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

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

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 $\begin{array}{l} R^1 = R^2 = R^3 = R^4 = H(a), \ R^1 = CI, \ R^2 = R^3 = R^4 = H(b), \ R^2 = CI, \ R^1 = R^3 = R^4 = H(c), \ R^2 = R^3 = R^4 = H(d), \ R^2 = I, \ R^1 = R^3 = R^4 = H(c), \ R^2 = CN, \ R^1 = R^3 = R^4 = H(c), \ R^1 = R^2 = R^3 = R^4 = H(c), \ R^1 = R^4 = R^4 = R^3 = R^4 = R^4 = R^4 = R^3 = R^4 = R^4 = R^4 = R^3 = R^4 = R^4 = R^4 = R^3 = R^4 = R^4$

The corresponding dimers are indicated by FF.

EXPERIMENTAL

The kinetics of the reversible recombination of radicals of 2-(p-dimethylaminophenyl)indane-1,3-dion-2-yl derivatives were investigated by the impulse photolysis method

$$FF \xrightarrow{2k_1} F + F$$
 (1)

The starting FF (a-i) were synthesized according to [5-7]. The measurements were carried out in benzene and mineral oil (MO). The viscosity of the binary benzene-MO mixture was measured with a Heppler viscometer by varying the composition of the binary mixture. When determining the thermodynamic parameters, the temperature variation interval was $\geq 50^{\circ}$ C. The solutions were thermostatted with an accuracy of $\pm 0.5^{\circ}$ C. The extinction coefficients of the radicals and the equilibrium constants (K) of the system dimer-free radicals were determined in [8] by means of accurate EPR and spectral measurements. The determined values were used for the determination of $2k_{-1}$ and $2k_1$. The photoexcitation of air-saturated FF solutions ($10^{-3}-10^{-4}$ mole/liter) was carried out using light of λ 280-380 nm. Using impulse photoexcitation of FF solutions, we obtained a super-equilibrium concentration of F^{*}. The relaxation of the system toward equilibrium proceeded with full reversibility, a fact that allowed the calculation of the $2k_{-1}$ value from anamorphic data using Eq. (2):

$$\ln \frac{\Delta D_0 (2\overline{D} + \Delta D)}{\Delta D (2\overline{D} + \Delta D_0)} = k_{-1} (4[F] + K) t$$
(2)

where \overline{D} is the absorption corresponding to the equilibrium concentration of F'; ΔD_0 is the variation of the optical density of the solution at the first instant following the flash. The thermodynamic parameters of the direct and reverse reactions were obtained from the temperature dependences of $2k_{-1}$ and K. FF (f and g), when photoexcited, give a very weak signal related to the formation of a slight superequilibrium concentration of F' (the mentioned dimers have significantly higher K values than the remaining ones); for this reason it was difficult to experimentally obtain the $(2k_{-1})$ constants.

RESULTS AND DISCUSSION

<u>Recombination Kinetics of Radicals</u>. High values of $2k_{-1} \sim 10^8 - 10^9$ liters/mole·sec were obtained for the F (a-i) recombination constants (Table 1). It is interesting to note that the values of ΔH_{-1}^{\neq} are close to zero and lower than the activation energy of the viscous flow of benzene, V = 10.4 ± 0.2 kJ/mole.

Figure 1 shows the linear dependence of $\Delta \log 2k_1$ on the sum of the Gametta $\Sigma \sigma$ constants:

$$\Delta \log 2k_{-1} = 0.32\Sigma\sigma, \quad r = 0.955 \tag{3}$$

The existence of a correlation with a low ρ value testifies to the weak effect of the electronic properties of the substituents on the recombination rate constant of F' (a-i). The values of magnitudes $2k_{-1}$ of F' (f and g) were obtained using Eq. (3). For F' (f), $\Sigma \sigma = 1.2$ [9]. In the case of F' (g), which contains four chlorine atom substituents which exert a complex combination effect, $\Sigma \sigma$ was obtained from equation $\Delta \log K = 0.87 \ \Sigma \sigma$ [8], and equals 1.58. $\Sigma \sigma$ of F' (i) was obtained in the same manner [8]; its high negative value ($\Sigma \sigma = -1.3$) satisfies well the correlations of $2k_{-1}$ (Fig. 1) and testifies to a substantial effect of steric hindrances (which distort the phthaloyl fragment and hinder the conjugation in the radical) on the equilibrium (K) and on the reverse reaction. It must be noted that in the series of 5-Cl, 5-Br, and 5-I substituted F' (c-e), the values of $2k_{-1}$ increase despite the approximately same electrophilic character of these substituents. This can be conditioned by an increase in the S = T relaxation rate of the radical pair as the ordinal number



Fig. 1. Dependence between $\Delta \log 2k_{-1}$ (1), $\Delta \log 2k_{1}$ (2), and $\Sigma \sigma$; in benzene at 293 K.

Fig. 2. Effect of the viscosity of the binary benzene-MO mixture at 294 K on the recombination rate constant of F (e) (η in sP). The hatched line represents the theoretical relationship.

TABI	E I	1.	Therm	nody	mami	LC	and	Kinetic	Parameters	of	Reaction
(1)	in	Ben	zene	at	293	K					

	K 10°, mole/l	2k-1.10-8, 1/mole. sec	-	ΔH°	ΔH_{-1}^{\neq}	ΔH_1^{\neq}	ΔS°	ΔS_{-1}^{\neq}	$\Delta S_1^{=}$
Compound			2k ₁ , sec ⁻¹	k	J/mole		J/mole • K		
a b c d e f g h i Error	$\begin{array}{c} 0,40\\ 1,08\\ 1,90\\ 2,20\\ 1,20\\ 4,60\\ 9,50\\ 0,06\\ 0,03\\ \pm 5\%\end{array}$	$5,97,96.8101219 *21 *4,12,0\pm 10\%$	$\begin{array}{c} 0,24\\ 0,87\\ 1,30\\ 2,20\\ 1,40\\ 8,70 \\ *\\ 20 \\ *\\ 0,025\\ 0,006\\ \pm 15 \\ \%\end{array}$	80 79 77 78 78 77 78 85 85 85 ±2	$ \begin{array}{r} -3 \\ -5 \\ -3 \\ -4 \\ 0 \\ - \\ -1 \\ -3 \\ \pm 2 \end{array} $	77 74 74 74 78 - 83 83 ± 4	$ \begin{array}{r} 94\\97\\96\\99\\94\\103\\112\\92\\90\\\pm6\end{array} $	88 90 86 86 71 - - 86 94 ±6	$ \begin{array}{c} 6 \\ 7 \\ 10 \\ 13 \\ 23 \\ - \\ - \\ 6 \\ 4 \\ \pm 12 \end{array} $

*Calculated values.

of the atom increases. The analogous effect of the heavy atom was examined in [10]. The influence of viscosity on $2k_{-1}$ was investigated using F' (e) as example (Fig. 2). The hatched line indicates the theoretical relationship, plotted on the assumption that for benzene $K_{dif} = (1/4)8RT/300 \eta$, and a straight line was drawn at $\tan \alpha = 0.5$ (the procedure was described in detail in [11]). It follows from Fig. 2 that at $0.6 \le \eta \le 2sP$ the reverse reaction depends only slightly on η and is activational, while at $\eta \ge 2sP$ the reaction is fully limited by the molecular mobility. The values of $2k_{-1}$ obtained at $\eta \ge 2sP$ are ~1.5 times lower than the corresponding k_{dif} values. It was shown in [2] that the recombination of F' (a) at $\eta \le 2sP$ is activational, and at $\eta \ge 2sP$ it is limited by molecular mobility. An analogous behavior can be predicted for F' (b-i).

<u>Dissociation Kinetics of Dimers</u>. The values of $2k_1$, ΔH_1^{\neq} , and ΔS_1^{\neq} were obtained from the found values of $2k_{-1}$, K, and their thermodynamic parameters (Table 1). Magnitude $2k_1$ depends strongly on the electronic and steric effects produced by the substituents in the indane fragment. It follows from Fig. 1 that for F[•] (a-i) the values of $\Delta \log 2k_1$ correlate very well with $\Sigma \sigma$:

$$\Delta \log 2k_1 = 1.20\Sigma\sigma, r = 0.993$$

The value $\rho = 1.20$ testifies to a significant increase in the dissociation rate of those FF which contain electrophilic substituents.



Fig. 3. Log $2k_1$ as a function of log K; in benzene at 293 K.

Figure 3 shows $\log 2k_1$ as a function of $\log K$ as determined by the Bela-Evans-Polianyi equation:

$$\lg 2k_1 = \alpha \lg K + \beta$$
, ($\alpha = 1.36, \beta = 12.8$) $r = 0.996$

It follows from the high value of $\alpha = 1.36$ that the transition state in the dimer dissociation reaction is closer in its structure to a pair of radicals than to a dimer. The same conclusion was drawn in [12] when investigating the dissociation of FF (a) in various solvents. An increase in the electrophilic character of substituents in the phthaloyl fragment resulted in an increased thermodynamic stability of the radicals (Table 1). The reason for this rule is understandable: The given radicals are ascribed a structure with a significant degree of intramolecular charge transfer [8].

In this way, the strong effect of a substituent on $2k_1$ as well as on K in the series of (a-i) compounds is conditioned by its influence on the stability of the radicals. In the FF (b-g) series, which have electrophilic substituents, the changes in $2k_1$ are determined mainly by a ΔS_1^{\neq} variation, as in the case of K [8].

CONCLUSIONS

1. We established linear relationships between $\Delta \log 2k_{-1}$, $\Delta \log 2k_{1}$, and $\Sigma \sigma$ of the Gammet constants with a positive ρ value, equal to 0.32 and 1.20, respectively.

2. We determined the kinetic and thermodynamic parameters of the recombination reaction of radicals and of the dissociation of dimers in the 2-arylindanedione-1,3 series.

3. The recombination rate constant of 2-arylindane-1,3-dion-2-yl radicals in benzene is activational. In the binary benzene-MO mixture at $\eta \ge 2sP$, the recombination rate constant is fully limited by molecular mobility. In the case of recombination of 5-iodo-2-(p-dimethylaminophenyl)indane-1,3-dion-2-yl radicals, we found that $2k_{-1} \sim \eta^{-0.5}$.

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KINETICS OF METHOXYCARBONYLATION OF 3-METHYL-1-BUTYN-3-OL

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Carbonylation of acetylenic alcohols in a methanol medium, in the presence of a $PdCl_2$ -CuCl_2-NaOAc catalytic system leads to the formation of methyl esters of acetylenic hydroxy-acids [1], which are promising intermediates in fine organic synthesis. We have previously [2] optimized the synthesis of methyl 4-methyl-4-hydroxy-2-pentynoate using multifactor planning. To find the parameters necessary for further improvement of the preparative reaction characteristics, we studied the kinetics of methoxycarbonylation of 3-methyl-1-butyn-3-ol (MB).

$$\begin{array}{c} Me & Me \\ Me & - & Cat & Me \\ Me & - & - & H \end{array} \xrightarrow{Me} & - & CO_2Me \\ OH & OH & OH \end{array}$$

$$Cat = PdCl_2 - CuCl_2 - NaOAc$$

The rate of reaction was measured on the consumption of CO with time at atmospheric pressure. The CO absorption curves were obtained at a temperature of from 16 to 34° C (five levels). The initial concentrations of MB were 0.1 and 0.2 mole/liter (two levels), and the concentration of the catalytic system components was: 0.35, 0.2, 0.1 and 0.005 mole/liter of (CuCl₂ and NaOAc) and 0.003, 0.005, 0.006, 0.025 mole/liter of (PdCl₂). From typical CO absorption curves it can be seen that almost up to reaching a plateau, they are satisfactorily approximated by straight lines (Fig. 1). The close to linear form of the kinetic curves up to the disappearance of the acetylenic alcohol (a control by TLC) formally corresponds to a general zero order at fixed concentrations of the reagents and the catalytic system components.

Since methanol appears as both a reagent and as a solvent in the carbonylation reaction of MB, the order with respect to methanol is zero. According to the experimental conditions, the order should also be zero with respect to CO, since its pressure was maintained constant.

The kinetic dependences obtained are approximately described by the simplest equations, corresponding to zero order with respect to CO, and having the most advantageous statistical characteristics (Table 1).

$$[CO] \cdot 10^3 = k_0 + kt \tag{1}$$

With the coefficients of the integral equations given in Table 1, we were able to obtain the value of the mean reaction rate V under various conditions (Table 2). The dependence of the reaction rate on the initial concentrations of the reagents and the catalytic additives can, in general, be described by the equation

$$V = k [C_1]^{n_1} [C_2]^{n_2} [C_3]^{n_3} [C_4]^{n_4}$$
(2)

where C_1 , C_2 , C_3 , and C_4 are concentrations of MB, PdCl₂, CuCl₂, and NaOAc, respectively, and n_1 are orders with respect to these components. By combining this equation with the Arrhenius equation ($k = A \exp - E/RT$), we obtain

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