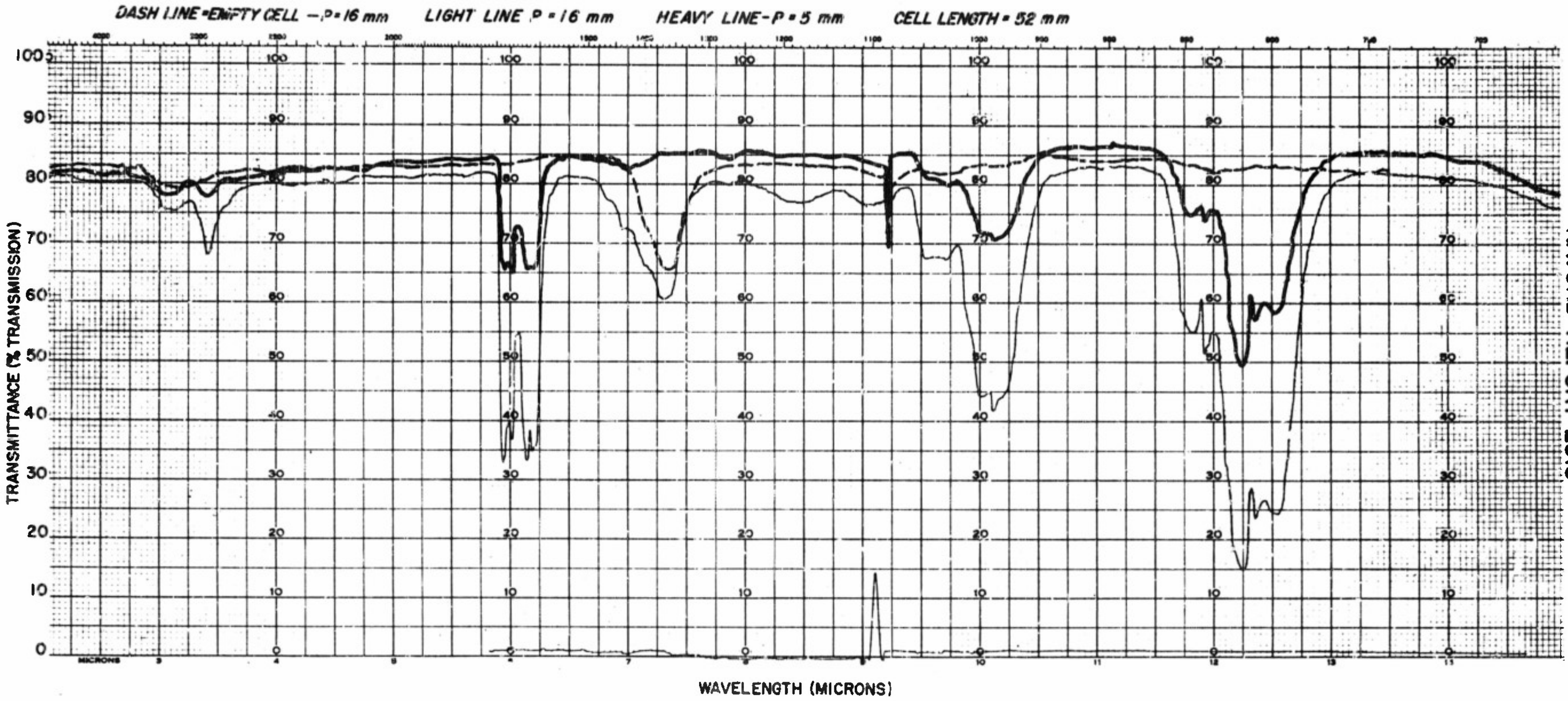


FIG. 17 METHYL NITRITE

P = 12.0 mm.   CELL LENGTH = 52 mm.

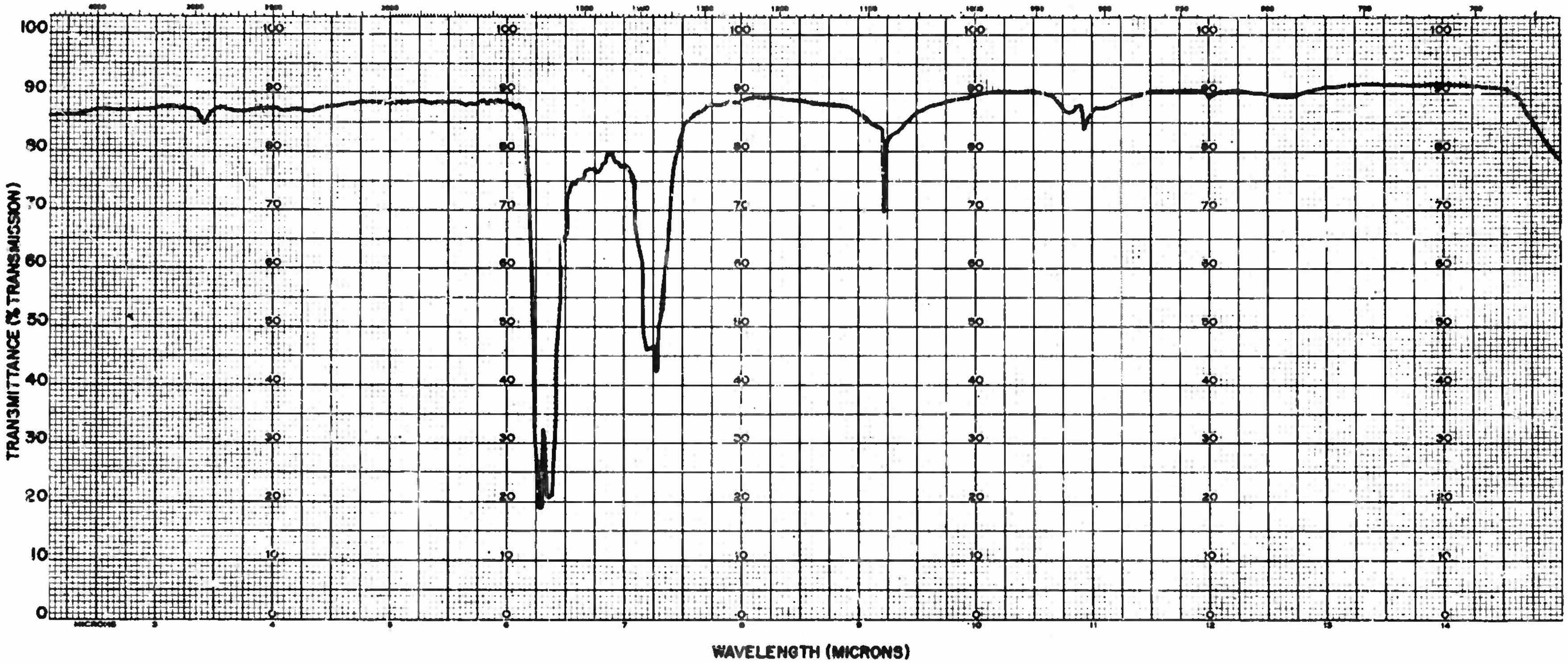


FIG. 18 NITROMETHANE

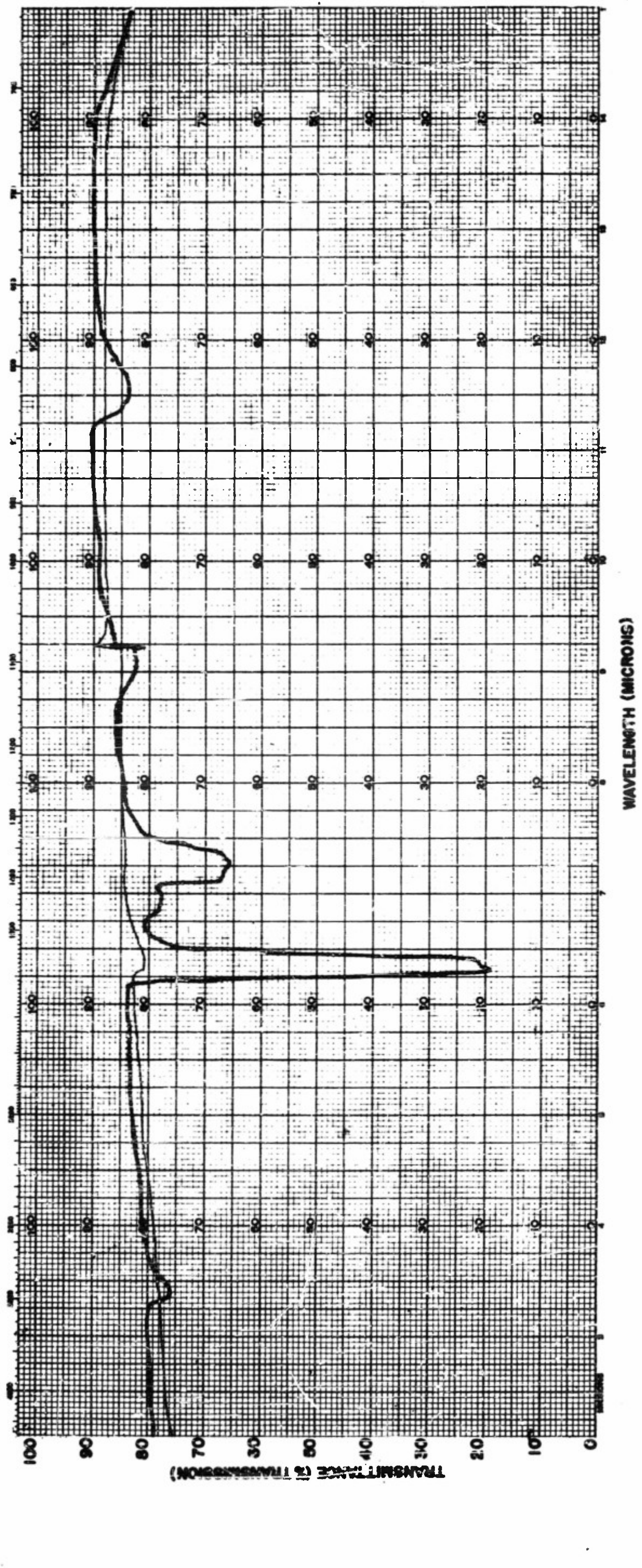


FIG. 19 NITROETHANE

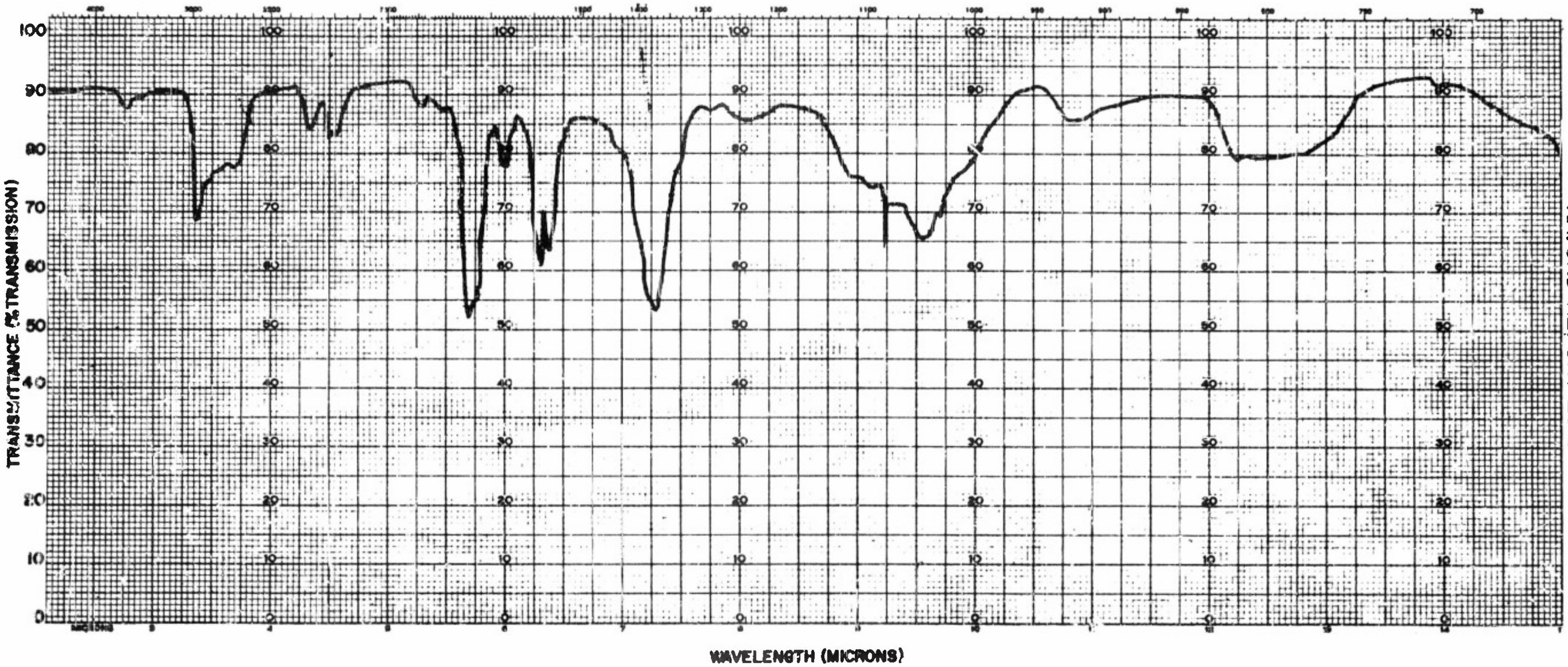


FIG. 20 PRODUCTS FROM THERMAL DECOMPOSITION OF ETHYL NITRITE AT 161°C, 7120 MINUTES

P = 19.0mm. CELL LENGTH = 52 mm

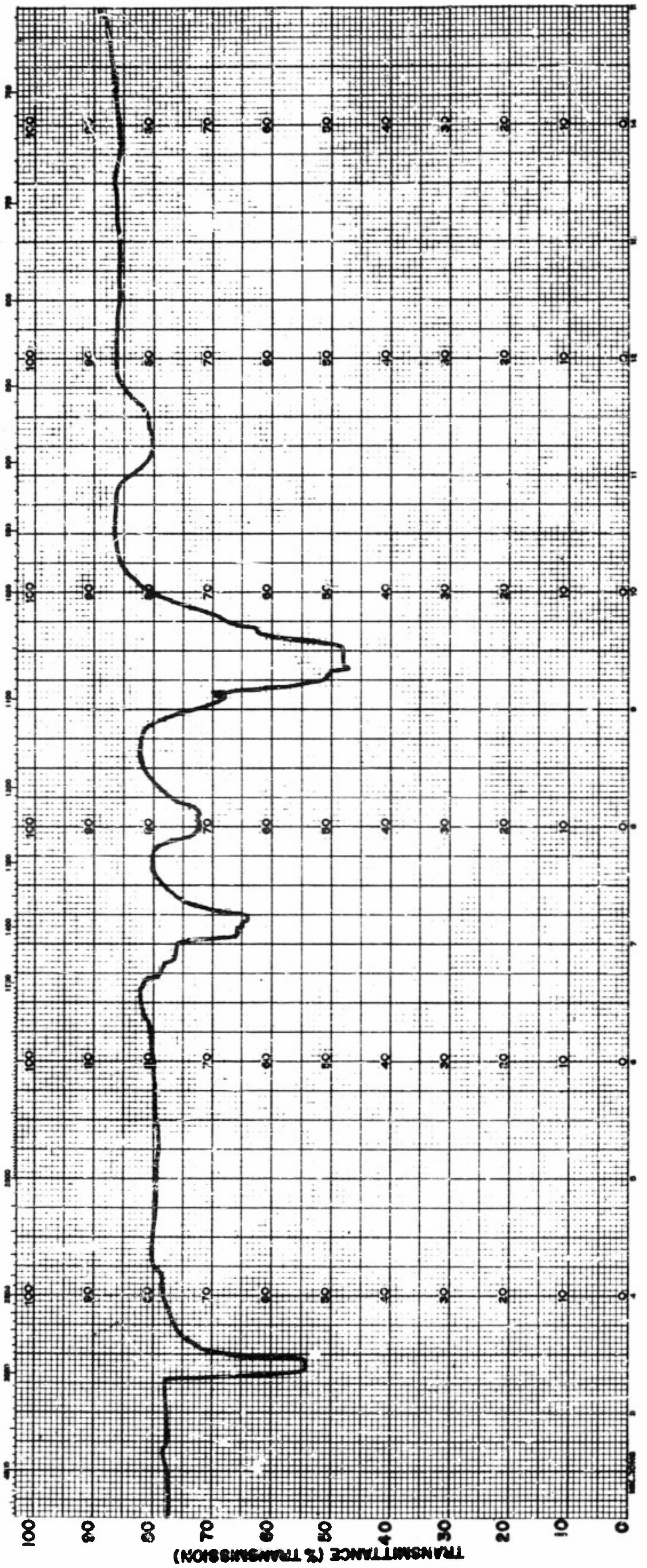


FIG. 21 ETHYL ALCOHOL

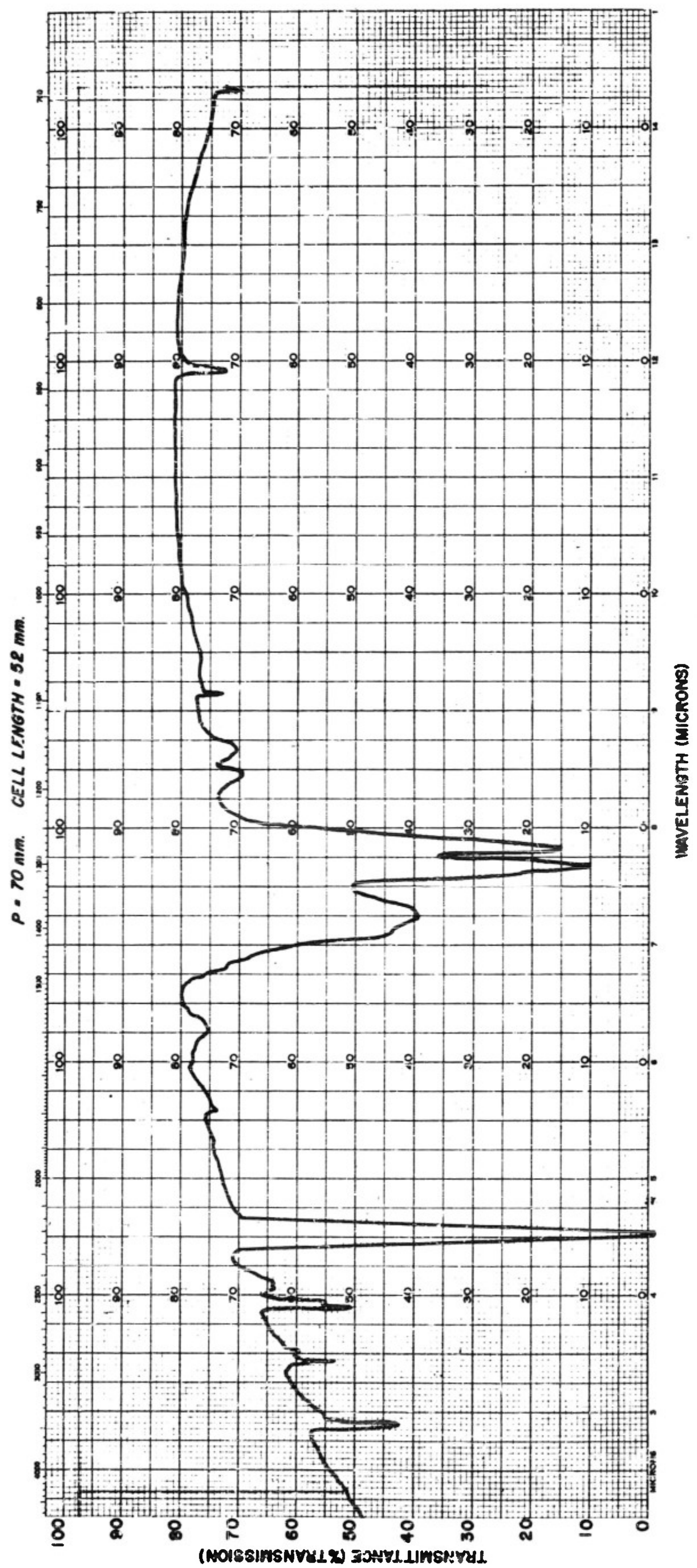


FIG. 22 NITROUS OXIDE

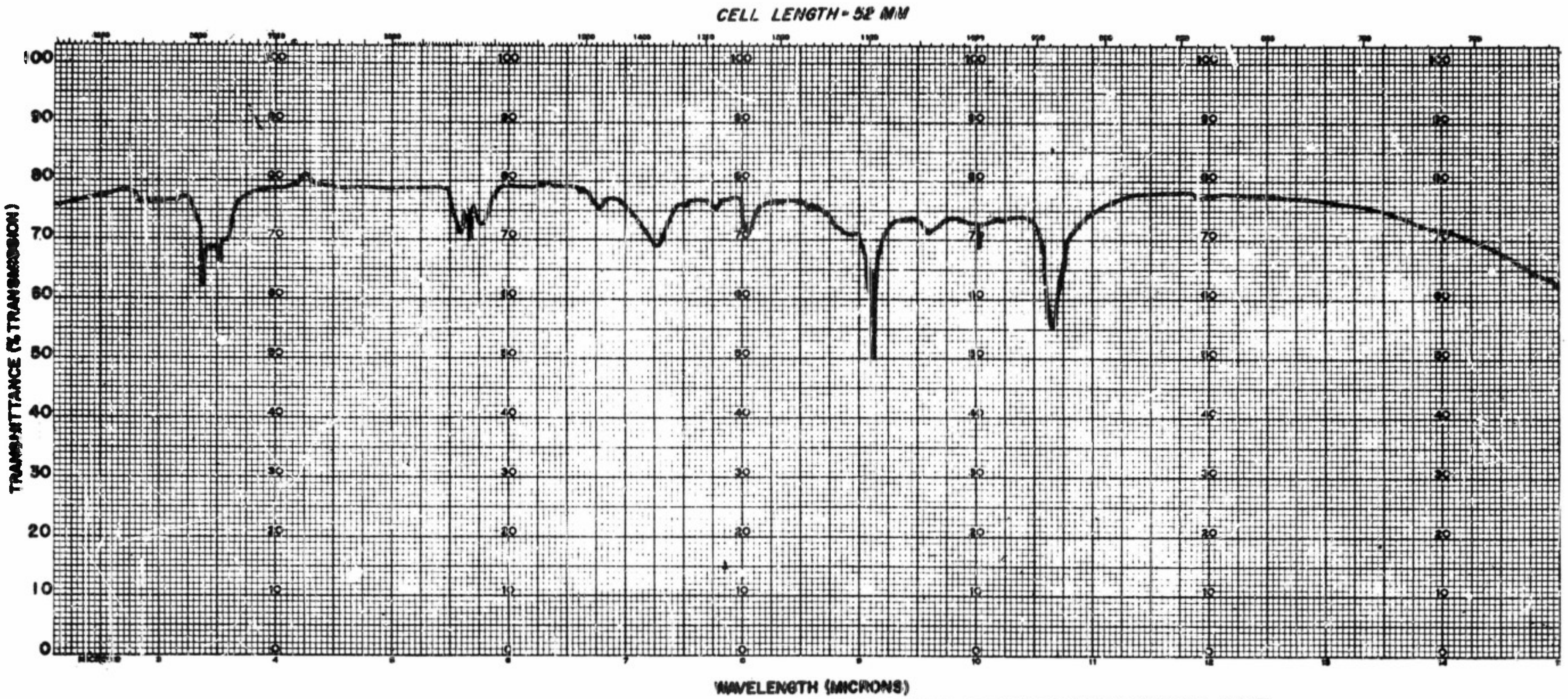


FIG. 23 FORMALDEHYDE AT VAPOR PRESSURE OF TRIOXYMETHYLENE

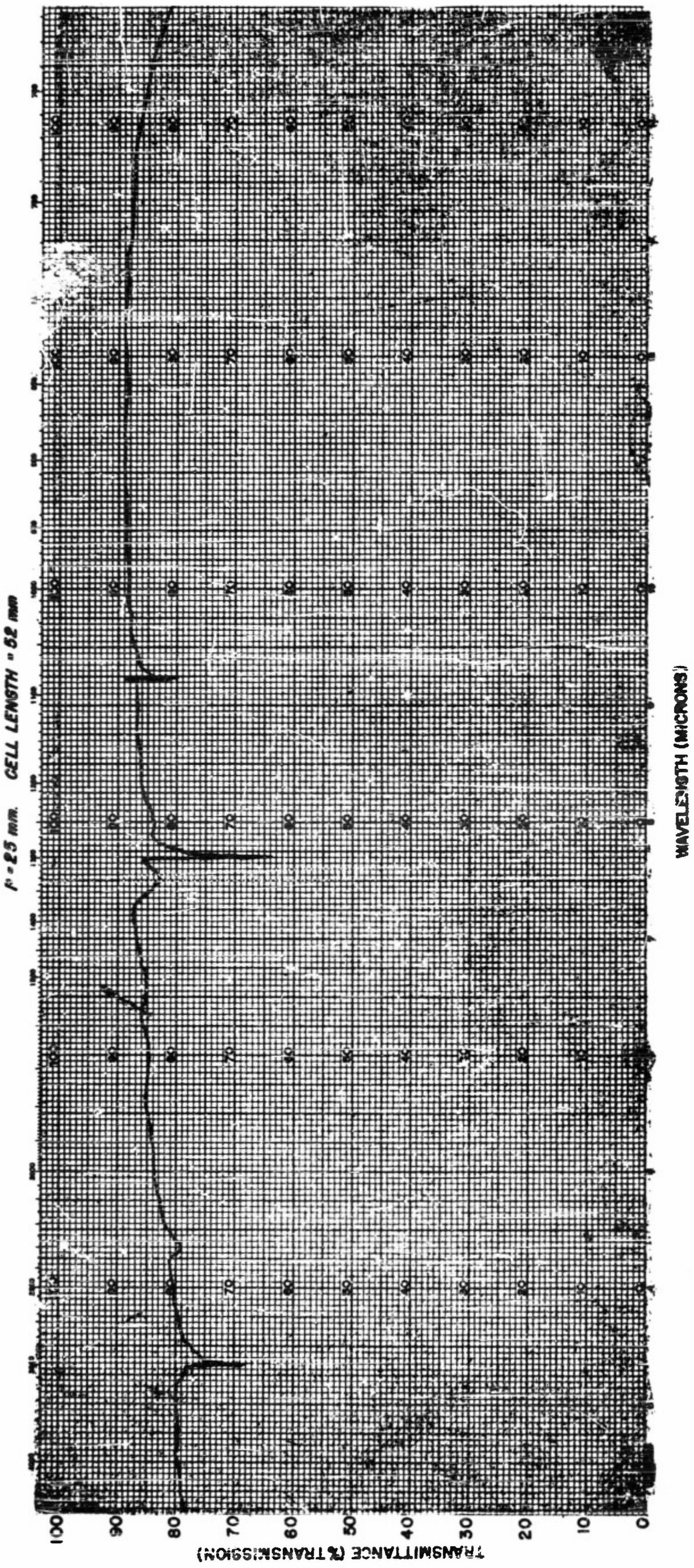


FIG. 24 METHANE

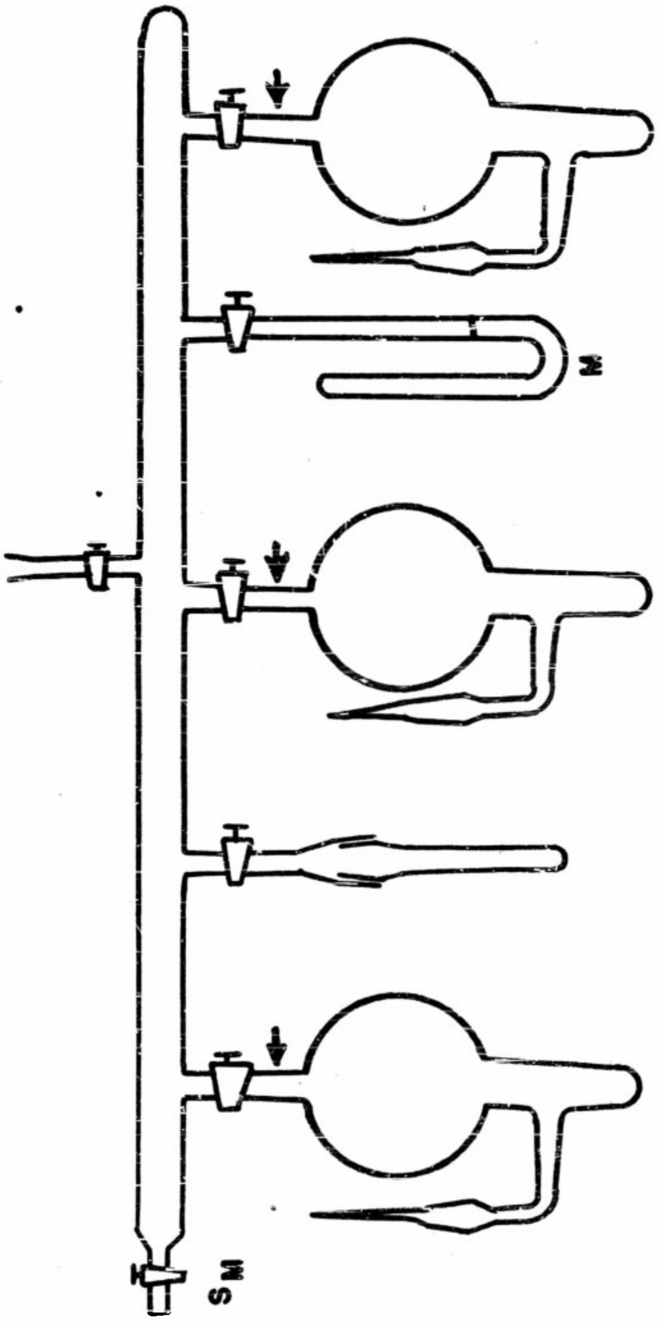


FIG. 25
BULB FILLING APPARATUS

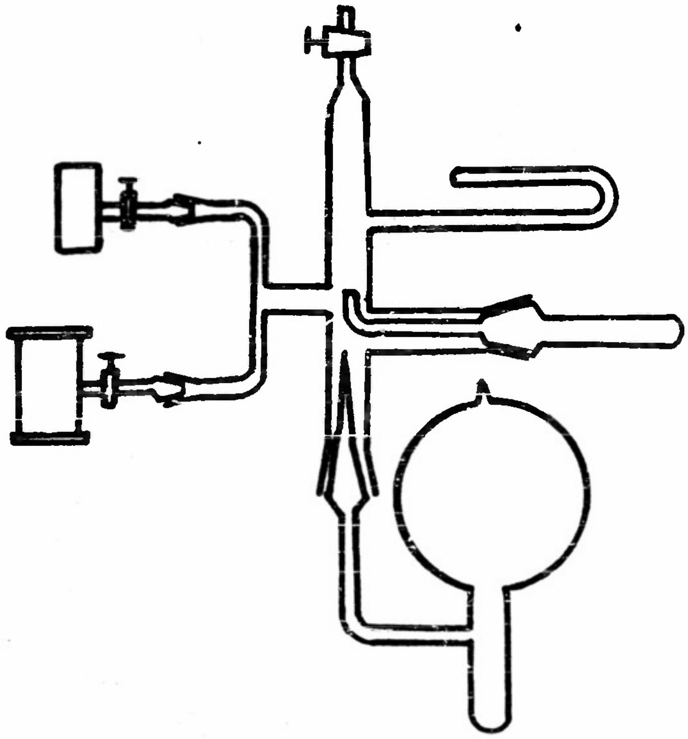


FIG. 26
BULB EXPANSION APPARATUS

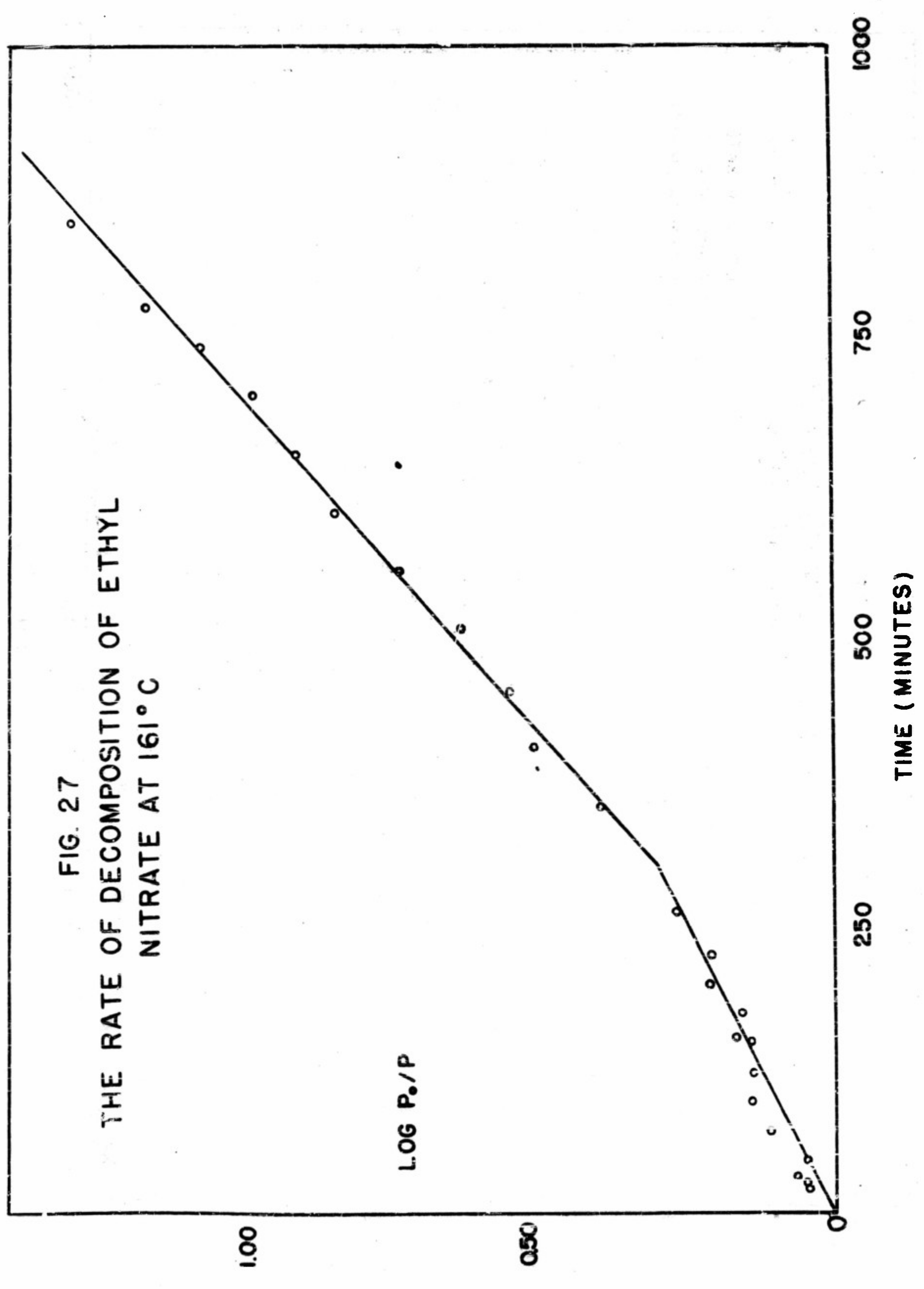
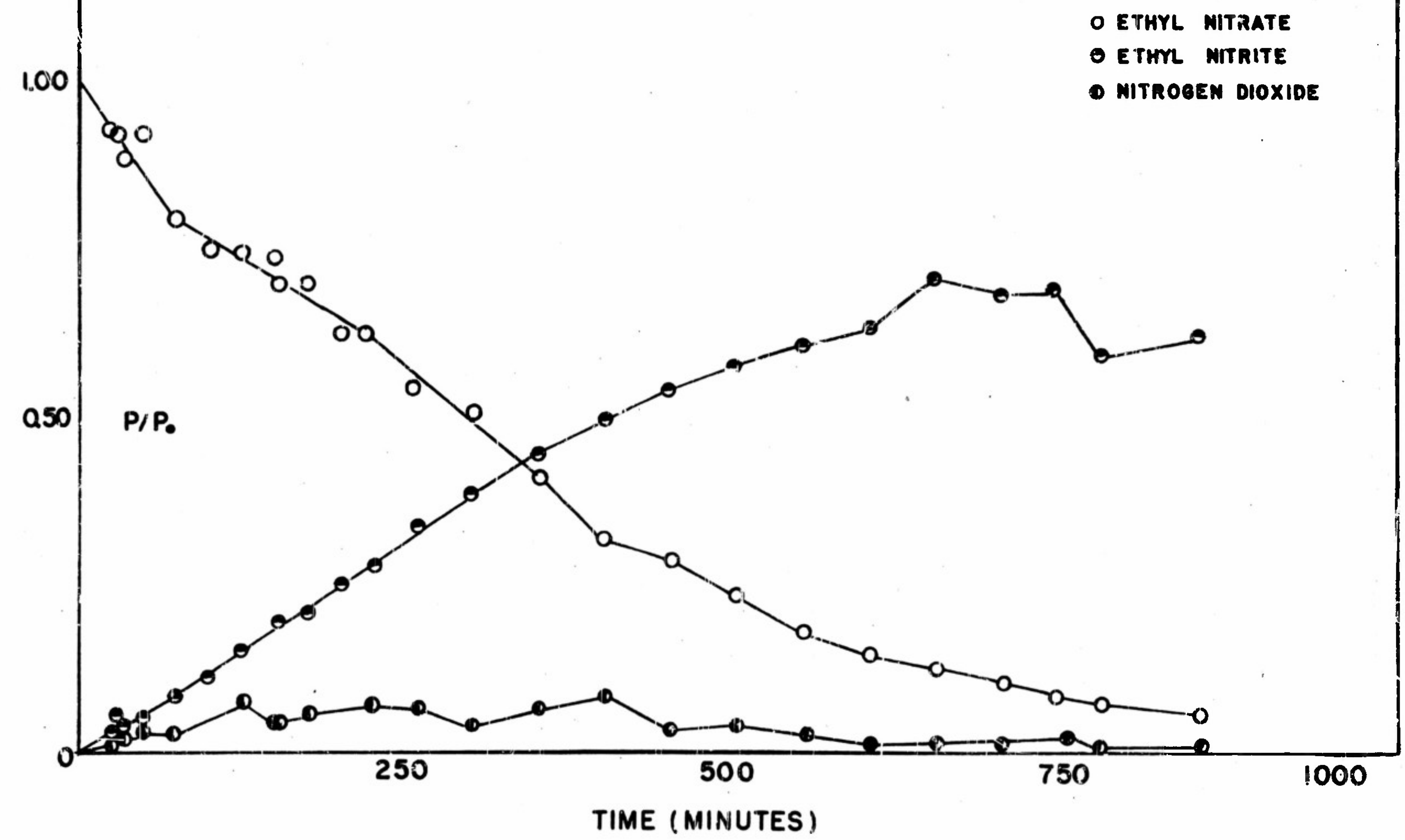


FIG. 27

THE RATE OF DECOMPOSITION OF ETHYL NITRATE AT 161° C

FIG. 28

THE THERMAL DECOMPOSITION OF
ETHYL NITRATE AT 161° C



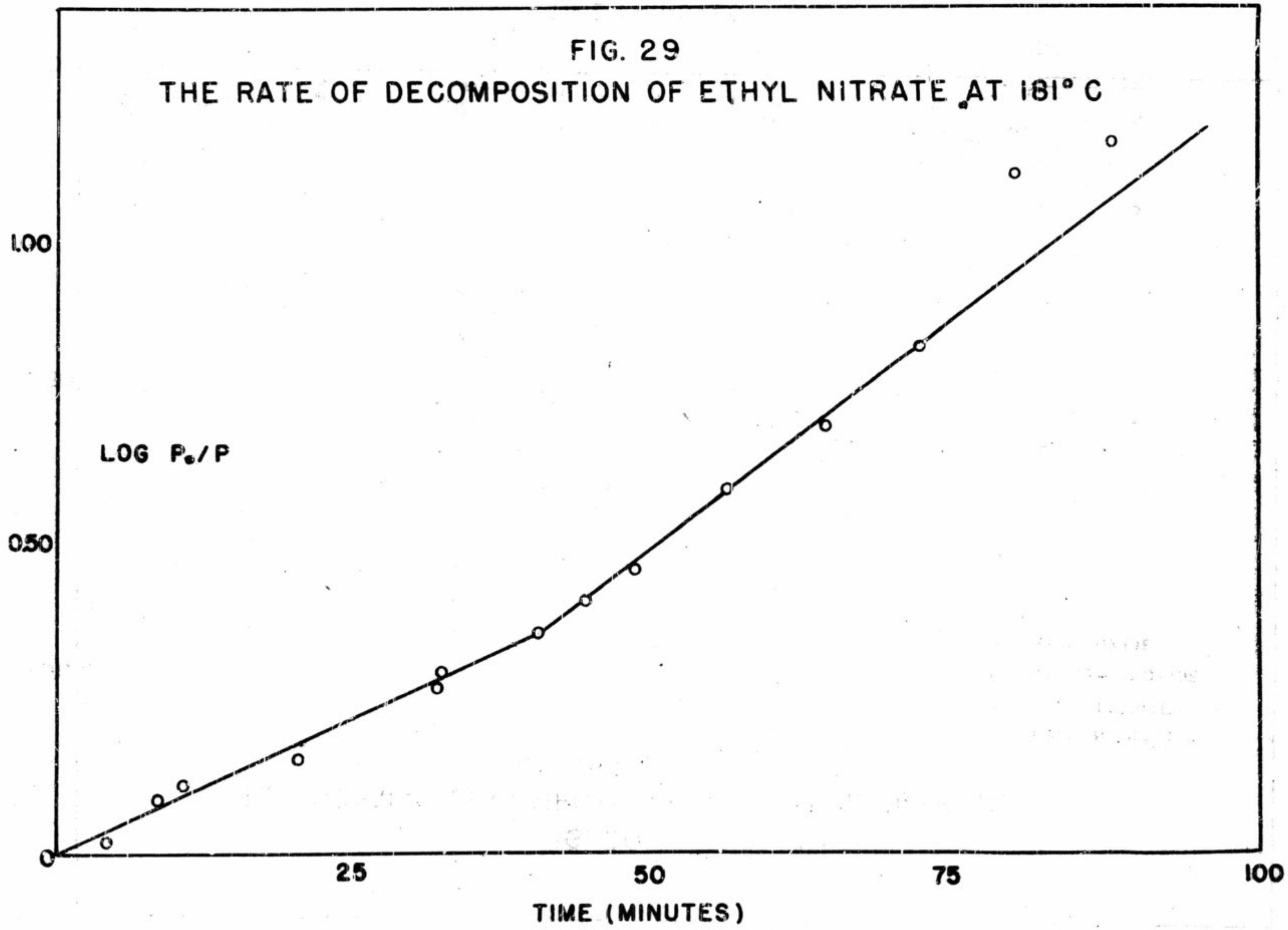


FIG. 29

THE RATE OF DECOMPOSITION OF ETHYL NITRATE AT 181° C

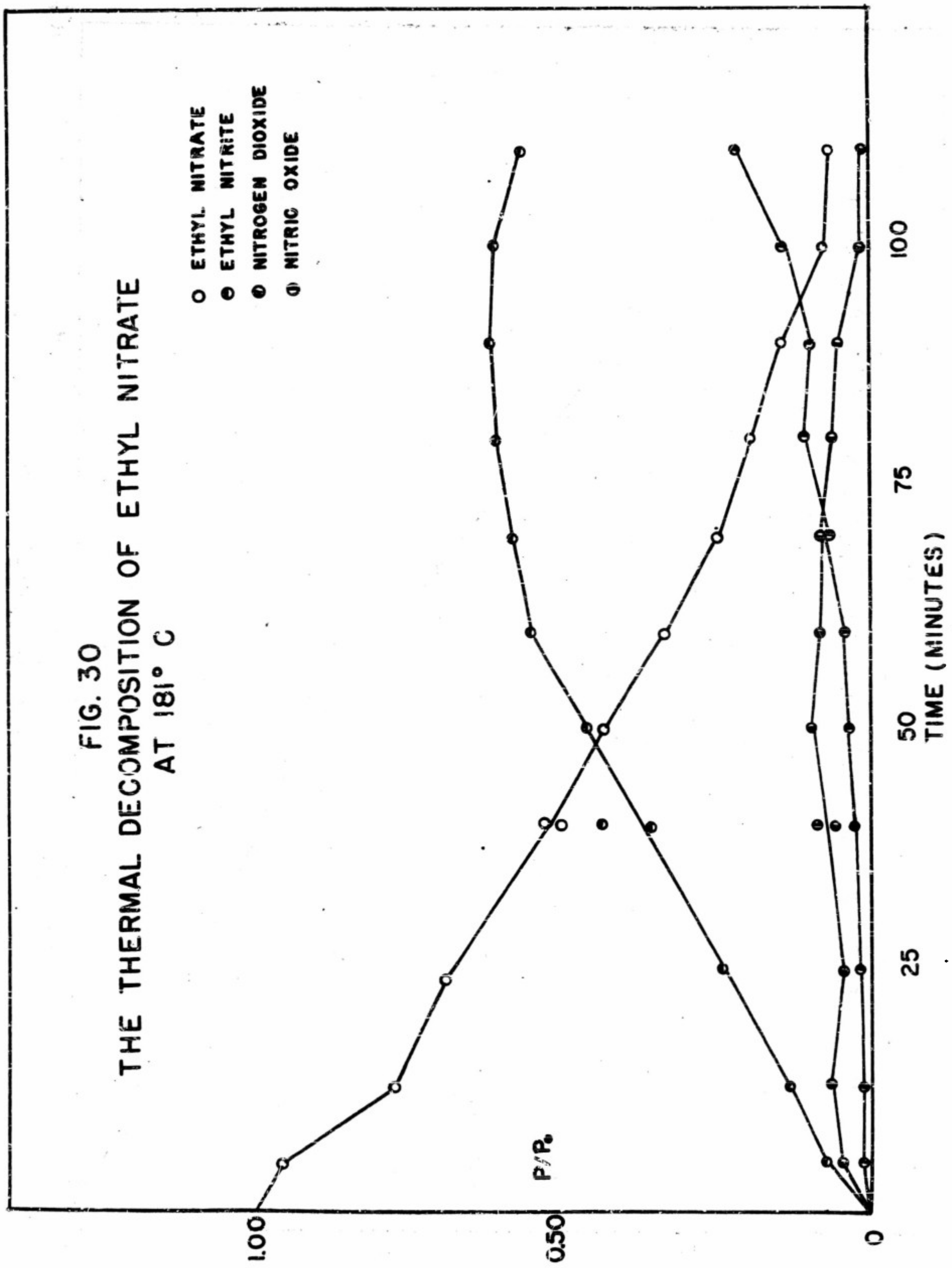


FIG. 30

THE THERMAL DECOMPOSITION OF ETHYL NITRATE AT 181° C

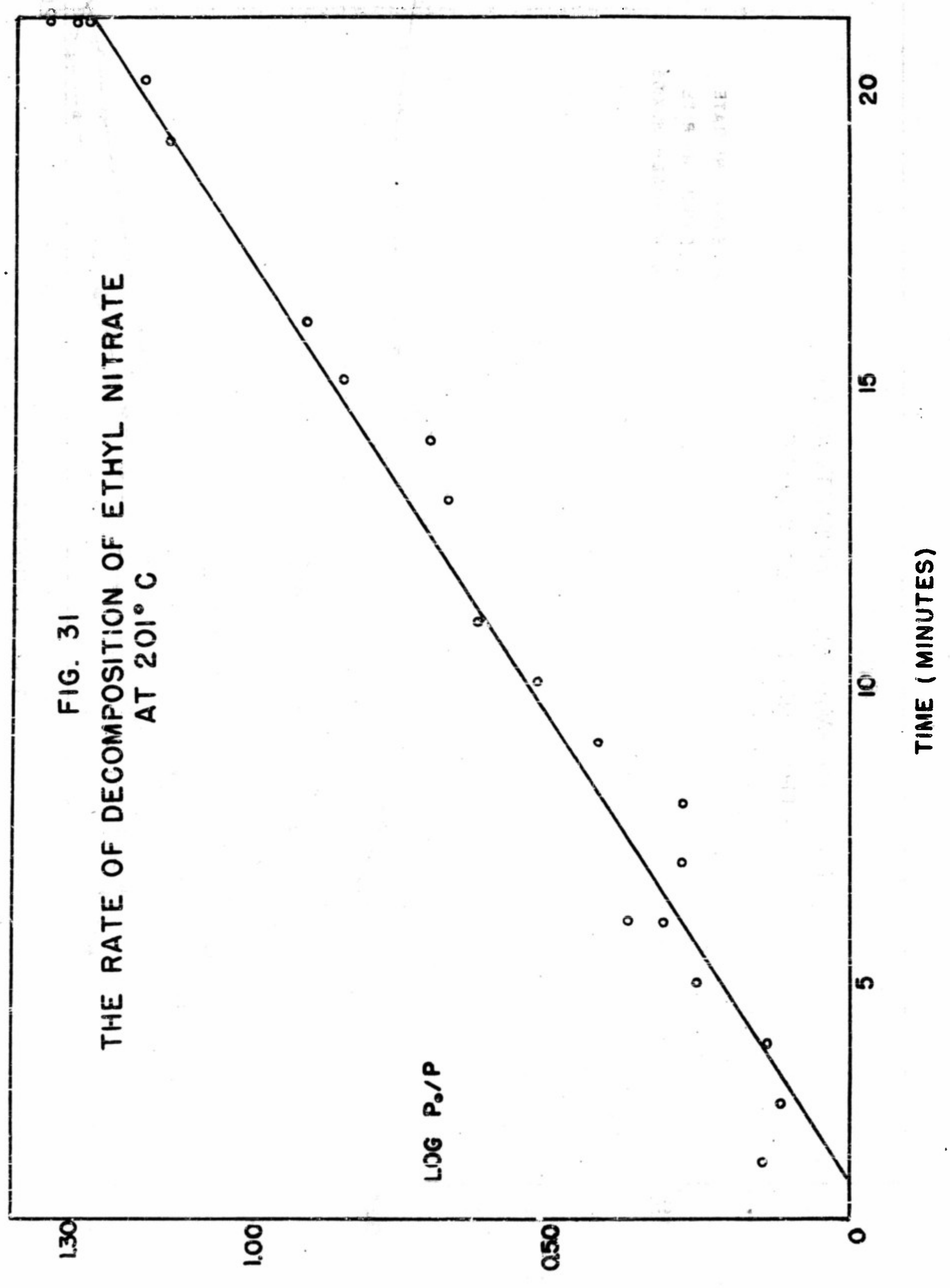
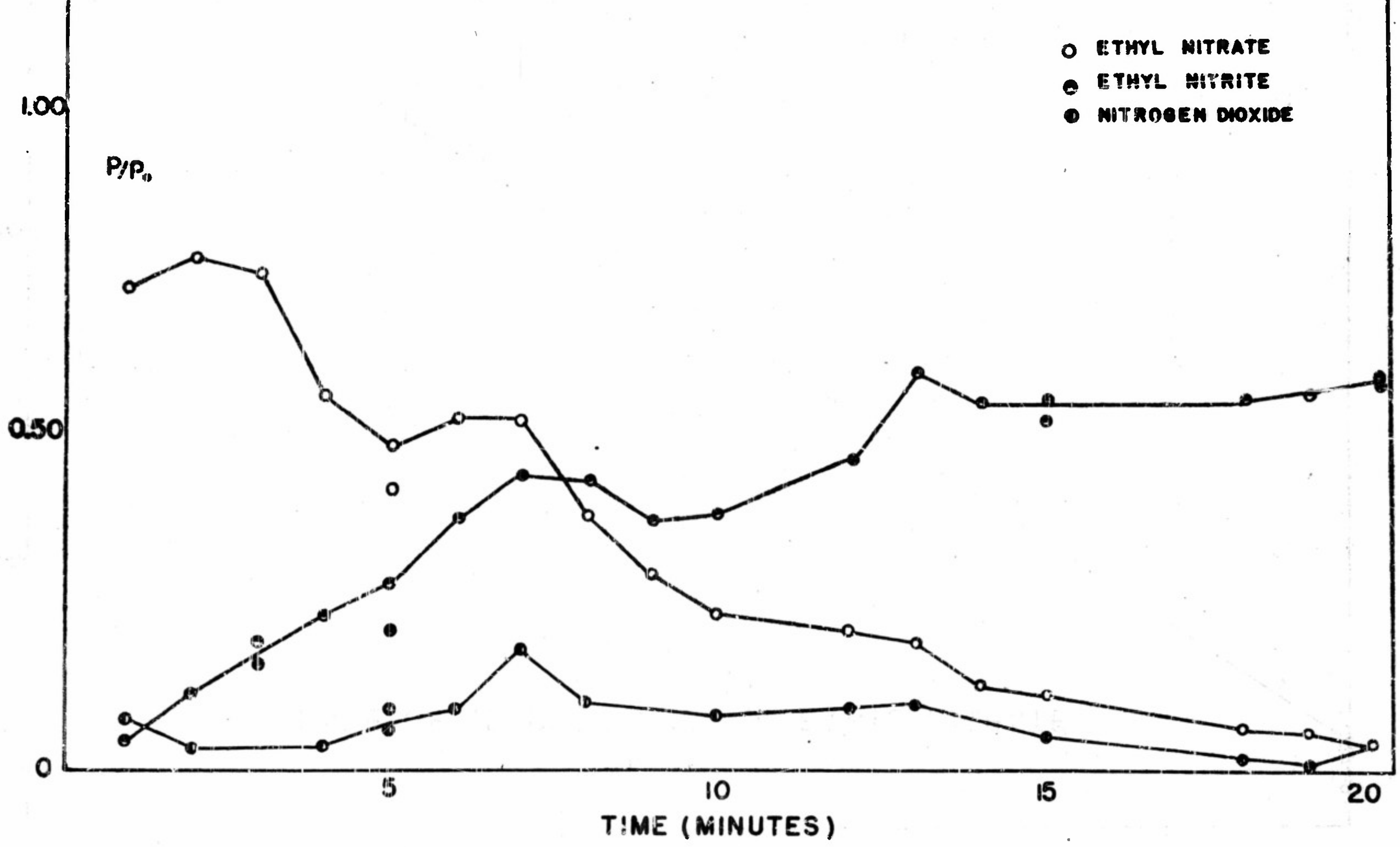


FIG. 31
THE RATE OF DECOMPOSITION OF ETHYL NITRATE
AT 201° C

FIG. 32

THE THERMAL DECOMPOSITION OF ETHYL NITRATE AT 201° C



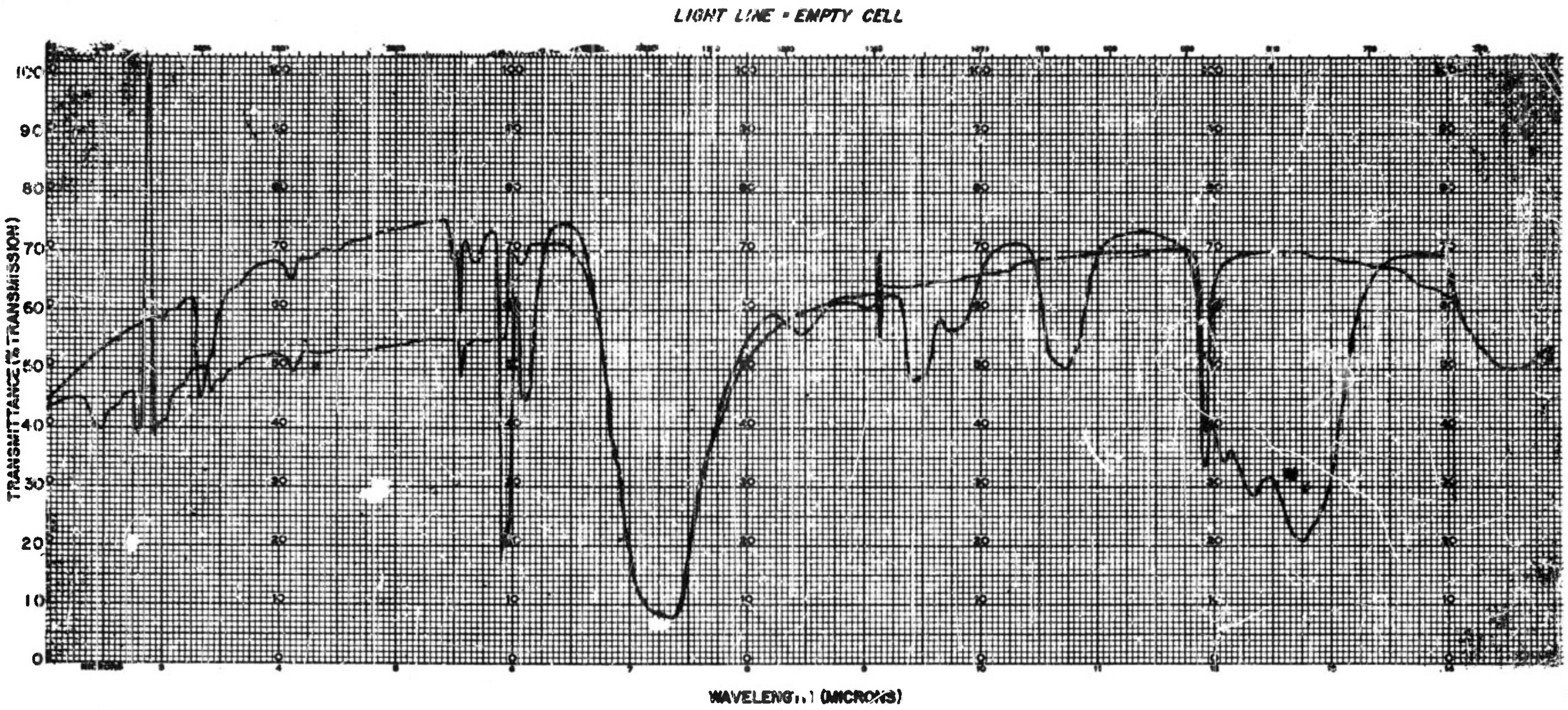


FIG. 33 THE PRODUCTS OF THE REACTION BETWEEN NITROGEN DIOXIDE AND ETHYL ALCOHOL

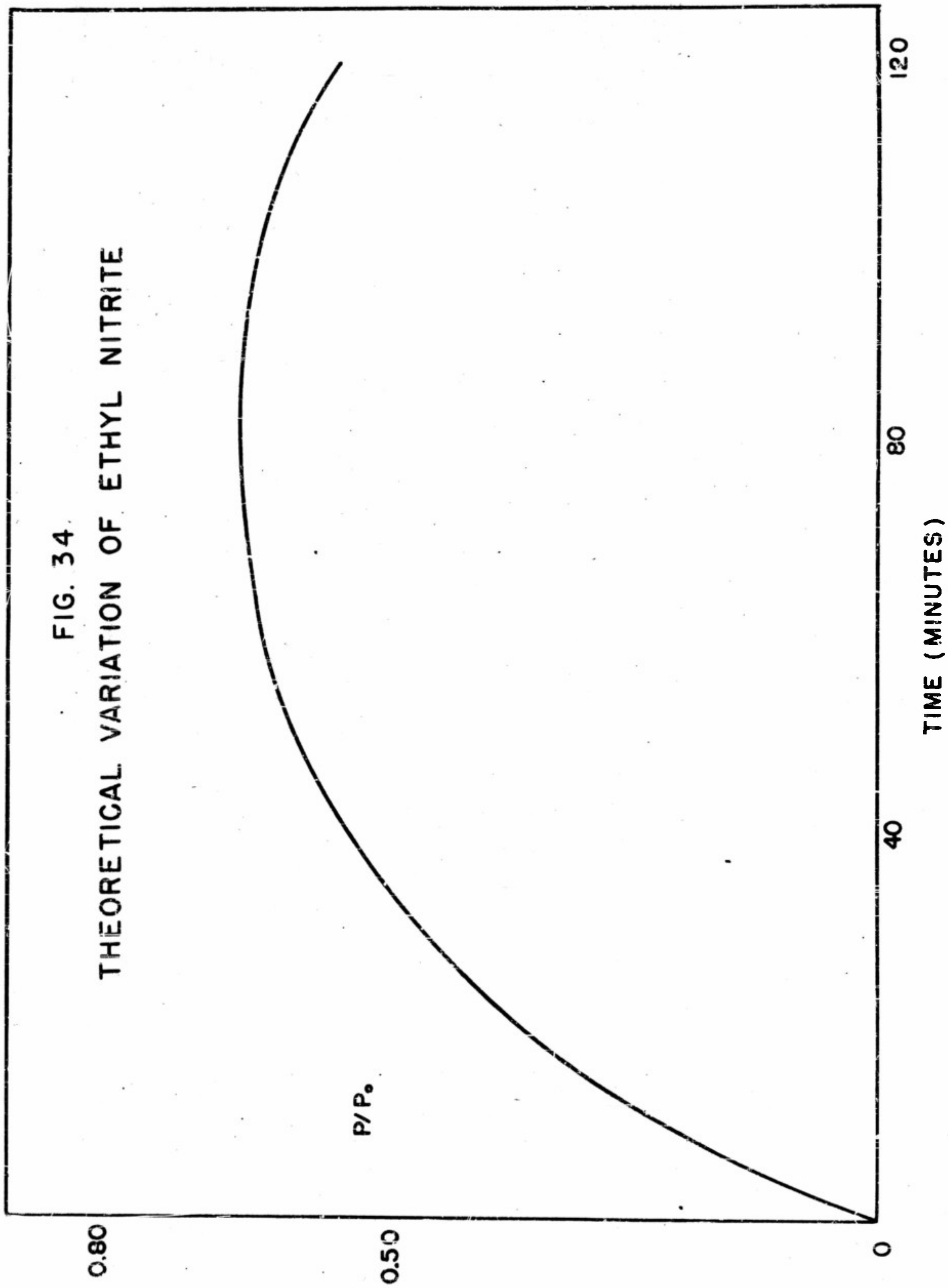


FIG. 34

THEORETICAL VARIATION OF ETHYL NITRITE

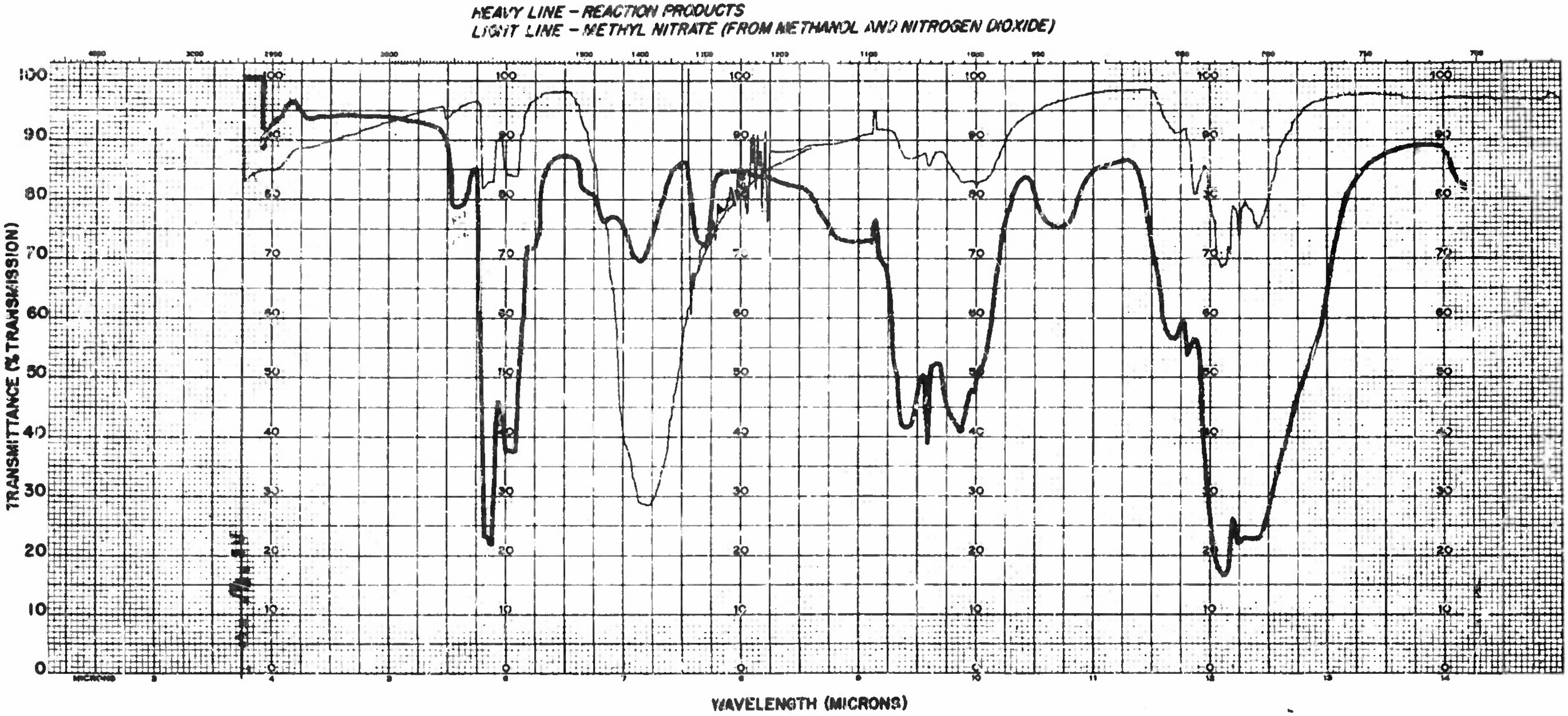


FIG. 35 THE DECOMPOSITION OF ETHYL NITRATE AT 201° C IN THE PRESENCE OF METHANOL

FIG.36 PRODUCTS OF THE REACTION BETWEEN ETHYL NITRITE AND METHANOL AT 199°C