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.[1] 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[2] 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[3] have reported kinetic measurements in several solvents of the rate of isomerization of 2-nitro-6-carboxy-2'-OR (R = CH_3, C_2H_5 and *n*-C_3H_7) diphenyl compounds. Observations of a more qualitative nature on several diphenyl compounds have also been made,[1] 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.[4] 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.

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[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).

A solution of *l*-base in diphenyl ether was heated for several hours at 380°. The mixture recovered melted at 130–132°. The pure *dl*-form melts at 136°. A sample of *l*-base was kept in the gas phase at 380° for eight hours. The mixture at the end of this time melted at 135°. A mixed melting point with the original *dl*-mixture melted at 134°. Thus the observed change in optical rotation is due to a simple racemization reaction.

The results of all runs are presented in Table I. The velocity constants have been calculated from the unimolecular expression $k = \frac{1}{2t} \ln \frac{\alpha_0}{\alpha_t}$ where α_0 is the initial rotation in degrees and α_t the value after t seconds of heating.

Due to the limited solubility of the *l*-base in diphenyl ether at room temperature the effect of concentration on the rate could not be studied over more than a six-fold range. In the gas phase runs have been made at calculated pressures of about 50 and 150 mm. The rate appears to vary slightly with concentration in solution, but as this effect is not observed in the gas phase it is believed to be due to the non-ideality of the solution rather than to the kinetics of the process. The reaction is undoubtedly unimolecular. Runs in tubes packed with 4-mm. Pyrex tubing show the reaction to be homogeneous in the gas phase.

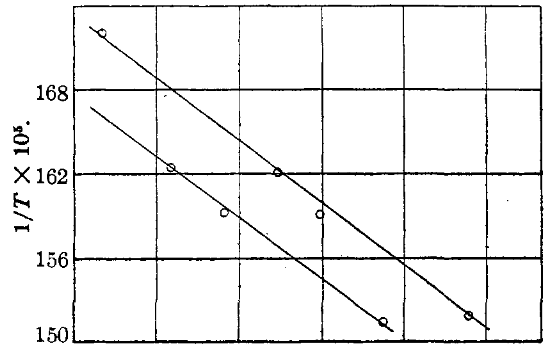

Fig. 1.—Upper curve, runs in solution; lower curve, runs in gas phase.

In Fig. 1 the temperature–rate data have been plotted in the usual manner both for solution and for gas phase. Within our experimental error the activation energy is the same in both cases, 45,100 ± 2000 cal. For the velocity constants in solution the rate expression is

$$k = 0.83 \times 10^{11} e^{-45{,}100/RT} \text{ sec.}^{-1}$$

In the gas phase the rate is about 3.5 times slower. Because of experimental inaccuracies it is not possible to say whether the difference is due to a smaller A factor or to an activation energy some 1000 calories greater.

TABLE I

RUNS IN DIPHENYL ETHER SOLUTIONS

T, °K.	Time, min.	Activity remaining, %	k, sec.−1	Concentration
658.2	10.25	85.26	1.30×10^{-4}	0.96 g. per 100 cc.
658.2	25.75	72.63	1.03	
658.2	31.00	69.47	0.98	
658.2	47.00	66.32	0.73	
629	177	71.10	1.60×10^{-5}	0.96 g. per 100 cc.
628	309	57.70	1.48	
629.2	450	43.30	1.55	
617.8	562	55.42	8.7×10^{-6}	0.96 g. per 100 cc.
617.0	640	49.40	9.1	
615.4	754	43.37	9.4	
580.1	1409	85.56	0.93×10^{-6}	0.96 g. per 100 cc.
582.6	2791	66.67	1.21	
581.0	3370	70.00	0.88	
629.8	161	70.09	1.84×10^{-5}	2.4 g. per 100 cc.
628.2	361	47.30	1.73	
627.8	434	42.86	1.62	
629.6	240	66.70	1.41×10^{-5}	0.4 g. per 100 cc.
629.6	353	55.60	1.39	
629.6	455	47.20	1.38	
		Runs in Gas Phase		
660.0[a]	122	63.16	3.14×10^{-5}	At pressure of 50 mm.
661	129	54.38	3.94	
661	202.5	52.63	2.64	
659.1	298.5	24.56	3.92	
629	163	91.25	4.69×10^{-6}	At pressure of 50 mm.
626.6	316	87.72	3.45	
628.2	937	52.63	5.71	
615	701	82.46	2.29×10^{-6}	At pressure of 50 mm.
615.8	995	73.68	2.56	
661	119.5	58.82	4.19×10^{-5}	At pressure of 150 mm.
660.5	126.5	60.00	3.37	
661	182.0	47.41	3.42	

[a] In a packed flask.

Racemization undoubtedly takes place when sufficient energy to initiate free rotation has accumulated in the torsional vibration of the phenyl groups around the bond joining them. As Adams has already suggested, this activation energy is needed to overcome the "steric hindrance" of the ortho substituents in the plane model of the molecule. The greater is the hindrance of the substituents, the larger should be the activation energy. In the case of 2,2′-diamino-6,6′-dimethyldiphenyl one finds an overlapping of the protons in the amino and the methyl groups in the plane model to the extent of *ca.* 0.5 Å. if Pauling's[5] internuclear distances and tetrahedral angles are

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[5] Pauling, *Proc. Nat. Acad. Sci.*, **18**, 293 (1932).

used as the basis of calculation. As the present work shows, 22,500 cal. are needed here to bend the bonds and to overcome the repulsions of non-bonding atoms of an amino and a methyl group to such an extent that a plane model can be realized. Although other vibrations, besides the torsional motion, may participate in the process of reaction, we believe that the main effect is due to the latter. Thus, the *A*-factor found in the present reaction (*ca.* 10^{11}) is considerably smaller than the usual *A*-factors found in unimolecular reactions (10^{13}–10^{14}),[6] but is of the same order of magnitude as the *A*-factors found in *cis-trans* isomerizations of stilbene and methyl cinnamate.[7] This is understandable qualitatively if in all these processes essentially the same motion—a rotation of heavy groups—is responsible for the reaction. Furthermore, the observations of Kuhn and Albrecht[2] and of Li and Adams[3] on other diphenyl compounds are consistent with an assumption of an *A*-factor identical with that now found. This shows that the nature of the substituent groups alters only the magnitude of the activation energy, but does not affect the essential mechanism of the reaction. Kuhn and Albrecht found nearly the same isomerization rates for both compounds studied but chose to represent the experimental data (in our units) by

$k = 0.76 \times 10^{12}\, e^{-26,570/RT}$ sec.–1 for 2,4′-dinitrodiphenic acid

and

$k = 0.83 \times 10^{9}\, e^{-22,400/RT}$ sec.–1 for 2,4,4′-trinitrodiphenic acid

A change of experimental velocity constants by only about 10–20% in the right direction, at the two temperatures studied, brings these expressions into the form

$$k = 10^{11}\, e^{-25,000/RT}$$

and

$$k = 10^{11} e^{-25,900/RT}$$

Their results are consistent, therefore, with the idea of an essentially constant *A*-factor for all such reactions and of activation energies determined by the extent of overlapping of the ortho substituents. The para substituent, as the above shows, has only a very slight effect on the activation energy, raising it by 900 cal.

Li and Adams[3] found the same activation energy for the three compounds studied, while the absolute rates were found to decrease in the ratio 7 : 5 : 1 in the methoxy to propoxy series. In view of the small temperature range covered, it is impossible to decide whether the activation energies of these compounds are really identical. If that is assumed, the *A*-factors are found to be of the order of 10^{11} to 10^{12} with an activation energy of 21,000 calories which appears to fit the data best.

In view of all these data it seems safe to assume that the *A*-factors for reactions involving rotations of heavy groups are considerably smaller than those typical of usual decomposition reactions. Hence, those diphenyl compounds for which the activation energy is appreciably less than *ca.* 20,000 calories should racemize at such a rate as to make a resolution of the racemic mixture impossible. This appears to be the case with the 2,2′-dibromo compounds,[8] while in diiodo compounds[9] the hindrance must just about reach the magnitude of 20,000 cal.

On the strength of the foregoing discussion we may venture to predict that further systematic study of the kinetics of racemization of diphenyl compounds will bring to light interesting information concerning the forces between non-bonding atoms and groups in close juxtaposition.

This work was made possible by a grant from the Bache Fund of the National Academy of Sciences, for which we wish to express our thanks.

Summary

1. The racemization of 2,2′-diamino-6,6′-dimethyldiphenyl has been studied in diphenyl ether solution and in the gas phase.
2. The reaction is homogeneous and unimolecular.
3. An activation energy of 45,100 cal. is found for the reaction in both phases.
4. The rate in solution is given by

$$k = 8.30 \times 10^{10}\, e^{-45,100/RT}\ \text{sec.}-1$$

and in the gas phase by

$$k = 2.35 \times 10^{10}\, e^{-45,100/RT}\ \text{sec.}-1$$

5. A nearly constant *A*-factor and an activation energy dependent mainly on the size of the ortho substituents appear to be in accord with various experimental results.

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[6] Kistiakowsky, *Chem. Rev.*, **17**, 47 (1935).

[7] Kistiakowsky and W. R. Smith, THIS JOURNAL, **56**, 638 (1934); *ibid.*, **57**, 269 (1935).

[8] (a) Searle and Adams, *ibid.*, **56**, 2112 (1934); (b) Patterson and Adams, *ibid.*, **57**, 762 (1935).

[9] Searle and Adams, *ibid.*, **55**, 1649 (1933).