degree of subdivision is attained. Positive assurance can be had, however, only when the surface structure of the quartz particles is definitely known.

Summary

Density measurements of silica and charcoal, using a series of liquids as the buoying fluid, indicate that polar liquids yield high density values for silica, non-polar yield low values. The more compressible liquids yield the higher density values for charcoal. Polar liquids having large compression coefficients yield high density values for both solids.

Density measurements of ground quartz of varying degrees of fineness were made by means of benzene and water as the buoying fluids. These measurements confirm the foregoing statements and indicate that a different degree of penetration of different liquids into the surface of the solid is probably not a factor of significance in the variations of apparent density.

PULLMAN, WASH. RECEIVED AUGUST 22, 1938

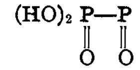
[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 652]

An Attempted Exchange of Phosphorus between Phosphorous and Phosphoric Acids

BY J. NORTON WILSON

The hydration of hypophosphoric acid, which takes place according to the equation

$$H_4P_2O_6 + H_2O \longrightarrow H_3PO_3 + H_3PO_4 \qquad (1)$$

has been shown[1,2] to proceed at a rate which is first order with respect to hypophosphoric acid and increases with increasing hydrogen ion concentration. It has been suggested[1] that this reaction is irreversible, but it seems probable that an equilibrium may be reached in which the concentration of hypophosphoric acid remaining is too small to be detected readily by chemical methods. If the structure of hypophosphoric acid is such that the phosphorus atoms are equivalent, as in the structure  $(HO)_2\underset{\substack{\| \\ O}}{P}-\underset{\substack{\| \\ O}}{P}(OH)_2$ which has been suggested on the basis of X-ray absorption spectra and chemical properties by Nylen and Stelling[3] and by Hantzsch,[4] the reverse of reaction (1) should lead to an exchange of radioactive phosphorus between phosphorous and phosphoric acids according to the following mechanism (the radioactive phosphorus atom is denoted by an asterisk)

$$H_3P^*O_4 + H_3PO_3 \rightleftarrows H_2O_3P^* - PO_3H_2 + H_2O \rightleftarrows H_3P^*O_3 + H_3PO_4 \qquad (2)$$

An attempt has been made to detect this exchange using radioactive phosphorus[5] obtained as a by-product of the formation of radio-sulfur by bombardment of sulfur with fast deuterons. The material was separated from most of the accompanying sulfur and oxidized to phosphoric acid; a small amount of ordinary phosphoric acid was added as a carrier. The phosphate was precipitated as magnesium ammonium phosphate and converted to lead phosphate which was treated with hydrogen sulfide to liberate radioactive phosphoric acid. The reaction mixtures were made up from this material and "C. P." phosphorous and phosphoric acids. The phosphorous acid used was found to contain a small amount of phosphoric; this was determined and corrected for.

In order to determine whether exchange had occurred the mixture was diluted and the phosphate precipitated as magnesium ammonium phosphate; this was dissolved in acid and reprecipitated to remove co-precipitated phosphite. The phosphate precipitate was dried and its electroscopic activity measured. The phosphite contained in the filtrates was oxidized with bromine and similarly precipitated; the electroscopic activity of this precipitate was determined as before. Occurrence of activity in the latter precipitate would be evidence either of exchange or faulty separation.

The reaction mixtures were made up in duplicate; one of the pair, used as a blank, was subjected immediately after mixing to the separation process and radioactivity measurements described above; the other was sealed in a glass

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[1] Van Name and Huff, *Am. J. Sci.*, **45**, 103, 18 (1918).

[2] Blaser, *Z. physik. Chem.*, **A167**, 441 (1934).

[3] Nylen and Stelling, *Z. anorg. allgem. Chem.*, **212**, 169 (1933); *ibid.*, **218**, 301 (1934).

[4] Hantzsch, *ibid.*, **221**, 63 (1934).

[5] This material was supplied through the generosity of Professor Edwin McMillan of the Radiation Laboratory of the University of California.

ATTEMPTED EXCHANGE OF PHOSPHORUS BETWEEN PHOSPHOROUS AND PHOSPHORIC ACIDS: EXPERIMENTAL RESULTS

No.	(H_3PO_4)	(H_3PO_3)	Other reagents	t, min.	T, °C.	Activity PO_3, div./min.	Activity PO_4, div./min.	β/α_0	β/α_0, blank
I	0.76	0.72		1440	100	+0.004 ± 0.005	0.79	$(5 \pm 6) \times 10^{-3}$	$\pm 6 \times 10^{-3}$
II	.46	.43	NaOH, 2.86	1400	100	− .002 ± .005	0.92	$(-2 \pm 5) \times 10^{-3}$	$\pm 5 \times 10^{-3}$
III	.60	.68	HCl, 5.31	11,500	100	+ .006 ± .006	4.85	$(1 \pm 1) \times 10^{-3}$	$\pm 1 \times 10^{-3}$
IV	.62	.70	HCl, 5.51	21,200	20-25	+ .013 ± .006	4.20	$(3 \pm 1) \times 10^{-3}$	$\pm 1 \times 10^{-3}$
V	.36	.35	HCl, 5.63	18,900	25	+ .010 ± .010	49.0	$(2 \pm 2) \times 10^{-4}$	$(1 \pm 1) \times 10^{-4}$
VI	.36	.35	HCl, 5.63	37,900	25	+ .006 ± .004	24.8	$(2 \pm 2) \times 10^{-4}$	$(1 + 1) \times 10^{-4}$

ampoule and allowed to stand for a convenient time before separation.

The probability of error due to faulty separation was greatly decreased in experiments V and VI in which after the precipitation and separation of the radioactive phosphate some inactive phosphoric acid equal in amount to that originally present in the solution was mixed with the phosphite in the filtrates and precipitated in the same way. This treatment should remove practically all of any radioactive phosphoric acid left in solution after the first precipitation. Measurement of the activity of the resulting precipitate indicated that about 0.1% of the radiophosphoric acid originally present was left in solution after the first precipitation. After the extra precipitation the phosphite in the filtrate was oxidized and precipitated as in the earlier experiments.

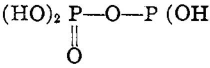
From the observed extent of an exchange occurring during the time t in accordance with the mechanism suggested in (2), one can calculate the rate at which reaction (1) and its reverse proceed at equilibrium. If the first order rate constant k_1 for the hydration of hypophosphoric acid is known, one can calculate from this result the equilibrium constant K, defined as $K = (H_4P_2O_6)/(H_3PO_4)(H_3PO_3)$. It may be shown that for the case where exchange occurs to a very small extent over a long time a good approximation is

$$K = \frac{2}{(H_3PO_4)k_1t}\frac{\beta}{\alpha_0} \qquad (3)$$

where α_0 is the fraction of phosphoric acid initially radioactive corrected for radioactive decay to the time t and β is the fraction of phosphorous acid radioactive at time t.

In the following table are listed the concentrations, in formula weights per liter, of the reagents used in the experiments; the time t between the original mixing of the solutions and the separation of the phosphate; the temperature; the electroscopic activities of equal weights of the precipitates from the phosphite and phosphate fractions, corrected for radioactive decay and for the normal leak of the electroscope; and the values of β/α_0, which has been taken as the ratio of these activities. The values of β/α_0 for the "blank" experiments are also included. The normal leak of the electroscope was about 0.07 division per minute; fluctuations about this value were large enough to make a comparatively large uncertainty in the value of the activity of the phosphite precipitate. This uncertainty was estimated from the root mean square deviation from the mean of a number of alternate measurements of the normal leak and the phosphite activity. The results of experiments V and VI are the most reliable because of the care used to eliminate the error due to faulty separation.

It is apparent that in no case was definite evidence of exchange obtained. It can be stated, however, that the extent of exchange was less than a certain value determined by the estimated uncertainty; on the basis of the assumptions made a limit can then be placed on the value of the equilibrium constant K. Thus in experiment VI, β/α_0 was very probably less than 5×10^{-4}; k_1 for the given conditions may be estimated from the data of Van Name and Huff[1] to be 1.0×10^{-3} min.$^{-1}$. Then $K < 8 \times 10^{-5}$ mole^{-1} liters at 25° in 5.6 formal hydrochloric acid.

Unfortunately, an alternative conclusion is possible: that the phosphorus atoms in hypophosphoric acid are not equivalent, as for instance in the structure  $(HO)_2\underset{\overset{\|}{O}}{P}{-}O{-}P(OH)_2$ proposed on the basis of some slight chemical evidence by Blaser and Halpern.[6] If this is the case it is unlikely that the reverse of reaction (1) would lead to exchange. According to the evidence at present available,[1,2] however, it seems quite probable that the molecule contains two equivalent phosphorus atoms bonded to one another.

The author is grateful to Professor R. G. Dickinson for his advice, criticism and encouragement in connection with this investigation.

Summary

No exchange of radioactive phosphorus between

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(6) Blaser and Halpern, *Z. anorg allgem. Chem.*, **215**, 33 (1933).

phosphorous and phosphoric acids in acid or alkaline solution was found to occur beyond the limits of experimental error. The results indicate that if the phosphorus atoms in hypophosphoric acid are equivalent, the equilibrium constant for the formation of hypophosphoric acid from phosphorous and phosphoric acids is less than 8×10^{-5} mole^{-1} liters at 25° in 5.6 formal hydrochloric acid.

PASADENA, CALIF. RECEIVED JUNE 13, 1938

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF HARVARD UNIVERSITY]

The Instability of Liquid Isobutene

BY EDWIN E. ROPER

In the course of measurements of the vapor pressure of a number of unsaturated hydrocarbons, the results of which are to be presented in a later paper, it was found that the vapor pressure of originally pure isobutene (2-methylpropene) decreases over a period of time and from this aged material a relatively high-boiling liquid was isolated. The most probable explanation of this instability of isobutene is that a polymer is formed. Since there appears to be no mention in the literature of any such uncatalyzed polymerization of isobutene, although it is well known that in the presence of certain catalysts isobutene is converted into polymers,[1] and since we do not plan to continue the study of this behavior further, it appears worth while to present our findings at this time.

Experimental

Apparatus.—A simple static system was used, consisting of a small (*ca.* 5 cc.) vapor pressure tube immersed in an ice-bath, which was maintained at 0.000 ± 0.001° for the observations. The washing procedure required to establish this temperature reproducibility in the ice-bath has been described.[2] The pressure was measured on an absolute manometer, of 15-mm. inside diameter Pyrex tubing, by a high grade cathetometer; meniscus corrections were determined for each observation and the pressure converted to international millimeters[3] (int. mm.) of mercury. Accessory apparatus included vacuum line, fore and condensation pumps, McLeod gage and a system of stopcocks; the manometer had a reservoir sealed on at the bottom, allowing the U to be used as a mercury cut-off, which was the only access to the vapor pressure system, so that no stopcocks were exposed to the vapor for long periods of time.

Material.—Four samples of isobutene were available. Sample D was from Dr. Harold S. Davis; it had been prepared by the dehydration of *t*-butyl alcohol by means of oxalic acid and purified in a Davis[4] low-temperature fractionating column. The boiling point range of this sample was given as ±0.05°. Sample R was one we had prepared by the method described by Davis,[4] with a boiling range of *ca.* 0.5°. Sample K, obtained from Professor Kistiakowsky of these Laboratories, had been highly purified for a determination of the heat of hydrogenation;[5] the consistent value of this heat of reaction for different fractions from the distillation,[5] the method of distillation,[6] the value of the freezing point,[5,6] and our vapor pressure measurements in conjunction with isothermal vaporization, gave indication of exceptional purity of the sample, of the order of 99.9%. Sample F was presented to us by Professor Forbes of these Laboratories; it had been prepared by the same investigators as had sample K and was the remnant of the material used in the photochemical investigation of Forbes and Nelson.[7] The boiling range was the same as that for sample K, namely, 0.02°. Samples K, F and R were dried by a physical method, which consisted of a filtration of the liquid through glass wool held at low temperatures;[8] this effectively dried the hydrocarbon and possibly removed some of the polymer. The samples were stored in the liquid phase in all-Pyrex glass containers, fitted with a glass internal break-off seal, externally operated by an electromagnet. High vacuum technique was used in all operations of filtering and transferring.

Procedure.—Immediately previous to the vapor pressure determinations, a distillation from the storage container at −80°, to a bulb on the vapor pressure line, via the manometer-cutoff, at −188° was carried out; this operation required some time, because of the low vapor pressure of the hydrocarbon at −80° (12 mm.). The first few tenths of a cc. that distilled was discarded, as was the last portion. In the subsequent examination of the latter, the container having been removed from the vacuum line, it was noticed that a small amount of residue, with a distinctive odor, was left after the admixed isobutene had been allowed to vaporize into the atmosphere; this residue was liquid at −80° and crystalline at −188°. It was obvious that the residue had formed during the several months of storage in the glass container, for during the

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[1] (a) Ellis, "The Chemistry of Petroleum Derivatives," The Reinhold Publishing Co., New York, N. Y., Vol. I, 1934, pp. 315, 378, 600; Vol. II, 1937, p. 641; (b) Whitmore and Wrenn, THIS JOURNAL, **53**, 3136 (1931); (c) Tongberg, Pickens, Fenske and Whitmore, *ibid.*, **54**, 3706 (1932).

[2] Roper, THIS JOURNAL, **60**, 866 (1938).

[3] Burgess, *Bur. Standards J. Research*, **1**, 635 (1928).

[4] Davis, *Ind. Eng. Chem.*, *Anal. Ed.*, **1**, 61 (1929).

[5] Kistiakowsky, Ruhoff, Smith and Vaughan, THIS JOURNAL, **57**, 876 (1935).

[6] Compare with Todd and Parks, *ibid.*, **58**, 134 (1936).

[7] Forbes and Nelson, *ibid.*, **59**, 693 (1937).

[8] Roper, *Ind. Eng. Chem.*, *Anal. Ed.*, **9**, 414 (1937).