polation the two runs numbered 14 and 17 were made with much larger amounts of solid to be transformed into double salt, and these were rotated for about a year before analysis. Although the equimolar ratio of the salts in the compound is quite clear from mere graphical extrapolation, it is more difficult to fix the hydration of the double salt, since the weight percentages of water in the mono-, di- and trihydrates of a 1:1 double salt are not very different, being 2.53, 4.93 and 7.21, respectively.

The tie-lines for complexes 12–19, in which the double salt was the sole saturating solid, were extrapolated algebraically to their intersections with the line representing the 1:1 salt ratio. The average number of moles of H_2O per $Ba(IO_3)_2 \cdot BaCl_2$ thus calculated is 2.13 with an average deviation from the mean of 0.18. The tie-lines were also extrapolated to the line representing the percentage of $Ba(IO_3)_2$ in a 1:1 double salt with 1, 2 and 3 moles of H_2O, respectively, in the formula. The intersections of the tie-lines with each of these fixed lines was then expressed as an "error" in terms (positive or negative) of percentage of $BaCl_2$ in the solid. The average (algebraic) error of extrapolation is then -0.71% $BaCl_2$ at the monohydrate, -0.08% at the dihydrate and $+0.52\%$ at the trihydrate.

The various tie-line extrapolations therefore seem to be sufficient to justify accepting the formula $Ba(IO_3)_2 \cdot BaCl_2 \cdot 2H_2O$ for the double salt. The other solid phases of the isotherm are $Ba(IO_3)_2 \cdot H_2O$ and $BaCl_2 \cdot 2H_2O$.

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Exchange of Deuterium Oxide with Bromodichloromethane and Chlorodibromomethane

BY R. H. SHERMAN AND R. B. BERNSTEIN

The base-catalyzed exchange of trichloromethane with deuterium oxide has been studied by Sakamoto,[1] who found that the rate of exchange was rapid compared with the rate of hydrolysis. Hine,[2] in a study of the basic hydrolysis of trichloromethane, proposed mechanisms involving the intermediates CCl_3^- and CCl_2 which were in concordance with the observed rapid exchange rates reported by Sakamoto. Newton and Rollefson[3] utilized the base-catalyzed exchange reaction as a method of preparation of trichloromethane-d.

Bromodichloromethane-d and chlorodibromomethane-d have been obtained in this Laboratory by the exchange reaction between the protium analogs and deuterium oxide in the presence of deuteroxide ion.[4] The reactions were carried out in heavy-walled Pyrex vessels of about 30 ml. volume, into

(1) Y. Sakamoto, Bull. Chem. Soc. Japan, 11, 627 (1936).
(2) J. Hine, THIS JOURNAL, 72, 2438 (1950).
(3) T. W. Newton and G. K. Rollefson. J. Chem. Phys., 17, 718 (1949).
(4) The procedure of ref. 3 employed carbonate as the base and was found to be unsatisfactory in the case of the bromomethanes. The carbonate was completely decomposed, resulting in explosion of the reaction vessels.

which were placed 0.1 mole of purified halomethane, 0.1 mole of 98% deuterium oxide and 0.01 mole of sodium deuteroxide. After outgassing the contents at $-78°$, the vessel was sealed and maintained at 105° in the absence of light for four days, with periodic shaking. The reactor was then cooled to $-195°$ and opened. The non-aqueous layer was dried and distilled through a small packed column.

The infrared absorption spectra of the purified products revealed appropriate bands attributed to the C–D bond stretching and bending vibrations. A determination of the isotopic purity of the deuterohalomethanes was carried out on the basis of the 3020 cm.$^{-1}$ band of the C–H bond. The results were 43% CBr_2ClD and 16% CCl_2BrD. Upon recharging the reactor with the enriched compound and a new supply of deuterium oxide and sodium deuteroxide in the original proportions the exchange reactions were repeated under similar conditions, resulting in 64% CBr_2ClD and 36% CCl_2BrD, respectively.

Considerable gas pressure (non-condensable at $-195°$) was observed at the end of each run. In one control experiment of two days using CBr_2ClH, the non-condensable gas was analyzed mass-spectrometrically and found to be essentially pure carbon monoxide, in a quantity accounting for approximately 3.5% of the total halomethane used. The aqueous phase was acid. The total halide ion found in the aqueous phase[5] corresponded to about 3% halomethane decomposition. In several experiments the ratio of Br^- to Cl^- exceeded 2:1. This ratio was found to vary; no explanation has yet suggested itself.

In one experiment of 16 days with CBr_2ClH, the total halide ion recovered was 10.5 millimoles; originally 11.8 millimoles of deuteroxide ion was available. This ratio of OD^-/X^- of 1.12 is in reasonable agreement with the stoichiometry of the hydrolysis according to the mechanisms of Hine.[2] The over-all reaction for decomposed halomethane may be written: $2CX_3H + 7OH^- = CO + 6X^- + HCO^-_2 + 4H_2O$, so that the ratio of hydroxyl consumed to halide produced would be 7/6 or 1.17. It thus appears that the extent of decomposition is limited by the hydroxyl ion available. It should also be noted that both of the purified halomethanes (and their deuterium analogs) were extremely stable to heat and light in the absence of oxygen, in contrast to the decomposition usually observed when exposed to the atmosphere.

It is clear from these results that the rate of exchange of bromodichloromethane and chlorodibromomethane is indeed more rapid than the rate of hydrolysis, in agreement with the previous data for chloroform. However, the apparent order of reactivity toward exchange for these two compounds is somewhat surprising from a point of view of electronegativity. Further kinetic studies in a single phase system appear necessary for an understanding of this observation.

(5) The concentrations of Br^- and Cl^- ions in the aqueous phase were obtained by potentiometric titration with silver nitrate.

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Condensation of Thiophene and Homologs with Ketones

BY JOHN W. SCHICK AND DUNCAN J. CROWLEY

The reaction of thiophene with aldehydes,[1] particularly formaldehyde,[2] in an acidic medium is known to produce 1,1-(2',2''-dithienyl)-alkanes which on further reaction result in resins and sub-

Although 72–75% sulfuric acid was the principal condensing agent employed, it was noted that 37% hydrochloric acid resulted in product yields comparable to sulfuric acid, while 85% phosphoric acid resulted in poorer yields. Table I summarizes the experimental data using 72% sulfuric acid as the condensing agent.

General Experimental Conditions

Thiophene or substituted thiophene (0.8–2.0 moles) and the ketone (1.0 mole) were allowed to react in the presence of 72–75% sulfuric acid (acid–thiophene ratio 1.5:1) at 50–90° for 3–8 hours. The reaction product was separated from the acid layer and washed with water, dilute carbonate, water again, then dried over anhydrous sodium sulfate. The unreacted thiophene or substituted thiophene was removed and the residue distilled at reduced pressure.

TABLE I

THIOPHENE-KETONE CONDENSATIONS[a]

Thiophene	Ketone	Mole ratio, thiophene: ketone	Product structure[b]	Formula	Yield,[c] %	B.p., °C.	Mm.	$n^{20}D$	Sulfur, % Calcd.	Found
Thiophene	Acetone	1.6	T–K–T	$C_{11}H_{12}S_2$	47	86	0.3	1.5855	30.8	30.9
			T–K–T–K–T	$C_{18}H_{20}S_3$	19	188	.3	1.6029	28.9	28.9
Thiophene	Methyl ethyl	2	T–K–T	$C_{12}H_{14}S_2$	66	97.5	.1	1.5806	28.8	29.0
			T–K–T–K–T[d]	$C_{20}H_{24}S_3$	8				26.6	25.9
			T–K–T₄–K–T[e]	$C_{44}H_{54}S_6$	11	...	ƒ		24.8	24.3
Thiophene	Cyclohexanone	1.6	T–K–T[g]	$C_{14}H_{16}S_2$	39	158	.3		25.8	25.7
			T–K–T₂–K–T	$C_{34}H_{40}S_4$	45	...	ƒ		22.3	22.4
Thiophene	Acetophenone	1.6	T–K–T	$C_{16}H_{14}S_2$	49	153	.5	1.6319	23.7	23.6
			T–K–T₂–K–T[h]	$C_{40}H_{34}S_4$	30	...	ƒ		19.9	20.2
Thiophene	Acetylthiophene	1.6	T–K–T	$C_{14}H_{12}S_3$	54	164	.1	1.6399	34.8	34.6
2-Chlorothiophene	Acetone	0.8	T–K–T	$C_{11}H_{10}S_2Cl_2$	61	143	.5		23.1	22.7
2-Methylthiophene	Acetone	1.6	T–K–T	$C_{13}H_{16}S_2$	79	110	.5	1.5691	27.1	26.5

[a] Condensation carried out in 72–75% H_2SO_4 with an acid:thiophene mole ratio of 1.5:1. [b] T = thiophene, K = ketone. [c] Yield based on thiophene consumed. [d] Mol. wt., calcd. 360, found 376. [e] Mol. wt., calcd. 774, found 772. [ƒ] Resinous composition. [g] M.p. 61–62.5°. [h] Mol. wt., calcd. 642, found 639.

resinous oils. However, no description of the reaction of thiophene and/or substituted thiophenes with ketones has been found in the literature.

The condensation is illustrated in the equation
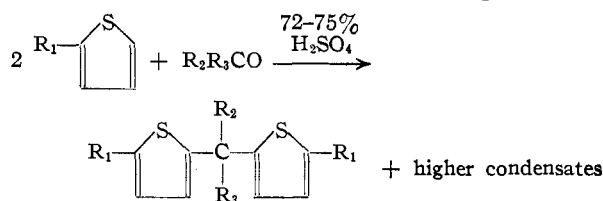
R_1 = H–, Cl–, CH_3–, R_2 = CH_3–
R_3 = CH_3–, C_4H_3S–, C_6H_5–, C_2H_5–

$R_2R_3C<$ may be cyclic, e.g., in cyclohexanone

This condensation has been carried out with thiophene, 2-methylthiophene and 2-chlorothiophene with ketones, such as acetone, methyl ethyl ketone, cyclohexanone, acetophenone and 2-acetylthiophene. For this particular reaction, the conditions are somewhat similar to those described for the phenol–ketone condensations.[3,4,5,6,7]

(1) Steinkopf, "Die Chemie des Thiophens," Edwards Brothers, Ann Arbor, Michigan, 1944, p. 138.
(2) Caesar and Sachanen, Ind. Eng. Chem., 40, 922 (1948).
(3) Greenalgh, U. S. Patent 1,977,627.
(4) Jordan, U. S. Patent 1,854,940.
(5) Baker and Besly, J. Chem. Soc., 1103 (1940).
(6) McGreal, Niederl and Niederl, THIS JOURNAL, 61, 345 (1939).
(7) DeBell, Goggin and Gloor, "German Plastic Practices," DeBell and Richardson, Springfield, Mass., 1946, p. 260.

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The Separation of Mixtures of Mono- and Disubstituted Alkyl Phosphoric Acids[1]

BY D. C. STEWART AND H. W. CRANDALL

A number of alkyl phosphoric acids are available commercially, but only as mixtures of the mono- (H_2RPO_4) and di- (HR_2PO_4) substituted forms. It seems probable that for many purposes it would be desirable to use one or the other of these in a separated state, as, for example, in studying the mechanisms involved in the extraction of amino acids by their use.[2] It has been found that this separation may be readily accomplished by taking advantage of the differences in the distribution of the two forms between two immiscible phases, generally water and some organic solvent. In this latter case, the disubstituted acid favors the organic phase, whereas the monosubstituted compound shows more affinity for the aqueous layer. By choosing the appropriate solvent, it is then possible to water wash all of the H_2RPO_4 out of the organic layer by a series of batch extractions, leaving only the HR_2PO_4;

(1) A portion of this work was performed under the auspices of the Atomic Energy Commission.
(2) E. V. McCollum, A. A. Rider and H. Suss, Proc. Soc. Exp. Biol. Med., 72, 709 (1949).