We are now in a position to summarize the existing knowledge of the mechanism of the *anodic* oxidation of PAP. Knobloch's work showed that in basic solutions the electron-transfer step is reversible and is the same in the anodic as in the homogeneous reaction. By analogy with the similar methyl-aminonaphthol, two electrons seem to be involved. Fieser's work on the *homogeneous* oxidation of PAP showed that the range of the linear portion of the potential–time plot decreased rapidly as the *p*H was lowered to 2.69 thus suggesting that in more acidic solutions the first-order character of the follow-up step (equation 2b) might disappear altogether. General considerations also suggest the possibility that a mechanistic inversion might occur in sufficiently acidic solutions because of the possibility of the semiquinone becoming appreciably stable[21] or of the *p*-hydroxyanilinium ion becoming the participating species of the reductant. Our work at *p*H 1.18 showed no evidence of a mechanistic inversion. Our data were in accord with a mechanism of type 2a-b. The agreement between our value for E_0' and Fieser's extrapolated value together with our accurately determined value of 2 for the number of electrons transferred show that the first step (2a) of the *anodic* oxidation is the same as that of the *homogeneous* reaction. Since the second step in the *anodic* reaction involves the same transitory intermediate reactant as the *homogeneous* oxidation and since, as we showed, its initial rate constant is a first-order constant, it seems almost certain that it is identical with the second step (1b) of the homogeneous oxidation which has been established, in basic solutions, to be the hydrolysis of quinoneimine.

It is barely conceivable that there might be a change, between *p*H 2.69 and 1.18, in the participating species of the reductant when homogeneous oxidation occurs although such is not the case for the heterogeneous reaction. This is very unlikely, however. We may therefore consider that our work has extended the knowledge of the homogeneous mechanism to *p*H 1.18.

Since our data are definitely not in accord with a mechanism involving a rate-controlling electron-transfer step, our work serves to emphasize that a voltammetric technique is able to distinguish between this mechanism and the Conant–Pratt mechanism even though the two are indistinguishable from the point of view of the theory of absolute reaction rates or, in the case of homogeneous oxidation, by Conant's electrochemical (A.O.P.) technique.

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[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT CENTER OF THE ARMSTRONG CORK CO.]

The Reaction of Neutral Esters of Trivalent Phosphorus Acids with Inorganic Acid Chlorides. I. The Reaction of Trialkyl Phosphites with Sulfuryl Chloride

BY ALGIRDAS C. POSHKUS AND JOHN E. HERWEH

RECEIVED JUNE 20, 1957

The reaction of sulfuryl chloride with trialkyl phosphites has been investigated. Dialkyl phosphorochloridates, sulfur dioxide and alkyl chlorides are formed. This constitutes a useful simple synthesis of dialkyl phosphorochloridates which avoids acidic by-products.

Interest in expanded or foamed plastics has stimulated the investigation of pneumatogens, thermolabile compounds which decompose into products at least one of which is gaseous.[1a,b] Attention was directed toward the reaction of sulfuryl chloride with trialkyl phosphites[2] which was expected to proceed in a manner analogous to the Michaelis–Arbuzov reaction as applied to acid chlorides of carboxylic acids.[3a,b] Extension of Michaelis–Arbuzov reaction to compounds bearing a halogen attached to elements other than carbon has been inadequately studied.

The reaction of sulfuryl chloride with dialkyl hydrogen phosphite occurs readily at about 30–45° in the absence of solvents to give dialkyl phosphorochloridates in good yields.[4] Hydrogen chloride, one of the reaction products, has a solvolytic effect on the chloridate as well as on the dialkyl phosphite,[5a,b] thus limiting the synthetic application of this reaction.[6,7]

It has now been found that sulfuryl chloride does indeed react with trialkyl phosphites extremely vigorously even at temperatures as low as −20° in a variety of solvents at low dilution. Stable intermediates reported by Bell[2] were not found. If intermediates are formed, they are extremely labile even at 0°. Thus, in a reaction carried out at temperatures below 20°, almost a quantitative amount (>95%) of sulfur dioxide was swept out by a stream of nitrogen and absorbed in an aqueous iodine–potassium iodide solution. The reaction apparently conforms to the stoichiometry

$$(RO)_3P + SO_2Cl_2 \longrightarrow (RO)_2P(O)Cl + SO_2 + RCl$$

The order of adding the reactants did not affect the

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[1] (a) F. Lober, *Angew. Chem.*, **64**, 65 (1952); (b) R. A. Reed, *Plastics Progress*, 51 (1955).

[2] A. Bell, U. S. Patent 2,508,364 (1950).

[3] (a) T. Reetz, D. H. Chadwick, E. E. Hardy and S. Kaufman, THIS JOURNAL, **77**, 3813 (1955); (b) T. B. Ackerman, T. A. Jordan, C. R. Eddy and D. Swern, *ibid.*, **78**, 4444 (1956); also see references cited in these papers.

[4] F. R. Atherton, H. T. Howard and A. R. Todd, *J. Chem. Soc.*, 1106 (1948).

[5] (a) W. Gerrard and E. G. G. Whitbread, *ibid.*, 914 (1952); (b) C. H. Campbell and D. H. Chadwick, THIS JOURNAL, **77**, 3379 (1955).

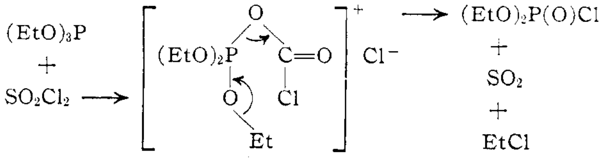
[6] G. W. Kenner, A. R. Todd and F. J. Weymouth, *J. Chem. Soc.*, 3675 (1952).

[7] F. R. Atherton, H. T. Openshaw and A. R. Todd, *ibid.*, 382 (1945).

results obtained. This reaction proceeds so readily in good to excellent yields without the formation of acidic by-products such as encountered in the chlorination of dialkyl phosphites with sulfuryl chloride or chlorine that it is a useful laboratory method for preparing phosphorochloridates when the trialkyl phosphite is readily available. This procedure also circumvents the disadvantage of using chlorine, reduces the preparation time, and permits easy isolation of the desired chloridate. Other sulfuryl halides are expected to react similarly.

The failure to obtain the desired addition products is not too surprising. Intermediates have not been observed in the reaction of trialkyl phosphites with sulfonyl or sulfenyl chlorides[8-10] or with sulfur monochloride.[10] Stable adducts were not reported in the reaction of sulfenyl chlorides with a variety of phenyl phosphinites.[11] Furthermore, neither Nylen[12] nor Saunders and his co-workers[13] could prepare compounds analogous to those claimed in Bell's patent.[2] Thus, we are drawn to the conclusion that sulfuryl chloride and other acid chlorides of sulfur acids do not give stable addition products with trialkyl phosphites.

It is proposed that the reaction proceeds through the formation of an unstable intermediate in which phosphorus is attached transitorily to the oxygen rather than to the sulfur atom



In the case of a sulfonyl chloride[8,9] oxygen transfer occurs through sulfinyl and sulfenyl chloride intermediates[14] without cleavage of the carbon–sulfur bond.

Hypotheses involving free radical intermediaries seem less tenable despite suggestions that quaternary ammonium[15,16] and phosphonium[17,18] salts can decompose through radical intermediaries. In order to ascertain whether radicals are formed in this reaction, sulfuryl chloride was added to a solution of triethyl phosphite in styrene. As in previous cases, the reaction proceeded very vigorously. Sulfur dioxide was evolved almost quantitatively and only a small amount of polymer was obtained. The failure to obtain a sulfur dioxide–styrene copolymer, the low yield of polymer, and the absence of low molecular weight adducts of styrene and sulfuryl chloride indicates strongly that at least active radical species were absent. The small amount of residue containing phosphorus probably consists of low molecular weight adducts of styrene and triethyl phosphite or diethyl phosphorochloridate.

Experimental

Materials.—With the exception of tris-(2-chloroethyl) phosphite, the trialkyl phosphites (Virginia-Carolina Corporation) were distilled prior to use.

Sulfuryl chloride (Eastman Kodak Co. purified grade) was redistilled at atmospheric pressure and the fraction boiling at 69° (760 mm.) used in these reactions.

Diethyl Phosphorochloridate.—Triethyl phosphite (166 g., 1.0 mole) in 200 ml. of anhydrous petroleum ether (low boiling) was added dropwise in five hours to a stirred solution of 135 g. (1.0 mole) of sulfuryl chloride in 300 ml. of anhydrous petroleum ether maintained at 0° in an atmosphere of dry nitrogen. Dropwise addition was necessary because the reaction proceeds vigorously with copious evolution of sulfur dioxide. The clear water-white reaction mixture was allowed to reach room temperature (about one hour); the solvent, sulfur dioxide and ethyl chloride were removed under reduced pressure at room temperature. The residue was distilled at low pressures, yielding 149.5 g. (87%) of diethyl phosphorochloridate, b.p. 52–54° (0.8 mm.), n^{26}_D 1.4162; reported[19] b.p. 61–63° (2.5 mm.).

Other phosphorochloridates (Table I) were prepared similarly. Although the addition of sulfuryl chloride to trialkyl phosphites gave equally good yields of phosphorochloridates, such a procedure is not recommended due to a possible Michaelis–Arbuzov reaction between the unreacted phosphite and the alkyl chloride.

Table I

Dialkyl Phosphorochloridates

$(RO)_2P(O)Cl$ R	Reaction temp., °C.	Yield, %	B.p. °C.	B.p. Mm.
C_2H_5	0	87	52–54	0.8
i-C_3H_7[a]	10	73	87–91	11–12
n-C_4H_9[b]	−10	89	121–126	8
$ClCH_2CH_2$[c]	0	48	118–125	0.35

[a] Reported[20] b.p. 95–96° (14 mm.). [b] Reported[21] b.p. 132–135° (15 mm.). [c] Reported[22] b.p. 137–139° (5 mm.), n^{20}_D 1.4742.

Diethyl N-Phenylphosphoramidate.—This derivative was prepared by adding 1.86 g. (0.02 mole) of aniline in 10 ml. of anhydrous diethyl ether to a solution of 1.72 g. (0.01 mole) of diethyl phosphorochloridate in 10 ml. of diethyl ether at room temperature. After a short induction period, the reaction mixture became warm and aniline hydrochloride slowly precipitated. The hydrochloride was filtered and the filtrate was evaporated on a steam-cone to yield a

Table II

Amidates of Dialkyl Phosphorochloridates

$(RO)_2P(O)NHR'$ R	R	Yield, %	M.p., °C. uncor.
C_2H_5	C_6H_5	87	93–96
i-C_3H_7	C_6H_5[a,b]	76	120–121.5
n-C_4H_9	CH_3[c]	73	[f]
$ClCH_2CH_2$	C_6H_5[d,e]	90	80.5–83.5

[a] Recrystallized from high boiling petroleum ether. [b] Reported[20] m.p. 121–121.5°. [c] Calcd. for $C_9H_{22}NO_3P$: N, 6.28; P, 13.89. Found: N, 6.14; P, 13.92. [d] Recrystallized from a petroleum ether–benzene mixture. [e] Calcd. for $C_9H_{14}O_3NCl_2P$: N, 4.89; Cl, 24.83; P, 10.84. Found: N, 4.70; Cl, 24.06; P, 10.40. [f] B.p. 116–119° (0.5–0.6 mm.).

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(12) P. Nylen, *Tids. Kjemi Bergwesen*, **18**, 59 (1938).

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(21) W. Gerrard, *ibid.*, 1464 (1940).

(22) M. I. Kabachnik and P. A. Rossiĭskaya, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 403 (1046); *C. A.*, **42**, 7242 (1948).

white solid. The solid, recrystallized from hexane, gave 2.0 g. (87%) of white crystals, m.p. 93–96° (reported[20] m.p. 96.5).

Other amidates (Table II) were made in the same manner except that in the case of di-*n*-butyl N-methylphosphoramidate anhydrous methylamine was passed directly into an ethereal solution of the chloridate and in the case of bis-(2-chloroethyl) N-phenylphosphoramidate the precipitated mixture of amidate and aniline hydrochloride was separated by washing out the latter with water.

Reaction of Sulfuryl Chloride with Triethyl Phosphite in Styrene.—Sulfuryl chloride (5.4 g., 0.04 mole) was added dropwise over a 15-minute period to a stirred solution of 6.65 g. (0.04 mole) of triethyl phosphite in 31.2 g. (0.3 mole) of freshly distilled styrene maintained at 0° in an atmosphere of dry nitrogen. The clear colorless mixture was then allowed to come to room temperature and stirred for two hours. During this time sulfur dioxide formed was swept out of the system by a stream of anhydrous nitrogen and passed through a known amount of standard iodine solution; 93% of the theoretical amount of sulfur dioxide was accounted for.

After diluting the mixture with 100 ml. of ethyl ether, an excess of dilute sodium hydroxide (125 ml. of a 5% solution) was added dropwise with cooling over a 30-minute period and the suspension was then stirred at room temperature for 30 minutes; the ether and aqueous layers were separated. The basic aqueous layer was extracted twice with 25-ml. portions of ethyl ether, the combined ether extracts were washed with three 25-ml. portions of water, and then dried over anhydrous sodium sulfate. The dry ether solution was concentrated under reduced pressure and the residual liquid was flash-distilled *in vacuo* yielding 25.0 g. (0.25 mole, 83.3% recovery) of styrene boiling at 47–50° (20 mm.). The residue, 4.28 g., was taken up in benzene; addition of an equal volume of methanol to the resulting clear solution gave 0.2 g. of a white amorphous solid in which phosphorus was absent and which appeared to be polystyrene. The filtrate was concentrated under reduced pressure and the residual oil was distilled, yielding a fraction boiling at 30–36° (0.04 mm.), and leaving approximately 2 g. of residue. The distillate gave a positive test for phosphorus and also for unsaturation but its identity could not be positively established.

Acknowledgments.—We wish to express our appreciation to R. W. Cogley for carrying out some of the experimental work.

LANCASTER, PENNA.

[CONTRIBUTION FROM THE REFINING RESEARCH AND DEVELOPMENT DIVISION, HUMBLE OIL AND REFINING CO.]

Cross Sections for Ionization by Electrons

BY F. W. LAMPE, J. L. FRANKLIN AND F. H. FIELD

RECEIVED MARCH 30, 1957

Cross sections for ionization by 75 v. electrons have been measured for 35 substances using the ion source of a CEC model 21-620 mass spectrometer. Values at variance with those reported by other workers are obtained, and as a consequence reservations concerning the validity of a proposed method of calculating ionization cross sections are expressed. It is found that the measured ionization cross sections are linearly related to polarizability, and a theoretical rationalization of this relationship is given.

Introduction

Total cross sections for ionization by electron impact of a wide variety of substances were reported recently by Otvos and Stevenson[1] (O. and S.). In addition, these authors assert that the atomic ionization cross sections of the elements are proportional to the number of valence electrons weighted by the mean square radii of these electrons as calculated using hydrogenic wave functions. Furthermore, they assert that the ionization cross section of a molecule can be obtained by adding the ionization cross sections of the constituent atoms.

Partially as a consequence of studies concerning ion–molecule reactions taking place in mass spectrometer ionization chambers, we have had occasion to measure total ionization cross sections by electron impact. We wish to report here our values since some of them disagree with those of O. and S., and this disagreement causes us to think that the proposed calculation of atomic ionization cross sections and postulate of additivity of atomic ionization cross sections are not so generally valid as O. and S. imply.

Experimental

In general, the method consisted of measuring the saturation ion-current collected on the ion-repeller of a CEC model 21-620, cycloidal focusing mass spectrometer when the repeller was biased negatively (5 volts) with respect to the ionization chamber. The ion-current was measured with a Keithley electrometer. The electron accelerating voltage was about 75 volts; the electron current was 10.0/μamp.; and the path length of the ionizing electrons was 0.56_3 cm.

At very low pressures in the reservoir the gas flow both in and out of the ionization chamber is effusive. In such a pressure region, the concentration of all gases in the ionization chamber will be the same for a given reservoir pressure and a plot of ion-current *versus* reservoir pressure will be linear, with the slope proportional to the total ionization cross section of the gas. Absolute total ionization cross sections are obtained from the slopes by comparison with the known absolute values of total ionization cross sections for argon and neon for 75 volt electrons as summarized by Massey and Burhop.[2]

At higher pressures in the reservoir mass flow into the ionization chamber begins to become important and, since there is still effusive flow out of the chamber, the ionization chamber pressure becomes proportional to a higher power of the reservoir pressure. The observed result is an upward curvature of the plot of ion-current *versus* reservoir pressure. A typical plot of ion-current *versus* reservoir pressure is shown in Fig. 1. The initial slope, shown by the dotted line, is used to determine the relative ionization cross section.

Results and Discussion

Table I gives our results and the results of previous workers. The cross-sections given in column III were calculated from the slopes of the ion current *vs.* pressure plots (column II) by taking the absolute total ionization cross section for argon to be $3.5_2 \times 10^{-16}$ cm.^{2} as given by Massey and Burhop.[2] Values for other gases summarized by Massey and Burhop[3] are given in column IV. Columns V and

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[1] J. W. Otvos and D. P. Stevenson, THIS JOURNAL, **78**, 546 (1956).

[2] H. S. W. Massey and E. H. S. Burhop, "Electronic and Ionic Impact Phenomena," Oxford University Press, London, 1952, p. 38.

[3] Reference 2, p. 265.