in ionization potential between As^{+2} and As^{+5} is 100 e.v. while the energies of peak C for As_2O_5 and As_2O_3 differ by only 5 e.v. There is also only a small correlation between the average electronegativity of the substituents and the energy of peak C, as can be seen from Table I. However, as expected, a high electron density on the arsenic atom consistently favors the escape of a 1s electron from the arsenic, represented by the escape-potential peak C.

Although the electrostatic model only poorly predicts the characteristics of the transitions in the lower energy regions, it fares much better when employed to estimate bond distances[2] from the C–D distance in Figure 1. This is shown by the following bond distances (Å.), where the values determined from diffraction studies[4] are given in parentheses behind those estimated from the K-edge absorption data: AsF_3, 1.9 (1.72); $AsCl_3$, 2.2 (2.25); AsI_3, 2.4 (2.54); Na_3AsO_4, 1.7 (1.75); and As_4O_6, 1.9 (1.79). We may conclude that, while details of σ and π bonding strongly influence the bound electronic levels on the arsenic atoms, a 1s electron with energy sufficient to surmount the attractive Hartree potential behaves approximately as a free electron in an ionic lattice.

The composite data on the arsenic compounds studied are presented in Table I.

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(4) L. E. Sutton, Ed., Tables of Interatomic Distances and Configuration in Molecules and Ions, The Chemical Society, London, 1958.

Correspondence

On the Supposed Reaction between Sulfur Hexafluoride and Hydrogen Iodide

Sir:

Padma and Murthy[1] have recently reported that sulfur hexafluoride is completely reduced by hydrogen iodide in the gas phase after 6 hr. at room temperature (30 ± 2°) and propose an analytical method based on the equation

$$SF_6 + 8HI = H_2S + 4I_2 + 6HF$$

Previously published work has shown that SF_6 undergoes chemical disruption only under powerful conditions such as exposure to alkali metal systems[2,3] and to attack by strong Lewis acids.[4] In the course of an investigation into the reactions of SF_5-containing compounds, we were unable to achieve reduction of the SF_5 group in the fluorocarbon derivatives $SF_5(C_2F_5)_nCl$[5] using either HI or H_2S at temperatures up to 200°. Furthermore, we could not detect any reaction between pure SF_6 and H_2S, contrary to an early report.[6] These observations prompted us to investigate the claim that reduction of SF_6 is readily brought about by hydrogen iodide.

In our experiments dry, oxygen-free gaseous mixtures of HI and SF_6 (8:1 molar ratio) under atmospheric pressure were allowed to stand in the dark at 25–35° for 72 hr. On analysis no trace of hydrogen sulfide, hydrogen fluoride, or free iodine could be detected, SF_6 being recovered unchanged. When the experiments were repeated with the gas mixtures exposed to ultraviolet radiation no products derivable from SF_6 were found, although iodine formed by the photodecomposition of HI was present.

The reducibility of the SF_5 group in compounds of the formula SF_5X depends largely on the nature of the attached group X. Perfluoroalkyl–SF_5 compounds and SF_6 are not reduced by sodium iodide in acetone, whereas SF_5Cl, S_2F_{10}, and $S_2F_{10}O$ react readily.[7] The trend is further illustrated by the reaction with anhydrous $AlCl_3$ in which chlorine and chlorides of sulfur are formed.[4] In this reaction SF_6 requires a temperature of 180–200° for its decomposition whereas $SF_5(C_2F_4)_nCl$ and S_2F_{10} react exothermally at room temperature.

The results reported by Padma and Murthy,[1] who did not state how they characterized their SF_6 sample, are consistent with the presence of a large proportion of S_2F_{10} (b.p. 29°) or even $S_2F_{10}O$ (b.p. 31°) in their material.

Sulfur hexafluoride was obtained as a by-product from the reaction of SF_4 with chlorine monofluoride.[8] The gas was freed from traces of SF_5Cl, SF_4, and Cl_2 by scrubbing with aqueous sodium hydroxide and aqueous potassium iodide consecutively, before being dried by passage through concentrated sulfuric acid and over phosphorus pentoxide. Gas–liquid chromatography on Florube A grease[8] indicated a single component. The infrared spectrum of the gas was identical in detail with the published spectrum[9] of pure SF_6 and no absorption attributable to S_2F_{10} (*e.g.*, the 826 cm.$^{-1}$ band[10]) was present.

Hydrogen iodide was prepared by the reaction of iodine with boiling tetralin.[11] The gaseous product was entrained in a stream of dry, oxygen-free nitrogen and collected in a liquid air cooled trap. Repeated transfer of the material between cooled traps *via* U tubes packed with powdered KI served to remove traces of tetralin and unreacted iodine.

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(1) D. K. Padma and A. R. V. Murthy, *Inorg. Chem.*, **3**, 1653 (1964).

(2) H. C. Cowen, F. Riding, and E. Warhurst, *J. Chem. Soc.*, 4168 (1953).

(3) G. C. Demitras and A. G. MacDiarmid, *Inorg. Chem.*, **3**, 1198 (1964).

(4) J. R. Case and F. Nyman, *Nature*, **193**, 473 (1962).

(5) J. R. Case, N. H. Ray, and H. L. Roberts, *J. Chem. Soc.*, 2070 (1961).

(6) H. Moissan and P. Lebeau, *Compt. Rend.*, **130**, 869 (1900).

(7) G. Pass and H. L. Roberts, *Inorg. Chem.*, **2**, 1016 (1963).

(8) F. Nyman and H. L. Roberts, *J. Chem. Soc.*, 3180 (1962).

(9) R. T. Lagemann and E. A. Jones, *J. Chem. Phys.*, **19**, 534 (1951).

(10) R. E. Dodd, L. A. Woodward, and H. L. Roberts, *Trans. Faraday Soc.*, **53**, 1545 (1957).

(11) J. Houben, J. Boedler, and W. Fischer, *Chem. Ber.*, **69B**, 1766 (1936).

The hydrogen iodide and sulfur hexafluoride were metered spearately into 1-l. glass vessels so that the respective partial pressures were in the ratio 8:1 and the total pressure was about 1 atm. at 20°. The charged vessels were then maintained thermostatically at 25 and 35° for 72 hr. in the dark. At the end of this period no pressure change was detected. A small volume of water was then injected into the gas mixtures to dissolve the HI. The residual gas was found to consist entirely of SF_6. Analysis of the aqueous extracts by means of the standard techniques[12] confirmed the absence of free iodine, hydrogen sulfide, and fluoride ion. When the experiments were repeated with the reaction vessels exposed to radiation from a mercury vapor lamp it was found that iodine was formed to the extent of about 5% of the hydrogen iodide originally taken. There was again no evidence of SF_6 decomposition.[13]

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[12] A. I. Vogel, "A Text-Book of Quantitative Inorganic Analysis," 3rd Ed., Longmans, Green and Co., London, 1961.

[13] NOTE ADDED IN PROOF.—Mr. W. G. Lawn, University of Pennsylvania, has confirmed our observations in a recent investigation of the reaction in question.

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Book Review

Friedel-Crafts and Related Reactions. Volume II, Parts I and II and Volume III, Parts I and II. Edited by GEORGE A. OLAH. John Wiley and Sons, Inc., New York, N. Y. 1964. 16.5 × 24 cm. Volume II: Part I, 658 pp.; Part II, 703 pp. $50.00. Volume III: Part I, 910 pp.; Part II, 695 pp. $60.00.

The key words in the title of these rewarding volumes are "Related Reactions," for "Friedel–Crafts Reactions" is liable to call to mind a too-restricted domain of organic and inorganic chemistry. Investigators with an interest in nearly any branch of chemistry will find rich fare in at least one chapter in these four volumes. As is to be expected, a majority of the chapters deal with "classical" Friedel–Crafts reactions, alkylations of aromatics with alkanes, alkenes, dienes, and alkynes, with ethers and carbonyl compounds, and acylations with acid derivatives. Volume III, Part I, for instance, consists mainly of two long chapters, one (381 pages, including 216 pages of tables and 2160 references) describing the synthesis of aromatic ketones and the other (375 pages, including 235 pages of tables and 1701 references) dealing with acylations with di- and polycarboxylic acid derivatives. Shorter chapters on the Houben–Hoesch synthesis and the Fries reaction are also included. These chapters are much like those which appear in "Organic Reactions," and they provide critical keys to the literature and discussions of mechanisms and catalytic and solvent effects. Volume III, Part II consists of shorter articles covering more varied grounds. A chapter on cycliacylation is followed by a short but illuminating one on the mechanism of acylations. The chapter on aliphatic acylations is an excellent example of the wide scope of these articles. The reactions of alkenes, alkanes, and alkynes with acid chlorides are considered, and, in addition to straightforward reactions, a host of fascinating rearrangements and unexpected transformations are described. Aromatic halogenation, sulfonation, nitration, and sulfonylation as well as the synthesis of aromatic acids and aldehydes are reviewed in other chapters.

Volume II follows somewhat the same pattern. Part I covers the alkylation of aromatics with alkenes, alkynes, and alkanes, with haloakanes, alcohols, and ethers, with aldehydes and ketones, and with esters of inorganic acids. In Part II generally less-familiar reactions are considered including cyclialkylation and dehydrogenation condensation reactions. Chapters dealing with isomerization of aliphatic and aromatic hydrocarbons and alkylation of saturated hydrocarbons again take us far afield from aromatic chemistry and provide a great deal of information which it is difficult to obtain elsewhere. A chapter on polymerization, one on hydrogen exchange, and others on the Prins reaction, the condensation of haloalkanes with alkenes, and haloalkylation complete this part.

With such a large number of authors, the quality of the chapters varies, but the average is high and the authors have obviously devoted a great deal of effort to their contributions. Since all the reactions considered have many elements of similarity, there is inevitably a rather high degree of redundancy in some of the sections—notably those dealing with mechanism and catalytic effects. Few readers (including even a reasonably conscientious reviewer) will read all of these volumes at one stretch. As a consequence, this redundancy is welcome, as chapters can be dipped into nearly at random.

These volumes will be available in any good chemistry library. They are expensive, and purchase for a personal collection will vary according to need. As a handy reference for synthetic work, Part I of both volumes can be recommended. My own preference is for the second parts. These chapters on less common reactions provide illuminating insights into many aspects of organic chemistry, some far afield from the Friedel–Crafts reaction.

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BOOKS RECEIVED

December 1965

JAMES B. HENDRICKSON. "The Molecules of Nature." W. A. Benjamin, Inc., 1 Park Ave., New York, N. Y. 1965. v + 189 pp. Hardback, $7.00; paperback, $3.95.