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The Thermal Decomposition of Benzalazines[1] in Solution

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The decomposition of several ring-substituted benzalazines is reported. Thermal decomposition of these azines in solution to form stilbenes and nitrogen has been shown to exhibit first-order kinetics. Positive values obtained for entropies of activation appear to preclude the operation of a cyclic mechanism for this process.

The bulk thermal decomposition of benzalazines was first reported by Curtius and Jay[3] who found that the principal decomposition products were nitrogen and stilbenes. Pascal and Normand[4] reported that a side reaction occurred on formation of the stilbenes in bulk, namely, the loss of *ortho* hydrogens on the phenyl rings as ammonia when the *ortho* positions were not occupied by a substituent, to give phenanthrene derivatives. These authors plotted the volume of nitrogen evolved and the rate of ammonia formation against temperature. Two curves were obtained which intersected the axis of temperature at a point defined by the authors as the decomposition temperature.

The reported catalysis of ethylene polymerization at 200–225° by benzal and benzhydryl azines[5] is indicative that a free radical or carbene is produced, at least to some extent, upon thermal elimination of nitrogen from the azines. It has also been shown that pyrolysis of benzalazine in the vapor phase exhibits first-order kinetics.[6]

The present work was undertaken in order to obtain kinetic and thermodynamic data which could aid in the elucidation of the mechanism of thermal decomposition of benzalazines in solution. Azines derived from *p*-chlorobenzaldehyde, *o*-chlorobenzaldehyde, anisaldehyde, veratraldehyde and piperonal were prepared in essentially quantitative yield by the reaction of hydrazine hydrate with either the corresponding free aldehyde or the cyanohydrin derived therefrom. The synthesis of azines from cyanohydrins has not been previously reported, though it offers no particular advantage over the direct aldehyde synthesis. Kinetic runs on all the azines were carried out in Aroclor 1242 (a mixture of chlorinated biphenyls, b.p. 322–365°, manufactured by the Monsanto Chemical Co.) at 287.6 ± 0.2°. The decomposition of the azines derived from *o*- and *p*-chlorobenzaldehyde was also studied at 260° in diphenyl ether.

Experimental

Preparation of Cyanohydrins.—Cyanohydrins were prepared by reaction of the substituted benzaldehyde directly with potassium cyanide and hydrochloric acid (method A) by the method of McCombie and Parry[7] or through the action of potassium cyanide on the bisulfite addition product (method B) by the procedure of Czaplicki, Kostanecki and Lampe.[8]

TABLE I

Aldehyde	Yield of cyanohydrin, %	Method	M.p., °C.
p-Anisaldehyde	70	A	62.5–63 (63,[9] 67[10])
p-Chlorobenzaldehyde	85	A	42–43 (43[10])
o-Chlorobenzaldehyde	61	B	46–47 (47[10])
Veratraldehyde	53	B	103–104 (103[10])
Piperonal	66	B	Liquid

Preparation of Azines.—All azines could be prepared quantitatively by admixture of hydrazine hydrate with the substituted benzaldehyde. Pure products were obtained after crystallization from benzene. The same yields were obtained using the corresponding cyanohydrin. A typical procedure is described below:

To a solution of 16.3 g. (0.10 mole) of *p*-anisaldehyde cyanohydrin dissolved in 35 ml. of absolute ethanol, 3.0 g. (0.051 mole) of hydrazine hydrate was added slowly at room temperature. A yellow precipitate formed immediately. After the reaction mixture was allowed to stand for 3 days, the precipitate was removed by filtration and washed with 100 ml. of 50% ethanol. Six recrystallizations from benzene gave golden colored crystals, transition point 167–168° (liquid crystals), m.p. 179–180° (95%). Curtius[11] and Jaeger[12] reported a melting range from 168 to 180° for anisalazine and showed that the compound on melting passed through a liquid crystal stage.

In this manner were prepared 4,4′-dichlorobenzalazine, m.p. 206.5–207° (211°[4]); 2,2′-dichlorobenzalazine, m.p. 143–143.5° (143.5°[13]); veratralazine, m.p. 191–191.5° (191°[14]) and piperonalazine, m.p. 201–201.5° (201.5°).[15]

Kinetic Measurements. I. Procedure.—The apparatus employed consisted of an air-bath and thermoregulator. The air-bath was well insulated and the air well circulated by fan blades. A multiple thermoregulator system was used. The temperature was recorded using a 300° thermometer graduated in tenths of a degree. At 287.6°, the temperature control was ±0.2°. The reaction was carried out in a 50-ml. flask equipped with two openings, one of which led to a 100-ml. gas buret through capillary tubing and the other was used for the introduction of the azine compounds and nitrogen. A test-tube containing dilute sulfuric acid or distilled water was placed between the reaction flask and the gas buret. The system was so devised that the gases were allowed to pass over the surface of the absorbent to avoid bubbling. Colored water was used in the buret, which was surrounded by a water jacket of constant temperature. All volumes of nitrogen were corrected. Aroclor 1242 was carefully redistilled. To initiate an experiment, the solvent was introduced into the reaction flask. The flask was then placed in the bath. Equilibrium was

(1) This is the 34th in a series of papers concerned with the decomposition of azo and related compounds; for the previous paper in this series, see C. G. Overberger and A. J. Rosenthal, THIS JOURNAL, **82**, 117 (1960).

(2) This paper comprises a portion of a thesis submitted by Pao-kung Chien in partial fulfillment of the requirements for the Master of Science Degree in the Graduate School of the Polytechnic Institute of Brooklyn, June, 1949.

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(4) P. Pascal and L. Normand, *Bull. soc. chim. France*, [4] **9**, 1029, 1059 (1911); [4] **11**, 21 (1912).

(5) M. J. Roedel, U. S. Patent 2,439,528, April 13, 1948.

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(11) T. Curtius, *J. prakt. Chem.*, [2] **39**, 44 (1889).

(12) F. M. Jaeger, *Z. anorg. Chem.*, **101**, 153 (1917).

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(15) T. Curtius, *J. prakt. Chem.*, [2] **85**, 437 (1912).

assumed when no further increases in the volume of the system were noted for 0.5 hour. The system was flushed with purified nitrogen. After flushing with pure nitrogen for 0.5 hour, the azine compound was introduced, the reaction flask was swirled to dissolve the compound, after which the control time and volume were recorded. These combined operations usually took between 20 and 40 seconds. The remainder of the procedure was essentially that reported earlier for the decomposition of azo nitriles.[16]

For the reactions at lower temperatures, purified diphenyl ether was used as the solvent and the reaction flask was heated in a wax-bath. The temperature was regulated to ± 0.1° (Table II).

TABLE II

DECOMPOSITION OF BENZALAZINES IN SOLUTION

Benzalazine	Concn. range, m./l.	k, sec.$^{-1}$ × 10^4
(A) In Aroclor at 287.6 ± 0.2°		
4,4′-Dichloro-	0.08056–.04888	1.31 ± 0.13
2,2′-Dichloro-	.08748–.01917	3.96 ± .40
4,4′-Dimethoxy-	.09502–.03494	0.80 ± .08
Veratralazine	.05236–.05124	0.83 ± .08
Piperonalazine	.01756–.02897	1.03 ± .10
(B) In diphenyl ether		
4,4′-Dichloro[a]	0.03650	0.14 ± 0.01
2,2′-Dichloro[b]	0.00905	0.34 ± 0.03

[a] 259.7° ± 0.1°; E_a kcal./mole 47 ± 4; A, sec.$^{-1}$, 5.03 × 10^{14}; $\Delta S^{\ddagger}$ +4.8 ±3. [b] 261.3° ± 0.1°; E_a 54 ± 4; A, 1.85 × 10^{18}; $\Delta S^{\ddagger}$ +10.0 ± 2.8.

II. Results and Discussion.—The decomposition of 4,4′-dichloro-, 2,2′-dichloro-, 4,4′-dimethoxy-, veratralazine and piperonalazine was carried out in Aroclor 1242 at 287.6 ± 0.2°. The decomposition of the 4,4′-dichloro- and the 2,2′-dichloroazines was also carried out at 260° in diphenyl ether. The results are summarized in Table II.

None of the benzalazines decomposed to give the theoretical amount of nitrogen. The amounts varied from 76 to 91% of the theoretical amount.

TABLE III

DECOMPOSITIONS OF BENZALAZINES IN AROCLOR

Benzalazine concn. m./l.	Theor. vol. of N_2, S. T. P.	Heating time, hr.	Vol. of N_2[a] observed S. T. P.	% N_2 evolved
4,4′-Dichloro- 0.002014	45.11	10	41.18	91.29
2,2′-Dichloro- 0.002187	48.99	4	39.07	79.74
Anisalazine 0.002376	53.21	20	45.81	86.10
Veratralazine 0.001309	29.32	23	25.78	87.94
Piperonalazine 0.0007243	16.23	24	12.46	76.78

[a] Value taken after no further volume increases were noted in from 2 to 6 hours.

(16) C. G. Overberger, M. T. O'Shaughnessy and H. Shalit, THIS JOURNAL, 71, 2661 (1949).

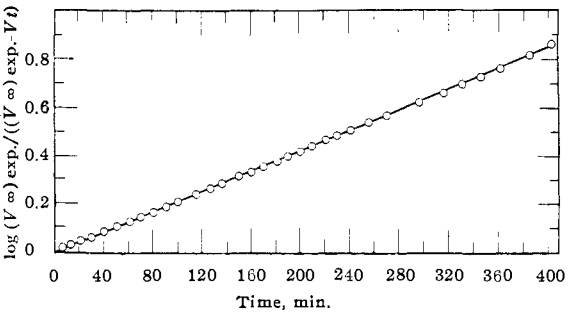

Fig. 1.—Decomposition of of anisalazine in Aroclor at 287.6 ± 0.2°; k = 0.808 × 10^{-4} sec.$^{-1}$.

It is nevertheless apparent that this is the main route of decomposition. Part of this discrepancy is undoubtedly due to the high temperature necessary for the decomposition resulting in some carbonization. The data are summarized in Table III.

A side reaction, loss of *ortho*-hydrogen to give ammonia, was determined semi-quantitatively by passing the evolved gases over standard acid (see Experimental Section). Two substituted benzalazines were studied in this manner and the results are summarized in Table IV. Hydrogen chloride was evolved upon decomposition of 2,2′-dichlorobenzalazine. This could be formed by combining the *ortho*-hydrogen atom at one ring and the *ortho*-chlorine of the other. Upon heating 2,2′-dichlorobenzalazine for 4.5 to 5.5 hours 17.10 to 18.52% of acid was evolved; 4,4′-dichlorobenzalazine gave only 3.98 to 4.41% of ammonia on heating for 17 to 23 hours. The rate of ammonia formation is much slower than that of loss of azine nitrogen.

TABLE IV

DECOMPOSITION OF BENZALAZINES IN AROCLOR

Benzalazine concn. m./l.	Heating, hr.	% NH_3[a] evolved
4,4′-Dichloro		
0.003758	17	3.98
0.00650	23	4.91
Veratralazine		
0.003944	20	12.70

[a] Blank experiments carried out with distilled H_2O as absorbent; no acid or ammonia found.

An estimation of errors such as variation in temperature control, volume readings, change in atmospheric pressure during an experiment, errors involved in determining control time and in the temperature buret are small but probably cumulative. A probable error of about 10% is estimated for the rate constants.

The results strongly indicate a first-order reaction. The detailed kinetic data are available on request. A representative curve is shown in Fig. 1. Although concentration of azine was not varied as much as might be desired, a fourfold variation does not materially affect the rate constant.

The data in Table II show that the effect of

substituents on the rate of decomposition is small. Electron-repelling substituents seem to cause slightly slower rates of decomposition.

The energy of activation for 4,4′-dichlorobenzalazine was 47 ± 4 kcal. per mole and that of 2,2′-dichlorobenzalazine 54 ± 4 kcal. per mole. The entropies of activation are positive and between 4 and 10 entropy units. The high activation energy is in accord with the difficulty in breaking the —C=N bond. The positive entropy of activation indicates that a cyclic mechanism which can be written for this decomposition probably is not operative.[17]

(17) The original work on this problem was carried out in 1948 and 1949, but since product analyses were not completed the research was not published. Recently an excellent detailed analysis of the products and reaction mechanism has been completed by Zimmerman and Somasekhara, THIS JOURNAL, **82**, 5865 (1960). Our kinetic data are not in conflict with their proposed mechanism.

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Conformational Analysis. XI. The Conformers of 2-Chlorocyclohexanone[1,2]

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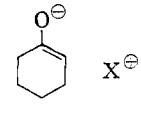
The *cis* and *trans* isomers of 2-chloro-4-*t*-butylcyclohexanone have been prepared and their structures have been assigned from their dipole moments. The infrared and ultraviolet spectra have been determined and differ in a manner analogous to that found earlier for the corresponding bromo compounds. The same properties have been measured for 2-chlorocyclohexanone. Using the data from the conformationally pure substituted compounds, the position of the conformational equilibrium in 2-chlorocyclohexanone has been determined in several independent ways. The isomers of 2-chloro-4-*t*-butylcyclohexanone have been equilibrated by treatment with anhydrous hydrogen chloride, and the position of equilibrium is similar to that found with 2-chlorocyclohexanone. These equilibria shift with changes in concentration, solvent and temperature. A consistent interpretation of the data is given.

Introduction

The original suggestion that the axial or equatorial configuration of a halogen (bromine) adjacent to a ketone could be determined from the frequency of the carbonyl absorption in the infrared was due to Jones and his co-workers.[3] Corey[4] applied this criterion to determine the conformations of various 2-halocyclohexanones, including 2-chlorocyclohexanone itself. Although cyclohexanone is often described as simple when contrasted with the steroids, the reverse is usually true with regards to conformational isomerism. In steroidal systems it is known that the introduction of a chlorine atom next to a carbonyl group causes a shift in the carbonyl absorption of 2–9 cm.$^{-1}$ if the chlorine is axial, but of 18–25 cm.$^{-1}$ if the chlorine is equatorial.[5]

Extensive studies have already been carried out with the related 2-bromocyclohexanone and the conformationally pure *cis*- and *trans*-4-*t*-butylcyclohexanones, and it was shown that when the same conformational arrangements are compared there is a nearly perfect correspondence in spectral properties between the monocyclic and steroidal compounds.[6–11] It therefore seems reasonable that such a correspondence would follow in the chloro series, yet the possibility of a reversal in spectral properties upon going from the monocyclic systems to the steroids has been suggested.[12]

The dipole moments of 2-bromo- and 2-chlorocyclohexanone were measured by Kumler and Huitric in different solvents.[10] It was found, somewhat unexpectedly, that the bromo compound consistently showed the smaller moment. An interpretation which was suggested was that the bromine atom tends to be in the axial position to a greater extent than does the chlorine atom. Since C–Br and C–Cl bonds have the same dipole moments, the steric effect was expected to dictate the relative positions of equilibria, but the results did not appear to correspond to the predictions. Corey and Burke[13] had previously noted cases of 2-halocyclohexanones in which chlorine seemed to show a greater preference for the equatorial position than did bromine, and they suggested that a reason for the apparent anomaly might be found in the valence bond structure I. Since this resonance would be



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expected to be more important when X was bromine, and could best occur when the halogen was axial, the effect of such resonance would be to shift the equatorial ⇄ axial equilibrium further to the right for the bromo compound.

An apparent analogy to the halo ketones exists with the *trans*-1,2-dihalocyclohexanes. The di-

(1) Paper X, N. L. Allinger and L. A. Freiberg, THIS JOURNAL, **82**, 2393 (1960).

(2) This Research was supported by the Office of Ordnance Research, U. S. Army, under Contracts No. DA-20-018-ORD-14652 and No. DA-20-018-ORD-20046.

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