amino group, since diethylamine yields no luminescence whatever. It thus seems logical to suppose that the machinery of the diethylaniline spectrum lies in the benzene ring as modified by the presence of the adjacent substituted amino radical. But if this assumption is correct, it seems equally applicable to the case of tetrahydroquinoline, for that compound also has a substituted amino radical in immediate proximity to the benzene nucleus.

We wish to express our thanks to the Chemical Society of London for a grant made from the Research Fund towards the expenses of this research. Some of the materials used in the work were obtained from the Eastman Kodak Company, and we wish to thank them for specially pure specimens, the use of which saved us much trouble. Part of the apparatus used in the investigation was procured with the aid of the Heron Fund of this University.

Summary

An examination has been made of the Tesla-luminescence spectra of a number of organic compounds belonging to various classes, and it has been shown that while each compound yields its own characteristic spectrum, the members of a given class show a general resemblance in the spectra which they emit. It has been found that slight changes in structure make their influence felt in the Tesla-luminescence spectra. A study of some heterocyclic compounds indicates that while furfurole, thiophene, pyrrole and pyridine emit no characteristic spectra of their own, the pyridine nucleus exerts a very marked influence when it is fused with a benzene ring, as in quinoline; and reduction of the pyridine structure produces a marked alteration in the spectrum of the compound.

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[CONTRIBUTION FROM THE FIXED NITROGEN RESEARCH LABORATORY, UNITED STATES DEPARTMENT OF AGRICULTURE]

THE MECHANISM AND THERMOCHEMISTRY OF THE REACTION BETWEEN CALCIUM CARBIDE AND NITROGEN

BY H. J. KRASE AND J. Y. YEE

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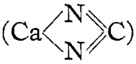
When calcium carbide reacts with nitrogen, calcium cyanamide and carbon are the end products of the reaction. There is, however, ample evidence that the reaction does not go as simply as is indicated by the equation,

$$CaC_2 \text{ (solid)} + N_2 \rightleftharpoons CaCN_2 \text{ (solid)} + C \text{ (solid)} \qquad (1)$$

for it appears that the system is not a monovariant one with three separate solid phases.

The evidence which demonstrates that the system is not a monovariant one is based on the work of earlier investigators in this field, some of whom have also reached this same conclusion. Thompson and Lombard[1] in measuring the equilibrium pressure of nitrogen over the system found an approximately linear relation between the nitrogen pressure and the temperature, and other workers, notably Le Blanc and Eschmann,[2] and V. Ehrlich[3] have found various curvilinear relations between these variables which, however, do not agree with each other. We, also, have obtained data on equilibrium pressures and concluded that the system was not a simple monovariant one because the heat of reaction calculated from the change in equilibrium pressure with the temperature did not agree with the measured heat of Reaction 1.

Evidence that some intermediate reactions are taking place and that Reaction 1 is a "summarized" reaction follows from the accepted structural formula for cyanamide (H_2CN_2) of which calcium cyanamide is the salt. The evidence for the structure of cyanamide, which will not be here reviewed, does not distinguish between the "cyanamide" and the "carbodiimide" structure so that the calcium compound may have either the structure, ($Ca{=}N{-}C{\equiv}N$) or  $(\mathrm{Ca}{<}\begin{smallmatrix}N\\N\end{smallmatrix}{>}\mathrm{C})$. However, we may say that both necessitate first the splitting of the calcium-carbide linkage of carbide and the subsequent reaction of the calcium with nitrogen. This hypothesis, of course, supposes first a dissociation of calcium carbide into its elements.

Various investigators have proposed hypotheses as to the thermal dissociation of calcium carbide. Erlwein, Warth and Beutner[4] concluded that calcium carbide, when heated, decomposed to a subcarbide of calcium and carbon. Briner and Kuhne[5] found no evidence of a subcarbide but concluded that the carbide dissociates into its elements when heated. Bredig[6] was not able to identify either a subcarbide or calcium as a product of the decomposition. E. Botolfsen,[7] although not making quantitative measurements of the decomposition, was able to identify volatilized calcium. V. Ehrlich[3] concluded on the basis of decomposition studies of pure calcium cyanamide $CaCN_2$ that calcium carbide decomposes into a subcarbide of calcium and carbon. He presented no conclusive experimental proof of the mechanism of the decomposition, however.

In the elaboration of our present theory as to the mechanism of the

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[1] Thompson and Lombard, *Met. Chem. Eng.*, **8**, 617 (1910).

[2] Le Blanc and Eschmann, *Z. Elektrochem.*, **17**, 20 (1911).

[3] Ehrlich, *ibid.*, **28**, 540 (1922).

[4] Erlwein, Warth and Beutner, *Z. Elektrochem.*, **17**, 177 (1911).

[5] Briner and Kuhne, *Chem.-Ztg.*, **37**, 442, 665 (1913); *Compt. rend.*, **156**, 620 (1913); *C. A.*, **7**, 2165, (1913); *J. chim. phys.*, **12**, 432 (1914), also *C. A.*, **9**, 565 (1915).

[6] Bredig, *Chem.-Ztg.*, **37**, 831 (1913).

[7] Botolfsen, *Ann. chim.*, **18**, 39 (1922).

carbide-nitrogen reaction, we shall first present some experimental work on the decomposition of calcium carbide by heat.

Experimental Method and Results

The method used for determining the mechanism of the calcium carbide decomposition was in general to heat a charge of about 10 g. of powdered and carefully analyzed calcium carbide for about 24 hours in a high vacuum. The product was then analyzed and the composition calculated. The sample was held in an iron crucible and the heating was carried out in a molybdenum-wound furnace. The heating element was contained in a water-cooled, steel shell which was connected with the high vacuum lime. Vacuum was obtained by means of a mercury-vapor pump backed by two oil pumps of suitable capacity. Pressures in the system were read with a McLeod gage.

The carbide sample was first subjected to a preliminary heating to about 800° in a vacuum in order to decompose the calcium hydroxide and volatilize the combined water, after which it was again analyzed, replaced in the furnace, and heated for the 24-hour period.

The experiments were carried out at 1000°, 1100°, 1200° and 1300°. Temperatures were measured by means of an optical pyrometer and observations were made through a glass window in the furnace. At the beginning of the heating period the temperature could be read very easily but later the glass window, which was vertically over the heated crucible, gradually became covered, at temperatures of 1100° and above, with a sublimate which was later identified as calcium. It is probable, however, that the furnace temperature did not vary more than 100° during these experiments.

The carbide used was specially prepared for this work by heating pure lime and graphite in an Acheson graphite crucible to about 2000° in an electric furnace. Except for one sample which contained a small amount of iron, the product contained only calcium carbide, calcium oxide and graphite, in addition to some moisture which had evidently been absorbed during the pulverizing of the carbide. This moisture was combined as calcium hydroxide. The carbide was ground to pass a 150-mesh screen, then thoroughly mixed and analyzed. All manipulations and handling of carbide were carried out in a suitably arranged desiccator over phosphorus pentoxide.

The material was analyzed for calcium carbide content by a method involving the evolution of acetylene, developed in this Laboratory by one of the authors, which gave very consistent and reliable results. Calcium was determined by precipitation as the oxalate and weighing as the oxide, and uncombined carbon by filtering and weighing. Water was determined in a combustion furnace.

The experimental results are given in Table I.

Table I

Results of Heating Calcium Carbide for 24 Hours in a High Vacuum

		Analytical results					Composition calculated from analysis					
Temp. °C.		CaC_2 %	Total Ca %	Free C %	H_2O %		CaC_2 %	CaO %	$Ca(OH)_2$ %	Free C %		Total %
1000	Original sample	72.08	56.32	8.45	3.75		72.08	4.05	15.43	8.45		100.01
	After preliminary heating to 800°	66.47	57.84	10.78	0.00		66.47	22.79	...	10.78		100.04
	After 24 hrs. at 1000° Pressure, 0.01 mm.	66.66	57.98	10.44	0.00		66.66	22.81	...	10.44		99.91
1100	Original sample	72.08	56.32	8.45	3.75		72.08	4.05	15.43	8.45		100.01
	After preliminary heating at 800°	66.47	57.84	10.78	0.00		66.47	22.79	...	10.78		100.04
	After 24 hrs. at 1100° Pressure, 0.003 mm.	60.71	55.34	15.52	0.00		60.71	24.41	...	15.52		100.64
					H_2O	Fe					Fe	
1200	Original sample[a]	57.43	52.94	13.02	5.60	0.35	57.43	6.36	23.04	13.02	0.35	100.20
	After preliminary heating at 800°	47.58	36.55	15.37	0.00	0.27	47.58	36.55	...	15.25	0.27	99.65
	After 24 hrs. at 1200° Pressure, 0.005 mm.	50.16	54.43	16.65	0.00	0.34	50.16	32.30	...	16.65	0.34	99.45
1300	Original sample	72.08	56.32	8.45	3.75	..	72.08	4.05	15.45	8.45	..	100.01
	After preliminary heating at 800°	65.40	58.10	10.47	..	..	65.40	24.15	...	10.47	..	100.02
	After 24 hrs. at 1300° Pressure, 0.0005 mm.	15.35	13.23	71.55	..	8.40[b]	15.35	5.05		71.55	8.40	100.35

[a] This sample is the exception mentioned on p. 1360. It was prepared in a small arc furnace from materials which contained a small amount of iron.

[b] The iron in this sample undoubtedly came from the iron crucible in which the charge was heated.

In each experiment after the preliminary heating at 800° the carbide had become black, as though carbon had separated. This has been previously observed, and described in the literature.[8] In fact it has been suggested that this phenomenon proves that calcium carbide when heated decomposes into a subcarbide and carbon.

It is quite apparent from our experimental results that the blackening of the carbide is due to the cracking of acetylene. The acetylene would, of course, be generated by the action on calcium carbide of water vapor from the decomposing calcium hydroxide.

The fact that there may be appreciable amounts of water combined as calcium hydroxide in powdered carbide, is here pointed out, it is believed, for the first time. In the commercial nitrification of calcium carbide in the cyanamide process it is usual to obtain a reaction efficiency based on the calcium combined as calcium carbide of about 85%. It is believed that this low reaction efficiency is due to the presence and decomposition of calcium hydroxide.

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[8] Bredig, Fraenkel and Wilke, *Z. Elektrochem.*, **13**, 608 (1907). Ref. 7, p. 38.

The results of heating calcium carbide at 1000° for 24 hours show no decomposition of carbide. The slight discrepancies between the calculated compositions before and after heating (66.47% and 66.66% of calcium carbide, respectively) are believed to be due to analytical error. The experiment at 1100° shows a slight decomposition of calcium carbide which can be calculated by assuming that the absolute weight of one constituent of the charge, say the calcium oxide, is unchanged. In the case of experiments at higher temperatures no one constituent of the charge remains unchanged in weight. At 1200° and 1300° appreciable amounts of lime are reduced by the carbon present with the formation of carbon monoxide. However, the amount of monoxide thus formed and calcium lost to the charge by volatilization may be computed by means of simultaneous equations.[9] This has been done in the case of the experiments at 1200° and 1300° and the results are assembled in Table II.

TABLE II

CARBON MONOXIDE FORMED AND CALCIUM VOLATILIZED FROM CARBIDE CHARGES

	Charge composition before heating					Resulting composition of charge calculated to same weight as before heating						
Temp. of Expt. °C.	CaC_2 %	CaO %	Free C %	Fe %	Total %	CaC_2 %	CaO %	Free C %	Fe %	CO formed %	Ca volatilized %	Total %
1000	66.47	22.79	10.78	0.00	100.04	66.66	22.81	10.44	0.00	0.00	0.00	99.91
1100	66.47	22.79	10.78	.00	100.04	56.65	22.91	14.53	.00	0.00	6.14	100.23
1200	47.58	36.55	15.25	.27	99.65	44.58	28.72	14.80	.30	3.64	7.49	99.53
1300	65.40	24.15	10.47	.00	100.02	5.96	1.95	27.78	.00	11.43	53.00	100.13

In all of the experiments in which calcium was volatilized, evidence of calcium metal was found on the interior of the furnace.

The mechanism of carbide decomposition is quite apparent from the above results. At temperatures of 1100° and higher, calcium carbide has an appreciable vapor pressure of calcium. At temperatures of 1200° and above, reduction of the free lime in the carbide with formation of carbon monoxide begins and increases with the temperature.

The agreement between theory and experiment is shown in Table III.

TABLE III

DECOMPOSITION OF CALCIUM CARBIDE

Temp. of expt., °C.	1000	1100	1200	1300
Carbon liberated: calcd. $CaC_2 = Ca + 2C$	0.00	3.68	1.12	22.32
Carbon found, increase	−0.34	+3.75	1.11	22.21

The first row of this table indicates the temperature; the results in the second row are calculated stoichiometrically from the carbide decomposed on heating at that temperature, and the third row indicates the actual

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[9] The "unknowns" in the equations were the amount of calcium volatilized and the amount of carbon monoxide formed.

increase in carbon which occurred on heating, taking into account the carbon used in the reduction of lime in the experiments at 1200° and 1300°.

The Thermal Dissociation of Calcium Carbide in the Presence of Calcium Chloride

The action of various inorganic salts, notably the alkali and alkaline earth halides as so-called catalyzers for the reaction of carbide with nitrogen has also been the subject of much work in this field. The action of calcium chloride and calcium fluoride in markedly speeding up the cyanamide reaction is well known, and these salts, especially the latter, are much used today in the operation of the calcium cyanamide process of nitrogen fixation. It is probable that the action of all these various salts is the same so that it will serve to consider here the action of calcium chloride.

In the following experiments finely powdered calcium carbide mixed with various amounts of calcium chloride were heated in a vacuum and then analyzed for carbide. The results are shown in Table IV.

TABLE IV

ACCELERATING EFFECT OF CALCIUM CHLORIDE ON CARBIDE DECOMPOSITION

Time of heating Hrs.	Temp. °C.	$CaCl_2$ added %	Decrease in CaC_2 content %
5	900	none	3.4
5	1100	none	7.7
$3^1/_2$	900	5.0	14.7
3	1100	5.0	13.9
$1^1/_2$	900	10.0	16.9
$2^1/_2$	1100	10.0	18.1

It is quite apparent from these results that calcium chloride has an accelerating effect on the carbide decomposition.

The Thermal Dissociation of Calcium Cyanamide

In the experiments listed in Table II it was shown that calcium carbide has an appreciable vapor pressure of calcium at as low a temperature as 1100°. It therefore follows that when carbide reacts with nitrogen the first compound to form will be calcium nitride which then reacts with the carbon present to give calcium cyanamide. On the other hand, carbon-free calcium cyanamide should have calcium nitride as one of its decomposition products. The following experiments show that such reactions occur.

1. Calcium nitride was mixed with sugar carbon and the mixture heated in a covered porcelain crucible to a red heat in air. The mass was cooled and shaken with water and the extract tested for cyanamide with ammoniacal silver nitrate. A copious yellow precipitate proved the presence of cyanamide. $Ca_3N_2 + 6C + 2N_2 = 3CaCN_2 + 3C$. This reaction was first presented by Polzeniusz[10] as part of his theory on the mechanism of

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[10] Polzeniusz, *Chem.-Ztg.*, **31**, 958 (1907).

catalysis, and since it is of considerable importance it was also studied thermochemically (see later).

2. Carbon-free calcium cyanamide made by heating dicyanodiamide with lime[11] was heated in a vacuum furnace to temperatures between 1000° and 1200°.

At 1000° and a pressure of 1 to 6 mm. a charge which originally contained 96.4% of $CaCN_2$ and 3.6% of CaO, after being heated contained 74.72% of $CaCN_2$, 15.8% of CaC_2, 2.01% of Ca_3N_2 and 7.47% of CaO.

At 1100° and 0.02 to 0.11 mm. a charge which originally contained 96.48% of $CaCN_2$, and 3.52% of CaO, after being heated contained 2.60% of $CaCN_2$, 77.20% of CaC_2, 0.75% of Ca_3N_2 and 18.38% of CaO.

At 1200° and 30 mm. a charge which originally contained 90% of $CaCN_2$, and 10% of CaO, after being heated contained 13.55% of $CaCN_2$, 5.24% of CaC_2, 5.23% of Ca_3N_2 and 28.82% of CaO.

These experiments show that calcium nitride and calcium carbide are products of the thermal decomposition of calcium cyanamide. Although calcium nitride itself has been recently shown to be quite stable[12] it is possible that in the presence of carbon and under these conditions some carbide is formed. These experiments are of course quite contrary to the findings of V. Ehrlich.[3]

3. Commercial calcium cyanamide, which contains both calcium cyanamide and carbon in the proportions of one molecule of $CaCN_2$ to one of C, was heated in the vacuum furnace at a temperature between 1000° and 1300° for various periods and then analyzed. The particular sample before heating contained 52% of $CaCN_2$ and 0.64% of CaC_2; it also contained carbon and calcium oxide.

After the product was heated to 1000° at a pressure of from 6 to 40 mm. for four hours, it contained 1.97% of $CaCN_2$ and 40.9% of CaC_2.

After another sample was heated to a temperature that fluctuated between 1000° and 1300° and at a pressure of 10 to 40 mm. for three hours, the product contained 0.00% of $CaCN_2$ and 46.6% of CaC_2. No calcium nitride was detected in either of these experiments.

Discussion of Results

It has been shown experimentally that calcium nitride reacts with carbon and nitrogen to give calcium cyanamide.

Carbon-free calcium cyanamide when heated in a vacuum decomposes into calcium carbide, calcium nitride and nitrogen. The presence of the calcium carbide can be explained by the decomposition of part of the calcium nitride in the presence of carbon formed in the primary decomposition of calcium cyanamide.

Commercial calcium cyanamide ($CaCN_2 + C$) when heated in a vacuum decomposes into calcium carbide and nitrogen. Calcium nitride does

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[11] Kameyama, *J. Coll. Eng. Tokyo Imp. Univ.*, **10**, [No. 8] 173 (1920).

[12] Kraus and Hurd, THIS JOURNAL, **45**, 2571 (1923).

not appear in this decomposition reaction both because of its tendency to react with carbon and also to decompose into calcium and nitrogen, the calcium combining with the carbon which is here present in large amounts.

The Thermochemistry of the Reactions

Heat of the Reaction, $CaC_2 + N_2 = CaCN_2 + C$.—The heat of this reaction is of interest mainly because it has found application in the fixation of nitrogen by the cyanamide process, where its exothermicity is of great practical value. The heat of this reaction had not previously been measured directly, but it has been computed by Kameyama[13] from the heat of combustion of pure calcium cyanamide in oxygen. This calculation involves the heats of formation of calcium oxide, calcium carbide and carbon dioxide, and consequently these must be known with sufficient accuracy. It is obvious that a direct method in which calcium carbide was caused to react with nitrogen in a calorimeter would be more desirable. We have employed such a method in the present work.

Experimental Method and Results

To carry out a determination of the heat of the reaction the bomb of an ordinary fuel calorimeter was modified as follows. The sample of calcium carbide was contained in an alundum crucible replacing the nickel cup that is commonly used in the fuel calorimeter. To raise the sample of carbide to the reaction temperature, an electrical heater, consisting of a small helix of platinum wire 0.43 mm. in diameter was embedded in the carbide and connected to the terminals within the bomb. The bomb was filled with nitrogen gas to about 33 atmospheres pressure and placed in the calorimeter containing a weighed quantity of water.

The cooling correction was obtained in the usual manner and amounted to considerably less than 5% of the total temperature rise. The mercury thermometer could be read to 0.002°, and current and voltage to 0.05 of a unit and time to 0.4 second. It is believed that the value of a single determination is correct within 5%, a sufficient accuracy considering the nature of the calculations.

Five successful determinations of the heat of the reaction by the method described above gave for the heat of the reaction the following values: 95,630; 105,290; 97,440; 101,130; 92,670; the average of these gives the heat of the reaction:

$$CaC_2 + N_2 = CaCN_2 + C + 98{,}430 \text{ cals.}^{14} \qquad (1)$$

at 25° and constant pressure.

Kameyama[13] by calculation from the measured heat of combustion of

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[13] Kameyama, *J. Coll. Eng. Tokyo Imp. Univ.*, **10**, 249 (1920); *C. A.*, **15**, 1110 (1921).

[14] The thermochemical usage is here employed.

calcium cyanamide has obtained the value of 78,420 cals. for this reaction.

The Heat of the Reaction, $Ca_3N_2 + 3C + 2N_2 = 3CaCN_2$.—Using the same apparatus and technique, described above, a determination of the heat of this reaction was made. The results of three successful experiments gave the following values: 186,000; 210,500; and 198,220 cals.; the average of these gives the heat of the reaction:

$$Ca_3N_2 + 3C + 2N_2 = 3CaCN_2 + 198{,}240 \qquad (2)$$

at 25° and constant pressure.

This value, together with that given in Equation 1 and the heat of formation[15] of Ca_3N_2 $[(3Ca:N_2) = +112{,}200]$, enables us to calculate the heat of formation of calcium carbide from calcium and graphitic carbon. The result is $Ca + 2C = CaC_2 + 5050$ cals. This value falls between the two published experimental values for this quantity which are[16] $(Ca : 2C) = +14{,}150$ cals. and $(Ca : 2C) = -6250$ cals.

The authors are indebted to Drs. R. C. Tolman and J. M. Braham for valuable assistance during the course of this work.

Summary and Conclusions

The thermal stability of calcium carbide has been investigated and its decomposition into the elements confirmed. The influence of calcium chloride in accelerating the reaction of nitrogen on calcium carbide is explained by showing that such salts accelerate the ordinarily slow decomposition of calcium carbide.

The thermal decomposition of both carbon-free calcium cyanamide and commercial calcium cyanamide shows very clearly that the reaction of nitrogen with calcium follows the carbide decomposition: thus $3CaC_2 = 3Ca + 6C$ (1) $3Ca + N_2 = Ca_3N_2$ (2) and that the carbon liberated in Reaction 1 reacts with calcium nitride: $Ca_3N_2 + 6C + 2N_2 = 3CaCN_2 + 3C$ (3) with the formation of calcium cyanamide and carbon.

It has been shown that the measured heat of the reaction of Equation 3 agrees thermochemically with that of the equation, $CaC_2 + N_2 = CaCN_2 + C$, provided that the heat of formation of calcium carbide is a small positive quantity.

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[15] (a) Guntz and Bassett, *Compt. rend.*, **140**, 863 (1905). (b) Ref. 12.

[16] Landolt-Börnstein-Roth, "Tabellen," Julius Springer, **1912**, 4th ed., p. 862. See also Ref. 15 a.