Table VIII

Kinetics of Reaction of Butyl Bromides in Pyridine at 27.6°

Bromide	Concn., mmoles/liter	Silver nitrate concn., mmoles/liter	10^3k, hr.$^{-1}$ acc. to eq. 1	10^3k, l.-mole^{-1} hr.$^{-1}$, acc. to eq. 6
n-Butyl	96.1	0	57 ± 1	
	46.4	49.3	85 ± 6	786 ± 23
	103.8	104.7	108 ± 10	737 ± 64
	132.7	136.3	117 ± 11	771 ± 140
sec-Butyl	102.6	0	2.5 ± 0.1	
	46.8	47.3	7.5 ± .6	147 ± 5
	103.9	104.4	13 ± .3	150 ± 3
	147.3	148.6	18 ± 3	157 ± 2

stant is practically the same over a threefold concentration range of halide and silver nitrate. In addition, with both bromides, calculation of first-order constants for the silver nitrate solutions resulted in markedly decreasing values of the constants as reaction proceeded. No trend was discernible in the values of the corresponding second order constants.

It is concluded that silver nitrate is reacting with the alkyl halides in pyridine. The primary compounds react with pyridine alone approximately twenty times more readily than the secondary halides. This is not unexpected for an SN2 reaction. Furthermore, the primary compounds react five times more rapidly with silver nitrate than the secondary halides, again as expected for a direct nucleophilic displacement which now has electrophilic assistance. In the solvent reaction, pyridine is, of course, a strong nucleophile but may also act as a weak electrophile, solvating the ion-pair which is being formed. Silver ion is, of course, a much more effective electrophile. In the present system it appears that "push" by the pyridine is more important than "pull" by the silver ion. This conclusion emerges from both the kinetic results and the analyses of the products of the reactions, in which the yields of olefin and quaternary salt were unchanged by the addition of silver nitrate.

Acknowledgments.—The authors express their appreciation to Drs. J. Greenspan and F. M. Beringer for helpful discussions.

Brooklyn 1, N. Y.

[Contribution from the School of Chemistry of the University of Minnesota]

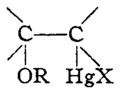
Reaction of 1-Iodomercuri-2-propanol and its Methyl Ether with Non-halogen Acids[1]

By Maurice M. Kreevoy

Received September 8, 1958

The reaction of $CH_3CH(OR)CH_2HgI$ with perchloric and acetic acids has been examined for R = H and R = CH_3. The products are propylene, HgI_2, HOR and $CH_3CHORCH_2Hg^{\oplus}$ (the latter either as the perchlorate or the acetate). The reaction rate is proportional to the hydronium ion concentration in dilute solution and is independent of the concentration of molecular acetic acid. For both R = H and R = CH_3, the reaction is faster in D_2O than in H_2O. These facts suggest very strongly that the first step in this reaction is a fast, reversible protonation of the substrate oxygen and that this is followed by a rate-determining step in which no covalent bonds to solvent or acetate ion are formed. The exact nature of the rate-determining step and the structure of the transition state are not yet known.

It has long been known that compounds of the general type I, where R is either a hydrogen atom or an alkyl group and X is a halogen atom, generate



Ia, R = H, X = I
Ib, R = CH_3, X = I

the corresponding olefin on treatment with halogen acids and sometimes also on treatment with acetic acid.[2] Several mechanisms have been proposed for this reaction,[3,4] but none seems to have been definitely established. In the present paper the stoichiometry and kinetics of the reactions with aqueous perchloric and acetic acid are reported, along with the effect on the rate of changing the solvent to D_2O. Solvent and salt effects are also briefly reported. Considerable information about the mechanism of the reaction is deduced.

Results

Products.—All of the results are consistent with the stoichiometry shown in eq. 1. On treatment

$$2CH_3CH(OR)CH_2HgI + H_3O^{\oplus} \longrightarrow CH_3CH{=}CH_2 + H_2O + CH_3CH(OR)CH_2Hg^{\oplus} + ROH + HgI_2 \quad (1)$$

$$CH_3CH(OR)CH_2HgI + H_3O^{\oplus} \longrightarrow CH_3CH{=}CH_2 + H_2O + HgI^{\oplus} + ROH \quad (2)$$

$$CH_3CH(OR)CH_2HgI + HgI^{\oplus} \longrightarrow CH_3CH(OR)CH_2Hg^{\oplus} + HgI_2 \quad (3)$$

$$R = H \text{ or } CH_3$$

with a large excess of 0.2 *M* aqueous perchloric acid, 3.49 mmoles of Ia produced 1.84 mmoles of gas (assumed to be propylene). Similarly 3.96 mmoles of Ib produced 2.03 mmoles of gas. It was shown that Ia produced no significant quantity of isopropyl alcohol, precluding an electrophilic displacement reaction.

The spectra of HgI_2 and $HgI^{\oplus}$ have been previously determined.[5] Redetermination gave good agreement in the case of HgI_2, but in the case of $HgI^{\oplus}$ the previously reported valley around 2500 Å. was partially filled in.[6] With both

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[1] Presented in part at the April, 1958, Meeting of the American Chemical Society, San Francisco, Calif.

[2] (a) F. C. Whitmore, "Organic Compounds of Mercury," The Chemical Catalog Co. (Reinhold Publ. Corp.), New York, N. Y., 1921, Chap. V. (b) G. F. Wright, *Ann. New York Acad. Sci.*, **65**, 436 (1957). (c) J. Chatt, *Chem. Revs.*, **48**, 7 (1951).

[3] A. Rodgman, D. A. Shearer and G. F. Wright, *Can. J. Chem.*, **35**, 1377 (1957).

[4] F. C. Whitmore, *Chem. Eng. News*, **26**, 672 (1948).

[5] M. M. Kreevoy, This Journal, **79**, 5929 (1957).

[6] The argument for the products of acid cleavage of CH_3HgI (ref. 4) are strengthened by the new spectrum for $HgI^{\oplus}$.

Ia and Ib, the product spectra were essentially identical with that predicted for HgI_2 in a concentration one-half that of the starting material. These spectra are significantly different from that of $HgI^{\oplus}$. Figure 1 compares a typical product spectrum with the spectra of HgI_2 and $HgI^{\oplus}$. The spectrum of $CH_3CH(OR)CH_2Hg^{\oplus}$, like that of $CH_3Hg^{\oplus}$,[5] is apparently much weaker than those of HgI_2 and $HgI^{\oplus}$. All of these results are in accord with the predictions of eq. 1 and preclude the stoichiometry shown in eq. 2.

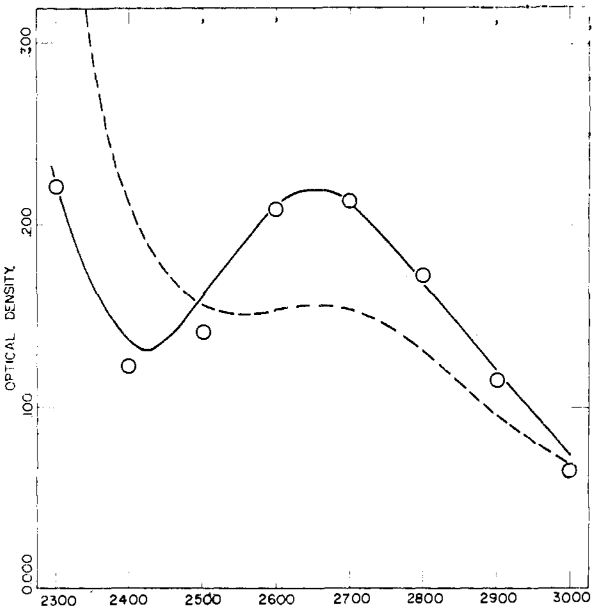

Fig. 1.—Typical product spectrum: ———, the calculated spectrum for 3.69×10^{-5} *M* HgI_2; – – – –, the calculated spectrum for 7.38 *M* HgI^+; ○, observed optical densities at 100 half-lives for a reaction mixture initially 7.38×10^{-5} *M* in $CH_3CH(OCH_3)CH_2HgI$.

Rate Law.—The course of each reaction was followed by observing the build-up of the HgI_2 spectrum in the ultraviolet. In the presence of excess perchloric acid, fairly good pseudo first-order kinetics were observed at initial substrate concentrations below 5×10^{-5} *M*. At higher concentrations the rate, $d(HgI_2)/dt$, did not fall off with time as fast as predicted by the first-order rate law, and closer examination showed small deviations from the first-order rate law even in the low-concentration experiments. It was shown (by adding the products to the initial mixture) that these deviations were due to catalysis by the products. The initial pseudo first-order rate constants were invariant, within experimental uncertainty, under a fourfold change in initial substrate concentration. Figure 2 shows typical first-order rate plots for high- and low-concentration experiments. Most of the data reported in this paper were taken from low-concentration experiments in which the curvature is hardly detectable, but it is clear from Fig. 2 that there is no difficulty in evaluating the initial slope even in the high-concentration experiments. Catalysis by the products was not further investigated. Since the making and breaking of mercury–iodine bonds in aqueous solution is presumably fast, it seems very likely that the observed stoichiometry was due to a slow reaction with the stoichiometry shown in eq. 2 and first-order in substrate, quickly followed by the reaction shown in eq. 3. This reaction scheme is analogous to the one suggested for the acid cleavage of methylmercuric iodide[5] and leads to the integrated rate law shown in eq. 4. In eq. 4,

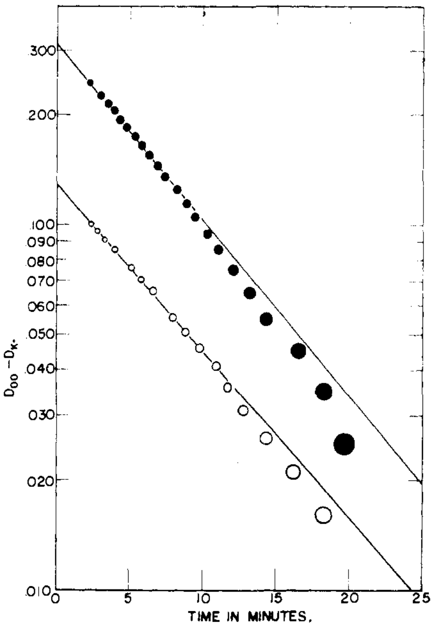

Fig. 2.—Typical first-order rate plots: ○, initial concn. of $CH_3CH(OH)CH_2HgI$ is 4.72×10^{-5} *M*; ●, initial concn. of $CH_3CH(OH)CH_2HgI$ is 18.9×10^{-5} *M*; the lines represent the initial slopes. The ordinate is $(D_{\infty} - D_t)$ on a logarithmic scale, where D_{∞} is the ultimate optical density and D_t is the optical density at time *t*.

$$k_1 = \frac{2.303}{2\,(t - t_0)} \log \frac{(D_{\infty} - D_0)}{(D_{\infty} - D_t)} \qquad (4)$$

k_1 is a pseudo first-order rate constant and D_t is the optical density at time *t*. Except for the factor 2 in the denominator, eq. 4 is the integrated form of the usual first-order rate law and it predicts the observed first-order dependence of the rate on the substrate concentration. All of the rate constants reported in the present paper were evaluated by eq. 4 and the initial slopes of plots such as those shown in Fig. 2.

Pseudo first-order rate constants measured under the same conditions were reproducible within 5–15%. Better reproducibility was obtained with the slower reactions. Some of the faster reactions had half-lives of the order of magnitude of one minute which made them hard to thermostat accurately and hard to follow with the present techniques.

Because of the very low substrate concentrations used, it was possible to study a considerable range of perchloric acid concentrations without going beyond the limits of very dilute solutions and yet always keeping the acid in large excess over the substrate. Within the limits of experimental uncertainty, k_1 for Ia is directly proportional to the perchloric acid concentration from 2.2×10^{-4} *M* to 1.3 × 10^{-3} *M*. For thirteen experiments within this range, $k_2 = k_1/(\mathrm{H}^{\oplus})$ and has a value 2.09 ± 0.26 l. mole^{-1} sec.$^{-1}$ at 25°. Similarly[7] for Ib, k_2 has a value 0.658 ± 0.083 l. mole^{-1} sec.$^{-1}$ determined from four experiments in which the perchloric acid concentrations varied from 6.6 × 10^{-4} to 4.4 × 10^{-3} *M*.

Specific Hydronium Ion Catalysis.[8]—Elimination from Ia is also brought about by acetic acid–acetate buffers. The rate, however, is directly proportional to the hydronium ion concentration and independent of the concentration of molecular acetic acid. The hydronium ion concentrations were evaluated by means of eq. 5. The ionization

$$(\mathrm{H}^{\oplus}) = \frac{K(\mathrm{HC_2H_3O_2})}{(\mathrm{C_2H_3O^-})f^2_{\pm}} \qquad (5)$$

$$\log f_{\pm} = \frac{0.3582\sqrt{\Gamma}}{1 + 1.30\sqrt{\Gamma}} \qquad (6)$$

constant of acetic acid at 25°, $K = 1.75 \times 10^{-5}$, was that cited by Harned and Owen.[9] The mean activity coefficient was evaluated in each case by eq. 6,[10] where Γ is the ional strength and the parameters are those required by theory.[11] The mean ionic radius (5.6 Å.) is that given by Harned.[12] For eight experiments covering a range of hydronium ion concentrations from 2.17 × 10^{-5} to 2.08 × 10^{-4}, k_2 had an average value of 2.13 ± 0.12 l. mole^{-1} sec.$^{-1}$. The concentration of molecular acetic acid varied from 1.9 × 10^{-2} to 1.9 *M*, and sodium acetate concentration varied from 1.6 × 10^{-3} to 1.6 × 10^{-1} *M*. The values of k_2 show no systematic trend whatsoever. Data given below indicate that this reaction is not particularly sensitive to salt or solvent effects. Estimating that, as a reasonable maximum, 20% of the rate at 1.9 *M* acetic acid is due to molecular acetic acid, a *maximum* value of 7 × 10^{-6} can be put on the catalytic constant,[13] k_A, of molecular acetic acid. The ratio k_2/k_A then has a *minimum* value of 3 × 10^5.

Salt and Solvent Effects.—Four experiments carried out with Ia in aqueous sodium perchlorate of concentrations up to 0.17 *M* failed to show any dependence of k_2 on ionic strength. In these experiments, k_2 had a value 2.13 ± 0.16 l. mole^{-1} sec.$^{-1}$.

Eight experiments were carried out with Ia in a solvent containing 4% water and 96% methanol.[14] The perchloric acid concentration varied from 1.66 × 10^{-4} to 2.03 × 10^{-3} *M*. For these experiments, k_2 had a value 1.31 ± 0.04 l. mole^{-1} sec.$^{-1}$ surprisingly similar to its value in pure water.

Solvent Isotope Effects.—Experiments were carried out with both Ia and Ib in aqueous solution containing up to 99 atom % deuterium. Ten experiments with Ia and solutions containing 98.6 atom % D gave a value of 4.43 ± 0.76 l. mole^{-1} sec.$^{-1}$ for k_2. The average deviation from the mean is rather large because these rates are inconveniently fast in reasonable perchloric acid concentrations. The *probable error*[15] in the mean value of k_2 is 0.20 l. mole^{-1} sec.$^{-1}$. Averaging all the values of k_2 for Ia in H_2O (25 perchloric acid and buffer experiments) a value of 2.11 l. mole^{-1} sec.$^{-1}$ is obtained with a probable error[15] of 0.03 l. mole^{-1} sec.$^{-1}$. Making the short extrapolation to 100% D, the ratio of the rate constant in D_2O to that in H_2O, k_2^D/k_2^H, is 2.16, with a probable error of 0.10. With Ib as the substrate, k_2 had a value of 1.84 ± 0.20 l. mole^{-1} sec.$^{-1}$ for four experiments in solutions containing 98.9 atom % D. For Ib, k_2^D/k_2^H therefore has a value of 2.80 with a probable error of 0.18.

Figure 3 shows how the rate constant for Ia increases with increasing deuterium concentration in the solution. Figure 4 shows the same increase for Ib; Fig. 4 also shows the curve predicted by the equations of Butler.[16–18] This curve and the fit of the experimental points to it are discussed below.

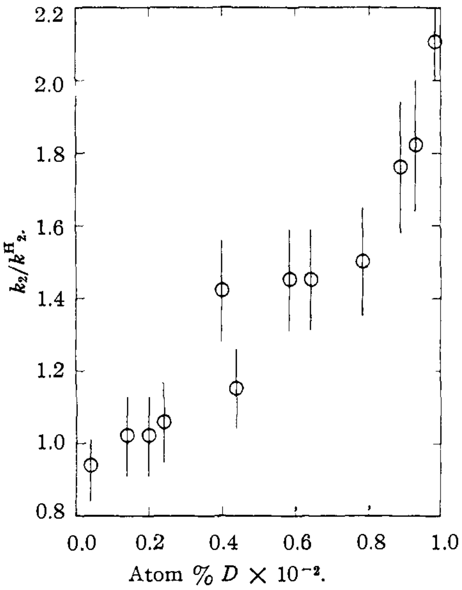

Fig. 3.—Plot of k_2/k_2^H for Ia in H_2O–D_2O mixtures; ϕ are experimental points; the length of the vertical line indicates a 10% uncertainty except that at 98.6% D the mean value of k_2/k_2^H is used and the vertical line indicates the probable error of the mean.

Discussion

The results presented above are all consistent with the mechanism shown in eqs. 7–9. The pres-

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[7] In this paper, whenever a quantity is followed by a measure of its uncertainty in this fashion, the quantity is a mean value and the measure of uncertainty is simply the average deviation from the mean value.

[8] This reaction is not truly acid catalyzed, as the acid is consumed in the course of the reaction, but the vocabulary of acid catalysis is otherwise applicable and is used.

[9] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 1943, p. 583.

[10] *Ibid.*, p. 39.

[11] *Ibid.*, pp. 118–120.

[12] H. S. Harned, *J. Phys. Chem.*, **43**, 275 (1938).

[13] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 209.

[14] The exact method of making up this solvent is described in the Experimental part.

[15] R. Livingston, "Physico Chemical Experiments," The Macmillan Co., New York, N. Y., 1948, pp. 29–30.

[16] W. J. C. Orr and J. A. V. Butler, *J. Chem. Soc.*, 330 (1937).

[17] W. E. Nelson and J. A. V. Butler, *ibid.*, 958 (1938).

[18] E. L. Purlee and R. W. Taft, Jr., THIS JOURNAL, **78**, 5807 (1956).

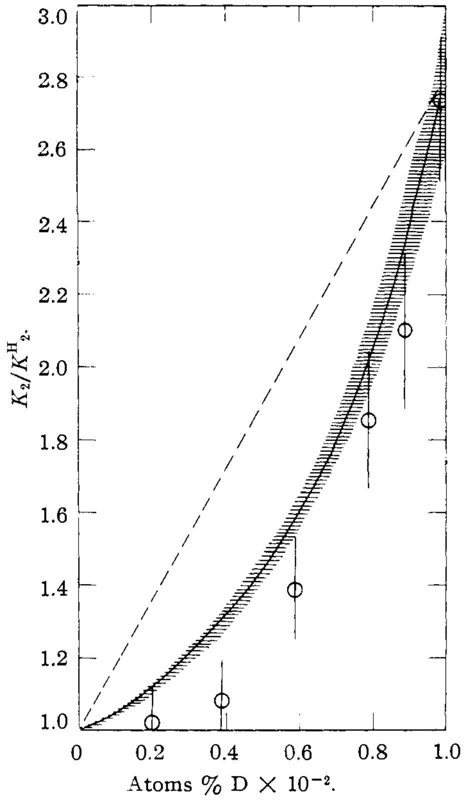
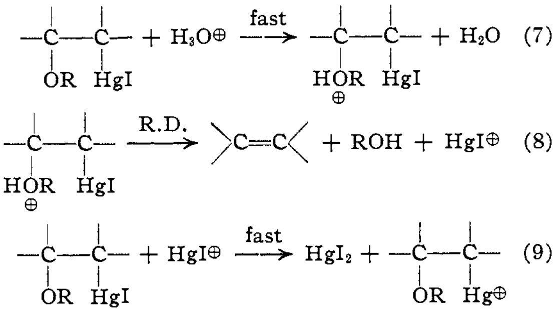


Fig. 4.—Plot of k_2/k_2^{H} for Ib in H_2O–D_2O mixtures; ϕ are experimental points; the length of the vertical line indicates a 10% uncertainty, except that at 98.9% D the mean value of k_2/k_2^{H} is used and the vertical line indicates the probable error of the mean; ——— is the curve calculated from the experimental value of $k_2^{\mathrm{D}}/k_2^{\mathrm{H}}$ and the equations of Butler. The shaded area is the uncertainty introduced into this curve by the probable error in $k_2^{\mathrm{D}}/k_2^{\mathrm{H}}$.

ence of a proton in the transition state is implied



$$-\overset{|}{\underset{\substack{|\\ \mathrm{OR}}}{\mathrm{C}}}-\overset{|}{\underset{\substack{|\\ \mathrm{HgI}}}{\mathrm{C}}}- + \mathrm{H_3O^{\oplus}} \xrightarrow{\text{fast}} -\overset{|}{\underset{\substack{|\\ \mathrm{HOR}\\ \oplus}}{\mathrm{C}}}-\overset{|}{\underset{\substack{|\\ \mathrm{HgI}}}{\mathrm{C}}}- + \mathrm{H_2O} \tag{7}$$

$$-\overset{|}{\underset{\substack{|\\ \mathrm{HOR}\\ \oplus}}{\mathrm{C}}}-\overset{|}{\underset{\substack{|\\ \mathrm{HgI}}}{\mathrm{C}}}- \xrightarrow{\text{R.D.}} {>}\mathrm{C{=}C}{<} + \mathrm{ROH} + \mathrm{HgI^{\oplus}} \tag{8}$$

$$-\overset{|}{\underset{\substack{|\\ \mathrm{OR}}}{\mathrm{C}}}-\overset{|}{\underset{\substack{|\\ \mathrm{HgI}}}{\mathrm{C}}}- + \mathrm{HgI^{\oplus}} \xrightarrow{\text{fast}} \mathrm{HgI_2} + -\overset{|}{\underset{\substack{|\\ \mathrm{OR}}}{\mathrm{C}}}-\overset{|}{\underset{\substack{|\\ \mathrm{Hg^{\oplus}}}}{\mathrm{C}}}- \tag{9}$$

by the observed, first-order dependence of the rate on the perchloric acid concentration. The oxygen atom seems by far the most reasonable point of attachment.

If a proton transfer to the substrate from molecular acetic acid were a part of the rate-determining transformation, general acid catalysis would be expected.[19,20] A rate-determining attack on the protonated substrate by acetate ion would also lead to an acetic acid term in the rate expression.[19,20] The very large *minimum* value of k_2/k_{A}, 3×10^6, obtained above, may be compared with the value of 50 obtained for the mutarotation of glucose.[21] The latter is a typical general acid-catalyzed reaction. The results presented above also show no signs of a reaction with water, which can function as an acid in general acid-catalyzed reactions. It is recognized that general acid catalysis can be obscured by a large value of the Brönsted constant, α.[22] There is no known case, however, in which a ratio of k_2/k_{A} as large as that reported here has been found for a reaction of one of the general acid-catalyzed types.

Since acetate ion does not attack the protonated substrate in the rate-determining step, it is suggested by analogy that no attack by water is needed either. Similarly, since proton transfer from molecular acetic acid to the substrate is not part of the rate-determining step, it is strongly suggested that proton transfer from hydronium ion to the substrate is not part of the rate-determining step. If the proton is part of the transition state but is not transferred in the rate-determining step, it must have been transferred in a prior, equilibrium step.

The observed values of $k_2^{\mathrm{D}}/k_2^{\mathrm{H}}$ are also consistent with a fast prototropic equilibrium preceding the rate-determining step, and inconsistent with a rate-determining step including a proton transfer from solvent to substrate.[23,24] For Ib, the ratio $k_2^{\mathrm{D}}/k_2^{\mathrm{H}}$ is very similar to that (3.1) found in acid-catalyzed acetal hydrolysis.[25] The latter reaction definitely involves a proton transfer to an ether oxygen in a fast equilibrium followed by a rate-determining cleavage of one of the carbon–oxygen bonds and does not require an attack on the protonated substrate by solvent. If the proton transfer from solvent to substrate were part of the rate-determining step it would be expected that $k^{\mathrm{D}}/k^{\mathrm{H}}$ would be equal to or (probably) less than unity for both Ia and Ib.[23,24]

If the rate-determining step is preceded by a fast, prototropic equilibrium, it would be expected that k_2/k_2^{H} for Ib at intermediate percentages of D_2O would follow Butler's equation.[16–18] (The rates for Ia would not be expected to follow Butler's equation in any event because Ia has an exchangeable hydrogen in the substrate, the isotopic nature of which has an important bearing on the rate.) Figure 4 shows that the fit is not too good.[26] It has been pointed out, however, that the assumptions made in obtaining Butler's equation are not exact,[27] and the data are also not as precise as one could wish. If the proton transfer were part of the rate-determining step, a *linear* relationship between k_2/k_2^{H} and the percentage D would be expected and this is clearly a poorer approximation to the data than Butler's equation.

The data specifically eliminate the possibility

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[19] R. P. Bell, "Acid–Base Catalysis," Oxford at the Clarendon Press, 1949, p. 124.

[20] Reference 13, p. 204.

[21] J. N. Brönsted and E. A. Guggenheim, THIS JOURNAL, **49**, 2554 (1927).

[22] Reference 13, p. 209.

[23] Reference 19, p. 145.

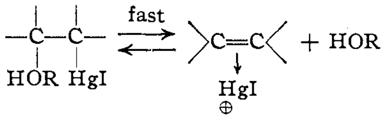
[24] K. B. Wiberg, *Chem. Revs.*, **55**, 713 (1955).

[25] M. M. Kreevoy and R. W. Taft, Jr., THIS JOURNAL, **77**, 3146 (1955).

[26] A theoretical curve only slightly different is obtained if a more modern value of the equilibrium constant for the reaction $H_2O + D_2O \rightleftarrows 2HOD$ is used; *cf.* ref. 18.

[27] Reference 19, p. 152.

that reaction 10 follows reaction 7 and precedes the rate-determining step. If such a step were included and were, in fact, fast and reversible, Ib would be converted rapidly to Ia in an aqueous solution, and the rates observed would have been the same for both compounds. In fact k_2 for Ib is only about one-third of k_2 for Ia.



$$-\underset{\text{HOR}}{\underset{|}{\overset{|}{C}}}-\underset{\text{HgI}}{\underset{|}{\overset{|}{C}}}- \underset{\longleftarrow}{\xrightarrow{\text{fast}}} \underset{\underset{\text{HgI}^{\oplus}}{\downarrow}}{>C{=}C<} + \text{HOR} \qquad (10)$$

The results discussed above show that the transition state in these reactions is composed of the substrate plus a proton. Beyond that its structure is not known. Neither is it known whether the rate-determining step leads directly to the products shown in eq. 8 or whether one or more intermediates intervene. These questions are currently under investigation in these laboratories and will be discussed when more evidence is available.

Experimental

Kinetic Procedure.—All rate measurements were made by following the appearance of the HgI_2 absorption at 2800 Å. with a Beckman DU spectrophotometer. The reaction mixtures were made up in volumetric flasks without the substrate and thermostated at 25.00 ± 0.05° in a water-bath of conventional design. The substrate then was added in a small volume of stock solution. Part of the reaction mixture was transferred to a 1.00-cm. silica spectrophotometer cell and the cell was placed in a water-jacketed cell compartment for the course of the reaction. Water was pumped through the jackets from the bath mentioned above and the temperature in the cells was never found to vary from the bath temperature by more than 0.1°. The optical density was determined at convenient intervals over a range of 70–90% of its total change. Infinity points were determined by making a number of measurements after eight or more half-lives had passed.

Stock solutions of substrate were made up in methanol, so that the "aqueous" solutions referred to above actually contained 1–4% methanol. In view of the small difference between the rates in nearly pure water and those in 96% methanol, this small percentage of methanol was not thought to be significant, and k_2 was shown to be invariant with changes in the percentage methanol between 1 and 4%. The 96% methanol solvents were made up in a 25-ml. volumetric flask, to which 1 ml. of water containing the requisite amount of acid had been added. The flask was then filled to the mark with methanolic stock solution of substrate plus pure, dry methanol.

Materials.—The preparation of solvents and standard acids has been described previously.[5] Compound Ia was prepared by the method of Hofmann and Sand,[28] m.p. 63–65°, and had an infrared spectrum characteristic of a secondary alcohol. Compound Ib does not seem to be previously known. It was prepared by essentially the method outlined by Wright[29] for the cyclohexene derivative, except that the olefin was passed into the reaction mixture as a gas; Ib is a liquid which freezes around 0° and could neither be recrystallized nor distilled. Fortunately, it seems to come out of the reaction mixture fairly pure. It had an infrared spectrum typical of an ether.

Anal. Calcd. for C_4H_9OHgI: C, 11.99; H, 2.26. Found: C, 11.51; H, 2.01.

Ultraviolet Spectra.—A standard solution of HgI_2 in methanol was diluted 25-fold with water in order to obtain the spectrum of a solution of reliably known concentration. The spectrum of $HgI^{\oplus}$ was obtained by mixing solutions containing one equivalent each of mercuric nitrate and sodium iodide.

Products.—In a typical determination of the volume of gas produced, 1.526 g. (0.00396 mole) of Ib was added to 50 ml. of water in a 500-ml. filter flask, which was then tightly stoppered with a dropping funnel passing up through the stopper. The side arm was connected to a gas buret through a short length of Tygon tubing and 1 ml. of 11 *M* $HClO_4$ was added through the dropping funnel, which was then tightly closed. Fifty-four ml. of gas was collected at 26° and 740 mm. on shaking for about 15 minutes, and no further gas could be collected after 30 minutes of shaking. The liquid Ib was converted to red mercuric iodide during this time. The same procedure yielded 3 ml. of gas in the absence of Ib—probably due to CO_2 evolution. The volume of propylene evolved was, therefore, 51 ml. Under these conditions only about 0.2% of the propylene would remain in the aqueous solution.[30] The total yield of gas was, therefore, 0.00203 mole.

When Ia was used, the solution was filtered to remove mercuric iodide, made basic with 2 *M* sodium hydroxide, and distilled. Ten ml. of this solution was treated with 1 ml. of 18.7 *M* sulfuric acid and 2.00 ml. of 0.102 *M* chromium(VI) oxide at 62° for 2.5 hours. No change in the visible spectrum of the chromium(VI) oxide could be detected spectroscopically. Under the same conditions, 10 ml. of 1.32×10^{-3} *M* isopropyl alcohol in water reduces 1.0 mole of chromium(VI) oxide to chromic ion, as determined spectroscopically. The spectrum of chromium(VI) oxide in these solutions was determined directly. The spectrum of the chromic ion was determined by heating 0.001 mole of isopropyl alcohol at 62° for 2.5 hours with 2.04×10^{-4} mole of chromic acid, 1 ml. of 18.7 *M* H_2SO_4 and 12 ml. of water.

Acknowledgment.—The author is pleased to acknowledge the financial support of the National Science Foundation through grant No. N.S.F.-G5434 during part of the period when this work was in progress. He also wishes to thank Mrs. Olga Hamerston for the troublesome analysis of Ib.

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[28] K. A. Hofmann and J. Sand, *Ber.*, **33**, 1354 (1900).

[29] G. F. Wright, THIS JOURNAL, **57**, 1993 (1935).

[30] E. W. Washburn, ed., "International Critical Tables," Vol. III, McGraw-Hill Book Co., Inc., New York, N. Y., 1928, p. 260.

[CONTRIBUTION FROM STAMFORD LABORATORIES, RESEARCH DIVISION, AMERICAN CYANAMID CO.]

The Cyanoethylation of Phosphine and Phenylphosphine

BY M. M. RAUHUT, I. HECHENBLEIKNER, HELEN A. CURRIER, F. C. SCHAEFER AND V. P. WYSTRACH

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Phosphine reacts with acrylonitrile at room temperature in the presence of strongly basic catalysts to give high yields of 2-cyanoethylphosphines. The primary, secondary or tertiary phosphine can be made the predominant product by choosing appropriate conditions. Phenylphosphine also reacts readily with acrylonitrile under these conditions to give a high yield of bis-(2-cyanoethyl)-phenylphosphine. A number of derivatives of tris-(2-cyanoethyl)-phosphine and bis-(2-cyanoethyl)-phenylphosphine have been prepared.

The reaction of active hydrogen compounds with acrylonitrile to produce derivatives containing a 2-cyanoethyl substituent is well known and has been reviewed.[1] The cyanoethylation of the hy-

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[1] H. A. Bruson, "Organic Reactions," Vol. 5, John Wiley and Sons, Inc., New York, N. Y., 1949, p. 79.