

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF INORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 52]

## The Dissociation of Carbon Dioxide in the Electrodeless Discharge

BY WALTER C. SCHUMB AND FRED A. BICKFORD

The present paper is concerned with an extension of previous work in this Laboratory upon the subject,<sup>1</sup> the experimental conditions under which the work was carried on being more definitely controlled by reason of improved apparatus, affording also much wider variation in the frequency employed. Our purpose, furthermore, was to verify the conclusions arrived at from pressure measurements by quantitative analysis of the gas mixtures resulting from the action of the discharge.

### Experimental

**Oscillator.**—The radio-frequency oscillator employed, designed and constructed by Mr. L. Jacobson, formerly of the Department of Electrical Engineering of this Institute, provided a constant number of ampere turns of magnetizing force over the wave length range covered, 60 to 600 meters. To accomplish this, one exciting coil was used at all wave lengths, and inductances, the fields of which were removed from the neighborhood of the reaction tube, were added to the plate and grid circuits as the wave length was increased. The ratio of inductance to capacitance was also maintained approximately constant. The oscillator supplied a current of 15 amperes to the exciting coil over the entire frequency range and a maximum of 20 amperes over most of it. This current was controlled by the plate voltage, which was adjusted by means of a General Radio Company Variac connected to the power pack. Variation in current affected the wave length but little, and the tank current meters were employed in such a way that their wave length error was kept at a low value. The set was calibrated over the entire frequency range, 475 to 5200 kc. Figure 1 shows in detail the design of the oscillator.

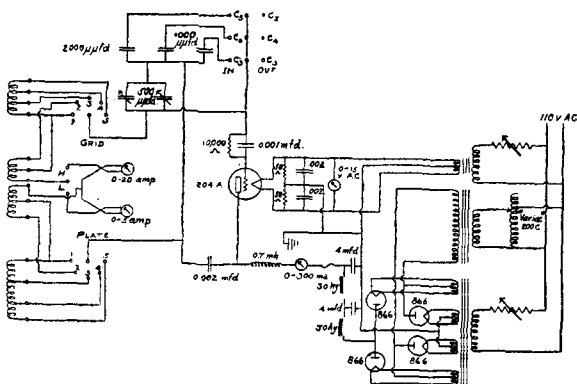


Fig. 1.

**Reaction System.**—The apparatus was similar in its essential features to that employed by Schumb and Gold-

(1) H. Hunt with W. C. Schumb, *THIS JOURNAL*, **52**, 3152 (1930).

man<sup>2</sup> in their study of the dissociation of ammonia in the electrodeless discharge. Figure 2 shows the general arrangement and Figure 2a the magnetic mercury switch devised to control the direction of rotation of the motor which operated the gas circulating pump. In Figure 2, (d) is a mercury seal, used to confine the carbon dioxide in

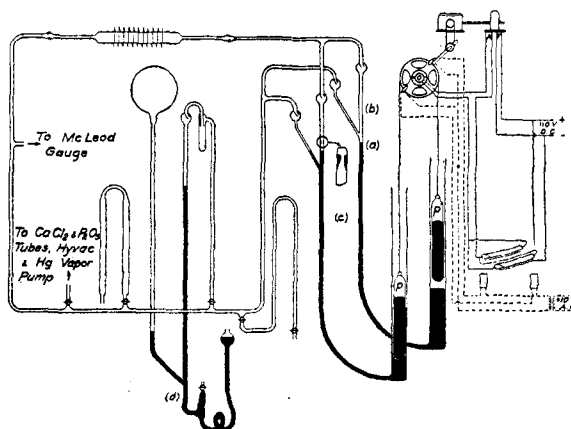


Fig. 2.

the storage bulb; (c) the circulating pumps which, operating alternately, forced the gas through the system. In the operation of these pumps, as the mercury-filled plungers p or p' sink in their respective wells, the mercury in tube (c) rises from (a) to above the capillary portion (b), which thereupon acts as a valve preventing backflow of gas as the mercury falls again to (a) on the return stroke. The proper construction of the capillary at (b), shown as an inset in the diagram, is of primary importance in the successful operation of the pump. The tapered sides prevent sticking of the mercury and the fairly large capillary opening prevents breakage by the "hammering" of the mercury on the upstroke.

The plungers were operated by a chain passing over a 20-cm. sprocket, driven by a 7.6-cm. sprocket, in turn connected with a small speed reducer, coupled to a small d. c. motor. The reversal of direction of rotation of the motor was accomplished by maintaining the current in the field (F) constant, and reversing the current in the armature (A) by means of the switch shown in Fig. 2a. The operation of this switch, con-

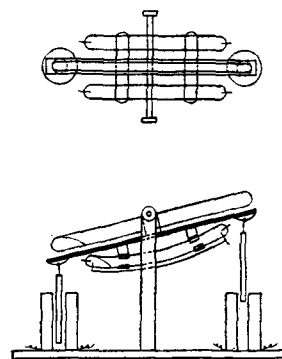


Fig. 2a.

(2) Schumb and Goldman, *Proc. Am. Acad. Arts Sci.*, **69**, 169 (1934).

trolled by small mercury switches attached to the 20-cm. sprocket, resulted from the alternate excitation of the two small electromagnets, and proved to be much superior to any of the previously used forms of reversing switches.

A safety mercury switch, connected in series with the motor, prevented rotation of the large sprocket in excess of 180°. This switch, attached to the face of the sprocket, was circular in form and constructed of 8-mm. glass tubing, with two sealed-in tungsten electrodes about 1 cm. apart. If the sprocket rotated more than 180°, contact in this switch was broken and the motor instantly stopped.

The reaction bulb shown in Fig. 2, was made of 52-mm. Pyrex glass tubing 33 cm. long and provided with ground joints at both ends so that the bulb might be removed and cleaned when necessary.

### Materials

Pure carbon dioxide was prepared by heating the purest available sodium bicarbonate contained in an all-glass system sealed to the apparatus shown in Fig. 2. The tube, loosely filled with bicarbonate, and the condensing system connected therewith, consisting of a series of traps, were thoroughly evacuated and the bicarbonate gently heated. The carbon dioxide passed successively through glass wool to remove solid particles and through three condensing traps cooled with a carbon dioxide-alcohol mixture to remove most of the water and finally through phosphorus pentoxide free from lower oxides of phosphorus. The gas was finally condensed by liquid air. When a sufficient amount had been collected, the trap containing it was sealed, isolating it from the generating system, and pumped very thoroughly to remove permanent gases. The carbon dioxide was now fractionally distilled, the middle third only being collected in a liquid air trap. This procedure was repeated twice more, the middle third only being retained each time, the final product being allowed to pass into the large globe provided with a mercury seal (d, Fig. 2) which served as a reservoir of the gas.

All the mercury used in the system was purified electrolytically<sup>3</sup> and was subsequently thoroughly washed and dried.

### Procedure

In order that the walls of the reaction tube should be in as nearly as possible the same condition at the beginning of each series of experiments, it was found that washing the tube with boiling hot, concentrated nitric acid, rinsing with distilled water and with reagent alcohol, drawing a stream of air through the tube, and subsequently baking the tube at 440° for one hour, pumping at the same time to the highest vacuum attainable with the Hyvac and the mercury diffusion pump, gave consistent readings when the tube was subsequently employed in a decomposition experiment.

The entire apparatus with the exception of the gas reservoir having been thoroughly evacuated, a sample of gas was admitted from the reservoir into the rest of the system and the initial pressure read on the McLeod gage. The first experiments were carried out at an initial carbon dioxide pressure of 1 mm., the current passing through the exciting coil being 15 amp., and the discharge operated for

thirty minutes, with the circulating pumps operating. The light blue glow in the reaction tube was small and well defined in the center of the tube. A series of experiments was made to determine the time required to reach a steady state, and it was found that sixty minutes sufficed for this purpose, no further pressure change being observed with longer intervals. To be on the safe side, however, seventy-five minutes were allowed as a general procedure. The wave length range covered in these experiments was from 250 to 450 meters, the amperage was varied from 13.5 to 20 amp., and the initial pressure used was changed from 0.5 to 1.0 mm.

The data at 250 meters showed the poorest agreement. In these runs a very slight brown film was deposited in the reaction tube, which has been attributed by other investigators to the formation of carbon suboxide. Whenever this film made its appearance, the tube was removed and cleaned with concentrated nitric acid, as already described, before continuing. At the other wave lengths used, no film could be detected and suboxide formation therefore presumably did not occur. Furthermore, the fact that the mercury surfaces remained clean and bright throughout makes it improbable that ozone formation was taking place, or that the mercury took part in the chemical changes.

The conclusions arrived at from the pressure measurements were subsequently tested by a quantitative analysis of the gas mixture left in the system after the final pressure reading had been taken. The purpose of this procedure was not only to corroborate the data previously obtained, but also to prove that the essential decomposition reaction is, as had been assumed in earlier work,  $2\text{CO}_2 \longrightarrow 2\text{CO} + \text{O}_2$ , and that no side reactions such as the formation of ozone or carbon suboxide had taken place to any appreciable extent. The analysis consisted of the determination of carbon dioxide and of carbon monoxide. The gas mixture resulting from the action of the discharge was swept from the apparatus by a current of pure, dry nitrogen at the rate of a liter an hour; the carbon dioxide was absorbed from this mixture by a Stetser-Norton absorption tube containing "Ascarite," which was weighed by the counterpoise method. Since the gas passing through the system was very dry, it was led from the Ascarite tube through a weighed U-tube containing purified phosphorus pentoxide, to correct for dehydration of the Ascarite.

Carbon monoxide was determined by the iodine pentoxide method,<sup>4</sup> the liberated iodine being titrated with 0.002 *N* sodium thiosulfate, prepared by dilution of 0.01 *N* standard solution, with the help of a 3-cc. microburet. The iodine pentoxide was freshly prepared according to the method of Nicloux.<sup>5</sup>

The nitrogen employed in sweeping the reaction mixture from the system was free from carbon dioxide and was dried thoroughly before entrance into the system.

The volume of the system must be known in order that the weights of carbon monoxide and dioxide may be calculated from pressure and temperature readings. This was determined by filling the system with pure carbon dioxide at a known temperature and pressure and then sweeping

(3) F. A. Wolf and C. E. Waters, *Bull. Bur. Standards*, **3**, 623; (4), 1 (1907).

(4) See J. S. Haldane and J. I. Graham, "Methods of Air Analysis," Charles Griffin and Company, Ltd., London, 1934, page 116.

(5) M. M. Nicloux, *Compt. rend.*, **154**, 1166 (1912).

the gas through an Ascarite absorption tube and determining the increase in weight. The volume so determined, the average of three determinations, was 1040 cc.

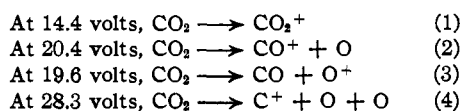
Ten analyses were made on gas mixtures produced from carbon dioxide by the electrodeless discharge under varying conditions of pressure, wave length and amperage and the results were in substantial agreement with those calculated from the pressure measurements within the experimental error.

The fact that no noticeable error was introduced by adsorption of carbon dioxide on the walls of the reaction vessel is indicated by the observation that when the apparatus had been evacuated thoroughly and filled with carbon dioxide at a given pressure this pressure would be maintained unchanged overnight; whereas in a similar experiment with ammonia gas an appreciable diminution in pressure occurred, due to adsorption of the gas by the walls.

**Reversibility of Reaction.**—The fact that the decomposition of carbon dioxide may be caused to take place reversibly under the influence of various forms of electrical excitation, has been demonstrated by a number of experimenters, as well as by previous work in this Laboratory.<sup>6</sup> Some additional preliminary experiments were carried out in the present investigation in further corroboration of this fact.

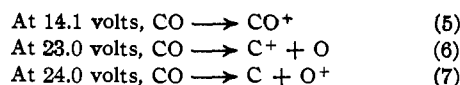
### Discussion of Results

The high frequency electrodeless discharge produces both electrostatic and electromagnetic fields, the intensities of which it is difficult to estimate.<sup>7</sup> It is probable that electron impact is responsible for the largest part of the decomposition. Although there are many positive ions, it is doubtful that they acquire sufficient velocity to produce either decomposition or ionization.<sup>8</sup> Collisions of the second kind must be of importance<sup>9</sup> especially after decomposition has become appreciable. Even under the favorable conditions existing in the mass spectrograph, the interpretation of the results obtained with carbon dioxide is attended with considerable difficulty.<sup>10</sup> However, in addition to molecular dissociation of the dioxide into the monoxide and oxygen, the following processes have been established:



Carbon monoxide similarly undergoes the following processes

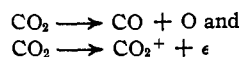
- (6) G. L. Wendt and M. Farnsworth, *THIS JOURNAL*, **47**, 2490 (1925); M. Pierre Jolibois, *Bull. soc. chim.*, [5] **2**, 2035 (1935).  
 (7) K. A. MacKinnon, *Phil. Mag.*, **8**, 605 (1929).  
 (8) K. T. Compton and I. Langmuir, *Rev. Modern Phys.*, **2**, 123 (1930).  
 (9) F. L. Arnot, "Collision Processes in Gases," Methuen and Company, Ltd., London, 1933, p. 86.  
 (10) See H. D. Smyth, *Rev. Modern Phys.*, **3**, 347 (1931).



That all of the above processes take place under the conditions prevailing in the present work is very improbable. The fact that as a rule the discharge required the additional excitation provided by a "leak detector" to start the discharge shows that the field within the exciting coil in the range of frequencies used is not strong enough to initiate ionization of the carbon dioxide, which requires 14.4 volts. Processes requiring high potentials are therefore unlikely, as the mean free path of the electrons is too small to allow them to acquire the necessary energy in the field used. Only at the lower wave lengths and pressures are processes (2) and (3) likely to take place. Vaughan<sup>11</sup> has shown that, under the more favorable conditions afforded in the mass spectrographic study of carbon monoxide, processes (6) and (7) are small in comparison with (5). Process (5) furthermore will not be anticipated until considerable decomposition of the dioxide has occurred.

A plot of the effective cross section of the carbon dioxide molecule against the energy of the colliding electron shows a sharp maximum at 4 volts, which corresponds to the molecular process:  $\text{CO}_2 \longrightarrow \text{CO} + \text{O}$ .<sup>12</sup> These facts add strength to the probability that the main reaction occurring in the electrodeless discharge is this molecular process. The curve falls to a minimum rising at much higher potentials to reach a broad maximum at 25 volts, where no doubt the other processes mentioned are taking place as well as excitation to various levels of the electrons within the carbon dioxide molecule.

Although it is admittedly difficult to postulate an entirely satisfactory mechanism for the processes occurring in the electrodeless discharge, on the simplifying assumption that, under the conditions of the present experimental work, the only significant processes are



a qualitative explanation of the observed effect of current, frequency and pressure upon the decomposition of carbon dioxide may be given.

Three sets of curves are given below, represent-

- (11) A. L. Vaughan, *Phys. Rev.*, **38**, 1687 (1931).  
 (12) "International Critical Tables," Vol. VI, p. 118. The value, 5.5 volts, assigned to the molecular dissociation of carbon dioxide calculated from thermal data, is expected to be somewhat high.

ing the experimental data. In the first set (Fig. 3) the effect is shown of variation of the *amperage* in the exciting coil upon the increase in pressure (which is an index of the extent of decomposition); the second set (Fig. 4) shows the effect of change of *wave length*, and the third (Fig. 5) the effect of variation of the *initial pressure* upon the percentage decomposition.

**Effect of Variation of Amperage.**—The curves shown correspond to initial pressures of 1.00, 0.75 and 0.50 mm. They are either straight lines or approach a horizontal asymptotically. The higher the frequency (or lower the wave length) and the lower the pressure, the more rapidly does a curve approach an asymptotic value; or, in other words, a state is reached wherein with an increase in power no greater decomposition of the carbon dioxide is effected.

The field is directly proportional to the amperage. At low amperage there is a low concentration of electrons, because only a few acquire sufficient energy to produce ionization, which is necessary to replace those lost due to recombination with ions or by migration to the walls. Consequently there can be only a small number of collisions which produce decomposition.

As the amperage increases the field strength increases with a corresponding increase in the amount of ionization. The greater concentration of electrons leaves more to produce decomposition of the carbon dioxide and hence there is a greater increase in pressure. This process does not continue indefinitely or else a steady state would not have been reached, as was actually observed. The attainment of a steady state is to be attributed to the fact that with increasing pressure the mean free path of the electrons decreases, fewer and fewer acquire sufficient energy before a collision is made to produce decomposition or ionization. When the amperage is sufficiently high so that the curve becomes rectilinear, a high population of electrons must have been created, with many having higher energies than is required to produce decomposition. As the content of carbon monoxide and oxygen becomes appreciable these gases must in turn begin to be ionized by the high energy electrons. The positive carbon monoxide and oxygen ions migrate toward the negative walls where they can collide and recombine to form carbon dioxide again. This seems to be the most probable mechanism at high amperages. It also serves to explain the fact

that at the higher frequencies where there is a strong field the variation in amperage for a constant initial pressure produces no variation in the percentage decomposition. In this case, regardless of the amperage, there is decomposition until the concentrations of carbon monoxide and oxygen become appreciable; then they are ionized and recombine close to the walls. The increase in amperage in these cases thus not only increases the rate of decomposition but also the rate of recombination.

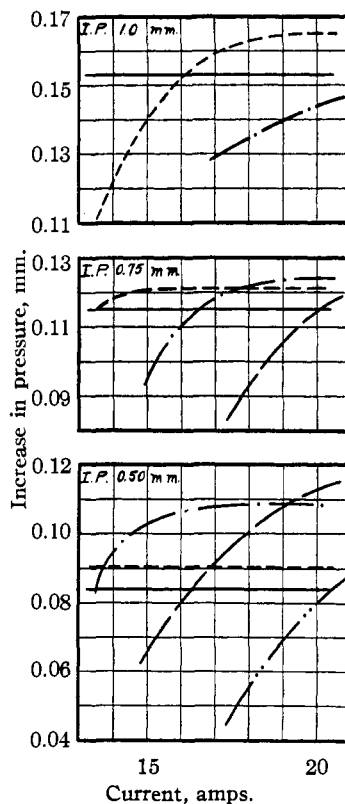


Fig. 3. ———— 250 m.;  
 - - - - - 300 m.;  
 ······ 350 m.;  
 —·—·—· 400 m.;  
 - · - · - · 450 m.

**The variation of the increase in pressure with wave length** is given in Fig. 4 for initial pressures of 1.00, 0.75 and 0.50 mm. These curves all have the same characteristics; as the wave length increases they pass through a maximum. The behavior of this maximum is interesting; for any particular initial pressure it shifts to the left with decrease in amperage and for any definite amperage it moves to the left with increase in pressure. For example, at 20 amperes the maximum at 0.500 mm. is about 400 meters, at 0.750 mm.

about 350 meters and at 1.00 mm. about 300 meters. Schumb and Goldman<sup>2</sup> in their work on ammonia obtained strong evidence for such a maximum but did not locate it or study its variations.

crease in energy the frequency must be increased, therefore the maximum is shifted in the direction of greater frequency. For the same reason, at constant pressure there is a shift in the maximum

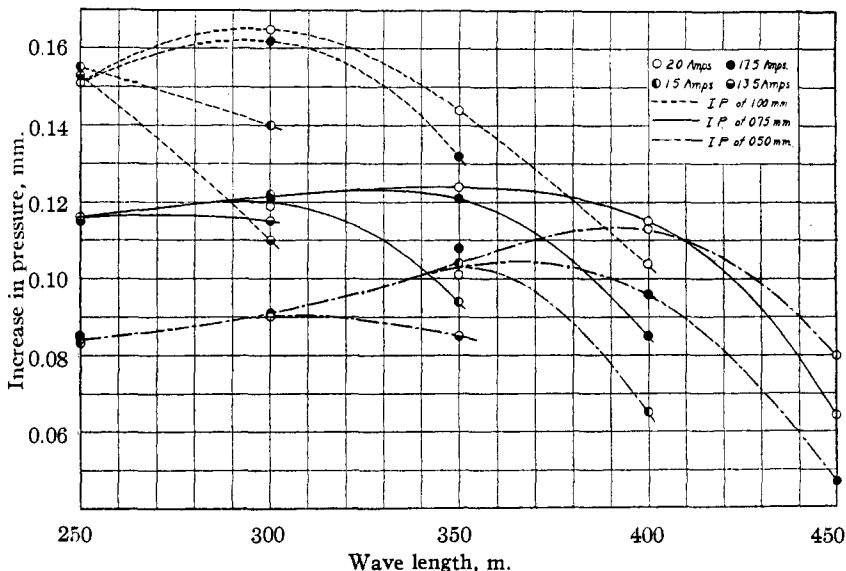


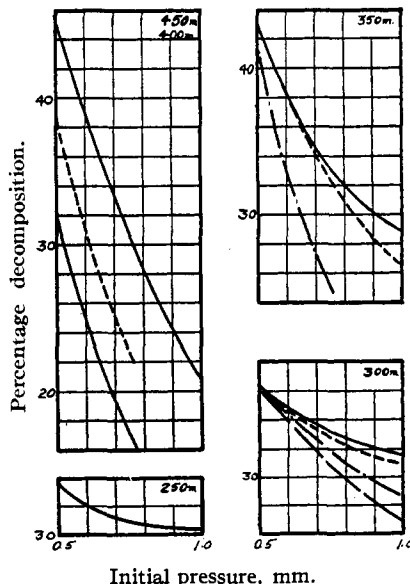
Fig. 4.

to the left as the current decreases. Here again the field strength is decreased with the falling current and to compensate for this the frequency must be increased.

The effect of pressure on the percentage decomposition is shown in Fig. 5. These curves all have the same general characteristics, namely, that as the pressure increases the percentage decomposition decreases. This result is similar to the observations made by Schumb and Goldman.<sup>2</sup> It is also worthy of note that as the wave length

The variation caused by change in wave length can be accounted for in a manner similar to that used to explain the effect of amperage. At the high wave lengths (low frequency) the field strength is low and therefore the energy of the electrons is low. Hence only a few electrons are able to produce ionization and, therefore, only a few cause decomposition. As shown in the similar case at low amperage, as the pressure increases the electrons lose their power due to the smaller mean free path. As the frequency increases the number of electrons and likewise their energy increases, so that there is more decomposition of carbon dioxide. Finally, when the field becomes sufficiently strong the carbon monoxide begins to be ionized and recombination commences. As the field further increases in strength the recombination becomes greater and consequently there is a falling off in the percentage decomposition of carbon dioxide.

decreases the slope becomes less steep.



Initial pressure, mm.  
In upper left plot: upper and dashed curves, 400 m.; lower curve, 450 m.  
Fig. 5. ———, 20 amps.;  
-----, 17.5 amps.;  
———, 15.0 amps.;  
———, 13.5 amps.

On the basis of this mechanism we can explain the shift in the maximum. It was pointed out that for any given current there was a shift to the left with increase in pressure, that is, a shift in the direction of greater field strength. As the pressure increases there is a corresponding decrease in the mean free path which cuts down the energy of the electrons. To compensate for this de-

The explanation of these curves is quite simple. As the pressure increases the mean free path de-

creases, so that an electron has less chance to acquire the energy necessary to produce decomposition or ionization before a collision is made. The change in slope of the curves is due to the change in field strength with wave length. At a high wave length where the field strength is low the shortening of the mean free path is much more effective in decreasing the energy of the electrons than it is at low wave length where there is a much stronger field.

### Summary

The decomposition of carbon dioxide under the

influence of the electrodeless discharge has been studied; the effect on the percentage decomposition of variation in frequency, amperage, and pressure has been determined, both by observation of the pressure changes produced and by chemical analysis of the resulting gas mixture.

The decomposition products over the range of experimental conditions employed were carbon monoxide and oxygen, the formation of suboxide being avoided by control of these conditions.

A mechanism for the decomposition process has been proposed.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

## The Kinetics of Racemization of 2,2'-Diamino-6,6'-dimethyldiphenyl

BY G. B. KISTIAKOWSKY AND WALTER R. SMITH

The racemization of optically active diphenyl compounds is a particularly simple type of intramolecular rearrangement.<sup>1</sup> While a great deal of work has been done on the preparation and separation of these compounds, very few quantitative data on the kinetics of the racemization are available. Kuhn and Albrecht<sup>2</sup> have studied the racemization of 2,4'-dinitrodiphenic acid and 2,4,4'-trinitrodiphenic acid in 2 *N* sodium carbonate at two temperatures. More recently Li and Adams<sup>3</sup> have reported kinetic measurements in several solvents of the rate of isomerization of 2-nitro-6-carboxy-2'-OR (R = CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub> and *n*-C<sub>3</sub>H<sub>7</sub>) diphenyl compounds. Observations of a more qualitative nature on several diphenyl compounds have also been made,<sup>1</sup> but no study of their racemization in the gaseous phase has ever been undertaken. The present paper describes measurements of the velocity of racemization of 2,2'-diamino-6,6'-dimethyldiphenyl in a solution of diphenyl ether and also in the gaseous phase.

### Experimental Details

**Materials.**—The 2,2'-diamino-6,6'-dimethyldiphenyl was kindly prepared for us by Professor Roger Adams according to the methods of Meisenheimer and Höring.<sup>4</sup> The *l*-base used in our experiments melted at 156°; 0.5973 g. of it in 25 cc. of diphenyl ether showed a molar rotation

at 25° of -77° with sodium light and -92.9° with mercury light.

The diphenyl ether was Eastman best grade, m. p. 26-27°. It was redistilled at reduced pressure, the middle fraction boiling at 138° at 22 mm. being employed. All polariscopic observations were made with a sodium vapor lamp and an all-glass cell 1.175 dm. in length and 6 cc. in volume.

**Experimental Procedure.**—Solutions of the desired concentration of the *l*-base in diphenyl ether were prepared and their rotation measured. Seven cubic centimeter portions of the solution, after careful degassing *in situ*, were sealed off in evacuated, heavy-walled quartz tubes 15 × 200 mm. These tubes were plunged into a molten lead bath for the desired length of time. The reaction was stopped by withdrawing the tube and plunging it into cold water. For the runs in the gas phase the desired amount of material was weighed out and transferred to Pyrex tubes 30 × 300 mm. The tubes were evacuated after carefully melting the compound to eliminate occluded air. They were plunged into the lead bath for the desired period. The reaction was stopped by withdrawing the tube and directing an air blast against the bottom. In about ten seconds all the material crystallized out. The top of the tube was then cracked off and 9 cc. of diphenyl ether introduced. The rotation of the resulting solution was compared with the rotation of a similar solution of pure *l*-base.

### Experimental Results

All runs were remarkably free from any indication of decomposition. At the highest temperature studied in solution a faint yellowish tint was observable in some of the longer runs. However, it was never sufficient to interfere with the reading of the polariscope. In the gas phase there was no indication of decomposition.

(1) Adams and Yuan, *Chem. Rev.*, **12**, 261 (1933).

(2) Kuhn and Albrecht, (a) *Ann.*, **455**, 272 (1927); (b) *ibid.*, **458**, 221 (1927).

(3) Li and Adams, *THIS JOURNAL*, **57**, 1565 (1935).

(4) Meisenheimer and Höring, *Ber.*, **60**, 1429 (1927).