pressure measurement. The mixed gases were admitted to the reaction cell, which was attached close to the right-side tube. The stopcock was then closed and the pressure read at liberty. At any predetermined time the stopcock was opened for a few seconds and another pressure measurement made. The rate of this reaction could thus be followed, since an increase in pressure at constant volume occurs in the reaction.

It is evident that at no time after the gases were once admitted to the gage did they come in contact with grease. The device is very compact when one considers the number of operations to be performed.

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[Contribution from the Chemical Laboratory of Stanford University]

# THE THERMAL DECOMPOSITION OF METHYL ISOPROPYL DI-IMIDE: A HOMOGENEOUS UNIMOLECULAR REACTION. THE THERMAL DECOMPOSITION OF HYDRAZOIC ACID AND METHYL AZIDE

By Herman C. Ramsperger[1]

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It is important that present theories of unimolecular reaction velocity should be thoroughly tested with a wide variety of reactions. All homogeneous unimolecular gas reactions so far discovered involve rather large molecules. Their reaction rate is too fast to be accounted for without ascribing to some of them as large a number of internal degrees of freedom as can be justified, while others require but few degrees of freedom. The decomposition of nitrogen pentoxide cannot at present be accounted for in this way, but the low-pressure data may still be questionable.

The author had previously found that the two azo compounds, azomethane[2] and azo-*iso*propane[3] decompose in a homogeneous unimolecular manner. A new azo compound, methyl *iso*propyl di-imide was recently prepared[4] by the author to provide an additional test of unimolecular reaction rate theories. Its decomposition will be shown to be first order at high pressures. However, the rate constant becomes lower at low pressures, as was also the case with azomethane.[5]

A unimolecular reaction involving a smaller molecule with a more limited number of degrees of freedom would provide another valuable test of reaction rate theories. For this reason the decomposition of hydrazoic acid and methyl azide was studied.

[1] National Research Fellow in Chemistry.

[2] Ramsperger, This Journal, **49**, 912 (1927).

[3] Ramsperger, *ibid.*, **50**, 714 (1928).

[4] Ramsperger, *ibid.*, **51**, 918 (1929).

[5] Ramsperger, *ibid.*, **49**, 1495 (1927).

## The Thermal Decomposition of Methyl *Iso*propyl Di-imide

Methyl *iso*propyl di-imide was prepared as described in a previous publication.[4] The thermal decomposition was carried out at pressures ranging from $5.8 \times 10^{-3}$ cm. to 13.12 cm. and at temperatures ranging from 250 to 332°.

**Nature of the Reaction Products.**—A rough analysis of the products of decomposition in Expt. 34 (Table I) was made. The final pressure in this experiment (and all other experiments with this sample) was 2.18 times the initial pressure at constant volume. We may write equations for the likely reactions analogous to those of the other two azo compounds previously studied. The main reaction products in these cases were nitrogen and a hydrocarbon as shown, for example, in the equation $CH_3N{=}NCH_3 = N_2 + C_2H_6$. In this new mixed azo compound, however, an analogous reaction may yield either a single hydrocarbon or a mixture of hydrocarbons according to whether the two radicals combine at the instant of disruption of the molecule or the separate radicals combine at random later.

The former case gives only butane and nitrogen. In the latter case we may expect combinations between two methyl radicals, between two *iso*propyl radicals and between methyl and *iso*propyl radicals. The equations for the two mechanisms are then as follows

$$CH_3N{=}NC_3H_7 = N_2 + C_4H_{10} \qquad \text{(a)}$$
$$CH_3N{=}NC_3H_7 = N_2 + xC_2H_6 + yC_4H_{10} + zC_6H_{14} \qquad \text{(b)}$$

Since the final pressure is greater than twice the initial pressure as would be required by both of these equations, there is a side reaction, as was also the case with the other azo compounds. Analogous side reactions are

$$2CH_3N{=}NC_3H_7 = 2N_2 + C_2H_4 + 2C_3H_8 \qquad \text{(c)}$$
$$CH_3N{=}NC_3H_7 = N_2 + CH_4 + C_3H_6 \qquad \text{(d)}$$

The gas to be analyzed was collected in a 250-cc. flask which had a manometer attached and had a tube sealed to the bottom. Liquid air, carbon dioxide snow and freezing mixtures were placed around this tube. After surrounding the tube with a constant temperature bath, the manometer pressures were read repeatedly until no further change was noted. This usually required only ten or fifteen minutes but a much longer time was usually taken to be sure of a constant reading. The initial pressure of the gas was 10.98 cm. At −78°, 17.6% of the gas was condensed by means of ether–carbon dioxide mixture. Most of this condensed out between −20 and −50°. Liquid air condensed 43.4%. The vapor pressures of all of the possible reaction products are known at least approximately. Hexane is the only hydrocarbon that should condense out at temperatures above −78°. Methane and nitrogen are the only gases that should remain uncondensed with liquid air. Since Reaction b is the only one producing hexane, the main reaction is to be represented by Equation b. If the side reaction c is to account for the final pressure, then 54.1% of the gas should be condensable with liquid air, while if Reaction d occurs only 45.9% of the gas should condense. Since the experimental result is even slightly lower than the latter value, it seems that Reaction d is the probable side reaction. An analysis made by the freezing out of vapors is not expected to be very accurate, but if a choice is to be made among these four reactions, the differences in the pressures expected are sufficiently great for this method to give the correct result. The 17.6% condensed at −78° is somewhat higher than one might expect. Collisions between the larger *iso*propyl radicals will occur more often than collisions between methyl radicals. If the diameter of an *iso*propyl radical be taken as 2.5 times that of a methyl radical and all combinations of the radicals are taken to be equally probable, then kinetic theory equations for the number of collisions[6] show that 37.1% of the mixed gases should be hexane and 14% of all of the gas should be condensable. It seems likely that the difference between the latter value and 17.6% may be due to butane and propylene dissolving in the condensed hexane, especially since the partial pressure of the butane is about two-thirds of its saturation pressure for this temperature.

**Preparation and Purification.**—Methyl *iso*propyl di-imide was prepared and purified in the manner described in a previous paper by the author.[4] Two different samples were used in this research. Experiments 1 to 30 (Table I) were made with the first sample and Expts. 31 to 47 were made with the second sample. An examination of the rate constants shows that the second sample gave the same rate constants as the first sample. However, the final pressures were about 2.12 times the initial pressure for Sample 1, and 2.18 times the initial pressure for Sample 2. The rate constants were calculated on the basis of the final pressures obtained. It is likely that the first sample contained a small amount of impurity, probably a hydrocarbon of similar boiling point.

**Reaction Rate Measurements.**—The same pyrex reaction cell, surrounded by mercury vapor boiling under a constant pressure, that was used with the previously studied azo compounds was used here. In addition, a similar apparatus made entirely of quartz was used in Expts. 1, 2, 31, 32 and 33. Experiments at pressures above 3 cm. were made exactly as with azomethane.[2] Experiments at low pressures were made with a combination of stopcock and McLeod gage described in the preceding article.[7] The first reading could be made within several seconds after the McLeod gage was open to the cell, and in only a few of the most rapid experiments was a correction necessary for the decomposition before this reading was made. The McLeod gage was kept closed between readings, and opened for only five to ten seconds before each pressure reading was made. The calculation of the partial pressure of the methyl *iso*propyl di-imide in the reaction cell was somewhat simpler than was the case with the apparatus used in the previous researches.

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[6] Tolman, "Statistical Mechanics," The Chemical Catalog Co., New York, 1927, p. 71.

[7] Ramsperger, This Journal, 51, 2132 (1929).

Let $P$ be the pressure read on the McLeod gage and $\Delta P$ the pressure increase during the preceding time interval. Let $V_1$ and $T_1$ be the volume and temperature of the McLeod gage and $V_2$ and $T_2$ the volume and temperature of the reaction cell. Then $P'$, the total pressure in the reaction cell just before the reading, is given by $P' = P + \Delta P V_1 T_2/V_2 T_1$. Now the increase in pressure from the previous reading at time $t'$ to the reading at time $t$ divided by 1.18 (or 1.12 for the first sample) gives the reduction in pressure of the methyl *iso*propyl di-imide in the cell. If $P'_{At}$ represents the partial pressure of methyl *iso*propyl di-imide before the reading at $t'$ and $P_{At'}$ represents its partial pressure at the end of the previous reading, we have

$$P'_{At} = P_{At'} - (P_{t'} - P'_{t})/1.18 \quad \text{and} \quad P_{At} = P'_{At}\, P_t/P'_t$$

The rate constant is then given by

$$K = \log_{10} \frac{P_{At'}}{P'_{At}} \times \frac{2.303}{t - t'}$$

where $t$ and $t'$ are given in seconds.

**Experimental Results.**—A summary of all of the experiments is given in Table I.

TABLE I

SUMMARY OF ALL EXPERIMENTS

| Expt. | Temp., °C. | Init. press., cm. | Av. $K \times 10^3$ | Expt. | Temp., °C. | Init. press., cm. | Av. $K \times 10^3$ |
|---|---|---|---|---|---|---|---|
| 37 | 250.0 | 4.53 | 0.0409 | 47 | 300.0 | 0.709 | 1.69 |
| 36 | 259.1 | 6.54 | .088 | 1 | 300.0 | 0.444 | 1.33 |
| 24 | 260.0 | 0.690 | .0544 | 2 | 300.0 | 0.0378 | 0.97 |
| 22 | 260.0 | 0.142 | .050 | 18 | 300.0 | 0.0058 | .445 |
| | | | | | | | |
| 35 | 270.0 | 9.32 | .220 | 32 | 310.0 | 4.04 | 3.94 |
| 38 | 270.0 | 3.24 | .210 | 43 | 310.0 | 0.604 | 3.22 |
| 39 | 270.0 | 0.673 | .171 | 30 | 310.0 | .195 | 2.47 |
| 40 | 270.0 | .637 | .157 | 4 | 310.0 | .0938 | 1.98 |
| 9 | 270.0 | .128 | .117 | 5 | 310.0 | .0215 | 1.39 |
| 10 | 270.0 | .0583 | .107 | | | | |
| 41 | 270.0 | .0430 | .106 | 45 | 322.0 | .690 | 6.90 |
| 25 | 270.0 | .0123 | .077 | 8 | 322.0 | .390 | 5.54 |
| | | | | 6 | 322.0 | .124 | 4.56 |
| 34 | 285.0 | 13.12 | .714 | 15 | 322.0 | .091 | 5.01 |
| 31 | 285.0 | 3.29 | .686 | 7 | 322.0 | .040 | 3.84 |
| 33 | 285.0 | 2.53 | .600 | 46 | 322.0 | .0233 | 3.50 |
| 42 | 285.0 | 0.781 | .533 | 16 | 322.0 | .0133 | 3.25 |
| 29 | 285.0 | .194 | .379 | | | | |
| 28 | 285.0 | .152 | .426 | 19 | 332.0 | .134 | 9.80 |
| 12 | 285.0 | .136 | .346 | 20 | 332.0 | .0175 | 5.53 |
| 13 | 285.0 | .0606 | .325 | 21 | 332.0 | .0080 | 4.20 |
| 26 | 285.0 | .0168 | .297 | | | | |

The complete data of two typical experiments are given in Table II.

## Discussion

Experiments 28, 29 and 30 were made with sufficient pyrex tubing in the cell to increase the surface five-fold. Since the rates fall in line with

TABLE II

COMPLETE DATA OF TWO EXPERIMENTS

Expt. 39. $V_1T_2/V_2T_1 = (15.2 \times 543)/(210 \times 298) = 0.130$

| $t$, min. | $P$, cm. | $P'$ | $P'_A$ | $P_A$ | $K \times 10^3$ |
|---|---|---|---|---|---|
| 0 | 0.673 | 0.673 | 0.673 | 0.673 | ... |
| 11 | .743 | .752 | .606 | .599 | 0.163 |
| 21 | .809 | .817 | .536 | .531 | .185 |
| 32 | .863 | .870 | .479 | .475 | .160 |
| 50 | .950 | .961 | .392 | .388 | .178 |
| 75 | 1.043 | 1.055 | .299 | .296 | .174 |
| 120 | 1.162 | 1.177 | .182 | .180 | .180 |
| 159 | 1.221 | 1.228 | .124 | .123 | .159 |

Expt. 46. $V_1T_2/V_2T_1 = 15.2 \times 595/210 \times 298 = 0.142$

Decomposition in filling cell = 0.0004 cm.

| $t$, min. | $P$, cm. | $P'$ | $P'_A$ | $P_A$ | $K \times 10^3$ |
|---|---|---|---|---|---|
| 0 | 0.02378 | 0.02378 | 0.0229 | 0.0229 | .. |
| 1.33 | .02968 | .03052 | .0172 | .0168 | 3.58 |
| 2.75 | .03401 | .03463 | .0126 | .0124 | 3.38 |
| 4.25 | .03779 | .03833 | .0087 | .0086 | 3.94 |
| 6 | .04028 | .04064 | .0062 | .0062 | 3.12 |
| 45 | .04599 | .04680 | .0007 | .0007 | .. |

the experiments made with the empty cell and with those made in the quartz cell, the reaction is homogeneous and not influenced by the walls.

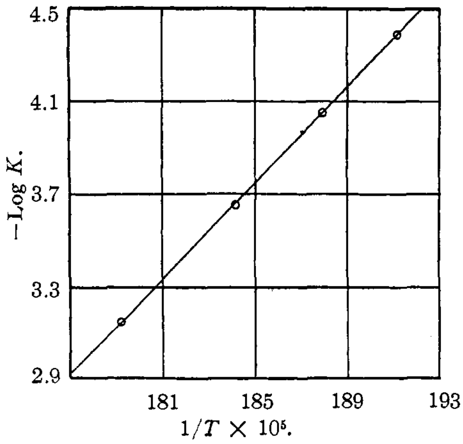

Fig. 1.

It is apparent that within experimental error and reproducibility the decomposition is first order in any given experiment. It is also apparent that the rate constant varies with the initial pressure, being lower for lower initial pressures. It does, however, approach a constant value at the higher pressures and lower temperatures as, for example, at 270 and 285°. Experiments were made at 250, 259.1, 270 and 285° at sufficiently high pressures to approach the value which would be obtained for very high pressures. The log of the rate constants for these experiments is plotted against $1/T$ in Fig. 1. These points should fall on a straight line according to the Arrhenius equation for the temperature coefficient of reaction velocity, namely, $d \ln K/d(1/T) = Q/R$. The line drawn through the points in Fig. 1 is a straight line. $Q$ is found to be 47,480 cal. per mole. The equation for the rate constant is $2.72 \times 10^{15} \times e^{-47480/RT}$. However, the asymptotic values of the rate constants have not quite been reached at the highest pressures studied. We may take roughly $2.80 \times 10^{15} \times e^{-47480/RT}$ as the best value of the rate constant for very high pressures.

This reaction is evidently very similar to that of azomethane, which was shown to be first order at high pressures and to fall off in rate at lower pressures. With methyl *iso*propyl di-imide the high pressure rate is maintained to somewhat lower pressures than with azomethane. The more complex azo-*iso*propane showed no dropping in rate at the lowest pressures studied. A collision theory of activation developed by Rice and the author[8] (Theory II) was shown to be in agreement with the experimental data on azomethane.[9] Kassel[10] has also developed a theory (Theory III) which is very similar to Theory II of Rice and the author. Another theory (Theory I) of Rice and the author, which is an extension of the theory of Hinshelwood and Lindemann[11] to low pressures, does not fit the azomethane data. It has also been shown by Kassel[10] and by Rice and the author that several reactions studied by Hinshelwood and his co-workers cannot be accounted for as well on Theory I as on Theory II or III. More recently Rice[12] and Kassel[13] have given quantum treatments based on Theories II and III. The quantum treatments are more difficult to apply and for large molecules are not sufficiently different from the earlier classical theories for experimental data of the usual accuracy to decide between them. There is also no appreciable difference between Theories II and III for a molecule having a large number of degrees of freedom involved in the reaction, as is the case with the azo compounds. I will therefore use Theory II to interpret the decomposition of methyl *iso*propyl di-imide.

Equation 19 of reference 8 (*cf.* p. 1624) has been integrated graphically, using a value of 33 for $n$, and values of 543, 573 and 603 for $T$, corresponding to 270, 300 and 330°. $E$ is 46,900 cal. per mole (from Equation 20 of reference 8). Log $K/K_\infty$ is then calculated for a series of values of $\beta_2/p$. The experimental data are plotted as in Fig. 2. The theoretical curves are then found to fit the data if the molecular diameter be taken as $6 \times 10^{-8}$ cm. The upper theoretical curve is for 270°, the middle curve for 300° and the lower curve for 330°. Most of the experimental points from 270 to 332° fall within the region bounded by the theoretical curves. It may also be observed that low temperature points fall above high temperature points. The small differences between the theoretical curve and experimental points should be ascribed to experimental errors of the indi-

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[8] Rice and Ramsperger, THIS JOURNAL, **49**, 1617 (1927).

[9] Rice and Ramsperger, *ibid.*, **50**, 617 (1928).

[10] Kassel, *J. Phys. Chem.*, **32**, 225 (1928).

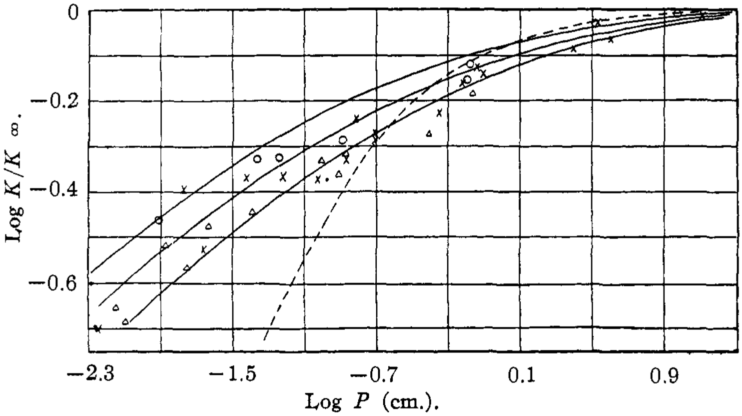
[11] Hinshelwood, *Proc. Roy. Soc. London*, **113A**, 230 (1928).

[12] Rice, *Proc. Nat. Acad. Sci.*, **14**, 114 (1928).

[13] Kassel, *J. Phys. Chem.*, **32**, 1065 (1928).

vidual points and to a small possible error in $K_\infty$ as calculated from Equation 1. The agreement is therefore as good as the experimental accuracy would justify.

The author would like to call attention to the significance of this agreement. If, for example, Theory I be applied with the same value for $n$ and for the molecular diameter as used for Theory II, the dotted curve of Fig. 2 is obtained. This curve has the wrong shape and so cannot be made to fit all of the experimental points by changing either the diameter or the number of degrees of freedom. The curves for Theory II have now been shown to fit the low pressure data for the two azo compounds, azomethane and methyl *iso*propyl di-imide. They have also been shown to fit the data for diethyl ether and dimethyl ether.[9] The only other reaction that has been carried to low enough pressures to test theories of reaction velocity is the decomposition of nitrogen pentoxide. Here, however, the data of the various investigators do not agree among themselves, and Loomis and Smith[14] have recently shown that the methods used in these experiments produce very large errors due to absorption and occlusion. Very recently it has been reported that the rate constant of this reaction falls off even at several mm. pressure,[15] so conclusions regarding this reaction must be withheld until the low pressure data are confirmed. It is also significant that all of the various theoretical treatments that are based on the assumption that reaction occurs whenever a definite amount of energy becomes localized in one or at most several degrees of freedom, give the correct shape of curve. Normal molecular diameters are used



○, Experiments at 270°; ×, experiments at 285–310°: △, experiments at 322 and 332°.

Fig. 2.

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[14] Loomis and Smith, This Journal, **50**, 1864 (1928).

[15] Rice, Urey and Washburn, *ibid.*, **50**, 2402 (1928).

and the number of degrees of freedom required is not greater than is allowable in applying these theoretical treatments.

If, however, reliable data on the decomposition of nitrogen pentoxide do not agree with these theories, we may expect to find other unimolecular reactions, especially of inorganic molecules, which will disagree. It is possible that the assumptions made in the derivation of the theories regarding energy transfer both between molecules at collision and between internal degrees of freedom are approximately obeyed in the organic molecules and not in the others.

Data on the three azo compounds studied by the author are collected in Table III. $P$(cm.) is the pressure range studied, $T$ the temperature range, $A$ and $Q$ are the quantities in the expression for the rate constant at high pressures, $K_\infty = Ae^{-Q/RT}$ and $n$ is the number of degrees of freedom required by Theory II.

TABLE III

COLLECTED DATA FOR THREE AZO COMPOUNDS

| Compound | $P$, cm. | $T$, °C. | $A$ | $Q$, cal. | $n$ |
|---|---|---|---|---|---|
| $C_2H_6N_2$ | 0.0259 to 70.79 | 278 to 327 | $1.07 \times 10^{16}$ | 51,200 | 25 |
| $C_4H_{10}N_2$ | 0.0058 to 13.12 | 250 to 332 | $2.80 \times 10^{15}$ | 47,480 | 33 |
| $C_6H_{14}N_2$ | 0.025 to 4.60 | 250 to 290 | $5.6 \times 10^{13}$ | 40,900 | >40 |

The heat of activation of the new compound is intermediate between that for dimethyl di-imide and di-*iso*propyl di-imide. If now the decomposition of these azo compounds occurs by the breaking of a single bond, then we may expect the heat of activation of methyl *iso*propyl di-imide to be very nearly that of di-*iso*propyl di-imide, namely, 40,900 cal. per mole, for the reaction will occur at the weaker *iso*propyl bond and the interchange of methyl for *iso*propyl should not greatly alter the binding energy of the *iso*propyl bond. If, however, the reaction occurs by the simultaneous rupture of both bonds, then we may expect an intermediate heat of activation, and this is the experimental result. From the fact that the main reaction gives a mixture of hydrocarbons, we conclude that the two radicals are not combined at the instant of reaction but are separately dislodged and combine at random later.

## The Thermal Decomposition of Hydrazoic Acid

Anhydrous hydrazoic acid vapor was found to decompose at 290° with measurable velocity. A white solid, probably ammonium azide, was formed and a gas, probably nitrogen, which was not condensable in liquid air was also produced. Only a small increase in pressure accompanied the reaction, so that the rate was followed by determining the percentage of gas not frozen out by liquid air. Three experiments, all at 290° and about 4-cm. pressure, showed that 9 to 11% of the hydrazoic acid was decomposed in twenty-five minutes. When pyrex tubing was placed in the reaction cell in sufficient amount to increase the surface to four times the original surface, three similar experiments showed that 12% was decomposed in eight minutes, 22% in twenty-five minutes and 31% in thirty-four minutes. While no great accuracy can be claimed for these experiments, they show conclusively that the reaction is catalyzed by the walls of the vessel. Since the reaction is not homogeneous it cannot be used to test gas phase reaction theories and so the reaction was not studied further.

## The Thermal Decomposition of Methyl Azide

Methyl azide ($CH_3N_3$) was prepared from sodium azide and methyl sulfate. Five experiments were carried out at 245°. The complete decomposition gave a final pressure of 1.55 times the initial pressure. No analysis of the products of reaction was made but a white solid formed similar to that from hydrazoic acid. The reaction may very likely be the following, $2CH_3N_3 = C_2H_4 + 2HN_3$. The reaction rate so measured by the pressure increase was not influenced by increasing the wall surface and is therefore homogeneous. The reaction rate was first order during a given experiment but the rate constant became much lower at low pressures. A summary of the five experiments is given in Table IV.

TABLE IV

SUMMARY OF EXPERIMENTS

| Expt. | 5 | 4 | 1 | 3 | 2 |
|---|---|---|---|---|---|
| Init. press., cm. | 5.75 | 4.06 | 3.37 | 0.226 | 0.0484 |
| Av. $K \times 10^3$ | 1.98 | 1.64 | 1.50 | 0.52 | 0.31 |

The reaction is somewhat uncertain because of the fact that it may be followed by the decomposition of hydrazoic acid, and the formation of the white solid would lead to inaccuracies at higher pressures. It seems likely, however, that this is really another homogeneous unimolecular reaction the rate of which falls off at low pressures.

The author wishes to take this opportunity to express an appreciation of the interest and encouragement Professor Gilbert N. Lewis has generously given throughout the author's researches on azo compounds made at the University of California and elsewhere.

## Summary

The thermal decomposition of methyl *iso*propyl di-imide was studied over a temperature range of 250 to 332° and a pressure range of 0.0058 to 13.12 cm. The reaction has been found to be homogeneous and first order at high pressures, but the rate constant falls off at pressures below several cm. The high-pressure rate constant is given by the expression $K_\infty = 2.80 \times 10^{15} \times e^{-47480/RT}$. Theory II of Rice and the author has been found to fit the data if the molecule be assumed to have 33 degrees of freedom. The significance of this agreement is discussed. All unimolecu-

lar reactions (with the possible exception of nitrogen pentoxide) agree with theories based on the assumption that reaction occurs whenever a definite amount of energy becomes localized in one or, at most, several degrees of freedom.

The thermal decomposition of hydrazoic acid was found to be catalyzed by the pyrex walls of the reaction vessel.

The thermal decomposition of methyl azide was found to be homogeneous and first order during a given experiment but the rate constant becomes lower at lower initial pressures.

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

# SOME THIOPHENE ANALOGS OF DI-, TRI- AND TETRAPHENYLMETHANE COMPOUNDS[1]

BY WESLEY MINNIS

RECEIVED OCTOBER 15, 1928 PUBLISHED JULY 5, 1929

In the course of an attempt to extend the results of a previous investigation[2] of free radicals containing the thiophene ring, studies were made of various analogs of di-, tri- and tetraphenylmethane compounds in which one phenyl group was replaced by the thienyl group.

In general, methods of synthesis used in the benzene series were successfully applied. Usually the thiophene analogs were isolated with more difficulty, probably because of the greater reactivity of the thiophene nucleus, which tends toward the formation of by-products. After isolation, decomposition often occurred under conditions which do not similarly affect the phenyl compounds. For example, phenylthienyl ketone dichloride could not be distilled under reduced pressure without decomposition, whereas benzophenone dichloride is readily purified in such manner. The diphenylcarbinol halides have been made and are moderately stable, but attempts to prepare phenylthienylcarbinol halides resulted in deep-seated decomposition. The reduction of diphenylthienylcarbinol gave only a 50% yield of methane as contrasted with the practically quantitative yield of triphenylmethane from its carbinol. Diphenylthienylcarbinol halides were much less stable than the triphenylcarbinol halides, and the same was true of the corresponding free radicals.

The instability of the free radical, diphenylthienylmethyl, was reminiscent of the behavior of phenylthioxanthyl,[3] and it is tentatively suggested

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[1] This article is an abstract of Part II of the dissertation submitted to the faculty of the University of Michigan, in partial fulfilment of the requirements for the degree of Doctor of Philosophy. 1922.

[2] Gomberg and Jickling, THIS JOURNAL, **35**, 446 (1913).

[3] Gomberg and Minnis, *ibid.*, **43**, 1940 (1921).