where

V = molecular vol. (computed from Traube's rule)
λ_0 = confocal elliptical coördinate (ratio of sum of focal distances of a point on surface of an ellipsoid of revolution to the interfocal distance, R), obeys relation $\lambda_0^3 - \lambda_0 = 6V/\pi R^3$ for such an ellipsoid, where V is the volume and other quantities have been defined above.

The charge separation distances for both diamines by whatever model is used fall within the region of 4.66 to 4.86 Å. These suggest similar backbone and steric configurations for these molecules so that the difference in ΔpK values, aside from an added inductive effect in II, is a result of a 25% decrease in effective cavity dielectric constant for the larger molecule.

The charge separation distances also fall within the limits for the theoretical H to H distance for a di-acidified ethylenediamine skeleton defined by the extended chain value of 5.10 Å. and by the free rotation value of 3.94 Å.[11] Structural parameters used in these latter calculations were as follows: $r_{\text{N-H}} = 1.03$ Å.[12], $r_{\text{C-N}} = 1.47$ Å.,[13] $r_{\text{C-C}} = 1.54$ Å.,[13] with all bond angles assumed to have the tetrahedral value of 109°28′.

The exceedingly good results obtained from the Kirkwood–Westheimer calculations may well be fortuitous, but the agreement is heartening.

Contributions from steric factors imposed by the added methyl group in II might play a role by increasing the energy in the conformation with "*trans*" dimethylamino groups so that the preferred orientation is skewed, resulting in a smaller value for the charge separation. However, scale molecular models of either the Fisher–Hirschfelder–Taylor or Stuart–Briegleb type would not suggest large contributions from this source.

Experimental

N,N,N′,N′-Tetramethyl-1,2-ethanediamine (I).—This diamine was prepared by a procedure analogous to that used for the propane homolog II[14] and in comparable yield. For the basicity measurements, a fraction was taken boiling at 119.4–119.5° at 724 mm. (lit.[15] b.p. 120° at 760 mm.), with $n^{18}\text{D}$ 1.4196 (lit. $n^{20}\alpha$ 1.4180, $n^{20}\beta$ 1.4298[16]). The freezing point, previously unreported, was −55.1°, as determined from cooling curves.

N,N,N′,N′-Tetramethyl-1,2-propanediamine (II).—The preparation and properties of this compound have been published elsewhere.[14]

Base Strengths.—For the determination of pK_{ai} values, aqueous solutions, about 10^{-2} M in diamine and 0.5 M in sodium perchlorate, were potentiometrically titrated at 30° with 0.1 N aqueous perchloric acid, using glass and saturated calomel electrodes with a Beckman model G pH-meter. The sodium perchlorate, added to swamp out effects from changing ionic strength, was reagent grade material further purified by recrystallization from water. It gave a neutral aqueous solution. The diamines and aqueous perchlorate solutions were each separately saturated with argon gas bubbled in for at least one half hour to displace carbon dioxide and prevent its influencing the titration. The argon, obtained from a high pressure cylinder, was purified and dried by passage through towers of soda-lime and anhydrous magnesium perchlorate.

The pK_{ai} values were determined from graphical interpolation on the titration curve plot for the pH at the half-neutralization point between each equivalent step. At least two independent titrations were performed on each diamine. The titration curves were clear and the equivalence points sharp so no difficulty was experienced in the determinations.

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[11] Computed from the formula of H. Eyring, *Phys. Rev.*, **39**, 746 (1932).

[12] This was taken from the work on ammonium halides wherein the neutron diffraction value of H. A. Levy and S. W. Peterson, *Phys. Rev.*, **86**, 766 (1952) and the nuclear magnetic resonance data of H. S. Gutowsky, G. E. Pake and R. Bersohn, *J. Chem. Phys.*, **22**, 643 (1954) and of R. Bersohn and H. S. Gutowsky, *ibid.*, **22**, 651 (1954), all agree within 0.01 Å. See also Table VI in H. A. Levy and S. W. Peterson, THIS JOURNAL, **75**, 1536 (1953).

[13] Concordant values were taken from electron diffraction data on simple aliphatic amines listed in the compilation by P. W. Allen and L. E. Sutton, *Acta Cryst.*, **3**, 46 (1950).

[14] R. W. Moshier and L. Spialter, *J. Org. Chem.*, **21**, 1050 (1956).

[15] G. F. Grail, L. E. Tenenbaum, A. V. Tolstoouhov, C. J. Duca, J. F. Reinhard, F. E. Anderson and J. V. Scudi, THIS JOURNAL, **74**, 1313 (1952).

[16] H. T. Clarke, *J. Chem. Soc.*, **101**, 1788 (1912).

WRIGHT–PATTERSON AIR FORCE BASE, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

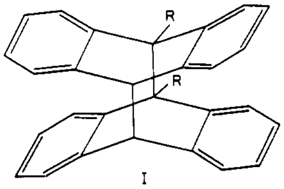
The Acid-catalyzed Dissociation of Bis-9-anthraldehyde[1]

BY FREDERICK D. GREENE, SANTIAGO ROBLEDO OCAMPO AND LOUIS A. KAMINSKI[2]

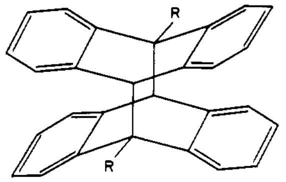
RECEIVED JULY 2, 1957

The photodimer of 9-anthraldehyde (I, R = CHO, bis-9-anthraldehyde) has been shown to undergo facile acid-catalyzed cleavage to 9-anthraldehyde in benzene solution. The cleavage reaction shows great sensitivity to the strength of the acid catalyst, exhibiting the following relative rate sequence at 25°: trifluoroacetic acid, 10^5; trichloroacetic acid, 10^4; dichloroacetic acid, 10^2; monochloroacetic acid, 0.45. The order in stoichiometric acid concentration is a function of the acid strength: trifluoroacetic acid, 2.44; trichloroacetic acid, 2.06; dichloroacetic acid, 1.96; monochloroacetic acid, 1.47. The isotope effect, $k_{\text{cH}}/k_{\text{cD}}$, for dichloroacetic acid and dichloroacetic acid-*d* is 1.1. The driving force for the cleavage reaction is attributed to the electrostatic repulsion between the carbonyl carbon atoms arising from coördination of acid moieties with the oxygen atoms of the formyl groups (V).

Sunlight effects the conversion of a wide variety of anthracene derivatives to dimeric structures in which the two anthracene units are bonded together at the 9,9′- and 10,10′-positions. For the dimerization of a 9-substituted compound, two such structures are possible, I and II. Structure I has been established for the photodimers derived from the 9-



I



II

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[1] Presented before the Organic Division of the 131st Meeting of the American Chemical Society in Miami, Florida, April, 1957.

[2] Cabot Solar Energy Fellow, 1956–1957.

substituted anthracenes in which R is formyl, carbomethoxy and hydroxymethyl.[3] Dimerization of 9-bromoanthracene affords a product possessing structure II.[4] The photodimers are stable for prolonged periods of time on storage but are quantitatively dissociated to the corresponding monomers at the melting (decomposition) point. The photodimer of 9-anthraldehyde (I, R = CHO; bis-9-anthraldehyde) has been shown to undergo a facile acid-catalyzed dissociation in benzene solution. The investigation of this cleavage reaction was the purpose of the present work.

Experimental[5]

Anthracene Derivatives.—9-Anthraldehyde and 9-methyl anthroate were prepared by the previously described methods.[3] 9-Anthraldehyde dissolves in concd. sulfuric acid to give a red solution from which the aldehyde may be quantitatively recovered by dilution with water.

Photodimers.—Bis-9-anthraldehyde was prepared as before.[3] Irradiation in degassed acetic acid minimized the formation of anthraquinone. The photodimer was recrystallized several times from benzene to obtain a colorless product suitable for kinetic studies, dec. p. 185–186°.

Irradiation of a 2-g. sample of 9-methyl anthroate in 30 ml. of chloroform afforded 1.2 g. of colorless prisms of dec. p. 222–223° after recrystallization from benzene.

Anal. Calcd. for $C_{32}H_{24}O_4$: C, 81.37; H, 5.12. Found: C, 81.04; H, 5.20.

Effect of Acid on Photodimers.—A solution of 0.1 g. of bis-9-anthraldehyde and 1.0 g. of trichloroacetic acid in 75 ml. of benzene was left at 25° for 24 hr. Extraction of the yellow solution with bicarbonate solution and removal of the benzene under reduced pressure afforded 0.095 g. of yellow solid, m.p. 104–106°, mixed m.p. with 9-anthraldehyde, 104–106°. Subjection of a sample of bis-9-methyl anthroate to identical conditions resulted in essentially quantitative recovery of the *photodimer*, dec. p. 222–223°, remelting at 112–113° (m.p. of 9-methyl anthroate) after cooling.

Determination of Wave Length for Dimerization of 9-Anthraldehyde.—Aliquots of a solution of 9-anthraldehyde in acetic acid were sealed in tubes under an atmosphere of nitrogen. The tubes were placed in separate compartments of a box and Corning glass filters were sealed over each compartment. After exposure to sunlight for one week, the tubes were opened and the dimer was recovered by filtration. The wave length necessary to effect dimerization lies between 390 and 460 mμ.

Materials for Kinetic Studies.—Reagent grade benzene was heated at reflux over sodium and distilled directly into the reaction flask. Trichloroacetic acid, Eastman Kodak Co. White Label, was recrystallized from benzene and dried over phosphorus pentoxide, m.p. 57–58°. Dichloroacetic acid was purified by vacuum distillation, b.p. 99.5–100.0° (19 mm.), $n^{20}\text{D}$ 1.4657. Monochloroacetic acid, Eastman Kodak Co., was recrystallized from benzene, m.p. 62–63°. Phenylpropiolic acid, prepared from cinnamic acid dibromide,[6] had m.p. 136–137°. α-Chloroallocinnamic acid was prepared by the method of Sudborough and James.[7] Initial separation of the allo isomer from the acid mixture was effected through the barium salts. Repeated recrystallization of the alloacid from petroleum ether afforded material of m.p. 110–111°.

Dichloroacetic Acid-*d*.—To 31.5 g. of dichloroacetic anhydride, b.p. 122–123° (20 mm.), frozen at 0° was added 3.14 g. of deuterium oxide (Stuart Oxygen Co., 99.5 wt.-% deuterium oxide). The mixture was allowed to warm to room temperature, maintained at 30–40° for 45 min. by intermittent cooling, and left at room temperature overnight. Distillation of the homogeneous solution afforded a small forerun and a main fraction, b.p. 97.5–98° (18 mm.). A midcut was taken for kinetic experiments and analysis. The infrared spectrum exhibited prominent bands at 3280, 2000–2500, 2800 cm.$^{-1}$ corresponding to carbon–hydrogen stretching and oxygen–deuterium stretching (associated and unassociated). No oxygen–hydrogen bands were observed. *Anal.* 50.4 ± 0.5 atom-% deuterium corresponding to 1.00 g.-atom deuterium per mole.

Kinetic Method.—The rate of appearance of 9-anthraldehyde was followed with a Beckman DU spectrophotometer, taking advantage of the strong absorption of 9-anthraldehyde in a region where bis-9-anthraldehyde is transparent. The 400 mμ maximum of 9-anthraldehyde in benzene is shifted to slightly longer wave lengths in the presence of the acids. The extinction coefficient of the 420 mμ band in 9-anthraldehyde and trichloroacetic acid (0.164 *M*) is constant over a variation in aldehyde concentration from 2×10^{-5} to 1×10^{-4} *M* (the range used in the rate measurements), indicating adherence to Beer's law and that the 9-anthraldehyde is complexed to the same extent throughout. The pertinent ultraviolet absorption spectra are reported in Fig. 1. Kinetic determinations were made by the following method. Benzene was distilled directly into a flask which had been baked at high vacuum. The flask was removed from the still, the desired amount of bis-9-anthraldehyde was added and the flask was stoppered. A solution of trichloroacetic acid in benzene was prepared in a duplicate flask, and one-third of the solvent was removed by distillation. The flask containing the acid solution was transferred to the flask containing the photodimer solution by means of a curved glass adapter with ground joints. The adapter was replaced by a stopper which consisted of a ground glass joint, a stopcock and a rubber cap. For the fast reactions at 25° (trifluoroacetic acid), a portion of the solution was transferred by a hypodermic syringe to a stoppered quartz cell in a thermostated cell holder and measurements of the optical density were begun. For the other experiments at 25 and 45°, the flask was immersed in a constant temperature bath with the stopcock shut. At suitable time intervals the stopcock was opened and aliquots were withdrawn through the rubber cap by means of a hypodermic syringe. For most of the kinetic experiments, the initial concentration of bis-9-anthraldehyde was about 8×10^{-5} *M* which permitted following the reaction to completion without making any dilutions of the reaction solution. The concentration of acid was determined by titration of a portion of the final solution. The concentration of water, determined by Karl Fischer titration,[8,9] was negligible. For measurements with the weaker acids (monochloroacetic acid and phenylpropiolic acid) the initial concentration of bis-9-anthraldehyde was made considerably greater because of the slowness of the reaction, and the reaction was only followed to about 25% completion. Addition of trifluoroacetic acid at this point, thus allowing the reaction to proceed rapidly to completion, permitted the determination of the infinity reading.

Calculation of the Rate Constants.—The rate constants were determined by use of equation 1 in which O.D._0, O.D._∞ and O.D._t are the optical densities at zero time, at complete reaction and at time *t* in sec., respectively, and *k* is the observed rate constant. Values of *k* were determined for each

$$2.303 \log (\text{O.D.}_\infty - \text{O.D.}_0/\text{O.D.}_\infty - \text{O.D.}_t) = kt \quad (1)$$

measurement of O.D._t; the arithmetic mean of the individual *k* values was taken for k_{obs}. The average deviation was between 1 and 2%.

Results

Kinetic Results.—The rate of the acid-catalyzed dissociation of bis-9-anthraldehyde to 9-anthraldehyde in benzene solution was determined for trifluoro-, trichloro- and dichloroacetic acid at 25° and for trichloro-, dichloro-, monochloroacetic acid, phenylpropiolic acid and α-chloroallocinnamic acid at 45°. The kinetic data are summarized

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(3) F. D. Greene, S. L. Misrock and J. R. Wolfe, Jr., THIS JOURNAL, **77**, 3852 (1955).

(4) D. E. Applequist, Abstracts of the 131st *meeting of the* American Chemical Society, Miami, Florida, April, 1957, p. 8-O.

(5) Melting points are corrected. We are indebted to Dr. S. M. Nagy and his associates for analyses and infrared spectra and to Josef Nemeth for the deuterium analysis.

(6) T. W. Abbott, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 515.

(7) J. J. Sudborough and T. C. James, *J. Chem. Soc.*, **89**, 105 (1906)

(8) The amount of water in benzene solutions of acids may be determined with great accuracy. See J. Mitchell and D. M. Smith, "Aquametry," Interscience Publishers, Inc., New York, N. Y., 1948.

(9) We wish to thank Professor Hume and Mr. Foreman for assistance in these determinations.

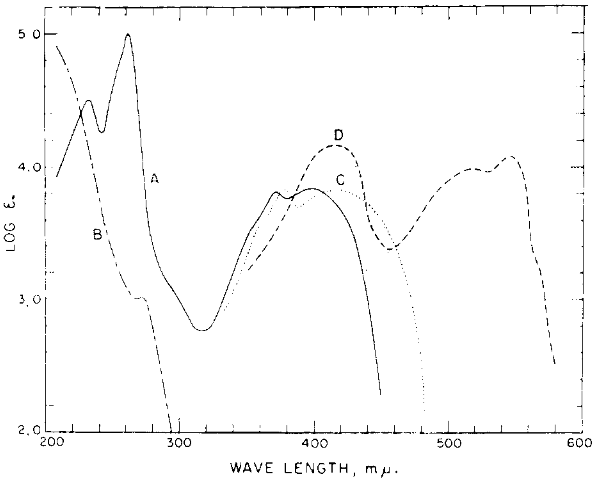

Fig. 1.—Ultraviolet absorption spectra of 9-anthraldehyde (A); bis-9-anthraldehyde (B); 9-anthraldehyde, 3.07 × 10^{-5} *M* in benzene solution containing 0.165 *M* trichloroacetic acid (C); 9-anthraldehyde in concd. sulfuric acid (D). Spectra were measured on a Beckman model DU spectrophotometer: 208–320 in *n*-heptane; 320–490 in benzene.

in Table I. In all of the cases studied, the reaction is first order in photodimer concentration, illustrated for two runs in Fig. 2. The reaction remains first order in bis-9-anthraldehyde throughout the entire course of the reaction, followed in some cases as far as 99%.

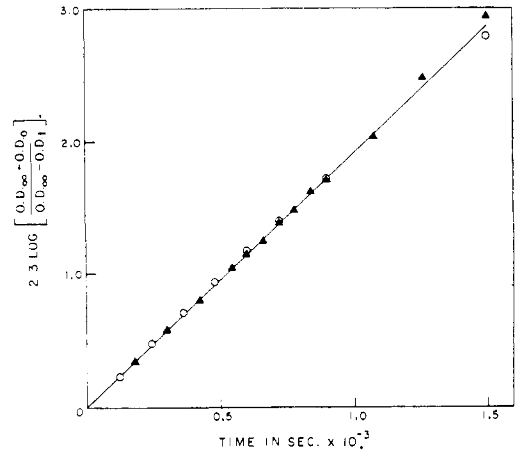

Fig. 2.—Dissociation of bis-9-anthraldehyde in benzene solution at 25° in the presence of 0.15 *M* trichloroacetic acid: ○, 2.92 × 10^{-5} *M*; ▲, 5.83 × 10^{-5} *M*.

The order with respect to acid concentration was determined by evaluation of the slope of the line (least squares method) defined by a plot of log k_{obs} against log of the stoichiometric acid concentration. These data are summarized in Fig. 3. The order in acid is dependent on the strength of the acid changing from 2.44 for trifluoroacetic acid to 2.06 for trichloroacetic acid, 1.96 for dichloroacetic acid and 1.47 for monochloroacetic acid.[10] From the data of Table I and those derived from Fig. 3, the catalytic constants have been determined by the use of equation 2 and are summarized in Table II.

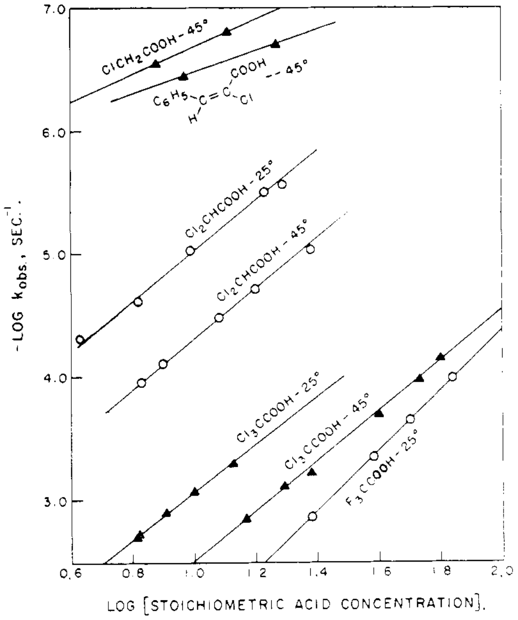

Fig. 3.—Relationship between observed rate constants (k_{obs}) and stoichiometric acid concentration for the dissociation of bis-9-anthraldehyde in benzene.

$$k_{\text{obs}} = k_0 + k_c[\text{HA}]^x \qquad (2)$$

Effect of Water.—In Fig. 4, the variation of the observed rate constant for a fixed concentration of trichloroacetic acid at 45° is recorded as a function of the water concentration.

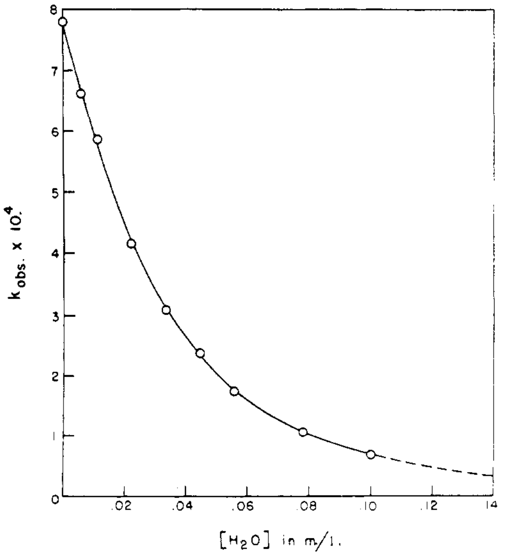

Fig. 4.—Effect of water on rate of dissociation of bis-9-anthraldehyde in benzene containing 0.0513 *M* trichloroacetic acid at 45°.

Discussion

The dissociation of bis-9-anthraldehyde to monomeric 9-anthraldehyde, a potentially simple process involving only a small change in bond angles and a

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[10] The range in acid concentration is limited at high concentrations of acid by the great speed of the reaction and a desire to minimize medium effects and at low concentrations by the retarding effect of traces of moisture.

TABLE I

SUMMARY OF KINETIC DATA ON THE ACID-CATALYZED DISSOCIATION OF BIS-9-ANTHRALDEHYDE IN BENZENE

Catalyst	Temp., °C.	Catalyst concn., *M*	Initial concn. of photodimer × 10^4	k_{obs}, sec.$^{-1}$
None	45	0	7.347	5.10 × 10^{-8a}
F_3CCOOH	25	0.0430	0.8075	13.9 × 10^{-4}
	25	.0265	.8075	4.40 × 10^{-4}
	25	.0200	.8075	2.24 × 10^{-4}
	25	.0146	.8075	0.996 × 10^{-4}
Cl_3CCOOH	25	.1500	.2917	1.92 × 10^{-3}
	25	.1500	.5825	1.91 × 10^{-3}
	25	.1238	.5115	1.31 × 10^{-3}
	25	.1000	.8075	0.847 × 10^{-3}
	25	.0750	.5825	0.501 × 10^{-3}
	45	.0670	.8075	14.1 × 10^{-4}
	45	.0513	.8075	7.79 × 10^{-4}
	45	.0420	.8075	6.06 × 10^{-4}
	45	.0254	.8075	2.05 × 10^{-4}
	45	.0187	.8075	1.03 × 10^{-4}
	45	.0159	.8075	0.694 × 10^{-4}
$Cl_2CHCOOD$	25	.2386	.8075	4.24 × 10^{-5}
$Cl_2CHCOOH$	25	.2354	.8075	4.58 × 10^{-5}
	25	.1509	.8075	2.45 × 10^{-5}
	25	.1027	.8075	0.944 × 10^{-5}
	25	.0595	.8075	.316 × 10^{-5}
	25	.0513	.8075	.276 × 10^{-5}
	45	.1475	.8075	11.0 × 10^{-5}
	45	.1254	.8075	7.84 × 10^{-5}
	45	.0837	.8075	3.33 × 10^{-5}
	45	.0627	.8075	1.97 × 10^{-5}
	45	.0438	.8075	0.932 × 10^{-5}
$ClCH_2COOH$	45	.1333	6.20	2.90 × 10^{-7}
	45	.0777	6.20	1.59 × 10^{-7}
α-Chloroallocinnamic acid	45	.1083	0.660	4.09 × 10^{-7}
	45	.0533	.505	1.99 × 10^{-7}
Phenylpropiolic acid	45	.107	8.61	1.14 × 10^{-6}

[a] k_0 for equation 2.

TABLE II

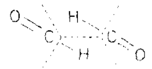
CATALYTIC CONSTANTS FOR THE DISSOCIATION OF BIS-9-ANTHRALDEHYDE IN BENZENE SOLUTION

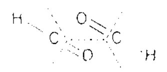
Catalyst	k_c, M^{-x} sec.$^{-1}$, 25°	x	k_c, M^{-x} sec.$^{-1}$, 45°	x
$ClCH_2COOH$			4.7 × 10^{-6} (2)	1.47
$Cl_2CHCOOH$	8.3 × 10^{-4} (5)[a]	1.93	5.2 × 10^{-3} (5)	1.96
$Cl_2CHCOOD$	7.5 × 10^{-4} (1)	[1.93]		
Cl_3CCOOH	6.8 × 10^{-2} (5)	1.96	3.4 × 10^{-1} (6)	2.06
F_3CCOOH	3.1 (4)	2.44		

[a] Number of determinations on which k_c is based.

redistribution of electronic charge, presents several points of interest: the novelty of this type of bond rupture, the great sensitivity of rate of cleavage to acid strength of the catalyst and the order in acid concentration and variation in order with different acids.

Molecular models of bis-9-anthraldehyde (Catalin or Stuart and Briegleb) are rigid but essentially strain-free, with considerable hindrance to free rotation of the formyl groups. A top view of two orientations of the formyl groups is shown in III and IV in which the sterically most favorable orientation is III and the electronically most favorable one is IV. Rough calculations of the dipole–dipole interaction energy[11] for IV are suggestive of a few kcal./mole of stabilization, but such orientation cannot be achieved in Stuart and Briegleb models without lengthening of the 9,9′-bond.[12]


III


IV

Variation in order in acid and occurrence of nonintegral orders in acid are phenomena that have been encountered in virtually all work associated with acid catalysis in aprotic media.[13] In its simplest form this is associated with variation in activities of acids in media of low dielectric constant. Interpretation of the results of previous studies of acid catalysis in aprotic solvents have suffered from incomplete data on the actual catalyst concentration, arising from the importance of complexing of catalyst with the products of the reaction where comparable concentrations of catalyst and substrate have been employed. In the present study such difficulties were avoided by use of a spectroscopic method which permitted operation at a catalyst to substrate ratio of greater than 200 to 1. Thus the variation in acid order (x, Table II) is largely associated with the particular acid and not with acid–substrate complexing. One of the principal sources of this variation is undoubtedly the association of the carboxylic acids in benzene to form the cyclic hydrogen-bonded acid dimers. Accurate data on the magnitude of the dissociation constants governing acid monomer–acid dimer equilibria are available for many of the substituted benzoic acids and simple aliphatic acids,[14] but the data pertaining to the dissociation constants for the halogenated acetic acids in benzene are limited (see Table III) to one determination for monochloroacetic acid at 30°, one oft-quoted but approximate value for trichloroacetic acid at 30° and freezing point data from which it was concluded that the acid was dimeric in benzene even at 0.01 *M*.[15] However, two points seem reasonably well established: first, the greater the ionization constant of an acid in water, the smaller is the tendency of the acid to associate in benzene[14,15b,16]; secondly, the variation in acid dimer dissociation constant in an inert medium is a fairly insensitive function of acid strength.[14,17] If the reported acid dimer dissociation constants are

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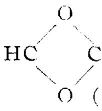
[11] W. R. Smythe. "Static and Dynamic Electricity," McGraw-Hill Book Co., Inc., New York, N. Y., 1939, p. 7; S. Winstein, E. Grunwald and L. L. Ingraham, THIS JOURNAL, **70**, 821 (1948).

[12] The carbonyl absorption band in the infrared is normal, excluding important contributions from (a). Thermochemical studies in progress on compounds in this series may provide more information on the influence of groups, R, on the stability of photodimers, I.


(a)

[13] (a) R. P. Bell, "Acid–Base Catalysis," Oxford University Press, London, 1941, Ch. VI; (b) R. P Bell, "Advances in Catalysis," Vol. IV, Academic Press, Inc., New York, N. Y., 1952, pp. 151–210; (c) C. G. Swain and J. F. Brown, Jr., THIS JOURNAL, **74**, 2534, 2538 (1952); (d) H. Kwart and L. B. Weisfeld, *ibid.*, **78**, 635 (1956).

[14] G. Allen and E. F. Caldin, *Quart. Revs.* (*London*), **7**, 255 (1953).

[15] (a) R. P. Bell and M. H. M. Arnold, *J. Chem. Soc.*, 1432 (1935); (b) however, see A. Weissberger, THIS JOURNAL, **65**, 102 (1943).

[16] R. J. W. Le Fèvre and H. Vine, *J. Chem. Soc.*, 1795 (1938).

[17] J. T. Harris, Jr., and M. E. Hobbs, THIS JOURNAL, **76**, 1419 (1954).

correct, then one is dealing with comparable amounts of monomeric and dimeric acids under the conditions of these experiments. The effective agent for cleavage may be acid monomer, acid dimer or both.[18] The observation that small amounts of water (see Fig. 4) have a marked retarding effect on the acid-catalyzed cleavage suggests that the acid–water complex is a less effective catalyst, in accord with other investigations.[19] The finding of second-order dependence on stoichiometric acid concentration requires at least two acid molecules in the transition state for the cleavage reaction. To the extent that the acids are dimeric under the conditions of these experiments, the number of acid molecules involved in the cleavage will be greater than the apparent order in acid. (Thus the occurrence of the larger orders with the stronger acids is consistent with the trend in dissociation constants of the hydrogen-bonded acid dimers.) It is of interest that the variation in acid order for this cleavage reaction closely parallels that observed in the acid-catalyzed conversion of N-bromoacetanilide to *p*-bromoacetanilide in benzene at 15° (order in acid: trichloroacetic acid, 0.98; dichloroacetic acid, 0.83; monochloroacetic acid, 0.67).[20]

The cleavage reaction shows great sensitivity to the acid strength of the catalyst. The rates of cleavage at a fixed acid concentration are shown in Table III.[21] Of particular importance is the observation that the variation in relative rates is substantially greater than the variation in ionization constants of the acids.[22] In terms of the Brönsted catalysis law, this corresponds to a Brönsted α of about 1.8 at 25°.[23] The occurrence of α-values greater than unity has been observed previously in cases involving orders in catalyst greater than unity.[24] The significance of the large value of α in the present case is the strong implication that *both* acid entities in the reaction are being used as *electrophilic agents*. The establishment of a minimum of two acid molecules in the transition state and of the use of the catalytic units as electrophilic agents still leaves a larger number of possible routes for the cleavage reaction. The two principal paths (leaving aside questions of the extent of hydrogen transfer from acid to substrate) are (a) two prior equilibrium steps followed by rate-determining cleavage of the complex (equations 3, 4, 5 with 5 rate-determining), and (b) one prior equilibrium step (eq. 3) followed by rate-determining reaction of the acid-substrate complex with a second acid unit (eq. 6).

TABLE III

ACID-CATALYZED DISSOCIATION OF BIS-9-ANTHRALDEHYDE IN BENZENE

Catalyst	Rel. *k* for HA = 0.05 *M*, 25°	K_a, water, 25°	K_d, benzene, 30°[a]
$ClCH_2COOH$	0.45[b]	1.4×10^{-3}	1×10^{-2}[c]
$Cl_2CHCOOH$	100	5.0×10^{-2}	
Cl_3CCOOH	10,000	6.3×10^{-1}	4×10^{-2}[d]
F_3CCOOH	100,000	1.8[e]	

[a] Dissociation constants for acid dimers, mole/l. units. [b] Estimated value, corrected for the non-catalyzed rate. [c] H. A. Pohl, M. E. Hobbs and P. M. Gross, *J. Chem. Phys.*, 9, 408 (1941). [d] R. J. W. Le Fèvre and H. Vine, *J. Chem. Soc.*, 1795 (1938). [e] G. C. Hood, O. Redlich and C. A. Reilly, *J. Chem. Phys.*, **23**, 2229 (1955).

$$D + HA \rightleftarrows D{\cdot}HA \qquad (3)$$

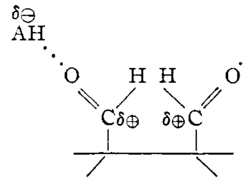
$$D{\cdot}HA + HA \rightleftarrows AH{\cdot}D{\cdot}HA \qquad (4)$$

$$AH{\cdot}D{\cdot}HA \longrightarrow 2M{\cdot}HA \qquad (5)$$

$$D{\cdot}HA + HA \longrightarrow 2M{\cdot}HA \qquad (6)$$

D = bis-9-anthraldehyde
M = 9-anthraldehyde
HA = the effective acid catalyst

Comparison of the effectiveness of dichloroacetic acid and dichloroacetic acid-*d* reveals an isotope effect, k_{cH}/k_{cD}, of 1.1. The smallness of this isotope effect is out of accord with a process in which proton transfer is involved in a rate-determining process and leads us to prefer path (a). The simplest representation for the cleavage reaction is that shown below. Coördination of acid units with both carbonyl oxygen atoms (by full proton transfer, hydrogen bonding or intermediate degrees of proton transfer) increases the positive charge on the carbonyl carbon atoms. The enhanced electrostatic repulsion between these atoms is suggested as the driving force for fission of the 9,9′-bond, which may be followed rapidly by, or occur synchronously with, fission of the 10,10′-bond. This suggestion is supported by the observation that bis-9-methyl anthroate is much less subject to acid-catalyzed cleavage than is bis-9-anthraldehyde.



V

The facile carbon–carbon cleavage reaction of bis-9-anthraldehyde is reminiscent of the benzidine rearrangement, in which the nitrogen–nitrogen cleavage reaction is second order in acid[25] and sub-

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[18] The closeness of the orders in acid for dichloro- and trichloroacetic acid to two raises the possibility that for these acids both monomeric and dimeric acid are effective catalysts. Expressing the catalytic constant as $k_c = k_M[HA]^2 + k_D[HA]_2^2 + k_{MD}[HA][HA]_2$, if the trichloroacetic acid dimer were a more effective catalyst than the acid monomer, the expression for k_c might be approximated by $k_c = k'([HA] + 2[HA]_2)^2$ which would account for second-order behavior in stoichiometric acid at all acid concentrations.

[19] A. Weissberger, THIS JOURNAL, **65**, 242 (1943); A. Weissberger and J. Högen, *Z. physik. Chem.*, **156A**, 321 (1931).

[20] R. P. Bell, *Proc. Roy. Soc.* (*London*), **A143**, 377 (1934). The reported catalytic constants were calculated on an assumed order in acid of unity. However, plots of log *k vs.* log of the acid concentration afford excellent straight lines, corresponding to the orders reported above.

[21] Rates have been compared at a fixed acid concentration rather than by use of the catalytic constants because of variation in units for the latter.

[22] For a series of acids of the same charge type the relative strength has been found to be approximately independent of the solvent. Leading references are cited on p. 108 of ref. 13a.

[23] Although a proper test of the Brönsted law for this reaction is precluded by the limited range in acid type, a plot of log rel. *k vs.* pK_A affords a straight line.

[24] See, for example, R. P. Bell, O. M. Lidwell and M. W. Vaughan-Jackson, *J. Chem. Soc.*, 1792 (1936).

[25] G. S. Hammond and H. J. Shine, THIS JOURNAL, **72**, 220 (1950).

ject to general acid catalysis in 50% ethanol.[26]

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[26] M. D. Cohen and G. S. Hammond, This Journal, **75**, 880 (1953). For the rearrangement of *p,p'*-dideuterohydrazobenzene, see G. S. Hammond and W. Grundemeier, *ibid.*, **77**, 2444 (1955).

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[Contribution from the Departments of Chemistry of DePaul University and Purdue University]

Kinetics of the Isomerization of Substituted 5-Amino-1,2,3-triazoles[1]

By Eugene Lieber,[2] C. N. Ramachandra Rao and Tai Siang Chao

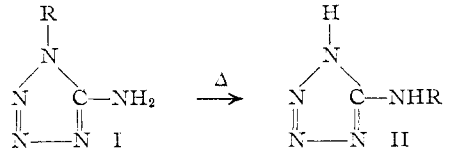
Received June 10, 1957

A study of the kinetics of the equilibrium reaction involved in the independent thermal isomerization of 1-(substituted (R))-4-phenyl-5-amino-1,2,3-triazoles and 5-(substituted (R))-amino-4-phenyl-1,2,3-triazoles has demonstrated that the same electronic mechanism and electrical effects of groups applies to both the corresponding 1,2,3-triazole and tetrazole ring systems. The kinetics of the equilibrium where R is $4\text{-}NO_2\text{-}C_6H_4$, $3\text{-}ClC_6H_4$, C_6H_5, $4\text{-}CH_3C_6H_4$, $4\text{-}CH_3OC_6H_4$ and $C_6H_5CH_2$ were studied in the range of 133–159°. In the initial stages of the isomerization, the first-order rate law is obeyed. For the forward reaction, the rates (k_1) decreased along the indicated series, the energies of activation increased from about 21,500 to 34,000 cal. per mole, and the heats of reaction varied from 11,840 cal. per mole (evolved) to about a value of 2200 cal. per mole (absorbed) extrapolated for the *p*-amino substituent. For the aryl substituted amino-1,2,3-triazoles, there was a good correlation between the logarithm of the rates of isomerization and Hammett's σ-value for groups.

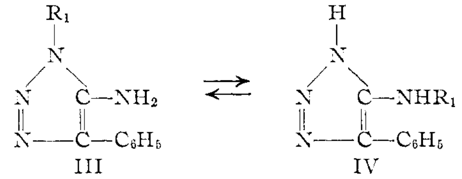
Introduction

1-Substituted-5-amino-1,2,3-triazoles and 5-(substituted)-amino-1,2,3-triazoles are thermally unstable and can be isomerized without appreciable decomposition in solvents or undisturbed melts to equilibrium mixtures of both isomers.[3] The present work is concerned with the kinetics of this isomerization.

In 1953, Henry, Finnegan and Lieber[4–7] as well as Herbst and Garbrecht[8] reported the observation that 1-substituted-5-aminotetrazoles I undergo a facile thermal rearrangement to substituted-5-aminotetrazoles II



Subsequent studies[6,7a] demonstrated the equilibrium nature of I ⇄ II and determined the effect of the electrical properties of R on the position of equilibrium and the kinetics of the forward and reverse reactions. In particular the kinetics[7a] of the forward and reverse reactions were decisive in aiding in the selection of a reasonable mechanism among a number of possibilities.[5–8] In view of the isosteric relationship of the 1,2,3-triazole and tetrazole nuclei, it appeared fairly certain that the isomerization of their corresponding 5-amino derivatives involved the same electronic mechanism and that the electrical effects of groups could be extrapolated from the tetrazole system to the triazole system.[6] The determination[5] of the position of equilibrium in homogeneous systems (undisturbed melts) for III ⇄ IV showed that K_{eq} (*i.e.*, the molar ratio of [IV]/[III]) is dependent on the electrical nature of R_1 in a manner very nearly parallel to the effect observed in the substituted 5-aminotetrazole system. Accordingly, it has remained for kinetic information in order to conclusively demonstrate the parallelism between the 1,2,3-triazole and tetrazole systems. One essential difference between the 5-aminotetrazole and 5-amino-1,2,3-triazole system lies in the fact that in the latter the 4-position may be varied with groups of distinctly different electrical properties. However, in the present study the 4-position is maintained constant as a phenyl group. Further studies on the effect of substituents in the 4-position of the 1,2,3-triazole nucleus are in progress and will be reported in a separate communication.



Experimental

Materials.—The 1-substituted-5-amino-1,2,3-triazoles and the 5-(substituted)-amino-1,2,3-triazoles were prepared as previously described.[3]

Apparatus and Procedure.—The apparatus used for the isomerizations consisted of a double walled flask. The reaction vessel consisted of a 25 mm., 7.6-cm. long tube sealed at one end, with the other end sealed to a 34/45 standard inner joint which in turn was sealed to a 24/40 standard outer joint. This was then fitted into the central neck (34/45 outer joint) of a 500-ml. 3-necked flask, a condenser being fitted to the outer end of the reaction vessel. Boiling *trans*-decalin, anisole, *n*-amyl alcohol, monoethanolamine and chlorobenzene enabled temperatures of 458, 432, 423, 406, and 401 °K. to be maintained. During any one experiment the temperature did not vary more than ±0.2°.

A solvent boiling at the desired bath temperature was placed in the three-necked flask, and the reaction vessel was fitted to the central neck of the flask. Ethylene glycol was placed in the reaction vessel and a thermowell and condenser fitted to it. The three-necked flask was also fitted with a condenser and thermowell. As soon as the ethylene glycol

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[1] Presented in part at the 128th National Meeting of the American Chemical Society, Minneapolis, Minn., September, 1955.

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[3] E. Lieber, T. S. Chao and C. N. R. Rao, *J. Org. Chem.*, **22**, 654 (1957).

[4] First reported at the 123rd Meeting of the American Chemical Society, Los Angeles, Calif., March, 1953.

[5] Henry, *et al.*, This Journal, **75**, 2023 (1953).

[6] Henry, *et al.*, **76**, 88 (1954).

[7] (a) Henry, *et al.*, **77**, 2264 (1955); (b) *J. Org. Chem.*, **18**, 781 (1953).

[8] R. M. Herbst and W. L. Garbrecht, *ibid.*, **18**, 1269 (1953).