easy to point out errors in the calculations of K. Iwasé and N. Nasu, but this will not greatly change the order of the figures.

Lastly may be mentioned that H. Müller[10] claims to have measured the equilibrium

$$V_2O_5 + H_2 = V_2O_4 + H_2O$$

He finds

$$K_p = p_{H_2O}/p_{H_2} = 7.6, 21.2, 23.3$$

at 496, 530 and 600°, respectively. If log K_p is plotted against $1/T$ in the usual way, it will be evident that the values for K_p do not refer to an equilibrium.

$VOSO_4$ and Contact Process for Sulfuric Acid. B. Neumann, H. Panzner and E. Goebel,[11] have shown that a V_2O_5-catalyst for the reaction

$$SO_2 + {}^1/_2O_2 = SO_3$$

showed a maximum catalytic effect at a certain temperature. The position of the maximum is shifted by a change in the rate of gas flow, but at moderate rates it is around 500–550°. They try to explain this by assuming that the maximum catalytic effect is related to the coexistence of the three phases V_2O_5, V_2O_4 and $VOSO_4$. This explanation is obviously incorrect (since three solid phases are coexistent at one temperature only). Our data, however, indicate that the maximum catalytic effect is obtained near the decomposition temperature of $VOSO_4$, according to reaction 4. For the working conditions of B. Neumann, H. Panzner and E. Goebel, this temperature has been calculated to about 530°.

Summary

The equilibria

$$2VOSO_4 = V_2O_4 + 2SO_3 \qquad (3)$$
$$2VOSO_4 = V_2O_5 + SO_2 + SO_3 \qquad (4)$$
$$V_2O_5 + SO_2 = V_2O_4 + SO_3 \qquad (5)$$

have been investigated by a flow method. The equations given below reproduce the results with good approximation

$$-\log K_3 = \frac{9{,}900}{T} - 9.84 \quad (520 - 581°)$$
$$-\log K_4 = \frac{18{,}600}{T} - 20.01 \quad (581 - 600°)$$
$$-\log K_5 = \frac{1{,}216}{T} + 0.353 \quad (550\text{-}650°)$$

By V_2O_5 reduction, ($VOSO_4$) a modification of V_2O_4 not previously described,[12] is found at temperatures below 615°.

From the data for reaction 4 $S^{\circ}_{298(VOSO_4)}$ has been calculated to 27.1.

By combination of the data for reaction 3 (above) with those for the reaction

$$SO_2 + {}^1/_2O_2 = SO_3$$

data for the equilibrium

$$V_2O_5\ (\text{solid}) = V_2O_4\ (\text{solid}) + {}^1/_2O_2$$

has been calculated.

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[10] H. Müller in W. Biltz's "Festschrift Hannover" (1927) (quoted by J. W. Mellor, Vol. IV, p. 744).

[11] B. Neumann, H. Panzner and E. Goebel, *Z. Elektrochem.*, **34**, 696 (1928).

[12] Compare ref. 4.

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[CONTRIBUTION FROM THE CENTRAL RESEARCH DEPARTMENT, MONSANTO CHEMICAL COMPANY]

Isomerization of Alkyl Phosphites. VI. Reactions with Chlorides of Singular Structure

BY GENNADY M. KOSOLAPOFF

The synthesis of phosphonic acids and their derivatives by the interaction of esters of phosphorous acid with alkyl halides is generally practicable only in the case of primary halides. The only recorded instance of a successful reaction involving non-primary halides is that of Arbuzov's synthesis of dialkyl triphenylmethanephosphonates from triphenylhalomethanes.

It was felt that it should be possible to effect the phosphonation reaction, with alkyl phosphite derivatives, with carbon tetrachloride, which in a number of instances displays a certain degree of reactivity of at least one chlorine atom. This expectation was realized and good yields of esters of trichloromethanephosphonic acid were obtained by the reaction of an excess of carbon tetrachloride with triethyl phosphite and tributyl phosphite. However, the reaction of carbon tetrachloride with an excess of the trialkyl phosphite, which was attempted with the expectation of poly-phosphonation, led to elimination of but two equivalents of alkyl chloride from the reaction mixture, which could not be resolved into definite products. Similarly, attempts to isolate definite products of poly-phosphonation from reaction mixtures of carbon tetrachloride with an excess of either sodium diethylphosphite or sodium dibutylphosphite were unsuccessful. In the first instance there was isolated only an undistillable gelatinous product which was chlorine free, as well as small amounts of diethyl phosphite and triethyl phosphate. In the second instance, a small amount of an unstable product, which was essentially chlorine free and which contained 25.5% phosphorus, was obtained.

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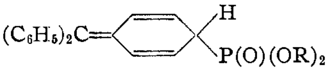
(1) A. E. and B. A. Arbuzov, *J. Russ. Phys.-Chem. Soc.*, **61**, 217 (1929).

These results were in general agreement with those obtained by similar reactions with methylene halides.[2]

It was also felt that the reactivity of the chlorine atom in the 9-position of the acridine nucleus should be sufficient for a successful phosphonation reaction. Such a reaction should then open the way to the synthesis of phosphonic acid derivatives of nitrogen heterocyclics. This expectation was realized and 9-phosphonoacridine was prepared in satisfactory yields from 9-chloroacridine and triethyl phosphite. The behavior of the product, however, was found to have some points of similarity to that of the phosphonation products of trityl halides[1] and indicated the possibility of tautomeric structures. The latter were obtained by Arbuzov in both colorless and colored modifications in a number of instances. An explanation for this observation has been lacking. However, a hypothesis may be advanced in an attempt to explain the apparent tautomerization on the basis of the reactions of triphenylhalomethane both in the benzenoid and the *p*-quinonoid forms with the trialkyl phosphite used by Arbuzov. On this basis the resulting products in the case of trityl halides could be assigned the structures $(C_6H_5)_3CP(O)(OR)_2$ and



the latter being that of the colored modification. Extension of this concept to the acridine derivatives may then be used in an attempt to explain the existence of two forms of 9-phosphonoacridine.

Experimental

Reactions with Carbon Tetrachloride

I. **Triethyl Phosphite.**—Triethyl phosphite (50 g.) was refluxed overnight with 250 cc. (large excess) of dry carbon tetrachloride. The colorless solution was distilled under reduced pressure to yield 72 g. (93.6%) of diethyl trichloromethanephosphonate, as a colorless mobile liquid, b. p. 135–137° at 16 mm., b. p. 127–128° at 13 mm., $n^{25}\mathrm{D}$ 1.4582.

Anal. Calcd. for $C_5H_{10}O_3Cl_3P$: Cl, 41.6; P, 12.1. Found: Cl, 41.2, 41.42; P, 12.11, 12.17.

II. **Tributyl Phosphite.**—Tributyl phosphite (50 g.) was refluxed for twenty-four hours with 150 g. (large excess) of dry carbon tetrachloride. On distillation of the colorless solution under reduced pressure there was obtained 15 g. (25%) of crude dibutyl trichloromethanephosphonate, as a colorless mobile liquid, b. p. 150–155° at 5 mm., $n^{25}\mathrm{D}$ 1.4490. The product showed evidence of thermal decomposition on distillation and could not be subjected to fractionation. Its analyses indicated the content of 11.0% phosphorus, which was in excess of the 10.1% indicated for the pure substance.

Reactions with 9-Chloroacridine

Triethyl Phosphite.—9-Chloroacridine (20 g.) and 50 g. (excess) of triethyl phosphite were heated under a reflux condenser, which was protected with a calcium chloride tube, for six hours at 150°. The loss of weight was 6.5 g. (slightly in excess over the calculated value for evolution of one equivalent of ethyl chloride). The dark mass was freed of the excess triethyl phosphite by distillation under reduced pressure and the residual mass was stirred with a small amount of absolute ethanol. It was possible in this manner to isolate from the viscous red mass a small amount of yellowish feathery crystals of crude diethyl 9-acridinephosphonate, m. p. 165–167°, which, however; could not be isolated in the state of analytical purity. The crude mass was freed of the alcohol under reduced pressure and the residual mass was refluxed overnight with 150 cc. of concentrated hydrochloric acid. The mixture was concentrated to approximately 75 cc. and was filtered upon cooling. The dark solid was extracted thoroughly with dilute sodium hydroxide and the filtered extract was cautiously acidified with dilute hydrochloric acid with stirring and cooling. There was obtained 15 g. (62%) of 9-phosphonoacridine in the form of lustrous green crystals, which decomposed at 247–249°. The product must be filtered and dried rapidly, because on prolonged standing in contact with dilute hydrochloric acid it was transformed slowly into a yellow crystalline solid which did not melt at 350° and retained these properties after solution in dilute sodium hydroxide and re-precipitation with dilute hydrochloric acid. However, at each re-precipitation, a small amount of acridine was isolated; this was not observed with the green modification.

Anal. Calcd.: equiv. wt., 129.5. Found: 131, 133. (Satisfactory results could not be obtained in combustion or peroxide bomb analyses.)

Sodium Dibutyl Phosphite.—9-Chloroacridine (25 g.) was added slowly to a solution of sodium dibutyl phosphite (from 25 g. of dibutyl phosphite) in 500 cc. of dry hexane. The solution acquired a brown color which remained after the mixture was refluxed for four hours. On cooling, the mixture was shaken with cold water and filtered. Substantially quantitative recovery of acridone was accomplished.

Summary

The reaction of carbon tetrachloride with trialkyl phosphites and with sodium dialkyl phosphites was studied. Diethyl- and dibutyl trichloromethanephosphonates were prepared. A similar reaction of 9-chloroacridine was investigated and 9-phosphonoacridine was synthesized.

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[2] P. Nylen, "Studien über Phosphororg. Verb.," Upsala, 1930; Arbuzov and Kushkova, *J. Gen. Chem.*, U. S. S. R., **6**, 283 (1936).