Aspects of Tautomerism. Part IV.[1] A Kinetic Study of the Dimerization Reaction of Pseudo-acid Chlorides

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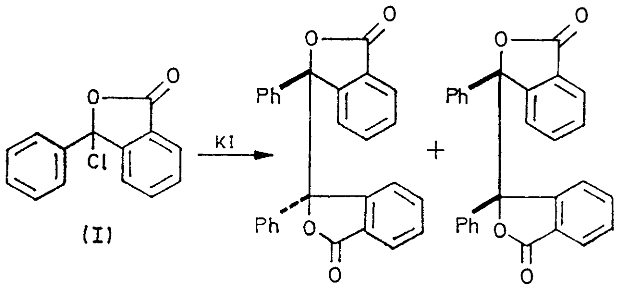
The kinetics of dimerization of 4′-substituted and unsubstituted *o*-benzoylbenzoyl chlorides, with iodide ion can be described by the expression, rate = k_2 [acid chloride][iodide]. The ρ value for the reaction in dimethylformamide solution is −0·38. The entropy of activation for the reaction is −34·2 cal mol^{-1} K^{-1} and the activation energy is 10·7 kcal mol^{-1}. These results have been interpreted as evidence for the formation of pseudo-iodide in the rate-determining step and its fast decomposition to radicals which combine to give a mixture of stereoisomeric dilactones.

We have reported earlier that the pseudo-acid chloride of *o*-benzoylbenzoic acid (I) reacts with alkali iodides under mild conditions to give an almost quantitative yield of a mixture of stereoisomeric dilactones [1,2] (II) and (III). It was also shown that the distribution of isomers was not 1 : 1 and that in all cases examined the *meso*-isomer always predominated. These observations were interpreted in terms of combination of radicals formed by the decomposition of the pseudo-iodide. We report in this paper a kinetic study of the dimerization in dimethylformamide solution. Substituent and temperature effects have been examined.



(I) (II) (III)

RESULTS AND DISCUSSION

The kinetics of dimerization of *o*-benzoylbenzoyl chloride and other *o*-(*p*-substituted benzoyl)benzoyl chlorides fit a first-order rate expression for the disappearance of the acid chloride. The order of the reaction was verified by the normal methods. First-order rate constants are tabulated in Table 1.

Table 1

Effect of changing acid chloride concentration on the rate of dimerization of *o*-benzoylbenzoyl chloride with potassium iodide *

[Acid chloride]/M	$10^4 k_1$/s^{-1}
0·0050	6·22
0·0075	6·44
0·0100	6·28

[KI] = 0·200M, solvent, anhydrous dimethylformamide, temp. 25°.

* Rate coefficients were reproducible to within ±3%.

The effect of changing the concentration of potassium iodide at constant acid chloride concentration (Table 2) gave good first-order rate plots for each concentration. Pseudo-first order rates were divided by the molar concentrations of potassium iodide to get second-order rate constants (k_2). The value of k_2 was found to be a constant, showing thereby the first-order dependence of the reaction on potassium iodide concentration.

The rate expression for the dimerization of the pseudo-acid chloride of *o*-benzoylbenzoic acid can be written as (1). The activation energy and entropy of activation are given in Table 3.

Table 2

Effect of change in concentration of potassium iodide on the rate of dimerization of *o*-benzoylbenzoyl chloride *

[KI]/M	$10^4 k_1$/s^{-1}	$10^3 k_2$/l mol^{-1} s^{-1}
0·1100	3·36	3·06
0·1502	5·05	3·36
0·1900	6·23	3·28
0·2700	9·21	3·41

[Acid chloride] = 0·005M, solvent, anhydrous dimethylformamide, temp., 25°.

* Rate coefficients were reproducible to within ±3%.

Table 3

Effect of temperature on the rate of dimerization of *o*-benzoylbenzoyl chloride with potassium iodide

t/°C	$10^3 k_2$/ l mol^{-1} s^{-1}	E_a kcal mol^{-1}	$\Delta H^‡$ kcal mol^{-1}	$\Delta S^‡$/ cal mol^{-1} K^{-1}
25	3·16			
30	4·31	10·7	10·1	−34·2
35	5·70			
40	7·25			
45	9·32			

[Acid chloride] = 0·005M, [KI] = 0·2107M, solvent, anhydrous dimethylformamide.

$$\text{Velocity} = k_2\,[\text{acid chloride}][\text{KI}] \qquad (1)$$

The effect of substituents in the 4′-position of *o*-benzoylbenzoyl chloride on the rate of dimerization was examined. Second-order rate constants are tabulated in Table 4. A methyl substituent in the 4′-position slightly increased the rate and a nitro-group slightly lowered it. In general it was found that electron-donating groups slightly increased and electron-withdrawing groups slightly lowered the rate. When log k_2 values were plotted against σ^+ constants a fairly good linear plot was obtained (Figure). The ρ value for the

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[1] Part III, M. V. Bhatt, K. M. Kamath, and M. Ravindranathan, *J. Chem. Soc.* (*C*), 1971, 3344.

[2] H. Manohar, V. Kalyani, M. V. Bhatt, and K. M. Kamath, *Tetrahedron Letters*, 1966, 5413.

dimerization reaction is —0·38 (correlation coefficient 0·996). It was found that the rates were correlated by

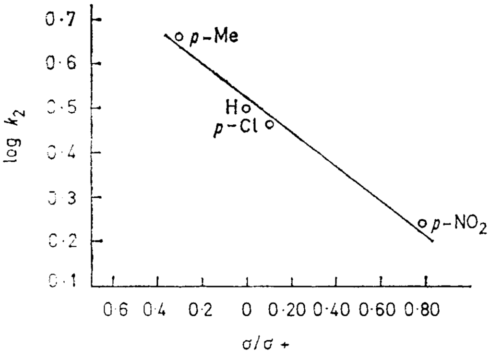
TABLE 4

Effect of substituents on the rate of dimerization of *o*-benzoylbenzoyl chloride with potassium iodide *

Substituents	$10^3 k_2$/l mol^{-1} s^{-1}
4′H	3·16
4′Me	4·49
4′NO_2	1·76
4′-Cl	2·85

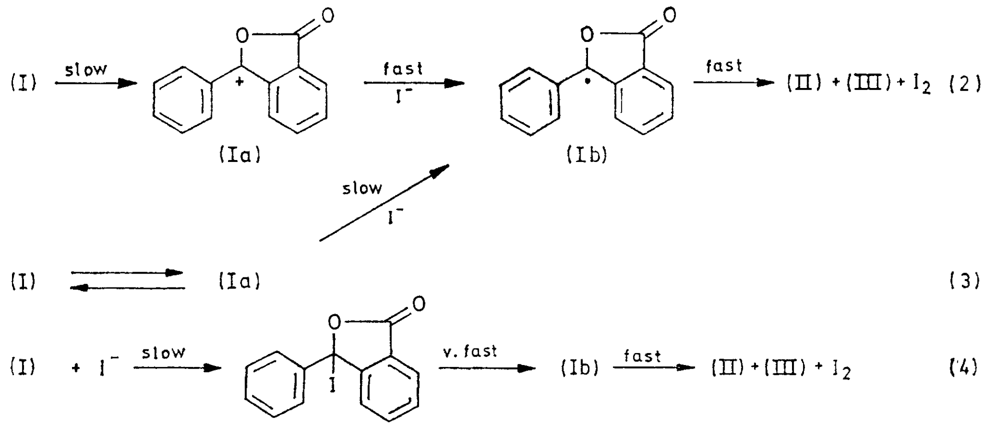
[Acid chloride] = 0·005M, [KI] = 0·2107M, solvent, anhydrous dimethylformamide, temp. 25°.

* See footnote to Table 1.



Substituent effect on the rate of dimerization of *o*-benzoylbenzoyl chloride with potassium iodide

σ+ values better than by σ values. The σ+ values were originally proposed for ionic reactions in which a positive charge capable of resonance interaction with the benzene ring is generated in the transition state.[3] Although these σ+ constants were successful in correlating rates of reactions in which there is considerable ionic character, it has been found that many homolytic reactions are correlated better by σ+ than by σ.[4]



Three reasonable mechanisms (2)—(4) could be conceived for the formation of dilactones from the acid chlorides. The present kinetic study makes it possible to decide among these possibilities. According to mechanism (2), the iodide ion concentration should have no influence on the rate, because the electron transfer reaction may be expected to be much faster than bond breaking. The reaction may be expected to be first order in acid chloride and zero order in iodide ion.

A rapid equilibrium ionization of the acid chloride leading to steady-state concentration of the ionic species [process (3)] is inconsistent with the small ρ value observed. One should expect a large negative ρ value for a reaction involving ionic species. The ρ value for the solvolysis of benzhydryl chlorides, for example, is —4·03.[5] The rate of hydrolysis of *o*-benzoylbenzoyl chloride in 90% aqueous dioxan at 25° is 1·35 × 10^{-3} s^{-1} which is only twice the rate of dimerization. The overall reaction involving an equilibrium ionization and slow electron transfer by iodide ion can therefore be safely discounted.

The reaction is first order in acid chloride and first order in iodide, clearly demonstrating that the nucleophilic displacement of the chloride by iodide is the rate-determining step. The entropy of activation is negative, as would be expected for a S_N2 type reaction. The small negative ρ value of —0·38 is consistent with this view. We suggest that the reaction follows path (4). The presence of radicals was further confirmed by trapping them as their acrylonitrile adducts (see Experimental section).

EXPERIMENTAL

Acids were prepared by literature procedures.[6-9] Acid chlorides were obtained by treating acids with thionyl chloride and purified by distillation under reduced pressure. *o*-Benzoylbenzoyl chloride had b.p. 177—178° at 3 mmHg, *o*-(*p*-methylbenzoyl)benzoyl chloride had b.p. 177—179° at

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[3] H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, 1958, **80**, 4979.

[4] W. A. Pryor, ‘ Free Radicals,’ McGraw-Hill, New York, 1966, p. 172.

[5] J. Hine, ‘ Physical Organic Chemistry,’ McGraw-Hill, New York, 1962, 2nd edn., p. 164.

[6] L. F. Fieser, ‘ Experiments in Organic Chemistry,’ Heath, Boston, 1955, 3rd edn., p. 160.

[7] L. F. Fieser, *Org. Synth.*, 1944, **1**, 517.

[8] P. H. Groggins and H. P. Newton, *Ind. Eng. Chem.*, 1919, **21**, 369.

[9] M. V. Bhatt and K. M. Kamath, *J. Chem. Soc.* (*B*), 1968, 1036.

2 mmHg, and *o*-(*p*-chlorobenzoyl)benzoyl chloride, had b.p. 182—185° at 2 mmHg. *o*-(*p*-Nitrobenzoyl)benzoyl chloride was crystallized from benzene–light petroleum (1 : 1), m.p. 147—148°. The purity of acid chlorides was checked by g.l.c. All inorganic compounds used were of reagent grade. Dimethylformamide was purified by distilling twice over phosphorus pentoxide, the temperature of the bath being maintained to $\pm 0{\cdot}1°$.

Kinetic Procedure.—Solutions of acid chloride and potassium iodide in anhydrous dimethylformamide were kept separately in the thermostat for 1 h to attain thermal equilibrium. The solutions were flushed with a current of dry nitrogen. A known volume of the acid chloride solution was pipetted into the potassium iodide solution. Aliquot portions were drawn at regular intervals and run into doubly distilled water (50 ml). The amount of iodine liberated was estimated by titrating against standard sodium thiosulphate solution using a 1% solution of starch as indicator.[10]

The stoicheiometry of the reaction was determined by product analysis. Using an excess of potassium iodide the reaction was allowed to go to completion. The mixture was diluted with water and the liberated iodine was estimated. It was extracted several times with ether, washed with sodium hydrogen carbonate solution, and dried (Na_2SO_4). Removal of solvent left the dilactone mixture. From the weight of the dilactone mixture and the amount of iodine liberated the stoicheiometry of the reaction was established as (5)

$$\text{2 acid chloride} + 2\,\text{KI} \longrightarrow \text{1 dilactone} + 2\,\text{KCl} + 1\,\text{I}_2 \quad (5)$$

When the dimerization of *o*-benzoylbenzoyl chloride was repeated in the presence of freshly distilled acrylonitrile, a semi-solid polymeric material was isolated along with the dilactones. The compound showed a sharp band at 2280 cm^{-1} in the i.r. spectrum characteristic of C≡N. No polymeric material formation was observed when the reaction was conducted in the absence of either acid chloride or potassium iodide.

Calculation of Rate Constants.—All kinetic runs were conducted under pseudo-unimolecular conditions. Pseudo-first-order rate constants k_1 were calculated from the normal rate equations.

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[10] A. I. Vogel, 'A Textbook of Quantitative Inorganic Analysis,' Longmans, London, 1964, p. 347.