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THERMAL DECOMPOSITION OF 1-AZO-BIS-1-PHENYLETHANE: ACCELERATION BY CHLORANIL

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THE rate of the thermal decomposition of 1-azo-bis-1-phenylethane, A, has been measured in the presence of chloranil, C, and MgO in N-methylpropionamide, NMP, solvent. It was found that chloranil produced a significant increase in the rate of decomposition, while the suspension of MgO was necessary to neutralize an acid reaction product which halted the decomposition, probably through catalyzing the isomerization of the azo compound to the corresponding hydrazone.

The course of the reaction was followed by measuring nitrogen evolution as a function of time with the reaction cell in a constant temperature bath which was maintained at 97.30 ± 0.14° throughout the runs reported here.

The decomposition was found to be first order in $\underline{A}$ to a high percentage reaction and the first-order rate constants were found to be proportional to $\underline{C}_o/\sqrt{\underline{A}_o}$ where $\underline{C}$ and $\underline{A}$ are mole fractions of C and A respectively, and the subscripts refer to zero time. Table I presents the first-order rate constants k together with values of $\underline{A}_o$, $\underline{C}_o$ and $\underline{C}_o/\sqrt{\underline{A}_o}$. The rate constants were obtained by a least squares treatment of values of ln $\underline{A}_o/\underline{A}$ vs. time $\underline{t}$, using data obtained between 10% and 60% reaction.

TABLE I

$A_o \times 10^3$ mole fract.	$C_o \times 10^3$ mole fract.	$C_o/\sqrt{A_o} \times 10^2$	$k \times 10^5$ sec^{-1}
8.046	0	0	3.773
6.914	2.475	2.977	4.312
8.469	4.159	4.519	4.420
2.188	2.161	4.620	4.600
5.958	5.099	6.606	4.985
2.149	3.166	6.830	4.723
8.078	7.950	8.845	5.182
7.892	7.858	8.845	5.198

A least squares treatment of k vs. $C_o/\sqrt{A_o}$ gives a slope of 1.575×10^{-4} and an intercept of 3.798×10^{-5} sec^{-1} with an average deviation of 1.47%. The intercept agrees almost perfectly with first-order rate constants obtained for the decomposition of A in both NMP and diphenylmethane with nothing added as it does with the value (3.78×10^{-5} sec^{-1}) obtained by extrapolation from the data of Cohen, *et al.*,[1] at two slightly higher temperatures in ethylbenzene.

The data can be fitted by assuming the following reactions to be the only kinetically significant ones:

$$A \xrightarrow{k_1} N_2 + 2R\cdot \tag{1}$$

$$R\cdot + C \xrightarrow{k_2} RC\cdot \tag{2}$$

$$RC\cdot + A \xrightarrow{k_3} RCR + N_2 + R\cdot \tag{3}$$

$$R\cdot + R\cdot \xrightarrow{k_4} R_2 \tag{4}$$

where R· is the 1-phenylethyl radical and RC· symbolizes the

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[1] S. G. Cohen, S. J. Groszos and D. B. Sparrow, *J. Am. Chem. Soc.* **72**, 3947 (1950).

product(s) of attack by R· on C. There is a wide variety of possibilities for the chemical identities of RC· and RCR, essentially unlimited by kinetic restrictions. In this situation, product analyses cannot identify with any certainty the species important in step 3.

Applying the steady-state approximation to R· and RC· yields the rate equation

$$-\frac{d\underline{A}}{d\underline{t}} = \underline{A}\left[k_1 + k_2\sqrt{\frac{k_1}{k_4}}\,\frac{\underline{C}}{\sqrt{\underline{A}}}\right]. \qquad (5)$$

Since individual runs are cleanly first order in $\underline{A}$, the experimental first order rate constant can be written

$$k = k_1 + k_2\sqrt{\frac{k_1}{k_4}}\,\frac{\underline{C}}{\sqrt{\underline{A}}} = k_1 + k_2\sqrt{\frac{k_1}{k_4}}\,\frac{\underline{C}_0}{\sqrt{\underline{A}_0}}. \qquad (6)$$

This is predictable since both $\underline{C}$ and $\underline{A}$ decrease as the reaction proceeds, with $\underline{C}$ decreasing less rapidly than $\underline{A}$, and under these conditions the function $\underline{C}/\sqrt{\underline{A}}$ is not very dependent on time regardless of the exact stoichiometry.

It is interesting to note that, while step 3 is most important in determining the functional dependence of rate on $\underline{C}$ and $\underline{A}$, k_3 does not appear in the final rate expression.

Applying the rate data to equation 6 gives $k_1 = 3.798 \times 10^{-5}$ sec $^{-1}$ and $k_2/\sqrt{k_4} = 2.555 \times 10^{-2}$ sec $^{-1/2}$. Rate constants are given in four figures for the least squares treatment, but the fourth figure is certainly doubtful. Also, there is evidence of side reactions with chloranil present which contribute an error to the value of $k_2/\sqrt{k_4}$.

Step 1 is kinetically indistinguishable from the sequence

$$A \rightleftharpoons [R\cdot + \cdot N{=}N{-}R] \longrightarrow N_2 + 2R\cdot \qquad (7)$$

where brackets indicate a solvent cage. The radical RC· can thus react with either A, the cage or both with no observable kinetic difference.

The nature of step 3 in the reaction scheme is of particular pertinence to the question of mechanism. It is improbable that this step represents an induced decomposition of A, since a separate study has shown that the rate of decomposition of A is increased by 1,1-diphenyl-2-picrylhydrazyl. In this case attack by the DPPH radical on A seems unlikely due to the size of the radical and to its relatively low reactivity.

A reasonable possibility involves formation of a complex between RC· and A,[2] which complex may then decompose to give N_2 at a faster rate than does A itself.

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[2] C. E. Boozer and G. S. Hammond, J. Am. Chem. Soc. **76**, 3861 (1954).