change in heat content of lead iodide as $-42,289$. And if we use Jones and Kaplan's[11] value for ΔH for silver iodide, *i. e.*, $-28,708$, we get ΔH for the change in heat content of lead iodide as $-41,077$. Gerke's value is $-41,859$.

From $NF(\mathrm{d}E/\mathrm{d}T) = \Delta S$ we calculate the change in entropy, ΔS, for the cell reaction to be -9.23 cal. In order to obtain the change in entropy, ΔS, for lead iodide from its elements, we combine the following reactions

$$\begin{array}{ll}
PbHg_x + 2AgI = xHg + PbI_2 + 2Ag; & \Delta S = -9.23 \\
Pb(s) + Hg = PbHg_x; & \Delta S = +0.74^{2} \\
\hline
Pb(s) + 2AgI = PbI_2 + 2Ag; & \Delta S = -8.49 \\
2Ag(s) + I_2 = 2AgI; & \Delta S = +9.60^{11} \\
\hline
Pb(s) + I_2 = PbI_2; & \Delta S = +1.11
\end{array}$$

Gerke[2] reports -1.20 for ΔS for lead iodide.

If now we use the third law, $\Delta F = \Delta H - T\Delta S$, using our values of $\Delta F = -41,479$ and $\Delta S = +1.11$, we obtain for ΔH the value $-41,148$. If next we use the value of Lewis and Randall,[12] $\Delta S = 6.8$ for 2AgI, with the above equations, we obtain ΔS for lead iodide from its elements as -1.69. Using this value with the third law, and our value $\Delta F = -41,479$, we obtain ΔH for lead iodide as $-41,983$.

We take as our values for lead iodide from its elements: $\Delta F = -41,479$; $\Delta H = -42,259$ and $\Delta S = 1.11$.

Summary

We have calculated the values of ΔF, ΔH and ΔS for the formation of lead iodide from its elements. We have also compared various calculations made from available data in the literature.

NORTHAMPTON, MASS.

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[11] Jones and Kaplan, THIS JOURNAL, **50**, 1845 (1928).

[12] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York City, 1923, p. 451.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY]

The Photolysis of Azomethane. II. The Effect of Temperature

BY MILTON BURTON,[1] THOMAS W. DAVIS AND H. AUSTIN TAYLOR

In a previous report[2] evidence was presented indicating that the photolysis of azomethane is not to be represented by the over-all equation

$$CH_3N{=}NCH_3 + h\nu \longrightarrow C_2H_6 + N_2 \quad (1)$$

On the other hand, there was no evidence that the primary step may be represented entirely by the equation

$$CH_3N{=}NCH_3 + h\nu \longrightarrow N_2 + 2CH_3 \quad (2)$$

We have shown that the gaseous products not soluble in hydrochloric acid contain approximately 55% nitrogen, 3% methane and 42% ethane when the photolysis is permitted to proceed to a 10% pressure increase at a temperature of 20°. These results and others reported are consistent with the ideas that there is a secondary reaction between free methyl radicals and azomethane and that some of the azomethane may decompose by a rearrangement process to yield ultimate molecules in one primary act, as shown by equation 1. The first idea has been justified further by a study of the effects of temperature. The results are reported herein.

The assumption hitherto has been that equation 1 represents in a rough way the principal course of the reaction even at high temperatures. We have now found this assumption to be absolutely unjustified. It is shown that as the temperature is increased the yield of ethane decreases markedly, methane becoming the chief hydrocarbon product.

Experimental Method

The procedure employed was similar to that hitherto reported.[2] The azomethane sample used throughout this work was a portion from the previous investigation. An air thermostat with Pyrex window was substituted for the water thermostat previously used. The temperature within the thermostat varied within a range of 2.5°. In the following statements the average temperature is reported.

As in the previous work,[2] there was interposed between the light source[3] and the reaction system a Corning No. 534 blue ultra filter which, according to the specifications, transmits only wave lengths longer than 3500 Å. This filter was used in all the experiments; the distance of the arc from the wall of the reaction vessel was rigidly fixed at 10.2 cm. As before, the total thickness of Pyrex between the arc and the reacting gas was of the order of 2 mm.

Photolysis of Azomethane.—The initial pressure of azomethane was fixed arbitrarily at approximately 100

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[1] Present address: Department of Chemistry, University of California, Berkeley, Calif.

[2] Burton, Davis and Taylor, THIS JOURNAL, **59**, 1038 (1937).

[3] Burton, *ibid.*, **58**, 1645 (1936).

TABLE I

SUMMARY OF ANALYTICAL RESULTS[a]

Experiment	I[c]	6	4	3	2	1	8	7[d]
Temp., °C.	20	75	118	163	214	216	223	257
P_0	100	99.2	100.4	101.3	99.0	101.9	99.5	100.0
$\Delta P/P_0$, %	10	10.6	10.5	10.5	10.6	10.5	10.4	10.2
Unsatd., %	0	0.4	0	0.4	0	0.5	0.0	0.0
CH_4, %	3.0	10.2	12.0	25.0	30.1	29.3	23.0	37.0
C_2H_6, %	42.0	29.7	23.7	5.4	0.6	1.2	4.9	4.4
C_3H_8, %	0	0	0	0	1.3	1.4	4.5	2.4
N_2, %	55.0	60.0	64.9	68.2	66.0	68.5	69.0	57.7
H_2, %	0	0	0	0.3	1.3	0	0	0
Total	...	100.1	100.6	99.3	99.3	100.9	101.4	101.3
M or D[b]	...	D	M	M	M	D	M	M
$V_{\text{Alk.}}/V$, %	8.5	7.8	9.3	8.9	...	8.3	7.2	7.3
N_2/V % $= a$	10.7	10.7	11.7	18.0	...	17.4	15.3	9.5
$\Delta P/P_F$ % $= b$	8.9	8.9	9.6	9.5	9.6	9.5	9.4	9.3
a/b	1.20	1.20	1.22	1.90	...	1.83	1.63	1.02

[a] Unless otherwise noted the percentages are on the basis of gas not soluble in hydrochloric acid or stannous chloride. P_0 refers to the initial pressure, ΔP to the pressure change, and P_F to the final pressure. V_{Alk} is the total volume of alkane gas (corrected for aqueous tension). V is the volume of product gases measured over mercury. [b] N_2 by actual measurement = M; by difference = D. [c] I represents the rough average of several experiments reported previously.[2] [d] Experiment 7 was a pyrolysis.

mm. for all the experiments, regardless of the temperature. The effect, consequently, was to produce a lower gas concentration at the higher temperatures. However, it has been shown[2] that the initial concentration is without substantial effect on the products of the photolysis of azomethane. The results may, therefore, be directly interpreted. The results of the analyses of the products are shown in Table I.

The initial and final pressure readings were checked over a period of three to five minutes with the system unilluminated. There was no appreciable temperature effect on the initial pressure up to the maximum temperature of 223°; however, it was found that at the latter temperature the pressure continued to increase after illumination ceased. This result is discussed below.

Pyrolysis of Azomethane.—One run was conducted at 257° in the same reaction system used for the photolyses. Neither the initial pressure nor the final one can be exactly fixed. Undoubtedly, pyrolysis started before the first reading and continued after evacuation of the reaction vessel began. The rough results so obtained have been included in this paper merely for the purpose of comparison.

The Formation of a Condensable Liquid.—In the photolyses conducted at a temperature of 163° and above and in the pyrolysis conducted at 257° it was noted during evacuation of the reaction vessel prior to analysis, that a liquid condensed in the Töpler pump at pressures somewhat below atmospheric. In the last experiments conducted, arrangements were made for removing this liquid. The second fraction for analysis was removed through a trap held at dry-ice–toluene temperatures. Azomethane and the various products of the decomposition hitherto encountered appeared to be readily removable at such temperatures; the condensable liquid was retained completely in the trap and subsequently was removed.

The pyrolysis at 257° did not furnish enough material for microanalysis. The typical "nitrogenous odor" was quite evident however and the sample showed nitrogen by a qualitative microanalysis conducted by Mr. W. H. Bromund. The photolysis at 223° yielded approximately 4.14 mg. of material, an amount sufficient for a carbon-hydrogen determination. The results of the microanalysis conducted by Dr. W. Saschek indicated 11.40% hydrogen and 32.61% carbon. The amount of nitrogen, by difference, therefore appears to be 55.99%. The percentages do not correspond to a true simple compound; the nearest empirical formula is $C_2N_3H_8$. The interpretation of this analysis is discussed below.

The calculated and "measured" initial volumes for all the experiments are compared in Table II. As before,[2] T is the temperature expressed in degrees centigrade. P_0 refers to the initial pressure, V is the total volume of gas collected over mercury at room temperature and $V_{\text{Alk.}}$ is the total volume of alkane gas at room temperature (corrected for the aqueous tension). V_0 (calcd.) is the initial volume of azomethane gas calculated to room temperature and pressure from a knowledge of the volume of the reaction system (1015 cc.) and the initial conditions. $V - V_{\text{Alk.}}$ is obviously the initial volume as calculated from a knowledge of the final conditions. The justification for this statement appears in the earlier report.[2] Obviously, reasonable correspondence between V_0 and $V - V_{\text{Alk.}}$ can be expected only if no condensable liquid forms. The difference between these figures, as shown in

TABLE II

COMPARISON OF CALCULATED AND "MEASURED" INITIAL VOLUME

Expt.	P_0	T	V	$V_{\text{Alk.}}$	V_0 (calcd.)	$V - V_{\text{Alk.}}$	Diff.
6	99.2	75	123.3	9.6	114.3	113.7	0.6
4	100.4	118	112.5	9.3	103.0	103.2	− .2
3	101.3	163	94.1	8.4	93.2	85.7	7.5
1	101.9	216	79.8	6.6	83.7	73.2	10.5
8	99.5	223	74.6	5.4	80.4	69.2	11.2
7	100.0	257	79.9	5.8	75.7	74.1	1.6

the last column, becomes notable at 163°, which is the lowest temperature at which liquid was observed in the Töpler pump.

It is to be noted that the discrepancy between V_0 and $V - V_{\mathrm{Alk.}}$ decreases at the highest temperature, *i. e.*, that of the pyrolysis at 257°. The results in experiment 8, in which case it was noted that the pressure continued to increase after illumination ceased, may explain this result. It is, perhaps, possible that the condensable product is itself unstable at the higher temperatures and decomposes to non-condensable gaseous products.

It should be noted that when the reaction vessel was opened to the atmosphere after experiment 8 a light deposit formed in one spot and then disappeared after about thirty seconds.

Discussion of Results

In our previous report[2] we have shown that in a general way the ratio of methane to ethane increases as the photolysis of azomethane proceeds. Furthermore, we have found that at 20° the yield of propane becomes marked at high initial pressures for a higher percentage decomposition.[4] These parallel results suggest an interesting relation. It is possible that subsequent to reactions 1 and 2 (the former must not be omitted as a possible primary act) the following reactions take place

$$CH_3 + C_2H_6 \longrightarrow C_3H_8 + H \qquad (10)$$
$$CH_3 + C_2H_6 \longrightarrow CH_4 + C_2H_5 \qquad (11)$$

Rice and Herzfeld[5] have estimated the energy of activation of reaction 11 to be about 20 kcal. If we are to assume that such a reaction is the principal source of methane, it seems that this would have to be a maximum estimate in order to explain the formation of methane at room temperatures. Inasmuch as the amount of propane in the initial stages of the reaction was shown to be much less than that of methane,[2] it would seem that the energy of activation of reaction 10 would have to be much greater than 20 kcal. to explain the result. On the other hand, the yields of propane actually observed in the more prolonged photolyses would then have been much too great to agree with such a high energy of activation. It is probable, therefore, that all of the propane is formed by some other reaction of the type

$$CH_3 + C_2H_5 \longrightarrow C_3H_8 \qquad (12)$$

Not all of the free ethyl formed in such a reaction as 11 would of necessity disappear by route 12. Some might disappear by an association reaction with azomethane to yield free radicals and associated molecules of the type already discussed. It thus appears that the propane yield can approach but not exceed the methane yield. (The anomalous results previously obtained at low temperatures do not fit in with this type of reasoning.)

It should be noted that neither in the previous work nor in this was an appreciable yield of hydrogen ever detected. The failure to find molecular hydrogen does not of itself necessarily eliminate the possibility of such a reaction as 10. Hydrogen atoms might be expected not to form molecules but to disappear much more readily by such reactions, as for example

$$C_2H_6 + H \longrightarrow CH_3 + CH_4 \qquad (14)$$

which has an energy of activation of about 7.2 kcal.[6]

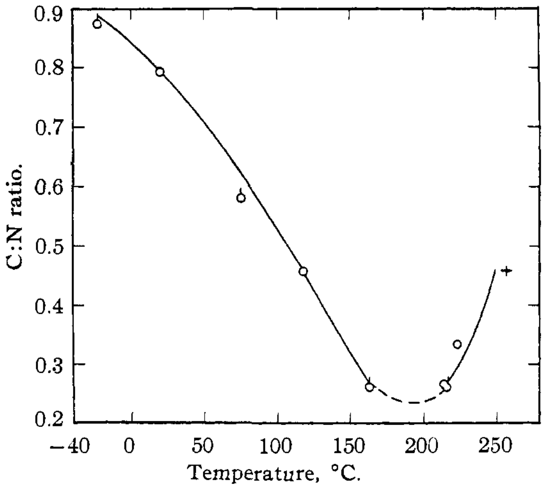

Fig. 1.—Carbon:nitrogen ratio in acid-insoluble product gases plotted against temperature. The experiment represented by + is a pyrolysis. The flagged circles represent points which are known to be low because unsaturated hydrocarbons have not been included in the calculation.

The results reported herein are precisely what might have been expected from the previous work. The increased yield of methane at higher temperatures, accompanied by a decrease in the ethane yield, suggests that reaction 11 may be responsible. Only a small portion of the ethyl so formed unites with methyl to form propane. Below 214° (with the exception of the case previously reported at −22°) the higher hydrocarbons have not been detected in the early stages of the reac-

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(4) In an experiment conducted at −22.5° without filter, propane was reported at lower decomposition. No explanation is advanced for this fact or for the fact that there may have been no methane at all produced in this case. The point at −22.5° is included in Fig. 1.

(5) Rice and Herzfeld, THIS JOURNAL, **56**, 284 (1934).

(6) *Cf.* Trenner, Morikawa and H. S. Taylor, *J. Chem. Phys.*, **5**, 203 (1937).

tion.[7] It would be fruitless to attempt a calculation of any energies of activation from the data at hand because there are too many competing reactions involved.

Mention should finally be made of the liquid condensate appearing at 163°, of which an analysis is reported. This condensate has an approximate empirical formula $C_2N_3H_8$. If we compare this with the formula of azomethane $C_2N_2H_6$, it is evident that there is a deficiency of C atoms. Evidently this material does not contain the product which is responsible for the deficiency of C atoms in the acid insoluble product gases. That such a deficiency exists and increases in amount up to about 200° may be seen in Fig. 1 in which the C:N atom ratio in those gases is plotted against temperature. Presumably, some other product may be formed at higher temperatures in which at one stage a hydrogen atom replaces a methyl group from azomethane, the H atom coming, for example, from a reaction such as 10. The liquid condensate is probably a mixture of such products. The sample analyzed came from experiment 8; a rough calculation shows that there was 190 mg. of azomethane originally present of which $\sim$ 25 mg. decomposed. Judging from the C:N ratio another $\sim$17 to 33 mg. of azomethane disappeared by an association reaction depending on whether one or two radicals added to an azomethane molecule. However, the total amount of material found in the liquid condensate was only a little over 4 mg. Thus, it is consistent with the calculation that this liquid contains a deficiency of C atoms for it may represent only a special kind of associated molecules.

The rise in the carbon–nitrogen ratio at $\sim$200° is probably due to the fact that the associated molecules, formed by reaction of azomethane with radicals or atoms, are unstable at higher temperatures. This surmise is supported by the fact, noted previously, that in experiment 8 conducted at 223°, the pressure continued to increase after illumination was cut off. The low value for propane in the pyrolysis at 257° is apparently out of line with the other figures. It should be noted that actually a much lower percentage decomposition is involved than in the lower temperature experiments. This fact may be seen clearly by referring to the *a/b* value in Table I.

The only previous estimate of the nature of the products in the photolysis of azomethane is that of Heidt and Forbes[8] based largely on volatility and pressures of the products at dry-ice and liquid air temperatures. In the work by Forbes, Heidt and Sickman[9] on the quantum yield of the photolysis the calculation was based definitely on the assumption that pressure changes were a measure of the percentage decomposition. The results reported in this paper now indicate that such an assumption is incorrect. When the studies were conducted at reasonably low partial pressures of azomethane ($\leq$180 mm.), Forbes, Heidt and Sickman obtained a limiting quantum yield Φ of $\sim$1.0. At higher partial pressures they found that deactivating collisions reduced the limiting value of Φ to $\sim$0.77. In that part of their investigation where they studied the effect of temperature, they worked at the higher partial pressures. It was their conclusion that variation of the temperature between 20 and 226° was practically without effect on Φ. It should be noted that Φ was based on pressure measurements. Using their data and recalculating on the basis of the *a/b* ratio of Table I, it appears that if $\Phi_{20°} \simeq 1.0$, then $\Phi_{223°} \simeq 1.36$ and $\Phi_{163°} \simeq 1.58$. It may be concluded, consequently, that their statement that the photochemical temperature coefficient if $t < 226°$ is found to be zero, is founded on insufficient evidence.[9a]

The results we have here reported are of such a nature as to indicate that even if the primary reaction is exclusively by mechanism 2 it is probable that not all the radicals so formed are available to initiate chains when azomethane is used in "mixed" reactions.[10] Consequently, it may be concluded that estimates of chain length computed on such a basis would at best be minimum values.

Summary

1. The analyses of the products of photolysis of azomethane have been extended so that a

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(7) The 1.5% of propane reported in Experiment 22 of the earlier report was based on an analysis of a very small gas sample.

(8) Heidt and Forbes, THIS JOURNAL, **57**, 2331 (1935).

(9) Forbes, Heidt and Sickman, *ibid.*, **57**, 1935 (1935).

(9a) The basis of this calculation is the assumption that nitrogen yield is the true measure of azomethane decomposition. This will be further substantiated in a third paper now in preparation. The *a/b* ratio is the fraction (% azomethane converted to nitrogen)/(% pressure increase). The values of Forbes, Heidt and Sickman are founded on per cent. pressure increase. According to our belief, if the quantum yields on the basis of per cent. pressure increase actually were constant from 20 to 226°, then the true quantum yields would be in the ratio of the *a/b* values at the different temperatures. Thus, if $\Phi_{20} = 1.20$, $\Phi_{163} \simeq 1.90$; if $\Phi_{20} = 1$, $\Phi_{163} \simeq 1.90/1.20 = 1.58$.—(M. B. and T. W. D.)

(10) *Cf.* Allen and Sickman, *ibid.*, **56**, 2031 (1934).

range of temperature from −22.5 to 223° is now covered.

2. The amount of nitrogen produced exceeds the amount of hydrocarbon gas. The discrepancy increases to a maximum at about 200°.

3. The amount of higher hydrocarbon produced (presumably propane) increases with increase in temperature. The amounts of hydrogen and unsaturated hydrocarbon produced are generally negligible.

4. The results substantiate the suggestion previously made that there is a secondary association reaction between free radicals and azomethane.

5. A recalculation of quantum yield data in the literature, on the basis of the analyses here reported, casts doubt on the validity of the conclusion that the temperature coefficient of the photolysis at temperatures $<226°$ is zero.

6. The results indicate that estimates of chain length initiated by azomethane would at best be minimum values.[11]

(11) Through a typographical error in THIS JOURNAL, **59**, 1044 (1937), we are made to say the opposite to this. The line in the middle of the second column should read "... since fewer but longer chains would *now* be required to explain the effects observed."

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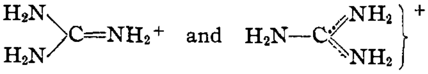
[CONTRIBUTION NO. 153 FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Studies in the Urea Series. XIV.[1] Structure of the Guanidonium Ion, Evidence from Electrolysis[2]

BY TENNEY L. DAVIS, WILLIAM E. YELLAND AND CHUK-CHING MA

The fact that guanidonium hydroxide is an extremely strong base, indistinguishable from potassium hydroxide in electrometric titration,[3] suggests that the guanidonium ion is not of the ammonium type, that guanidine owes its salt-forming properties to some cause other than its being a substituted ammonia. A comparison of the basicities of various alkyl-substituted guanidines and a study of the behavior of these substances on nitration[4] show definitely that the salt-forming properties of these bases cannot be attributed to any particular one of the three nitrogen atoms which each of them contains. The perfect stability of guanidonium nitrite in boiling aqueous solution[5] is not a property of a nitrite of an ammonium base. Edsall,[6] from Raman spectrum measurements, recently has concluded that the guanidonium ion possesses trigonal symmetry and contains three amino groups attached to the central carbon atom. Some years ago Madelung[7] formulated guanidonium hydrochloride $[C(NH_2)_3]^+Cl^-$, considered it to be a carbonium salt and compared it in an interesting manner with pararosaniline hydrochloride—which he formulated $[C(C_6H_4{\vdots}NH_2)_3]^+Cl^-$—pointing out that carbonium salts are not necessarily colored and that pararosaniline hydrochloride owes its color rather to the phenylene groups by which the amino groups are attached to the central carbon atom. Lecker and Graf[8] in consequence of their study of peralkylated guanidines concluded that guanidonium salts contain three amino groups (or six hydrogen atoms capable of being replaced by alkyl groups), but judged that the position of carbon in the periodic table made it unlikely that it would have a positive function and supposed the charge to be resident upon one of the nitrogen atoms. They assigned to the guanidonium ion two formulas which they regarded as identical, namely



$$\left.\begin{matrix}H_2N\\ H_2N\end{matrix}\right\rangle C{=}NH_2^+ \quad \text{and} \quad \left.H_2N{-}C\begin{matrix}\nearrow NH_2\\ \searrow NH_2\end{matrix}\right\}^+$$

While the discharge of such ions might be expected to yield guanidine and hydrogen, we find that hydrogen is not a primary product of the electrolysis and that there is no evidence of a doubling up, through a nitrogen–nitrogen linkage, of molecules of this type. Indeed the products which we find are not those which would be expected from the discharge of an ammonium type ion or of any other in which the charge is resident upon a nitrogen atom, but are those which would be expected if the guanidonium ion is the

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(1) No. XIII of this series, THIS JOURNAL, **58**, 1800 (1936).

(2) Paper read before the Organic Chemistry Division, A. C. S., at the meeting at Rochester, New York, September 7, 1937.

(3) Davis and Elderfield, THIS JOURNAL, **54**, 1499 (1932).

(4) Davis and Elderfield, *ibid.*, **55**, 731 (1933).

(5) Davis and Abrams, *Proc. Am. Acad. Arts Sciences*, **61**, 444 (1926).

(6) Edsall, *J. Phys. Chem.*, **41**, 133 (1937).

(7) Madelung, *Ann.*, **427**, 35 (1922).

(8) Lecker and Graf, *ibid.*, **438**, 154 (1924); **445**, 61 (1925).