Temperature: 60.0°; 5.05-ml. aliquots at 24°; [bromotetralone]: 0.0200 *M*; [NEt_4Br]: 0.00955 *M*; titers are in ml. of 0.0100 *M* silver nitrate; the initial [NEt_4Br] is equivalent to a titer of 4.82 ml.; the integrated first-order rate coefficients, k_1 (sec.$^{-1}$), are calculated with respect to the bromotetralone I

Time, min.	0	8	20	40	60	90	180
Titer	5.16	5.50	6.01	6.65	7.12	7.72	8.61
$10^5 k_1$	..	7.3	7.6	6.9	6.2	5.6	4.0

By extrapolation to zero reaction of a plot of k_1 against the extent of reaction, expressed in ml. of 0.0100 *M* Br^- produced, an initial value for k_1 of 8.5×10^{-5} sec.$^{-1}$ is obtained, corresponding to an initial second-order coefficient of 8.9×10^{-3} l. moles^{-1} sec.$^{-1}$

an 81% yield calculated as unsaturated ketone, was obtained. A solution in acetonitrile of a portion of the product gave a slight precipitate with silver nitrate indicating the presence of a trace of unreacted bromotetralone I.[2c] The melting point of the crude product was 105–109°. After recrystallization of a portion from methanol the melting point 113–114° corresponded to that for pure endocyclic unsaturated ketone II[2a]; the recrystallized product gave no precipitate with an acetonitrile solution of silver nitrate.

The infrared spectrum of the crude product had $\gamma_{C=O}$ 1662/95, corresponding to the endocyclic unsaturated ketone II.[2a] No disturbance was observed at 1673 cm.$^{-1}$, where the exocyclic unsaturated ketone III would give a peak.[2a] A small shoulder was observed at $\gamma_{C=O}$ 1687/38, where the reactant bromotetralone I shows a peak.[2a] The recrystallized material had $\gamma_{C=O}$ 1663/96 and no shoulder at 1687 cm.$^{-1}$, where the absorption was 28%. The ultraviolet spectrum of the crude product had the form predicted for endocyclic unsaturated ketone II[2a]; λ_{max} 254 mμ (ε 14,800); λ_{min} 228 mμ (ε 8,200).

The ultraviolet spectra of II and III are quite different in character[2a] and in particular in the region 320–340 mμ III absorbs strongly while II has virtually no absorption. Absorption in this region was found to be extremely low.

(B) **Elimination Promoted by Piperidine Hydrobromide.**—Twenty-five ml. of a solution initially 0.0200 *M* in bromotetralone I and 0.00500 *M* in piperidine hydrobromide was left for 13 days at 60.0° and the solution then evaporated to dryness. After ether extraction the filtrate was evaporated to dryness. A 0.10-g. amount of brownish residue was isolated. The yield calculated as unsaturated ketone was 77%. The infrared spectrum of the crude material had $\gamma_{C=O}$ 1663/92 and a shoulder 1686/41 with no disturbance at 1673 cm.$^{-1}$. The product was endocyclic unsaturated ketone II with a little unreacted bromotetralone I.[2a] On recrystallization from methanol a white solid, m.p. 111–112°, was obtained which was endocyclic unsaturated ketone II.[2a]

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[CONTRIBUTION FROM AVERY LABORATORY, UNIVERSITY OF NEBRASKA, LINCOLN 8, NEBR.]

Elimination Reactions of α-Halogenated Ketones. VI.[1] Kinetics of Piperidine Promoted Elimination from 2-Benzyl-2-bromo-4,4-dimethyl-1-tetralone in Solvent Acetonitrile

BY DENNIS N. KEVILL AND NORMAN H. CROMWELL

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2-Benzyl-2-bromo-4,4-dimethyl-1-tetralone (I) has been found to undergo a facile piperidine-promoted elimination in solvent acetonitrile to yield mainly the endocyclic α,β-unsaturated ketone, 2-benzyl-4,4-dimethyl-1-keto-1,4-dihydronaphthalene (II) together with a smaller amount of the exocyclic α,β-unsaturated ketone 2-benzal-4,4-dimethyl-1-tetralone (III). The reaction was found to be kinetically of first order in the bromotetralone I and of both a zero order and a first order component in piperidine. A merged substitution and elimination mechanism for the dehydrobromination reactions of bromotetralone I is proposed.

Introduction.—It has been shown in a previous publication[2b] that dehydrobromination of 2-benzyl-2-bromo-4,4-dimethyl-1-tetralone (I) with amines leads to mainly the endocyclic α,β-unsaturated ketone, 2-benzyl-4,4-dimethyl-1-keto-1,4-dihydronaphthalene (II) together with some of the exocyclic α,β-unsaturated ketone, 2-benzal-4,4-dimethyl-1-tetralone (III).

Discussion of Results

This investigation shows that the actual composition ratios in the product must be treated with reservation as regards representation of the way in which the piperidine-promoted elimination reaction divides between the two unsaturated ketones. As reaction proceeds a bromide ion-promoted elimination reaction becomes of increasing importance and this reaction has been shown[1] to produce only the endocyclic unsaturated ketone II. In this investigation an acetonitrile solution 0.0200 *M* in bromotetralone I and 0.0400 *M* in piperidine after reacting to completion at 60.0° gave 87% of II and 13% of III. The figure of 13% must, however, be regarded as only a minimum figure for the percentage of *exo*-elimination in the piperidine promoted reaction.

The elimination reaction promoted by piperidine was found to be kinetically first order in bromotetralone I but of indefinite order in piperidine. The order in piperidine was found to consist of two components, one of zero order and one of first order. The velocity of the piperidine promoted elimination reaction (v) could be expressed

$$v = [\text{bromotetralone}](k_1^0 + k_2^0[\text{piperidine}])$$

where k_1^0 and k_2^0 are the first- and second-order rate coefficients for the piperidine promoted elimination. During each individual run the kinetics were complicated by an autocatalysis due to the formation of piperidine hydrobromide.[1] To avoid consideration of this intervention, the kinetic data were analyzed in terms of initial values for the rate coefficients.

(1) For paper V in this series see D. N. Kevill and N. H. Cromwell, *J. Am. Chem. Soc.*, **83**, 3812 (1961).

(2) (a) A. Hassner and N. H. Cromwell, *ibid.*, **80**, 893 (1958); (b) **80**, 901 (1958); (c) N. H. Cromwell, R. P. Ayer and P. W. Foster, *ibid.*, **82**, 130 (1960).

Although piperidine does not enter into the rate equation for the first-order reaction, it must in some way enter into the mechanism which leads to this rate equation since the value at 60.0° for the first-order rate coefficient in the presence of piperidine, 7.1×10^{-6} sec.$^{-1}$, is considerably greater than the first-order rate coefficient for the self-decomposition of the bromotetralone I in acetonitrile at 60.0°, 3.2×10^{-7} sec.$^{-1}$.[1]

The frequency factors for both the first and second order rate coefficients, $10^{5.7}$ sec.$^{-1}$ and $10^{5.3}$ liters moles^{-1} sec.$^{-1}$, respectively, are somewhat low in value as would be predicted for reaction between two formally uncharged species. The activation energy for the first-order process is 16.5 kcal./mole and for the second-order process 12.1 kcal./mole. A rise in temperature will increasingly favor the first-order process over the second-order process.

Mechanism of Dehydrobromination Reactions of 2-Benzyl-2-bromo-4,4-dimethyl-1-tetralone (I) in Solvent Acetonitrile.—Consideration of the product studies and especially of the kinetic data for dehydrobromination of the bromotetralone I as promoted by both bromide ions and by piperidine allows conclusions to be drawn concerning the mechanism of the dehydrobromination reactions.

Bromide ions have been shown[1] to promote dehydrobromination of the bromotetralone I with formation of the endocyclic unsaturated ketone II; only bromide ions possessing at least a certain degree of freedom are capable of promoting the elimination reaction, those bound in ion-pairs being ineffective.

Piperidine-promoted elimination has both a zero-order and a first-order component as regards the piperidine concentration. The presence of a first-order component (zero order in piperidine) to the kinetics suggests that a fairly facile rupture, or at least elongation, of the axial bromine–carbon bond[2] can occur and it is probable that even in bimolecular reaction a considerable bond elongation occurs prior to reaction.

It is suggested that in the dehydrobromination reactions of the bromotetralone I the first stage is an elongation of the axial bromine–carbon bond

$$R\text{-}Br \underset{\longleftarrow}{\overset{1}{\longrightarrow}} R^{\delta+}\text{-----}Br^{\delta-}$$

The intermediate can then either collapse to return to the unactivated bromotetralone I or alternatively it can undergo reaction. In the self-decomposition reaction it is not known whether the subsequent decomposition is promoted by attack of solvent acetonitrile molecules or whether the decomposition is truly unimolecular. Irrespective of mechanism, however, the rate of self-decomposition is lower than the rate of first-order decomposition in the presence of piperidine and it is necessary to assume that the piperidine assists in the first-order component of the reaction in other than the rate-determining step. It is proposed that in the general case the second stage in the mechanism is the attack of a nucleophilic reagent upon the activated intermediate

$$X^- + R^{\delta+}\text{-----}Br^{\delta-} \underset{\longleftarrow}{\overset{2}{\longrightarrow}} \underset{A}{X^{\delta-}\text{---}R^{\delta+}\text{-------}Br^{\delta-}}$$

Attack produces what is essentially an ion-pair (A) with, however, the probable existence of weakly developed covalent binding and the possible retention of weak binding to the outgoing group. Whether the kinetics observed are of first or second order depends upon the relative rates of these first and second stages of the mechanism.

Attack by negatively charged bromide ions at the positively charged carbon center of the activated intermediate previously formed in the first stage will be favored and especially favored will be attack by bromide ions possessing a considerable degree of freedom from association with a cation. The proposed picture is consistent with the finding that only sufficiently dissociated bromide ions promote elimination.

In piperidine-promoted elimination the formally uncharged piperidine molecules will be less favored than negatively charged nucleophiles as regards orientation for attack at the positively charged center of the activated intermediate. It is found that in some instances sufficient elongation of the carbon–bromine bond occurs prior to attack by a piperidine molecule for the first stage of the mechanism to be rate determining. It is, however, proposed that, whether the first or second stage of the mechanism is rate determining, piperidine enters into the mechanism in much the same way by promoting reaction of an activated intermediate as an alternative to deactivation.

The weakly bound A can be considered as an intermediate which either collapses to give substitution products or alternatively the nucleophile abstracts a β-proton. The elimination reaction will be especially favored if steric factors inhibit collapse to the substitution product. As proposed the mechanism has the characteristics of a borderline SN1–SN2 mechanism, but the nucleophilic attack is finally diverted from the carbon atom center to the axial β-hydrogen atom. It appears that the piperidine molecule is sufficiently inhibited as regards close approach to the positively charged carbon center for abstraction of a β-proton to provide the sole reaction path. When the attacking agent is a base Y, such as piperidine, some coördination of Y with the carbonyl carbon of the α-halogenated ketones in the transition state is also to be expected (see Fig. 1).

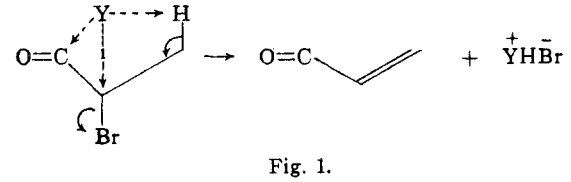


Fig. 1.

This scheme is a more detailed description of the mechanism first suggested for such reactions of α-halogenated ketones.[3]

It is not proposed that all elimination reactions proceed through this type of merged substitution

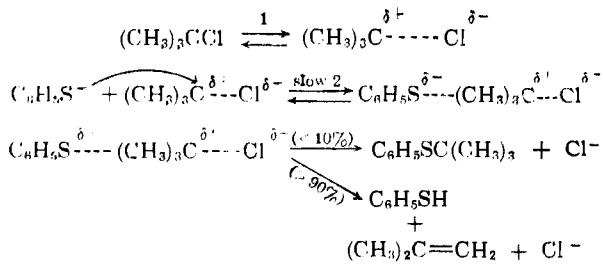
(3) A. Hassner, N. H. Cromwell and S. J. Davis, *J. Am. Chem. Soc.*, **79**, 230 (1957).

and elimination mechanism. There probably exists a whole spectrum of elimination mechanisms with a gradual gradation away from mechanisms with pure E2 characteristics as increasing amounts of SN2 character enter into the mechanism which, however, eventually leads to an elimination product. Indeed it is further possible that this mechanism represents only one of several types of merged substitution and elimination mechanisms.[4]

It is, however, predicted that under favorable circumstances various reactions will proceed by this type of merged substitution and elimination mechanism.

At least one apparent anomaly in the literature occurs for a reaction favorable to this type of merged substitution and elimination mechanism. De la Mare and Vernon tentatively proposed an E2 mechanism for reaction of *t*-butyl chloride and thiophenoxide ions in ethanol.[5] Reaction yielded about 90% olefin and only a small amount of the substitution product *t*-butyl phenyl sulfide. The bimolecular elimination reaction proceeded at an abnormally large rate when considered as an E2 attack by somewhat weakly basic but strongly nucleophilic thiophenoxide ions at a carbon atom center.

The *t*-butyl chloride was present in a polar solvent with possibility of considerable dipolar development in the carbon–chlorine bond prior to reaction. Further, steric hindrance to bimolecular substitution at the carbon center is common to tertiary structures, and the thiophenoxide ion although strongly nucleophilic is somewhat bulky. Finally, no fewer than nine β-protons are available for abstraction as an alternative to collapse of the *t*-butyl-thiophenoxide ion-pair.



Experimental Results

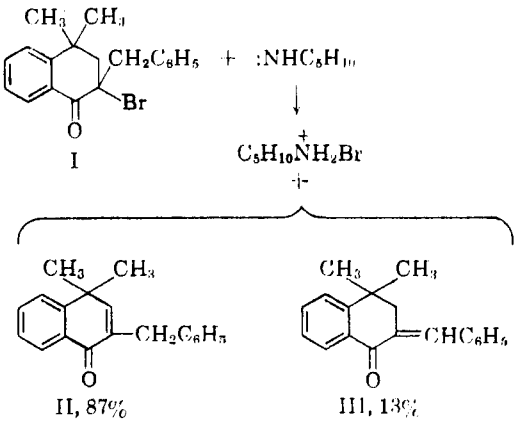
The concentrations quoted in this paper are uncorrected for expansion of the solvent from room temperature to the reaction temperature. Other entities which are concentration dependent are similarly uncorrected.

2-Benzyl-2-bromo-4,4-dimethyl-1-tetralone (I) has been shown to give fairly stable solutions in acetonitrile.[1] When piperidine is also present in solution decomposition is greatly accelerated and the kinetics of this decomposition reaction have been investigated.

(4) S. Winstein, D. Darwish and H. J. Holness, *J. Am. Chem. Soc.*, **78**, 2915 (1956).

(5) (a) P. B. D. de la Mare and C. A. Vernon, *J. Chem. Soc.*, 41 (1956); (b) E. L. Eliel and R. S. Ro, *Tetrahedron*, **2**, 353 (1958), in supporting the mechanism proposed by Winstein,[4] stated, "The operation of the merged mechanism may well be responsible for the remarkably high elimination rates observed in the reaction of cyclohexyl tosylate, *cis*-4-*t*-butyl-cyclohexyl tosylate and *t*-butyl chloride with sodium thiophenolate."

Reaction at 60.0° of an acetonitrile solution 0.0200 *M* in bromotetralone I and 0.0400 *M* in piperidine for 100 hours gave at least a 73% yield, calculated as unsaturated ketone, of a pale yellow solid. Analysis of the ultraviolet spectrum indicated the product to consist of 87% endocyclic unsaturated ketone II together with 13% of the exocyclic unsaturated ketone III. No evidence for any substitution product was found. The reaction scheme can be expressed



A solution, in acetonitrile at 60.0°, 0.0100 *M* in bromotetralone I and 0.0200 *M* in piperidine, was found by titration against standard hydrochloric acid in methanol to have after 3 days 48% of the initial piperidine concentration remaining. After 6 days 47% of the initial piperidine concentration remained. It appears that essentially one piperidine molecule is neutralized for each bromotetralone molecule which decomposes. It further appears that over relatively long periods of time a slow side reaction also removes a little piperidine from solution.

The kinetics of the elimination reaction have been followed both by titration of the rate of disappearance of piperidine from solution and by titration of the rate of appearance of bromide ions in solution. For any given set of reaction conditions both titration techniques lead to identical results.

The kinetic results were analyzed in terms of integrated second-order coefficients. The coefficients were found to rise in value throughout each individual run and further at a given temperature their initial values obtained by extrapolation to zero extent of reaction fell in value as the concentration of piperidine increased. The piperidine-promoted elimination reaction appears kinetically to have both a first- and a second-order component, with further complication due to autocatalysis resulting from the formation during the reaction of piperidine hydrobromide which has previously been shown to promote elimination from the bromotetralone I.

At a given temperature the mixed-order kinetics can be expressed by the relationship

$$k_2[\text{bromotetralone}][\text{piperidine}] = k_1^0[\text{bromotetralone}] + k_2^0[\text{bromotetralone}][\text{piperidine}]$$

A plot of the initial values for the second-order coefficient k_2 against the reciprocal of the piperidine concentration for the runs at 60.0° was found to be

TABLE I

INITIAL VALUES FOR THE SECOND-ORDER RATE COEFFICIENTS FOR PIPERIDINE NEUTRALIZATION, $k_2^{(H^+)}$ (LITERS MOLES^{-1} SEC.$^{-1}$), AND FOR THE SECOND-ORDER RATE COEFFICIENT FOR BROMIDE ION PRODUCTION, $k_2^{(Br^-)}$ (LITERS MOLES^{-1} SEC.$^{-1}$), IN THE REACTION OF 2-BENZYL-2-BROMO-4,4-DIMETHYL-1-TETRALONE (I) WITH PIPERIDINE IN SOLVENT ACETONITRILE AT VARIOUS TEMPERATURES

t, °C.	[Bromotetralone]	[Piperidine]	$10^3\ k_2^{(Br^-)}$	$10^3\ k_2^{(H^+)}$
29.0	0.0100	0.00250	..	0.57
29.0	.0100	.0100	..	0.41
60.0	.0100	.00250	..	4.6
60.0	.0200	.00250	4.4	...
60.0	.00500	.00500	..	3.2
60.0	.0100	.00500	..	3.2
60.0	.0200	.00500	3.5	3.5
60.0	.0100	.0100	..	2.8
60.0	.0200	.0100	2.7	...
60.0	.0100	.0200	..	2.3
60.0	.0200	.0200	2.3	...
60.0	.0200	.0400	..	2.0
75.0	.0100	.00500	..	9.0
75.0	.0100	.0200	..	5.8
90.3	.00500	.00500	..	19.8
90.3	.0200	.00500	..	22.2
90.3	.0200	.0400	..	11.9

linear, consistent with the proposed mixed-order reaction path

$$k_2 = k_2^0 + k_1^0[\text{piperidine}]^{-1}$$

Values for the first-order rate coefficient, k_1^0 and the second-order rate coefficient, k_2^0, were obtained from the slope and intercept of the plot; values were obtained similarly at each of the other three temperatures which were briefly studied.

TABLE II

VALUES FOR THE FIRST-ORDER RATE COEFFICIENT, k_1^0 (SEC.$^{-1}$), AND THE SECOND-ORDER RATE COEFFICIENT, k_2^0 (LITERS MOLES^{-1} SEC.$^{-1}$), FOR ACID PRODUCTION IN THE MIXED-ORDER REACTION OF 2-BENZYL-2-BROMO-4,4-DIMETHYL-1-TETRALONE WITH PIPERIDINE IN SOLVENT ACETONITRILE AT VARIOUS TEMPERATURES

t, °C.	29.0	60.0	75.0	90.3
$10^6\ k_1^0$	0.55	7.1	21.5	52
$10^3\ k_2^0$	0.35	1.9	4.7	10.1

Arrhenius plots of both the first-order and the second-order coefficients were linear. The first-order rate coefficient, k_1^0, gave values for the frequency factor of $10^{5.7}$ and for the activation energy of 16.5 kcal./mole. The second-order rate coefficient, k_2^0, gave values for the frequency factor of $10^{5.3}$ and for the activation energy of 12.1 kcal./mole.

Experimental Methods

Materials.—Preparation of the 2-benzyl-2-bromo-4,4-dimethyl-1-tetralone has been described previously.[1] Technical grade piperidine was dried over potassium hydroxide and fractionated. The middle fraction was dried over sodium wire and refractionated. The acetonitrile used was Matheson, Coleman and Bell spectroquality reagent.

Kinetic Methods.—All runs were carried out by means of the sealed bulb technique. The sealed bulbs were prepared from 16 × 150 mm. test-tubes and each aliquot of reaction mixture was of 5.05 ml. at room temperature. After each bulb was removed from the thermostat, reaction was quenched by immersion in solid CO_2–alcohol slush until analyzed.

Measurement of the Rate of Disappearance of Piperidine from Solution.—Analysis was by titration in 20 ml. of acetone, previously rendered neutral to the Lacmoid indicator against a standard solution of hydrogen chloride in methanol.

The analyses of a few runs illustrating the method of obtaining initial values for the rate coefficient from the determination of the extent of olefin formation by piperidine concentration measurements are given below.

In each case the integrated second-order rate coefficients k_2 (liters moles^{-1} sec.$^{-1}$), are calculated with respect to the bromotetralone I and to piperidine, and an initial value for the second order rate coefficient, k_2 (liters moles^{-1} sec.$^{-1}$), is obtained by extrapolation to zero extent of reaction of a plot of k_2 against the extent of reaction, expressed as ml. of standard hydrogen ion produced as determined by titration of remaining piperidine.

(A) Temperature: 60.0°; 5.05-ml. aliquots at 24°; [bromotetralone]: 0.0200 *M*; [piperidine]: 0.00500 *M*; titers are in ml. of 0.0105 *M* HCl

Time, min.	0	22	44	66	88	132	262
Titer	2.22	2.02	1.82	1.63	1.47	1.13	0.19
$10^3\ k_2$	..	3.7	3.9	4.1	4.2	4.7	9.4

Initial k_2 is 3.5×10^{-3} l. moles^{-1} sec.$^{-1}$

(B) Temperature: 60.0°; 5.05-ml. aliquots at 24°; [bromotetralone]: 0.0200 *M*; [piperidine]: 0.0400 *M*; titers are in ml. of 0.0525 *M* HCl

Time, min.	0	30	60	90	146	276	342
Titer	3.61	3.36	3.12	2.95	2.67	2.21	2.11
$10^3\ k_2$	..	2.2	2.4	2.6	2.8	3.6	3.7

Initial k_2 is 2.0×10^{-3} l. moles^{-1} sec.$^{-1}$

(C) Temperature: 90.3°; 5.05-ml. aliquots at 24°; [bromotetralone]: 0.00500 *M*; [piperidine]: 0.00500 *M*; titers are in ml. of 0.0105 *M* HCl

Time, min.	0	14	24	36	48	76	100
Titer	2.34	2.16	2.04	1.90	1.74	1.41	1.14
$10^3\ k_2$	..	20.3	20.9	22.0	24.6	29.6	36.0

Initial k_2 is 19.8×10^{-3} l. moles^{-1} sec.$^{-1}$

Measurement of the Rate of Formation of Bromide Ion in Solution.—Several runs were analyzed by means of potentiometric titration against standard aqueous silver nitrate in a titration medium consisting of 30 ml. of acetone containing about 1 ml. of 1 *N* nitric acid. A silver wire electrode and a potassium nitrate–agar bridge to a dip-type calomel reference electrode were used. The analyses of two runs illustrating the determination of the extent of reaction through bromide ion development are given below.

In each case the integrated second-order rate coefficients, k_2 (liters moles^{-1} sec.$^{-1}$), are calculated with respect to the bromotetralone I and to piperidine and an initial value for the second-order coefficient is obtained by extrapolation to zero reaction of a plot of k_2 against the extent of reaction, expressed in ml. of standard bromide ion produced as determined by titration.

(A) Temperature: 60.0°; 5.05-ml. aliquots at 24°; [bromotetralone]: 0.0200 *M*; [piperidine]: 0.00500 *M*; titers are in ml. of 0.0100 *M* $AgNO_3$

Time, min.	0	28	46	76	132	186	270
Titer	0.15	0.37	0.58	0.81	1.25	1.59	2.22
$10^3\ k_2$	..	(2.9)	3.7	3.9	4.2	4.7	7.4

Initial k_2 is 3.5×10^{-3} l. moles^{-1} sec^{-1}

(B) Temperature: 60.0°; 5.05-ml. aliquots at 24°; [bromotetralone]: 0.0200 *M*; [piperidine]: 0.0100 *M*; titers are in ml. of 0.0100 *M* $AgNO_3$

Time, min.	0	30	68	96	136	211	278
Titer	0.15	0.60	1.07	1.43	1.88	2.66	3.33
$10^3\ k_2$	..	2.8	2.7	2.9	3.0	3.4	4.0

Initial k_2 is 2.7×10^{-3} l. moles^{-1} sec.$^{-1}$

Product Studies.[6]—A 60-ml. solution of 0.0200 *M* in bromotetralone I and 0.0400 *M* in piperidine was allowed to react for 100 hours at 60.0°. The solution was evaporated to dryness. After ether extraction of the residue the filtrate was evaporated to dryness. A 0.230-g. amount of a pale yellow solid was obtained. This represented a 73% yield, calculated as unsaturated ketone. A solution of a portion in acetonitrile gave no precipitate with an acetonitrile solution of silver nitrate, indicating the absence of any unreacted bromotetralone I.[2c] The melting point was indefinite, but complete melting occurred lower than 109°. A portion recrystallized from methanol gave a white solid, m.p. 112–113°, the endocyclic unsaturated ketone II.[1]

The infrared spectrum of the crude product had $\gamma_{C=O}$ 1662/95 corresponding to the endocyclic unsaturated ketone II[2a]; no other carbonyl peaks or shoulders were present.

The ultraviolet spectrum had considerable absorption in the region 320–340 mμ, where the exocyclic unsaturated ketone III absorbs strongly and where the endocyclic unsaturated ketone II has virtually no absorption.[2a] A detailed comparison of the ultraviolet spectrum with those of the pure components II and III showed the product to be a mixture of 87% endocyclic unsaturated ketone II and 13% exocyclic unsaturated ketone III.

(6) Melting points were read with a calibrated thermometer. Ultraviolet absorption spectra were determined with a Cary model 11-MS recording spectrophotometer using reagent grade methanol solutions. Infrared spectra were measured with a Perkin-Elmer model 21 double beam recording instrument employing sodium chloride optics and matched sodium chloride cells with carbon tetrachloride solutions.

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE SPRAGUE ELECTRIC CO., NORTH ADAMS, MASS.]

Solvent Effects in the Decomposition of 1,1'-Diphenylazoethane and 2,2'-Azobis-(2-methylpropionitrile)

BY RAYMOND C. PETERSEN, J. HODGE MARKGRAF[1] AND SIDNEY D. ROSS

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Rates of decomposition of 1,1'-diphenylazoethane and 2,2'-azobis-(2-methylpropionitrile) were measured by a very precise technique in several solvents. Significant differences in rate were found, but no simple structural order was evident. A linear relationship was observed between enthalpy and entropy of activation for 2,2'-azobis-(2-methylpropionitrile) in four solvents, but this observation was dismissed as a likely consequence of experimental error. The relationship between errors in rate constants and errors in activation parameters is discussed in detail.

The thermal decomposition of azo compounds in solution is a first-order reaction.[2,3] The rate has been found by many workers to be nearly independent of the medium, while others claim to observe differences in rate in different solvents.

Lewis and Matheson,[4] Overberger, *et al.*,[5] and Arnett[6] offer the conclusion that the rate of decomposition of various azo compounds, including 2,2'-azobis-(2-methylpropionitrile) in each case, is independent of the solvent. The work of Leffler, *et al.*,[7-9] presents an example of a study which led to the conclusion that there are significant rate differences in different solvents. In the decomposition of phenylazotriphenylmethane in several solvents[7,8] it was concluded that the difference lies in solvation of the reactant molecule through complex formation and that in each case the activation process probably involves desolvation. In the case of *p*-nitrophenylazotris-(*p*-anisyl)-methane[9] it was inferred that some solvents solvate the transition state more than the ground state of the reactant molecule while other solvents function in the opposite manner.

These observations are, of course, limited by experimental errors which are often quite large, and it is recognized that apparent variations in rate may be merely reflections of experimental inaccuracies and that random errors in turn may obscure real rate changes.

The present work represents a study of solvent effects on the rate of the thermal decomposition of two azo compounds, 1,1'-diphenylazoethane and 2,2'-azobis-(2-methylpropionitrile), utilizing a precise measuring technique and striving for accuracy approaching the precision of the technique.

Experimental

Rate Measurement.—Rates of decomposition were determined by measuring nitrogen evolution as a function of time. The measuring apparatus is outlined in Fig. 1. It consists of a reaction cell, gas buret and manometer with a leveling bulb to adjust the mercury in the manometer and buret.

A solution of azo compound was prepared by weight and a known quantity by weight was transferred to the cell. The cell was connected to the measuring system through a standard taper joint and nitrogen was bubbled through the solution, saturating the solution and replacing the air in the measuring system. The nitrogen, which enters the system through stopcock A, leaves through stopcock B, then passes through a bubbler containing a high-boiling liquid to prevent diffusion of air back into the system.

After bubbling N_2 for at least 0.5 hour, stopcock A was closed, the mercury level in the buret was raised to a point near zero and stopcock B was closed. Stopcock C remains open throughout the procedure, its purpose being to aid in detection of leaks and in calibration.

The cell, connected to the measuring system through long capillary tubing and short flexible couplings, was placed in a constant-temperature bath and magnetic stirring was begun. Measurements of buret volume readings and buret (room) temperature were made at constant pressure, using the mercury-leveling bulb, the manometer with a scale and a barometer. Bath temperature varied in a regular cycle by about ±0.1° around the central temperature.

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