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The synthesis and thermal decomposition of 3, 3-disubstituted-[delta]'-pyrazoli

Boston University
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Dissertation

The Synthesis and Thermal Decomposition of 3,3-Disubstituted-Δ^1-pyrazolines.

by

Harry Raymond Snyder, Jr.

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A.M., Boston University, 1952)

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Approved

by

First Reader J. Philip Mason
Professor of Chemistry

Second Reader Norman N. Lichtin
Ass't. Professor of Chemistry

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The microanalyses reported throughout were performed by Dr. Carol K. Fitz, Needham Heights, Massachusetts.

The author thanks his wife who worked so endlessly that this dissertation might be finished.

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Introduction: A Statement of the Problem

Unlike the aromatic azo compounds which are quite stable towards heat, the aliphatic azo compounds can be decomposed thermally at temperatures below 300°C. (28). The first member of the series of aliphatic azo compounds is azomethane (I) which undergoes decomposition when heated above 200°C.. Kinetic studies which have been carried out on azomethane

$$CH_3\text{-}N{=}N\text{-}CH_3$$

I

show that the activation energy for the thermal decomposition is 52.5 kcal. per mole (28) and that the reaction takes place in a homogeneous unimolecular manner (28).

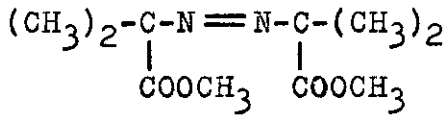
Extensive studies which have been performed employing several homologues of azomethane demonstrate that substitution of the α-hydrogens by alkyl groups lowers the activation energy of the thermal decomposition; e.g. methyl azoisopropane (II), 47.5 kcal. per mole (30); azoisopropane (III), 40.9 kcal. per mole (29).

$$CH_3\text{-}N{=}N\text{-}CH(CH_3)_2 \qquad\qquad (CH_3)_2CH\text{-}N{=}N\text{-}CH(CH_3)_2$$

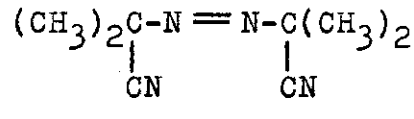
II III

The results of investigations concerning aliphatic azo compounds show that decrease in the activation energy could be effected also by the substitution of negative groups, i.e. cyano and carboxy groups, on the α and α'-carbon atoms.

For example, dimethyl 2-azo-bis-isobutyrate (IV), and 2-azo-bis-isobutyronitrile (V) have activation energies of 35.8 and 31.3 kcal. per mole respectively (20).

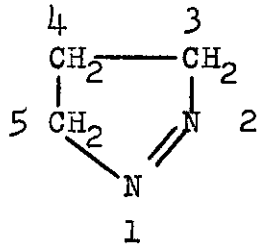


IV



V

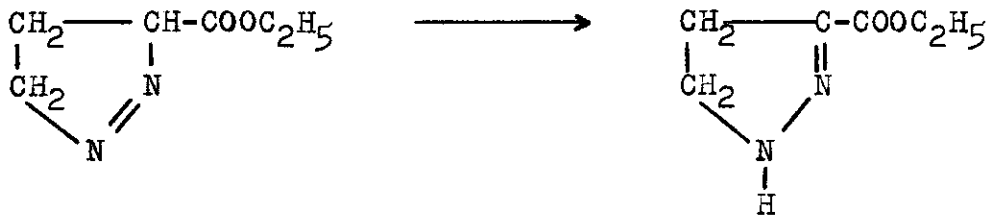
Keeping the above facts concerning the aliphatic azo compounds in mind, it is of interest to examine a class of heterocyclic compounds known as pyrazolines. The pyrazolines possess a five-membered ring system which contains a double bond and two adjacent nitrogen atoms. Although the double bond may appear in any position within the ring, attention is focused specifically upon the isomer which has the double bond between the adjacent nitrogen atoms, i.e. the Δ^1-pyrazolines (VI).



VI

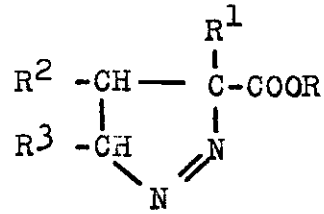
As seen from the above structure (VI), the Δ^1-pyrazolines can be considered as being cyclic aliphatic azo compounds and, as such, might be expected to behave similarly. A known fact is that pyrazolines in general will decompose

thermally to give nitrogen together with cyclopropane derivatives and/or unsaturated compounds (34). Von Auwers found that many pyrazolines would decompose around 200°C. and that the presence of a carboxyl group on carbon 3 would lower the decomposition temperature (34). It seemed desirable to extend the work of Von Auwers and his co-workers by replacing the carboxyl group with other groups and also by introducing various groups in the 3, 4, and 5 positions of the pyrazoline ring. It was hoped that a rather wide range of decomposition temperatures of various substituted pyrazolines would thus be made available. Previous work has shown that Δ^1-pyrazolines which have a hydrogen atom and a carboxyl group on carbon 3 isomerize very readily to Δ^2-pyrazolines (34), as follows:



In order to prevent the isomerization from occurring, the pyrazolines studied were substituted at carbon 3 by an alkyl or phenyl group.

To summarize, the following system has been studied:



Δ^1-Pyrazolines were prepared in which one or more of the groups R, R^1, R^2, R^3 are alkyl or phenyl, the others being hydrogen. In addition, the molecule was modified by the use of four activating groups (other than the carboxyl group), i.e. -CN, $-CONH_2$, $-COCH_3$, and $-NO_2$. The compounds were decomposed thermally and the kinetics of the decomposition was followed by measuring the volume of nitrogen liberated as a function of time. From the data obtained, the rate constants and energies of activation were calculated. The purpose of the investigation was to determine the effects upon the rate constants and energies of activation produced by the alteration of the molecule at the above-indicated positions.

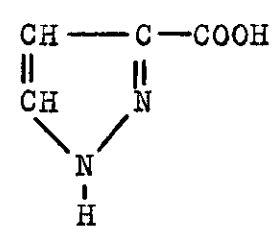
The Synthesis of the Pyrazolines.

The majority of the pyrazolines studied were prepared by the addition of diazomethane to the appropriate olefinic compound. All of the olefins were compounds which contained the double bond α, β to an electron withdrawing group, e.g. cyano, nitro, carboxyl, aceto, and carbamyl. The remainder of the pyrazolines studied were prepared by the addition of the appropriate diazoalkane to ethyl methacrylate.

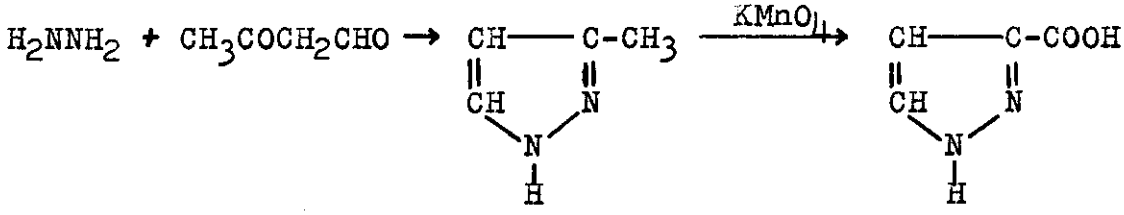
Since the above methods were used to prepare the pyrazolines, the mode of addition of diazomethane, or diazoalkane, to the olefinic compound must be known in order to assign the correct structures to the pyrazolines. There is a great deal of evidence in the chemical literature which shows that in adding to an activated double bond, the methylene carbon of the diazoalkane is attached to the β-carbon of the olefin.

Diazomethane adds to ethyl acrylate to form a substituted pyrazoline which on oxidation by bromine in chloroform solution, followed by hydrolysis in acidic medium, yields pyrazole-3-carboxylic acid (34).

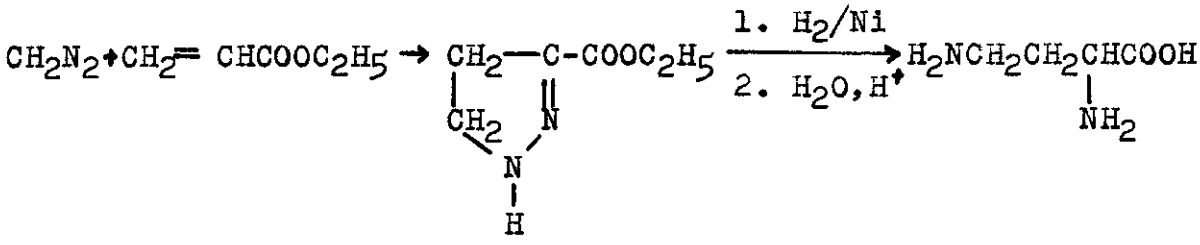
$$CH_2N_2 + CH_2{=}CHCOOC_2H_5 \xrightarrow[2.\ H_2O,\ H^+]{1.\ Br_2/HCCl_3}$$



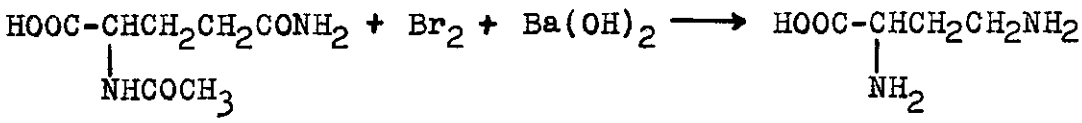
Pyrazole-3-carboxylic acid had been independently prepared by the oxidation with potassium permanganate of 3-methylpyrazole which was formed by the condensation of hydrazine and formylacetone (15).



In another experiment, the addition product of diazomethane and ethyl acrylate was reduced with hydrogen and Raney nickel. Hydrolysis of the reduced material produced α, γ -diaminobutyric acid (6).

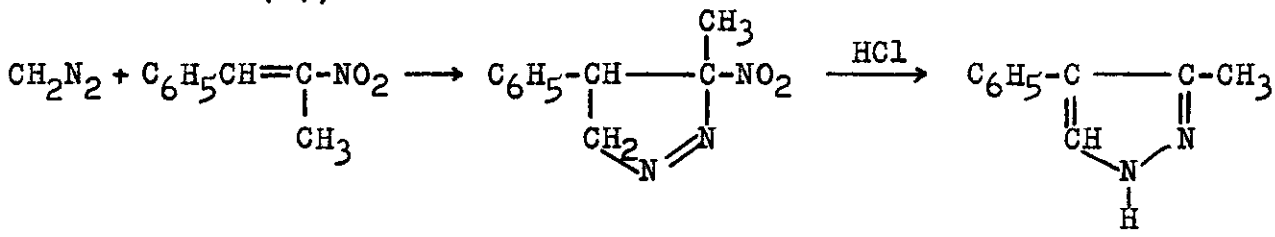


The diamino acid had been prepared previously by other methods, e.g. the action of bromine and barium hydroxide on acetylglutamine followed by hydrolysis (14).

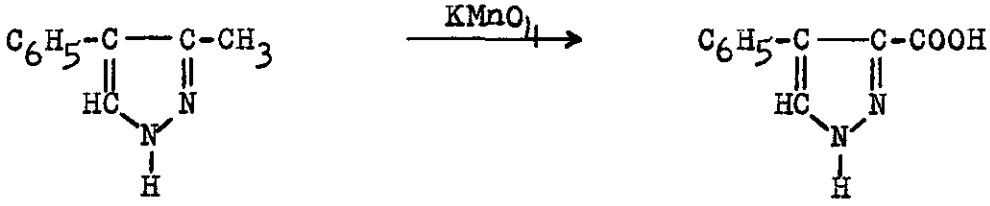


So far the evidence presented shows that diazoalkanes add to acrylates with the methylene carbon attaching itself to the β -carbon of the olefinic ester. More experimental evidence shows that the same behavior is observed with other electronegative groups in the olefin.

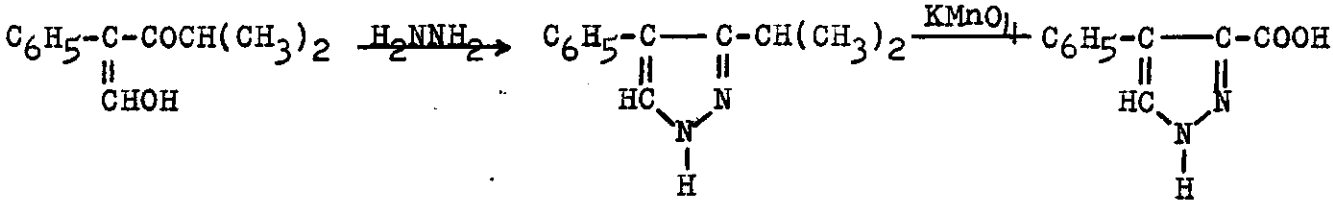
When 2-nitro-1-phenylpropene-1 and diazomethane were added together, a pyrazoline was obtained which formed nitrous acid and 4-phenyl-3-methylpyrazole by treatment with hydrochloric acid (27).



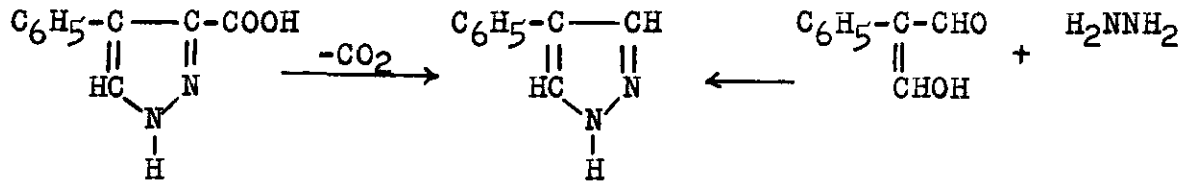
The structure of 4-phenyl-3-methylpyrazole was confirmed by oxidation with potassium permanganate to 4-phenylpyrazole-3-carboxylic acid (27).



The structure of the acid was demonstrated in two ways: a) the acid was synthesized by the oxidation with potassium permanganate of 4-phenyl-3-isopropylpyrazole prepared from the condensation of hydroxymethylenebenzylisopropyl ketone and hydrazine (16),

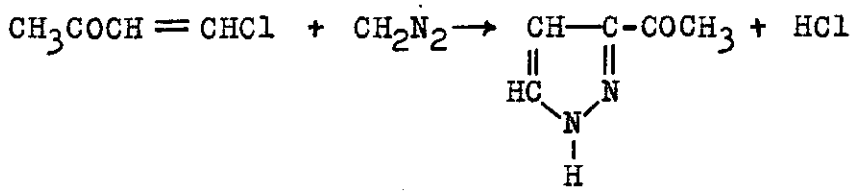


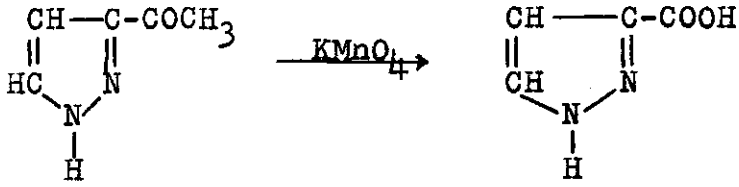
and b) by decarboxylation of the acid to 4-phenylpyrazole which was independently prepared by the condensation of hydroxymethylenephenylacetaldehyde and hydrazine (18, 33).



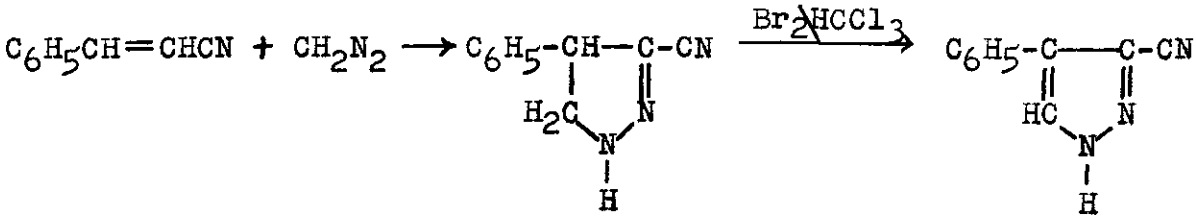
The above reactions show that the addition of diazomethane to 2-nitro-1-phenylpropene-1 proceeded as indicated.

The reaction between diazomethane and 1-chloro-1-butene-3-one yielded 3-acetopyrazole (23). The correct structure was demonstrated by the oxidation of 3-acetopyrazole with potassium permanganate to pyrazole-3-carboxylic acid (23) whose structure was already known (15).

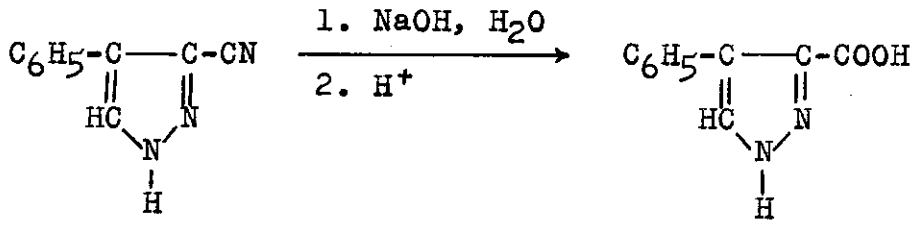




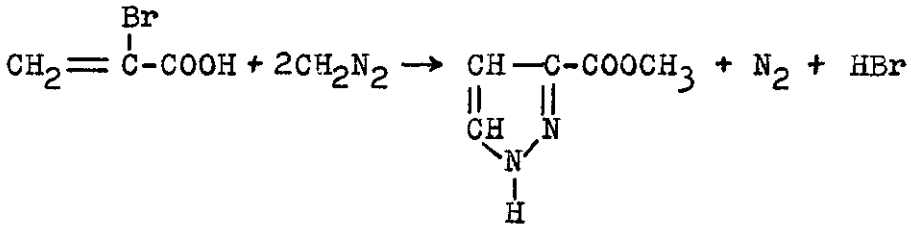
The addition of diazomethane to cinnamonitrile produced a pyrazoline which was oxidized by bromine in chloroform to 4-phenyl-3-cyanopyrazole (36).



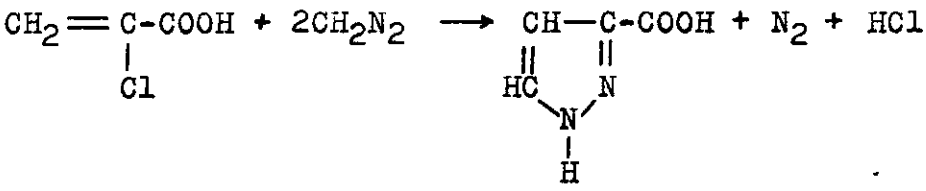
The structure of 4-phenyl-3-cyanopyrazole was confirmed by alkaline hydrolysis, followed by acidification, to 4-phenyl-pyrazole-3-carboxylic acid (36).



α-Bromoacrylic acid reacted with two moles of diazomethane forming one mole each of nitrogen and hydrogen bromide. The product was methyl pyrazole-3-carboxylate (26).

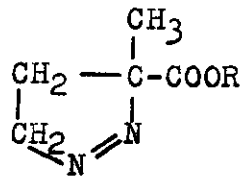


The same reaction took place when α-chloroacrylic acid was used (26).



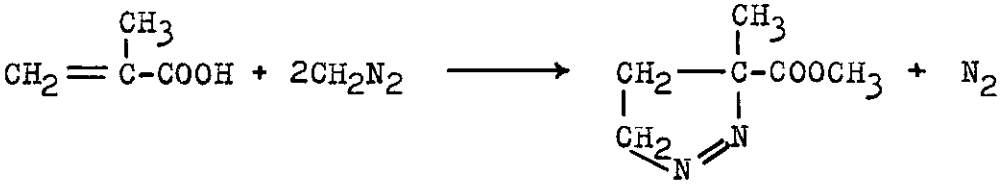
The evidence presented shows that when a diazoalkane adds to an olefinic double bond which is α, β to an electron withdrawing group, the methylene carbon is attached to the β-carbon of the olefin. Thus, the structure of the resulting pyrazoline can be predicted.

The first step in the synthetic work involved the preparation of the necessary precursors. For the series of pyrazolines in which the alcohol group was varied (I), methacrylates having the following alcohol groups were desired:



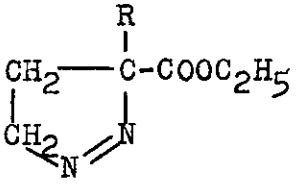
methyl, ethyl, n-propyl, isopropyl, n-butyl, and t-butyl. It was possible to obtain the ethyl and n-butyl esters from the Rohm and Haas Co.. All of the remaining methacrylates, except methyl methacrylate, were prepared by reacting methacrylyl chloride with the proper alcohol (13). The reaction was carried out in a pyridine solution. The acid chloride was made by an acid interchange, in pyridine, between methacrylic acid and benzenesulfonyl chloride (12).

The pyrazoline with the methyl ester group (II) was prepared by reacting methacrylic acid with moles of diazomethane.



II

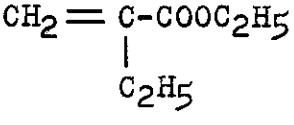
The next series of pyrazolines involved the variation of the group at carbon 3 (III).



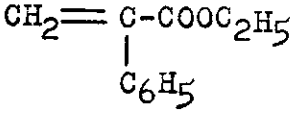
R = C_2H_5-, C_6H_5-

III

Two different synthetic routes were utilized in preparing the two olefinic esters IV and V.

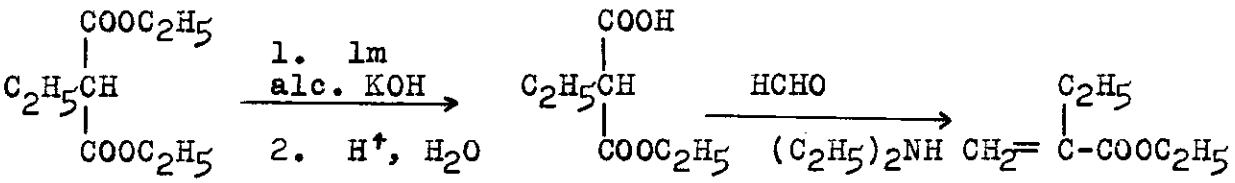


IV



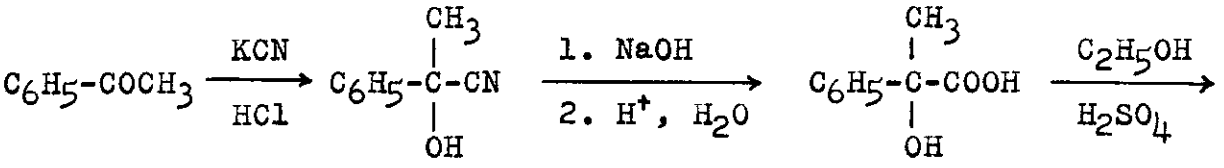
V

Diethyl ethylmalonate was hydrolyzed with one mole of methanolic potassium hydroxide to yield, upon acidification, ethyl hydrogen ethylmalonate (VI) (13). The half ester (VI) was treated with formaldehyde and diethylamine in a Mannich reaction to yield the desired product, ethyl α-ethylacrylate (IV) (21).

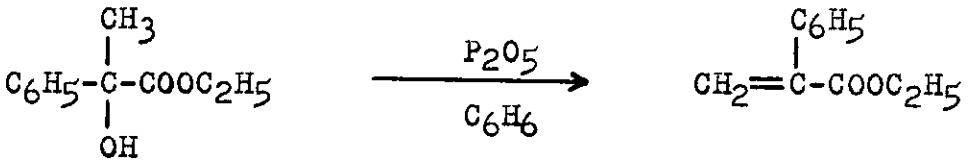


VI IV

Ethyl atropate (V) was synthesized starting with acetophenone (VII) (22) which was treated with potassium cyanide and hydrochloric acid to yield acetophenone cyanohydrin (VIII). Hydrolysis of the cyanohydrin with sodium hydroxide, followed by acidification, produced atrolactic acid (IX) which was esterified with ethyl alcohol. Ethyl atrolactate (X) was dehydrated to ethyl atropate (V) by the action of phosphorus pentoxide in refluxing benzene.



VII VIII IX

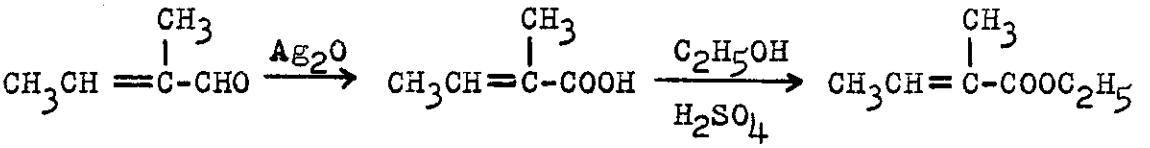


X V

In order to obtain ethyl 3,4-dimethyl-Δ^1-pyrazolin-3-carboxylate (XI) it was necessary to make ethyl tiglate (XII).

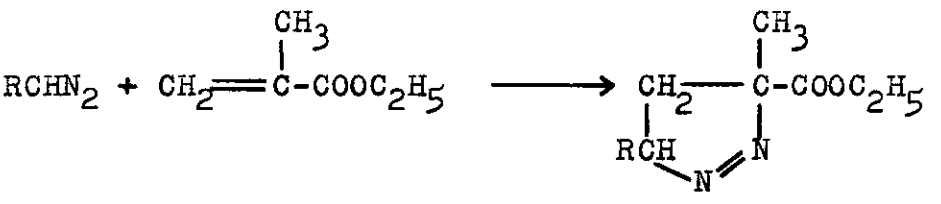
XI XII

Silver oxide oxidation of tiglaldehyde (XII) furnished tiglic acid (8) (XIV) which was then esterified by a standard procedure.



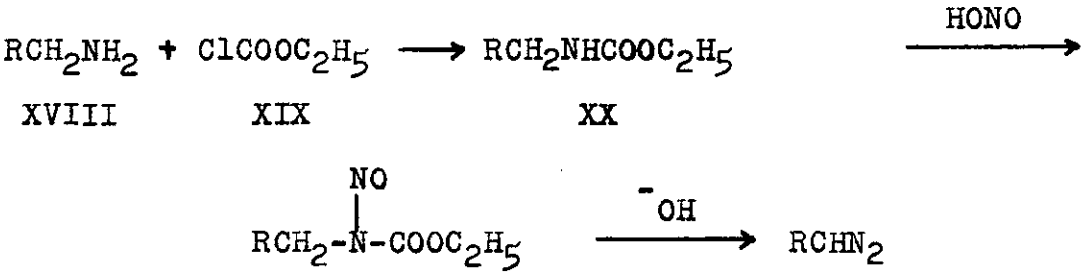
XIII XIV XII

The series of pyrazolines in which the group at carbon 5 was varied (XVII) was prepared by adding the appropriate diazoalkane (XV) to ethyl methacrylate (XVI) as follows (34);



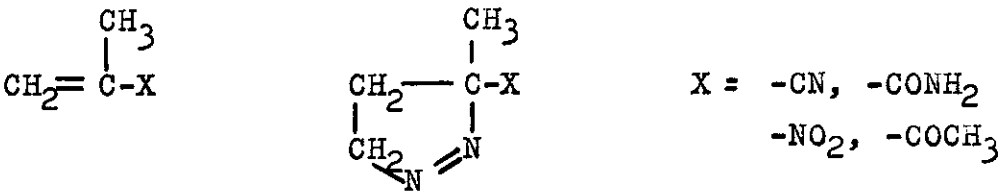
XV XVI XVII

The diazoalkanes (XV) were prepared by the alkaline decomposition of N-nitroso-N-alkyl carbamates (XXI) (38). Nitrosation of the carbamates, which were made by reacting the amine (XVIII) with ethyl chloroformate (XIX), gave the necessary nitroso carbamates (XXI) (34). The reactions are outlined below.



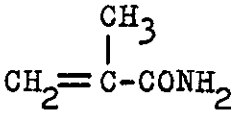
XVIII XIX XX XXI XV

The last series of olefins which was needed had the structure shown by formula XXII and were used to prepare the series of pyrazolines possessing the structure shown by formula XXIII.

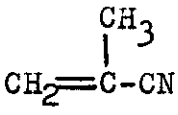


XXII XXIII

Methacrylamide (XXIV) and methacrylonitrile (XXV) were obtained from commercial sources (Monomer-Polymer Co., Leominster, Massachusetts and Shell Development Co. respectively). Methyl isopropenyl ketone (XXVI) was prepared by dehydrating with potassium acid sulfate the ketol (37).

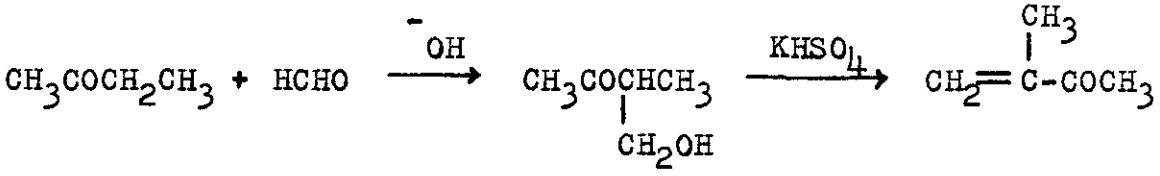


XXIV



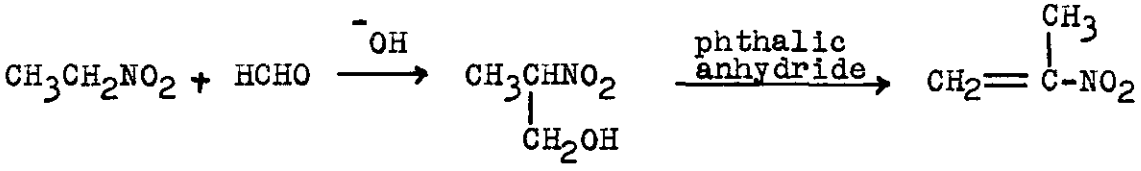
XXV

(XXVII) resulting from the condensation of formaldehyde and methyl ethyl ketone (19).



XXVII XXVI

The dehydration of the nitro alcohol (5) (XXVIII) obtained by the condensation of nitroethane and formaldehyde (3) yielded the desired nitro-olefin (XXIX). Phthalic anhydride served as the dehydrating agent.



XXVIII XXIX

In the following section, the detailed experimental procedures are given for the reactions discussed in this section.

The Preparation of Methacrylyl Chloride (12).

$$CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{C}}\text{-}COOH + C_6H_5SO_2Cl \xrightarrow{C_5H_5N} CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{C}}\text{-}COCl + C_6H_5SO_3H \cdot C_5H_5N$$

Experiment I

One-hundred and fifty eight grams (2 moles) of pyridine (E.K., practical grade, dried over potassium hydroxide pellets) was mixed with 172g. (2 moles) of methacrylic acid (Matheson, practical grade, freshly distilled, b.p. 160-163°C.). The mixture was then added very slowly with continuous shaking and cooling to 424g. (2.4 moles) of freshly distilled benzenesulfonyl chloride (E.K., b.p. 127-127.5°/22 mm.) in a 1-liter flask. The methacrylyl chloride was distilled immediately from the reaction mixture, under reduced pressure, into a receiver cooled by a salt-ice bath. The reaction flask was heated by an oil bath kept at 140-185°C. (never above 190°C.), and the distillation was carried out at approximately 35 mm.. The product distilled at 65-75°C.. A small amount of white material appeared in the condenser and receiver. The crude product was redistilled at atmospheric pressure to give a final yield of 165.5g. (80% yield), b.p. 98.5-101°C.. The material was placed in a brown, glass stoppered bottle and stored in the refrigerator.

Caution! Methacrylyl chloride is a strong lachrymator and should be handled in the hood. All glassware used in the preparation should be rinsed immediately after use with

concentrated ammonium hydroxide. All work with methacrylyl chloride should be conducted with protection against direct radiation to reduce polymerization.

Experiment II

The same procedure was followed as in Experiment I using 430g. (5 moles) of methacrylic acid, 1060g. (6 moles) of freshly distilled benzenesulfonyl chloride, and 395g. (5 moles) of pyridine dried over potassium hydroxide pellets. The yield of pure product was 360g. (70%), b.p. 98-100°C..

Lit: (12): 86%, b.p. 98-100°C..

The Preparation of Alkyl Methacrylates (13).

$$CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{C}}\text{-}COCl + ROH \xrightarrow{C_5H_5N} CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{C}}\text{-}COOR + C_5H_5N \cdot HCl$$

The procedure which was followed in the preparation of each ester is described in detail for the preparation of t-butyl methacrylate. Following the experimental details is a table which summarizes the results of the preparation of the methacrylates.

Seventy-nine grams (1 mole) of pyridine (E.K., practical dried over potassium hydroxide pellets) and 37g. (0.5 mole) of freshly distilled t-butyl alcohol were placed together in a 250 ml. reaction flask and cooled to approximately 10°C. in an ice bath. After adding 1g. of powdered copper to the mixture (to reduce polymerization), 52g. (0.5 mole) of methacrylyl chloride was introduced gradually with agitation and cooling; the temperature was kept under 45°C.. After the methacrylyl chloride had been added, the reaction flask was equipped with a reflux condenser, protected with a calcium chloride drying tube, and the mixture refluxed for two hours.

The contents of the flask were then poured into one liter of water containing 60 ml. of concentrated hydrochloric acid. The mixture was extracted with petroleum ether (b.p. 30-65°); the combined extracts were dried over anhydrous calcium chloride. A few crystals of hydroquinone were added to inhibit polymerization during the drying process and subsequent

distillations.

The solvent was removed and the residue distilled under vacuum. The yield of product was 26g. (36.6%) which boiled at 72-73°C. at 91 mm. pressure.

TABLE I

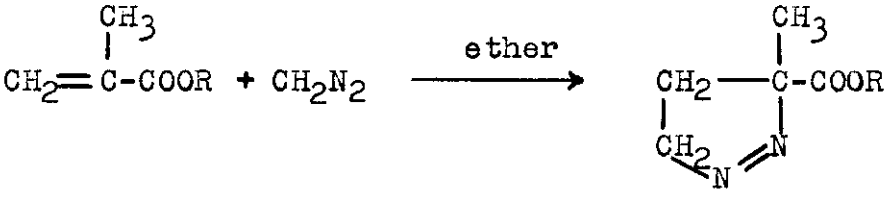
The Alkyl Methacrylates.

R	Yield	B.P./mm.
$CH_3CH_2CH_2$-	30.0 g. (47%)	137-138°C./760
CH_3>CH- *CH_3	21.6 g. (41%)	39-40°C./33
**$(CH_3)_3C$-	26.0 g. (36.6%)	72-73°C./91

* Prepared by W. R. Browne

** Lit: (13); 48%, b.p. 72-74°C./96 mm..

The Preparation of the Alkyl 3-Methyl- Δ^1-pyrazolin-3-carboxylates (34).



An ethereal solution of diazomethane was prepared from 41.2g. (0.4 mole) of N-nitroso-N-methylurea (2,10).

To the ethereal solution of diazomethane was added a solution of 22.8g. (0.2 mole) of ethyl methacrylate in 50 ml. of ether. The mixture was placed in the refrigerator and allowed to stand for four hours. The excess diazomethane and ether were removed by distillation from a steam bath under the hood. The residual liquid was distilled under reduced pressure to yield 28.2g. (90%) of the pyrazoline, b.p. 53-53.5°C./0.5 mm., $n_D^{24} = 1.4476$.

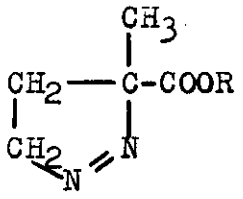
Lit.: (34); 79% yield, b.p. 99-100°C./11 mm.

Anal: for $C_7H_{12}N_2O_2$: Calc.: C, 53.83; H, 7.75; N, 17.9. Found: C, 53.7; H, 7.7; N, 17.7.

The above procedure was followed in the preparation of all of the pyrazoline esters except the methyl ester. The results are summarized in the following table.

TABLE IIa

The Alkyl 3-Methyl-Δ^1-pyrazolin-3-carboxylates.



R	Yield, %	B.P.	n_D^{24}
C_2H_5-	(90%)	53-53.5°C./0.5	1.4476
$CH_3CH_2CH_2$-	(77.6%)	67-68°C./1.0	1.4477
*$(CH_3)_2CH$-	(79%)	73-74°C./2.0	1.4422
$CH_3CH_2CH_2CH_2$-	(78%)	72-73°C./1.0	1.4485
$(CH_3)_3C$-	(80.5%)	57-58°C./1.0	1.4429

* Prepared by W. R. Browne

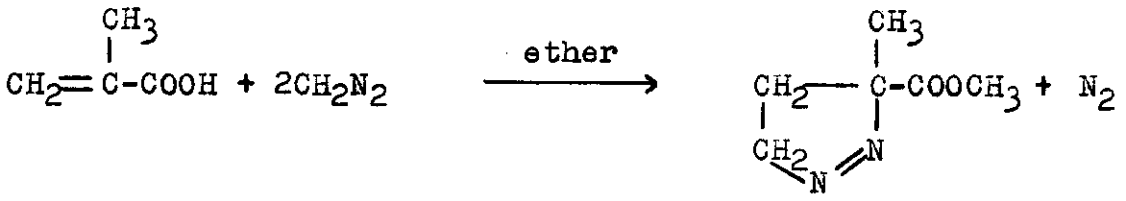
TABLE IIb

The Alkyl 3-Methyl-Δ^1-pyrazolin-3-carboxylates:

Analytical Data

		Cal'c.			Found		
R	Mol. Form.	C	H	N	C	H	N
C_2H_5-	$C_7H_{12}N_2O_2$	53.8	7.8	17.9	53.7	7.7	17.7
$CH_3CH_2CH_2$-	$C_8H_{14}N_2O_2$	56.5	8.3	16.5	56.2	8.1	16.4
$(CH_3)_2CH$-	$C_8H_{14}N_2O_2$	56.5	8.3	16.5	56.3	8.1	16.3
$CH_3CH_2CH_2CH_2$-	$C_8H_{14}N_2O_2$	58.8	8.8	15.3	58.8	8.7	15.2
$(CH_3)_3C$-	$C_9H_{16}N_2O_2$	58.8	8.8	15.3	58.5	8.6	15.2

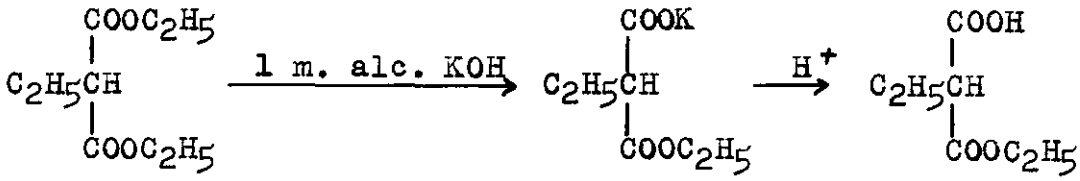
The Preparation of Methyl 3-Methyl-Δ^1-pyrazolin-3-carboxylate.



An ethereal solution of diazomethane was prepared from 41.2g. (0.4 mole) of N-nitroso-N-methylurea. To the diazomethane was added 8.6g. (0.1 mole) of methacrylic acid dissolved in ether. There was a vigorous evolution of gas immediately following the addition. As soon as the bubbling stopped, the solution was placed in the refrigerator for two hours. The ether and excess diazomethane were removed by distillation from a steam bath. The residue of crude pyrazoline was distilled under reduced pressure. The final yield of product was 10.0g. (70%), b.p. 45-46°C./1.0 mm., $n_D^{24} = 1.4535$.

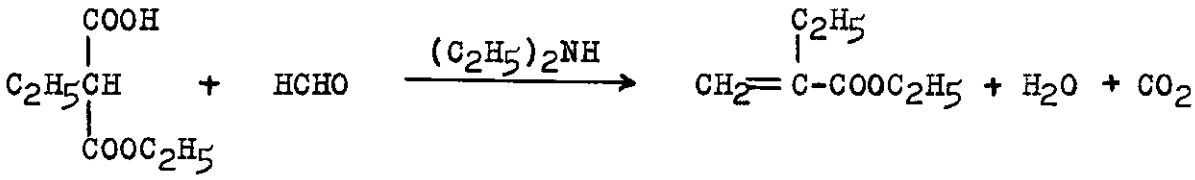
Anal. for $C_6H_{10}N_2O_2$. Calc. C, 50.7; H, 7.1; N, 19.7. Found: C, 50.5; H, 7.0; N, 19.4.

The Preparation of Monoethyl Ester of Ethylmalonic Acid (4).



One-hundred and eighty-eight grams (1 mole) of diethyl ethylmalonate (Eastman Kodak) was placed in a 5-liter flask together with 600 ml. of ethanol. To the mixture was added a solution of 56g. (1 mole) of potassium hydroxide in 600 ml. of ethanol. The resulting mixture was allowed to stand at room temperature for twenty-four hours with occasional shaking. The mixture was then poured into an evaporating dish and heated on a steam bath until the alcohol was removed. The concentrated liquor was then distributed between chloroform, to remove unreacted ester, and a minimum amount of water to dissolve the potassium salt of the half-ester. The aqueous layer was separated, cooled in an ice bath, and acidified with a slight excess of concentrated hydrochloric acid. The acidified solution was extracted several times with ether. The ethereal extracts were dried over anhydrous sodium sulfate and the ether removed by distillation over a steam bath. The final traces of ether were removed under vacuum, and the residue dried in vacuo over phosphorus pentoxide for twenty-four hours. The crude yield of 82g. (51%) was used directly in the next step.

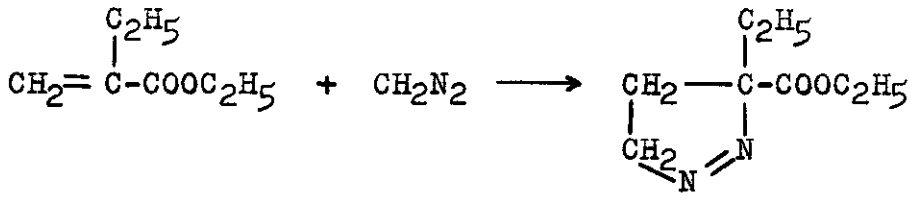
The Preparation of Ethyl α-Ethylacrylate (21).



The Mannich reaction was utilized in the preparation of ethyl α-ethylacrylate. The half-ester of ethylmalonic acid, 82g. (0.51 mole), was neutralized with 36.5g. (0.5 mole) of diethylamine. To the mixture was added 50 ml. of 30% aqueous formaldehyde. The evolution of carbon dioxide began as soon as the formaldehyde solution had been added. After about two hours, a second layer of liquid began to separate from the homogeneous solution. The mixture stood overnight at room temperature. The upper layer, which was the product, was separated and dried over anhydrous sodium sulfate. After drying, the material was distilled at atmospheric pressure to yield 40g. (62%) of product boiling at 137-138°C..

Lit.: (21); 63%, b.p. 138°C..

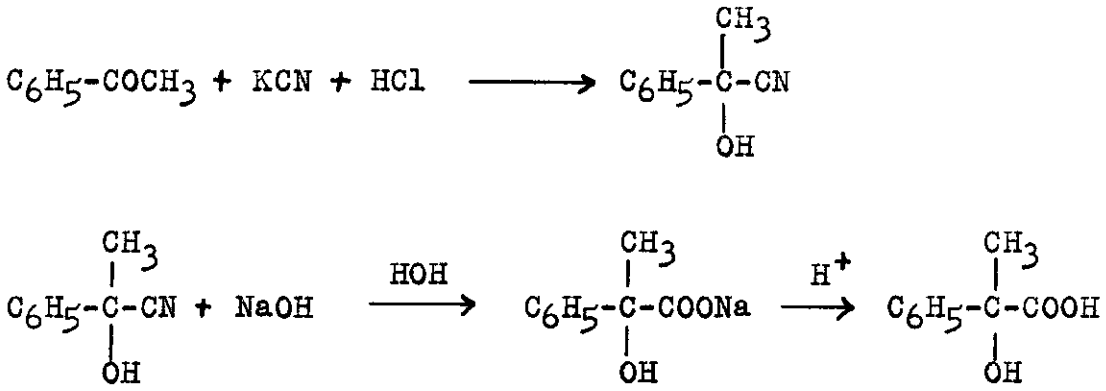
The Preparation of Ethyl 3-Ethyl-Δ^1-pyrazolin-3-carboxylate.



An ethereal solution of diazomethane was prepared from 41.2g. (0.4 mole) of N-nitroso-N-methylurea. To the diazomethane was added 25.6g. (0.2 mole) of ethyl α-ethylacrylate in 50 ml. of ether. The mixture was placed in the refrigerator for two hours. The ether and excess diazomethane were removed by distillation using a steam bath. The crude residue, which weighed 32.3g., was distilled under reduced pressure to yield 10.9g. (32.0%) of the pyrazoline boiling at 71-72°C. at 1.0 mm., $n_D^{24} = 1.4521$.

Anal. for $C_8H_{14}O_2N_2$: Calc.: C, 56.45; H, 8.29; N, 16.46. Found: C, 56.4; H, 8.3; N, 16.3.

The Preparation of Atrolactic Acid (22).



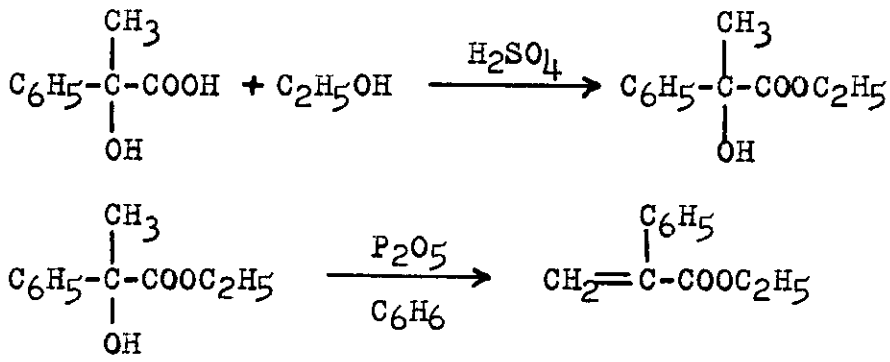
One-hundred and twenty grams (1 mole) of acetophenone, 96g. (1.4 mole) of 96% potassium cyanide, and 6 ml. of water were placed in a 3-necked flask equipped with a stirrer and dropping funnel. Concentrated hydrochloric acid, 115 ml., was added very slowly with vigorous stirring. The addition took place over a five-hour period with 20 ml. being added during each of the first two hours and 25 ml. during each of the remaining hours. During the first three hours of addition, the reaction mixture was kept at room temperature so that the acetophenone would not solidify, but towards the end of the addition, the mixture was cooled in an ice-cold water bath. After the addition had been completed, the reaction mixture was allowed to stand for one-half hour. After the oily layer was separated and washed with water, it was poured into 240 ml. of concentrated hydrochloric acid and left standing at room temperature overnight.

Sodium hydroxide solution was added until the hydrochloric acid mixture was neutral and then 120g. (3 moles) of base

added. The alkaline mixture was steam distilled until ammonia ceased to evolve. The unreacted acetophenone, 67.3g. (0.56 mole), was recovered from the distillate. The solution in the distillation flask was evaporated on the steam bath until crystals formed. After cooling, the crystals were collected and acidified using concentrated hydrochloric acid and Congo Red indicator. The atrolactic acid was collected together with some sodium chloride. The acid was separated from the salt with ether extraction using a Soxhlet extractor. The ethereal solution was dried over anhydrous magnesium sulfate. Upon evaporation of the ether, the acid crystallized. The crude yield of 19.9g. (19% based upon acetophenone used) of atrolactic acid was used directly in the next step.

Lit.: (22); 73% (based on converted ketone).

The Preparation of Ethyl Atropate.



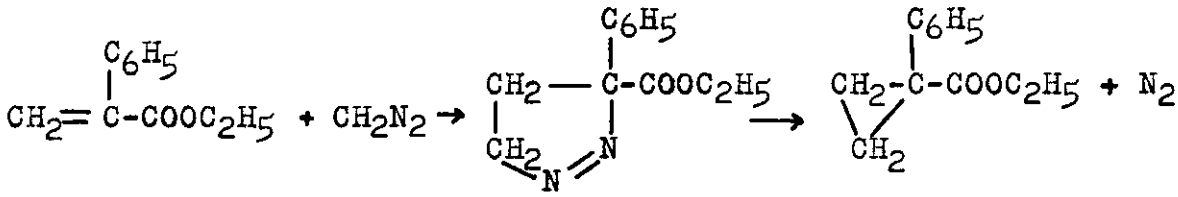
The atrolactic acid, 19.9g. (0.11 mole), was placed in a reaction flask equipped with a reflux condenser. Fifty ml. of commercial absolute ethanol and 5 ml. of concentrated sulfuric acid were added and the mixture refluxed for three hours. The excess alcohol was removed by distillation and the residue poured into 50 ml. of water. Solid sodium carbonate was added until the mixture was neutral. The ester was extracted with ether, and the ethereal solution was dried over anhydrous sodium sulfate. Removal of the ether by distillation left 12.9g. (61% yield) of crude ethyl atrolactate which was used directly in the dehydration reaction.

The ethyl atrolactate, 12.9g. (0.066 mole), was dissolved in 50 ml. of dry benzene and placed in a reaction flask equipped with a reflux condenser which was protected with a calcium chloride drying tube. Phosphorus pentoxide, 7.1g. (0.05 mole), was added to the benzene solution and the mixture refluxed for two hours. After pouring the reaction mixture into water, the benzene layer was separated and dried

over anhydrous sodium sulfate. The benzene was partially removed by distillation on the steam bath. The residue was then distilled under reduced pressure. After all of the benzene had been removed, the ethyl atropate distilled at 53-54°C./0.2 mm.. The yield was 5.7g. (50%).

Lit.: (35); b.p. 124°C./16 mm.; 120°C./14 mm.

The Preparation of Ethyl 3-Phenyl-Δ^1-pyrazolin-3-carboxylate.

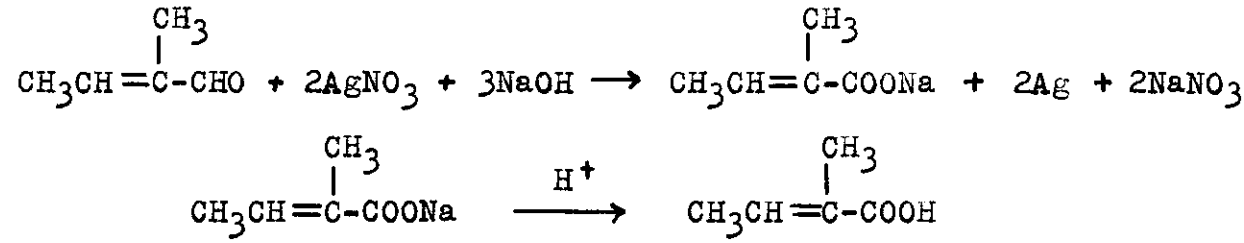


An ethereal solution of diazomethane was prepared from 10.3g. (0.10 mole of N-nitroso-N-methylurea and added to a solution of 5.8g. (0.033 mole) of ethyl atropate in 25 ml. of ether. The mixture was placed in the refrigerator for two hours. Removal of the ether and excess diazomethane on the steam bath left a crude residue of approximately 7g.. However, the material decomposed quite readily at room temperature as evidenced by the evolution of gas. No attempt was made to purify the material since it was so unstable. Heating the material on the steam bath in an effort to decompose it completely resulted in a violent eruption with subsequent loss of considerable material. The remainder of the material was heated cautiously until the decomposition was completed.

The decomposition product gave negative results for olefinic unsaturation when treated with bromine and potassium permanganate. The material was refluxed for two hours with excess sodium hydroxide solution. After cooling, the reaction mixture was acidified with 5% sulfuric acid solution with the formation of crystals. The crystalline product was filtered and recrystallized from water and air dried. The melting point was 86-87°C.. The amide was prepared as a

derivative and recrystallized from water. The melting point of the amide was 100-101°C.. These two values agree with the literature values of 1-phenylcyclopropanecarboxylic acid and its amide (17).

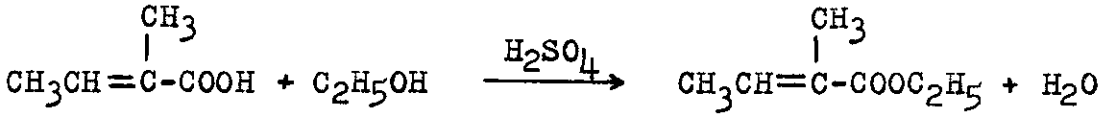
The Preparation of Ethyl Tiglate (8).



Two hundred and twenty-five grams (1.5 moles) of silver nitrate was added to 50g. (0.595 mole) of tiglaldehyde (E.K., practical) together with enough 95% ethanol to form a homogeneous mixture. A sodium hydroxide solution, 84.0g. (2.09 moles) in 4 liters of water (approximately N/2), was placed in a 5-liter, 3-necked flask equipped with a stirrer, dropping funnel, and thermometer. The flask and sodium hydroxide solution were cooled in a salt-ice bath to approximately 10°C. and stirred while the silver nitrate-tiglaldehyde solution was slowly added over a two-hour period. After the addition was completed, the reaction mixture was stirred at room temperature overnight.

The reaction mixture was then filtered through a fluted filter to remove the reduced silver. The filtrate was acidified with a few drops of concentrated hydrochloric acid until just neutral to phenolphthalein. The alcohol was removed by distillation, and the residue was acidified with excess concentrated hydrochloric acid. The acidified solution was extracted thoroughly with ether, and the combined ether extracts were dried over anhydrous sodium sulfate. Upon

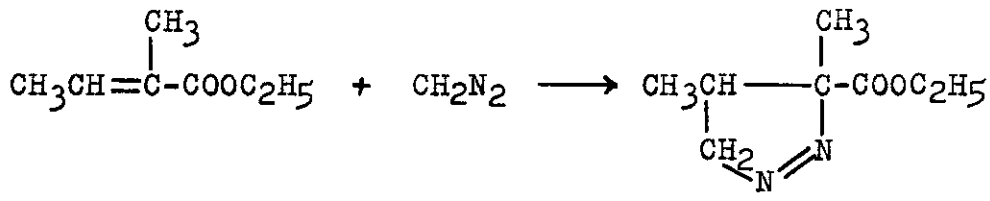
removal of the ether by distillation, the residue crystallized to yield crude tiglic acid when cooled.



The crude product was dissolved in 100 ml. of commercial absolute ethanol and 5 ml. of concentrated sulfuric acid added. The mixture was refluxed for 24 hours and then the excess alcohol removed by distillation. The residue was poured into 250 ml. of water and the organic layer separated. The aqueous layer was extracted with three 50 ml. portions of ether which were combined with the organic layer. The ethereal solution, after having been washed with water and 10% sodium bicarbonate solution, was dried over anhydrous magnesium sulfate. Upon removal of the ether by distillation, the crude product was distilled under reduced pressure. The final product weighed 37.5g., which represents a 49% over-all yield in the two-step process. The product boiled at 47-48°C. at 10 mm. pressure.

Lit.: (31); b.p. 100°C./30 mm..

The Preparation of Ethyl 3,4-Dimethyl-Δ^1-pyrazolin-3-carboxylate.



An ethereal solution of diazomethane was prepared from 41.2g. (0.4 mole) of N-nitroso-N-methylurea. A solution of 25.6g. (0.2 mole) of ethyl tiglate in 50 ml. of ether was added to the diazomethane and the mixture placed in the refrigerator two hours. The ether and excess diazomethane were removed by distillation from a steam bath. The crude residue was distilled under reduced pressure to yield 13.7g. (40.3%) of the pyrazoline boiling at 52.5°C./0.05 mm., $n_D^{24} = 1.4498$.

Anal. for $C_8H_{14}O_2N_2$: Calc: C, 56.45; H, 8.29; N, 16.46. Found: C, 56.4; H, 8.3; N, 16.6.

The Preparation of the Ethyl N-Alkylcarbamates (38)

$$RCH_2NH_2 + ClCOOC_2H_5 + NaOH \longrightarrow RCH_2NHCOOC_2H_5 + NaCl + H_2O$$

The procedure used for the synthesis of the ethyl N-alkylcarbamates is that which is described below for ethyl N-ethylcarbamate. A table which follows the procedure summarizes the preparation of the carbamates which were needed for subsequent reactions leading to the formation of the diazoalkanes.

A solution of 270.0g. (2 moles) of 33% ethylamine and 80.0g. (2 moles) of sodium hydroxide in 120 ml. of water was placed in a one-liter, 3-necked flask which was equipped with a stirrer, dropping funnel, and thermometer. The flask was surrounded by a salt-ice bath. When the amine-hydroxide solution had cooled to about 5°C., 100 ml. of ether was added. While stirring the solution, 217.0g. (2 moles) of ethyl chloroformate in an equal volume of ether was added slowly so that the temperature of the reaction mixture never rose above 20°C.. After the addition had been completed, about four hours, the ether layer was separated and dried over anhydrous potassium carbonate. The ether was removed by distillation on a steam bath. The residue was distilled at reduced pressure to yield 226g. (96%); b.p. 79-80°C./14 mm..

Lit.: (38); (86-92% yields), b.p. 58-60°C./3 mm., or 79-80°C./14 mm..

TABLE III

Preparation of the Ethyl N-Alkylcarbamates

Amine	Amine Moles	$ClCOOC_2H_5$ Moles	NaOH Moles	Yield %	B.P. Product
Ethyl, 33% aq.	2	2	2	96	79-80°C./14 mm.
n-Propyl	1.7	1.6	2.07	78	190-190.5°C.*
n-Butyl	3.2	3	3.68	84	207-209°C.**

*Lit.: (24), b.p. 191.5-192.5°C./758 mm.

**Lit.: (24), b.p. 208-211°C./770 mm.

The Preparation of the Ethyl N-Nitroso-N-Alkylcarbamates (38).

$$RCH_2NHCOOC_2H_5 + NaNO_2 + HNO_3 \longrightarrow RCH_2\text{-}\underset{\displaystyle NO}{\underset{|}{N}}\text{-}COOC_2H_5 + NaNO_3 + H_2O$$

To 226g. (1.92 moles) of ethyl N-ethylcarbamate and 600 ml. of ether in a 5-l. flask was added 200g. of ice together with 650g. (9 moles) of sodium nitrite dissolved in one liter of water. The flask was equipped with a thermometer, a tube to lead off evolved nitric oxide, and a separatory funnel with an extension tube reaching to the bottom of the flask.

A cold solution of 426 ml. (6.7 moles) of concentrated nitric acid and 600g. of ice was then added cautiously through the funnel during one and one-half hours. The flask was swirled occasionally to ensure some mixing, but most of the stirring was done by the evolved gases. Ice was added as required to keep the temperature below 15°C..

After the addition was completed, the ether layer was separated and washed twice with water. The ethereal solution was washed with cold potassium carbonate solution until carbon dioxide was no longer evolved. After drying over anhydrous potassium carbonate, the ether was removed under reduced pressure. The crude material was distilled under reduced pressure to yield 207.0g. (74%), b.p. 54-56°C./6 mm..

Lit.: (38); 76-80% yields, b.p. 52.5-53.5°C./5 mm..

The above procedure was used for the preparation of ethyl

N-nitroso-N-ethylcarbamate and ethyl N-nitroso-N-butyl-carbamate. However, in the preparation of ethyl N-nitroso-N-propylcarbamate, sulfuric acid was used in the place of nitric acid and only a small excess of sodium nitrite was used.

The results are summarized in Table IV.

TABLE IV

Preparation of the Ethyl N-Nitroso-N-Alkylcarbamates.

Carbamate	Carbamate Moles	Acid	$NaNO_2$ Moles	Yield %
$C_2H_5NHCOOC_2H_5$,	1.92	HNO_3, 426 ml.	9	74
n-$C_3H_7NHCOOC_2H_5$,	0.5	H_2SO_4, 196g.	0.6	98*
n-$C_4H_9NHCOOC_2H_5$,	1	HNO_3, 300 ml.	4.5	87**

*Product was not distilled

**Prepared by W. R. Browne

The Preparation of Diazoalkanes (38).

$$RCH_2\text{-}\underset{\displaystyle NO}{\underset{|}{N}}\text{-}COOC_2H_5 + 2KOH \xrightarrow{\text{ether}} RCHN_2 + C_2H_5OH + H_2O + K_2CO_3$$

R = CH_3-, C_2H_5-, n-C_3H_7-

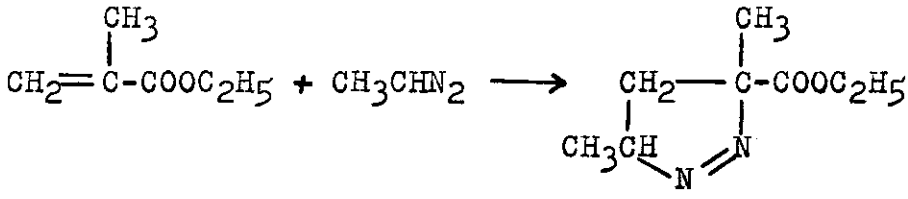
The ethereal solutions of the diazoalkanes which were used were prepared by procedures similar to that described below for diazoethane.

A one-liter, 3-necked flask was fitted with an addition funnel, a mechanical stirrer, and a bent glass tubing leading to a condenser. The condenser was attached to an adapter which dipped below the surface of anhydrous ether in the receiver. The receiver was a 500 ml. suction flask, equipped with a calcium chloride drying tube, cooled in an ice bath.

Two hundred ml. of anhydrous ether and a solution of 50g. (0.89 mole) of potassium hydroxide in 200 ml. of n-propyl alcohol were placed in the flask. The mixture was heated with a water bath, while stirring, until the ether began to distill. Keeping the water bath at 50°C., a solution of 50g. of ethyl N-nitroso-N-ethylcarbamate (0.342 mole) in 150 ml. of ether was added rapidly from the addition funnel in five minutes at such a rate that frothing was not serious. After the addition was completed, fresh portions of ether were added until the distillate was coming over colorless.

The ethereal solution was used directly in the addition to the desired olefins.

The Preparation of Ethyl 3,5-Dimethyl-Δ^1-pyrazolin-3-carboxylate.

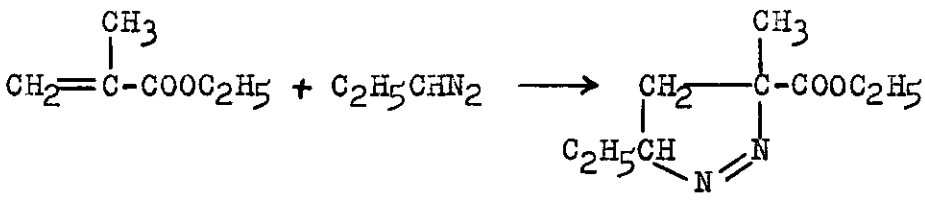


An ethereal solution of diazoethane was prepared from 50g. (0.342 mole) of ethyl N-nitroso-N-ethylcarbamate and was added to a solution of 45.6g. (0.4 mole) of ethyl methacrylate in 50 ml. of ether. The resulting solution was kept in the refrigerator for two hours during which time the orange color was completely discharged.

The ether and excess ethyl methacrylate were removed by distillation from a steam bath under reduced pressure. The crude residue was distilled under vacuum to yield 24.1g. (41%) of the pyrazoline, b.p. 44-44.5°C. at 0.1 mm., $n_D^{24} = 1.4437$.

Anal. for $C_8H_{14}O_2N_2$: Calc.: C, 56.45; H, 8.29; N, 16.46. Found: C, 56.4; H, 8.3; N, 16.2.

The Preparation of Ethyl 5-Ethyl-3-methyl-Δ^1-pyrazolin-3-carboxylate.

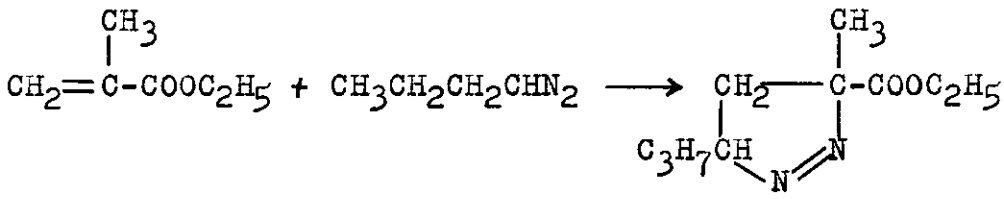


An ethereal solution of diazopropane was prepared from 78g. (0.488 mole) of ethyl N-nitroso-N-propylcarbamate. The solution was added to 57g. (0.5 mole) of ethyl methacrylate, dissolved in 50 ml. of ether, and the mixture was placed in the refrigerator for two hours. The orange color of the ethereal solution was completely bleached so the ether and excess ethyl methacrylate were removed by distillation from a steam bath under reduced pressure.

The crude residue was distilled under vacuum to yield 21.4g. (24.0%) of the pyrazoline boiling at 56-57°C./0.3 mm., $n_D^{24} = 1.4458$.

Anal. for $C_9H_{16}O_2N_2$. Calc.: C, 58.76; H, 8.75; N, 15.3. Found: C, 58.7; H, 8.5; N, 15.4.

The Preparation of Ethyl 5-Propyl-3-methyl-Δ^1-pyrazolin-3-carboxylate.



An ethereal solution of n-diazobutane was prepared from 69.6g. (0.4 mole) of ethyl N-nitroso-N-butylcarbamate. A solution of 57.0g. (0.5 mole) of ethyl methacrylate in 50 ml. of ether was added to the diazobutane, and the resulting mixture was placed in the refrigerator for two hours. The orange color of the diazo solution was completely removed during the two hours. Removal of the ether and excess ethyl methacrylate on a steam bath under reduced pressure left a residue which was distilled under vacuum. The yield of the pyrazoline was 12.0g. (15.2%), b.p. 73-74°C./0.3 mm., $n_D^{24} = 1.4468$.

Anal. for $C_{10}H_{18}N_2O_2$. Calc.: C, 60.5; H, 9.2; N, 14.1. Found: C, 60.4; H, 9.1; N, 14.0.

The Preparation of 3-Methyl-4-hydroxy-2-butanone (19).

$$CH_3COCH_2CH_3 + HCHO \xrightarrow[KOH]{alc.} CH_3COCHCH_3 \quad (CH_2OH)$$

Three hundred and fifty grams (4.85 moles) of methyl ethyl ketone was mixed with 30g. (1 mole) of paraformaldehyde in a 500 ml. 3-necked flask which was equipped with a stirrer, reflux condenser, and a thermometer. The mixture was heated, while stirring, to 40°C. and 3.5 ml. of 0.5N alcoholic potassium hydroxide solution was added. Upon addition of the alkali, the suspended paraformaldehyde soon depolymerized to produce a clear solution. The mixture was kept at 40-45°C., and the stirring was continued until a negative Tollen's test for formaldehyde was achieved. One ml. of 2N acetic acid solution in 5 ml. of methyl ethyl ketone was then added to neutralize the alkali. The excess ketone was removed by distillation. The residue of crude product was distilled under vacuum. The yield of final product was 73g. (71.5%), b.p. 86-89°C./15 mm..

Lit.: (19); 80-89% yield of crude material.

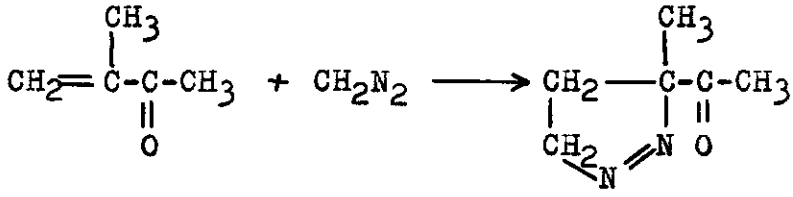
The Preparation of Methyl Isopropenyl Ketone(37).

$$CH_3COCH(CH_2OH)CH_3 \xrightarrow[\text{hydroquinone}]{KHSO_4} CH_3COC(CH_3){=}CH_2 + H_2O$$

Five grams of freshly fused potassium acid sulfate and 0.4g. of hydroquinone were ground together and placed in a 250 ml. reaction flask which was fitted with a Claisen head leading to a condenser for distillation. The mixture was heated by an oil bath to about 140°C. (oil bath temperature). The ketol, 73g. (0.715 mole), was preheated to 95°C. and allowed to drop upon the potassium acid sulfate in a steady stream. The unsaturated ketone and water distilled together and were separated when the reaction had ceased. The crude ketone, after drying over anhydrous magnesium sulfate, was distilled under reduced pressure to yield 32.0g. (53.5%) of product boiling at 47-48°C. at 110 mm. pressure.

Lit.: (37); 80% yield, b.p. 58°C./200 mm..

The Preparation of 3-Methyl-3-aceto-Δ^1-pyrazoline.



An ethereal solution of diazomethane was prepared from 41.2g. (0.4 mole) of N-nitroso-N-methylurea. To the diazomethane solution was added 16.8g. (0.2 mole) of isopropenyl methyl ketone in 50 ml. of ether. The mixture was placed in the refrigerator for two hours. The ether and excess diazomethane were removed by distillation from a steam bath. The crude residue was distilled under reduced pressure to yield 20.2g. (80%) of the pyrazoline, b.p. 79-80°C./0.5 mm..

Anal. for $C_6H_{10}N_2O$: Calc.: C, 57.1; H, 8.0; N, 22.2. Found: C, 57.0; H, 8.1; N, 22.0.

The Preparation of 2-Nitro-1-propanol (3).

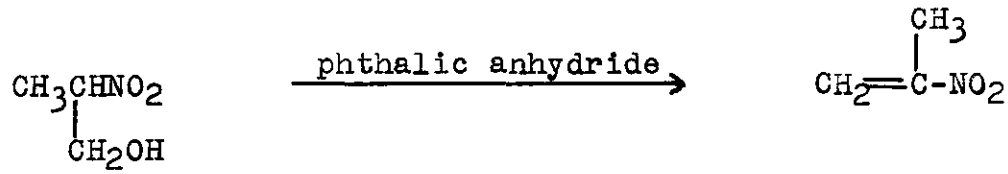
$$CH_3CH_2NO_2 + HCHO \xrightarrow{Ca(OH)_2} \begin{matrix} CH_3CHNO_2 \\ | \\ CH_2OH \end{matrix}$$

Two hundred and twenty-five grams (3 moles) of nitroethane, 255 ml. of 95% ethanol, and 0.9g. of calcium hydroxide were placed together in a 2-liter, 3-necked flask equipped with a stirrer, thermometer, and dropping funnel. Then 240g. (3 moles) of 37.5% aqueous formaldehyde solution was added to the stirred nitroethane mixture. The addition was accompanied by a slight temperature rise. After the completion of the addition, the mixture was allowed to stand for forty-eight hours.

The mixture was next treated with an excess of carbon dioxide, and the calcium carbonate, which formed, was removed by filtration through a sintered glass filter. Alcohol, water and any unreacted materials were removed by distillation on the steam bath, and the residue was distilled under reduced pressure. The final yield of product which distilled with difficulty was 116.0g. (37%), b.p. 100-105°C./13 mm..

Lit.: (3); 46% yield, b.p. 100-105°C./13 mm..

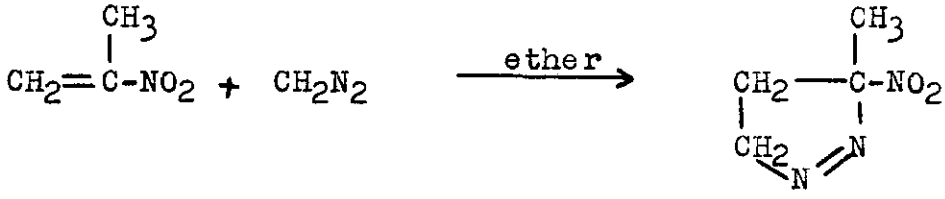
The Preparation of 2-Nitro-1-propene (5).



Seventy-five grams (0.5 mole) of phthalic anhydride and 52.5g. (0.5 mole) of the nitroalcohol were mixed together in a 250 ml. reaction flask fitted with a short fractionating column and heated with an oil bath. After evacuating the apparatus to 80 mm., the mixture was heated at 140-150°C. until homogeneous. The bath temperature was then raised to 175-180°C. and kept there until distillation had ceased. The distillate, dried over anhydrous calcium chloride, was redistilled under vacuum to give 18.0g. (41%) of nitroolefin which boiled at 57-57.5°C. at 85 mm. pressure. The product was a yellow oil which turned green quickly; it was used immediately in the preparation of the pyrazoline.

Lit.: (5); 55.5% yield, b.p. 58°C./90 mm..

The Preparation of 3-Nitro-3-methyl-Δ^1-pyrazoline.



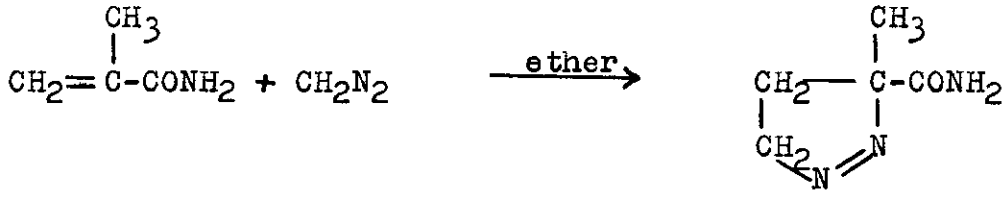
An ethereal solution of diazomethane prepared from 41.2g. (0.4 mole) of N-nitroso-N-methylurea was redistilled in order to remove all traces of alkali which would polymerize the nitro-olefin.

Eighteen grams (0.207 mole) of 2-nitropropene dissolved in 50 ml. of ether was added to the ethereal diazomethane solution. Although a very vigorous reaction took place, the solution was cooled down and placed in the refrigerator overnight.

The excess diazomethane and ether were removed by distillation on a steam bath. The residue was distilled under reduced pressure to yield 20.6g. (77%), b.p. 66-66.5°C./ 1.0 mm..

Anal. for $C_4H_7N_3O_2$: Calc.: C, 37.2; H, 5.5; N, 32.5. Found: C, 37.1; H, 5.5; N, 32.2.

The Preparation of 3-Methyl-3-carbamyl-Δ^1-pyrazoline.

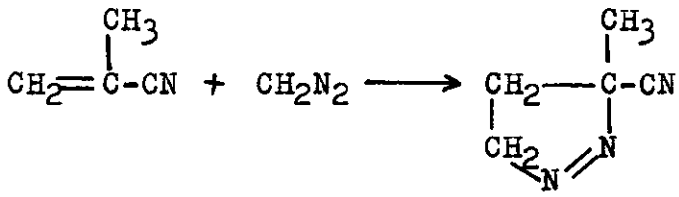


An ether-chloroform solution of diazomethane was prepared from 41.2g. (0.4 mole) of N-nitroso-N-methylurea. To the diazomethane was added 17g. (0.2 mole) of methacrylamide dissolved in 500 ml. of chloroform. The combined solution was kept at room temperature overnight (cooling the solution caused the amide to crystallize).

The solvent and excess diazomethane were removed by distillation; the residue crystallized upon cooling. The crude material was recrystallized from 95% ethanol to yield 17.8g. (70%), m.p. 109-109.5°C.. Although the material was first believed to be the starting material (m.p. 108-110°C.), a mixed melting point of 70-82°C. dispelled this belief.

Anal. for $C_5H_9N_3O$: Calc.: C, 47.24; H, 7.14; N, 33.06. Found: C, 47.0; H, 7.1; N, 32.9.

The Preparation of 3-Cyano-3-methyl-Δ^1-pyrazoline.

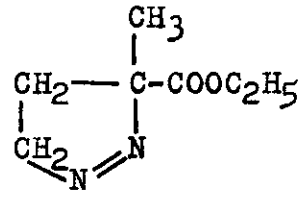


An ethereal solution of diazomethane was prepared from 41.2g. (0.4 mole) of N-nitroso-N-methylurea. To the diazomethane was added 13.4g. (0.2 mole) of methacrylonitrile dissolved in 50 ml. of ether. After the mixture had stood in the refrigerator for two hours, the excess diazomethane and ether were removed by distillation from a steam bath to yield 20.7g. of crude material. The pyrazoline was distilled under reduced pressure; the fraction distilling between 45 and 46°C. at 0.3 mm. was collected. The final yield was 14.0g. (64.2%), $n_D^{24} = 1.4518$.

Anal. for $C_5H_7N_3$: Calc.: C, 55.02; H, 6.46; N, 38.5. Found: C, 54.9; H, 6.5; N, 38.3.

The Kinetics of the Thermal Decomposition of the Pyrazolines.

Since the Δ^1-pyrazolines decompose thermally to give off nitrogen, the reaction lends itself readily to kinetic study. The course of the reaction can be easily followed by measuring the volume of nitrogen evolved as a function of time. Because the decomposition of aliphatic azo compounds follows first order kinetics (28), it was believed that the thermal decomposition of the Δ^1-pyrazolines would also obey first order kinetics. Preliminary studies made at the laboratories of the Armstrong Cork Co. (1), showed that the nitrogen liberation of ethyl 3-methyl-Δ^1-pyrazolin-3-carboxylate (I) gave first order plots.



(I)

The first step in the kinetic study was the construction of the decomposition apparatus. The most important part of the decomposition apparatus is the constant temperature bath because small changes in the temperature of the reaction cause relatively large errors in the final kinetic rate. The bath was made from a 4-liter silvered Dewar flask which was set into a large wooden box. The flask was then surrounded with rock wool insulation. The top of the flask was shielded with

a cover made from 1" insulating material. The heat source was a 50 watt flexible heater which was coiled to fit the inside of the flask. The heater was activated by an electronic relay which was operated by a Magna-Set Mercury Thermoregulator. The electronic relay employed was built by the author according to the wiring diagram shown in Figure 1 (32). A stirrer and a Beckmann thermometer completed the constant temperature bath. The insulating cover of the Dewar flask was cut into two pieces to permit the removal of the reaction flask. Dibutyl phthalate was employed as the heat exchange medium.

It was soon discovered that the 50 watt heater provided too much heat input to maintain a narrow range of temperature control. For this reason, a variable resistance (Fig. 1, Resistance No. 1) was inserted in series with the heater so that the heat input, when called for by the control circuit, would be only a fraction of the 50 watt total. The adjustment of the resistance usually was dependent upon the temperature at which the bath was operating. The heating circuit with the resistance in it is labeled "Low Heater" ih the wiring diagram. Since it was advantageous to use the total input of the 50 watt heater when heating the bath from room temperature, an external circuit from the relay was provided; this heating circuit is referred to as the "High Heater" in the wiring diagram.

A third heating circuit had to be installed when it was

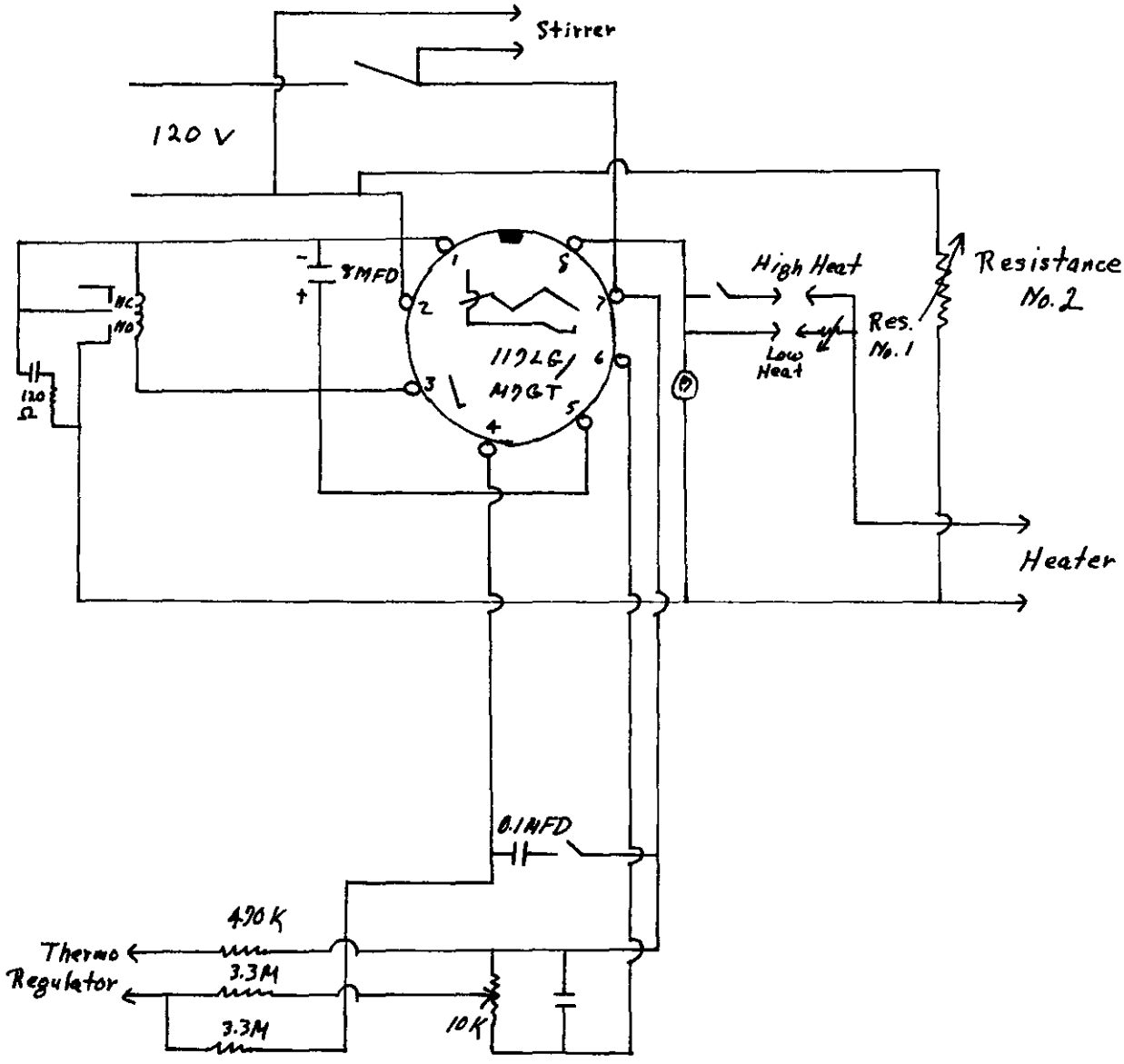


Figure No. 1

Electronic Relay Circuit

found that the loss of heat from the dibutyl phthalate was too rapid for efficient operation. In order to effectively retard the loss of heat from the butyl phthalate, a small input of heat was constantly fed into the bath by means of a circuit which by-passed the relay. The heat input of this latter circuit was controlled by a variable resistance (Fig. 1, Resistance No. 2). The adjustment of this resistance was also dependent upon the operating temperature of the bath.

The reaction flask was a 100 ml. round bottom flask fitted with an inlet tube extending to the bottom for the carbon dioxide, which was used to sweep the nitrogen from the flask into the gas buret, and an outlet which led, via a capillary tube, to the gas buret. The flask also had an arm made of capillary tubing which extended above the top of the control bath with a stopcock. The sample (the pyrazoline) was introduced through the stopcock by a hypodermic syringe. Originally, the side arm was stoppered with a self-sealing rubber stopper, but it was found that the butyl phthalate attacked the rubber at the operating temperature of the bath. The reaction flask is shown in Figure 2. When the reaction flask was placed in the constant temperature bath, it rested in a small wire strainer which was suspended across the heating coils of the bath. The flask was filled with 140 ml. of tetrahydronaphthalene (E.K., practical grade) which was used as the diluent.

The gas collecting tube was a 100 ml. gas buret equipped

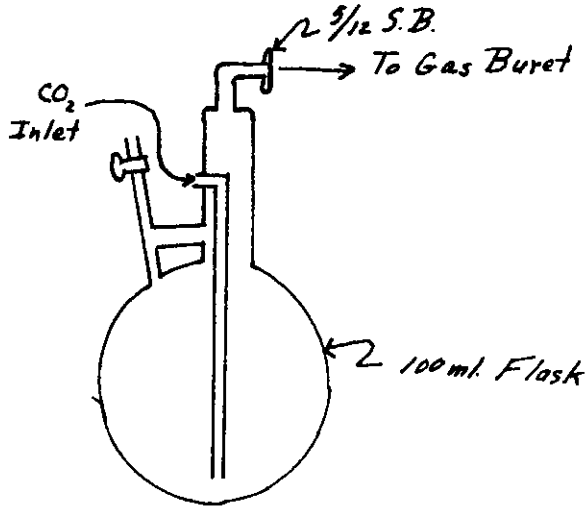


Figure No. 2

Reaction Flask

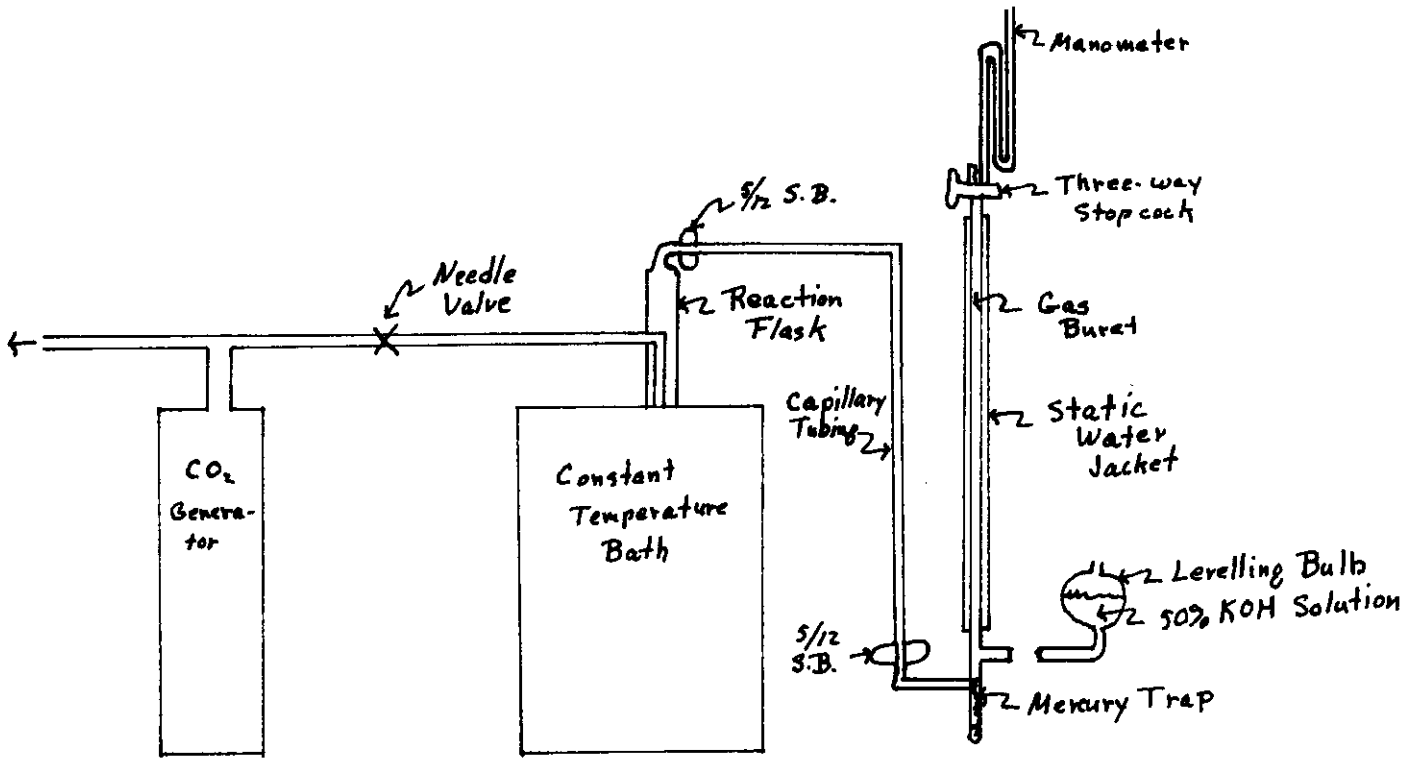


Figure No. 3

Decomposition Apparatus

with a leveling device similar to the burettes used in the Dumas method for the determination of nitrogen (7). The gases from the reaction flask entered the buret at the bottom through a mercury trap. The carbon dioxide which was used to sweep the nitrogen through the system was dissolved by 50% potassium hydroxide solution in the gas buret. The nitrogen was collected in the buret and its volume read as a function of time. The top of the gas buret was equipped with a three-way stopcock. In one position, the buret was opened to the atmosphere; in the other position, the buret was opened to a manometer which operated against atmospheric pressure. The manometer, which was filled with butyl phthalate, facilitated volume readings since it was easier to determine when the gas in the buret was at atmospheric pressure. The gas buret was surrounded by a static water jacket to reduce temperature fluctuations of the nitrogen collected. The gas buret is shown in Figure 3.

The sublimation of dry ice was found to be the best source of carbon dioxide used to sweep the system. The dry ice was stored in a silvered 500 ml. Dewar flask equipped with a T-joint. One arm of the T-joint was connected with tubing to the inlet tube of the reaction flask. The flow of carbon dioxide through the system was controlled by a needle valve set between the Dewar flask and the reaction flask. The rate of flow of carbon dioxide was adjusted to approximately one liter per hour. The other end of the T-joint on the Dewar flask was

connected to a safety valve which maintained constant pressure and prevented excessive pressure from building up in the flask.

In carrying out a kinetic run, the system was first allowed to come to thermal equilibrium. Carbon dioxide was passed through the apparatus to remove the air and fill the system with the gas. Before the sample of pyrazoline could be introduced, the blank had to be determined. The buret was filled with 50% potassium hydroxide solution and closed at the top. A zero volume reading and the time were noted. Carbon dioxide was bubbled through the system for a period of time ranging from one to two hours. A final volume reading, the time, the atmospheric pressure, and the temperature of the water jacket (which is taken as the temperature of the gas in the buret) were noted. The data obtained could then be used to calculate the blank in terms of milliliters per minute at standard temperature and pressure. The use of the blank is shown under the section of calculations.

After the gas buret was refilled with fresh 50% potassium hydroxide solution, the apparatus was set for a kinetic run. The zero volume reading was noted and recorded. The sample of pyrazoline dissolved in tetralin was injected with the syringe into the reaction flask through the stopcock and side arm. The time of the start of the run was noted by starting a stopwatch. The volume of nitrogen in the buret was recorded after the pressure in the buret was balanced with the atmospheric

pressure by the aid of the leveling-bulb and manometer. The time of the reading, the atmospheric pressure, and the temperature of the water jacket were also recorded. Readings were made at convenient intervals which were dependent upon the rate of decomposition. Usually six to nine readings were made over one to two hours. In some cases, there were more readings taken and the time period was over three hours. The process of reducing the raw data to the final form which was used in calculating the rate constant of a reaction is shown in the next section.

The size of the sample was arbitrarily set at 0.003 mole which provided for a final volume of nitrogen of about 70-75 ml. at room conditions. The concentration of the pyrazolines was about 0.3-0.5g. in 140 ml. of tetralin. In a few cases, a smaller amount of sample was used. The results of the kinetic runs are shown in table form and graphs at the end of the section.

For each compound, the rate constant was determined at two different temperatures which were usually fifteen to twenty degrees apart. From the two constants, the energy of activation for each compound could be determined. The calculations and results are also shown in the next section.

Calculation of the Rate Constants.

Since it was established that the nitrogen evolution gave good first order kinetics, the equation of a first order reaction could be used as follows

$$k = \frac{2.303}{t} \log \frac{a_o}{a_o - x}$$

where a_o = the original concentration of the reactant, and x = the amount of reactant which has reacted in time interval t (which can be expressed in any time units). Because the thermal decomposition of a Δ^1-pyrazoline evolves one mole of nitrogen per molecule of pyrazoline, the volume of nitrogen, expressed at standard temperature and pressure, can be used as a measure of concentration of reactant. Thus the rate expression takes on the form of

$$k = \frac{2.303}{t} \log \frac{V_\infty}{V_\infty - V}$$

where V_∞ is the volume of nitrogen, at S. T. P. equivalent to the original concentration of the pyrazoline (expressed in moles), and V is the volume of nitrogen evolved during the interval t (expressed in minutes). A plot of the quantity $\log \frac{V_\infty}{V_\infty - V}$ vs. t will result in a straight line. The slope of the line obtained multiplied by 2.303 will be equal to the rate constant.

In order to show how the calculations are made, the raw data obtained during a kinetic run are shown below. The material being decomposed is n-propyl 3-methyl-Δ^1-pyrazoline-3-carboxylate at 109.5°C..

Time (min.-sec.)	Vol. ml. of N_2 evolved	Gas Temp. °C.	Press. mm. Hg.
12-30	2.70	27.5	770.0
28-25	8.65	27.7	770.0
44-24	14.30	27.9	770.0
84-35	26.35	28.0	770.0
103-32	31.10	28.0	770.0
117-24	34.30	28.0	770.0
140-31	39.00	27.8	770.0

The first three steps consist of a) converting the temperature readings to degrees absolute, b) correcting the pressure readings by substracting the vapor pressure of 50% potassium hydroxide solution (7), and c) changing the seconds to hundredths of a minute. The results of the first three steps as applied to the above data are shown below.

Time	Gas Temp. °T	Press. mm. Hg.
12.50	300.7	759.9
28.42	300.9	759.8
44.40	301.1	759.7
84.58	301.2	759.6
103.53	301.2	759.6
117.40	301.2	759.6
140.52	301.0	759.7

The volume readings are next reduced to standard temperature and pressure values by use of the following equation

$$V = \frac{(273.2)}{(760)} \times \frac{(P')}{(T')} \times (V')$$

$$= (0.359) \times \frac{(P')}{(T')} \times (V')$$

e.g. $$V = (0.359) \times \frac{(759.9)}{300.7} \times (2.70) = 2.45$$

The result of this calculation is to give a series of volumes at standard temperature and pressure as shown. However, the blank must be substracted from the volumes to give a true value. The uncorrected volumes are listed below.

2.45
7.84
12.95
23.85
28.15
31.05
35.33

The value for the blank had been pre-determined to be 0.0068 ml./min.. The correction which had to be substracted was calculated by multiplying the blank by the time interval, e.g. for the first volume, the correction is: 0.0068 x 12.50 = 0.09 and the S.T.P. volume should be 2.36 ml. instead of 2.45 ml.. The corrected volumes are shown below together with the values of $V_\infty - V$ where V_∞ had been previously calculated to be 63.44 ml.

S.T.P. Vol.	$V_\infty - V$
2.36	61.08
7.63	55.81
12.65	50.79
23.23	40.21
27.45	35.99
30.25	33.19
34.37	29.07

The value for the term $\frac{V_\infty}{V_\infty - V}$ was then determined and its logarithm obtained from tables. The final results are shown in Table VII, Run No. 2. In plotting the values of time vs. log $\frac{V_\infty}{V_\infty - V}$, time is plotted to one decimal place and the logarithm to three. The plot of the results is shown in

the graph on page 71, Run No. 2. The value of the slope of the line formed is 0.0025. The slope must be multiplied by 2.303 to obtain the rate constant in $min.^{-1}$ which, in this example, is 0.0058.

The tables and graphs at the end of the section show the results of the kinetic data obtained.

As another means of comparing the ease of nitrogen evolution, the half-lives of each compound were also calculated by means of the following formula (11a):

$$t_{\frac{1}{2}} = \frac{2.303 \log 2}{k} = \frac{0.6932}{k},$$

where $t_{\frac{1}{2}}$ is the half-life for the reaction and k is the rate constant. The half-lives were calculated from each rate constant.

Calculation of the Energy of Activation.

The following equation represents the solution for the Arrhenius activation energy (E_a) of a reaction (11b):

$$E_a = \frac{(2.303) \times (R) \times (T_2) \times (T_1) \times (\log k_2 - \log k_1)}{T_2 - T_1},$$

where k_2 and k_1 are rate constants at T_2 and T_1 where the latter are expressed in ^{o}A, and R is the gas constant expressed in calories.

The rate constants, half-lives, and activation energies are listed in the following tables and are summarized in Table XX, p. 115.

In the following tables, the observed and calculated data for each run are recorded. The observed volumes of collected nitrogen are listed under "Accum. Vol."; the observed volumes reduced to standard temperature and pressure and corrected for the blank (which is also at S.T.P.) are listed under "S.T.P. Vol.".

TABLE V

The Observed and Calculated Data for the Decomposition of Methyl 3-Methyl-Δ^1-pyrazolin-3-carboxylate in Tetralin.

Run #1 Blank = 0.0064 ml./min. V_∞ = 67.88 ml.

Weight of Sample = 0.4305g. Temp. = 125.9°C.

Time (min.)	Accum. Vol. (ml.)	Gas Temp. (abs.)	Gas Press. mm (corr.)
7.3	8.10	298.1	768.0
13.5	21.85	298.2	767.9
23.5	40.10	298.2	767.9
35.4	52.95	298.4	767.8
50.5	63.74	298.7	767.7
62.5	67.90	299.0	767.5

S.T.P. Vol. (ml.)	$\frac{V_\infty}{V_\infty - V}$	$\log \frac{V_\infty}{V_\infty - V}$
7.44	1.123	0.050
20.11	1.421	0.153
36.92	2.193	0.341
48.68	3.535	0.548
58.49	7.229	0.859
62.17	11.888	1.075

2.303 x Slope = 0.0431 = k $min.^{-1}$

$t_{\frac{1}{2}}$ = 16 min.

Run #2 Blank = 0.0064 ml./min. V_∞ = 67.88 ml.

Weight of Sample = 0.4305g. Temp. = 125.9°C.

Time (min.)	Accum. Vol. (ml.)	Gas Temp. (abs.)	Gas Press. mm (corr.)
7.0	8.55	299.9	765.3
13.0	21.90	300.0	765.3
20.0	36.80	300.0	765.3
28.1	47.30	300.1	765.2
33.0	52.50	300.1	765.2
41.0	59.10	300.1	765.2
48.3	63.95	300.1	765.2

S.T.P. Vol. (ml.)	$\frac{V_\infty}{V_\infty - V}$	$\log \frac{V_\infty}{V_\infty - V}$
7.79	1.130	0.053
19.98	1.417	0.151
33.57	1.978	0.296
43.12	2.742	0.438
47.82	3.384	0.529
53.84	4.835	0.684
58.23	7.034	0.847

$2.303 \times \text{Slope} = 0.0435 = k \text{ min.}^{-1}$

$t_{\frac{1}{2}} = 16$ min.

Run #3 Blank = 0.0068 ml./min. V_∞ = 67.88 ml.

Weight of Sample = 0.4305g. Temp. = 109.5°C.

Time (min.)	Accum. Vol. (ml.)	Gas Temp. (abs.)	Gas Press. mm (corr.)
7.4	1.20	300.0	758.7
14.6	4.10	300.1	758.6
27.5	9.65	300.1	758.6
42.5	15.60	300.2	758.6
56.4	20.90	300.2	758.6
74.7	26.90	300.2	758.6
90.1	31.45	300.2	758.6
105.5	35.60	300.2	758.6

S.T.P. Vol. (ml.)	$\frac{V_\infty}{V_\infty - V}$	$\log \frac{V_\infty}{V_\infty - V}$
1.04	1.016	0.007
3.62	1.056	0.032
8.57	1.144	0.058
13.86	1.257	0.099
18.58	1.377	0.139
23.89	1.543	0.188
27.92	1.699	0.230
31.57	1.869	0.271

$2.303 \times \text{Slope} = 0.0062 = k \text{ min.}^{-1}$

$t_{\frac{1}{2}} = 112$ min.

$E_a = 36$ kcal./mole

Decomposition of Methyl 3-Methyl-Δ^1-pyrazolin-3-carboxylate in Tetralin

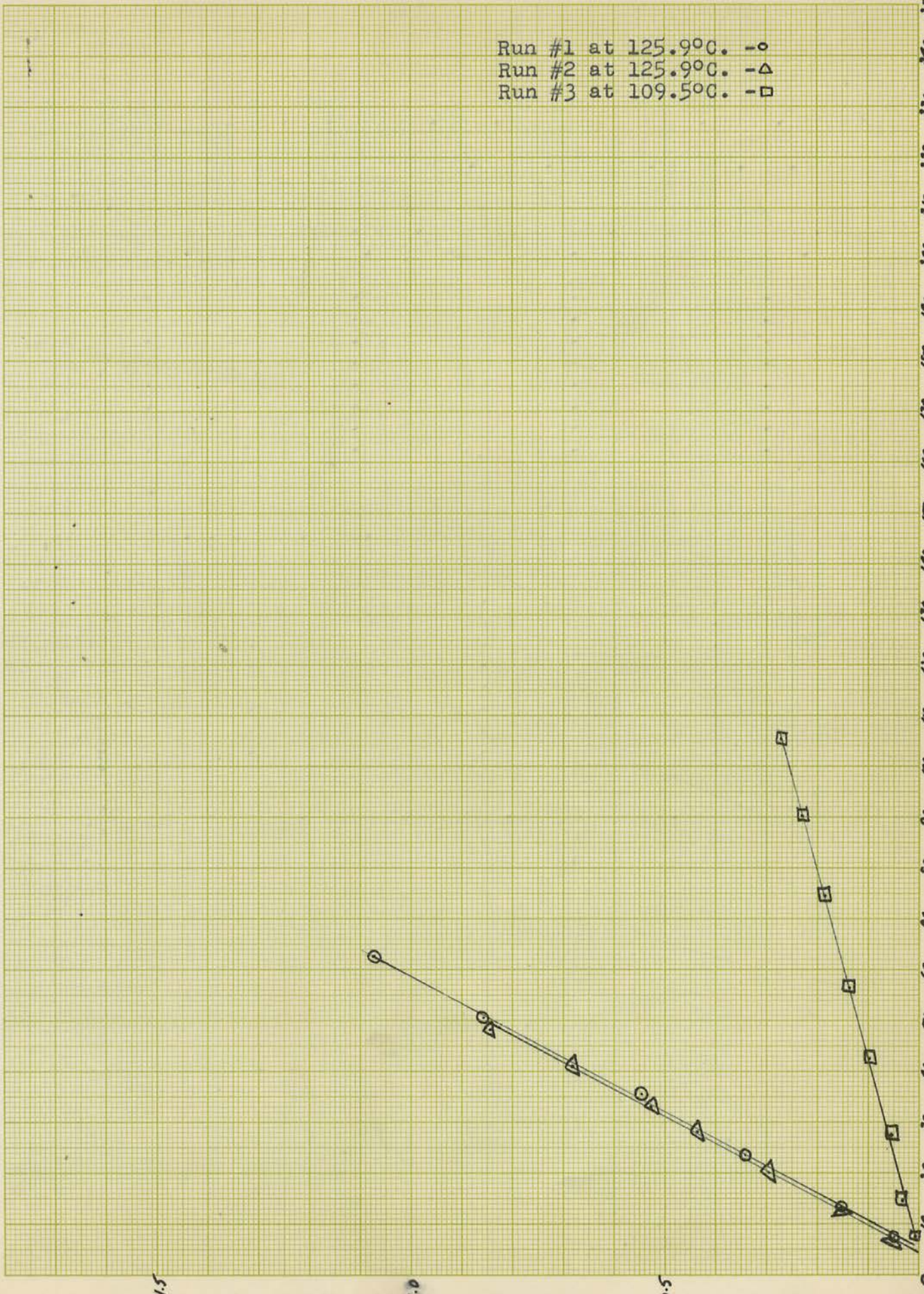


TABLE VI

The Observed and Calculated Data for the Decomposition of Ethyl 3-Methyl-Δ^1-pyrazolin-3-carboxylate in Tetralin.

Run #1 Blank = 0.0052 ml./min. V_∞ = 67.02 ml.

Weight of Sample = 0.4676g. Temp. = 109.5°C.

Time (min.)	Accum. Vol. (ml.)	Gas Temp. (abs.)	Gas Press. mm (corr.)
8.7	1.70	298.1	749.2
18.4	5.75	298.2	749.1
29.3	10.30	298.3	749.1
47.5	17.30	298.5	749.0
58.8	20.85	299.0	748.8
72.4	25.40	299.2	748.7

S.T.P. Vol. (ml.)	$\frac{V_\infty}{V_\infty - V}$	$\log \frac{V_\infty}{V_\infty - V}$
1.48	1.023	0.010
5.09	1.082	0.034
9.14	1.158	0.064
15.34	1.297	0.113
18.44	1.380	0.140
22.44	1.503	0.177

2.303 x Slope = 0.0060 = k $min.^{-1}$

$t_{\frac{1}{2}}$ = 116 min.

Run #2 Blank = 0.0079 ml./min. V_∞ = 67.02 ml.

Weight of Sample = 0.4676g. Temp. = 125.9°C.

Time (min.)	Accum. Vol. (ml.)	Gas Temp. (abs.)	Gas Press. mm (corr.)
11.4	12.70	300.2	752.4
15.3	19.60	300.2	752.4
21.5	29.75	300.4	752.3
27.7	38.45	300.6	752.2
35.4	47.15	300.9	752.0
45.4	55.35	301.1	751.9
55.9	61.50	301.2	751.8
64.4	64.95	301.4	751.7

S.T.P. Vol. (ml.)	$\frac{V_\infty}{V_\infty - V}$	$\log \frac{V_\infty}{V_\infty - V}$
11.34	1.204	0.081
17.52	1.354	0.132
26.58	1.657	0.219
34.32	2.050	0.312
42.02	2.681	0.428
49.26	3.774	0.577
54.67	5.427	0.735
57.64	7.145	0.854

$2.303 \times \text{Slope} = 0.0341 = k \text{ min.}^{-1}$

$t_{\frac{1}{2}} = 20$ min.

$E_a = 32$ kcal./mole

Decomposition of Ethyl 3-Methyl-Δ^1-pyrazolin-3-carboxylate in Tetralin

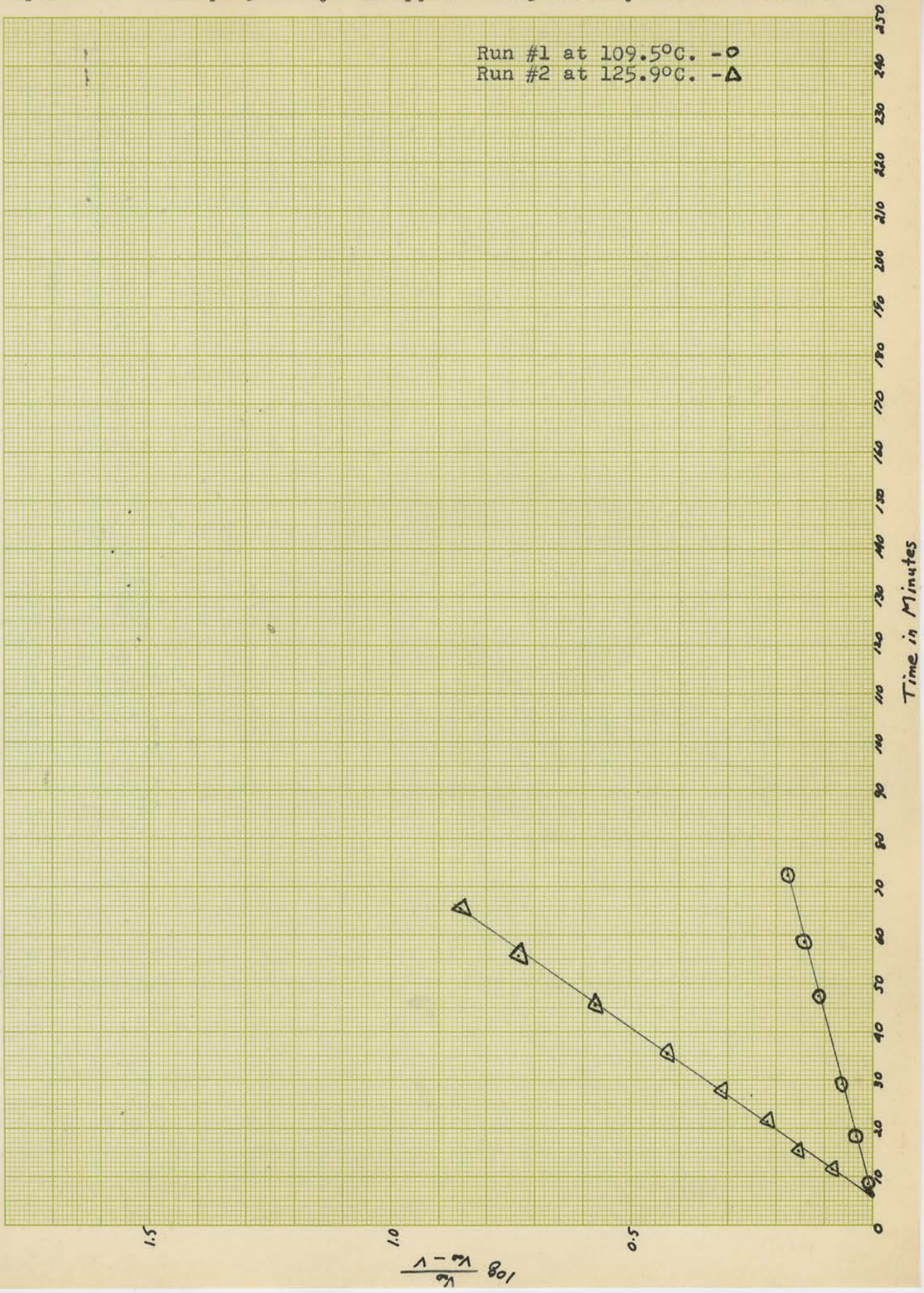


TABLE VII

The Observed and Calculated Data for the Decomposition of n-Propyl 3-Methyl-Δ^1-pyrazolin-3-carboxylate in Tetralin.

Run #1 Blank = 0.0095 ml./min. V_∞ = 63.44 ml.

Weight of Sample = 0.4822g. Temp. = 125.9°C.

Time (min.)	Accum. Vol. (ml.)	Gas Temp. (abs.)	Gas Press. mm (corr.)
9.5	10.60	300.3	755.3
16.5	23.75	300.3	755.3
23.5	33.20	300.4	755.3
30.5	47.25	300.5	755.2
38.5	49.35	300.6	755.2
47.5	55.10	300.6	755.2
55.5	59.05	300.7	755.1

S.T.P. Vol. (ml.)	$\frac{V_\infty}{V_\infty - V}$	$\log \frac{V_\infty}{V_\infty - V}$
9.48	1.176	0.070
21.28	1.505	0.178
29.75	1.883	0.275
37.84	2.478	0.394
44.15	3.289	0.571
49.25	4.471	0.650
52.70	5.907	0.771

2.303 x Slope = 0.0351 = k $min.^{-1}$

$t_{\frac{1}{2}}$ = 20 min.

Run #2 Blank = 0.0068 ml./min. V_∞ = 63.44 ml.

Weight of Sample = 0.4822g. Temp. = 109.5°C.

Time (min.)	Accum. Vol. (ml.)	Gas Temp. (abs.)	Gas Press. mm (corr.)
12.5	2.70	300.7	759.9
28.4	8.65	300.9	759.8
44.4	14.30	301.1	759.7
84.6	26.35	301.2	759.6
103.5	31.10	301.2	759.6
117.4	34.30	301.2	759.6
141.5	39.00	301.0	759.7

S.T.P. Vol. (ml.)	$\frac{V_\infty}{V_\infty - V}$	$\log \frac{V_\infty}{V_\infty - V}$
2.36	1.039	0.017
7.63	1.137	0.056
12.65	1.249	0.097
23.23	1.578	0.198
27.45	1.763	0.246
30.25	1.911	0.281
34.37	2.185	0.339

$2.303 \times \text{Slope} = 0.0058 = k \text{ min.}^{-1}$

$t_{\frac{1}{2}} = 120$ min.

$E_a = 33$ kcal./mole

ecomposition of n-Propyl 3-Methyl-Δ^1-pyrazolin-3-carboxylate in Tetralin

TABLE VIII

The Observed and Calculated Data for the Decomposition of Isopropyl 3-Methyl-Δ^1-pyrazolin-3-carboxylate in Tetralin.

Run #1 Blank = 0.0065 ml./min. V_∞ = 64.33 ml.

Weight of Sample = 0.4901g. Temp. = 125.9°C.

Time (min.)	Accum. Vol. (ml.)	Gas Temp. (abs.)	Gas Press. mm (corr.)
13.2	16.40	296.9	762.4
19.2	26.45	297.0	762.4
27.3	37.15	297.2	762.3
36.4	46.05	297.2	762.3
45.3	52.75	297.3	762.2
57.4	58.80	297.5	762.1
67.4	62.35	298.0	761.9
77.4	64.70	298.1	761.8

S.T.P. Vol. (ml.)	$\frac{V_\infty}{V_\infty - V}$	$\log \frac{V_\infty}{V_\infty - V}$
15.03	1.305	0.116
24.25	1.605	0.205
34.03	2.123	0.327
42.17	2.903	0.463
48.26	4.003	0.602
53.70	6.052	0.782
56.79	8.532	0.931
58.86	11.761	1.070

2.303 x Slope = 0.0343 = k $min.^{-1}$

$t_{\frac{1}{2}}$ = 20 min.

Run #2 Blank = 0.0065 ml./min. V_∞ = 64.33 ml.

Weight of Sample = 0.4901g. Temp. = 125.9°C.

Time (min.)	Accum. Vol. (ml.)	Gas Temp. (abs.)	Gas Press. mm (corr.)
10.6	12.35	297.2	748.1
18.5	26.00	297.2	748.1
27.5	38.30	297.4	748.0
48.8	55.75	297.7	747.8
56.6	59.60	297.7	747.8
67.5	63.40	297.7	747.8
77.3	65.85	297.7	747.8

S.T.P. Vol. (ml.)	$\frac{V_\infty}{V_\infty - V}$	$\log \frac{V_\infty}{V_\infty - V}$
11.09	1.208	0.082
23.38	1.571	0.196
34.40	2.155	0.333
49.96	4.477	0.651
53.37	5.870	0.769
56.73	8.464	0.928
58.88	11.804	1.072

2.303 x Slope = 0.0341 = k $min.^{-1}$

$t_{\frac{1}{2}}$ = 20 min.

Run #3 Blank = 0.0044 ml./min. V_∞ = 64.33 ml.

Weight of Sample = 0.4901g. Temp. = 109.5°C.

Time (min.)	Accum. Vol. (ml.)	Gas Temp. (abs.)	Gas Press. mm (corr.)
12.8	2.55	296.4	758.5
27.0	7.55	296.6	758.4
37.1	10.90	296.8	758.4
52.5	15.75	297.1	758.2
84.6	24.65	298.0	756.0
104.1	29.40	298.2	755.8
120.6	33.00	298.6	756.4
136.9	36.75	299.0	756.3
165.6	41.55	299.2	756.2

S.T.P. Vol. (ml.)	$\frac{V_\infty}{V_\infty - V}$	$\log \frac{V_\infty}{V_\infty - V}$
2.28	1.037	0.016
6.81	1.118	0.048
9.84	1.181	0.072
14.20	1.283	0.108
22.08	1.523	0.183
26.29	1.691	0.228
29.48	1.846	0.266
32.77	2.038	0.309
36.97	2.351	0.371

$2.303 \times \text{Slope} = 0.0053 = k \text{ min.}^{-1}$

$t_{\frac{1}{2}} = 128$ min.

$E_a = 34$ kcal./mole

omposition of Isopropyl 3-Methyl- Δ^1-pyrazolin-3-carboxylate in Tetralin

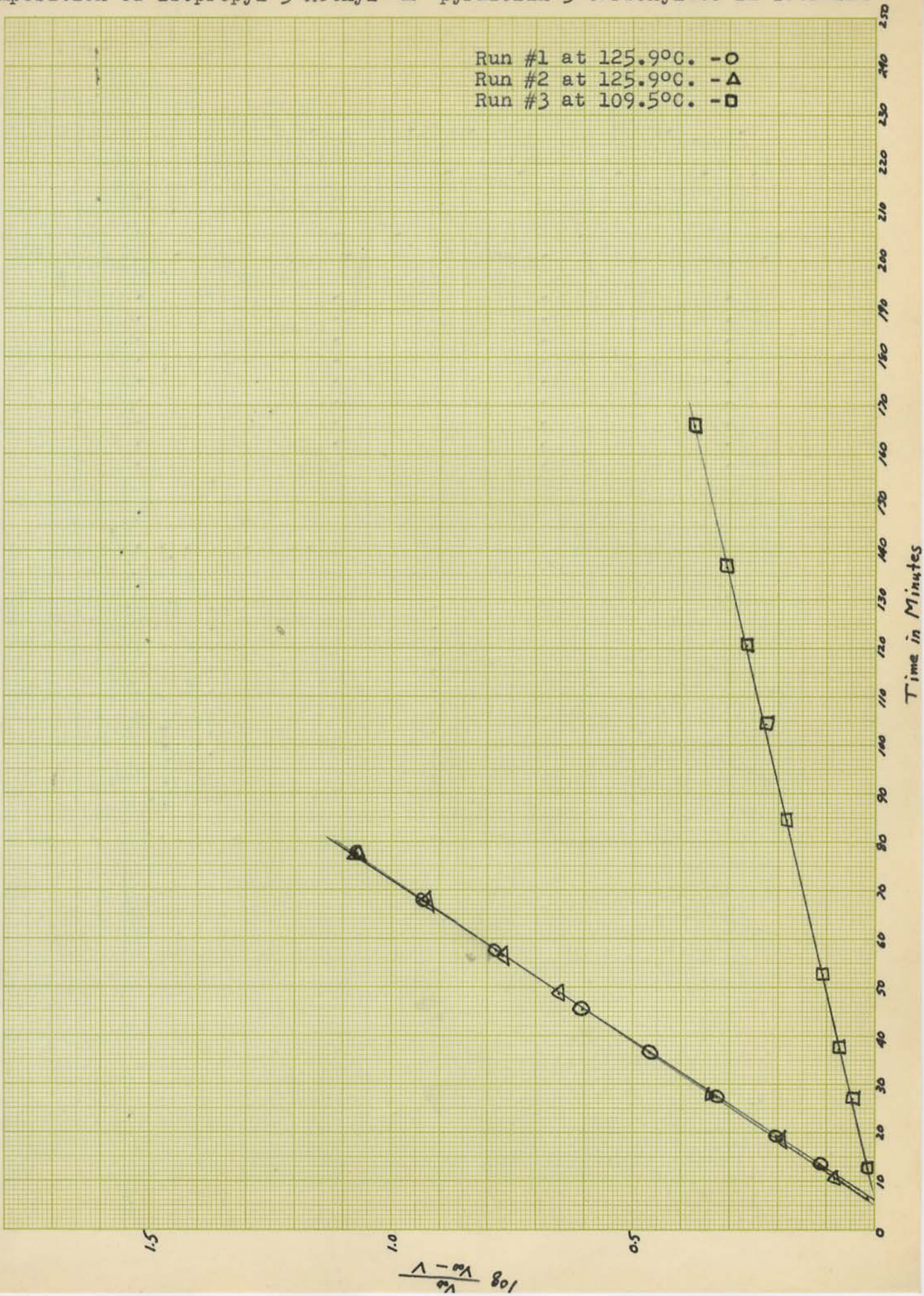


TABLE IX

The Observed and Calculated Data for the Decomposition of n-Butyl 3-Methyl-Δ^1-pyrazolin-3-carboxylate in Tetralin.

Run #1 Blank = 0.0087 ml./min. V_∞ = 67.26 ml.

Weight of Sample = 0.5568g. Temp. = 125.9°C.

Time (min.)	Accum. Vol. (ml.)	Gas Temp. (abs.)	Gas Press. mm (corr.)
13.4	19.65	296.6	753.4
20.4	31.65	296.8	753.4
29.4	43.30	297.0	753.3
39.6	53.00	297.1	753.2
48.5	58.45	297.1	753.2
56.0	63.60	297.1	753.2
68.5	66.95	297.1	753.2

S.T.P. Vol. (ml.)	$\frac{V_\infty}{V_\infty - V}$	$\log \frac{V_\infty}{V_\infty - V}$
17.80	1.360	0.134
28.66	1.742	0.241
39.17	2.394	0.379
47.90	3.474	0.541
52.78	4.645	0.667
57.39	6.815	0.833
60.32	9.692	0.986

2.303 x Slope = 0.0357 = k $min.^{-1}$

$t_{\frac{1}{2}}$ = 19 min.

Run #2 Blank = 0.0054 ml./min. V_∞ = 67.26 ml.

Weight of Sample = 0.5568g. Temp. = 109.5°C.

Time (min.)	Accum. Vol. (ml.)	Gas Temp. (abs.)	Gas Press. mm (corr.)
13.5	3.20	301.0	768.9
28.4	8.95	301.0	768.9
43.3	14.35	301.0	768.9
58.3	19.30	301.0	768.9
73.3	23.90	300.7	769.1
92.4	29.20	300.5	769.2
107.4	32.95	300.9	769.0
149.5	42.20	301.5	768.7

S.T.P. Vol. (ml.)	$\frac{V_\infty}{V_\infty - V}$	$\log \frac{V_\infty}{V_\infty - V}$
2.86	1.044	0.019
8.06	1.136	0.055
12.93	1.238	0.093
17.39	1.349	0.130
21.55	1.471	0.168
26.33	1.643	0.216
29.65	1.788	0.252
37.82	2.284	0.359

$2.303 \times \text{Slope} = 0.0058 = k \text{ min.}^{-1}$

$t_{\frac{1}{2}} = 120$ min.

$E_a = 34$ kcal./mole

composition of n-Butyl 3-Methyl- Δ^1-pyrazolin-3-carboxylate in Tetralin

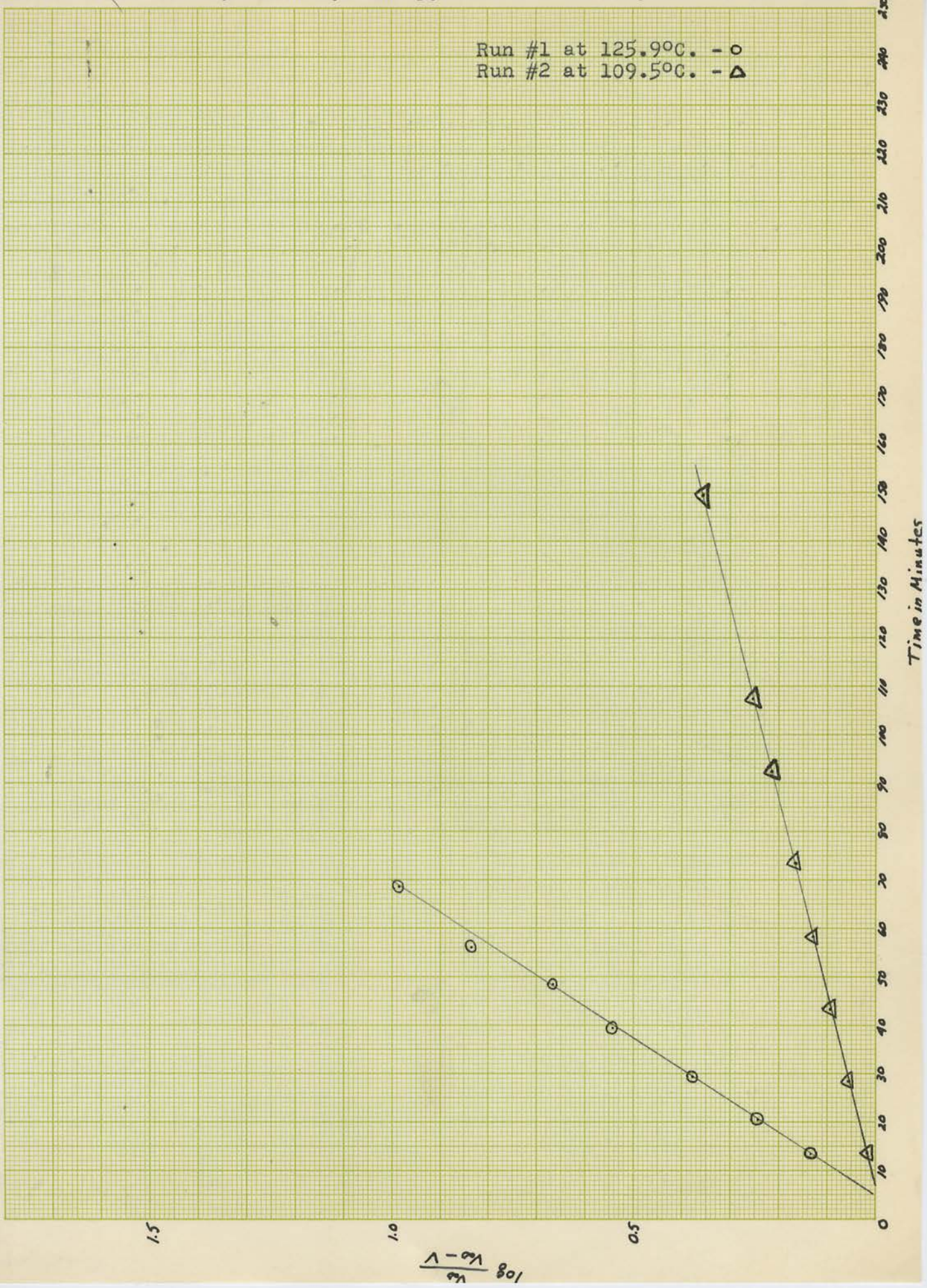


TABLE X

The Observed and Calculated Data for the Decomposition of t-Butyl 3-Methyl-Δ^1-pyrazolin-3-carboxylate in Tetralin.

Run #1 Blank = 0.0087 ml./min. V_∞ = 67.26 ml.

Weight of Sample = 0.5544g. Temp. = 125.9°C.

Time (min.)	Accum. Vol. (ml.)	Gas Temp. (abs.)	Gas Press. mm (corr.)
8.6	7.00	300.2	760.1
17.6	20.30	300.3	760.0
32.5	37.95	300.5	759.9
46.6	49.20	300.8	759.7
57.4	55.65	301.0	758.1
72.7	62.10	301.1	758.1
86.4	66.00	301.1	758.1

S.T.P. Vol. (ml.)	$\frac{V_\infty}{V_\infty - V}$	$\log \frac{V_\infty}{V_\infty - V}$
6.29	1.103	0.043
18.29	1.373	0.138
34.17	2.033	0.308
44.20	2.917	0.465
49.82	3.857	0.586
55.50	5.719	0.757
58.91	8.055	0.906

2.303 x Slope = 0.0256 = k $min.^{-1}$

$t_{\frac{1}{2}}$ = 28 min.

Run #2 Blank = 0.0087 ml./min. V_∞ = 67.26 ml.

Weight of Sample = 0.5544g. Temp. = 125.9°C.

Time (min.)	Accum. Vol. (ml.)	Gas Temp. (abs.)	Gas Press. mm (corr.)
11.6	14.35	296.2	758.3
19.7	25.30	296.3	758.3
32.5	39.10	296.7	758.1
53.6	53.70	297.1	757.9
64.6	58.75	297.1	757.9
74.6	62.40	297.2	757.9
86.8	65.50	297.3	757.9
99.6	68.25	297.5	757.8

S.T.P. Vol. (ml.)	$\frac{V_\infty}{V_\infty - V}$	$\log \frac{V_\infty}{V_\infty - V}$
13.09	1.242	0.094
23.08	1.522	0.182
35.59	2.124	0.327
48.71	3.626	0.559
53.24	4.797	0.681
56.48	6.239	0.795
59.20	8.345	0.921
61.55	11.779	1.061

$2.303 \times \text{Slope} = 0.0258 = k \text{ min.}^{-1}$

$t_{\frac{1}{2}} = 27$ min.

Run #3 Blank = 0.0068 ml./min. V_∞ = 67.26 ml.

Weight of Sample = 0.5544g. Temp. = 109.5°C.

Time (min.)	Accum. Vol. (ml.)	Gas Temp. (abs.)	Gas Press. mm (corr.)
16.5	3.35	301.0	750.3
29.4	7.00	301.2	750.2
45.5	11.55	301.3	750.1
64.4	16.55	301.5	750.0
85.4	21.55	301.8	750.0
145.5	33.95	302.2	748.8
177.5	39.35	302.2	748.8

S.T.P. Vol. (ml.)	$\frac{V_\infty}{V_\infty - V}$	$\log \frac{V_\infty}{V_\infty - V}$
2.89	1.045	0.019
6.06	1.099	0.041
10.01	1.175	0.070
14.34	1.271	0.104
18.64	1.383	0.141
29.21	1.768	0.247
33.79	2.010	0.303

$2.303 \times \text{Slope} = 0.0041 = k \text{ min.}^{-1}$

$t_{\frac{1}{2}} = 164$ min.

$E_a = 34$ kcal./mole

ecomposition of t-Butyl 3-Methyl-Δ^1-pyrazolin-3-carboxylate in Tetralin

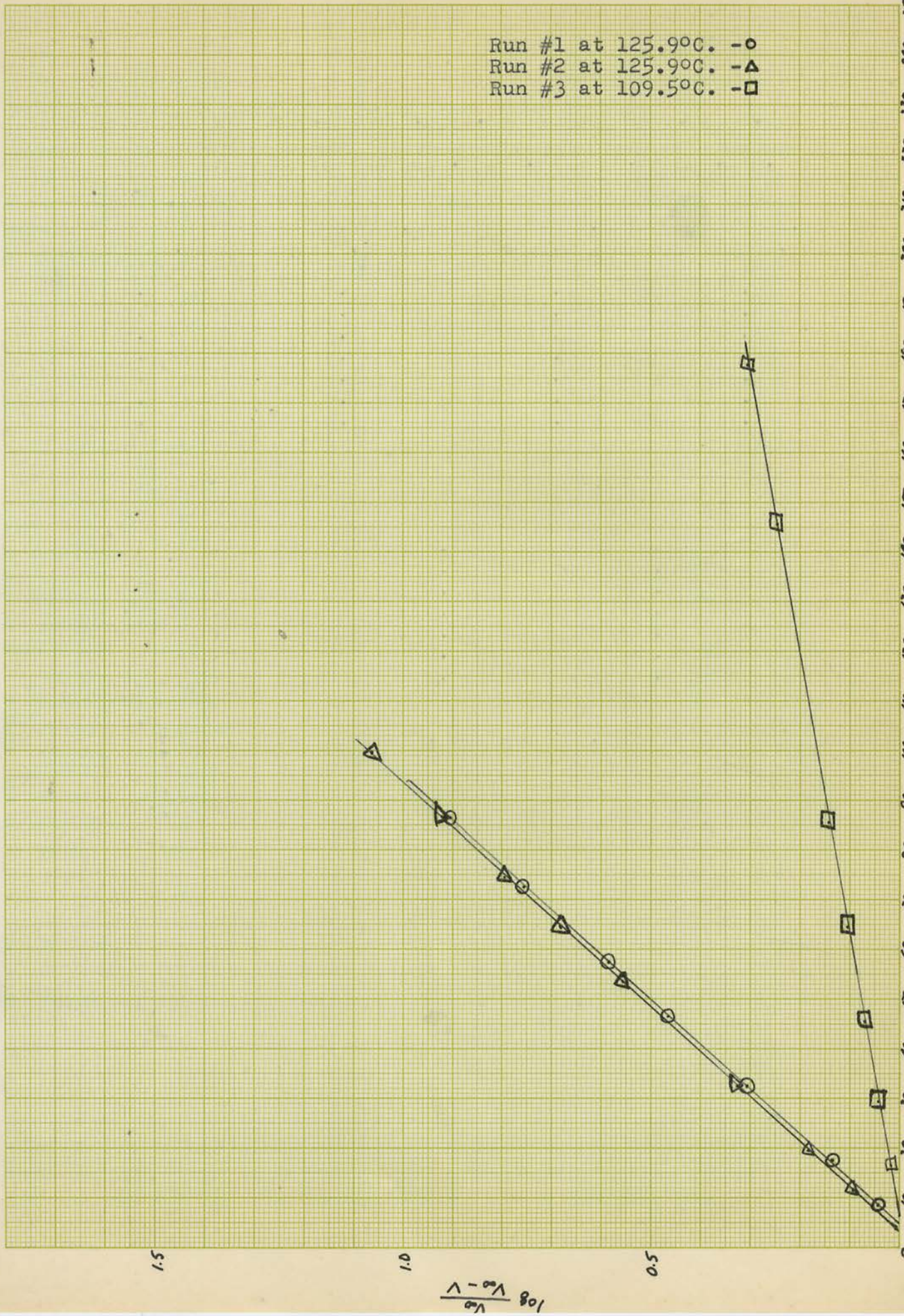


TABLE XI

The Observed and Calculated Data for the Decomposition of Ethyl 3-Ethyl-Δ^1-pyrazolin-3-carboxylate in Tetralin.

Run #1 Blank = 0.0067 ml./min. V_∞ = 67.02 ml.

Weight of Sample = 0.5097g. Temp. = 125.9°C.

Time (min.)	Accum. Vol. (ml.)	Gas Temp. (abs.)	Gas Press. mm (corr.)
7.5	3.35	297.6	764.2
15.4	10.85	297.7	764.2
20.4	16.95	297.7	764.2
27.4	22.65	297.9	764.1
34.3	29.60	297.9	764.1
41.9	34.20	298.0	764.1
60.4	44.80	298.1	764.0
75.4	50.90	298.1	764.0
90.4	55.40	298.1	764.0

S.T.P. Vol. (ml.)	$\frac{V_\infty}{V_\infty - V}$	$\log \frac{V_\infty}{V_\infty - V}$
3.04	1.048	0.020
9.90	1.173	0.069
15.48	1.300	0.114
20.68	1.446	0.160
27.03	1.676	0.224
31.20	1.871	0.272
40.82	2.558	0.408
46.32	3.238	0.510
50.36	4.023	0.605

2.303 x Slope = 0.0164 = k $min.^{-1}$

$t_{\frac{1}{2}}$ = 42 min.

Run #2 Blank = 0.0068 ml./min. V_∞ = 67.02 ml.

Weight of Sample = 0.5097g. Temp. = 143.96°C.

Time (min.)	Accum. Vol. (ml.)	Gas Temp. (abs.)	Gas Press. mm (corr.)
5.3	11.20	300.9	754.7
8.4	22.50	300.9	754.7
10.3	29.60	300.9	754.7
12.4	36.20	301.0	754.6
14.4	41.90	301.1	754.6
16.4	46.50	301.1	754.6
18.4	50.45	301.1	754.6
22.4	56.35	301.1	754.6

S.T.P. Vol. (ml.)	$\frac{V_\infty}{V_\infty - V}$	$\log \frac{V_\infty}{V_\infty - V}$
10.04	1.176	0.070
20.20	1.431	0.156
26.58	1.657	0.219
32.50	1.941	0.288
37.60	2.278	0.358
41.73	2.650	0.423
45.26	3.080	0.489
50.55	4.069	0.609

$2.303 \times \text{Slope} = 0.0758 = k \text{ min.}^{-1}$

$t_{\frac{1}{2}} = 9$ min.

$E_a = 28$ kcal./mole

Decomposition of Ethyl 3-Ethyl- Δ^1-pyrazolin-3-carboxylate in Tetralin

TABLE XII

The Observed and Calculated Data for the Decomposition of Ethyl 3,4-Dimethyl-Δ^1-pyrazolin-3-carboxylate in Tetralin.

Run #1 Blank = 0.0079 ml./min. V_∞ = 67.70 ml.

Weight of Sample = 0.5142g. Temp. = 125.9°C.

Time (min.)	Accum. Vol. (ml.)	Gas Temp. (abs.)	Gas Press. mm (corr.)
15.4	7.75	300.0	754.8
25.3	15.05	300.0	754.8
35.4	22.10	300.1	754.8
45.3	28.05	300.1	754.8
58.4	35.95	300.1	754.8
68.4	40.60	300.1	754.8
90.4	49.15	300.2	754.7
108.4	54.50	300.2	754.7

S.T.P. Vol. (ml.)	$\frac{V_\infty}{V_\infty - V}$	$\log \frac{V_\infty}{V_\infty - V}$
6.88	1.113	0.047
13.39	1.247	0.096
19.67	1.410	0.149
24.97	1.584	0.200
32.00	1.896	0.278
36.12	2.144	0.331
43.65	2.815	0.449
48.24	3.479	0.541

$2.303 \times \text{Slope} = 0.0122 = k \text{ min.}^{-1}$

$t_{\frac{1}{2}} = 57$ min.

Run #2 Blank = 0.0079 ml./min. V_∞ = 67.70 ml.

Weight of Sample = 0.5142g. Temp. = 109.5°C.

Time (min.)	Accum. Vol. (ml.)	Gas Temp. (abs.)	Gas Press. mm (corr.)
8.6	0.70	298.3	747.6
23.3	3.25	298.3	747.6
39.6	5.85	298.3	747.6
89.4	12.85	298.3	747.6
105.4	15.00	298.3	747.6
123.4	17.35	298.3	747.6
137.5	19.00	298.3	747.6
170.5	22.95	298.3	747.6

S.T.P. Vol. (ml.)	$\frac{V_\infty}{V_\infty - V}$	$\log \frac{V_\infty}{V_\infty - V}$
0.56	1.008	0.003
2.74	1.042	0.018
4.95	1.079	0.033
10.85	1.191	0.076
12.67	1.230	0.090
14.63	1.276	0.106
16.00	1.309	0.117
19.30	1.399	0.146

$2.303 \times \text{Slope} = 0.0020 = k \text{ min.}^{-1}$

$t_{\frac{1}{2}} = 347$ min.

$E_a = 34$ kcal./mole

ecomposition of Ethyl 3,4-Dimethyl- Δ^1-pyrazolin-3-carboxylate in Tetralin

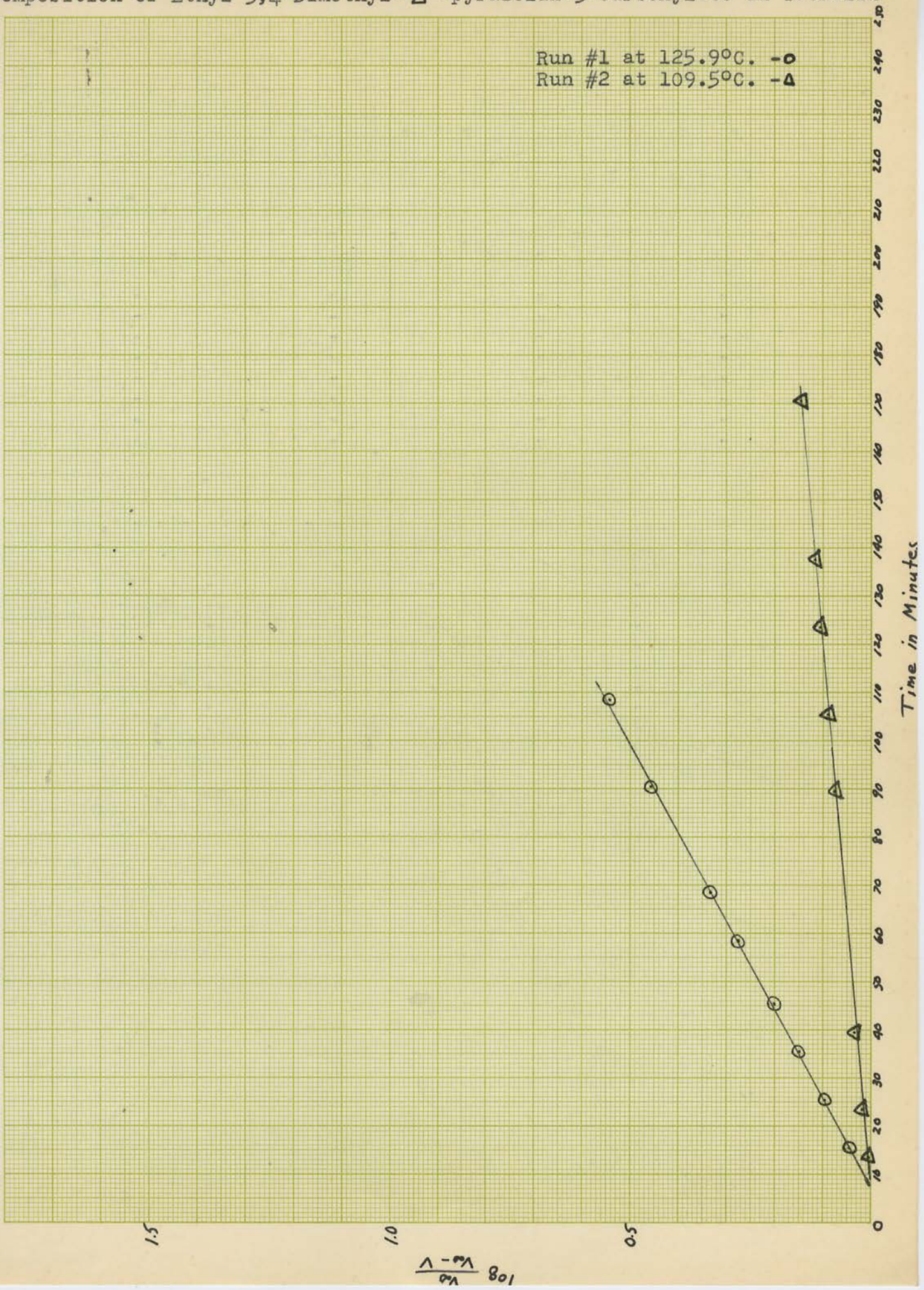


TABLE XIII

The Observed and Calculated Data for the Decomposition of Ethyl 3,5-Dimethyl-Δ^1-pyrazolin-3-carboxylate in Tetralin.

Run #1 Blank = 0.0079 ml./min. V_∞ = 66.35 ml.

Weight of Sample = 0.5042g. Temp. = 109.5°C.

Time (min.)	Accum. Vol. (ml.)	Gas Temp. (abs.)	Gas Press. mm (corr.)
14.3	21.40	302.2	742.3
20.6	33.70	302.3	742.2
26.4	43.60	302.3	742.2
31.6	50.10	302.5	742.1
36.4	55.50	302.6	742.1
46.5	62.60	302.9	741.9

S.T.P. Vol. (ml.)	$\frac{V_\infty}{V_\infty - V}$	$\log \frac{V_\infty}{V_\infty - V}$
18.76	1.394	0.144
29.54	1.802	0.256
33.22	2.359	0.373
43.87	2.952	0.470
48.57	3.732	0.572
54.67	5.681	0.754

2.303 x Slope = 0.0435 = k $min.^{-1}$

$t_{\frac{1}{2}}$ = 16 min.

Run #2 Blank = 0.0086 ml./min. V_∞ = 66.35 ml.

Weight of Sample = 0.5042g. Temp. = 88.75°C.

Time (min.)	Accum. Vol. (ml.)	Gas Temp. (abs.)	Gas Press. mm (corr.)
16.4	3.25	304.8	749.9
24.3	6.10	305.0	749.8
32.3	9.10	305.1	749.8
55.4	17.20	305.4	749.6
75.4	23.80	305.7	749.4
92.4	28.60	306.0	749.3
197.4	32.45	306.1	749.2

S.T.P. Vol. (ml.)	$\frac{V_\infty}{V_\infty - V}$	$\log \frac{V_\infty}{V_\infty - V}$
2.73	1.043	0.018
5.17	1.085	0.035
7.75	1.132	0.054
14.68	1.284	0.109
20.30	1.441	0.159
24.35	1.580	0.199
27.59	1.712	0.234

$2.303 \times \text{Slope} = 0.0055 = k \text{ min.}^{-1}$

$t_{\frac{1}{2}} = 126$ min.

$E_a = 27$ kcal./mole

Decomposition of Ethyl 3,5-Dimethyl-Δ^1-pyrazolin-3-carboxylate in Tetralin

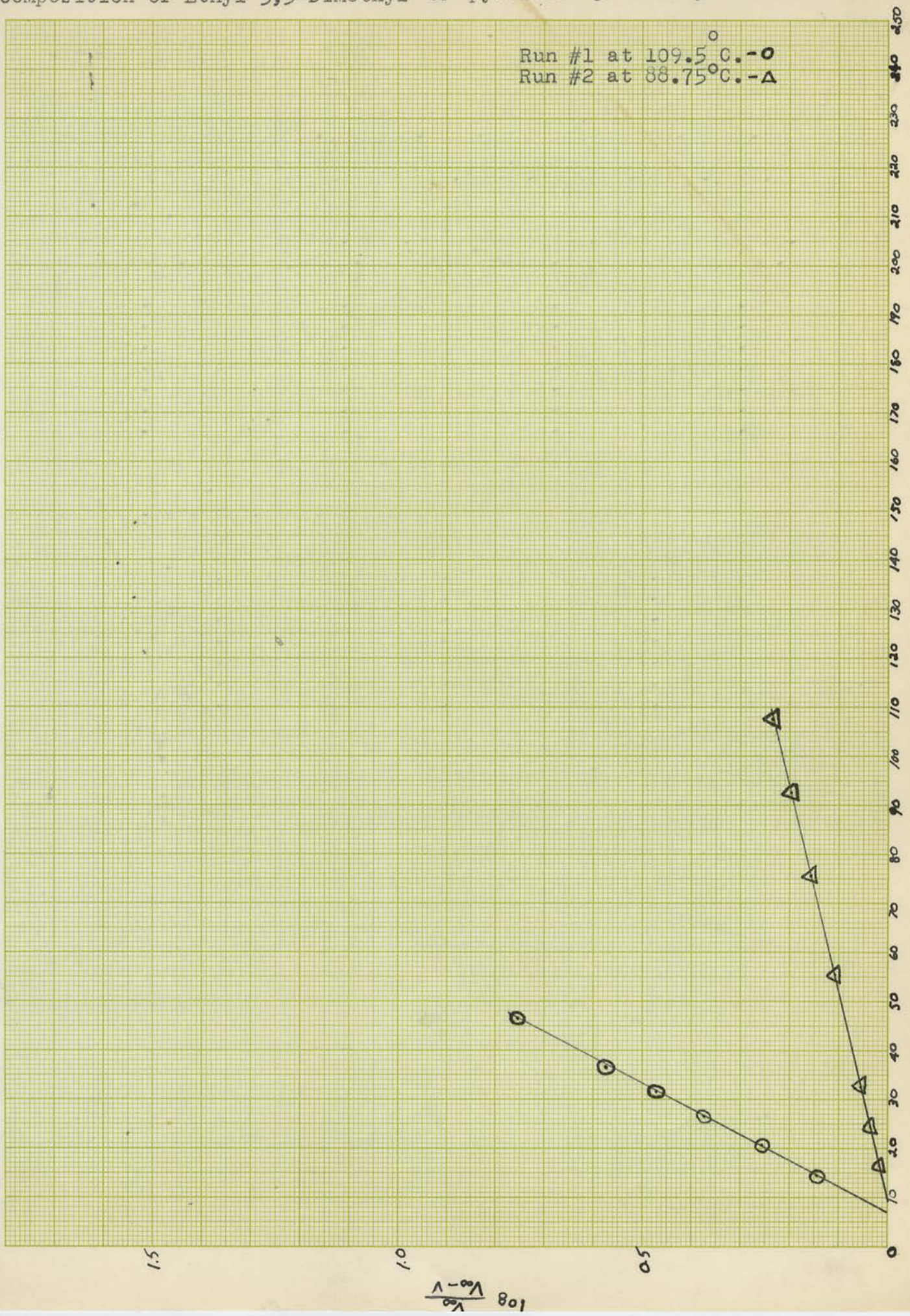


TABLE XIV

The Observed and Calculated Data for the Decomposition of Ethyl 5-Ethyl-3-methyl-Δ^1-pyrazolin-3-carboxylate in Tetralin.

Run #1 Blank = 0.0079 ml./min. V_∞ = 64.78 ml.

Weight of Sample = 0.5509g. Temp. = 109.5°C.

Time (min.)	Accum. Vol. (ml.)	Gas Temp. (abs.)	Gas Press. mm (corr.)
7.5	8.80	302.1	744.6
12.3	19.30	302.1	744.6
18.4	31.85	302.2	744.6
23.4	39.70	302.3	744.5
28.6	47.45	302.5	744.4
40.8	55.75	302.8	744.3
49.9	63.45	303.1	744.1

S.T.P. Vol. (ml.)	$\frac{V_\infty}{V_\infty - V}$	$\log \frac{V_\infty}{V_\infty - V}$
7.73	1.135	0.055
16.98	1.355	0.132
28.02	1.762	0.246
34.92	2.169	0.336
41.69	2.806	0.448
48.87	4.072	0.610
55.53	7.003	0.845

2.303 x Slope = 0.0438 = k $min.^{-1}$

$t_{\frac{1}{2}}$ = 16 min.

Run #2 Blank = 0.0088 ml./min. V_∞ = 64.78 ml.

Weight of Sample = 0.5509g. Temp. = 88.75°C.

Time (min.)	Accum. Vol. (ml.)	Gas Temp. (abs.)	Gas Press. mm (corr.)
15.6	2.30	304.1	744.5
33.3	7.90	304.2	744.4
45.4	11.70	304.2	744.4
60.5	15.15	304.2	744.4
76.4	20.55	304.3	744.3
90.3	24.25	304.4	744.3
105.6	28.00	304.4	744.3
120.9	31.30	304.4	744.3

S.T.P. Vol. (ml.)	$\frac{V_\infty}{V_\infty - V}$	$\log \frac{V_\infty}{V_\infty - V}$
1.88	1.030	0.013
6.65	1.114	0.047
9.88	1.180	0.072
12.78	1.246	0.096
17.37	1.366	0.135
20.50	1.463	0.165
23.65	1.575	0.197
26.42	1.689	0.228

$2.303 \times \text{Slope} = 0.0048 = k \text{ min.}^{-1}$

$t_{\frac{1}{2}} = 144$ min.

$E_a = 28$ kcal./mole

Decomposition of Ethyl 5-Ethyl-3-Methyl-Δ^1-pyrazolin-3-carboxylate in Tetralin

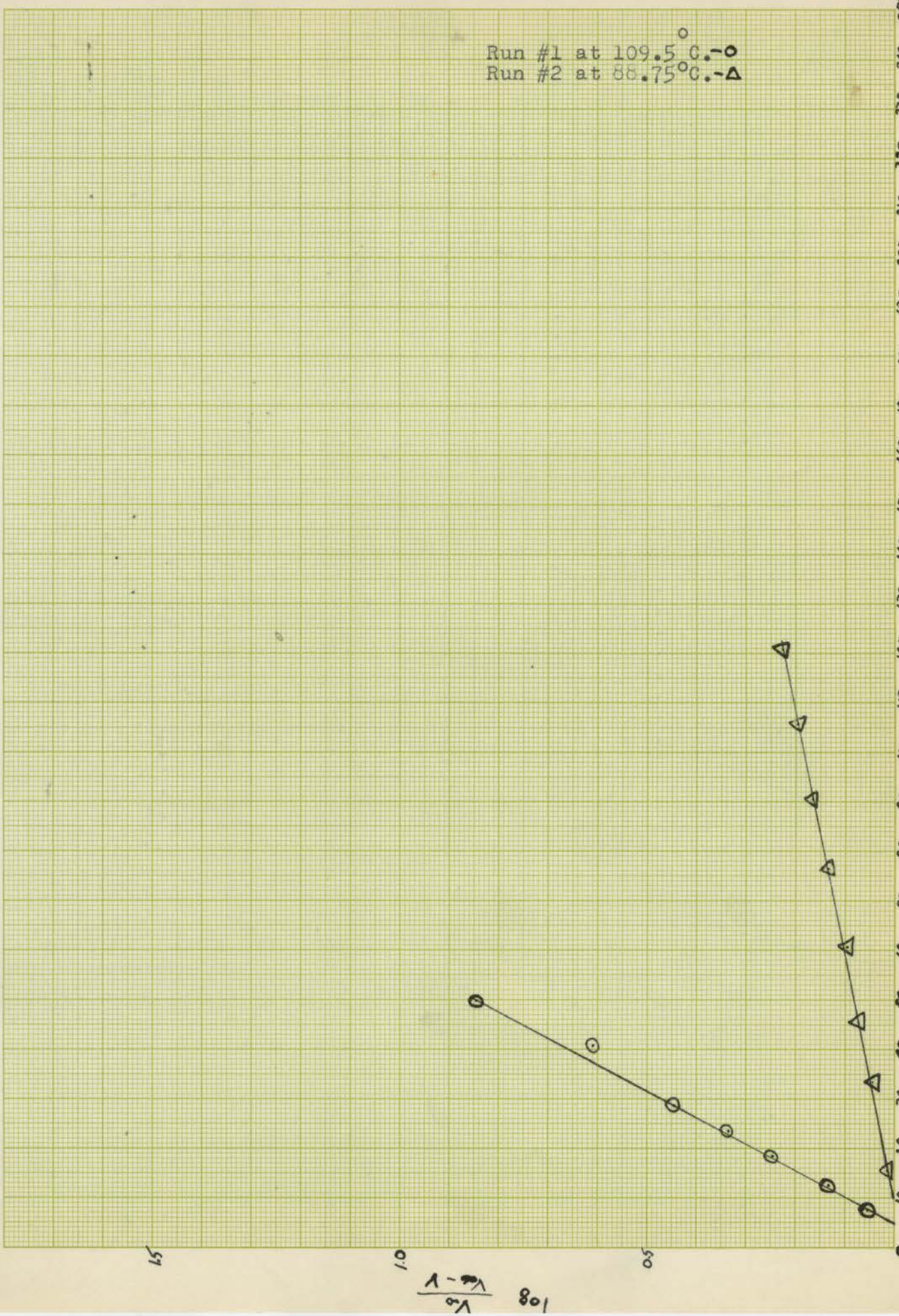


TABLE XV

The Observed and Calculated Data for the Decomposition of Ethyl 5-Propyl-3-methyl-Δ^1-pyrazolin-3-carboxylate in Tetralin.

Run #1 Blank = 0.0067 ml./min. V_∞ = 43.71 ml.

Weight of Sample = 0.3868g. Temp. = 109.5°C.

Time (min.)	Accum. Vol. (ml.)	Gas Temp. (abs.)	Gas Press. mm (corr.)
14.3	13.75	295.6	765.6
18.4	18.85	295.9	765.5
25.3	26.45	296.2	765.4
35.5	34.40	296.5	765.3
45.4	39.30	297.0	765.1
60.9	43.45	297.3	765.0

S.T.P. Vol. (ml.)	$\frac{V_\infty}{V_\infty - V}$	$\log \frac{V_\infty}{V_\infty - V}$
12.68	1.409	0.149
17.39	1.661	0.220
24.37	2.260	0.354
31.64	3.621	0.559
36.05	5.706	0.756
39.73	10.980	1.041

2.303 x Slope = 0.0440 = k $min.^{-1}$

$t_{\frac{1}{2}}$ = 16 min.

Run #2 Blank = 0.0088 ml./min. V_∞ = 43.71 ml.

Weight of Sample = 0.3868g. Temp. = 88.75°C.

Time (min.)	Accum. Vol. (ml.)	Gas Temp. (abs.)	Gas Press. mm (corr.)
15.6	2.00	301.6	749.8
30.4	5.60	301.9	749.6
58.4	12.40	302.2	749.5
72.8	15.55	302.2	749.5
96.4	19.90	302.3	749.4
112.4	22.65	302.5	749.3
139.4	26.70	302.8	749.2

S.T.P. Vol. (ml.)	$\frac{V_\infty}{V_\infty - V}$	$\log \frac{V_\infty}{V_\infty - V}$
1.65	1.039	0.017
4.72	1.121	0.050
10.53	1.317	0.120
13.21	1.431	0.156
16.86	1.628	0.212
19.15	1.780	0.250
22.49	2.060	0.314

$2.303 \times \text{Slope} = 0.0054 = k \text{ min.}^{-1}$

$t_{\frac{1}{2}} = 128$ min.

$E_a = 28$ kcal./mole

Decomposition of Ethyl 5-Propyl-3-Methyl-Δ^{1} pyrazolin-3-carboxylate in Tetralin.

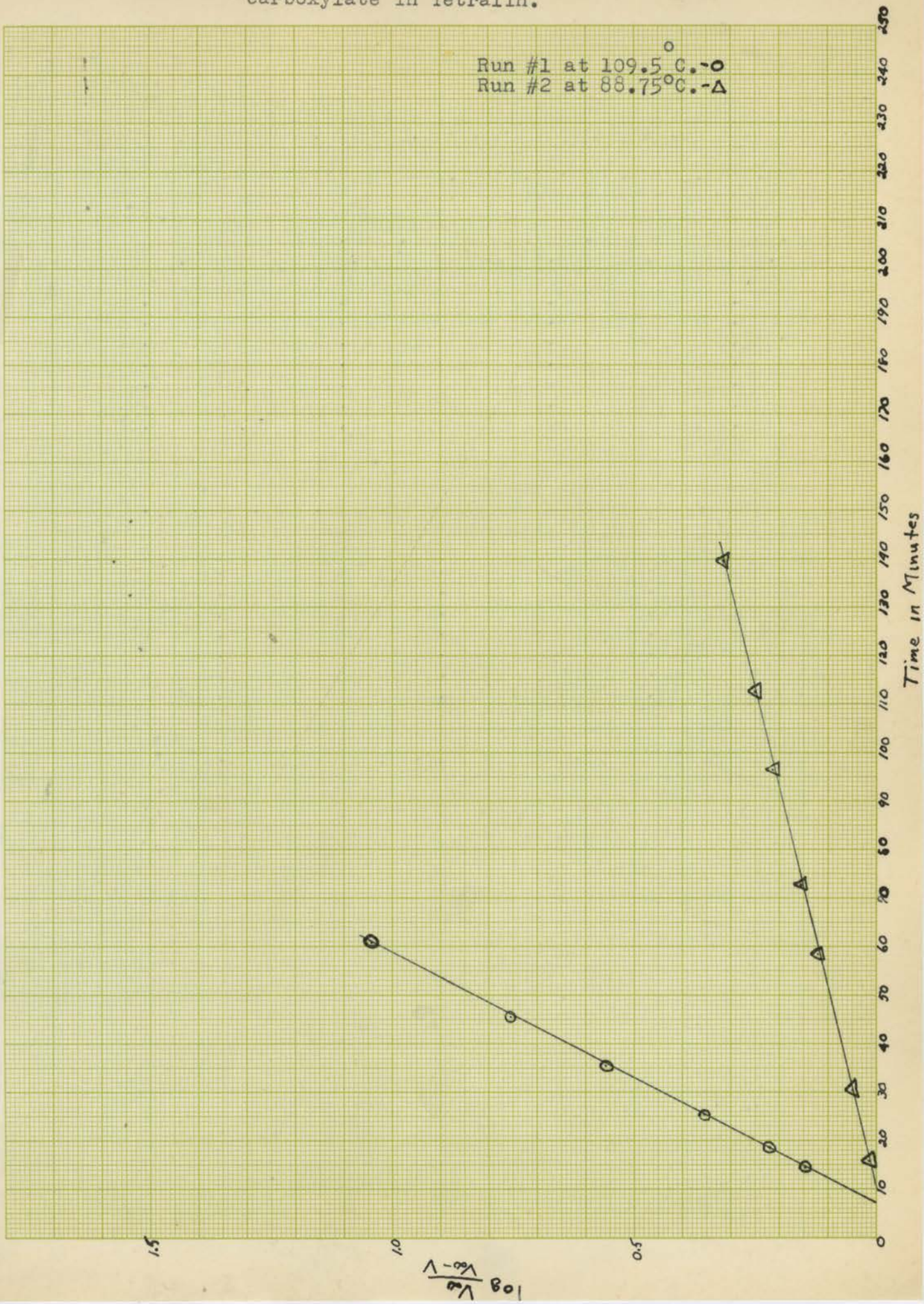


TABLE XVI

The Observed and Calculated Data for the Decomposition of 3-Aceto-3-methyl-Δ^1-pyrazoline in Tetralin.

Run #1 Blank = 0.0039 ml./min. V_∞ = 63.21 ml.

Weight of Sample = 0.3558g. Temp. = 125.9°C.

Time (min.)	Accum. Vol. (ml.)	Gas Temp. (abs.)	Gas Press. mm (corr.)
13.3	14.75	298.2	763.5
17.3	23.40	298.2	763.5
21.3	31.25	298.4	763.4
25.8	39.25	298.7	763.3
30.7	46.15	298.7	763.3
35.5	51.05	298.7	763.3
40.4	55.05	298.7	763.3
45.5	58.25	298.9	763.2

S.T.P. Vol. (ml.)	$\frac{V_\infty}{V_\infty - V}$	$\log \frac{V_\infty}{V_\infty - V}$
13.51	1.272	0.104
21.43	1.513	0.180
28.62	1.827	0.262
35.90	2.315	0.365
42.21	3.010	0.479
46.69	3.826	0.583
50.34	4.911	0.691
53.21	6.321	0.801

$2.303 \times \text{Slope} = 0.0496 = k \text{ min.}^{-1}$

$t_{\frac{1}{2}} = 14$ min.

Run #2 Blank = 0.0044 ml./min. V_∞ = 63.21 ml.

Weight of Sample = 0.3558g. Temp. = 109.5°C.

Time (min.)	Accum. Vol. (ml.)	Gas Temp. (abs.)	Gas Press. mm (corr.)
9.4	2.80	299.2	753.9
15.4	7.35	299.2	753.9
28.4	14.70	299.6	753.7
43.4	22.85	300.1	753.4
58.4	29.90	300.2	753.4
75.4	36.55	300.6	752.2
92.5	42.25	300.9	752.0
121.5	50.10	301.1	751.9
134.5	52.85	301.2	751.8

S.T.P. Vol. (ml.)	$\frac{V_\infty}{V_\infty - V}$	$\log \frac{V_\infty}{V_\infty - V}$
2.49	1.041	0.017
6.58	1.116	0.048
13.15	1.263	0.101
20.40	1.477	0.169
26.68	1.730	0.238
32.50	2.058	0.313
37.50	2.459	0.391
44.38	3.357	0.526
46.77	3.845	0.585

$2.303 \times \text{Slope} = 0.0104 = k \text{ min.}^{-1}$

$t_{\frac{1}{2}} = 67$ min.

$E_a = 29$ kcal./mole

Decomposition of 3-Aceto-3-Methyl- Δ^1-pyrazoline in Tetralin

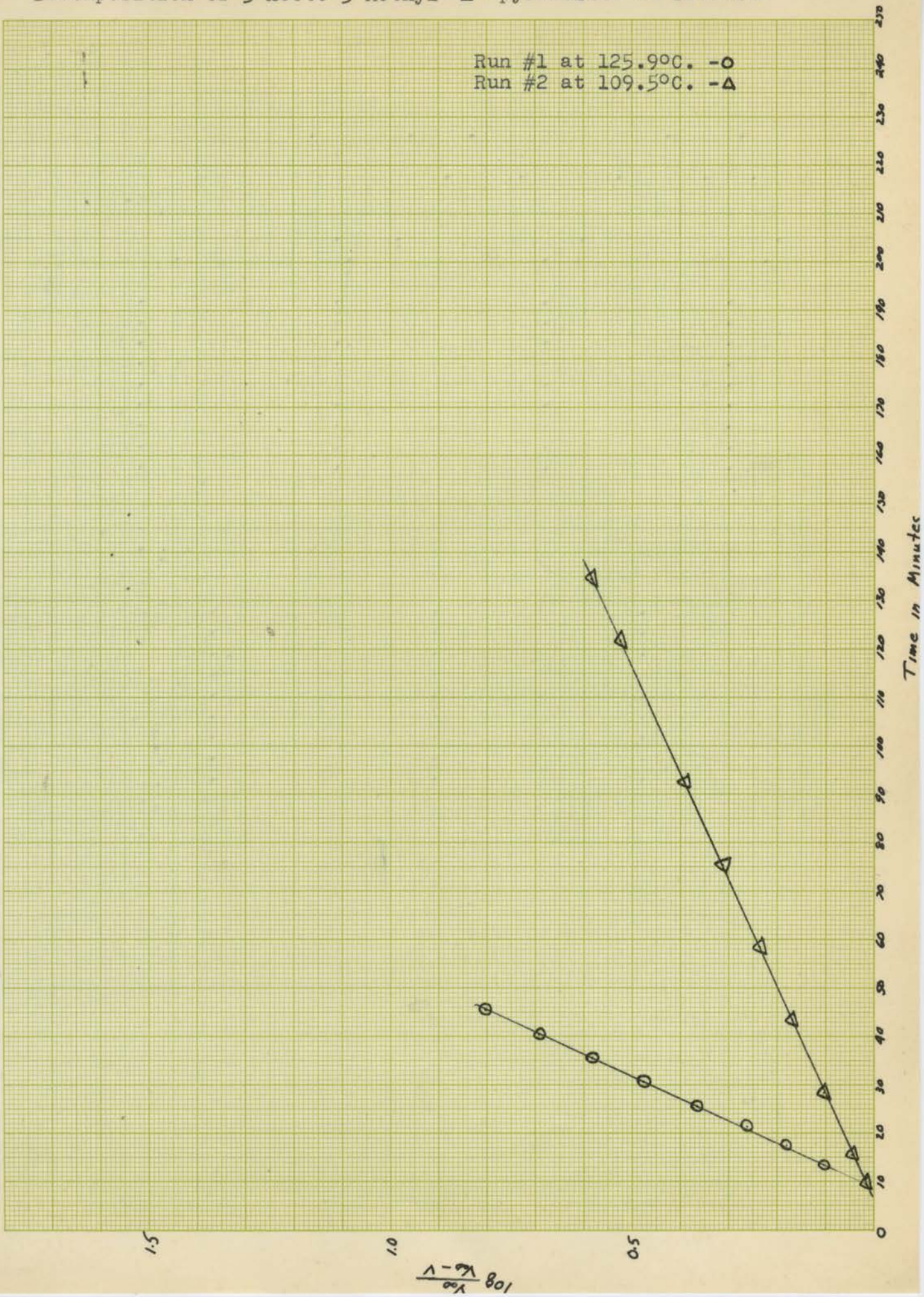


TABLE XVII

The Observed and Calculated Data for the Decomposition of 3-Nitro-3-methyl-Δ^1-pyrazoline in Tetralin.

Run #1 Blank = 0.0077 ml./min. V_∞ = 67.02 ml.

Weight of Sample = 0.3865g. Temp. = 125.9°C.

Time (min.)	Accum. Vol. (ml.)	Gas Temp. (abs.)	Gas Press. mm (corr.)
7.3	6.40	300.3	757.5
11.6	13.50	300.3	757.5
17.4	22.50	300.3	757.5
23.5	31.00	300.3	757.5
35.9	44.50	300.3	757.5
45.4	52.10	300.3	757.5
67.5	62.80	300.3	757.5

S.T.P. Vol. (ml.)	$\frac{V_\infty}{V_\infty - V}$	$\log \frac{V_\infty}{V_\infty - V}$
5.74	1.094	0.039
12.14	1.221	0.087
20.25	1.433	0.156
27.88	1.712	0.234
40.02	2.482	0.395
46.83	3.319	0.521
56.35	6.281	0.798

2.303 x Slope = 0.0290 = k $min.^{-1}$

$t_{\frac{1}{2}}$ = 24 min.

Run #2 Blank = 0.0052 ml./min. V_∞ = 67.92 ml.

Weight of Sample = 0.3918g. Temp. = 109.5°C.

Time (min.)	Accum. Vol. (ml.)	Gas Temp. (abs.)	Gas Press. mm (corr.)
11.4	2.85	299.6	747.5
23.3	8.05	299.6	747.5
35.3	13.20	299.8	747.4
47.6	17.80	299.7	747.4
61.4	22.80	299.7	747.5
78.0	27.95	299.5	747.6
95.1	32.60	299.5	747.6
114.3	37.35	299.4	747.7
133.2	41.75	299.1	747.8

S.T.P. Vol. (ml.)	$\frac{V_\infty}{V_\infty - V}$	$\log \frac{V_\infty}{V_\infty - V}$
2.49	1.038	0.016
7.09	1.117	0.048
11.63	1.207	0.082
15.69	1.300	0.114
20.10	1.420	0.152
24.64	1.569	0.196
28.72	1.733	0.239
32.90	1.939	0.288
36.78	2.181	0.339

$2.303 \times \text{Slope} = 0.0061 = k \text{ min.}^{-1}$

$t_{\frac{1}{2}} = 114$ min.

$E_a = 29$ kcal./mole

Decomposition of 3-Nitro-3-Methyl-Δ^1-pyrazoline in Tetralin

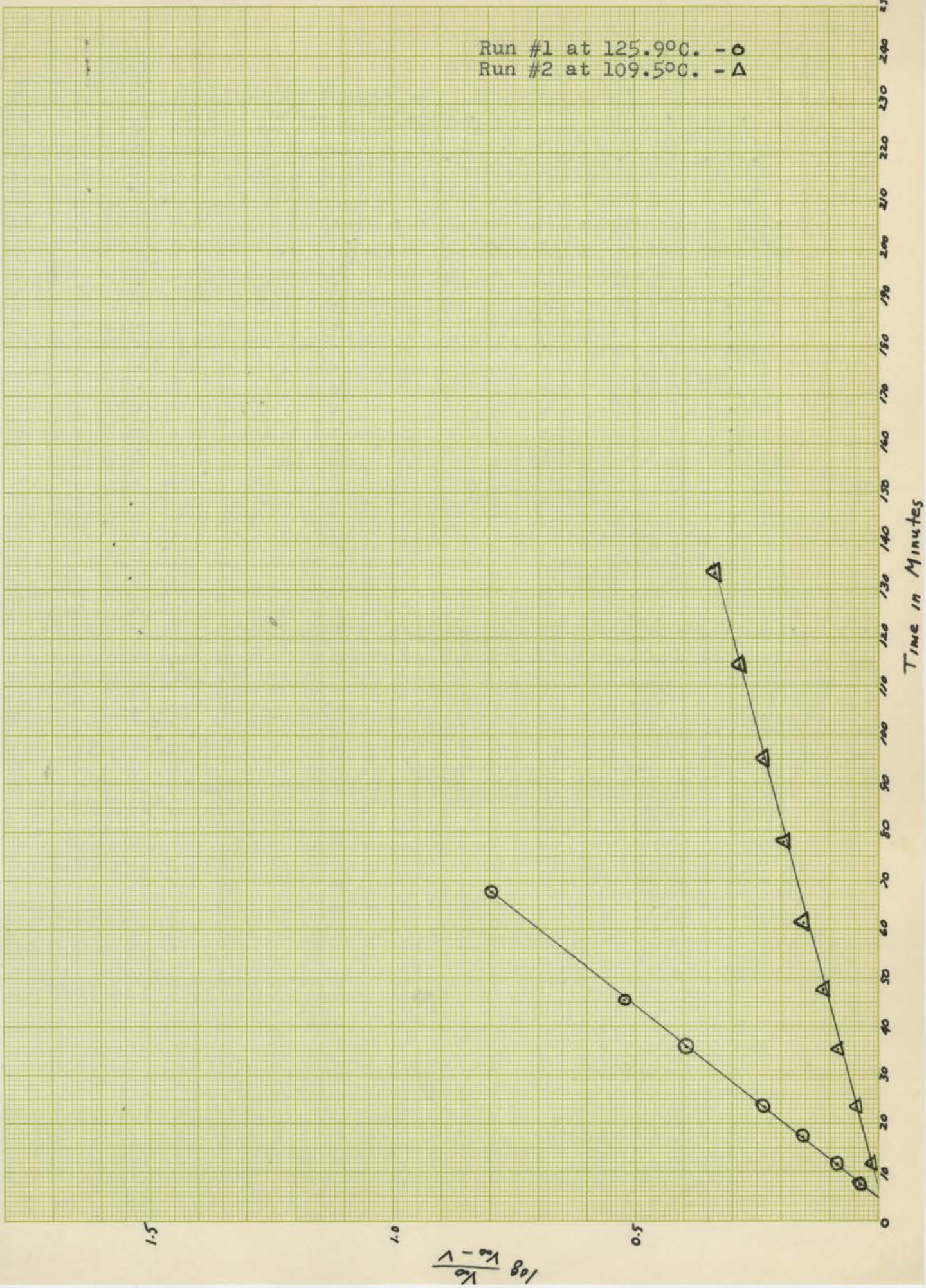


TABLE XVIII

The Observed and Calculated Data for the Decomposition of 3-Carbamyl-3-methyl-Δ^1-pyrazoline in Tetralin.

Run #1 Blank = 0.0079 ml./min. V_∞ = 46.40 ml.

Weight of Sample = 0.2638g. Temp. = 125.9°C.

Time (min.)	Accum. Vol. (ml.)	Gas Temp. (abs.)	Gas Press. mm (corr.)
15.3	0.60	299.2	753.7
30.2	1.60	299.4	753.6
45.4	2.60	299.9	753.3
60.3	3.60	300.1	753.2
75.5	4.55	300.2	753.2
105.5	6.36	300.4	753.1
136.3	8.40	300.6	753.0
165.9	9.96	300.8	752.8

S.T.P. Vol. (ml.)	$\frac{V_\infty}{V_\infty - V}$	$\log \frac{V_\infty}{V_\infty - V}$
0.42	1.009	0.004
1.21	1.027	0.012
1.98	1.045	0.019
2.76	1.063	0.027
3.50	1.082	0.034
4.90	1.118	0.048
6.47	1.162	0.065
7.64	1.197	0.078

$2.303 \times \text{Slope} = 0.0012 = k \text{ min.}^{-1}$

$t_{\frac{1}{2}} = 578$ min.

Run #2 Blank = 0.0068 ml./min. V_∞ = 46.40 ml.

Weight of Sample = 0.2638g. Temp. = 143.96°C.

Time (min.)	Accum. Vol. (ml.)	Gas Temp. (abs.)	Gas Press. mm (corr.)
15.4	3.85	301.2	755.2
30.3	9.05	301.2	755.2
45.3	13.85	301.3	755.1
60.6	18.15	301.3	755.1
75.4	21.95	301.4	755.1
103.4	28.25	301.8	754.9
120.5	31.45	301.9	754.8

S.T.P. Vol. (ml.)	$\frac{V_\infty}{V_\infty - V}$	$\log \frac{V_\infty}{V_\infty - V}$
3.37	1.078	0.033
7.94	1.206	0.081
12.15	1.355	0.132
15.92	1.522	0.182
19.23	1.708	0.232
24.67	2.135	0.329
27.41	2.443	0.388

$2.303 \times \text{Slope} = 0.0078 = k \text{ min.}^{-1}$

$t_{\frac{1}{2}} = 89$ min.

$E_a = 34$ kcal./mole

Decomposition of 3-Carbamyl-3-Methyl- Δ^1-pyrazoline in Tetralin

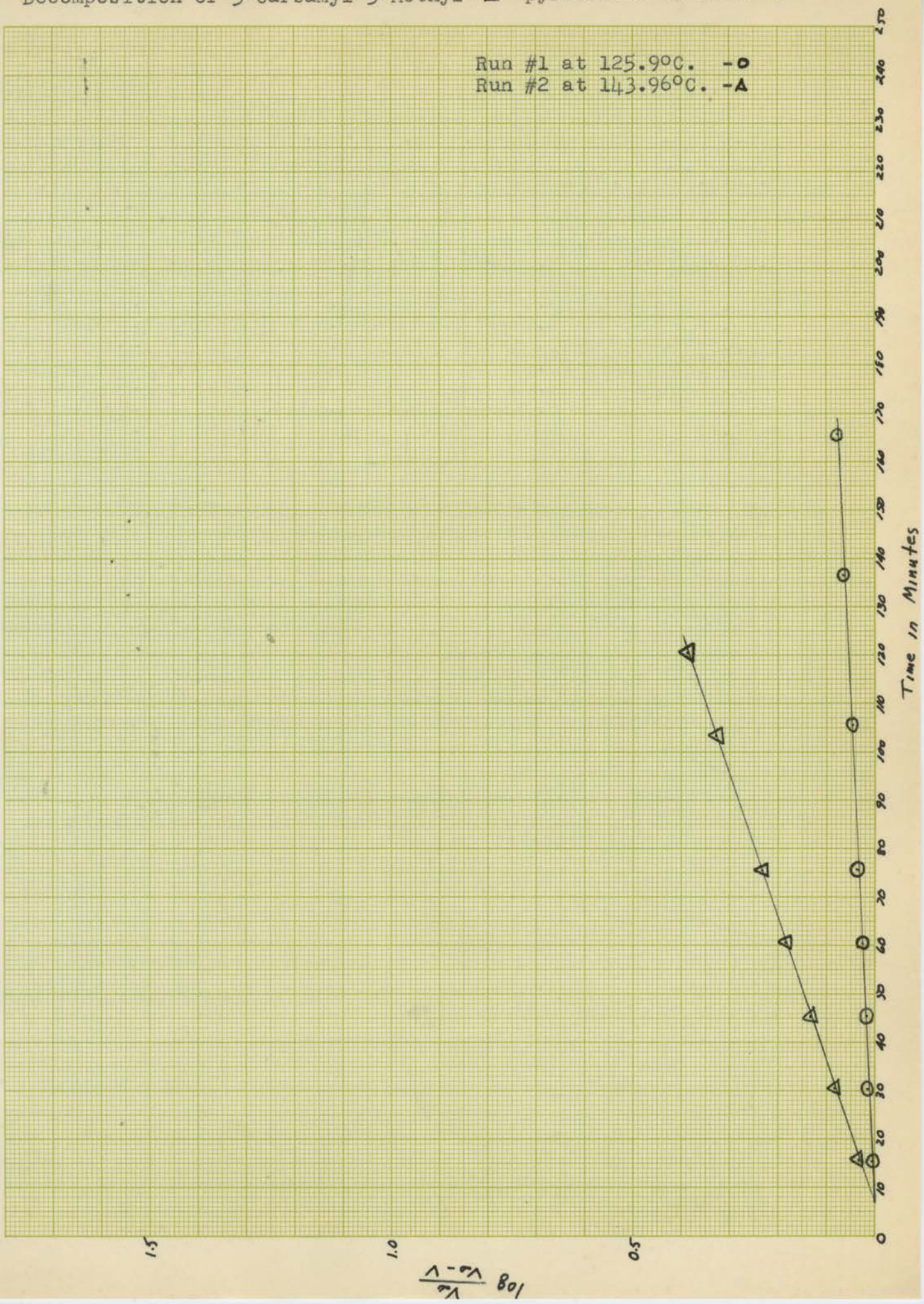


TABLE XIX

The Observed and Calculated Data for the Decomposition of 3-Cyano-3-methyl-Δ^1-pyrazoline in Tetralin.

Run #1 Blank = 0.0079 ml./min. V_∞ = 61.87 ml.

Weight of Sample = 0.3014g. Temp. = 109.5°C.

Time (min.)	Accum. Vol. (ml.)	Gas Temp. (abs.)	Gas Press. mm (corr.)
7.3	7.65	300.2	757.5
13.3	20.40	300.3	757.4
18.2	30.00	300.4	757.4
23.4	38.45	300.6	757.3
28.4	44.80	300.9	757.1
33.4	49.90	301.0	757.0
41.9	56.30	301.1	757.0
47.9	59.25	301.2	757.0

S.T.P. Vol. (ml.)	$\frac{V_\infty}{V_\infty - V}$	$\log \frac{V_\infty}{V_\infty - V}$
6.87	1.125	0.051
18.36	1.422	0.153
27.01	1.775	0.249
34.59	2.268	0.356
40.25	2.862	0.457
44.79	3.622	0.559
50.48	5.432	0.735
53.07	7.031	0.847

2.303 x Slope = 0.0461 = k $min.^{-1}$

$t_{\frac{1}{2}}$ = 15 min.

Run #2 Blank = 0.0086 ml./min. V_∞ = 61.87 ml.

Weight of Sample = 0.3014g. Temp. = 88.75°C.

Time (min.)	Accum. Vol. (ml.)	Gas Temp. (abs.)	Gas Press. mm (corr.)
16.8	2.45	303.5	749.3
30.3	6.65	303.8	749.2
45.3	11.10	304.2	748.9
61.4	15.75	304.3	748.8
75.4	19.45	304.5	748.7
90.5	23.25	304.8	748.5
105.5	26.65	305.0	748.4
120.4	29.95	305.1	748.4
175.1	40.15	305.8	747.0

S.T.P. Vol. (ml.)	$\frac{V_\infty}{V_\infty - V}$	$\log \frac{V_\infty}{V_\infty - V}$
2.03	1.034	0.015
5.63	1.100	0.041
9.42	1.180	0.072
13.38	1.276	0.106
16.52	1.364	0.135
19.72	1.468	0.167
22.57	1.574	0.197
25.33	1.693	0.229
33.70	2.196	0.342

$2.303 \times \text{Slope} = 0.0048 = k \text{ min.}^{-1}$

$t_{\frac{1}{2}} = 144$ min.

$E_a = 30$ kcal./mole

Decomposition of 3-Cyano-3-Methyl-Δ^1-pyrazoline in Tetralin

Discussion

The object of this research was to investigate the thermal stability of 3,3-disubstituted-Δ^1-pyrazolines. Interest in these compounds lies in their thermal decomposition liberating nitrogen. Several pyrazolines were prepared with varying substituents on the ring. The effect produced by the various substitutions was determined by measuring the rate of nitrogen evolution. The results obtained are believed to be useful in preparing tailor-made pneumatogens.

The pyrazolines prepared were easily decomposed thermally to liberate nitrogen together with olefin and/or cyclopropane derivatives. Since the rate of nitrogen evolution was the primary interest, no attempt was made to make further studies of the kinetics of the decomposition. A complete study of the kinetics of the reaction would involve an examination of the products of the decomposition, e.g. the ratio of olefin to cyclopropane derivatives. Furthermore, the order of the reaction would have to be determined more rigorously. The present results are consistent with first order kinetics but the dependence of rate on initial concentration of pyrazoline was not investigated. However, it is interesting to note that the thermal decomposition of the aliphatic azo compounds has been demonstrated to be first order. It is believed that the results obtained serve the object of the research.

During the course of the decomposition studies, two

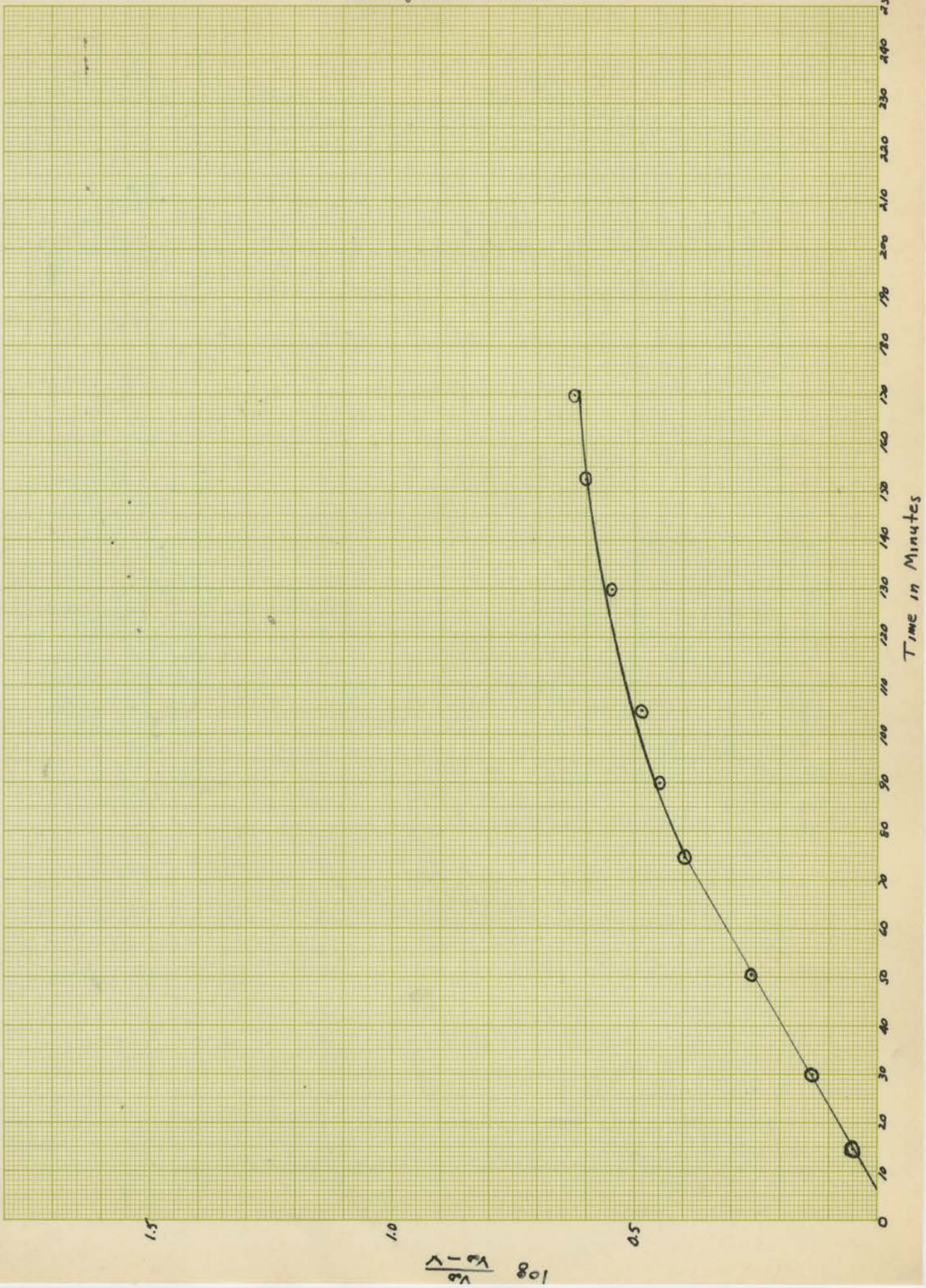
unusual effects were noticed. First, a solvent effect was noticed in the early stage of the decomposition study. Second, it was observed that the plots of $\log \frac{V_\infty}{V_\infty - V}$ vs. time fail to go through the origin.

At the start of the decomposition work diethyl phthalate was used as the solvent. However, when the decomposition data were plotted, the resulting graph was curved as shown in Graph No. 16, page 112. The conclusion was reached that one of two things was happening: a) some of the nitrogen was lost, or b) some of the pyrazoline was removed before it could decompose. A very careful check showed that there were no leaks in the apparatus through which nitrogen could escape. When tetralin (tetrahydronaphthalene) was used as the solvent in the reaction flask, the evolution of nitrogen gave good first order plots. No further study of the observed effect was made.

In a first order reaction, a plot of $\log \frac{V_\infty}{V_\infty - V}$ vs. time should produce a straight line which passes through the origin. Although the exact cause for the failure of the plots to go through origin is not known, there are several factors which can contribute. The reaction may have an induction period or may produce some minor volatile products. Possibly the corrections for volatile impurity in the CO_2 were not sufficient. Another factor is the length of the path which the gas travels from the reaction flask to the gas buret.

A word should be said concerning the accuracy of the

Decomposition of Isopropyl 3-Methyl-Δ^1-pyrazolin-3-carboxylate in Dibutyl Phthalate



rate constants and energies of activation obtained. The errors of measurement of time and pressure are negligible compared to the errors in measuring the volume and temperature of the gas evolved.

The volume of gas in the buret was read to the nearest 0.05 ml.. Since the change in volume from one reading to the next is the important factor, the volume reading could represent an error as great as $\pm$ 2.5%. The temperature of the gas in the buret was taken as the temperature of the water jacket surrounding the buret. In most cases, the temperature of the water changed appreciably during a run. Therefore, the temperature of the evolved gas could be in error by as much as 1%. The thermostat was kept constant to within $\pm$ 0.03°C.. From the Arrhenius equation, the temperature variation corresponds to an error of approximately 0.15%. It is believed that the rate constants calculated represent values having an error of $\pm$ 5%. The accuracy of the energies of activation are dependent upon the rate constants, and the ratio of the rate constants; the calculated values are believed to be accurate to within $\pm$ 10%.

The determination of the rate constants was made using calculated values for V_∞ . The agreement between V_∞ (calculated) and V_∞ (observed) was checked with isopropyl 3-methyl-Δ^1-pyrazolin-3-carboxylate. The value of V_∞ (observed) was 99.2% of V_∞ (calculated).

The investigation of the thermal liberation of nitrogen

of the Δ^1-pyrazolines was the main objective of this research. For the purposes of this discussion, attention is focused upon the rates of nitrogen evolution at 109°C., since all but two of the pyrazolines were studied at this temperature. The nitrogen evolution rates for ethyl 3,4-dimethyl-Δ^1-pyrazolin-3-carboxylate and 3-carbamyl-3-methyl-Δ^1-pyrazoline at this temperature are calculated values. Table XX lists the compounds studied in their order of decreasing rate and increasing half-lives together with their energies of activation. In the following discussion, the nitrogen evolution rate of ethyl 3-methyl-Δ^1-pyrazolin-3-carboxylate is arbitrarily taken as a convenient reference point.

As seen by examining the table, the rates can be divided into five groups representing eight major changes which influence the rate of nitrogen evolution.

There is relatively little change in the rate of decomposition as the alcohol portion of the ester group at position 3 is varied with one exception. The tert.-butyl group in the alcohol portion of the ester significantly decreases the decomposition rate.

In comparison with the standard, the substitution of the carboxyl group at position 3 by a nitro group has little effect upon the decomposition rate.

A decrease in the rate of nitrogen evolution which is of the same order as that produced by the tert.-butyl group at the alcohol portion is brought about by the substitution of an

TABLE XX

Summary of Kinetic Data.

Compound	k min.$^{-1}$ at 109.5°C.	$t_{\frac{1}{2}}$ min. at 109.5°C.	k min.$^{-1}$(°C.)	$t_{\frac{1}{2}}$ min.	Ea(kcal.)
3-Cyano-3-methyl-Δ^1-pyrazoline	0.0461	15	0.0048(88.75)	144	30
Ethyl 5-Propyl-3-methyl-Δ^1-pyrazolin-3-carboxylate	0.0440	16	0.0054(88.75)	128	28
Ethyl 5-Ethyl-3-methyl-Δ^1-pyrazolin-3-carboxylate	0.0438	16	0.0048(88.75)	144	28
Ethyl 3,5-Dimethyl-Δ^1-pyrazolin-3-carboxylate	0.0435	16	0.0055(88.75)	126	27
3-Aceto-3-methyl-Δ^1-pyrazoline	0.0104	67	0.0496(125.9)	14	29
Methyl 3-Methyl-Δ^1-pyrazolin-3-carboxylate	0.0062	112	0.0431(125.9) 0.0435(125.9)	16 16	36
3-Nitro-3-methyl-Δ^1-pyrazoline	0.0061	114	0.0290(125.9)	24	29
Ethyl 3-Methyl-Δ^1-pyrazoline-3-carboxylate	0.0060	116	0.0341(125.9)	20	32
n-Propyl 3-Methyl-Δ^1-pyrazolin-3-carboxylate	0.0058	120	0.0351(125.9)	20	33
n-Butyl 3-Methyl-Δ^1-pyrazolin-3-carboxylate	0.0058	120	0.0357(125.9)	19	34

Compound	k min.$^{-1}$ at 109.5°C.	$t_{\frac{1}{2}}$ min. at 109.5°C.	k min.$^{-1}$(°C.)	$t_{\frac{1}{2}}$ min.	E_a(kcal.)
Isopropyl 3-Methyl-Δ^1 -pyrazolin-3-carboxylate	0.0053	128	0.0343(125.9) 0.0341(125.9)	20 20	34
t-Butyl 3-Methyl-Δ^1 -pyrazolin-3-carboxylate	0.0041	164	0.0256(125.9) 0.0258(125.9)	28 27	34
Ethyl 3-Ethyl-Δ^1 -pyrazolin-3-carboxylate*	0.0039(calc.)	178	0.0164(125.9)	42	28
Ethyl 3,4-Dimethyl-Δ^1 -pyrazolin-3-carboxylate	0.0020	347	0.0122(125.9)	57	34
3-Carbamyl-3-methyl-Δ^1 -pyrazoline**	0.0019(calc.)	3648	0.0012(125.9)	578	34

* Second k = 0.0758 min.$^{-1}$ at 143.96°C., $t_{\frac{1}{2}}$ = 9 min.
** Second k = 0.0077 min.$^{-1}$ at 143.95°C., $t_{\frac{1}{2}}$ = 89 min.

ethyl group for the methyl group at position 3.

The most significant decreases in the decomposition rates are effected by one of two ways: a) the substitution of a methyl group at position 4, and b) the replacement of the carboxyl group with a carbamyl group at position 3.

Going in the other direction, the use of an aceto group at position 3 for the carboxyl group results in a significant increase in the rate of nitrogen evolution. Very great increases in the rate of decomposition can be accomplished in one of two ways: a) the substitution of an alkyl group, e.g. methyl, ethyl, or n-propyl, at position 5, and b) the use of a cyano group in place of the carboxyl group at position 3.

There is a fourth way by which the rate may be increased. The use of a phenyl group to replace the methyl group at position 3 resulted in a pyrazoline which decomposed noticeably at room temperature and vigorously at steam bath temperature.

Thus, it appears that there are four ways by which the rate of nitrogen evolution can be reduced: A) the use of tert.-butyl alcohol in the carboxyl group at position 3, B) the substitution of an ethyl group for the methyl group at position 3, C) the substitution of a methyl group at position 4 and D) the use of a carbamyl group in place of the carboxyl group at position 3.

In addition, there are four ways by which the rate of nitrogen evolution can be increased: A) the substitution of

the carboxyl group at position 3 by an aceto group, B) the substitution of an alkyl group at position 5, C) the use of a cyano group to replace the carboxyl group at position 3, and D) the replacement of the methyl group at position 3 by a phenyl group.

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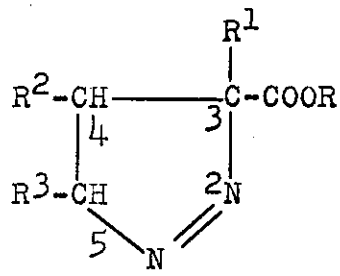
Abstract

The Synthesis and Thermal Decomposition of 3,3-Disubstituted-Δ^1-pyrazolines

Harry Raymond Snyder, Jr.
Major Professor: J. Philip Mason
Chemistry Department, Boston University

The following system has been studied:



Δ^1-Pyrazolines were prepared in which one or more of the groups R, R^1, R^2, R^3 are alkyl or phenyl and the other groups are hydrogen. In addition, the molecule was modified by the use of four other activating groups in the place of the carboxyl group, i.e. -CN, $-CONH_2$, $-COCH_3$, and $-NO_2$. The compounds were decomposed thermally and the kinetics of the decomposition was followed by measuring the volume of nitrogen evolved as a function of time. From the data obtained, the rate constants and energies of activation were calculated. The purpose of the investigation was to determine the effects upon the rate constants and energies of activation produced by the alteration of the molecule at the above-indicated positions.

The pyrazolines were prepared by the addition of diazomethane to the appropriate olefin, or by the addition of the

appropriate diazoalkane to ethyl methacrylate.

The following table summarizes the compounds prepared and the kinetic data obtained.

In order to facilitate a discussion of the conclusions drawn from the kinetic data, attention is focused upon the rates of nitrogen evolution at 109.5°C. since all but two of the pyrazolines were studied at this temperature. The nitrogen evolution rates for ethyl 3,4-dimethyl-Δ^1-pyrazolin-3-carboxylate and 3-carbamyl-3-methyl-Δ^1-pyrazoline at this temperature are calculated values. The rate of nitrogen evolution of ethyl 3-methyl-Δ^1-pyrazolin-3-carboxylate is arbitrarily taken as a convenient reference point.

An examination of the kinetic data shows that there are eight major changes which influence the rate of nitrogen evolution:

I. There are four ways by which the nitrogen evolution can be reduced:

A. The use of tert.-butyl alcohol in the carboxyl group at position 3.

B. The substitution of an ethyl group for the methyl group at position 3.

C. The substitution of a methyl group at position 4.

D. The use of a carbamyl group in the place of the carboxyl group at position 3.

II. There are four ways by which the rate of nitrogen evolution can be increased:

A. The substitution of the carboxyl group at position 3 by an aceto group.

B. The substitution of an alkyl group at position 5.

C. The use of a cyano group to replace the carboxyl group at position 3.

D. The replacement of the methyl group at position 3 by a phenyl group.

Summary of Kinetic Data.

Compound	k min.$^{-1}$ at 109.5°C.	k min.$^{-1}$(°C.)	E_a(kcal.)
3-Cyano-3-methyl-Δ^1-pyrazoline	0.0461	0.0048(88.75)	30
Ethyl 5-Propyl-3-methyl-Δ^1-pyrazolin-3-carboxylate	0.0440	0.0054(88.75)	28
Ethyl 5-Ethyl-3-methyl-Δ^1-pyrazolin-3-carboxylate	0.0438	0.0048(88.75)	28
Ethyl 3,5-Dimethyl-Δ^1-pyrazolin-3-carboxylate	0.0435	0.0055(88.75)	27
3-Aceto-3-methyl-Δ^1-pyrazoline	0.0104	0.0496(125.9)	29
Methyl 3-Methyl-Δ^1-pyrazolin-3-carboxylate	0.0062	0.0431(125.9) 0.0435(125.9)	36
3-Nitro-3-methyl-Δ^1-pyrazoline	0.0061	0.0290(125.9)	29
Ethyl 3-Methyl-Δ^1-pyrazoline-3-carboxylate	0.0060	0.0341(125.9)	32
n-Propyl 3-Methyl-Δ^1-pyrazolin-3-carboxylate	0.0058	0.0351(125.9)	33
n-Butyl 3-Methyl-Δ^1-pyrazolin-3-carboxylate	0.0058	0.0357(125.9)	34
Isopropyl 3-Methyl-Δ^1-pyrazolin-3-carboxylate	0.0053	0.0343(125.9) 0.0341(125.9)	34
t-Butyl 3-Methyl-Δ^1-pyrazolin-3-carboxylate	0.0041	0.0256(125.9) 0.0258(125.9)	34
Ethyl 3-Ethyl-Δ^1-pyrazolin-3-carboxylate*	0.0039***	0.0164(125.9)	28
Ethyl 3,4-Dimethyl-Δ^1-pyrazolin-3-carboxylate	0.0020	0.0122(125.9)	34
3-Carbamyl-3-methyl-Δ^1-pyrazoline**	0.0019***	0.0012(125.9)	34

* Second k = 0.0758 min.$^{-1}$ at 143.96°C., $t_{\frac{1}{2}}$ = 9 min.
** Second k = 0.0077 min.$^{-1}$ at 143.95°C., $t_{\frac{1}{2}}$ = 89 min.
*** calc.

Note: An attempt to prepare ethyl 3-phenyl-^{1}-pyrazolin-3-carboxylate resulted in a pyrazoline which decomposed noticeably at room temp. and vigorously at steam bath temp.

Harry Raymond Snyder, Jr.

Birthday: January 19, 1924

Birthplace: Lawrence, Massachusetts

Parents: Harry Raymond and Marjorie Ward Snyder

Education: Public schools of Carver, Massachusetts and Providence, Rhode Island.

Classical High School, Providence, Rhode Island, 1941.

University of Rhode Island - one semester 1942-1943.

University of Alabama - three semesters under Army Specialized Training Program, 1943-1944.

Brown University - Sc.B., June 1949

Boston University - M.A., June 1952

Boston University - Ph.D., June 1958

Military Service: U. S. Army March 1943 - February 1946.

Fellowship: Boston University Teaching Fellow 1949-1952.

Armstrong Cork Co. Research Grant 1952-1954.

Wife: Edna Frances Gay married June 1949.

Son: Herbert Ward born June 1955.

Employment: Research Department, R. J. Reynolds Tobacco Co., Winston-Salem, N. C. July 1954-October 1956.

Eaton Laboratories, Div. Norwich Pharmacal Co., Norwich, New York November 1956 to present.