THE GAS-PHASE OXIDATION OF ACETIC ACID BY NITROGEN DIOXIDE

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A Thesis
submitted in partial fulfillment of
the requirements for the degree of
Master of Science

March, 1967

Memorial University of Nfld.,
St. John's

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DISCUSSION.

ABSTRACT

This thesis presents the results of a preliminary investigation of the gas-phase oxidation of acetic acid by nitrogen dioxide and is an example of a chemical process in which nitration competes with destructive oxidation of an organic molecule. The products of the reaction are CO, CO_2, CH_3NO_2, NO, H_2O and possibly small quantities of N_2O and N_2. Carbon and nitrogen balances within 95% were obtained, about as expected when the analytical errors are considered. Small quantities of other products cannot be excluded. An induction period of ∿ 900 seconds was observed at low temperature (∿ 190°C) but no induction period was observable at 253.5°C. The induction period at low temperature indicates a complicated reaction mechanism. The rate using CH_3COOD indicated that carboxyl hydrogen abstraction reactions were kinetically important. For the same initial pressure of acetic acid and NO_2 the total pressure rise is not greatly changed by adding NO, or by using D- acid as the reactant. The reaction is autocatalysed by NO. With the techniques used the reaction rate was found to depend on the CH_3COOH and NO_2 concentrations but accurate orders could not be determined. As will be seen in the result section the method used is not suitable due to concurrent decomposition of NO_2. Although a final complete mechanism

can not be written at this time, the partial one discussed in this thesis has been suggested because it explains the formation of products and stimulates further study.

ACKNOWLEDGEMENTS

The author is greatly indebted to Dr. Donald Barton for his encouragement, patience and advice offerred so freely during the course of this investigation. Acknowledgement is also made to the Department of Chemistry for a graduate teaching fellowship. Finally, the author wishes to express sincere gratitude to Dr. W. D. Machin for his valuable advice.

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INTRODUCTION

In the last twenty years much interest has been taken in NO_2 reactions and many investigations of importance have been carried out. The interest in the oxidation of acetic acid arose from the observed autocatalysis in the reaction between formic acid and NO_2(1,2) and the absence of the same in several other organic molecules containing C, H and O atoms.

Rate controlling association reactions between the organic molecule and NO_2 have been proposed by Walsh(3), and by Pollard, see Pedler and Pollard(4), for example. Rate controlling hydrogen abstraction reactions have been proposed by Thomas(5). In a later study of the isotope effects in the reaction between formaldehyde and nitrogen dioxide Barton(6) has shown that hydrogen abstraction is kinetically important. In addition the relationship between comparative and competitive isotope effects was interpreted as arising in a chain mechanism in which the chain carrier was OH or HONO, and that the rate was not controlled by a single elementary reaction as was previously supposed.

Apart from the problem of hydrogen abstraction reactions it is of interest, as mentioned above to see that some reactions exhibit autocatalysis for example CH_3Cl(7), CH_2Cl_2 and $CHCl_3$(8). The products hydrogen chloride and nitrosylchloride have been found to catalyse the reactions. The autocatalysis has been explained by a mechanism involving chlorine atoms. An explanation for autocatalysis is not available in the case of compounds containing C, H and O atoms. It has been postulated by Pollard(1) that catalysis by NO was via hydrogen abstraction by N_2O_3. However such a simple mechanism breaks down when order is observed with respect to NO(2).

The work of Pollard(4) on the reaction between acetaldehyde and NO_2 (which incidentally shows no autocatalysis with NO) reveals some interesting features about the fate of the methyl group. Although the products of methyl oxidation were not identified, they were supposed to be nitromethane, methyl nitrate and methyl nitrite.

The present work on acetic acid preliminary though it is, is of considerable interest as it provides useful information on the products of the reaction, rate controlling reactions in the mechanism and on NO catalysis.

EXPERIMENTAL SECTION

1. MATERIALS

(i) Acetic acid.

Fisher Scientific Co., cat. No. A-38 of stated purity 99.7% CH_3COOH. This acid was used without treatment for most experiments.

(ii) Acetic acid prepared from anhydride.

Fisher Reagent grade anhydride cat. No. A-10 of expected purity 97.2% from a fresh bottle was distilled through a fractionating column heated electrically 10°C below the boiling point of the anhydride. The middle fraction which distilled at 140°C was used for the preparation of the acid 28.33 gms. of anhydride was added slowly to 5.00 gms of water with stirring. The acid prepared by the above method was distilled on a spinning band column. The middle fraction of the acid was collected.

(iii) Preparation of CH_3COOD.

25.48 gms of acetic anhydride was mixed with 5.00 gms of D_2O exactly in the manner described for CH_3COOH and the whole process repeated. The sample appeared to be about 98% deuterated from observation of the n.m.r. spectra.

(iv) Nitrogen dioxide.

Nitrogen dioxide, obtained from Matheson Company, was treated with oxygen to remove nitric oxide and was passed through phosphorous pentoxide to remove moisture. The infrared spectrum of 6 cms of NO_2 in a 10 cm. cell showed no bands other than those due to NO_2 and N_2O_4. A number of experiments were carried out with untreated NO_2 with no apparent effect on the rate or products.

(v) Nitric oxide.

Possible impurities are: N_2, NO_2, N_2O_3 and N_2O. A procedure similar to that described in reference (9) was carried out in the vacuum line; see fig.2.

The system was evacuated to the cylinder head. Nitric oxide was then let into the line and by opening stopcock # 19 the NO storage was filled up to one atmosphere. The NO was then transferred to storage bulb L at liquid nitrogen temperature where any N_2 present could be pumped away. At this point the condensate appeared blue, particularly around the top due to N_2O_3. The liquid nitrogen bath was replaced by a dry ice-trichloroethylene bath and NO and any N_2O present were distilled wnto the NO storage section leaving behind NO_2, N_2O_3 and H_2O trap L. The dryice-trichloroethylene bath around L was kept raised in order to achieve an effective separation of NO from NO_2 and N_2O_3 as these impurities should have condensed near the top of the trap L at liquid nitrogen temperature. The residue was discarded and the process repeated until there was no trace of blue colour in the condensate.

Finally NO, possibly with N_2O, was transferred from the NO storage section to trap L at liquid nitrogen temperature. The liquid nitrogen trap was then lowered so that NO evaporated first, to a larger extent, filling the NO storage bulb.

(vi) Carbon monoxide, carbon dioxide, nitrous oxide and nitric oxide.

These were obtained from Matheson Co. and were used without purification for comparison purposes in the identification of the products and in analysis by infrared spectra and in the chromatograph.

(vii) Nitromethane.

Nitromethane of unknown origin and Matheson, Coleman and Bell spectroquality were used. The IR spectra were indistinguishable. It was frozen at liquid nitrogen temperature and dissolved gases were pumped away. It was further purified by repeated vacuum distillation, finally retaining the middle fraction.

2. APPARATUS.

(i) Reactor and pressure measuring device.

The reactor, fig.1, was vycor glass, of volume 203.00 cm^3 and surface area 240 cm^2. For measuring the pressure rise and administering reagents a quartz spiral gauge was used. The hollow end of the spiral gauge was attached to the reactor at its one end and to a needle at the other. Such a gauge is quite suitable below one atmosphere pressure. The pressure could be measured to ± 0.02 cm. of Hg. The whole spiral system was enclosed in a pyrex glass tube.

The reactor described above is represented by R in Fig. 2. The gauge is connected to one of the arms of the manometer M_1 and to a fore pump via a two-way stopcock. A glass window was fixed on the gauge protecting tube. The image of the needle could be focussed on a telescope and the pressure read on manometer M_1.

To begin with the reactor and gauge were evacuated and the image of the needle was focussed on the cross-wire of the telescope. This was taken as the null position of the needle. A pressure of air equal to the required reactant pressure was leaked to the gauge side. This displaced the needle from its original position and now the reactant was administered into the reaction vessel until the needle came back to the null position.

(ii) Furnace.

The reactor (11) was heated electrically and thermostated by means of thermistor and relay. It was enclosed in a hollow steel cylinder. The ends of the steel cylinder were closed by the same material with parts suitably designed to leave a space for thermocouple inlets and neck of the reactor. In the wall of the cylinder there was a hole four inches deep which could allow the placing of a thermistor. The steel cylinder was wound in two layers of heaters of chromel-A wires of resistance 4.28 ohms per foot. Each layer had three sets of separate heaters, controlled by separate variacs mounted on a wooden board. Fig. 1, illustrating the heaters and insulation, is self explanatory.

(iii) Thermocouple calibration.

Thermocouples were calibrated by means of melting and freezing tin. For heating the metal uniformly a furnace shown in Fig. 3 was constructed. A cylindrical steel can of 35 cms height and 25 cms diameter was taken. The bottom of the steel can was properly insulated and on it was placed a brass metal cylinder of 25 cms height and 11 cms in diameter. A thin asbestos sheet was wrapped around the metallic cylinder and on it were imbedded 11 turns of heating wire of resistance 1.01 ohms per foot. The heating wires were covered with layers of asbestos. The space between the steel can and the heating cylinder was filled with vermiculite. The graphite crucible was placed, inside the brass cylinder, on a tripod stand made up of an insulating material. The reference metal was placed in the crucible and heaters switched on. To avoid contamination thermocouple wires were not directly immersed into the molten metal but instead were placed in a pyrex protection tube. The reference junction was placed in ice water. The metal was brought to a temperature of 10°C above its melting point for several minutes and then cooled slowly by stirring the molten metal with the thermocouple protection tube. Thermal e.m.f's were measured on a K_3 potentiometer by observing a null point deflection in a 2430-A L & N galvanometer. The standard cell used was from

Thermocouple #1 (while melting)

e.m.f.	Time
9.4360 m. volts	
9.4360 "	
9.4360 "	for 900 seconds
9.4455 "	
9.4455 "	
9.4450 "	
9.4450 "	

Thermocouple #1 (while freezing)

e.m.f.	Time
9.4360 m. volts	
9.4630 "	
9.4630 "	for 600 seconds
9.4630 "	
9.4630 "	

Eppley Lab. Inc. (U.S.A.), Cat. No. 100 and serial no. 689764. This cell was calibrated against the certified standard cell no. 796228 from the same manufacturer. The constant e.m.f. was taken as the corresponding f.pt. e.m.f. A typical freezing point and melting point datum is given below. Since the deviations observed from the tabulated values were < 0.5°C no attempt was made to make any corrections whatsoever.

(iv) Temperature control.

Eight thermocouples of chromel alumel material, calibrated by the method described earlier, were used to measure the temperature at the various points of the reactor. The thermistor was used to control the temperature. Unfortunately thermistors arn't very sensitive in this temperature range. On the average the temperature control was obtainable within ± 0.25°C and ± 0.1°C in the well of the reactor, a point close to the thermistor. It is to be admitted that, in spite of our months' effort to bring all thermocouples as close as possible, three of them placed near the ends of the reactor were hopelessly out, by approximately 5°C from the rest of them. In our final effort we changed the position of the thermistor to the reactor well but this too could not improve the results as much as expected. The average of all readings was taken as the experimental temperature. A typical reading (in millivolts) of eight thermocouples are taken from run 38. Thermocouple # 4 was in the reactor well.

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
10.275	10.355	10.355	10.395	10.410	10.130	10.190	10.380

Average = 10.31 millivolts or 253.50°C

(v) Vacuum system (see fig.2).

I sincerely wish to thank Dr. Donald Barton for accomplishing most of the glass blowing in Fig.2. The following accessories were used:

(a) forepump
    Duo-Seal 1403B or 1400 B
(b) diffusion pump
    C.V.C. MCF-60 and VMF-10
(c) thermocouple pressure gauge
    C.V.C. GTC-100

3. INTRODUCTION OF REACTANTS.

In all runs acetic acid was introduced first. To introduce the acid above 2 cms Hg a small drop of acid was frozen in a finger trap between stopcocks #1 and #2. Then this section was electrically heated until the required pressure in reactor R was obtained. Care was taken to prevent the acid from overheating. NO_2, stored in D at liquid nitrogen temperature, was warmed to ice temperature, and, keeping stopcock # 4 closed, the storage section L of about 500 ml capacity was filled up. The stopcock at storage section D was then closed and the ice bath was replaced by liquid nitrogen. Stopcocks #4 and #2 were opened so that NO_2 could reach stopcock #1. Stopcock #1 was then cautiously opened until the required pressure in R was obtained. Time measurement followed immediate closure of stopcock #1, and the pressure increase due to reaction was followed. The NO_2 from the section between stopcocks #1 and #4 was discarded and the rest stored back in D.

4. ANALYTICAL PROCEDURES.

The reaction was quenched in trap A at -220°C. This temperature was attainable by freezing liquid nitrogen in a thermos flask, shown by a dotted line in the figure, under continual pumping until an approximate pressure of 2 cms Hg was recorded on a manometer connected in series with this system. The non-condensable part was removed by means of the toepler pump by opening the stopcocks leading to T.P. and closing the others. Finally the gases were forced into the calibrated section of the manometer, M_2. (Volume of the bulbs V_1, V_2 and the entire section connecting it through the stopcock (19) to (18) was known). Here the pressure of the gases at various positions of the manometer and at room temperature could be measured.

The majority of runs were carried out using a slight excess of NO_2. Under these conditions the NO and NO_2 of the condensable products, retained in the trap cooled at solid nitrogen temperature, remain as N_2O_3 to a large extent and their separation by warming the trap to -80°C or -120°C is not at all satisfactory as was observed in the separation of a standard mixture of the two.

[redacted]

Material not condensable at solid nitrogen.

The amount of product not condensable at solid nitrogen temperature was measured by noting the pressure it exerted in a portion of the calibrated volume. This product was completely combusted over copper oxide at $\sim$ 250°C between stopcocks #15 and # 16, Fig. 2. This gas was completely absorbed by caroxite. In one run the emerging gas after oxidation through copper oxide was examined by infrared which identified it as CO_2. It* was further confirmed as CO by examination of its infrared spectrum. Further testing revealed that none of the gases such as hydrogen, methane or nitrogen were present to an extent which could be measured with confidence on our pressure and volume measuring device. If these materials were present, there could not be more than 0.02×10^{-4} moles - a lower limit of detection manometrically.

When an incomplete reaction was quenched, oxygen as a result of the dissociation of NO_2, also made its appearance with CO. In an excess of NO_2 one would naturally expect oxygen as a result of the dissociation of residual NO_2, however no oxygen was found in the analysis of complete reactions at the pressure of NO_2 used. One possible reason for its absence, besides any other reactions (see mechanism) of O_2, could be reaction with the accumulated NO which makes the O_2 concentration in the dissociation reaction,

* the unoxidized gas

$$2NO_2 \rightleftharpoons 2NO + O_2,$$

small.

Material condensible at temperature of solid nitrogen.

The trap A was warmed to -120° C using an ethanol slush bath. The mixture of gases volatile at this temperature was collected with the toepler pump and placed in the appropriate portion of the calibrated volume section where the pressure was noted on the manometer M_2. The separation of nitric oxide was effected by circulating the mixture through a trap at -160° C (isopentane slush) and collecting NO. The gas held at -160° C was identified as CO_2 with the suspicion of a trace of N_2O. See below for attempts to detect N_2O.

Quantitative analysis of CH_3NO_2 in presence of NO_2(i.r.).

The residue, after removing gases at -120° C, was distilled into a 200 c.c. infrared cell equipped with CaF_2 windows. The CH_3NO_2 peak near 1625 cm^{-1} was used for quantitative purposes. NO_2 at room temperature exists as

$$2\ NO_2 \rightleftharpoons N_2O_4$$

NO_2 also has a strong absorption band at 1625 cm^{-1}, therefore, it interferes with the CH_3NO_2 peak in the mixture. To estimate the absorption due to NO_2 a peak at 1750 cm^{-1} was used, and the corresponding absorption at 1625 cm^{-1} was found from a calibration curve. This was subtracted from the total absorption at 1625 cm^{-1} and the remaining absorption was due to that of CH_3NO_2. To check the validity of the method, a standard mixture of CH_3NO_2 was prepared and analysis done.

Standard mixture.

CH_3NO_2 = 0.257×10^{-4} moles

NO_2 = 0.15×10^{-4} moles

A(1750) = 0.067

I-R 51

A(1625) = 0.60

From NO_2 calibration curve,

if A(1750) = 0.067, then A(1625) 0.15

A(1625) (mixture) - A(1625) (NO_2)

= 0.60 - 0.15

= 0.45

A(CH_3NO_2) = 0.45

From the calibration curve of CH_3NO_2

CH_3NO_2 = 0.25×10^{-4} moles

CH_3NO_2 from standard mixture = 0.257×10^{-4} moles

CH_3NO_2 from calculation = 0.25×10^{-4} moles.

Analysis of N_2O.

The analysis of N_2O in a mixture of NO and CO_2 presented a special difficulty. The vapour pressure of N_2O is such that it would probably be with both CO_2 and NO. The following procedures were carried out to assess the amount of nitrogen present as N_2O in the CO_2.

Caroxite method.

Materials condensible at liquid N_2 trap were warmed to $-120^\circ C$ and the mixture of CO_2, NO and N_2O collected as described earlier. The gases held at $-160^\circ C$ were passed through a U-tube containing caroxite, which was expected to retain all of the CO_2 but not the N_2O. The success of the method was dependent upon a prolonged pumping until the absorbent ceased to show any appreciable vapour pressure. A standard mixture of N_2O (1.32×10^{-4} moles) and CO_2 (1.64×10^{-4} moles) was analysed and the separation was reasonably satisfactory provided a $-120^\circ C$ trap was placed in series to hold up water vapour. Using this method we have estimated that N_2O could not be more than 1.4% of the total CO_2 produced in the system, by measuring the gas not absorbed by caroxite.

Hydrocarbons.

V.P.C. analysis and good carbon balance indicate that no hydrocarbon was present.

Hydrogen.

No hydrogen was present determinedby oxidation of the CO fracton over CuO. (i.e. no water was observed when the CO fraction was oxidized).

Chromatographic analysis.

The gas chromatographic apparatus was a Dynatronic Instrument Chromalyzer-100. The detector was of the thermal conductivity cell type.

Throughout the investigation a 10' long spiral column of 3/16" dimaeter copper tubing was employed. Sixty to two hundred mesh silica gel, obtained from B.D.H., was used as an adsorbent. The silica gel was dried over night in a furnace at 150°C. The column was then packed with dried silica gel as quickly as possible. After the column was attached to the apparatus it was heated up to 260°C and a flow of helium established for a long time to free the absorbent from moisture.

The sample cell was all pyrex glass with two separate arms of known volume. These arms could be filled with a partial or complete sample from the vacuum line and transferred to the chromatographic apparatus after flushing out the air from the side arms with nitrogen.

The carrier gas was helium under a pressure of 20 pounds per square inch at a flow which varied from 45 ml per minute for the reduced temperature (-78°C) to 30 ml per minute at room temperature studies. A good separation was obtained for each component in a standard mixture of N_2O and CO_2 at room temperature. It was estimated that the instrument could not detect less than approximately 0.006×10^{-4} moles of N_2O at its maximum sensitivity. The N_2O amount is, if present at all, therefore,

less than this quantity. This is contrary to what we have estimated the maximum quantity of N_2O to be from the caroxite method ($\sim 0.02 \times 10^{-4}$ moles). It must also be mentioned that in several identical runs N_2O estimated by caroxite method varied to an inadmissible extent.
The contradiction between the two methods was not resolved.
At lower temperature ($-78^{\circ}C$) where a mixture of CO, NO, CO_2 and N_2O from the product was passed through the column a good separation of CO and NO was obtained. On raising the column to room temperature no trace of N_2O was visible except for little shouldering near the CO_2 leading to an ambiguity.

Water.

Water was assumed to be the other major product of the reaction. The band at 3600 cm^{-1} in the infrared spectrum of the products condensible at $-120^{\circ}C$ is thought to be due to water. See the infrared spectrum of the $-120^{\circ}C$ product of run # 26 in the appendix.

RESULTS

1. Pressure-time data.

Examples of pressure-time curves are shown in figures 6,7,8, 9 and 10. Other examples are given in the appendix. The curves are of the sigmoid type; the reaction rate increasing to a maximum and then decreasing. Observe that in experiments 27, 28B and 29 the initial NO_2 and acetic acid pressures are identical, that in # 28B CH_3COOD was used, and in # 27 NO was added initially. Experiments #50 and # 52 illustrate pressure-time curves at high reactant pressures.

2. Material balance.

The carbon balance is shown for two experiments in Table 1, and nitrogen balance for two experiments in Table 2. More material balance data can be extracted from Table 5. The perfect agreement in some cases illustrated is fortuitous, because of analytical errors and also because of the possible presence of small quantities of N_2O and N_2. The products shown account for over 95% of the carbon balance and nitrogen in every case examined.

3. Summary of data.

The results of all experiments at 526.5°K are given in Table 7. Some results at lower temperature are given in the appendix.

4. Special experiments.

Analytical data from experiments using CH_3COOD, and with NO added are given in Tables 3 and 4.

5. Efforts to determine order using initial rate of pressure change.

When kinetic investigations in systems containing NO_2 are carried out at high temperatures the reaction

$$NO_2 \rightleftharpoons NO + \frac{1}{2} O_2$$

becomes important. Some work has been carried out without a consideration of the effect of decomposition of NO_2, for example see reference(10). Gagarina and Emanuel(11) have, in the reaction between NO_2 and CH_4, attempted to overcome the problem by introducing NO_2 first, allowing time for the attainment of equilibrium before introducing the CH_4. In the present study the initial rate of pressure rise was measured and from this was subtracted the rate of pressure rise caused by decomposition of NO_2. The method proved unsuccessful and reaction orders could not be obtained; complete details of the attempted corrections follow.

According to Ashmore and Burnett(12) the initial rate of the reaction

$$NO_2 \rightleftharpoons \frac{1}{2} O_2 + NO$$

is

$$\frac{d}{dt} [NO_2] = (k_1 + k_2) [NO_2]^2$$

where

$$k_1 = 10^{12.6} e^{-\frac{26,900}{RT}} \text{ cc mole}^{-1} \text{ sec}^{-1}$$

and $k_2 = 10^{11.89} e^{-\frac{23,900}{RT}}$ cc mole^{-1} sec^{-1}

From these rate constants the correction to the pressure rise due to decomposition of NO_2 is,

$$\left.\frac{\Delta P}{\Delta T}\right._{\text{initial}} = 1.85 \times 10^{-5} \times P^2{NO_2} \text{ cm sec}^{-1}$$

from which

$k_1 = 28.2,$

$k_2 = 93.4,$ and

$k_1 + k_2 = 121.6$ cc moles^{-1} sec^{-1}

in the system.

The corrections for various initial pressures of NO_2 are given in Table 5.

In a separate experiment we measured the rate of decomposition of NO_2, see run # 40 in the appendix. At 6 cms pressure the measured initial rate of decomposition was found to be approximately 0.17×10^{-3} cm sec^{-1}. From it the rate constant k was calculated to be 0.47×10^{-5} cm^{-1} sec^{-1}. Using this value of the rate constant the correaction for various initial pressures of NO_2 are listed in Table 6. This is a very rough correction for the second order rate constant is actually dependent upon the concentration of NO and is decreasing over the interval. See reference (12) for the details. In addition, in our experiments NO is produced independently, therefore the rate of NO_2 decomposition would be smaller than in pure NO_2.

Using the correction of Tables 5 and 6 the corrected and uncorrected rates have been plotted in Figs. 11 and 12 for various initial pressures of acetic acid and NO_2.

For the experiments using 2 cm. of CH_3COOH and 6 cm of NO_2 the average deviation in rate calculated from 21 experiments is shown on the figures. The difference in rates observed in pairs of experiments at other pressures (e.g. those at high acetic acid pressure) appears to be greater than that expected from any experimental error*. We believe this to have some other cause, such as a non-reproducible surface effect.

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* After run # 36 we discovered a drift in the standard cell used. This could have caused a temperature reading ~1° below the true value for some of the experiments. From the approximate temperature dependence observed, we note that this could not have caused such large deviations.

The corrections using the Ashmore rate constants are too large (see Figure 11); the rough correction using data obtained in this study is reasonable. However the uncertainty in the correction, the small number of data, and the scatter in the data prevent a determination of the order. All that can be stated is that the rate is dependent upon the concentrations of NO_2 and CH_3COOH (as well as NO).

Another fault with the pressure increase methods is that the stoichiometry is a function of reactant concentration, see Table 7. A given pressure rise may, therefore, represent slightly varying quantities of reactants consumed or products formed. Future work should probably make use of the method of reference(11) and initial rate of product formation should be obtained as a function of the reactant concentrations.

6. Fate of the methyl group.

The assumption is made (see Discussion) that the carboxyl group appears entirely as CO_2. With this assumption the mole fraction of CH_3 appearing as CO, CO_2 or CH_3NO_2 has been calculated and the results are given in Table 8.

7. Data at low temperature.

A number of experiments were carried out at 197°C. The sigmoid pressure time curve is found at this temperature also. The product distribution is approximately the same as at 253°C but the total pressure change is smaller.

An induction period was observed in all experiments at 197°C but not at ~253°C. See the low temperature data in the appendix.

DISCUSSION

Autocatalysis and Isotope Effect.

The shape of the pressure-time curve shows autocatalysis(13); the rate passes through a maximum at about 30% of the reaction. Nitric oxide was found to increase the rate as can be seen in Experiment # 27, Fig.8. The catalytic behaviour of other reaction products was not tested.

Prior to this investigation formic acid was the only molecule containing C,H and O atoms* known to be autocatalytic in nitric oxide, with the exception of methane(11), which was studied at a relatively high temperature. In an unpublished work(2), P. E. Yankwich and Donald Barton therefore, held the view that autocatalysis is connected to the carboxyl group in an important manner. The present work on acetic acid allowed a test of this hypothesis - although kinetic data with respect to nitric oxide are yet to be obtained in future work on this problem. A recent work on methanol and nitrogen dioxide, now in progress in this laboratory(14), also shows autocatalysis. The methanol study therefore contradicts the original supposition but nevertheless offers an interesting problem in itself. The reaction with D- acid (with D on the carboxyl group), as can be seen in run # 28B, Fig.7, indicates that a hydrogen abstraction reaction is kinetically important.

* We exclude the chloromethanes because autocatalysis in those cases is believed to involve chlorine.

2. Some possible products from the methyl radical.

(i) Methyl nitrate (CH_3ONO_2).

The decomposition of methyl nitrate has been studied(15,16). At 253° the preexponential factor, activation energy and rate constant are 2.5×10^{14}, 39000 cal. mole^{-1} and 8.87×10^{-3} sec^{-1}. From these date one can assess the half-life as 100 sec for the decomposition. The following stoichiometry has been reported:

$$\begin{aligned} CH_3ONO_2 \rightarrow\ & 0.95NO + 0.025N_2 \\ & + 0.75CO + 0.25CO_2 \\ & + 0.7H_2 + 0.8H_2O. \end{aligned}$$

The nitrate, therefore, cannot be present as a final product as the rate of decomposition is rapid.

(ii) Methyl nitrite (CH_3ONO).

Steacie and Shaw(17) studied the thermal decomposition at temperatures between 170 and 240°C; the preexponential factor, activation energy and rate constant (253°C) are 1.84×10^{13} sec^{-1}, 36,400 cal mole^{-1} and $\sim 14.7 \times 10^{-3}$ sec^{-1} respectively. The reaction would be rapid at 253°C with a half-life of about 50 seconds. A later study(18) which consisted of a detailed analysis of the products, indicated CO and N_2O as byproducts of the reaction. In a complete course of decomposition one would therefore expect formaldehyde*, methanol*, nitric oxide,

* Both are oxidized by NO_2 and would not appear in this reaction as final products.

and water together with CO and N_2O as the minor products.

(iii) Nitrosomethane (CH_3NO_2).

The reaction between methyl radical and nitric oxide has been extensively studied, and no attempt will be made to completely review the problem here. D. E. Hoare(19) studied the reaction, at 200°C, in which methyl radicals were produced by the photolysis of acetone. The nitrosomethane formation was observed to be third order with acetone as M.

$$CH_3 + NO + M \rightarrow CH_3NO + M$$

It was also shown that the nitrosomethane formed reacts with methyl radical or nitric oxide. (At high pressures of NO no reaction such as $CH_3 + CH_3 \rightarrow C_2H_6$ was detectable. This observation is of special interest in the present investigation as we could not observe any ethane in the presence of NO and NO_2 in the system:.

In another study Batt and Gowenlock(20 measured the rate of isomerization of CH_3NO to CH_2NOH. The rates were so sensitive to surface conditions and other factors that it is difficult to predict the reactions of CH_3NO in our system. There appears to be a possibility that some CH_2NOH could be formed.

They also found that NO accelerated the disappearance of CH_3NO and that a compound was formed which produced N_2 when condensed and then warmed.

Christie(21) also studied a reaction of NO with CH_3NO in the gas phase which produced N_2. The absence of appreciable N_2 in this study excludes the possibility of reactions proposed by Batt and by Christie; if CH_3NO were formed some N_2 might have been expected, at least in the later stages of the reaction when NO concentration is large.

(iv) Formaldoxime, CH_2NOH.

Gowenlock and Trotman(22) have shown that CH_3NO dimerizes in the gas phase and rearranges to give formaldoxime in solution. The equilibrium constant for dimer formation was studied in detail by Christie(21). The results show that dimer formation would not be important in this study. See reference(23) for a discussion of this and other problems related to CH_3NO and CH_2NOH. As mentioned in the preceeding section and in reference(23) it is impossible to extrapolate from one set of conditions to another. For the decomposition of oxime*(24) the pre-exponential factor, activation energy and first order rate constant (253°) are, $10^{9.5}$ sec^{-1}, 39,000 cal and 1.99×10^{-1} S^{-1} giving $t \frac{1}{2}$ of about 10^6 seconds. If CH_3NO isomerizes to oxime, the oxime might be stable. However, the decomposition of CH_3NOH is accelerated by air and by NO(24), and both O_2 and NO are present in this system. The good carbon and nitrogen balance with the measured products shows that CH_2NOH is either not formed in large quantities or it is oxidised by NO_2 or decomposed to the observed products of the reaction. Another piece of evi-

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* formaldoxime

dence which led us to this conclusion is from the experiment with added NO, Table 4, which shows no detectable change in stoichiometry of the reaction within the analytical errors. This further suggests that if CH_3 and NO react substantially to form CH_3NO the products are similar to those from CH_3 and NO_2; or CH_3 and NO do not react appreciably. We suppose that the former statement is inadequate and the latter is preferably true.

(v) Nitromethane (CH_3NO_2).

Nitromethane is the only observed nitro product of the methyl radical and NO_2 in this study. The decomposition of nitromethane has been studied$^{(25)}$. The pre-exponential factor, activation energy and first order rate constant for decomposition are, 2.7×10^{13} sec^{-1}, 50,000 cal/mole and $\sim 4.80 \times 10^{-8}$ sec^{-1} respectively at 253°C. The half-life is $\sim 10^7$ seconds. We thus expect that any nitromethane formed would remain intact during the course of the experiment.

3. Some reasonable elementary reactions.

The elementary reactions [1] to [26] are expected to occur, and account qualitatively for the products, but they do not account for the variation in stoichiometry with reactant quantities as illustrated in Table 7.

[1] $CH_3COOH + No_2 \rightarrow CH_3CO_2 + HONO$

[2] $CH_3CO_2 \rightarrow CH_3 + CO_2$

[3] $CH_3 + NO_2 \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} CH_3NO_2^*$

[3a] $CH_3NO_2^* + M \rightarrow CH_3NO_2 + M$

[4] $CH_3 + NO_2 \rightarrow CH_3O + NO$

[4a] $CH_3 + NO_2 \underset{k_{-4a}}{\overset{k_{4a}}{\rightleftharpoons}} CH_3ONO^*$

[5] $CH_3ONO^* + M \rightarrow CH_3ONO + M$

[6] $CH_3ONO^* \rightarrow CH_3O + NO$

[6a] $CH_3 + NO + M \rightarrow CH_3NO + M$

[7] $CH_3O + NO_2 \rightleftharpoons CH_3ONO^*_2$

[7a] $CH_3ONO^*_2 + M \rightarrow CH_3ONO_2 + M$

[7b] $CH_3ONO_2 \rightleftharpoons CH_3O + NO_2$

[7c] $CH_3O \rightarrow HCHO + H$

[7d] $CH_3O + NO_2 \rightarrow HCHO + HONO$

[8] $\mathrm{HCHO + NO_2 \rightarrow HCO + HONO}$

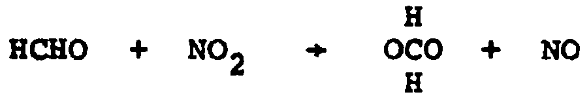
[9] $\mathrm{HCO + NO_2 \rightarrow HCO_2 + NO}$

[10] $\mathrm{HCO + M \rightarrow H + CO + M}$

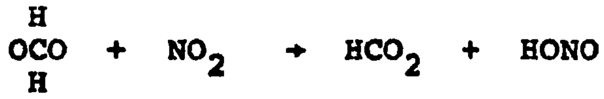
[11] $\mathrm{HCO_2 + M \rightarrow H + CO_2 + M}$

[12] $\mathrm{HCO_2 + NO_2 \rightarrow CO_2 + HONO}$

[13] $\mathrm{HCO + NO_2 \rightarrow CO + HONO}$

[14] 
$\mathrm{HCHO + NO_2 \rightarrow \overset{H}{\underset{H}{OCO}} + NO}$

[15] 
$\mathrm{\overset{H}{\underset{H}{OCO}} + M \rightarrow \underset{H}{OCO} + M + H}$

[15a] 
$\mathrm{\overset{H}{\underset{H}{OCO}} + NO_2 \rightarrow HCO_2 + HONO}$

[16] $\mathrm{CH_3COOH + HONO \rightarrow CH_3CO_2 + HOH + Ne}$

[17] $\mathrm{HONO + M \rightleftharpoons OH + NO + M}$

[18] $\mathrm{CH_3COOH + OH \rightarrow CH_3CO_2 + HOH}$

[19] $\mathrm{CH_3 + O_2 + M \rightarrow CH_3O_2 + M}$

[20] $\mathrm{CH_3O_2 \rightarrow HCHO + OH}$

[21] $CH_3O_2 + OH \rightarrow CH_3OH + O_2$

[22] $CH_3COOH + CH_3O \rightarrow CH_3COO + CH_3OH$

[23] $CH_3OH + NO_2 \rightarrow CH_3O + HONO$

[24] $CH_3COOH + NO \rightarrow CH_3COO + HNO$

[25] $H + NO_2 + M \rightarrow HNO_2 + M$

[25a] $H + NO_2 \rightarrow OH + NO$

[26] $2HNO_2 \rightarrow H_2O + NO + NO_2$

The above listed reactions are supported from previous and present experimental work. The isotope effect pointed out earlier suggests step [1]. There could also be a possibility of hydrogen abstraction from methyl group,

[27] $CH_3COOH + NO_2 \rightarrow CH_2COOH + HNO_2$

Since CH_4 does not react rapidly with NO_2 at this temperature, and we suppose that methyl has some of the properties of CH_4, we ignore the possibility of reaction [27] to occur. However this argument is not quite certain and [27] can not be definitely excluded.

The proposed acetoxy radical, CH_3CO_2, may decompose or react with some abundant species such as NO_2 and NO, e.g.

[28] $CH_3CO_2 + NO_2 \rightarrow CH_3NO_2 + CO_2$

[2] $CH_3CO_2 \rightarrow CH_3 + CO_2$

Pollard and Pedler(4) have supposed reaction [2] to occur in their acetaldehyde and NO_2 reaction. This type of decomposition has also been postulated by Christie, Collins and Voisey(26) in a study of the reaction between acetyl radicals and nitric oxide.

The rate constant for [2] in hydrocarbon solvents was estimated to be $1.6 \times 10^9 S^{-1}$ at 60° with an activation energy of 6.6 kcal(27) and would therefore be expected to be the dominant reaction in competition with [28].

Methyl radicals from step [2] enter into a set of competing reactions from [3] to [6a]. Because of such competition the overall reaction initiated by hydrogen abstraction becomes complicated. The nitromethane, reaction [3], possesses an excess energy and may break up yielding the original, as shown by [3a]. Useful bond strengths are(28):

$$D(CH_3\text{-}NO_2) = 57.3 \text{ Kcal mole}^{-1}$$

$$D(CH_3\text{-}ONO) = 56.2 \text{ Kcal mole}^{-1}$$

$$D(CH_3O\text{-}NO) = 38.9 \text{ Kcal mole}^{-1}$$

From the bond energies it can be seen that stabilization of the nitrite is much more difficult than is the stabilization of nitromethane. The C-O bond formed is not the weakest bond in the molecule. The O-N bond needs only 38.9 Kcal for its rupture and consequently it is almost impossible to stabilize nitrite in the gas-phase. In the gas-phase one might expect stable nitrite molecules not to be formed at all by direct association of CH_3 and NO_2, although they may be produced by reaction [6b].

$$[6b] \quad M + CH_3O + NO \rightarrow CH_3ONO + M$$

in the later stages of the reaction when NO concentration is appreciable. Gray and Style(29) have shown that in the acetaldehyde and NO_2 reaction the methyl radicals which are produced form a small amount of methyl nitrate in the initial stages of the reaction. It was of considerable interest to notice that methyl nitrite did not appear until the end of the reaction. This, therefore, confirms the view that in the gas-phase reaction the direct association of methyl radical and NO is not possible. Pedler and Pollard(4) suggest that the addition of methyl radical and NO_2 to form nitrite has a greater activation energy than the corresponding addition reaction giving CH_3NO_2.

The temperature dependence of the stoichiometry is small in the present study but the proportion of CH_3 going to CH_3NO_2 appears to be greater at 197°C (see appendix) supporting Pedler and Pollard.

The bond strengths in CH_3NO_2 and CH_3ONO compounds are such that one would expect a greater stabilization of the association product forming CH_3NO_2 and that it would be impossible to stabliize any appreciable CH_3ONO at the moderate pressures used here. The rate of formation of CH_3NO_2 might therefore be in a strongly pressure dependent region. We observe an increasing trend of nitromethane with increasing pressures of acetic acid, as can be seen from the CH_3NO_2 and pressure change data in Tables 6 and 7. We presume that the substrate molecule functions here as a third body to bring about the stability of CH_3NO_2.

One would expect a similar effect by increasing the NO_2 concentration. However we did not observe this trend. A glance at Table 7 shows that the ratio $[CO + CO_2] / [CH_3NO_2]$ from CH_3 (a fall in CH_3NO_2 quantity with increasing NO_2) is inconsistent with the above argument. It seems that at higher NO_2 pressure the reaction is complicated in some different manner and with our limited data we are unable to resolve this problem. We can only say that either the proposed path for formation of CO, CO_2 and CH_3NO_2 from methyl radical is incorrect or only partly correct, that is there are some other reactions to explain their formation at higher NO_2 concentration.

The NO_2 molecule is triangular in shape and there will be approximately twice as many collisions at oxygen as at nitrogen. One might therefore expect the number of nitrite producing reactions to be twice that of CH_3NO_2 producing reactions. In the mechanism proposed here all of the nitrite type of collisions produce CO and CO_2. The maximum ratio $[CH_3NO_2] / [CO + CO_2]$ would be 1/2 if all of the CH_3NO_2 were stabilized; note that this ratio is exceeded at high CH_3COOH pressure.

It has been discussed before that the reaction [5] will be improbable. The methoxy radical produced in reaction [4] or [6] might further complicate the mechanism by abstracting a hydrogen atom from the substrate molecule.

[29] $CH_3O + CH_3COOH \rightarrow CH_3OH + CH_3CO_2$

Besides the abstraction reaction [29], methoxy radical can also produce HCHO by reactions [7c] and [7d]. The methoxy radicals may also give rise to methyl nitrate via reactions [7] and [7a]; the formation and stability of this compound has been discussed earlier. See reference(30) on the reactions of nitrates.

Steps [8] to [13] follow in accordance with the previous work of Donald Barton(6). This sequence of reactions presents an interesting feature of the mechanism of formation of CO and CO_2 from methyl radical. The average value of $\frac{[CO]}{[CO + CO_2]}$ from the CH_3 group, where NO_2 pressure is not high, as observed in this investigation, is 0.67 which compares with that of Pollard and Wyatt of 0.63 at 220°C in the reaction between HCHO and NO_2. This supports the idea that CO and CO_2 originate from formaldehyde. However, in the reaction of HCHO with NO_2, the [CO] / [CO_2] ratio decreases as NO_2 increases, but the opposite was found in this study. Therefore formaldehyde may not be the source of CO and CO_2 in this reaction, or at least not the only source. We propose [14], [15] as HCHO might receive an oxygen atom. HCO is thought to decompose very rapidly so that [9] may not occur very much. We have written HONO as a chain carrier and also OH from [17] and [20]. The ΔH for [17] can be calculated as ∿ 50 Kcal.(36) This would give a high concentration of HNO_2. Pedler and Pollard(4) have suggested that HNO_2 formed can disappear bimolecularly as in reaction [26]. This thermoneutral reaction [26] is more likely and is to be preferred over reaction [17].

Another possible way of removal of HNO_2 could be that proposed by McDowell and Thomas(32),

$$CH_3O + HNO_2 \rightarrow CH_3OH + NO_2$$

but we have no evidence for or against it.

The reaction [25]

$H + NO_2 \rightarrow HNO_2$

was mentioned in connection with the NO_2 sensitized reaction between hydrogen and oxygen by Lewis and Von Elbe(33). They stated that the reaction is exothermic by about 80 Kcal. The association would be rapidly followed by dissociation into OH and NO. The reaction has more recently been studied by others, for example see reference(34).

Reaction [24] is a possible step giving NO catalysis. This cannot be definitely suggested since we do not have enough kinetic information. In the reaction between formic acid and NO_2 [2] the order is approximately 2/3 in NO and a mechanism is not yet found which gives this order.

The oxygen produced due to NO_2 decomposition can complicate the reaction further. Reactions [19], [20] and [21] are taken as the possible reactions in accordance with reference(35) and other references therein*. Reaction [22] seems quite likely as CH_3O may abstract hydrogen from substrate molecule; Pollard(4) has also suggested it. One would think that high CH_3NO_2 is due to formation of CH_3OH, if CH_3OH could be converted to CH_3NO_2, but Donald Barton in a recent study did not observe any nitromethane formed in the reaction between methanol and NO_2. Therefore while it seems likely that [22] occurs, it does not account for the high CH_3NO_2 with increasing acetic acid.

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* Note that from reaction [20] and [7C] O_2 has the same effect on products as NO_2 through [4] and [7C].

4. Suggestions for further work.

(1) A kinetic study using the method of reference(11), introducing the NO_2 first, adjusting pressures so as to separate the effects of NO_2, NO and O_2.

(2) A study of the rate-time data, and time and extent of reaction at which the maximum rate occurs.

(3) A more detailed study of the rate of formation of the products as a function of reactant and catalyst pressures.

(4) The effect of inert gases should be studied in order to observe the effect upon the rate of formation of CO or CO_2 and of CH_3NO_2 from CH_3.

(5) A study of the effect of O_2 on the rate and products, if possible, see item (1), to try to separate the two different pathways of oxidation, by O_2 and by NO_2.

(6) An extensive study of the effect of NO is required, to determine the order with respect to NO.

(7) A detailed isotope effect study, to see the effect of placing D on the methyl group, for example.

(8) Rates of formation of products should be determined, as opposed to pressure rise.

(9) Modifications of the apparatus are required; continuous photometric estimation of NO_2, a routine instrumental method of analysis, etc.

Appendix

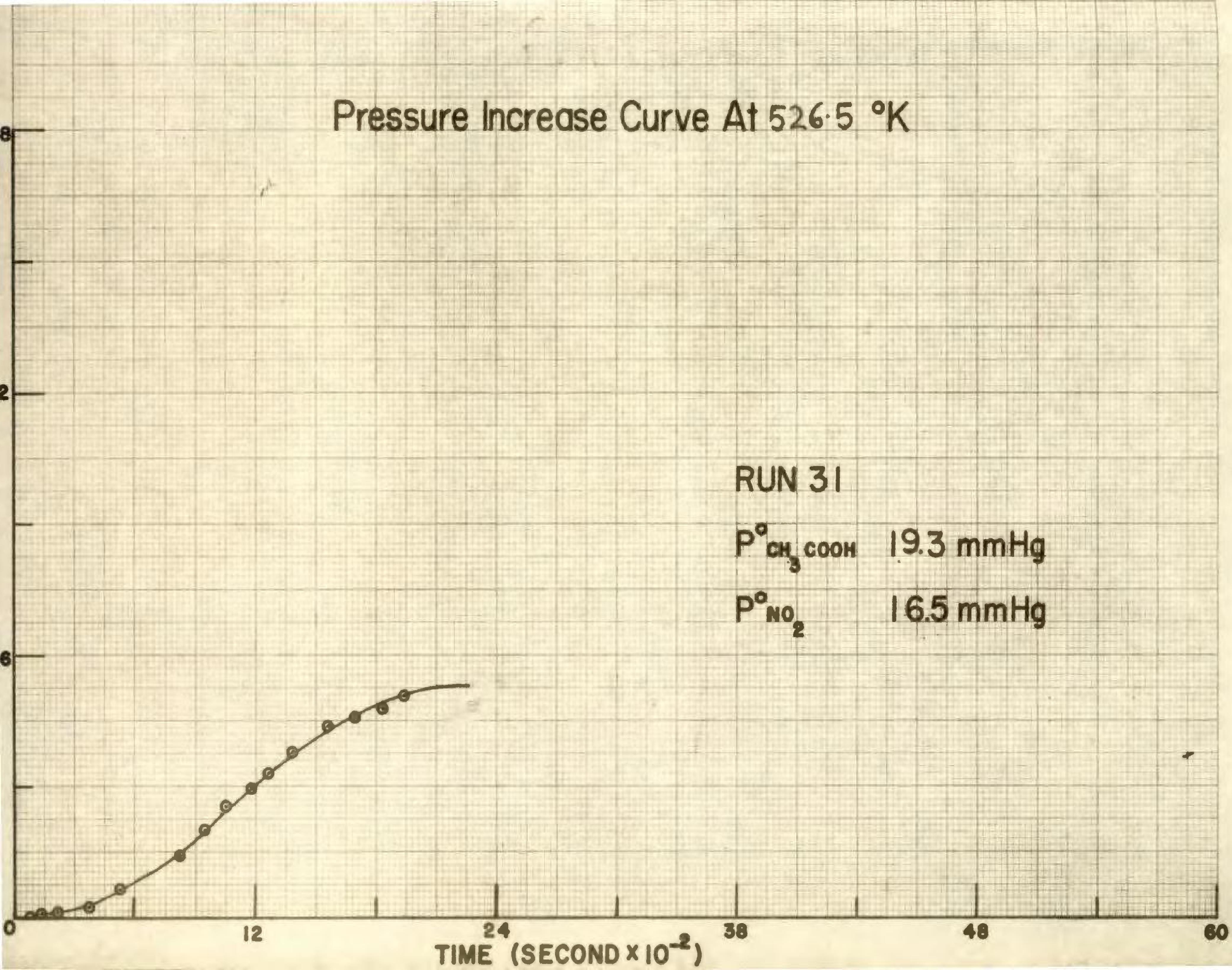
A1. Pressure-time curves, run 31.

A2. Some results at low temperature, run 31.

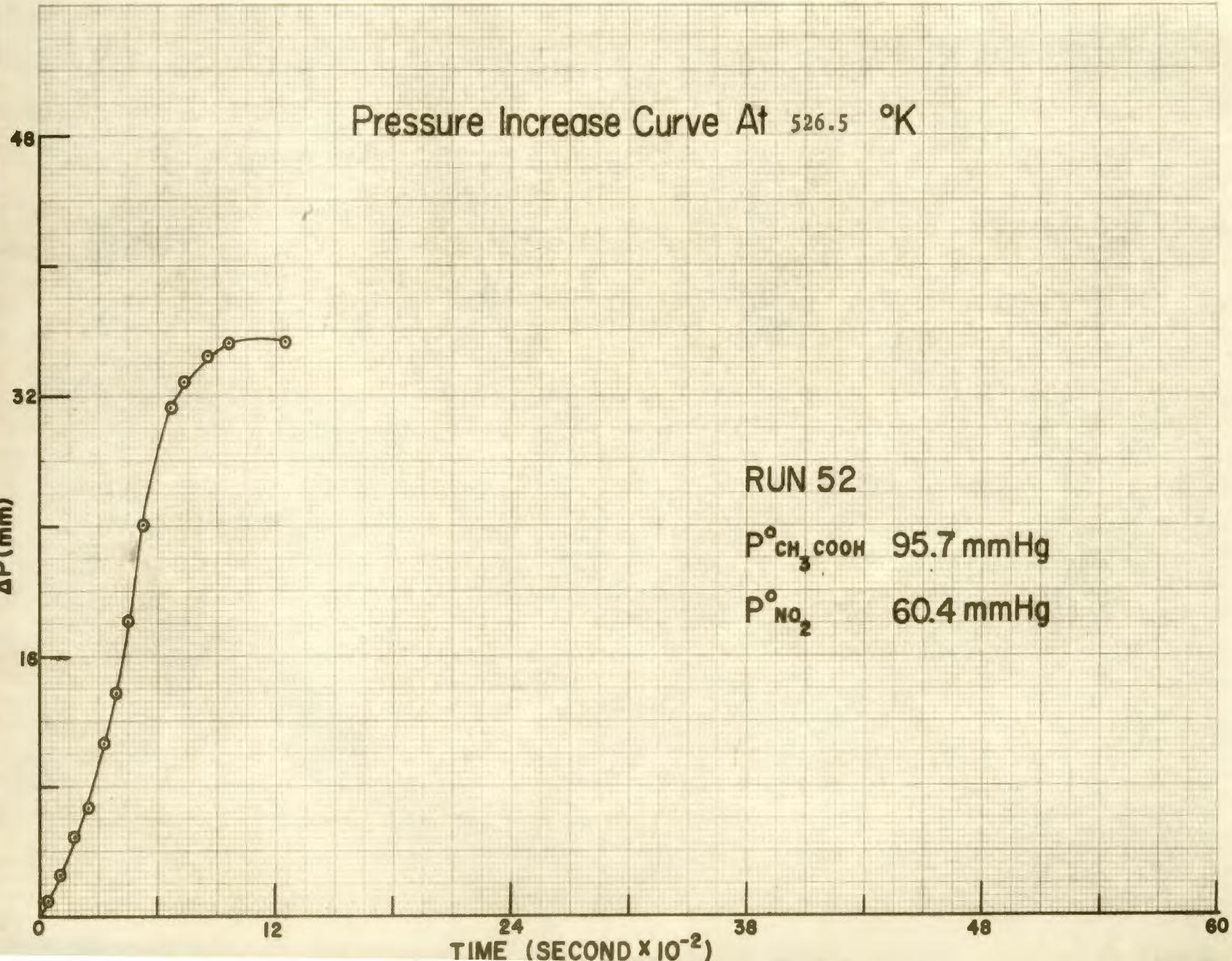
A3. IR spectrum of condensable products, run 26.

A4. IR spectrum of condensable products, run 51.

A1 Pressure-time curve, run 31.


Pressure Increase Curve At 526·5 °K
RUN 31
$P^{\circ}_{CH_3COOH}$ 19.3 mmHg
$P^{\circ}_{NO_2}$ 16.5 mmHg
8
2
6
0
0
12
24
38
48
60
TIME (SECOND × 10^{-2})

A2 Pressure-time curve, run 52.


Pressure Increase Curve At 526.5 °K

RUN 52

$P^{\circ}_{CH_3COOH}$ 95.7 mmHg

$P^{\circ}_{NO_2}$ 60.4 mmHg

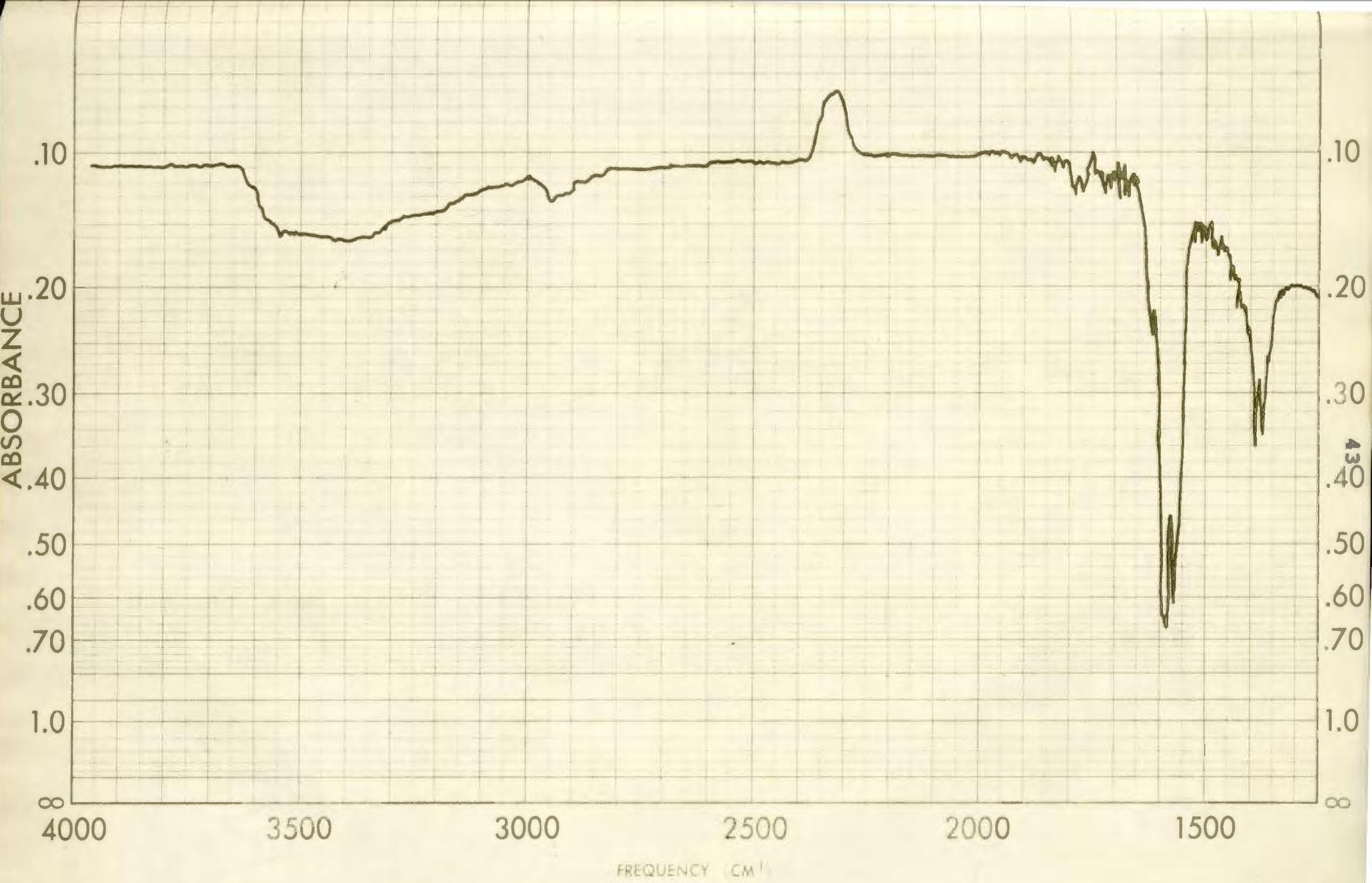
Some Results at Low Temperature (464°K)

Run Number	Moles x 10^4				
	CH_3COOH	NO_2	CO	CO_2	CH_3NO_2*
11	1.28	4.42	.50	1.57	.50
12	1.28	4.42	.50	1.66	.41
17	1.28	4.40	.59	1.56	.37

* Calculated assuming no other carbon product.

The activation energy for pressure rise is about 35 kcal but this includes a contribution from the NO_2 decomposition so the contribution due to the oxidation reaction cannot be determined.

A3. IR spectrum of condensable products, run 26.



SAMPLE CH_3NO_2 Brown Run 26 with H_2O All water	CURVE NO.	SCAN SPEED	OPERATOR
	CONC.	SLIT	DATE Dec 11 64
ORIGIN was warmed and let	CELL PATH	REMARKS	
SOLVENT in to Cell.	REFERENCE		

PERKIN ELMER

A4. IR spectrum of condensable products, run 51.

SAMPLE -120 Residue

expt. 51

ORIGIN

SOLVENT

CURVE NO.

CONC.

CELL PATH

REFERENCE

SCAN SPEED

SLIT N

OPERATOR Rud

DATE July 31 65

REMARKS

PERKIN-ELMER

Experiment No. 40

Rate of Pressure Increase for Pure NO_2 at 253.5°C

t(s)	P(cm)
0	6.03
95	6.03
210	6.06
320	6.07
748	6.14
996	6.25
1270	6.25
1690	6.30
2400	6.42
2554	6.42
2936	6.42
3000	6.42

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TABLE I

Carbon Balance at 526.5°K

Run 25

Material	Moles x 10^4
CH_3COOH	1.21
NO_2	3.73
CO	0.61
CO_2	1.48
CH_3NO_2	0.32
Total carbon (initial)	2.42
Total carbon in the product	2.41

Run 26

Material	Moles x 10^4
CH_3COOH	1.21
NO_2	3.73
CO	0.62
CO_2	1.50
CH_3NO_2	0.29
Total carbon (initial)	2.42
Total carbon in the product	2.41

TABLE II

Nitrogen Balance at 526.5°K

Run 30

Material	Moles x 10^4
CH_3COOH	1.21
NO_2	1.78
CO	0.24
CO_2	0.85
NO	1.65
CH_3NO_2	0.13
Total Nitrogen (initial)	1.78
Total Nitrogen in product	1.78

Run 31

Material	Moles x 10^4
CH_3COOH	1.19
NO_2	1.02
CO	0.12
CO_2	0.54
NO	0.88
CH_3NO_2	0.08
Total Nitrogen (initial)	1.02
Total Nitrogen in the product	0.96

TABLE III

Analysis with CH_3COOD at 526.5°K

Run 28B

CH_3COOD = 1.21×10^{-4} moles

NO_2 = 3.73×10^{-4} moles

Δ P = 4.68 cms Hg

CO = 0.61×10^{-4} moles

*CO_2 = 1.71×10^{-4} moles

*NO = 2.49×10^{-4} moles

*CH_3NO_2 = 0.27×10^{-4} moles

*Products analysis was delayed for a week.

TABLE IV

Analysis of Experiment with NO at 526.5°K

Run # 27

CH_3COOH = 1.21×10^{-4} moles

NO_2 = 3.73×10^{-4} moles

NO (initial) = 1.22×10^{-4} moles

ΔD = 4.76 cms Hg

CO = 0.62×10^{-4} moles

CO_2 = 1.51×10^{-4} moles

NO (final) = 4.20×10^{-4} moles

CH_3NO_2 = 0.27×10^{-4} moles

*N_2O = 0.057×10^{-4} moles

* Using fresh absorbent.

TABLE V

Correction to Initial Rate using Ashmore's data

Expt. No.	Pressure of NO_2	$1.85 \text{ x } 10^{-5} \text{x} P^{2}_{NO_2}$	Correction cm. sec^{-1}.
30	2.79 cms.	$1.85 \text{ x } 10^{-5} \text{ x } (2.79)^{2}$	$0.144 \text{ x } 10^{-3}$
31	1.62 cms.	$1.85 \text{ x } 10^{-5} \text{ x } (1.62)^{2}$	$0.049 \text{ x } 10^{-3}$
43	6.00 cms.	$1.85 \text{ x } 10^{-5} \text{ x } (6.00)^{2}$	$0.666 \text{ x } 10^{-3}$
54	.69 cms.	$1.85 \text{ x } 10^{-5} \text{ x } (8.69)^{2}$	$1.40 \text{ x } 10^{-3}$

TABLE VI

Correction to Initial Rate Using Data from this Study

Expt. No.	Initial pressure of NO_2	$0.47 \times 10^{-5} P^2_{NO_2}$	Correction cm $\overline{\text{sec}}^{-1}$
30	2.79 cms.	$0.47 \times 10^{-5} \times (2.79)^2$	0.0367×10^{-3}
31	1.62	$0.47 \times 10^{-5} \times (1.62)^2$	0.0124×10^{-3}
43	6.00	$0.47 \times 10^{-5} \times (6.00)^2$	0.169×10^{-3}
54	8.69	$0.47 \times 10^{-5} \times (8.69)^2$	0.355×10^{-3}

TABLE VII

Summary of Results at 526.5°K

Run	CH_3COOH	NO_2	ΔP cm.	CO	CO_2	NO	CH_3NO_2	Rate x 10^3 cm sec^{-1}
19	1.96 cm 1.21	6.10 cm 3.77	4.67	0.64	1.52	-	-	1.20
21	1.96 cm 1.21	6.20 cm 3.84	4.78	0.60	1.52	-	-	1.10
22	1.96 cm 1.21	6.21 cm 3.84	-	-	-	-	-	1.07
23	1.96 cm 1.21	6.19 cm 3.83	4.68	-	-	-	-	0.98
24	1.96 cm 1.21	6.04 cm 3.74	4.82	0.63	1.56	-	-	-
25	1.96 cm 1.21	6.05 cm 3.74	4.62	0.61	1.50	-	0.32	1.12
26	1.96 cm 1.21	6.00 cm 3.72	4.70	0.62	1.50	-	0.29	1.38

TABLE VII (cont'd)

Run	CH_3COOH	NO_2	ΔP cm	CO	CO_2	NO	CH_3NO_2	Rate x 10^3 cm sec^{-1}
28A	1.96 cm 1.21	5.96 cm 3.69	4.66	0.62	-	-	0.29	0.91
29	1.96 cm 1.21	6.06 cm 3.75	4.61	0.62	-	-	0.29	1.00
30	1.96 cm 1.21	2.79 cm 1.73	2.30	0.24	0.85	1.64	0.13	0.53
31	1.93 cm 1.19	1.62 cm 1.00	1.35	0.12	0.54	0.88	0.08	0.35
34	1.02 cm 0.63	5.98 cm 3.69	2.43	0.29	0.82	-	0.22	0.70
36	4.55 cm 2.81	6.00 cm 3.71	4.54	0.58	1.68	3.07	0.34*	1.20
38	1.08 cm 0.67	5.99 cm 3.72	-	-	-	-	-	0.620

TABLE VII (cont'd)

Run	CH_3COOH	NO_2	ΔP cm.	CO	CO_2	No	CH_3NO_2	Rate x 10^3 cm.sec^{-1}
39	5.62 cm 3.48	5.98 cm 3.71	-	-	-	-	-	1.72
42	1.94 cm 1.20	6.00 cm 3.72	4.60	0.61	1.50	-	0.24	0.90
44	1.96 cm 1.21	6.05 cm 3.74	-	-	-	-	-	0.92
45	1.98 cm 1.23	5.98 cm 3.71	-	-	-	-	-	0.98
46	1.94 cm 1.20	6.05 cm 3.74	-	-	-	-	-	1.10
49	1.02 cm 0.63	6.03 cm 3.74	-	-	-	-	-	0.68
50	5.60 cm 3.47	6.01 cm 3.72	-	-	-	-	-	2.15
51	4.54 cm 2.81	6.08 cm 3.76	4.51	0.50	1.72	3.12	0.53	1.50

TABLE VII (cont'd)

Run	CH_3COOH	NO_2	ΔP cm.	CO	CO_2	NO	CH_3NO_2	Rate x 10^3 cm sec^{-1}
52	9.57 cm	6.04 cm						
	5.92	3.74	3.55	-	-	-	-	2.35
53	9.57 cm	6.07 cm						
	5.92	3.75	3.95	-	-	-	-	2.90
54	1.96 cm	8.69 cm						
	1.21	5.37	4.77	0.61	1.59	-	-	2.00

* Two similar experiments (# 36 and # 51) produced widely different quantities of CH_3NO_2. For use in the discussion section the CH_3NO_2 data of # 36 has been omitted for the following reasons:

(1) The CH_3NO_2 analysis was unavoidably delayed,

(2) The N balance, which is normally good is very poor in this experiment, while the quantity of NO is identical within experimental error to that in # 51.

(3) The pressure rise is similar to that in # 51, and in the absence of any products, other than those reported, this smaller pressure rise indicates a large quantity of CH_3NO_2.

Occasionally attempts were made to find N_2 in the CO fraction and N_2O in the CO_2. In run # 19, .02 x 10^{-4} of gas not absorbed in caroxite was found, similarly .057 x 10^{-4} moles was found in run # 27. In run # 52 in the CO fraction, .006 x 10^{-4} moles of gas was not oxidized by CuO.

≠ Pressure changes and analysis are for reactions which were allowed to go to completion. Molar quantities are moles x 10^4.

TABLE VIII

The Fate of the Methyl Group at 526.5°K≠

CH_3COOH Initial Pressure cm.	NO_2 Pressure cm.	moles$\times10^4$ CH_3	moles$\times10^4$ CO	moles$\times10^4$ CH_3NO_2	moles$\times10^4$ CO_2	$\frac{CO}{CO + CO_2}$	CO	CH_3NO_2	CO_2
1.96	1.62	.36	.12	.08	.17	.41	.33	.22	.47
1.96	2.79	0.61	0.24	0.13	0.24	0.50	0.39	0.21	0.39
*1.96±01	6.06±.05	1.21±.01	0.62±.01	0.30±.01	0.31±.01	0.67	0.50	0.24	0.25
1.96	8.69	1.21	0.61	0.22	0.38	0.62	0.55	0.18	0.31
1.02	5.98	0.66	0.24	0.22	0.16	0.64	0.43	0.33	0.24
*1.96±.01	6.06±.01	1.21±.01	0.62±.01	0.30±.01	0.31±.01	0.67	0.50	0.24	0.25
4.55	6.00	1.30	0.58	0.34	0.38	0.60	0.45	0.26	0.29
4.54	6.08	1.38	0.50	0.53	0.35	0.59	0.36	0.38	0.25

*Change and average deviation using all appropriate data in Table 7.

≠ CO_2 is calculated using the assumption that all of the carboxyl group reacts to CO_2; is mole fraction.

FIGURE 1

A schematic diagram of reactor and pressure gauge.
All parts are not at the same scale.

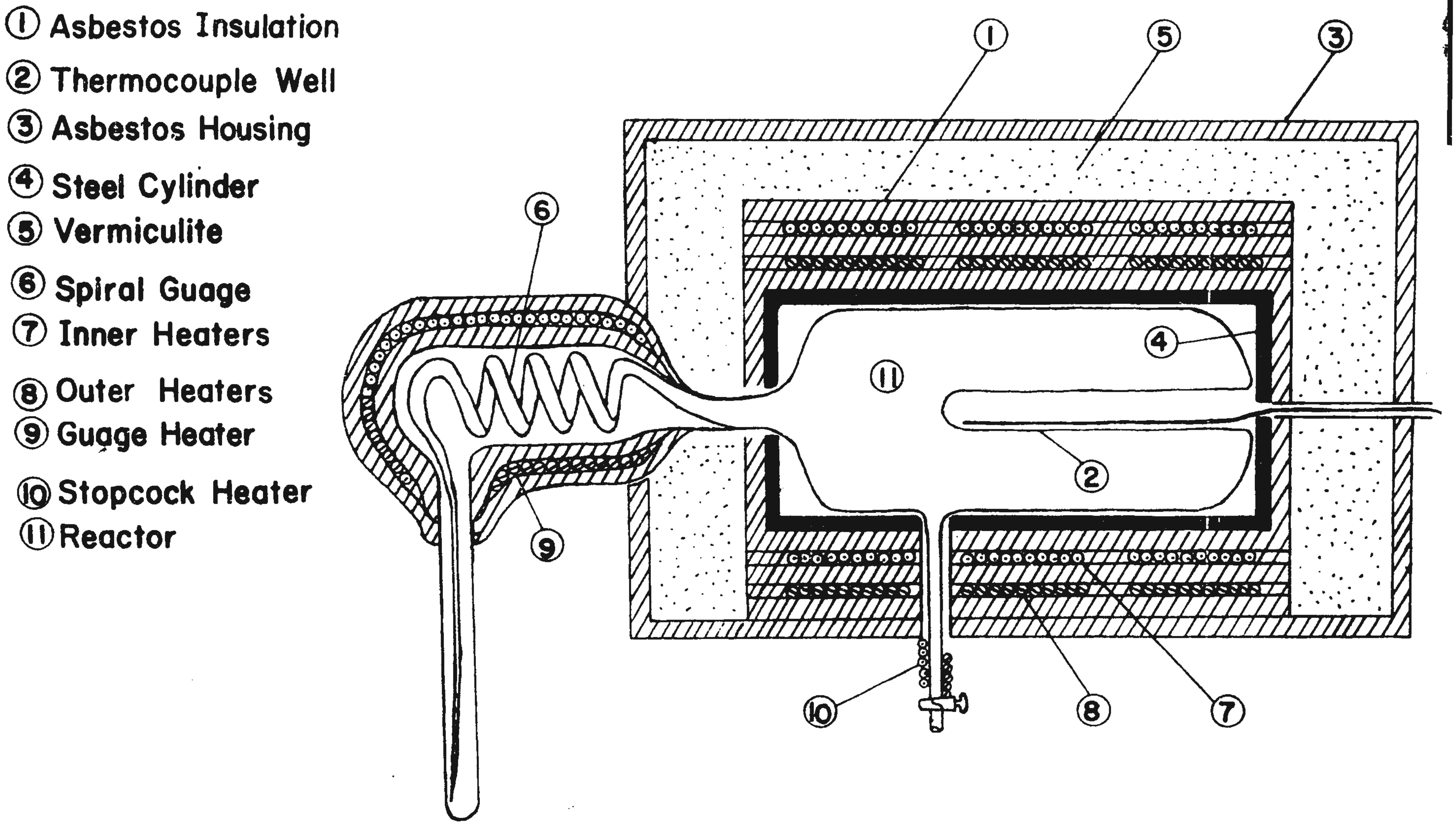

① Asbestos Insulation
② Thermocouple Well
③ Asbestos Housing
④ Steel Cylinder
⑤ Vermiculite
⑥ Spiral Guage
⑦ Inner Heaters
⑧ Outer Heaters
⑨ Guage Heater
⑩ Stopcock Heater
⑪ Reactor
①
⑤
③
⑥
④
⑪
②
⑨
⑩
⑧
⑦

FIGURE 2

A schematic diagram of the apparatus used:

F.P.	Fore pump
D.P.	Diffusion pump
T.G.	Thermocouple gauge
G.	Infrared gas cell
R	Reactor
M_1,M_2	Manometer

Schematic Diagram Of Apparatus Used

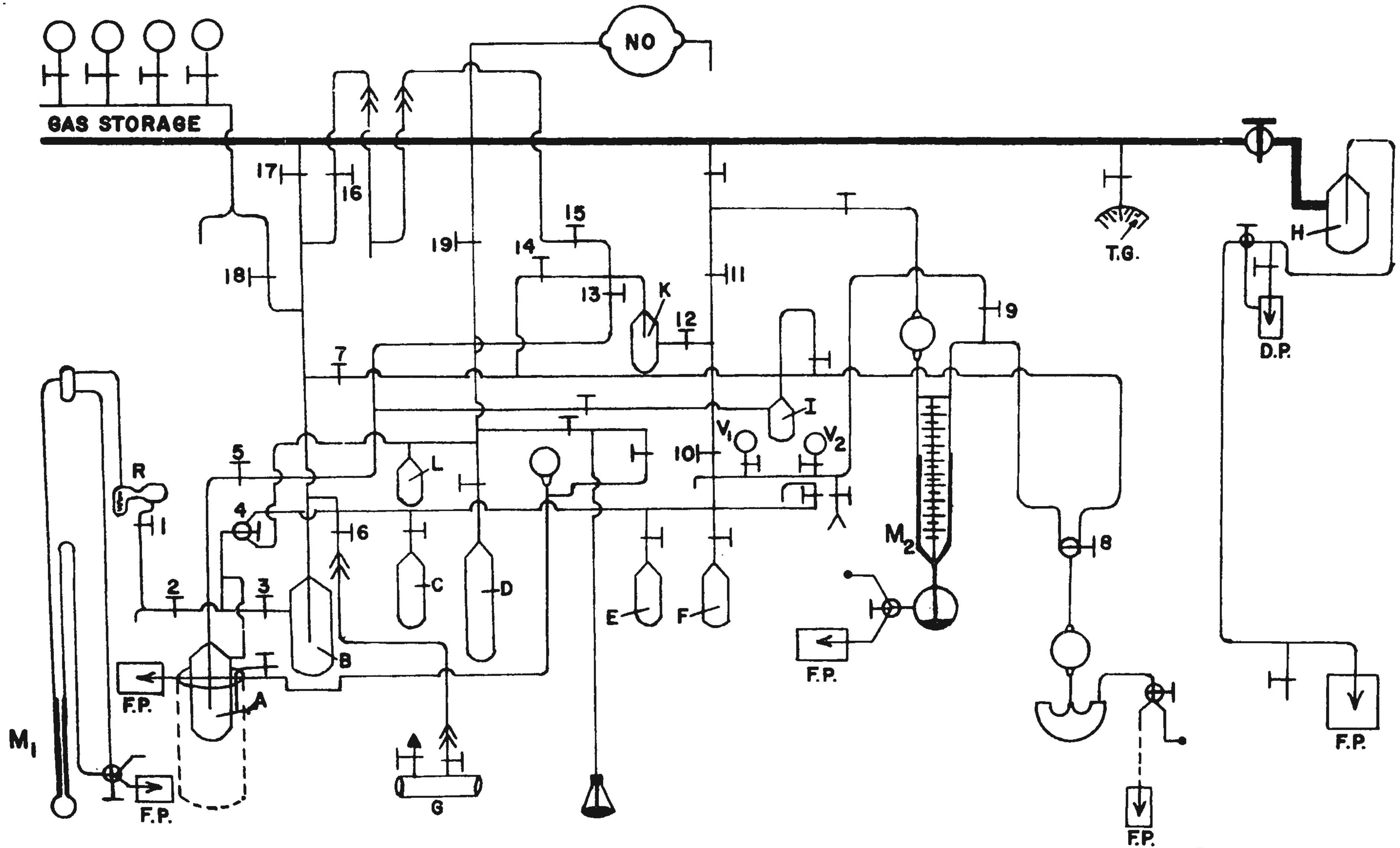
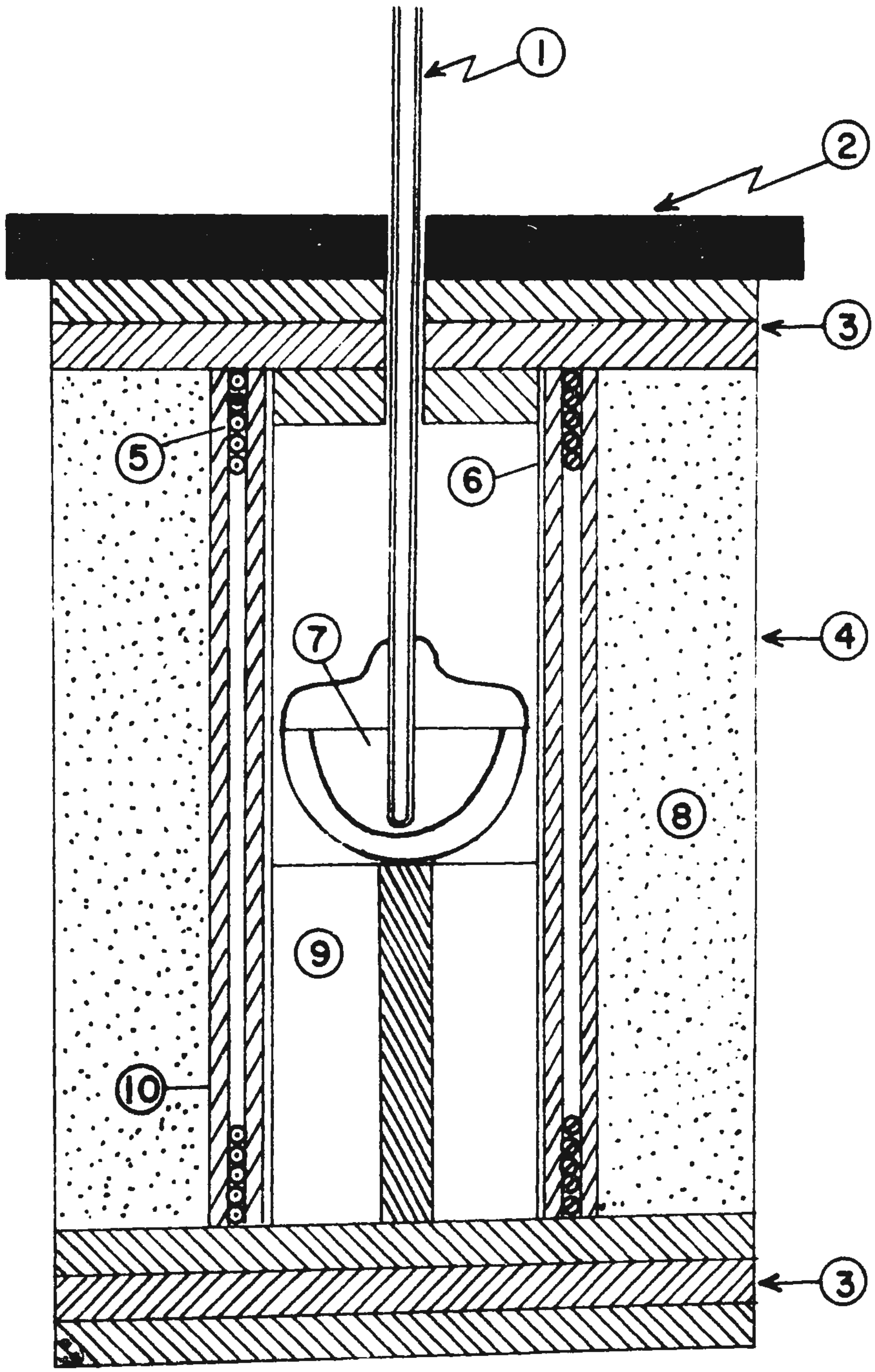


Fig. 2.

FIGURE 3

Thermocouple furnace. All parts now shown to same scale.

Fig. 3



THERMOCOUPLE FURNACE

① Glass Tube
② Cover
③ Insulating Rings
④ Steel Can
⑤ Heating Element
⑥ Brass Cylinder
⑦ Graphite Cruecible
⑧ Vermiculite
⑨ Stand
⑩ Asbestos Insulating

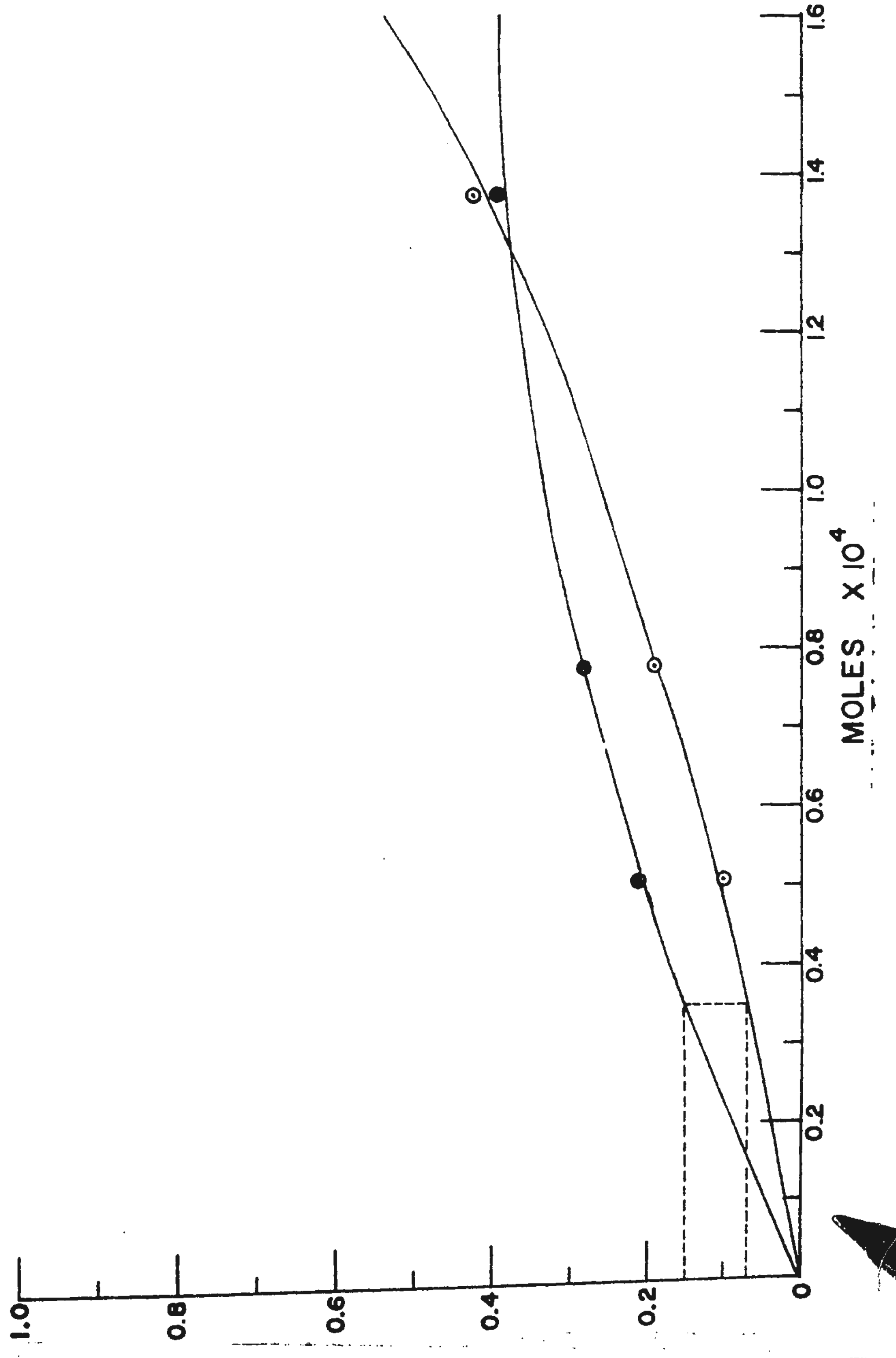
FIGURE 4

Infrared calibration curve for $2NO_2 \rightleftharpoons N_2O_4$

Absorption at 1750 cm^{-1}, •

Absorption at 1625 cm^{-1}, •

Fig. 4.



Calibration Curve For $2NO_2 \rightleftharpoons N_2O_4$ (I.R.)

FIGURE 5

Infrared calibration curve for nitromethane analysis

○ Curve used for analysis.

● Points observed.

Fig. 5.

Nitromethane Calibration Curve

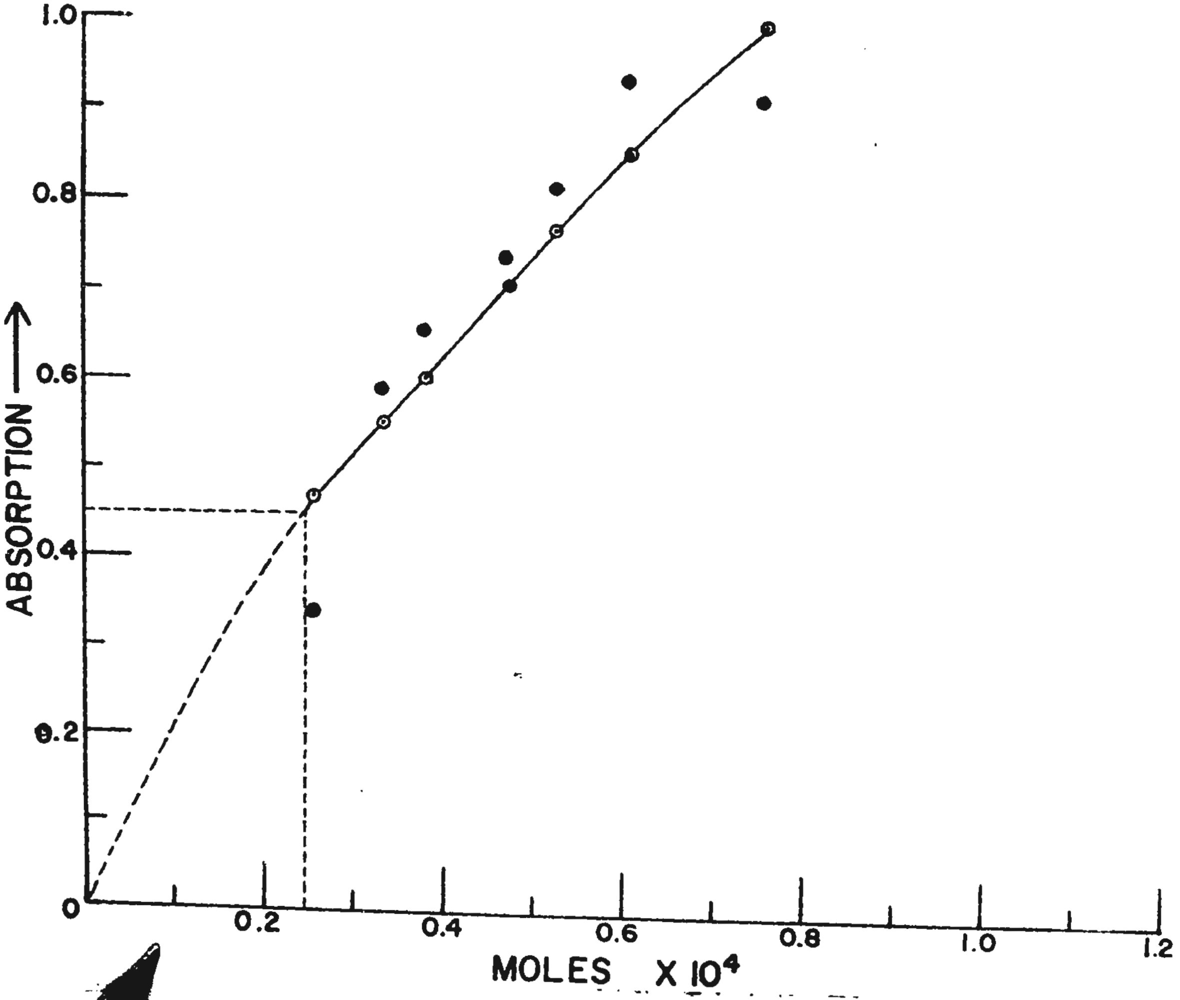
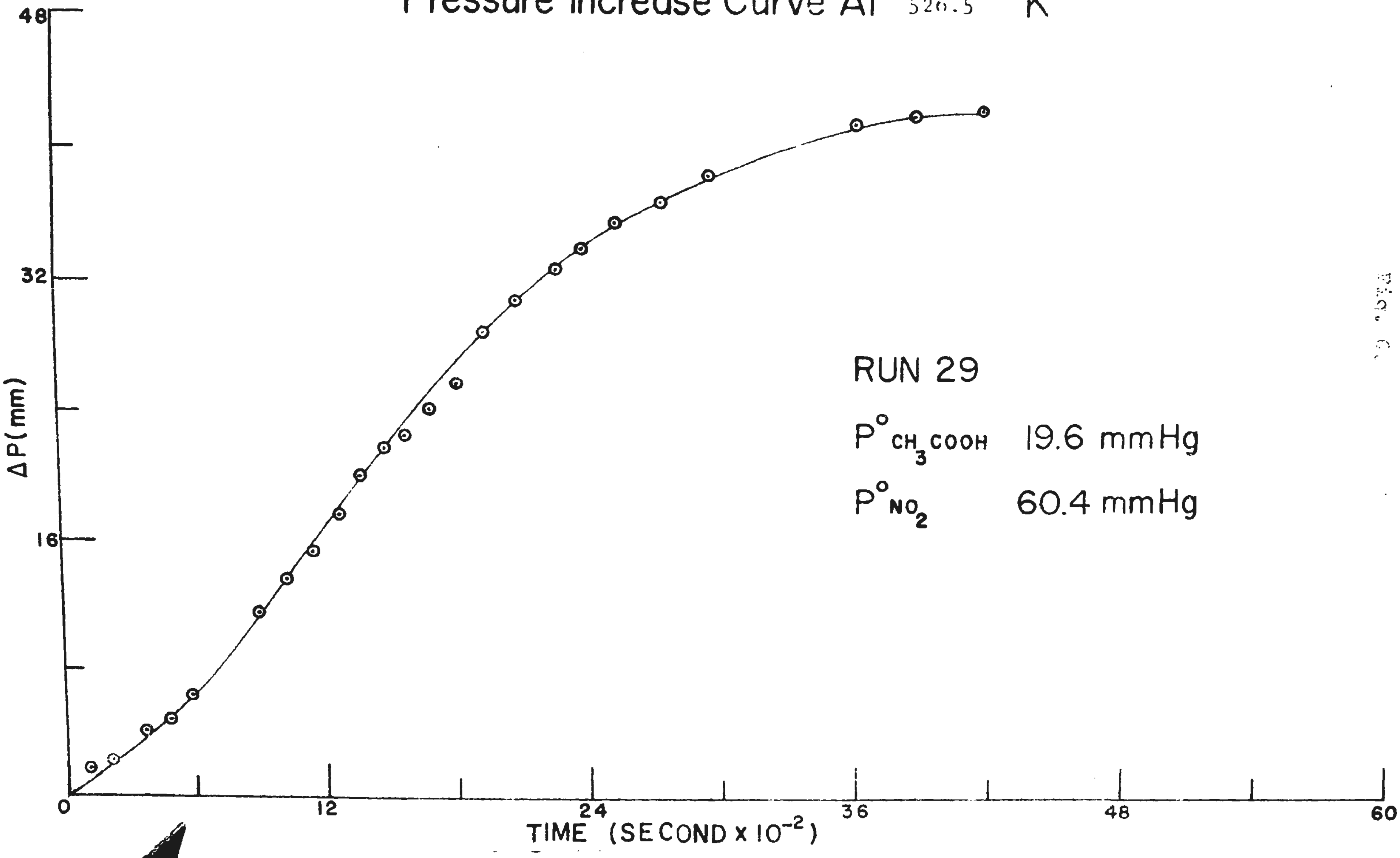


FIGURE 6

Pressure increase curve.



Pressure Increase Curve At 526.5 °K

Fig. [illegible]

FIGURE 7

Pressure increase curve with CH_3COOD.

Pressure Increase Curve At 526.5 °K

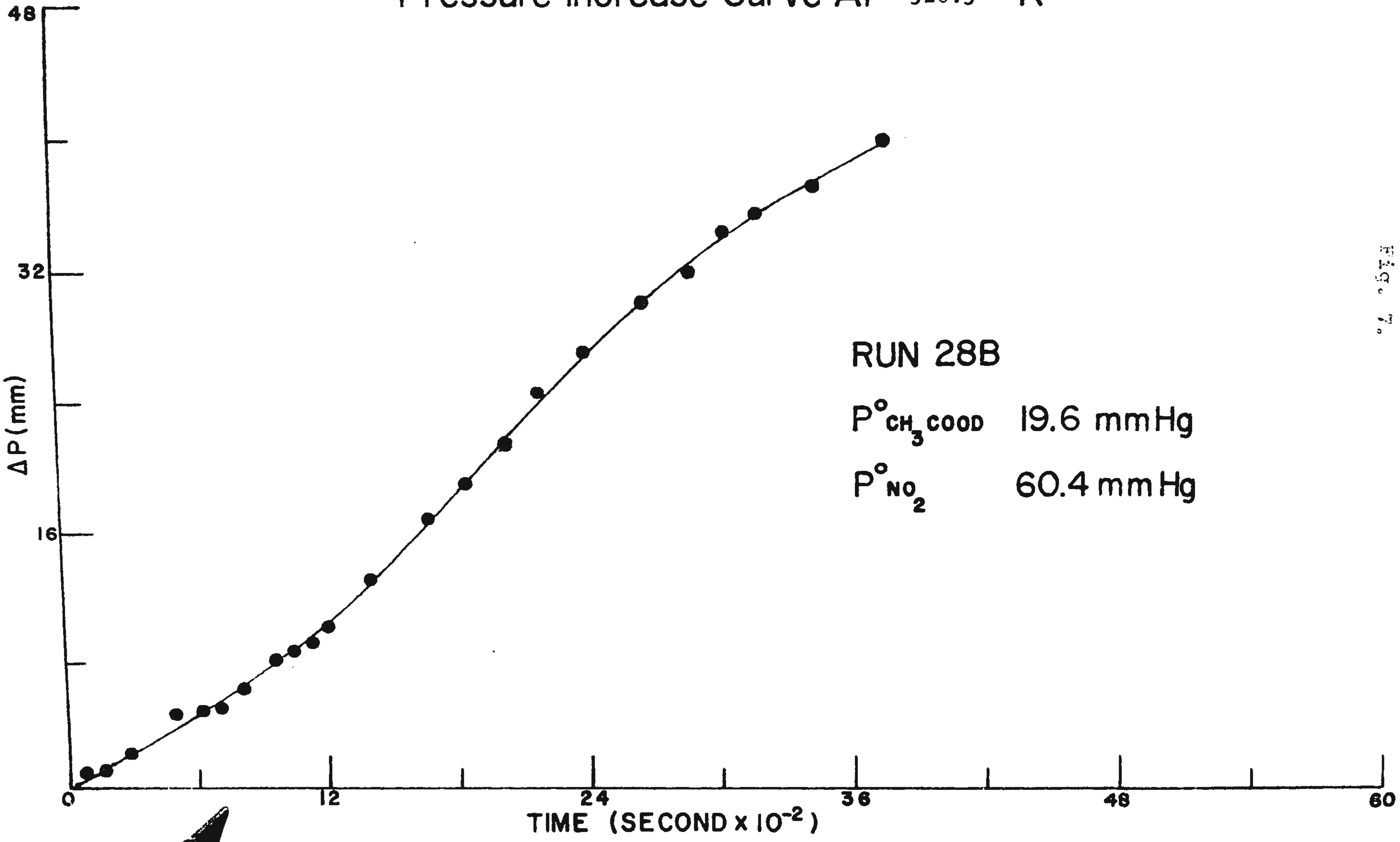


Fig. 7.

FIGURE 8

Pressure increase curve with NO.

Pressure Increase Curve At 526.5 °K

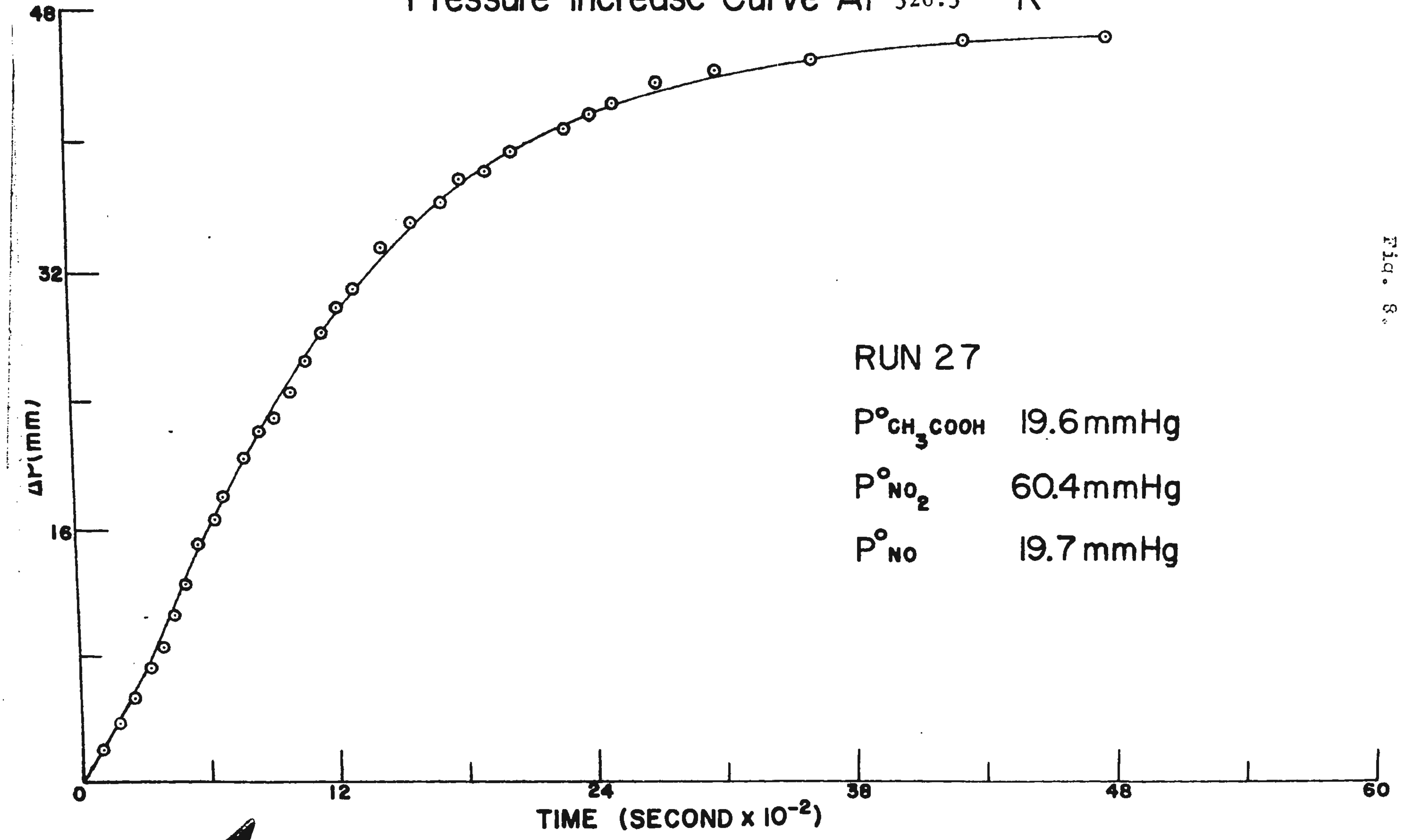


Fig. 8.

FIGURE 9

Pressure increase curve.

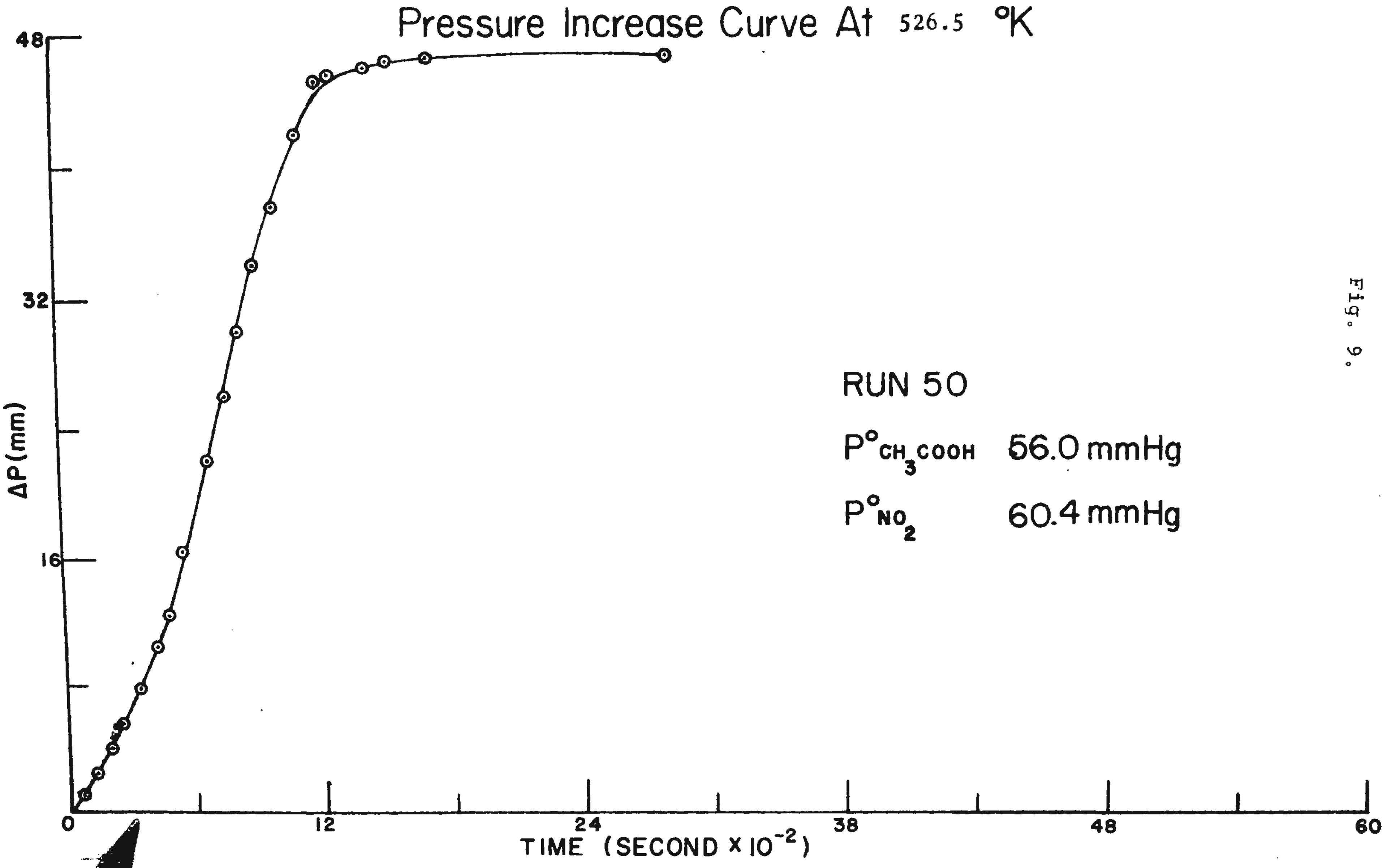
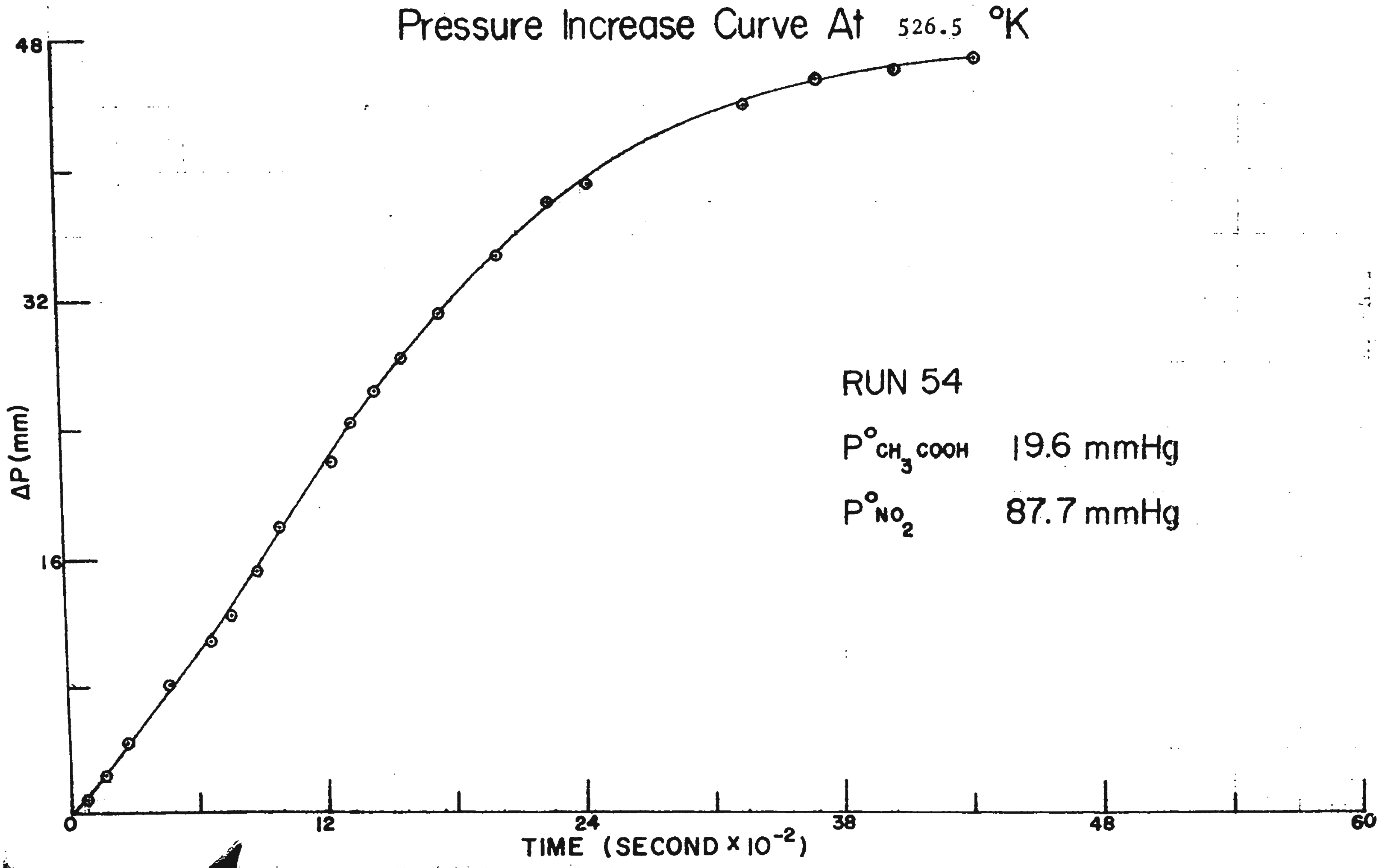


Fig. 9.

Pressure Increase Curve At 526.5 °K
ΔP (mm)
48
32
16
0
12
24
38
48
60
TIME (SECOND × 10^{-2})
RUN 50
$P^\circ_{CH_3COOH}$ 56.0 mmHg
$P^\circ_{NO_2}$ 60.4 mmHg

FIGURE 10

Pressure increase curve.


Pressure Increase Curve At 526.5 °K

RUN 54

$P^{\circ}_{CH_3COOH}$ 19.6 mmHg

$P^{\circ}_{NO_2}$ 87.7 mmHg

FIGURE 11

Initial rate as a function of acetic acid pressure. ○ uncorrected. ▽, corrected using data from this study. □, corrected using Ashmore's data.

Fig. 11

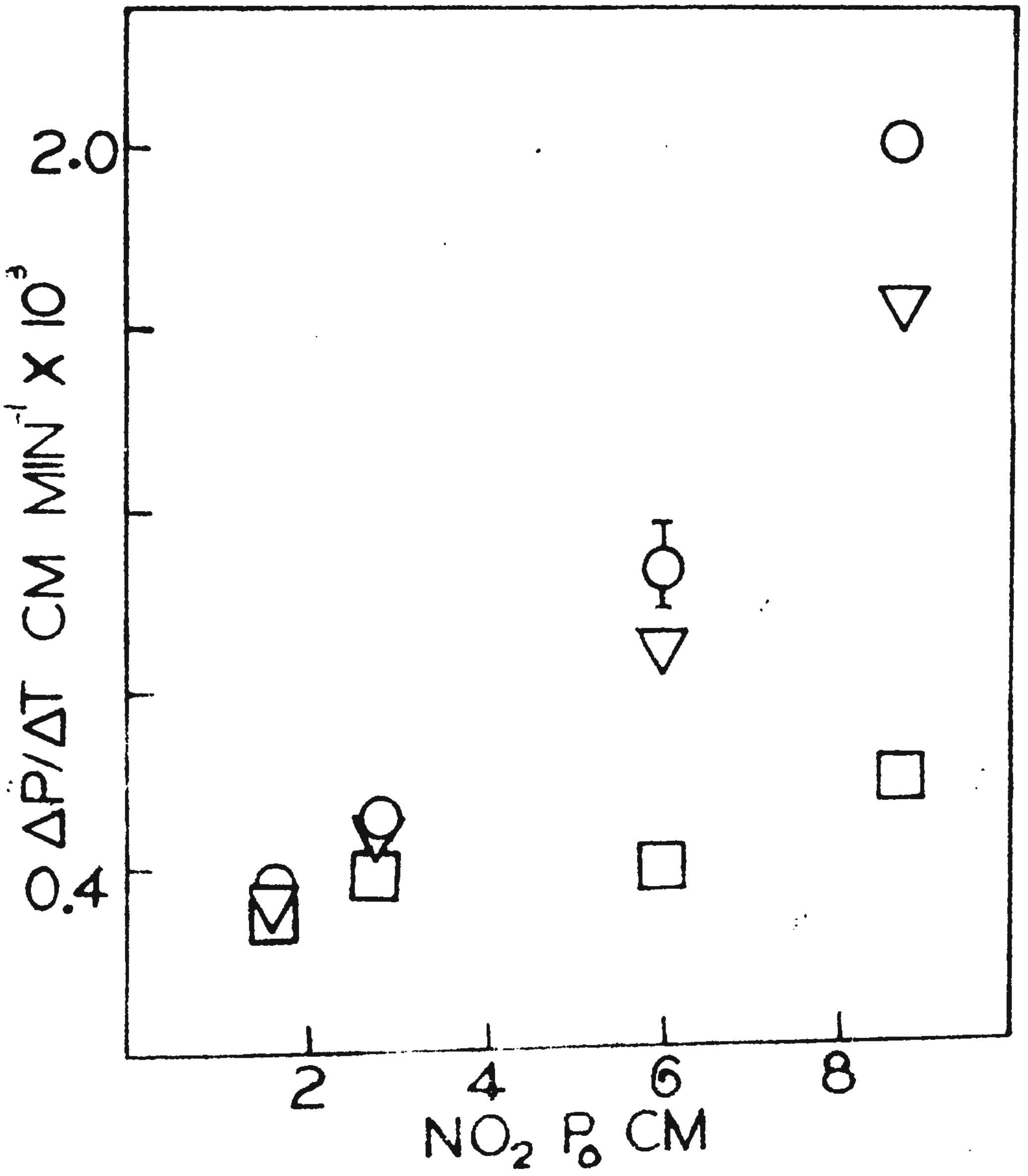


FIGURE 12

Initial rate as a function of NO_2 pressure. ○, uncorrected. ▽ , corrected using data from this study. □, corrected using Ashmore's data.

Fig. 12