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The Thermal Decomposition of 2,2'-Azo-bis-isobutyronitrile. Part II. Kinetics of the Reaction

BY M. TALÂT-ERBEN[1] AND S. BYWATER

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The kinetics of the thermal decomposition of 2,2'-azo-bis-isobutyronitrile have been investigated using an ultraviolet absorption technique. Kinetic analysis of the optical density changes at 320 mμ confirm the evidence given in Part I, that a ketenimine is formed in the reaction by an abnormal radical recombination reaction.

The over-all kinetics of the thermal decomposition of 2,2'-azo-bis-isobutyronitrile has been studied by several workers.[2–6] The rate of decomposition follows accurately a first-order law, and the rate constants are almost independent of the nature of the solvent. These observations indicate that the reaction is not complicated by attack of the free radicals formed on the azo compound as is the case with many compounds which decompose to give free radicals. Since 2,2'-azo-bis-isobutyronitrile has a symmetrical absorption band in the near ultraviolet ($\lambda_{\max}$ 345 mμ, $E_{\max}$ 14.9, in toluene), the rate of decomposition can be followed by changes in the optical density of solutions if measured in this wave length range. This method is not susceptible to the difficulties associated with the gas evolution methods used by previous workers, and has been used in the present work.

Experimental

The decomposition of 2,2'-azo-bis-isobutyronitrile was carried out in toluene (C.P.) solution in a two-necked flask immersed in an oil-bath controlled to ±0.1°. Nitrogen, purified as described in Part I, was passed in a slow stream one-half hour before and during the reaction. The standard taper joint on the nitrogen inlet was closed by a mercury seal since grease was slowly extracted from any greased joint. Excess nitrogen passed out through the side arm which was fitted with an ungreased cap. The azonitrile, lightly compressed into a narrow glass tube, was added through this side arm and dissolved rapidly. Samples were removed at definite times by pipet and cooled quickly to room temperature in a test-tube under running water. The samples were then transferred into 1 cm. quartz optical cells and the optical density (D) was measured at a series of wave lengths between 310–390 mμ using a Beckman D.U. spectrophotometer. A residual optical density measurement was made after 24 hours reaction time (D_∞). The optical density at zero time (D_0) was calculated from the initial concentration and the molar extinction coefficient at the appropriate wave length. Measurements on the pure azo compound showed that the optical density of the solutions was accurately proportional to their concentration in the range used.

Results

Experiments were carried out at five temperatures between 70 and 105° and over a concentration range. At 80.4° the range in concentration was about ten-fold. At wave lengths above 340 mμ, the optical density decreased exponentially with time. Measurements at 360, 370 and 380 mμ were plotted according to the first order equation $\ln(D_0 - D_\infty)/D - D_\infty) = k_1t$. All were good straight lines (Fig. 1) of identical slope. The largest variation in k_1 values at one temperature and different concentrations was around ±2% but usually smaller. The mean values at each temperature are given in Table I and the corresponding Arrhenius plot in Fig. 2. The experimental results are best fitted by the relation $k_1(\text{sec.}^{-1}) = 2.67 \times 10^{15} \exp.(-31.1/RT)$.

Below 340 mμ the optical density first increased with time and then slowly decreased. Measurements of this effect were made at 310 and 320 mμ, since at lower wave lengths toluene is not transparent and at higher wave lengths the azo compound absorbs too strongly. A small correction for the optical density due to the azo compound was made using the measured molar extinction coefficient at these wave lengths and the experimentally determined rate of disappearance of the azo compound. A typical family of curves showing the corrected change in optical density (D^{320}) with time and initial concentration at 80.4° is shown in Fig. 3. Similar sets of curves differing only in the time of the maximum ($t_{\max.}$) were obtained at other temperatures. At every temperature the maximum optical density and initial rate of increase of optical density at the above wave lengths were found to be directly proportional to the first power of the initial azo compound concentration.

The experimental data are summarized in Table I.

TABLE I

REACTION CONSTANTS AT VARIOUS TEMPERATURES

(Time in seconds throughout.)

T (°C.)	$k_1 \times 10^4$	$\frac{10^3}{[\text{azo}]_0}\left(\frac{\text{d}(D^{320})}{\text{d}t}\right)_0$	$\frac{D^{320}_{\text{m}}}{[\text{azo}]_0}$	$t_{\max} \times 10^{-3}$	$k_1t_{\max}$
70.0	0.40	0.81	9.5	29	1.2
80.4	1.55	2.9	9.2	6.6	1.0
90.0	4.86	7.8	9.0	2.2	1.1
100.0	16.0	22.8	8.9	0.6	~1
105.0	26.1				

The initial rates of change of corrected optical density (D^{320}) per unit concentration are plotted logarithmically against reciprocal temperature in Fig. 1, giving an activation energy of 29 ± 2 kg. cal. per mole.

Discussion

The agreement between individual measurements at 360, 370 and 380 mμ indicates that the optical density at these wave lengths is due only to the azonitrile, otherwise the relative contributions would be expected to vary at the three wave lengths and destroy the agreement. This is confirmed by

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(1) National Research Council of Canada Postdoctoral Fellow, 1952–1954. Faculty of Mineral Engineering, Technical University of Istanbul, Turkey.

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

(3) C. E. H. Bawn and S. F. Mellish, *Trans. Faraday Soc.*, **47**, 1216 (1951).

(4) F. M. Lewis and M. S. Matheson, THIS JOURNAL, **71**, 747 (1949).

(5) J. W. Breitenbach and A. Schindler, *Monatsh.*, **83**, 724 (1952).

(6) L. M. Arnett, THIS JOURNAL, **74**, 2027 (1952).

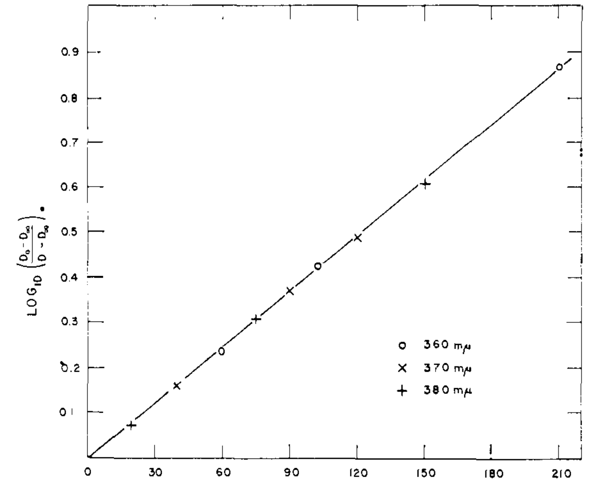

Fig. 1.—A typical first-order plot of optical density changes at 360, 370, 380 mμ.

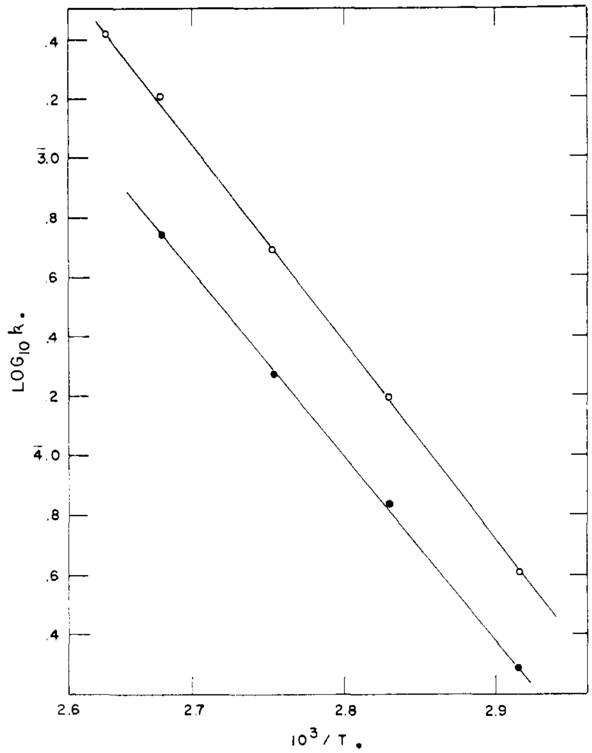

Fig. 2.—Temperature coefficients of k_1 (O), and initial rate of formation of intermediate (●). Arbitrary k units in the latter case.

the fact that the k_1 values obtained check well with those obtained by other methods. The rate constants reported by Bawn[3] at 69.5°, Overberger[2] at 69.8°, Matheson[4] at 80°, and Arnett[6] at 77° are in good agreement with the present work. Those of Overberger at 80.2° and Breitenbach[5] at 70° are about 7 and 17% higher, respectively, and that of Arnett at 82° is about 20% lower. In general the experimental points from this paper together with those of Bawn can be fitted to a good straight line with little scatter of points extending over the temperature range 40–105°.

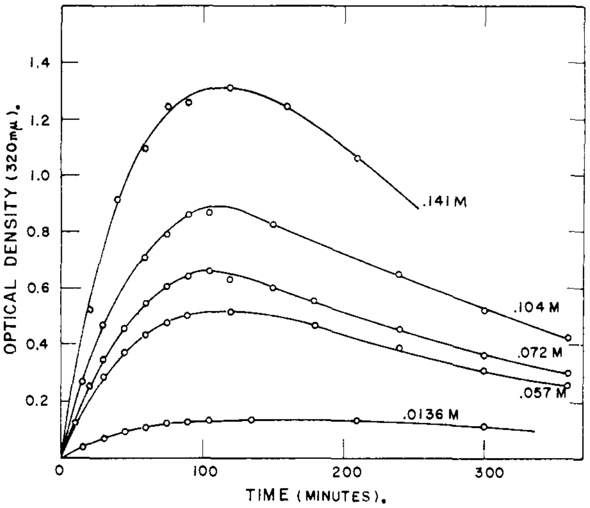

Fig. 3.—A typical set of curves showing optical density changes at 320 mμ, at constant temperature and varying initial azo compound concentration.

Walling[7] has reviewed the published values for k_1 in aromatic solvents and came to the conclusion that the inhibitor method used by Bawn yielded lower values than those given by the nitrogen evolution method. It was supposed that the nitrogen evolution method measured the total rate of production of free radicals, while the inhibitor method measured the rate of production of radicals available for reactions other than a rapid dimerization. The light absorption method used in this work should measure the total rate of production of free radicals. The agreement with Bawn's results suggests that no real difference exists between the different experimental methods. In fact at 70° the scatter in k_1 values obtained by the nitrogen evolution method is as great as the supposed difference between the two methods. At 60° the k_1 value of Arnett is *lower* than that of Bawn and not higher as reported by Walling.

The changes in optical density at 320 mμ indicate that an intermediate is formed which subsequently decomposes. Light absorption measurements were made on isobutyronitrile, methacrylonitrile and tetramethylsuccinodinitrile. None of these compounds absorbs appreciably at 320 mμ and so the final products do not account for the absorption at this wave length. Evidence has been presented in Part I that the compound responsible is dimethylketenecyanisopropylimine, an unstable intermediate formed by the abnormal recombination of the cyanisopropyl radicals formed in the reaction. This conclusion can be checked by a kinetic analysis of the following reaction scheme involving dimerization of radicals to form both a normal addition product and an unstable intermediate. This analysis should predict the changes of optical density (D^{320}) actually observed, assuming these are strictly proportional to the concentration of intermediate.

$R{-}N{=}N{-}R \longrightarrow 2R\cdot + N_2$ k_1
$R\cdot + R\cdot \longrightarrow$ TMSDN or (ISBN + MAN) k_2
$R\cdot + R\cdot \longrightarrow$ intermediate (I) k_3
intermediate $\longrightarrow$ stable products k_4

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(7) C. Walling, *J. Polymer Sci.*, **14**, 214 (1954).

No attack of radicals (R·) on the azo compound, either to form the intermediate or other products has been postulated since this would cause appreciable deviations from first-order kinetics easily observable over the tenfold range of initial concentrations used. Nor has any radical-induced polymerization of the ketenimine been suggested, since no significant amount of high molecular weight material is found in the final products.[8] Attack of the radicals on the products of reaction (2) has been neglected. This is almost certainly justifiable for tetramethylsuccinodinitrile (TMSDN) and isobutyronitrile (ISBN) but may not be so for methacrylonitrile (MAN). However, according to the data of Bickel and Waters,[8] the trimer which they assume is formed by attack of radicals on methacrylonitrile is only present in the final products to the extent of 6–7 mole % so this reaction too is not important. No data are available on the decomposition of the intermediate, but it is clear that since Bickel and Waters isolated 97% of the reaction products, it must either redissociate to form radicals or rearrange directly to form tetramethylsuccinodinitrile or isobutyronitrile and methacrylonitrile. The above scheme assumes direct rearrangement, but this point is dealt with later.

Solution of the above equations using the steady-state hypothesis gives

(a) $k_1 \neq k_4$

$$t_{\max} = (k_4 - k_1)^{-1} \ln (k_4/k_1)$$

$$\left(\frac{\mathrm{d}[\mathrm{I}]}{\mathrm{d}t}\right)_0 = k_1 k_3 [\mathrm{azo}]_0/(k_2 + k_3)$$

$$[\mathrm{I}]_{\max} = \{k_3[\mathrm{azo}]_0/(k_2 + k_3)\} \text{ exp. } \{-k_1/(k_4 - k_1)\}$$

(b) $k_1 = k_4$

$$[\mathrm{I}]_{\max} = k_3[\mathrm{azo}]_0/(k_2 + k_3)e;\ k_1 t_{\max} = 1$$

$$\left(\frac{\mathrm{d}[\mathrm{I}]}{\mathrm{d}t}\right)_0 = k_1 k_3 [\mathrm{azo}]_0/(k_2 + k_3)$$

Both solutions are in accord with the experimental results in that they predict that both the initial rate of formation of the intermediate $(\mathrm{d}[\mathrm{I}]/\mathrm{d}t)_0$, and its maximum concentration ($[\mathrm{I}]_{\max}$) should be proportional to the first power of the initial azo compound concentration. The equations also predict that the activation energy associated with the initial rate of formation of the intermediate should be close to E_1 as observed (Fig. 1) since the temperature coefficients of k_2 and k_3 will be small. The observed $k_1 t_{\max}$ values indicate that k_1 and k_4 and their activation energies must be almost equal, *i.e.*, scheme (b) applies. In this case also, $D^{320}_{\max}/[\mathrm{azo}]_0$ values almost independent of temperature are predicted as observed experimentally. Qualitatively, no intermediate would be observable at all if there was more than a factor of ten difference in k_1 and k_4.

The close agreement between the rates of reactions (1) and (4) found experimentally would suggest reactions of a very similar type. Fission of a C–N bond in the ketenimine to reform two radicals might be expected to occur at a rate almost equal to the rate of fission of a C–N bond in the azo compound since the adjacent bonds are similar

$$\mathrm{CN{\cdot}C(CH_3)_2} \overset{|}{\downarrow} \mathrm{N{=}N{-}(CH_3)_2C{\cdot}CN}$$

$$\mathrm{CN{\cdot}C(CH_3)_2} \overset{|}{\downarrow} \mathrm{N{=}C{=}C(CH_3)_2}$$

Solution of the analogous set of rate equations assuming the intermediate decomposes to re-form cyanisopropyl radicals rather than decomposing by a molecular process, and again assuming $k_1 = k_4$, gives an expression for the initial rate of formation of the intermediate identical with case (b) above and still predicts that the maximum concentration of intermediate will be proportional to the first power of the initial azo compound concentration. The expression for $t_{\max}$ becomes

$$k_2/(k_2 + k_3) = \exp \{-k_1 k_3 t_{\max}/(k_2 + k_3)\}$$

Since however $k_2/(k_2 + k_3)$ must be about 0.6–0.7,[9] then $k_1 t_{\max}$ will only be increased to around 1.2. This is not experimentally distinguishable from case (b) above.

OTTAWA, CANADA

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[8] A. F. Bickel and W. A. Waters, *Rec. trav. chim.*, **69**, 1490 (1950).

[9] 11–12 mole % of hydrolysis products were isolated in the experiments reported in Part I. The above schemes indicate that this is $1/e$ of the total amount formed. Hence 30–33 mole % of the radicals will recombine to form the intermediate.