analyses. The substrate concentration was determined from the amount originally added.

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OAK RIDGE, TENNESSEE RECEIVED JULY 2, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLLEGE OF ARTS AND SCIENCES, UNIVERSITY OF LOUISVILLE]

Base-catalyzed Decomposition of α-(Benzene- and *p*-Toluenesulfonamido)-phenylacetyl Chlorides

BY RICHARD H. WILEY, HOBERT L. DAVIS, DAVID E. GENSHEIMER[1a] AND NEWTON R. SMITH[1b]

It has been observed that α-(benzenesulfonamido)-phenylacetyl chloride undergoes decomposition when treated with aqueous sodium hydroxide forming benzaldehyde, benzenesulfonamide and carbon monoxide. A possible mechanism for this reaction is presented and coördinated with the decomposition of the free acid in pyridine and acetic anhydride to diphenyl disulfide and carbon dioxide. Data on the preparation, properties and reactions of the previously undescribed α-(benzenesulfonamido)- and α-(*p*-toluenesulfonamido)-phenylacetyl chlorides and the corresponding amides are given.

In a previous communication we have reported[2] the unusual formation of diphenyl disulfide in the pyridine–acetic anhydride catalyzed decarboxylation of α-(benzenesulfonamido)-propionic acid. Since then we have observed a similar reaction with α-(benzenesulfonamido)-phenylacetic acid. This reaction was explained in terms of the rupture of the sulfur–nitrogen linkage in a hypothetical carbanion intermediate, $C_6H_5SO_2NH\overset{\ominus}{C}H(CH_3)$, to form the sulfinite ion and acetaldimine. This was visualized as a β-elimination type of reaction at a carbon–nitrogen bond. The cleavage products apparently undergo disproportionation and oxidation resulting in the reduction of the sulfinite ion to the disulfide. In continuing these studies we have also observed that aqueous sodium hydroxide cleaves α-(benzenesulfonamido)-phenylacetyl chloride with formation of benzenesulfonamide, benzaldehyde and carbon monoxide.

The α-(benzenesulfonamido)-phenylacetyl chloride and its *p*-toluene analog used in these studies were prepared using purified thionyl chloride, a procedure preferred to the phosphorus pentachloride method previously described.[3a,b] Attempts to analyze and characterize these acid chlorides were beset with unusual difficulties. The crude yellow solids showed wide melting point ranges that indicated presence of impurities. Although they are soluble in hydrocarbon solvents, attempts at purification by recrystallization were unsuccessful. Neutral equivalent values were uniformly high. The presence of a neutral impurity or decomposition product was indicated by the observation that part of the sample was insoluble in alkali at the end of the titration. It is to be noted that nitrogen analysis previously used to characterize arylsulfonamido acid chlorides[3a] is insufficiently precise to distinguish between the free acid and the acid chloride. On the basis of further observations on the reactions of these chlorides on heating or treatment with alkali, it is believed that these compounds are not stable enough to permit purification, analysis and identification by the usual methods. Both acid chlorides were converted in 50–70% yields to the previously undescribed amides by reaction with aqueous ammonium hydroxide at room temperature and the benzenesulfonamido acid chloride was hydrolyzed to the acid in 67% yield. The α-(benzenesulfonamido)-phenylacetyl chloride was used as the crude yellow solid obtained after thorough evacuation of the reaction mixture to remove sulfur dioxide, hydrogen chloride, and unreacted thionyl chloride.

The alkaline decomposition reactions were carried out under a variety of conditions as described in Table I. The benzaldehyde was extracted from the alkaline reaction mixture and isolated as its 2,4-dinitrophenylhydrazone. The benzenesulfonamide precipitated on acidification of the reaction mixture. Carbon monoxide was present in the gas evolved as evidenced by the combustibility and solubility in aqueous cuprous chloride of the gas. The yields of benzaldehyde, isolated as its 2,4-dinitrophenylhydrazone, and benzenesulfonamide, using different reagents, temperatures of 30° and nearly boiling, and concentrations of sodium hydroxide from 5–50%, are given in Table I. The yield of the aldehyde varies from 3 to 65% and the yield of the amide from 10–54%. The highest yields were obtained using hot 5% sodium hydroxide. No attempt has been made to determine the loss of benzaldehyde through the Cannizzaro reaction. On one run using the chloride obtained from 1.5 g. of acid and 5% hot sodium hydroxide 130 ml. of gas (uncorrected for air in the system) was collected. Of this, 55 ml. (48% of the theoretical amount of carbon monoxide) was soluble in acidic cuprous chloride.

The data given in this and the previous paper[2] show that α-(benzenesulfonamido)-phenylacetic acid derivatives undergo decomposition with the possibility of rupture at either the sulfur–nitrogen (a) or nitrogen–carbon (b) bond depending on

$$C_6H_5SO_2 \overset{(a)}{\text{———}} NH \overset{(b)}{\text{———}} CH(C_6H_5)COX$$

the conditions. This behavior is reminiscent of the "acid" and "ketone" cleavages of acetoacetic esters. To account for this phenomenon it is proposed that

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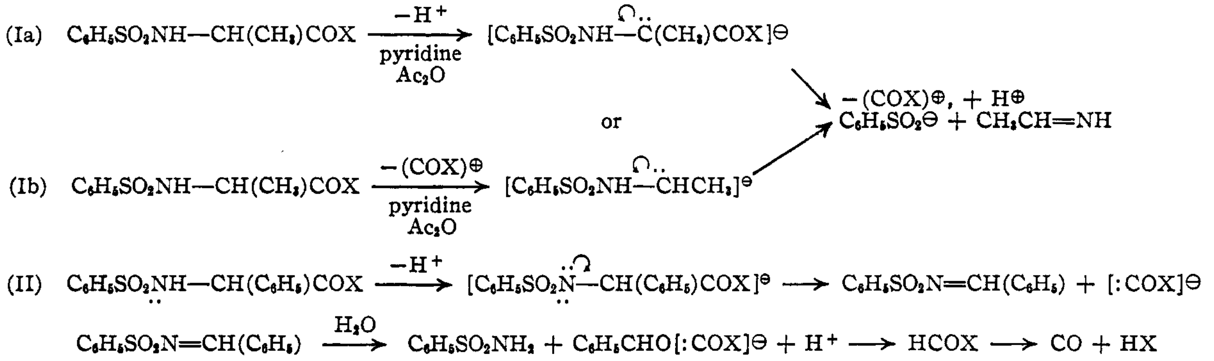
[1] (a) A portion of this work was presented in partial fulfillment of the Honors requirement by David E. Gensheimer. (b) The authors express their appreciation for a grant from the Research Fund of the College in partial support of this work.

[2] R. H. Wiley and N. R. Smith, THIS JOURNAL, **73**, 4719 (1951).

[3] (a) H. E. Carter and J. Hinman, *J. Biol. Chem.*, **178**, 403 (1949). (b) H. Bovarnick and H. T. Clarke, THIS JOURNAL, **60**, 2426 (1938).

the reactions take place through a base-catalyzed β-elimination[4] at the nitrogen–carbon bond in a manner similar to that taking place at carbon–carbon bonds. If the transitory carbanion is formed, either by removal of a proton by the base (Ia) or decarboxylation of the acid or its derivative (Ib), the cleavage takes place at the S–N bond with elimination of the sulfinite ion. Reactions Ia and Ib can be envisioned as a concerted β-elimination reaction in which no separate existence need be assigned to a transitory carbanion.[5] If the base removes a proton from the nitrogen atom, a likely possibility since sulfonamides are soluble in aqueous base, the cleavage occurs at the N–C bond (Equation II), with elimination of a carboxyl carbanion derived from formic acid.



(Ia) $C_6H_5SO_2NH{-}CH(CH_3)COX \xrightarrow[\text{pyridine}\ Ac_2O]{-H^+} [C_6H_5SO_2NH{-}\overset{\frown ..}{C}(CH_3)COX]^\ominus$

$\searrow -(COX)^\oplus, + H^\oplus$

or

$\nearrow C_6H_5SO_2^\ominus + CH_3CH{=}NH$

(Ib) $C_6H_5SO_2NH{-}CH(CH_3)COX \xrightarrow[\text{pyridine}\ Ac_2O]{-(COX)^\oplus} [C_6H_5SO_2NH{-}\overset{\frown ..}{C}HCH_3]^\ominus$

(II) $C_6H_5SO_2\underset{..}{N}H{-}CH(C_6H_5)COX \xrightarrow{-H^+} [C_6H_5SO_2\overset{..\frown}{\underset{..}{N}}{-}CH(C_6H_5)COX]^\ominus \longrightarrow C_6H_5SO_2N{=}CH(C_6H_5) + [:COX]^\ominus$

$C_6H_5SO_2N{=}CH(C_6H_5) \xrightarrow{H_2O} C_6H_5SO_2NH_2 + C_6H_5CHO[:COX]^\ominus + H^+ \longrightarrow HCOX \longrightarrow CO + HX$

In equation Ia and Ib, X may be OH or $-OCOCH_3$ and in equation II, hydroxy or chloro. Hydrolysis of the chloro to hydroxyl may take place prior to any step indicated with the ultimate formation of the formate ion.

Reaction II can also be stated as a nucleophilic displacement on carbon. The hydroxyl ion may displace either the carboxyl carbanion $(:COX)^\ominus$ or the sulfonamido anion, $(C_6H_5SO_2NH\text{-})^\ominus$. In either reaction the ultimate products are, as in the β-elimination reaction, benzenesulfonamide, benzaldehyde and some decomposition product of formic acid. Since the latter possibility requires the formation and cleavage of mandelic acid chloride, for which there is no known analogy, this type of displacement offers a less satisfactory explanation. The interpretation does, however, raise the question as to the possibility of an optical inversion during the reaction.

The isolation of carbon monoxide as one of the reaction products needs further comment. If the precursor of the carbon monoxide is formic acid as indicated, there should be some evidence that formic acid treated with aqueous sodium hydroxide gives carbon monoxide. Such data are available[6] from studies which have shown that the products of this reaction are in fact carbon monoxide, carbon dioxide and hydrogen. In the absence of additional data on the composition of the evolved gas, a complete interpretation of the fate of this fragment of the cleavage cannot be made. It is believed, however, that the identification of the fragments given in this paper is sufficient to establish without doubt the general course of the reaction.

It is to be noted that other examples of the cleavage of α-substituted acids to carbon monoxide or carbon dioxide and an aldehyde are known. Several of the types of acids which undergo this reaction—α-hydroxy acids,[7] α-amino acids,[8] and α-acyloxy- or alkoxy- acids[9] have, as does the α-sulfonamido acid, an atom with an unshared pair of electrons attached to the α-carbon. Apparently the alternative decarboxylation reaction (Equations Ia and Ib) has not been observed with these types.

In the course of this work we have also observed that when α-(benzenesulfonamido)-phenylacetic acid is decomposed by pyridine in acetic anhydride, benzaldehyde, diphenyl disulfide and benzenesulfonamide are formed. This indicates that reactions Ia-b and II may take place at the same time.

Experimental

α-(Benzenesulfonamido)-phenylacetyl Chloride and Amide.—α-(Benzenesulfonamido)-phenylacetic acid, 1 g., prepared as previously described[10] was dissolved in 4 ml. of purified[11] thionyl chloride and heated on a steam-bath for 2–3 minutes during which time the acid went into solution. The gaseous products and excess thionyl chloride were removed under vacuum leaving a yellow solid, m.p. 101–108°, which was used without further purification. Neutral equivalent values varied from 165–256. The amide, m.p. 211–212°, was prepared by reaction with ammonia at room temperature in 50% yield.

Anal. Calcd. for $C_{14}H_{14}N_2O_3S$: N, 9.6. Found: N, 9.5, 9.7.

α-(p-Toluenesulfonamido)-phenylacetyl chloride was prepared as above, m.p. 110–115°. Although soluble in benzene and toluene and apparently recrystallizable from benzene–petroleum ether mixtures, the chloride could not be obtained analytically pure. Titration with alkali gave values of 197–250 without complete solution. The amide, m.p. 219–220°, prepared from ammonium hydroxide at room temperature and recrystallized from methanol, was obtained in up to 70% yield.

Anal. Calcd. for $C_{15}H_{16}N_2O_3S$: C, 59.20; H, 5.26; N, 9.2; S, 10.5. Found: C, 59.18; H, 5.39; N, 9.21; S, 10.6.

Conversion of α-(Benzenesulfonamido)-phenylacetyl Chloride to Carbon Monoxide, Benzaldehyde and Benzenesulfonamide.—A series of experiments, summarized in Table I, was carried out using the following general procedure.

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[4] E. R. Alexander, "Ionic Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1950, pp. 105–107.

[5] The authors are indebted to a referee for pointing out this possibility.

[6] M. C. Boswell and J. V. Dickson, THIS JOURNAL, **40**, 1779 (1918).

[7] H. R. LeSueur, *J. Chem. Soc.*, **85**, 827 (1904); **87**, 1888 (1905).

[8] F. A. Baddar, *ibid.*, Supp. No. 1, PS 163 (1949).

[9] I. P. Bagard, *Bull. soc. chim.*, [4] **1**, 307 (1907).

[10] R. H. Wiley and H. L. Davis, THIS JOURNAL, **73**, 494 (1951).

[11] L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Boston, Mass., 1941, p. 381.

To the crude acid chloride obtained from 1 g. of the acid was added 15 ml. of one of the various reagents. After the times stated the reaction mixture was rapidly cooled if hot and extracted with ether, the ether removed, and the residue taken up in ethanol and treated with an excess of 2,4-dinitrophenylhydrazine solution. The precipitated 2,4-dinitrophenylhydrazone was dried, weighed, and characterized by melting point and in some instances by absence of depression in melting point in mixtures with authentic samples. From the alkaline mother liquors there were isolated on acidification α-(benzenesulfonamido)-phenylacetic acid and benzenesulfonamide as noted. One run using the chloride from 1.5 g. of acid was made in a closed system filled with air. The 130 ml. of evolved gas was collected over water. Of this gas, uncorrected for the air in the system, 55 ml. or 48% of the theoretical amount of carbon monoxide was soluble in acidic cuprous chloride.

Decomposition of α-(Benzenesulfonamido)-phenylacetic Acid in Pyridine and Acetic Anhydride.—This reaction was carried out as previously described[2] for the propionic acid derivative using 3 g. of acid. The yield of carbon dioxide evolved at the end of 10 minutes was 81% of theory. The reaction mixture was poured on ice and hydrochloric acid and extracted with ether. The ether extracts were washed with water and bicarbonate and divided into two portions. The ether was removed from one portion leaving a residue from which a 2,4-dinitrophenylhydrazone, m.p. 236–237°, was obtained. This showed no depression in melting point when mixed with an authentic sample of the benzaldehyde derivative. The yield corresponded to 53% of the theoretical amount of benzaldehyde. The other portion was extracted with sodium hydroxide. The alkaline extract was acidified and extracted with ether. The ether extracts on evaporation deposited less than 0.1 g., *ca.* 7%, of benzenesulfonamide, m.p. 152–153°. The alkali-extracted ether extract was evaporated to remove the ether and steam distilled to give *ca.* 0.05 g., *ca.* 5%, of diphenyl disulfide, m.p. 55°.

TABLE I

ALKALINE DECOMPOSITION OF α-(BENZENESULFONAMIDO)-PHENYLACETYL CHLORIDE

Reagent[a]	Time, min.	Yield,[b] %	Other products[c] (% yield)
5% NaOH	5	24	BSPA (10)
5% NaOH	5	33	BSPA (27)
15% NaOH (hot)[d]	5	43	BSA (15)
C_2H_5OH[e]	5	5	....
C_2H_5OH[e]	5	4	....
NH_4OH	4 hr.	..	BSPAM (50)
Pyridine	1 hr.	13	....
H_2O	20 hr.	3	BSPA (67)
5% NaOH (hot)[d]	3	65	BSA (54)
50% NaOH	1	0	....

[a] The reaction was run at room temperature (30°) except as noted. [b] Of the isolated 2,4-dinitrophenylhydrazone of benzaldehyde. [c] Yield in parentheses; BSPA, α-(benzenesulfonamido)-phenylacetic acid; BSPAM, amide of BSPA; BSA, benzenesulfonamide. [d] The reagent was heated to boiling and added to the chloride. [e] Reaction mixture tested for benzaldehyde directly.

LOUISVILLE 8, KENTUCKY RECEIVED JUNE 18, 1951

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Monoradical and Diradical Polymerization of Styrene[1]

BY D. H. JOHNSON AND A. V. TOBOLSKY

Relations between reciprocal number average degree of polymerization and rate of polymerization have been derived for monoradical and diradical initiation to account for the effects of termination of combination and disproportionation and also for the effect of chain transfer to catalyst. These equations were applied to experimental data on the polymerization of styrene at 60° initiated by various catalysts and by light. The chain transfer constant of styrene of 2-azo-bis-isobutyronitrile is effectively zero. The chain transfer constants of cumene hydroperoxide and *t*-butyl hydroperoxide are 0.063 and 0.035, respectively. The chain transfer constant for benzoyl peroxide calculated by our equation agrees closely with that reported by Mayo, Gregg and Matheson. The catalyst efficiencies for benzoyl peroxide and 2-azo-bis-isobutyronitrile are found to be nearly unity and the results indicate that the termination step occurs mainly by combination of radicals. Photopolymerization appears to proceed *via* chains growing in one direction only.

Introduction

In a recent paper by Mayo, Gregg and Matheson[2] a very careful analysis of the benzoyl peroxide catalyzed polymerization of styrene at 60° was made which enabled these authors to calculate the chain transfer constants to monomer and to catalyst, to evaluate the catalyst efficiency for benzoyl peroxide, and to conclude that the termination step probably occurs by recombination of radicals.

We present in this paper a similar series of experiments on the polymerization of styrene initiated by benzoyl peroxide, 2-azo-bis-isobutyronitrile, *t*-butyl hydroperoxide, cumene hydroperoxide and ultraviolet light. Our results offer an independent verification of the conclusions and results of Mayo, *et al.*, discussed above. In addition, we calculate the catalyst efficiency of 2-azo-bis-isobutyronitrile, the chain transfer constants for *t*-butyl hydroperoxide, cumene hydroperoxide, 2-azo-bis-isobutyronitrile, and show that photopolymerization proceeds *via* chains growing in one direction only. Our method of analyzing the kinetic data[3,4] is different from, but not contradictory to, the method of Mayo, *et al.*, and has, we think, attractive features of simplicity.

Chain Transfer Constants for Monoradical Catalyzed Polymerization.—Catalysts for vinyl polymerization such as benzoyl peroxide, 2-azo-bis-isobutyronitrile, *t*-butyl hydroperoxide and cumene hydroperoxide (which we shall hereinafter refer to as Bz_2O_2, Azo, *t*-BHP, and CHP, respectively) cleave to produce monoradicals, some of which initiate polymer chains. In the case of styrene (but not all vinyl monomers) there is in addition a spontaneous thermal initiation which occurs independently of the cata-

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(1) This paper was presented at the September, 1950, Meeting of the American Chemical Society in Chicago. Earlier results were presented at the September, 1949, meeting of the American Chemical Society in Atlantic City, N. J. See Abstracts of the A.C.S., September, 1949, Meeting at Atlantic City, p. 10 N; and Abstracts of the A.C.S., September, 1950, Meeting at Chicago, Ill., p. 2J.

(2) F. R. Mayo, R. A. Gregg and M. S. Matheson, THIS JOURNAL, **73**, 1691 (1951).

(3) D. H. Johnson, A. Escoruela and A. V. Tobolsky, Princeton University Plastics Report 14A, Signal Corps Contract W-36-039-SC-32011, May 3, 1949. Copies may be obtained by writing to Plastics Laboratory, Princeton University.

(4) H. Mark and A. V. Tobolsky, "The Physical Chemistry of High Polymeric Systems," Interscience Publishers, New York, 1950, pp. 401–408.