single type of heterolytic cleavage can account for all of the products.[12] Experimentation is in progress which should allow us to distinguish between these two possible routes to the *o*- and *p*-chloroanilines.

Since N-chloroaniline derivatives can be prepared rapidly in high yield and in a high state of purity *via* reaction of the corresponding aniline with sodium hypochlorite, the use of these intermediates in the synthesis of a wide variety of substituted aromatic amines should be possible. We are presently investigating a variety of applications of this potentially important nucleophilic aromatic substitution reaction.

Acknowledgment. We wish to thank the National Cancer Institute of the Public Health Service for Grant CA-07110 which supported this research.

---

[12] We have previously shown that chlorine can migrate from nitrogen to carbon with dramatic silver ion catalysis in high yield[1c] *via* the intermediacy of a tight ion pair.

[13] Alfred P. Sloan Research Fellow, 1967–1969.

[14] National Defense Education Act Predoctoral Fellow, 1967–1969.

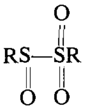
Paul G. Gassman,[13] Gerald Campbell,[14] Ronald Frederick
Department of Chemistry, The Ohio State University
Columbus, Ohio 43210

Received October 4, 1968

Synthesis and Properties of a Sulfinic Anhydride[1]

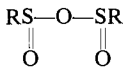
Sir:

Previously all attempts[2,3] to prepare the anhydride **2** of any sulfinic acid have led to the preparation of the isomeric sulfinyl sulfone **1**. We wish to report the first



$$\mathrm{R\underset{\underset{O}{\|}}{S}-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}R}$$

1

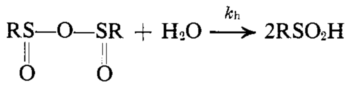


$$\mathrm{R\underset{\underset{O}{\|}}{S}-O-\underset{\underset{O}{\|}}{S}R}$$

2

preparation of such an anhydride (**2a**, R = *t*-Bu) and to indicate some significant differences between its properties and those of **1**.

Careful acidification of a cold solution of magnesium 2-methyl-2-propanesulfinate[4] gives 2-methyl-2-propanesulfinic acid (**3a**), which can be converted to the corresponding sulfinyl chloride by treatment with an equimolar quantity of thionyl chloride in ether. The sulfinyl chloride was added to a stirred suspension of silver 2-methyl-2-propanesulfinate[4] in ether at −5 to −10°. After 3 hr the mixture was filtered, and the ether was removed at 0°. The residue was purified by several low-temperature recrystallizations from ether, giving 2-methyl-2-propanesulfinic anhydride (**2a**, R = *t*-Bu) in 50% yield, mp 45–46°.[5] Proof that the compound was a sulfinic anhydride was provided (1) by its facile hydrolysis (eq 1) to **3a**, isolated in 73% yield by

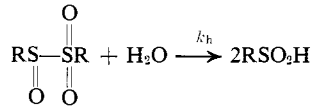


$$\mathrm{R\underset{\underset{O}{\|}}{S}-O-\underset{\underset{O}{\|}}{S}R + H_2O \xrightarrow{k_h} 2RSO_2H} \qquad (1)$$

2a **3a**

precipitation as its benzenediazo sulfone derivative, $C_6H_5N{=}NSO_2Bu$-*t* (**4**), mp 65–66°,[6] and (2) by its infrared spectrum (in $CHCl_3$), which was entirely different in the 7.5–9.3-μ region from those of three known sulfinyl sulfones (**1b**,[7] R = CH_3; **1c**,[7] R = *n*-Bu; and **1d**,[2] R = *p*-$CH_3C_6H_4$). All three of the latter possess a strong band at 7.6 μ due to the sulfone group, another absorption due to this group in the region 8.5–9.0 μ, and a strong band due to the sulfinyl group at 9.2 μ. In contrast, **2a** shows *only* a *single* strong band at 8.8 μ, an appropriate wavelength for a sulfinyl group which is bonded to carbon and an electron-withdrawing oxygen function.[9]

Sulfinic anhydride **2a** differs markedly from sulfinyl sulfones **1b–d** in the susceptibility of its hydrolysis to acid catalysis. In aqueous dioxane the hydrolysis of sulfinyl sulfones (eq 2) is not subject to acid catalysis



$$\mathrm{R\underset{\underset{O}{\|}}{S}-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}R + H_2O \xrightarrow{k_h} 2RSO_2H} \qquad (2)$$

(Table I and ref 3a). In sharp contrast the hydrolysis of sulfinic anhydride **2a** (eq 1) in the same medium shows definite acid catalysis (Table I), k_h being given by an expression of the form

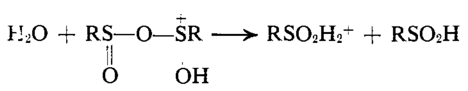
Table I. Rates of Hydrolysis in Acidic 60% Dioxane at 21.4° [a]

	$k_h \times 10^3$, sec^{-1}				
	C_{HClO_4}, *M*				
Compound	0.01	0.10	0.30	0.50	0.60
1b, R = CH_3	12	12			
1c, R = *n*-Bu	2.7	2.6		2.6	
2a, R = *t*-Bu	0.15	0.20	0.35	0.51	0.61

[a] Followed spectrophotometrically by measuring the decrease in optical density at 250 mμ for **1b** and **1c** and at 238 mμ for **2a**.

$$k_h = k_0 + k_H(H^+) \qquad (3)$$

Since $(k_H^{D_2O}/k_H^{H_2O}) = 1.35$, the $k_H(H^+)$ term in eq 3 is presumably associated with a mechanism (eq 4) involving attack of water on protonated **2a** (**5**).[10]



$$\mathrm{H_2O + R\underset{\underset{O}{\|}}{S}-O-\underset{\underset{OH}{|}}{\overset{+}{S}}R \longrightarrow RSO_2H_2^+ + RSO_2H} \qquad (4)$$

5

---

[1] This research was supported by the National Science Foundation, Grant GP-6952.

[2] (a) H. Bredereck, A. Wagner, H. Beck, and R. J. Klein, *Ber.*, **93**, 2736 (1960); (b) H. Bredereck, A. Wagner, E. H. Beck, H. Berlinger, and K.-G. Kottenhahn, *Angew. Chem.*, 70, 268 (1958).

[3] (a) J. L. Kice and G. Guaraldi, *J. Am. Chem. Soc.*, **89**, 4113 (1967); (b) J. L. Kice and N. E. Pawlowski, *ibid.*, **86**, 4898 (1964).

[4] H. Rheinbolt, F. Mott, and E. Motzkus, *J. Prakt. Chem.*, [2] **134**, 257 (1932).

[5] *Anal.* Calcd for $C_8H_{18}O_3S_2$: C, 42.45; H, 7.96. Found: C, 42.60; H, 7.64. The nmr spectrum (CCl_4) showed a sharp singlet at τ 8.78; the ultraviolet spectrum (dioxane) showed λ_{max} 238 mμ (ϵ 2300); upon addition of water to the solution this λ_{max} gradually disappears due to hydrolysis of 2a to 3a.

[6] *Anal.* Calcd for $C_{10}H_{14}N_2O_2S$: C, 53.07; H, 6.23. Found: C, 53.36; H, 5.97.

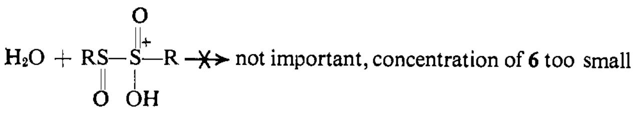
[7] The two sulfinyl sulfones **1b** and **1c**, previously unreported, were synthesized from the appropriate sulfinyl chloride and the sodium salt of the corresponding sulfinic acid by procedures analogous to those used for the synthesis of **1d**.[2,3,8]

[8] Satisfactory analyses were obtained for **1b** and **1c**. Their ultraviolet spectra (dioxane) have no clearly defined maximum above 220 mμ, only a broad shoulder extending from about 240–260 mμ (ϵ ~3000); on addition of water to the solution this absorption at 240–260 mμ disappears more or less rapidly due to hydrolysis of **1**. The nmr spectrum of **1b** consists of two sharp singlets, one at τ 7.15 and the other at τ 6.83.

[9] L. J. Bellamy in "Organic Sulfur Compounds," Vol. *1*, N. Kharasch, Ed., Pergamon Press, Oxford, 1961, p 48. See also the spectrum of ethyl *p*-toluenesulfinate shown in ref 2a.

[10] If the $k_H(H^+)$ term were due to unimolecular dissociation of **5** (an A1 mechanism), $k_H^{D_2O}/k_H^{H_2O}$ would be much larger (1.9–2.6).[11]

We suggest that the reason such an acid-catalyzed mechanism can make a contribution to the hydrolysis rate of **2a** but not to that of **1** is because sufinyl groups are so much more basic than sulfone groups.[12] Thus, at a given acidity, the equilibrium concentration of **5** is orders of magnitude larger than the equilibrium concentration of sulfonyl-protonated **1** (**6**). As a result, the acid-catalyzed reaction in eq 4 can compete with the uncatalyzed hydrolysis of **2a**, but this is not possible with **1** because of the extremely minute equilibrium concentration of **6**.



6

$$\mathrm{H_2O} + \mathrm{RS(=O)\!-\!\overset{+}{S}(=O)(OH)\!-\!R} \not\longrightarrow \text{not important, concentration of } \mathbf{6} \text{ too small}$$

The important general mechanistic significance of this result is that it suggests that the function of acid catalysis in these and related substitutions at sulfinyl sulfur is *protonation of the leaving group*, and *not* protonation of the sulfinyl group at which substitution is to occur. Otherwise there would be no reason for the different behavior exhibited by **1** and **2**.

The chemistry of sulfinic anhydrides and their possible interconversion with sulfinyl sulfones is currently under intensive study.

John L. Kice, Katsuyata Ikura
Department of Chemistry, Oregon State University
Corvallis, Oregon 97331

Received August 5, 1968

The value observed is in the range considered[11] typical for an A2-type process of the sort shown in eq 4.

(11) C. A. Bunton and V. J. Shiner, Jr., *J. Am. Chem. Soc.*, **83**, 3207 (1961); J. G. Pritchard and F. A. Long, *ibid.*, **78**, 6008 (1956); **80**, 4162 (1958).

(12) See ref 3a for a discussion of this point.

Book Reviews

Theory of Energy Transfers and Conversions. By FEDERICO GRABIEL, Space Systems Division, Hughes Aircraft Co., Culver City, and Loyola University, Los Angeles, Calif. John Wiley and Sons, Inc., 605 Third Ave., New York, N. Y. *1967.* xii + 217 pp. 16 × 24 cm. $10.95.

In this small volume, Federico Grabiel has provided a novel linear theory of energy transfers and conversions, which includes, as special cases, the second and third laws of thermodynamics. The development is axiomatic, with definitions and postulates induced from experience, and theorems deduced with the aid of elementary set theory and calculus. The chapter headings convey the flavor of the book: 1, Introduction; 2, Mathematical Preliminaries; 3, The Fundamental Theorems on Functions of State; 4, The Second Law of Energy Transfers and the General Gradient Law; 5, The Convertibility Equation. The Increment of the Associated Extensive Parameter or Coparameter, Its First Two Properties: Additivity and Extensiveness; 6, Interpretation of the Coparameter Increment; 7, Evaluation of the Irreversible Production of the Coparameter: Parasitic Conversions. Frictional Dissipation; 8, Evaluation of the Irreversible Production of the Coparameter: Internal Gradients; 9, The Finite Propagation Hypothesis and the Law of Degradation; 10, Third Fundamental Property of the Coparameter: Function of State; 11, Irreversible Production of the Coparameter: Internal Gradients—General Case; 12, Criteria for Equilibrium; 13, The Physicochemical Potentials; 14, The Fundamental Physicochemical Equation; 15, General Conditions for Equilibrium; 16, Processes in the Neighborhood of Absolute Zero Value of an Intensive Parameter; 17, The Process Velocity and the Affinity Function. The Direction of Time; 18, Systems Far from Equilibrium. Negative Absolute Values of the Intensive Parameter.

The contents are highly original, and Grabiel obviously has keen insight into his subject matter. It is, therefore, rather unfortunate that he chose to minimize the number of examples, omit exercises, and select his few concrete illustrations from phenomena other than heat. The net result is a succinct, fairly abstract text, faintly reminiscent of the difficult writings of Gibbs, in that the meaning is sometimes difficult to decipher. For example, on p 45 we find: "The symbol A_0^p, called the *absolute zero value of the parameter p*, represents the lowest p-value that can be *conceptually predicated* of the whole universe $U = \mathcal{S} \cup \mathcal{E}$." The four appendixes, however, were written in a more leisurely style, and the reviewer found considerable pleasure in reading them.

Thus, one criticism of the book is that it is too tightly constructed. Another criticism, common to all formal treatments of physical subjects, is that statements obvious to the author are not necessarily self-evident to others. By the way of illustration, let us consider the important Definition 4-1: "A δ_p-*set* (or δ_p-*cell*) is the smallest subsystem (or subset) of $\mathcal{S}$ at which property p is measurable." It is not clear to the reviewer that such a smallest subsystem is always well defined. He also wonders whether it is possible to formulate properly the definition without extended consideration of the meaning of the term "property" and of the role of experimental uncertainties.

In summation, the "Theory of Energy Transfers and Conversions," as developed by Grabiel, merits serious study by scholarly students of thermodynamics. However, the reviewer fears that, because of its unfamiliar format and closely knit structure, it will suffer the temporary fate of Gibbs' treatise on statistical mechanics, which was said by Poincare to be a "little book, little read, because it is a little hard."

Richard J. Bearman
Department of Chemistry, University of Kansas
Lawrence, Kansas 66044

Statistical Mechanical Theories of Transport Processes. By ROBERT M. MAZO. Pergamon Press Inc., 44-01 21st St., Long Island City, N. Y. 1967. xiii + 166 pp. 15.5 × 23 cm. $9.50.

The kinetic theory of dilute gases was brought to a theoretical high point by the studies of Enskog and of Chapman in the first quarter of this century. This work, which assumed the validity of the Boltzmann equation, developed algorithms for the calculation of the thermal conductivity, viscosity, and other transport coefficients in terms of the properties of the intermolecular pair potential. In the period 1920–1946 little of fundamental significance was added to the theoretical structure, and, aside from an isolated study by Enskog in 1922 and the model activated state theories of Eyring, little attention was devoted to transport phenomena in dense fluids. Interest in the theory of transport phenomena was stimulated by the publication, in 1946, of a paper by Kirkwood on the general theory of irreversible processes. Since that time, many investigators have made contributions that have greatly deepened our understanding of the nature of irreversible phenomena, have provided formalisms for the calculation of transport coefficients as general as the partition function formalism for the calculation of the free energy, and have provided models of varying degrees of sophistication (usually solved approximately) which describe with moderate accuracy the steady-state transport coefficients in a dense fluid. The monograph by Mazo touches on most of these subjects. Throughout the treatment is clear and clean, with the approximations made stated openly and their meaning discussed. The first three chapters deal with macroscopic relations, general dynamical