THERMAL DECOMPOSITION OF BENZOYL AZIDE AND DIAZOACETONE IN THE GAS PHASE

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The thermal decomposition of benzoyl azide (I) and diazoacetone (II) in solutions has been studied earlier. In the present work the thermal Curtius and Wolff rearrangements for (I) and (II), respectively, have been studied under gas-phase conditions and over a broader range of temperatures than previously. The kinetic parameters obtained have been used to examine the possible alternative mechanisms of the monomolecular conversions of (I) and (II).

EXPERIMENTAL

Compound (I) was synthesized by the method described in [1], T_m 26°C (cf. [1]). Compound (II) was synthesized by the method in [2], T_m 43-45°C (14 mm) (cf. [2]).

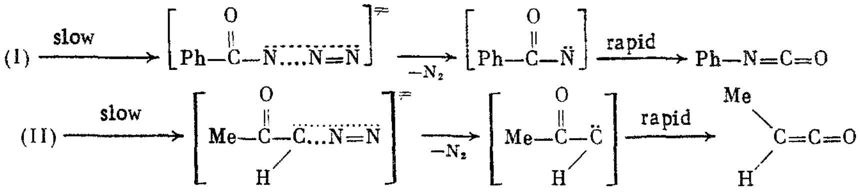
The kinetics of thermal decomposition was studied with the aid of an automated experimental set-up that continuously recorded the pressure in a 500-cm^3 glass reactor, $S/V = 0.6$ cm^{-1}. Complete transition of the weighed sample to the gas phase was monitored as the reactor was heated to the temperature of the run and then maintained at this temperature to within ±0.1 C. The initial vapor pressure was 0.5-0.7 torr for (I) and 1.0-1.3 torr for (II).

The kinetic curves are described by a first-order equation to a percent conversion of at least 90%; 2 moles of gaseous products were produced per mole reactant. The following activation parameters were calculated from the measured rate constants: (I) $E = 27.28 \pm 0.92$ kcal/mole, $\log A = 13.19 \pm 0.54$ sec^{-1}; (II) $E = 30.10 \pm 1.05$ kcal/mole, $\log A = 13.18 \pm 0.57$ sec^{-1}.

RESULTS AND DISCUSSION

The values given in [3a] for the rate constants for the decomposition of a 0.067 M solution of (I) in toluene at 60-75°C differ from the values we obtained using the Arrhenius equation by an average of ±1.5%.*

The observed stoichiometries and the first-order decomposition of compounds (I) and (II) may correspond to two different mechanisms. When the benzoyl nitrene intermediates form from (I) and acetocarbene forms from (II) according to reaction scheme (A)



(A)

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*Judging from the activation parameters given in [4], the rate constants for the decomposition of (I) at 65°C in benzene, pyridine, butanol, triethylamine, ethyl acetate, dioxane, chlorobenzene, and n-heptane are higher by an average of 15% (the maximum difference being ±60%) than in toluene, and in acetic acid, aniline, and nitromethane they are ~3.5 times higher. Only one value ($k = 1.68 \cdot 10^{-4}$ sec^{-1}) is given in [5] for the decomposition of (II) in tert-butanol at 80°C.

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TABLE 1. Experimental Values $10^4 \cdot k_1$, (sec^{-1}) for the Gas-Phase Thermal Decomposition of Compounds (I) and (II)

t, °C	85	90	100	110	115	120	130	140	150	155
(I)	3.55	5,77	16.5	42,8	64.0	110				
(II)				0,98	1.76	2,90	7,01	16,8	45,3	64,3

TABLE 2. Experimental Decomposition Parameters*

Azides $RN{=}N_2$					Diazo compounds $\overset{R}{\underset{H}{>}}C{=}N_2$			
R	t, °C	E	log A	ref.	t, °C	E	log A	ref.
H	1000–1200	40,0	11,25	[8]	225–450	34,0	12.08	[9]
Ph	160–200	33,9	13,35	[6]	85	30.18	†	[10]
PhCO	85–120	27,28	13,18		100–140	32,7	13,8	‡
MeCO					100–155	30,1	13,18	
EtCO	–5–0	21,2	†	[3b]				

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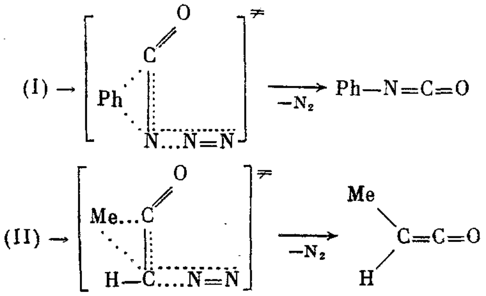
*E, kcal/mole, log A, sec^{-1}. The experimental values E = 60, log A = 11.9 correspond to the spin-forbidden process $N_2O \rightarrow N_2 + O(^3P)$. For $N_2O \rightarrow N_2 + O(^1D)$ $\Delta H_0{}^0 = 84$ [11].

†Estimated from the value of k(t) and the condition $\Delta S^{\neq} = 0$.

‡Preliminary data we obtained for the unimolecular decomposition of diazoacetylphenol in nitrobenzene.

the rate of conversion is controlled by the N_2 elimination step. The experimental conditions (gas phase, low pressure) rule out the possibility of bimolecular reactions involving electron-deficient species.

In reaction scheme (B) the rate of decomposition is controlled by the abstraction of nitrogen



(B)

which occurs simultaneously with the framework rearrangement to phenylisocyanate for (I) and to methylketene for (II).

It is shown in [6] that the abstraction of N_2 during the thermal decomposition of alkyl azides to form the corresponding singlet nitrenes is allowed, and the triplet forms are forbidden by the laws of orbital symmetry at the reaction coordinate corresponding to a linear antisymmetric vibration of the N atoms of the azide group.

This conclusion, which holds for the thermal decomposition of 1,3-dipolar molecules generally (azides, diazo compounds, etc.) is a natural consequence of the necessity for simultaneous breaking of mutually perpendicular σ bonds and the allyl 1,3-dipolar π system, while the number of σ and p electrons in the activated complex occupying orbitals of every type remains unchanged. Clearly identifying the reaction coordinate also makes it possible to analyze the entropy and enthalpy factors, since the energy barrier of such a conversion should in general be the same as the magnitude of the endothermic heat of formation of the corresponding singlet electron-deficient species. In fact, in the reverse process along the same coordinate the unoccupied valence orbital of the carbene or nitrene should approach the unshared pair of the N_2. In terms of the energetics, this is analogous to the most favorable approach of two monoradicals.

If we assume that the structures and frequencies of the starting molecules in scheme (A) are similar to those of the activated complex, then by transition-state theory the rate constants of the monomolecular reaction is given by

$$k_1 = kT/h\left[1-\exp\left(-\frac{h\nu}{kT}\right)\right]\exp\left(-E_0^{\neq}/RT\right)$$

where h and k are the Plank and the Boltzmann constants, E_0 is the true activation energy; ν is the vibration frequency converted to motion along the reaction coordinate $\nu = \nu_{as} \simeq 2100\ \text{cm}^{-1}$. At $T \ll h\nu_{as}/k$, regardless of the detailed structure of the molecule, the normal magnitude of the preexponential factor $A = ekT/h$ corresponds to a value of $\Delta S^{\neq} = 0$ and the condition $E_0^{\neq} = \Delta H^{\neq}$.

The values of log A we obtained differ only slightly from the normal values ($\Delta S^{\neq} = -0.60$ and -0.80 cal/(mole·deg) for (I) and (II), respectively), as do those of $\log A = 13.34$ (sec^{-1}), $\Delta S^{\neq} = -0.26$ cal/(mole·deg) for the decomposition of PhN_3 studied in [6] on the same experimental set-up at P = 0.9-2.1 torr and t = 160-200°C.

The internal rotation of the CH_3 group in (II) can be regarded as free, and that of the phenyl group in (I) as partially hindered by conjugation with the rest of the molecule. In the activated complex of the reactions in (B), these groups migrate, and their rotation should cease. Therefore, lower and different values of the preexponential factors for compounds (I) and (II) are more likely for (B).

It was established in [3a] that the rate constants at 65.2°C for the thermolysis of m- and p-substituted benzoyl azides (R = NO_2, CH_3, CH_3O, Cl, Br) in toluene are on average 17% lower (with maximum differences of +16 and −41%) than for unsubstituted (I). For o-substituted benzoyl azides, the rates of decomposition are higher than for (I), by a factor of 120 on the average, and increase for the R groups listed from 53 to 200 times [3b]. This result has not as yet been convincingly explained.

In scheme (A) the activated complex may be stabilized by approaching and interacting through space of the unoccupied orbital that forms as the reactant moves along the reaction coordinate of the corresponding species and the electron clouds of the given R group. A similar mechanism for stabilizing a radical reaction site formed by the homolytic cleavage of the $C{-}NO_2$ bond of some polynitro derivatives of pentane was argued for in [7]. For the (B) scheme the activated complex is more likely destabilized due to additional steric hindrances to the migration of the $-C_6H_4R$ group developing in the activated complex.

Thermal stability (with respect to the unimolecular abstraction of nitrogen) is greatly reduced in a number of the simplest 1,3-dipoles: N_2O, HN_3, H_2CH_2 (Table 2). The difficulty in forming the unoccupied valence orbital $O(^1D)$, ^1NH, $^1CH_2$ upon moving along the reaction coordinate is due to the dominant role of the nucleus of the O, N, and C atoms.

The unfilled state of this orbital in the activated complex formed in the decomposition of more complex molecules must be the reason for the intramolecular shift in electron density that stabilizes the activated complex increasingly with increasing nuclear charge due to the absence of screening of the electrostatic field of the nucleus by the given orbital. From this it follows that HN_3 should be the most stable of the azide series, just as H_2CN_2 is the most stable of the diazo compounds. The decrease in the stability should be greater for the more complex molecules in the azide series than in the analogous diazo compounds, however (cf. Table 2).

In the reaction mechanisms in (B), a most important role must be played by the cyclic group of the activated complex. In three-member rings in the molecules and the transition states, the energy increments are often fairly large, up to 20-25 kcal/mole [12]. The rearrangement occurring simultaneously with the elimination of N_2 therefore requires both a higher energy of activation and a lower value of the preexponential factor, which was not observed in the experiment (Table 2).

In our opinion, this discussion supports a number of well-known arguments [13-15] in favor of the Curtius and Wolff rearrangements being two-step (nitrogen elimination—framework rearrangement) reactions. The lack of examples of insertion products of some nitrenes, the major argument in favor of a one-step Curtius rearrangement [4, 14], may be due to the low energy barrier to unimolecular rearrangement of the corresponding nitrenes and is not inconsistent with the hypotheses outlined above.

CONCLUSIONS

1. The activation parameters for the thermal decomposition of benzoyl azide and diazoacetone in the gas phase have been measured.

2. Available kinetic data favor the Curtius and Wolff rearrangements being two-step mechanisms. In the step controlling the observed rate of unimolecular decomposition, a molecule of N_2 is eliminated, and a singlet electron-deficient intermediate species forms.

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KINETICS OF THE REVERSIBLE RECOMBINATION OF SUBSTITUTED 2-(p-DIMETHYLAMINOPHENYL)INDANE-1,3-DION-2-YL RADICALS

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Aromatic 2-arylindane-1,3-dion-2-yl free radicals ($F^\cdot$) present an interest as intermediate reagents in inhibited liquid-phase oxidation of alkylaromatic hydrocarbons in photo- and thermochromic systems [1, 2]. The investigation of the reactivity of $F^\cdot$ presents also an interest by itself in the investigation of kinetics of radical reactions. The high reactivity of $F^\cdot$ in recombination reactions, its inertness toward other reagents (including solvents), and the possibility of synthesizing various types of derivatives make $F^\cdot$ suitable investigation subjects to study the connection between structure and reactivity.

The kinetics of reversible recombination of $F^\cdot$, having substituents in the 2-phenyl ring, were investigated in [3, 4]. The present work was dedicated to investigate the recombination of $F^\cdot$ having different substituents in the indane cycle.

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