

for one reaction only, whereas the benzene data in Table V represent the median value of σ calculated from a number of different reactions.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF UTAH]

Application of Absolute Reaction Rate Theory to the Racemization of Certain Sterically Hindered Compounds¹

BY F. WM. CAGLE, JR., AND HENRY EYRING

The racemization of certain sterically hindered biphenyls and related compounds has been investigated by the use of the absolute reaction rate theory. It is possible to correlate structure and the observed values of ΔH^\ddagger and ΔS^\ddagger calculated from rate data. An approximate calculation of the resonance energy of biphenyl due to π bonding between the rings gives 5,000 cal./g. mole.

Introduction

The optical activity which may arise from steric hindrance introduced by the substitution of the O-O'-positions in biphenyls and related compounds was discovered by Christie and Kenner in 1922.² Since that date, the kinetics involved in the racemization of these compounds have received considerable study especially by Adams and his students. These studies have been made by the use of the familiar Arrhenius equation

$$\ln k' = \ln A - \frac{E}{RT}$$

The purpose of this paper is the application of the Absolute Reaction Rate Theory to the investigation of available data. This is done to permit an examination of the nature of the activated complex in the process of racemization. In this way, it is possible to study the relation between structure and reaction rate. These unimolecular racemiza-

tions provide information which may be interpreted in terms of a relatively very simple activated complex.

Theoretical Treatment

Consider the racemization of an optical antipode



This is a reversible first order reaction with the same rate constant, k' , in both directions. This constant may be expressed in terms of the measured optical rotation of a solution, α_t , at time, t , as

$$k' = \frac{1}{2t} \ln \alpha_0/\alpha_t$$

The theory of absolute reaction rates may be expressed as³

$$k' = \frac{\kappa k T}{h} \exp\left(-\frac{\Delta H^\ddagger}{RT}\right) \exp\left(\frac{\Delta S^\ddagger}{R}\right)$$

In the equation, k' is the rate constant; k , Boltzmann's constant; h , Planck's constant; T , absolute temperature; κ , the transmission coefficient; ΔH^\ddagger the enthalpy of activation; ΔS^\ddagger the entropy of activation; and R , the gas constant. If one makes the usual assumption that the transmission coefficient is unity, the absolute rate equation may be written

$$\log_{10} \frac{k'}{T} = 10.319 - \frac{1}{T} \left(\frac{\Delta H^\ddagger}{4.574} \right) - \left(\frac{\Delta S^\ddagger}{4.574} \right)$$

From this it is seen that the linear plot of $\log_{10} k'/T$ versus $1/T$ will have as its slope $-\Delta H^\ddagger/4.574$ and that ΔS^\ddagger may be evaluated from the same data.

The Gibb's free energy of activation may be calculated since $\Delta F^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$.

Discussion

Figure 1 is a plot of the experimental data of Kistiakowsky and Smith⁴ for the racemization of the *l*-antipode of 2,2'-diamino-6,6'-dimethyldiphenyl both in the vapor phase and in solution in diphenyl ether. From this graph ΔH^\ddagger and ΔS^\ddagger may be determined.

In Table I values of ΔH^\ddagger and ΔS^\ddagger for the racemization of optically active antipodes of various compounds are given. The sources of the experimental

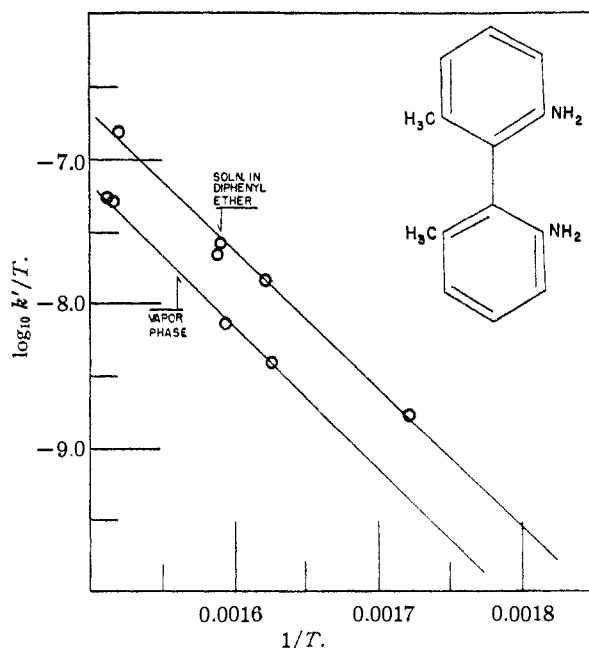


Fig. 1.—Data for the racemization of *l*-2,2'-diamino-6,6'-dimethyldiphenyl.

(1) This paper was presented before the Physical and Inorganic Division of The American Chemical Society, Cleveland, Ohio, March, 1951.

(2) C. H. Christie and J. Kenner, *J. Chem. Soc.*, 614 (1922).

(3) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., New York, N. Y., 1941.

(4) G. B. Kistiakowsky and W. R. Smith, *THIS JOURNAL*, **58**, 1043 (1936).

TABLE I

No.	Compound	Solvent	(cal./g. mole) ΔH^\ddagger	(e.u.) ΔS^\ddagger	Literature reference
I	4,6,4'-Trinitro-2,2'-diphenic acid	2 N NaOH solution	21,200	-18.5	5
II	6,4'-Dinitro-2,2'-diphenic acid	2 N NaOH solution	25,700	-4.2	6
III	2,2'-Diamino-6,6'-dimethyldiphenyl	Vapor phase diphenyl ether solution	45,600 44,100	-11.48 -11.54	4 4
IV	2-Nitro-6-carboxy-6'-methoxydiphenyl	Absolute ethanol	19,300	-9.19	7
V	2-Nitro-6-carboxy-6'-ethoxydiphenyl	Absolute ethanol	20,100	-9.38	7
VI	2-Nitro-6-carboxy-6'-propoxydiphenyl	Absolute ethanol	20,000	-10.5	7
VII	5,5'-Octamethylenedioxy-2,2'-diphenic acid	Dioxane	22,100	-9.24	8
VIII	5,5'-Decamethylenedioxy-2,2'-diphenic acid	Dioxane	22,800	-6.27	8
IX	Sodium N-acetyl-N-methyl- <i>p</i> -toluidine-3-sulfonate	Water	22,800	-1.60	9
X	N-Succinyl-1-methylamino-2,4-dimethyl-6-chlorobenzene	<i>n</i> -Butanol and methyl acetate	19,300	-26.9	10

data upon which these calculations are based are indicated.

If one considers the values of ΔH^\ddagger it will be seen that these show relatively little variation except in the case of the fully O,O'-substituted compound III. In this case as one might expect the value of ΔH^\ddagger is markedly increased. The entropies of activation ΔS^\ddagger exhibit most interesting behaviors. Note the increase in negative entropy as one proceeds through the series IV, V and VI. With an increase in size of the alkoxy group the positions in which it may be and still permit the formation of an activated complex becomes more limited. Thus if we consider a carbon atom which might freely occupy one of three equivalent positions in the normal state but which could occupy but one of these positions in the activated state, a change of entropy of $-(1.99 \ln 3)$ or -2.19 e.u., would be expected.

In the cases of compounds VII and VIII, one obtains a slight increase in ΔH^\ddagger with an increase in chain length; however, the entropy of activation, ΔS^\ddagger , decreases. This arises from the fact that the proper situation of the eight membered carbon chain in VII is just such as will permit racemization, the slipping of one carboxy group past the other. On the other hand, in the case of the ten membered chain in compound VIII, more freedom of configuration is possible in the activated complex. It is interesting to note that in these two compounds repeated complete rotation is quite impossible. Thus the relative agreement of these values of ΔH^\ddagger and ΔS^\ddagger with those of similar compounds indicates that the assumption $\kappa = 1$ is justified. Conceivably a substituted biphenyl once possessing sufficient free energy to pass over the higher of the two barriers will continue rotating until the energy in the reaction coordinate is dissipated, into other degrees of freedom. If, for example, an activated barrier were passed over repeatedly, say one hundred times, this would reduce κ to 1/100. The fact that in cases VII and VIII there is no indication of the chain affecting κ suggests the latter must be near unity in all

cases. Thus we conclude the apparent entropy is a real entropy of activation.

It is interesting to note that in general the choice of solvent has relatively little effect on the rate of racemization. This will be seen from examining the data for compound III in Table I where we see the liquid and vapor phase reaction proceed with almost the same heats and entropies of activation. This is in accord with the findings of Li and Adams in other cases.⁷ This further suggests that the assumption $\kappa = 1$ is valid. One exception to this statement is the greater rate of racemization of the substituted diphenic acids in sodium hydroxide solution. Unfortunately, suitable data are not available, in this case, to ascertain whether this effect arises from an alteration of ΔH^\ddagger or ΔS^\ddagger or both.

In the case of compound X the very negative value of ΔS^\ddagger is probably due to the fact that the long succinyl chain must so arrange itself as to clear either the methyl or chloro group during the rotation. This arrangement is unlikely and thus one observes the high negative value of ΔS^\ddagger .

An interesting though approximate calculation of the resonance energy due to the π bonding between the rings of biphenyl may be made. If one considers ΔH^\ddagger for compound III it will contain in first approximation two terms. One, which we shall call b , is the work necessary to distort bonds so that the molecule can be brought into a coplanar configuration. The other term, which is a , is the resonance energy which results from this configuration. Thus for compound III one writes $\Delta H^\ddagger = 2b - a = 45,000$ cal./g. mole. Now for compound V, one may write $\Delta H^\ddagger = b - a = 20,000$ cal./g. mole. If one assumes the values of b , the energy necessary to displace the O,O'-groups so they do not interfere in the planar configuration of the rings, are the same in the two cases, the value of a is 5,000 cal./g. mole. This is in substantial agreement with the value of 6,800 cal./g. mole given by Syrkin and Dyatkina.¹¹ Experimental results designed to measure this result more precisely would be especially valuable.

The work of Mayer and Westheimer^{12,13} should

(11) Y. K. Syrkin and M. E. Dyatkina, "Structure of Molecules and the Chemical Bond," Interscience Publishers, Inc., New York, N. Y., 1950.

(12) F. H. Westheimer and J. E. Mayer, *J. Chem. Phys.*, **14**, 733 (1946).

(13) F. H. Westheimer, *ibid.*, **15**, 252 (1947).

(5) R. Kuhn and O. Albrecht, *Ann.*, **458**, 221 (1927).

(6) R. Kuhn and O. Albrecht, *ibid.*, **455**, 272 (1927).

(7) C. C. Li and R. Adams, *THIS JOURNAL*, **57**, 1565 (1935).

(8) R. Adams and N. Kornblum, *ibid.*, **63**, 188 (1941).

(9) W. H. Mills and R. M. Kelham, *J. Chem. Soc.*, 274 (1937).

(10) R. Adams and J. R. Gordon, *THIS JOURNAL*, **72**, 2454 (1950).

be mentioned. They estimated theoretically an activation energy of 18,000 cal./g. mole for the racemization of 2,2'-dibromo-4,4'-dicarboxybi-phenyl. It

is unfortunate that this value cannot be compared with experimental data for this compound.

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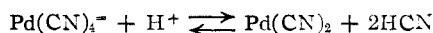
[CONTRIBUTION FROM THE LAB. PROD. MINERAL, MINISTERIO DA AGRICULTURA, RIO DE JANEIRO]

Salts of Tetracyanopalladic(II) Acid

BY F. FEIGL AND G. B. HEISIG¹

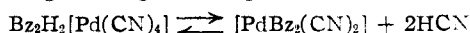
Tetracyanopalladic(II) acid forms insoluble salts of silver and copper and of their amines. It also forms normal salts of benzidine, β -naphthoquinoline and oxine, and the acid salt of nitron. On heating aqueous solutions of the benzidine, β -naphthoquinolinium salts, hydrocyanic acid is lost and the corresponding diammine is formed.

It is well known that palladium(II) cyanide dissolves in an excess of cyanide ions and that tetracyanopalladate(II) ion is formed. We found that by acidifying such a solution with a mineral acid there is no immediate precipitation of palladium(II) cyanide according to the equation



The time required for the precipitation depends on the temperature and on the concentration of the cyanide ion in the solution. Tetracyanopalladic(II) acid, $\text{H}_2[\text{Pd}(\text{CN})_4]$, is stable only in the presence of an excess of hydrocyanic acid. An acid having this formula should form insoluble salts with inorganic and organic cations.

The general method of preparing salts of this acid is to add a solution of the compound which gives the appropriate cation to a slightly acid, neutral or alkaline solution containing the tetracyanopalladate(II) ion. Thus by adding solutions of copper(II) sulfate and silver nitrate to a solution containing the tetracyanopalladate(II) ion, the corresponding salts precipitated. By adding a solution of copper(II) tetrammine sulfate or silver diammine nitrate to solutions containing the tetracyanopalladate(II) ion, impure diammines of copper and silver tetracyanopalladate(II) precipitated. From their hydrochloric acid solutions the salts of the following organic bases were precipitated: benzidine, β -naphthoquinoline, nitron and β -hydroxyquinoline (oxine). Aqueous suspensions of the salts of benzidine and β -naphthoquinoline when heated lose hydrogen cyanide according to the general equation



and diammines of palladium(II) cyanide were formed. Hydrocyanic acid was lost almost quantitatively from crystals of β -naphthoquinolinium tetracyanopalladate(II).

Experimental

A solution of potassium tetracyanopalladate(II) was prepared by adding potassium cyanide to freshly prepared palladium(II) cyanide until all was dissolved. Just before it was to be used, an acid solution of tetracyanopalladate(II) ion was prepared by adding a slight excess of dilute hydrochloric, sulfuric or acetic acid to a cold solution of the potassium salt. The palladium cyanide was prepared by treating 0.01 mole of palladium(II) chloride with 0.02 mole of mercuric cyanide and allowing the mixture to stand over-

night. The cream-colored precipitate, palladium(II) cyanide, was washed by decantation four or five times, filtered and washed with hot water.

A solution of crystals of potassium tetracyanopalladate(II)² was used to prepare the copper and silver salts.

Metals and Metal Ammine Salts of Tetracyanopalladic(II) Acid. Copper(II) Tetracyanopalladate(II), $\text{CuPd}(\text{CN})_4$.—Blue copper(II) tetracyanopalladate(II) was prepared by adding a solution of copper sulfate to a solution of the crystals of $\text{K}_2\text{Pd}(\text{CN})_4$. The residue obtained by ignition was 68.0%. The calculated value is 67.8%. The salt contained 19.9% of nitrogen and the calculated value is 20.4%.

Copper(II) Diamminetetracyanopalladate(II) $[\text{Cu}(\text{NH}_3)_2][\text{Pd}(\text{CN})_4]$.—This salt was prepared by adding a solution of copper(II) tetrammine nitrate to a solution of potassium tetracyanopalladate(II). A blue copper salt precipitated and was crystallized from hot water containing a little ammonia. The dried salt was ignited. The ratio $\frac{\text{Pd} + \text{CuO}}{\text{wt. of sample}}$

$\times 100$ was 60.0. The value calculated from the formula $[\text{Cu}(\text{NH}_3)_2][\text{Pd}(\text{CN})_4]$ is 60.5. Analysis of the product from another experiment gave the ratio $\frac{\text{Pd} + \text{CuO}}{\text{wt. of sample}} = 61.7$. The per cent. of carbon was 15.1, hydrogen 2.6 and that of nitrogen 28.8. The percentages calculated for the diammine are 15.6, 2.0 and 27.3, respectively.

Silver Tetracyanopalladate(II) $\text{Ag}_2[\text{Pd}(\text{CN})_4]$.—Silver tetracyanopalladate(II) was prepared by adding a slight excess of silver ions to a solution of the crystals of potassium tetracyanopalladate(II). The ratio of $\frac{\text{Pd} + \text{Ag}}{\text{wt. of sample}} \times 100$ was 75.5. The calculated value is 75.6.

Silver Diamminetetracyanopalladate(II) $[\text{Ag}(\text{NH}_3)_2][\text{Pd}(\text{CN})_4]$.—The white crystalline precipitate obtained by adding an ammoniacal solution of silver nitrate to a solution of potassium tetracyanopalladate(II) after recrystallization from hot, dilute ammonia was ignited. The ratio

$\frac{\text{Pd} + \text{Ag}}{\text{wt. of sample}} \times 100$ was 71.8. The value calculated for silver diamminetetracyanopalladate(II), $\text{Ag}_2[\text{Pd}(\text{CN})_4]$ is 75.6. The product was, therefore, a mixture of the two salts. Since the diammines of silver are unstable and lose ammonia the suspension of the product was heated until no more ammonia was evolved. Ignition of the white residue gave a ratio of $\frac{\text{Pd} + \text{Ag}}{\text{wt. of sample}} \times 100$ of 76.3, showing that the mixture had been changed to silver tetracyanopalladate(II), $\text{Ag}_2[\text{Pd}(\text{CN})_4]$.

Organic Salts of Tetracyanopalladic(II) Acid.—These salts were obtained by mixing dilute hydrochloric acid solutions of the respective bases with solutions of tetracyanopalladic(II) acid, $\text{H}_2[\text{Pd}(\text{CN})_4]$. The pure salts were obtained by crystallization from hot water. The dry salts were analyzed by weighing the palladium obtained upon igniting the salts.

Benzidiniumtetracyanopalladate(II) $\text{Bz}_2\text{H}_2[\text{Pd}(\text{CN})_4]$.—When the precipitate formed by the reaction of the hydrochloric acid solutions of tetracyanopalladic(II) acid and benzidine (Bz) was recrystallized from hot water, a residue

(1) On sabbatical leave from the University of Minnesota, Minneapolis, Minnesota.

(2) W. C. Fernelius, *et al.*, "Inorganic Syntheses," Vol. II, McGraw-Hill Book Company, Inc., New York, N. Y., 1946, p. 245.