# ORGANIC AND BIOLOGICAL CHEMISTRY

[CONTRIBUTION FROM THE PIONEERING RESEARCH DIVISION, TEXTILE FIBERS DEPARTMENT, E. I. DU PONT DE NEMOURS AND CO., INC.]

## Kinetics of Reactions of Acyl Chlorides. IV.[1] Solvolysis of Acyl Halides in Dimethylformamide

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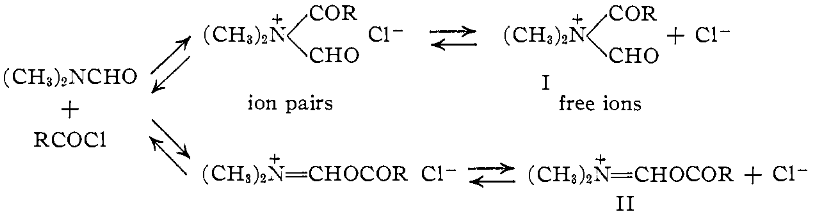
Acyl chlorides and bromides, dissolved in dimethylformamide, behave as weakly and strongly dissociated electrolytes, respectively. The latter yielded crystalline 1:1 salts when treated with a limited amount of the amide. These are formulated as $(CH_3)_2N^+{=}CHOCOR\ X^-$ on the basis of their reactions with aniline and water to give benzanilide and benzoic acid, respectively. The reaction occurs with other carboxamides, but not with nitrosamides, cyanamides or sulfamides.

Recently Rochow and co-workers[2] demonstrated that chlorosilanes dissolved in dimethylformamide yield conducting solutions of ionic substances. Since acyl chlorides display many similarities to chlorosilanes in their reactions, and since we have been interested in the ionization of acyl halides in water solution, it was of interest to study solutions of acyl halides in dimethylformamide.

Acetyl and benzoyl chlorides, ethyl chloroformate and benzenesulfonyl chloride when dissolved in pure dimethylformamide formed conducting solutions. Acetyl chloride reacted instantaneously and benzoyl chloride nearly so, while the other two chlorides reacted with half-lives of 9.5 and 6.8 minutes, respectively, at 20°.

This order of reactivity corresponds to that observed for displacement reactions (S$_N$2) rather than that for ionization (S$_N$1). On this basis the reaction is formulated in either of two ways



I

II

(1)

Covalent compounds such as $(CH_3)_2N{-}CHCl{-}OCOR$ are also possible. Conductivity curves were determined for these acyl chlorides. The data are plotted in Fig. 1. The curves are those characteristic of slightly dissociated substances. Therefore the over-all reaction 1 is reversible, with a small equilibrium constant. Moreover, ion pairs can probably be neglected in a solvent of dielectric constant 36.7. No extrapolation of the curves to infinite dilution was possible, so that the degree of dissociation and the dissociation constant cannot be calculated. Rochow, in agreement with these findings, observed equilibrium constants of the order of $10^{-2}$ to $10^{-4}$ for the chlorosilanes.

The observed conductivities were not caused by reaction of the acyl halides with impurities, but by reaction with the solvent itself. The following arguments support this contention: (1) The conductivity of the pure solvent is low ($7.8 \times 10^{-7}$ ohm$^{-1}$ cm.$^{-1}$) so that no appreciable concentration of ionic species is present initially. Furthermore, if dimethylamine or formic acid were reacting with the acyl halides (a) the curves would more likely be those of highly dissociated, rather than slightly dissociated, electrolytes; (b) a discontinuity or a leveling of the curve would appear when the impurity had been consumed; (c) reaction of dimethylamine with the acyl halides would be too fast to measure. Finally, isolation of the conducting species (see below) has been accomplished in the case of acyl bromides.

The structure of the cations can be formulated as either I or II. Since the reaction proceeds only slightly toward the right, it was difficult to obtain decisive evidence in favor of one or the other structure. For example, infrared examination of a solution of benzoyl chloride in dimethylformamide showed no new species to be present. The ionized material must therefore be present at less than *ca.* 3% concentration, in harmony with the conductance results. The lack of indication of new species supports our contention that ion pairs can be ignored. Attempted isolations of the adducts were unsuccessful.

Indirect evidence and analogy lead us to favor structure II. Since reaction 1 is reversible, chloride ion must react with the cation in the back step. If the cations had structure II, only benzoyl chloride would be formed. On the other hand, if structure I were correct, either benzoyl or formyl chloride would be expected to form. The latter would undergo decomposition to carbon monoxide and the amide hydrochloride. No gas evolution was noted. Further, amide hydrochlorides, which would be the other product, would probably be highly dissociated electrolytes in dimethylformamide solution. The weak electrolyte behavior of the acid chlorides is incompatible with this fact.

Analogy also supports structure II. Stephens, Branco and Pilgrim[3] have described a reaction of sulfonyl chlorides with primary amides which is plausibly ascribed to O-acylation. Coppinger,[4]

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(1) Part III, *J. Org. Chem.*, **21**, 248 (1956).

(2) K. Gingold, E. G. Rochow, D. Seyferth, A. C. Smith, Jr., and R. West, THIS JOURNAL, **74**, 6306 (1952).

(3) C. R. Stephens, E. J. Branco and F. J. Pilgrim, *ibid.*, **77**, 1701 (1955).

(4) G. M. Coppinger, *ibid.*, **16**, 1372 (1954).

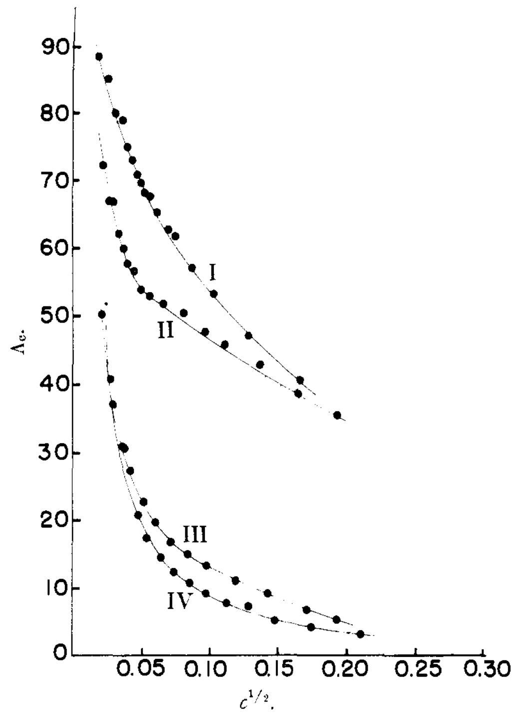

Fig. 1.—Conductivities of acyl halides in dimethylformamide at 20.1°: I, benzoyl bromide; II, acetyl bromide; III, benzoyl chloride; IV, acetyl chloride.

on the other hand, found that acyl chlorides were converted by dimethylformamide into the dimethylamides of the corresponding acids. However, this reaction required prolonged boiling of the dimethylformamide solution, and is doubtless a different one from the one under scrutiny here.

Acetyl and benzoyl bromides were examined in the hope that these reactions would go further to completion.[5] The acid bromides exhibited the behavior of strongly dissociated electrolytes (Fig. 1). No extrapolation to infinite dilution was performed, however, since the data are not of sufficient accuracy to give reliable results.

When either acetyl or benzoyl bromide was mixed with dimethylformamide in equimolar proportions, a crystalline salt formed immediately. These salts were unstable and hygroscopic, but the analytical data were sufficiently precise to identify them as 1:1 adducts. Evidence as to the structure of these compounds was provided by their reactions with aniline and with water. The salt from benzoyl bromide gve benzanilide in 84.8% yield with aniline in acetonitrile, and gave benzoic acid in 79.3% yield with water. Structure II best represents the facts, since structure I would predict the predominant formation of formanilide or formic acid.

These results are in accord with those of Haszeldine[6] who found that Lewis acids also react with dimethylformamide at the oxygen atom.

It was of interest to discover whether other carboxamides would react as rapidly with acyl halides as does dimethylformamide. For this purpose it was convenient to dissolve sodium perchlorate in the amide studied. The rate of appearance of chloride ion could be followed visually by the rate of precipitation of insoluble sodium chloride. Some amides failed to dissolve sodium perchlorate, so an alternative procedure was devised. Sodium perchlorate is quite soluble in acetonitrile. Although this solvent possesses a dielectric constant comparable to that of dimethylformamide, acid chlorides formed no precipitate of sodium chloride with such a solution. This is further evidence against the $S_N1$ mechanism for the reaction in dimethylformamide solution. When, however, small amounts of dimethylformamide were added to the acetonitrile, precipitation of sodium chloride occurred rapidly.

By these methods, other carboxamides were found to react similarly to dimethylformamide. Dimethylacetamide and N-methylpyrrolidone reacted at rates comparable to that of dimethylformamide, while N-vinylpyrrolidone and N-methylformanilide reacted more slowly. The reduction in rate was not that which would have been expected on the basis of electronic considerations, however, had acylation been occurring at the nitrogen atom.

The reaction appears to be specific to carboxamides, since the following amides reacted to a negligible extent under the above conditions with benzoyl chloride: dimethylmethanesulfonamide, tetraethylsulfamide, diethylcyanamide, dimethylnitrosamine and hexamethylphosphoramide. The amides derived from strong acids would be expected to be inert whether acylation occurred at oxygen or nitrogen. The inertness of those derived from weak acids, however, provides additional evidence in favor of acylation occurring at oxygen in carboxamides, since amides lacking the oxygen atom do not react.

**Acknowledgments.**—We are indebted to Dr. P. W. Morgan for guidance and to Mr. Donald G. Preis for excellent technical assistance.

## Experimental

**Materials.**—The purification of the acyl chlorides has been described previously.[7] Acetyl and benzoyl bromides were obtained from Eastman Kodak Co. as water-white liquids.

Dimethylformamide was dried over a mixture of KOH and BaO, filtered and fractionally distilled in a glass helix-filled column, b.p. 152.5°. Its specific conductance was $7.8 \times 10^{-7}$ ohm$^{-1}$ cm.$^{-1}$.

Dimethyl methanesulfonamide, b.p. 112° (10 mm.), m.p. 48–49°, was prepared from methanesulfonyl chloride and dimethylamine in 71.7% yield in a stirred methylene chloride–sodium hydroxide mixture. Tetraethylsulfamide, b.p. 124.5–125.5° (8 mm.), was prepared in methylene chloride solution from sulfuryl chloride and diethylamine. Diethylcyanamide and dimethylacetamide (Eastman) and hexamethylphosphoramide (Monsanto) were purified by distillation. Dimethylnitrosamine was obtained from Dr. V. Shashoua of this Laboratory.

**Conductivity Measurements.**—The conductimetric measurements were made with an Industrial Instruments Co. Conductivity Bridge Model RC-1B (1000 cycles). The dip-type cell (smooth platinum) had a cell constant of 0.118 cm.$^{-1}$, as the resistance of a 0.01 *N* KCl solution at 20° was found to be 93 ohms. The cell was placed in one neck of a special 500-ml. 3-neck flask, an electrically driven stirrer occupying the center one. For the kinetics measurements the acid chloride was added with stirring and the resistance change measured as a function of time. A plot of the quan-

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(5) Crystalline complexes of acyl bromides with urethans have been described; see D. Ben-Ishai and E. Katchalski, *J. Org. Chem.*, **16**, 1025 (1951).

(6) R. N. Haszeldine, *J. Chem. Soc.*, 4150 (1954).

(7) H. K. Hall, Jr., This Journal, **77**, 5593 (1955).

tity log ($K_\infty - K_t$), where $K_\infty$ and $K_t$ are the reciprocals of the observed resistance at times $\infty$ and $t$, respectively, against $t$ was made. The half-life was read from the graph. For the conductivity curves an accurately weighed amount of the acyl halide was added from a weight buret to the dimethylformamide (500 ml.) with stirring. The readings changed instantly to their final values except in the case of benzoyl chloride, where 1–2 minutes was required.

**Qualitative Kinetics Measurements.**—The experiments involving solutions of sodium perchlorate in the amides were carried out with 5–10% solutions of the salt. To 5–10 ml. of such a solution was added 2–4 drops of acid chloride and the rate of appearance of a white precipitate noted. The results are as follows (Table I).

TABLE I

Rapid denotes precipitation in <5 minutes; moderate, 5–30 minutes; slow > 30 minutes.

| Acyl chloride | Dimethylformamide | Diethylcyanamide | Dimethylacetamide | N-Methylpyrrolidone | N-Methylacetamide |
|---|---|---|---|---|---|
| Benzoyl chloride | Rapid | No reacn. | Rapid | Slow | Slow |
| Ethyl chloroformate | Moderate | No reacn. | Rapid | Slow | Slow |
| Benzenesulfonyl chloride | Moderate | No reacn. | Mod. | Slow | Slow |
| Dimethylcarbamyl chloride | Very slow | ...... | ... | .. | .. |

A 5–10% solution of sodium perchlorate in acetonitrile was prepared, and to 10–15 ml. of this solution was added 2–4 drops each of acid halide and amide. The results for benzoyl chloride were as follows: dimethylformamide, formamide and N-methylpyrrolidone, rapid; N-vinylpyrrolidone and N-methylformanilide, moderate; dimethyl methanesulfonamide, tetramethylsulfamide, diethylcyanamide and hexamethylphosphoramide, negligibly slow.

**Synthetic Experiments.**—To 15 ml. of pure dimethylformamide was added 10 ml. of benzoyl bromide. The mixture solidified almost completely. It was filtered and washed with anhydrous ether under a nitrogen blanket. The precipitate weighed 12.67 g.

*Anal.* Calcd. for $C_{10}H_{12}O_2NBr$: N, 5.43. Found: N, 4.59, 4.58.

This material, 4.0 g., was slurried with 46 ml. of pure acetonitrile, in which it did not completely dissolve. Heat was absorbed. To this was added a solution of 2.88 g. of aniline in 46 ml. of acetonitrile. An exothermic reaction occurred and the solution became clear. It was evaporated overnight under a jet of nitrogen. The solid residue was taken up in 10 ml. of water, triturated, and filtered. It was washed twice more with 5-ml. portions of water and air-dried. There was obtained 2.59 g. (84.8%) of benzanilide, m.p. 158°.

Reaction of the crystalline salt with water was carried out by mixing the former, 2.0 g., in 10 ml. of water. After several hours at room temperature, the mixture was filtered and the precipitate was air-dried. There was obtained 0.75 g. (79.3%) of benzoic acid, m.p. 115–116°.

The preparation of acetyl bromide–dimethylformamide was carried out by slowly adding the amide (5 ml.) to the acid bromide (15 ml.) with chilling in ice under a nitrogen blanket. The adduct crystallized nicely from the excess acid bromide and was filtered and rinsed with ether.

*Anal.* Calcd. for $C_5H_{10}O_2NBr$: N, 7.15. Found: N, 7.31, 7.56.

Under these conditions the mixture remains colorless. If, however, the preparation is performed by adding the acid bromide to excess amide, the mixture rapidly turns a deep red color. This does not appear to be bromine, since pouring an aliquot into water and extracting with carbon tetrachloride does not extract the color. Styrene fails to decolorize the solution. The nature of the colored species is unknown.

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# The Thermal Decomposition of Diol Dinitrites. II

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The vapor phase decomposition of compounds having the formula $R_2C(ONO)(CH_2)_nC(ONO)R_2$, where R is H and methyl, and $n$ is 1 through 4 has been studied. On the basis of the products formed, mechanisms have been proposed which have as their first step the cleavage of one nitrite group to form an alkoxy radical and nitric oxide. The fate of the unstable alkoxy radical depends upon the value of $n$ and to a lesser extent upon whether R is H or methyl. When $n$ is 1 and R is H and methyl, the alkoxy radical decomposes to olefin, aldehyde and nitrogen dioxide. When $n$ is 2 and R is methyl, the radical yields ethylene, 2 moles of acetone and nitric oxide. When R is H and $n$ is 2, 3 or 4 no cleavage of C–C bonds takes place. Instead a hydrogen transfer takes place yielding nitric oxide and a hydroxyaldehyde ($\alpha$-hydrogen transfer) or nitrogen dioxide and hydroxyolefin ($\beta$-hydrogen transfer). The nature of the product requires that the hydrogen transfer be intra- rather than intermolecular which precludes the participation of nitric oxide as a hydrogen acceptor. The liquid phase decomposition of propane-1,3-diol dinitrite in paraffin oil solution differs from the gas phase reaction. The initially formed alkoxy radical does not undergo C–C cleavage. It abstracts a hydrogen atom from the solvent and the final product is propane-1,3-diol.

This is a continuation of Part I of this series in which the decomposition of various 1,2-diol dinitrites was described.[1] The present work is concerned with the vapor phase decomposition of compounds having the formula $R_2C(ONO)(CH_2)_nC(ONO)R_2$, where R is H or methyl and $n$ is 1, 2, 3 and 4.

## Experimental

All but one of the diol dinitrites were prepared by reaction of the diol with aqueous nitrous acid.[2] Two moles of 6 $N$ hydrochloric acid were added slowly with mechanical stirring to an aqueous solution containing 1 mole of diol and 2.2 moles of sodium nitrite at 0°. Stirring was continued for 15 minutes after all the acid was added and the reaction mixture was poured into a separatory funnel. The aqueous layer was removed and the nitrite ester was washed with a 5% solution of sodium carbonate, dried over calcium chloride, and distilled. The dinitrite of 2,5-dimethyl-2,5-hexanediol was prepared by the addition of 2 moles of NOCl to an ether solution containing 1 mole of diol and 2 moles of pyridine at 0°. The ether solution was filtered, washed with dilute acid, and 5% sodium carbonate, and dried over calcium chloride. The product was purified by distillation. The physical constants and analytical data are given in Table I.

The vapor phase decompositions were performed by passing the vapor of the dinitrite in a stream of nitrogen through

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[1] L. P. Kuhn and L. DeAngelis, THIS JOURNAL, **76**, 328 (1954).

[2] L. Gattermann and H. Wieland, "Laboratory Methods of Organic Chemistry," 24th edition, The Macmillan Co., New York, N. Y., 1943, p. 147.